Reactions of Small Organic Rings and Activated Olefins With Transition Metal Complexes.

William Dudley Pitts Jr

Louisiana State University and Agricultural & Mechanical College

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WITH TRANSITION METAL COMPLEXES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
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Doctor of Philosophy

in

The Department of Chemistry

by

William Dudley Pitts, Jr.
B.S., Union University, 1969

August, 1976
To Nancy
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LIST OF ABBREVIATIONS

Ph$_3$P  triphenylphosphine
diphos  bis(1,2-diphenylphosphino)ethane
dars  o-phenylenebis(dimethylarsine)
TCNE  tetracyanoethylene
TCNEO  tetracyanoethylene oxide
dpcp  diphenylcyclopropenone
Me  methyl
TLC  thin layer chromatography
This Dissertation describes the reactions of various substituted epoxides, cyclic unsaturated ketones, and cyano-substituted ethylenes with a number of noble metal substrates. A number of new complexes have been prepared and characterized and the coordinating abilities of these compounds have been noted.

Reactions of tetracyanoethylene oxide with coordinatively unsaturated Pt(Ph₃P)₂ and MX(CO)(Ph₃P)₂ [M = Ir; X = Cl, Br; M = Rh; X = Cl] yield stable well characterized 1:1 complexes. These complexes result from nucleophilic attack of the metal atom on one of the ring carbons of the epoxide ring causing the cleavage of the bond between that carbon and the oxygen atom. The metal atom then is included in the final ring by attachment of the generated alkoxide to the metal saturating its coordination requirement. The resultant metallocycles are stable well characterized complexes. The complexes IrH(CO)(Ph₃P)₃, IrH(CO)₂(Ph₃P)₂, [Ir(diphos)₂]Cl, RhCl(Ph₃P)₃, Ni(CO)₂(Ph₃P)₂, and Pd(Ph₃P)₄ reacted but did not form well characterized products.

trans-1-Cyano-1,2-diphenyloxirane and trans-stilbene oxide were allowed to react with Pt(Ph₃P)₄ to give products which were described as [Pt(Ph₃P)₂]₂(oxirane). No reactions were observed to occur between these substituted oxiranes and IrCl(CO)(Ph₃P)₂ or Pd(Ph₃P)₄.
Diphenylcyclopropenone was found to react with Pt(Ph₃P)₂ to give the well characterized product Pt(Ph₃P)₂⁻ (diphenylcyclopropenone). This complex is also the product of a metal insertion into a small ring compound. The platinum atom inserts into one of the carbon-carbon single bonds forming a metalloccyclobutenone with the carbonyl function and the double bond intact in the ring. The reactions of [Ir(diphos)₂]Cl and Pd(Ph₃P)₄ with diphenylcyclopropenone gave evidence of forming 1:1 complexes but did not afford well characterized complexes. Diphenylcyclopropenone failed to react with IrH(CO)(Ph₃P)₃, IrH(CO)₂⁻(Ph₃P)₂, and IrCl(CO)(Ph₃P)₂. Other saturated ketone substituted rings which showed no reaction with Pt(Ph₃P)₄ were tetraphenylocyclopentadienone, 2,5-dimethyl-3,4-diphenylcyclopentadienone, cycloheptatrienone, and N-acetyl-diphenylcyclopropenoxime.

The reactions of three diaminodicyanoethylenes with various metal substrates revealed that the olefins react only with the most reactive metal complexes. The reaction of Pt(C₂H₄)(Ph₃P)₂ with 1,1-diamino-2,2 dicyanoethylene resulted in a 1:1 complex. RhCl(Ph₃P)₃ reacts with this ligand but does not afford a well characterized product. No reaction was observed between MX(CO)(Ph₃P)₂ [M = Ir; X = Cl, F; M = Rh; X = Cl] and 1,1-diamino-2,2-dicyanoethylene. Pt(Ph₃P)₄ reacts with diaminomaleonitrile to form a 1:1 complex. The complex RhCl(Ph₃P)₃ reacts with
diaminomaleonitrile but no well characterized product is isolated. Diaminomaleonitrile failed to react with IrX(CO)-(Ph₃P)₂ [M = Ir; X = Cl, Br, I; M = Rh; X = Cl] and IrH(CO)-(Ph₃P)₃. Reaction occurred between RhCl(Ph₃P)₃ and 1,1-bis(dimethylamino)-2,2-dicyanoethylene but no well characterized product was isolated. No reaction was observed with 1,1-bis(dimethylamino)-2,2-dicyanoethylene and Pt(C₂H₄)-(Ph₃P)₂ or IrCl(CO)(Ph₃P)₂.

Tetracyanoethylene reacts with Ir(NO)(Ph₃P)₃ to give a well characterized 1:1 product, Ir(NO)(Ph₃P)₂(TCNE). The reaction of tetracyanoethylene with Ir(NO)(CO)(Ph₃P)₂ yielded two products which are described as 1:1 and 2:1 ligand to metal reaction products. The complexes [IrH(NO)(Ph₃P)₃]ClO₄ and [IrCl(NO)(CO)(Ph₃P)₂]BF₄ reacted with tetracyanoethylene but did not afford well characterized products. Tetracyanoethylene failed to react with IrCl₂(NO)(Ph₃P)₂. Other activated olefins which did not react with the iridium-nitrosyl complexes Ir(NO)(CO)(Ph₃P)₂ and Ir(NO)(Ph₃P)₃ were fumaronitrile and cinnamonicitrile.
I. INTRODUCTION - METAL-EPOXIDE COMPLEXES

A. Review of Metal Complex-Epoxide Reactions

Reactions of epoxides with low oxidation state noble metal complexes have heretofore been studied very little. However, there are several reports in the literature dealing with reactions of other metal complexes reacting with epoxides. Catalytic processes, with the emphasis being on the nature of the transformed organic moieties instead of the metal complex-epoxide intermediates, have been the subject of several studies.

Direct oxygen addition to ethylene oxide was reported to take place over a metallic silver catalyst which involved adsorption of oxygen on the metal surface and transfer of the oxygen to the ethylene molecule through a possible silver oxide-ethylene linkage to silver-ethylene oxide linkage.\(^1\) Other researchers have contributed to this area of study.\(^2\)\textendash\(^10\)

Zinc was used to reduce ethylene oxides before the advent of complex metal hydrides. This reduction required the interaction of ethylene oxide with the metal forming some sort of short lived intermediate combination of the two reactants.\(^11\)\textendash\(^16\) Also before the introduction of complex metal hydrides, the most commonly used method for reducing ethylene oxides was catalytic hydrogenation. There were essentially only three catalysts for the hydrogenation
of ethylene oxides: nickel, palladium on charcoal and platinum black. Several excellent reviews discussed the interaction of metal and ethylene oxide.\textsuperscript{17-19} Ethylene oxides have also been reduced by the use of chromous chloride and chromous acetate.\textsuperscript{20-23}

Several of the few examples of controlled oxidation of ethylene oxides involve transition metals. The uses of platinum black,\textsuperscript{24} chromic acid,\textsuperscript{25-27} silver perchlorate or nitrate,\textsuperscript{28} and ruthenium tetroxide\textsuperscript{29} to oxidize epoxides have been described. The reactions of certain metal salts with epoxides were investigated including the reaction of ferric chloride with epoxides.\textsuperscript{30-33}

Eisenmann postulated in 1962 that the coordination of propylene oxide to the cobalt was involved in the isomerization of epoxides by dicobalt octacarbonyl.\textsuperscript{34} Muller and Muller allowed ethylene oxide to react with cobalt compounds very similar to vitamin B\textsubscript{12} and isolated a derivative. The ethylene oxide was bound to the cobalt but the ring had been opened, eq. 1.\textsuperscript{35} Heck, in a similar study allowed ethylene oxide to react with hydridotetra-carbonylcobalt(I) in ether at 0°C and isolated a similar compound, (CO)\textsubscript{4}Co-CH\textsubscript{2}CH\textsubscript{2}OH.\textsuperscript{36} This compound was treated with carbon monoxide to give carbonyl insertion into the
cobalt-carbon bond. Addition of triphenylphosphine yielded an isolable product, I. This work was done in an attempt

\[(\text{Ph}_3\text{P})(\text{CO})_2\text{Co-CH}_2\text{CH}_2\text{OH}\]

I

to elucidate the mechanism of the reaction of ethylene oxide with carbon monoxide and methanol wherein, in the presence of sodium tetracarbonylcobaltate(-I) at 65°C and 2000 psi, \(\beta\)-hydroxy acid esters were formed. Schrauzer and Windgassen reported the reaction of pyridinebis(dimethylglyoximato)cobalt(I) with ethylene oxide in the presence of water to give an analogous compound. This compound is a very good model for vitamin B_{12}. Jensen, Madan and Buchanan reported that the same reaction proceeds with inversion of configuration at carbon, establishing the \(S_N^2\) nature of the process. Dowd and Kang, in reporting the use of dicobalt octacarbonyl as a stereospecific deoxygenation agent for epoxy-esters, suggest that an intermediate cobalt heterocycle, II, is formed in the reaction.
Strohmeier and Hartman reported that monoepoxides were polymerized in good yields by ultraviolet irradiation in the presence of $\text{Mn}_2(\text{CO})_{10}$.

Allen, Bruce, and Hutchinson reported the synthesis of dimethyl- and diphenyl-zinc etherates. Similar zinc complexes may be present in the polymerization of epoxides. The proton magnetic resonance spectra of benzene solutions of the diarylzinc-ethylene oxide complexes were measured and gave evidence for a 1:2 molar ratio of diphenylzinc to ethylene oxide.

A stereospecific reduction of epoxides with sodium (cyclopentadienyl)dicarbonylferrate(II) was reported by Giering, Rosenblum, and Tancrede. This reaction is a new route to cationic iron-olefin complexes, eq. 2 and 3.

\[
[Fp]^- + \begin{array}{c} \text{O} \end{array} \rightarrow Fp - O^- \quad (2)
\]

\[
Fp - O^- \xrightarrow{H^+} Fp - OH^- \quad (3)
\]

\[
Fp = (\pi-C_5H_5)Fe(\text{CO})_2
\]

Treatment of the epoxide at ambient temperature with tetrahydrofuran solutions of the iron complex results in the rapid conversion to the alkoxides. Addition of two equivalents of fluoroboric or hexafluorophosphoric acid to
the reaction solution concerted the alkoxide to the olefin complex, which may be precipitated with ether.

Lithium diorganocuprates(I) have been used as reagents for the nucleophilic ring opening of oxiranes in the trans manner. Johnson, Herr, and Wieland reported that these reagents could selectively open oxirane rings in the presence of unprotected carbonyl functions, eq. 4.43

\[
\begin{align*}
\text{LiMe}_2\text{Cu} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2(\text{CH}_2)_8\text{O} - \text{CH}_3 \\
\text{(CH}_2)_8\text{O} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2(\text{CH}_2)_8\text{O} - \text{CH}_3 \\
\text{eq. 4.43}
\end{align*}
\]

During the course of the work described in the first section of this Dissertation, Milstein, Buchman, and Blum reported the homogeneous isomerization of aryl-substituted epoxides catalyzed by several noble metal complexes.44 Thus, trans-stilbene oxide was converted primarily into desoxybenzoin, eq. 5, by RhX(Ph$_3$P)$_3$ [X = Cl, Br] and RhCl(CO)(Ph$_3$P)$_2$. The reactions were carried out at 210°C under an inert atmosphere. Possible mechanisms were not discussed, nor were any intermediate metal complexes isolated.

Also during the course of this investigation described herein, Lenarda, Graziani, and Belluco reported
the carbon-carbon bond rupture in 1,1,2,2-tetracyanocyclopropane and tetracyanoethylene oxide. A later report by Schlodder, Ibers, Lenarda, and Graziani detailed an X-ray crystallographic study on a crystal of Pt(Ph₃As)(C₆N₄C)₂. Since the reaction of platinum phosphine complexes with various epoxides is included in the research described in this Dissertation, further comment on these reactions will be held until this topic is considered in the appropriate Discussion section of this work.

The objective of the work described in the first part of this Dissertation was the preparation and characterization of complexes of activated ethylene oxides with transition metals. An understanding of the reactivity of a variety of epoxides with these low valent transition metals and an understanding of the mechanism of the reactions were also goals of the work. The number of catalytic processes mentioned in this brief survey which involve interaction between ethylene oxides and transition metals or complexes provide a strong need to understand more fully the nature of this chemistry.

B. Chemistry of Epoxides

In 1859 the French chemist Wurtz announced the isolation of a new substance isomeric with acetaldehyde which he called ethylene oxide. This discovery opened the door to a new and important segment of organic
chemistry. Ethylene oxide is the simplest member of a class of compounds named "oxiranes" but often referred to as epoxides. Epoxides have been the subject of several reviews.49-53

The physical properties of epoxides are determined in the main by the substituents on the carbon atoms of the oxirane ring. For example, the boiling point of ethylene oxide is 10.5°C whereas with the substitution of one methyl group on the ring, as in propylene oxide, the boiling point is raised to 35°C. With the substitution of two phenyl groups on the ring, the compound, stilbene oxide, is a solid at room temperature.54

The interatomic distances and angles in the oxirane ring have been shown to vary very little with respect to the substituents on the carbon atoms of the ring. The distances and angles of ethylene oxide55-59 have been reported to be very close to those for tetracyanoethylene oxide.60

\[ \begin{align*}
\alpha &= 61^\circ 25 \\
\beta &= 59^\circ 18 \\
C-O &= 1.44 \text{ Å} \\
C-C &= 1.47 \text{ Å}
\end{align*} \]

\[ \begin{align*}
\alpha &= 63.4^\circ \\
\beta &= 58.3^\circ \\
C-O &= 1.42 \text{ Å} \\
C-C &= 1.49 \text{ Å}
\end{align*} \]

The vast majority of epoxide reactions involve the opening of the epoxide ring and the addition of a molecule of reagent.61 Due to the huge body of literature which the reactions of epoxides constitute, only a few
representative reactions will be mentioned here.

Reaction of ethylene oxide with metals is the oldest process for changing the epoxide to ethanol. Wurtz treated the epoxide with sodium amalgam in water.\textsuperscript{62} Catalytic hydrogenation was the most commonly used reaction for the reduction of epoxides using nickel, palladium, and platinum black as catalysts. However, catalyst and reaction condition determine the products obtained. Reduction of 1,2-epoxy-3-butene over Raney nickel at 76°C gives 1-butanol, whereas palladium on charcoal merely causes reduction of the double bond and isomerization to n-butyraldehyde.\textsuperscript{63} The discovery of complex metal hydrides as reductive agents for epoxides showed previous methods to be less desirable, because of the gentleness and directional selectivity of the complex hydrides. Trevoy and Brown found that the reaction of epoxides with lithium aluminum hydride followed the classical $S_N^2$ mode, eq. 6.\textsuperscript{64}

\begin{equation}
\text{R'}\text{R''}\text{R'''O} + \text{LiAlH}_4 \rightarrow \text{H}_2\text{O} \quad \text{(6)}
\end{equation}

There have been surprisingly few reactions involving controlled oxidation of ethylene oxides. An interesting
example was reported in 1879 by Richter which detailed the conversion of epichlorohydrin and epibromohydrin into the corresponding $\alpha$-hydroxy acid with concentrated nitric acid at 100°C.65

Ethylene oxides have long been known to isomerize to carbonyl compounds. Wurtz reported that ethylene oxide was related to acetaldehyde66 and later Ipatieff and Leontovich reported that passing ethylene oxide over alumina at 200-300°C or at 500°C without the catalyst, produced acetaldehyde.67 Isomerization catalyzed by acid and base also constitute many reported reactions concerning epoxides.53

Nucleophilic attack on epoxides has shown these three membered rings to be one of the most reactive classes of organic compounds due to relief of the strain in the opening of the ring.61 Hydroxylic nucleophiles, ammonia and amine nucleophiles, sulfur-containing nucleophiles, mineral and organic acids as nucleophiles, organomagnesium, -sodium, and -lithium nucleophiles, Grignard nucleophiles, carbanion nucleophiles, and others have been reported and utilized for many years.53 The majority of these reactions result in ring opening of the epoxide ring to yield an acyclic product. However, the reaction of a carbanion such as diethylsodiomalonate with ethylene oxide at ambient temperature and in equimolar amounts resulted in the formation of $\alpha$-carbethoxybutyrolactone, as reported by Traube and Lehmann in 1899, eq. 7.66 Reaction with
excess ethylene oxide gave further condensation and produced a spirolactone. Other reactions which produce cyclic products include the reaction of tetracyanoethylene oxide with olefins, acetylenes, and aromatics, all of which formed five membered rings as reported by Lynn and Benson in 1965, eq. 8. These examples showed graphically the two different ways the oxirane ring can be opened with a nucleophile. Another type of reaction of an epoxide with a nucleophile has been reported by Lynn, Webster, and Benson.
Reaction of tetracyanoethylene oxide with aqueous potassium iodide produced cyanogen iodide and the tricyanovinyl alcohohlate ion, eq. 9. Another reaction with tertiary

\[
\begin{align*}
\text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad + \quad I^- & \quad \rightarrow \quad ICN & \quad + \quad O\text{C}\equiv\text{C}\equiv\text{CN} \\
\text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN}
\end{align*}
\]  

(9)

nitrogen bases such as pyridine with tetracyanoethylene oxide gave a compound that contains one mole each of pyridine and dicyanomethane, eq. 10. The other product was

\[
\begin{align*}
\text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad + \quad \text{CN} & \quad + \quad \text{N} \quad \rightarrow \quad \text{CN} & \quad + \quad \text{CN} \\
\text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN}
\end{align*}
\]  

(10)

thought to be carbonyl cyanide. A very similar reaction in which carbonyl cyanide was isolated was the reaction of dialkyl sulfides with tetracyanoethylene oxide, eq. 11.

\[
\begin{align*}
\text{SR}_2 & \quad + \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \rightarrow \quad \text{R}_2\text{S} & \quad \text{C} & \quad (\text{CN})_2 & \quad + \quad \text{CO(CN)}_2 \\
\text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN} & \quad \text{CN}
\end{align*}
\]  

(11)

Another significant portion of the epoxide literature deals with electrophilic additions to the epoxide ring. These reactions yield either open-chained or cyclic
compounds, the distinction arising out of the nature of the reactants involved, eq. 12.\(^{53}\) Aryl halides, acyl halides, anhydrides, sulfinylchlorides, nitrosyl chlorides and dinitrogen tetroxide, alkyl dichloro- and dialkylchlorophosphines, halogens and other halogenating agents, metal halide salts, and other reagents react with the epoxide ring and yield the acyclic products with addition to oxygen and the carbon atoms and without the free hydroxyl groups of the conventional nucleophilic substitution reactions.\(^{61}\)

Reagents which yield cyclic products on reaction with epoxides are not as numerous as those which produce acyclic products. Carbon dioxide, carbon oxysulfide, carbon disulfide, organic isocyanates, sulfur trioxide and sulfur dioxide, ketenes and others form the heterocycles predicted by the equation above.\(^{73}\) Ethylene oxides in the presence of a catalyst will undergo dimerization to form the cyclic 1,4-dioxan. Aldehydes and ketones condense to form the cyclic acetals and ketals respectively.\(^{53}\) Imines and nitriles also form cyclic products with epoxides.\(^{73}\)

Epoxides have been shown to fragment upon exposure
to ultraviolet light to form carbenes and aldehydes or ketones depending on the substitution of the ring.\textsuperscript{74}

In summary, epoxides are reactive compounds that undergo a variety of transformations with numerous organic reagents. Utilization of inorganic reagents, such as transition metal substrates, would seem to be of some fundamental interest.
II. EXPERIMENTAL: Metal Complexes with Epoxides

A. General

1. Materials

Literature Preparations were followed to synthesize the following complexes: IrX(CO)(Ph$_3$P)$_2$ [X = Cl, Br, I, F], IrH(CO)(Ph$_3$P)$_3$, IrH(CO)$_2$(Ph$_3$P)$_2$, Ir(diphos)$_2$Cl, Ir(NO)(CO)(Ph$_3$P)$_2$, Ir(NO)(Ph$_3$P), [IrH(NO)(Ph$_3$P)$_3$]ClO$_4$, [IrCl(NO)(CO)(Ph$_3$P)$_2$]BF$_4$, IrCl$_2$- (NO)(Ph$_3$P)$_2$, RhCl(CO)(Ph$_3$P)$_2$, RhCl(Ph$_3$P)$_3$, Pt(Ph$_3$P)$_n$ [n = 3, 4], Pt(CO)$_2$(Ph$_3$P)$_2$, Pt(C$_2$H$_4$)(Ph$_3$P)$_2$, Pd(Ph$_3$P)$_2$. The nickel complex, Ni(CO)$_2$(Ph$_3$P)$_2$, was purchased from Alfa Inorganics, Inc. and used without further purification.

Tetracyanoethylene oxide, trans-1-cyano-1,2-diphenyloxirane, tetraphenylcyclopentadienone, 2,5-dimethyl-3,4-diphenylcyclopentadienone, N-acetyl-cyclopropenoxime, 1,1-diamino-2,2-dicyanoethylene, and 1,1-bis(dimethylamino)-2,2-dicyanoethylene were prepared by literature methods.

Tetracyanoethylene, fumaronitrile, cinnamonitrile, dimethylacetylene dicarboxylate, trans-stilbene oxide, diaminomaleonitrile, and cycloheptatrienone were purchased from Aldrich Company and used without further purification.

2. Instrumentation
Infrared spectra were measured on a Perkin-Elmer 621 grating infrared spectrophotometer over the 4000-200 cm\(^{-1}\) range with cesium iodide plates for solid mulls of Nujol or hexachlorobutadiene. Benzene, chloroform, or dichloromethane solutions were measured in 0.9 mm sodium chloride cells over the 4000-600 cm\(^{-1}\) range. Abbreviations used to describe infrared band intensities and widths are: s-strong; vs-very strong; m-medium; w-weak; sp-sharp; br-broad; and sh-shoulder. Band positions are reported in cm\(^{-1}\).

The proton nmr spectra were measured in CDCl\(_3\) on a Varian model VA-60 spectrophotometer at 60 MHz.

Melting points were taken on a Fisher-Johns Melting Point Apparatus and are uncorrected.

A Hewlett-Packard Model 302 Vapor Pressure Osmometer with a non-aqueous probe was used to determine molecular weights. Benzil solutions from 0.005-0.010 m concentrations were measured to give a calibration curve for chloroform and dibromomethane.

Elemental Analyses were performed by Mr. Ralph Seab, Department of Chemistry, Louisiana State University-Baton Rouge.

3. General Preparative Techniques

Reactions were carried out in solvents under a nitrogen atmosphere using Schlenk glassware. In reactions
in which precipitation occurred in the reaction solvent, the product was filtered and dried under nitrogen or vacuum. Recrystallizations from appropriate solvents or solvent systems followed when necessary. Air sensitive products were recrystallized under inert atmosphere. If the product did not precipitate during the course of the reaction either a polar solvent such as methanol or ethanol or a hydrocarbon solvent such as hexane or petroleum ether was added to the reaction solution to cause precipitation.
B. Epoxide Reactions

1. Reactions of Pt(Ph₃P)ₙ [n = 3, 4] with Tetracyanoethylene Oxide

a) Preparation and Characterization of Pt(Ph₃P)₂-
   \([C₂(CN)₄O]^{-}\) from Pt(Ph₃P)₄

To a 30 ml solution of tetrakis(triphenylphosphine)platinum(0) (0.62 g, 0.50 mmol) in benzene was added an equimolar amount of tetracyanoethylene oxide (0.72 g, 0.50 mmol) at room temperature. The initial yellow solution turned golden brown upon addition of the cyano-substituted oxirane. Methanol was added to the solution and under reduced pressure solvent was removed until precipitation occurred. The precipitate was filtered and dried in the air and was recrystallized from dichloromethane/methanol yielding light yellow crystals [0.38 g, 86%; mp, 210°C (dec)].

**Anal.** Calcd for C₄₃H₃₀N₄OP₂Pt: C, 58.30; H, 3.50; N, 6.49; mol wt, 863. Found: C, 58.04; H, 3.32; N, 6.43; mol wt, 890 (dibromomethane).

Infrared (Nujol): 2218 s (CN), 1080 s (Pt-O-C)

b) Preparation and Characterization of Pt(Ph₃P)₃-
   \([C₂(CN)₄O]^{-}\) from Pt(Ph₃P)₃

The bright orange crystals of tris(triphenylphosphine)platinum(0) (0.50 g, 0.50 mmol) were stored under an inert atmosphere to prevent reaction with oxygen and a 50 ml dichloromethane portion was used to dissolve these crystals. Tetracyanoethylene oxide (0.10 g, 0.7 mmol) was
added with the exclusion of oxygen and the solution stirred for 0.5 hr. The initial bright orange solution changed to a golden brown upon addition of the epoxide. Methanol was added to the solution and under reduced pressure solvent was removed until precipitation occurred. The yellow crystals were filtered and dried under vacuum and then recrystallized from dichloromethane/methanol to yield light yellow crystals (0.4 g, 90%).

The analytical and spectral data matched that reported for the reaction product in (a).

2. Reaction of Pt(CO)$_2$(Ph$_3$P)$_2$ with Tetracyanoethylene Oxide: Preparation and Characterization of Pt(Ph$_3$P)$_2$-[C$_2$(CN)$_4$O]

Solid dicarbonylbis(triphenylphosphine)platinum(0) (0.38 g, 0.50 mmol) was dissolved in 50 ml of dichloromethane. Excess tetracyanoethylene oxide (0.10 g, 0.70 mmol) was added with stirring. Methanol was added to effect solution of the ligand and the solution was stirred for 0.25 hr. Under reduced pressure solvent was removed until precipitation occurred. The yellow crystals were recrystallized from dichloromethane/methanol (0.4 g, 90%).

The analytical and spectral data match that for the two complexes reported above in 1(a) and 1(b).

3. Reactions of trans-MX(CO)(Ph$_3$P)$_2$ [$M = Ir$, $X = Cl, Br$; $M = Rh$, $X = Cl$] with Tetracyanoethylene Oxide
a) Preparation and Characterization of IrCl(CO)-(Ph₃P)₂[C₂(CN)₄O]

Solid trans-chlorocarbonylbis(tripheny!lphosphine)-iridium(I) (0.39 g, 0.50 mmol) was dissolved in a minimum amount (50 ml) of deoxygenated benzene under nitrogen and heated to reflux. Tetracyanoethylene oxide (0.072 g, 0.50 mmol) was also dissolved in a minimum amount (10 ml) of deoxygenated benzene and heated to reflux. The solutions were mixed under nitrogen and stirred for 2 hr while refluxing. The precipitation of a light brown powder [0.20 g, 44%; mp, 235-240°C (dec)] during this time was observed. The precipitate was filtered and dried under vacuum for 1 hr.

Anal. Calcd for C₄₃H₃₀ClIrN₄O₂P₂: C, 55.82; H, 3.27; N, 6.06; mol wt, 925. Found: C, 55.52; H, 3.13; N, 5.96; mol wt, 902.(dibromomethane).

Infrared (Nujol): 2218 m (CN), 2040 s (CO), 1075 s (Ir-O-C), and 310 w (Ir-Cl).

b) Preparation and Characterization of IrBr(CO)-(Ph₃P)₂[C₂(CN)₄O]

The compound trans-bromocarbonylbis(triphenylphosphine)iridium(I) (0.39 g, 0.50 mmol) was dissolved in a minimum amount (60 ml) of deoxygenated benzene under nitrogen and heated to reflux. Tetracyanoethylene oxide (0.72 g, 0.050 mmol) was dissolved in a minimum amount of deoxygenated benzene and heated to reflux. These two heated solutions were mixed and stirred under nitrogen at reflux temperature
for 1 hr. The solution changed from a bright yellow to a dark brown. A brown precipitate formed during this time and was filtered and dried under vacuum [0.2 g, 35%; mp, 230-235°C (dec)].

**Anal.** Calcd for C_{43}H_{30}BrIrN_{4}O_{2}P_{2}: C, 53.31; H, 3.12; N, 5.78. Found: C, 53.40; H, 2.85; N, 5.62.

Infrared (Nujol): 2220 m (CN), 2080-2070 s (CO), 1080 s (Ir-O-C).

c) Preparation and Characterization of RhCl(CO)-(Ph_{3}P)_{2}[C_{2}(CN)_{4}O]

To a 50 ml deoxygenated benzene solution of chlorocarbonylbis(triphenylphosphine)rhodium(I) (0.35 g, 0.50 mmol) heated to reflux was added as 10 ml solution of tetracyanoethylene oxide (0.072 g, 0.50 mmol) dissolved in benzene at reflux. The solution was stirred under nitrogen. There was an immediate orange precipitate which was filtered and dried under vacuum [0.34 g, 75%; mp, 182-185°C (dec)].

**Anal.** Calcd for C_{43}H_{30}ClN_{4}O_{2}P_{2}Rh: C, 61.85; H, 3.62; N, 6.71; mol wt, 833. Found: C, 61.98; H, 3.74; N, 6.44; mol wt, 890 (dibromomethane).

Infrared (Nujol): 2220 m (CN), 2080-2070 s (CO), 1080 s (Rh-O-C).

4. Reaction of IrH(CO)(Ph_{3}P)_{3} with Tetracyanoethylene Oxide
Yellow crystals of hydridocarbonyltris(triphenylphosphine)iridium(I) (0.50 g, 0.50 mmol) were dissolved in a minimum amount (40 ml) of deoxygenated toluene and cooled to -78°C. Tetracyanoethylene oxide (0.072 g, 0.50 mmol) was also dissolved in a minimum amount (5 ml) of deoxygenated toluene and cooled to -78°C. The reactant solutions were mixed under nitrogen at -78°C. There was no immediate visual change in the reaction solution. The solution was stirred and the temperature was allowed to rise to ambient condition. The reaction solution changed from a light yellow to an almond-brown. Deoxygenated absolute ethanol was added under nitrogen to cause further precipitation. There was a very small amount (0.01 g) of a brown-black solid which was filtered. The filtered material changed to an oil at room temperature under vacuum. Attempts to crystallize the oil were unsuccessful.

5. Reaction of IrH(CO)₂(Ph₃P)₂ with Tetracyanoethylene Oxide

To a 25 ml dichloromethane solution of hydridocarbonylbis(triphenylphosphine)iridium(I) (0.38 g, 0.48 mmol) was added solid tetracyanoethylene oxide (0.072 g, 0.50 mmol) under nitrogen at room temperature. The solution was stirred for 0.5 hr. Solvent was removed under reduced pressure and ether was added to precipitate a yellow-brown solid which was collected an a fritted filter and dried under vacuum for 0.5 hr.
Anal. Calcd for \( \text{C}_{44}\text{H}_{31}\text{IrN}_{4}\text{O}_{3}\text{P}_{2} \): C, 56.70; H, 3.13; N, 6.11. Found: C, 54.35; H, 3.15; N, 7.49.

Infrared (Nujol): 2220 m (CN), 2193 m, 2081 m, 1984 m, 1610 s.

NMR (CDCl\(_3\)): 7.75 br multiplet, 1.23 w doublet.

To a 100 ml deoxygenated toluene solution of hydridodicarbonylbis(triphenylphosphine)iridium(I) (0.78 g, 1 mmol) at -78°C was added a 20 ml solution of tetracyanoethylene oxide (0.144 g, 1 mmol) in deoxygenated toluene also at -78°C. The light yellow reaction solution was allowed to rise slowly in temperature with stirring to 0°C. At this temperature a slight darkening of the solution was observed. As the solution temperature rose to 15°C precipitate formed in the solution. The precipitate was filtered and dried under vacuum for 1.5 hr [(0.4 g; mp, >300°C)].


Infrared (Nujol): 2207 m (CN), 2196 m, 2173 m, 2150 m, 2078 m, 2051 m, 2028 s, 2004 vs, 1601 vs.

This yellow solid was chromatographed on a column of silica gel and three broad bands separated. Infrared spectrophotometric analysis on the brown solids showed loss of absorptions between 2000 and 2200 cm\(^{-1}\).

6. Reaction of \([\text{Ir(diphos)}_{2}]\text{Cl}\) with Tetracyanoethylene Oxide

Solid bis(1,2-diphenylphosphinoethane)iridium(I)
(0.50 g, 0.49 mmol) was dissolved in a minimum amount (25 ml) of dichloromethane under nitrogen. Colorless crystals of tetracyanoethylene oxide (0.072 g, 0.50 mmol) were added with stirring and 2 ml of methanol was also added to effect solution of the epoxide. The solution was stirred for 0.5 hr and then placed under reduced pressure to remove solvent until precipitation occurred. On formation of the precipitate the reaction mixture was cooled to -20°C overnight. A dark oil formed which was separated from the liquid layer. This oil was crystallized from chloroform/ethanol to give a dark brown solid [0.2 g, mp, 180-185°C].

Anal. Calcd for C_{58}H_{48}ClIrN_{4}OP_{4}: C, 59.20; H, 4.12; N, 4.79. Found: C, 52.37; H, 3.33; N, 6.48.

Infrared (Nujol): 2198 m, 2130 w, 1600 s br.

7. Reaction of RhCl(Ph₃P)₃ with Tetracyanoethylene Oxide

To a 50 ml dichloromethane solution of chlorotris(triphenylphosphine)rhodium(I) (1.25 g, 1 mmol) was added solid tetracyanoethylene oxide (0.288 g, 2 mmol). The solution changed from a deep burgandy to deep orange-brown on addition of the epoxide. The reaction was stirred for 1 hr with no visible change. Under reduced pressure approximately half the solvent was removed and methanol was added slowly to cause precipitation of an orange-brown solid [0.3 g; mp, 98-140°C] which was filtered and dried under a nitrogen stream for 0.5 hr.
Calcd for C\(_{42}H_{30}Cl_2N_4OP_2\)Rh\(_2\): C, 53.36; H, 3.19; N, 5.93. Found: C, 53.20; H, 3.30; N, 6.13.

Infrared (Nujol): 2220-2200 m (CN), 2170 sh, 1612 s br.

Recrystallization of the solid from dichloromethane/methanol yielded a brown solid.

Calcd for C\(_{42}H_{30}N_4\)NiOP\(_2\): C, 63.82; H, 4.13; N, 7.71. Found: C, 38.00; H, 2.45; N, 17.63.

Infrared (Nujol): 2250 sh, 2220 s br, 2175 s, 1600 s br.

Attempts at recrystallization yielded darker solids with essentially the same infrared spectral features but variant analytical data.

8. Reaction of Ni(CO)\(_2\)(Ph\(_3\)P)\(_2\) with Tetracyanoethylene Oxide

Off-white crystals of dicarbonylbis(triphenylphosphine)nickel(0) (0.32 g, 0.50 mmol) were dissolved in deoxygenated dichloromethane and cooled to -78°C. Tetracyanoethylene oxide (0.072 g, 0.50 mmol) was added to the solution with stirring. The light yellow solution was allowed to rise in temperature to -20°C and kept at this temperature overnight. A light yellow precipitate was formed during this time and this solid was filtered and dried under vacuum. As the solid warmed to room temperature it slowly darkened.

Calcd for C\(_{42}H_{30}N_4NiOP_2\): C, 63.82; H, 4.13; N, 7.71. Found: C, 38.00; H, 2.45; N, 17.63.

Infrared (Nujol): 2250 sh, 2220 s br, 2175 s, 1600 s br.

Attempts at recrystallization yielded darker solids with essentially the same infrared spectral features but variant analytical data.
9. Reaction of Pd(Ph$_3$P)$_4$ with Tetracyanoethylene Oxide

To a 100 ml deoxygenated benzene solution of tetrakis(triphenylphosphine)palladium(0) (1.1 g, 1 mmol) heated to reflux was added tetracyanoethylene oxide (0.144 g, 1.0 mmol) under nitrogen. The solution was stirred for 1 hr at reflux. The volume of the solution was reduced under lower pressure and deoxygenated methanol was added until precipitation occurred. The light yellow solid was filtered and dried under vacuum for 1 hr [0.4 g, mp, 235-240°C].

Anal. Calcd for C$_{44}$H$_{30}$N$_2$OP$_2$Pd: C, 65.71; H, 4.02; N, 5.60. Found: C, 65.41; H, 4.21; N, 5.51.

Infrared (Nujol): 2185 m, 2165 sh, 2135 w, 1590 s.

Recrystallization of the light yellow solid from dichloromethane/methanol gave a yellow powder, mp, 180-190° C.

Anal. Found: C, 65.41; H, 4.04; N, 5.88.

Infrared (Nujol): 2180 w, 2140 w, 1600 s.

10. Reaction of Pt(Ph$_3$P)$_4$ with trans-1-Cyano-1,2-Diphenyloxirane

The yellow crystalline complex tetrakis(triphenylphosphine)platinum(0) (0.21 g, 0.15 mmol) was dissolved in 30 ml of benzene under nitrogen. Solid trans-1-cyano-1,2-diphenyloxirane (0.04 g, 0.20 mmol) was added. The solution was stirred for 2 hr and then under reduced pressure solvent was removed. The residue was dissolved
in a minimum amount of dichloromethane and methanol slowly added causing a yellow solid to precipitate. The yellow solid was filtered and dried under vacuum for 0.5 hr [0.1 g, mp, 265 - 272°C].

**Anal.** Calcd for C₈₇H₇₁NOP₄Pt₂: C, 62.98; H, 4.32; N, 0.84. Found: C, 62.63; H, 4.66; N, 1.40.

Infrared (Nujol): 2183 w, 1606 s.

11. Attempted Reaction of trans-IrCl(CO)(Ph₃P)₂ with trans-1-Cyano-1,2-diphenyloxirane

To a solution of trans-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.39 g, 0.50 mmol) in 100 ml of benzene at room temperature was added solid trans-1-cyano-1,2-diphenyloxirane (0.11 g, 0.5 mmol). The solution was stirred for 0.5 hr and a sample portion taken and analyzed by infrared spectroscopy. The sample showed no change in the absorption patterns of the reactants. This monitoring system was continued for 24 hr. There was no reaction.

12. Attempted Reaction of Pd(Ph₃P)₄ with trans-1-Cyano-1,2-diphenyloxirane

The yellow crystalline complex tetrakis(triphenylphosphine)palladium(0) (0.50 g, 0.43 mmol) was dissolved in a minimum amount (30 ml) of dichloromethane. Solid trans-1-cyano-1,2-diphenyloxirane (0.12 g, 0.55 mmol) was added to the solution with stirring. The solution was stirred for 1 hr. Methanol was added to cause precipitaion
of a yellow solid. An infrared spectrum of the solid showed it to be the unreacted starting complex, Pd(Ph₃P)₄. There was no reaction.

13. Reaction of Pt(Ph₃P)₄ with trans-stilbene oxide

Tetrakis(triphenylphosphine)platinum(0) (0.47 g, 0.38 mmol) was dissolved in 40 ml of dichloromethane at room temperature. Trans-stilbene oxide (0.074 g, 0.38 mmol) was added. The solution was stirred for 48 hr. Methanol was added and the mixture allowed to stand until a gold solid precipitated. The solid was filtered and dried under vacuum [0.2 g; mp, 260-280°C (dec)].

Anal. Calcd for C₈₆H₇₂O₂P₄Pt: C, 63.14; H, 4.44; Found: C, 62.44; H, 4.72.

Infrared (Nujol): 1250 w.

The filtrate was placed under reduced pressure and solvent removed. Methanol was added and the mixture allowed to dry leaving a white solid, mp, 270-280°C (dec).


Infrared (Nujol): 1250 w.

This reaction was repeated in the same manner except the reaction time was shortened to 1 hr. Tetrakis(triphenylphosphine)platinum(0) (1.24 g, 1 mmol) was dissolved in 40 ml of dichloromethane. Trans-stilbene oxide (0.192 g, 1 mmol) was added to the reaction solution and a precipitate was formed. The gold crystals were
filtered and dried under vacuum [0.4 g; mp, 270 - 300°C (dec)].
Anal. Found: C, 62.96; H, 4.66.
Infrared (Nujol): 1570 w.
The gold crystals decompose slowly at room temperature.

14. Attempted Reaction of trans-IrCl(CO)(Ph₃P)₂ with trans-Stilbene Oxide

Yellow crystals of trans-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.39 g, 0.50 mmol) were dissolved in 100 ml of benzene at room temperature. Trans-stilbene oxide (0.10 g, 0.50 mmol) was added and the mixture stirred at reflux temperature under nitrogen for 6 hr. A sample portion of the reaction solution was taken and analyzed by infrared spectroscopy to determine if any change had occurred. The spectra revealed that there had been no change in either of the absorption patterns of the reactants. There was no reaction.

15. Attempted Reaction of Pd(Ph₃P)₄ with trans-Stilbene Oxide

Tetrakis(triphenylphosphine)palladium(0) (0.47 g, 0.38 mmol) was dissolved in 40 ml of dichloromethane. Trans-stilbene oxide (0.10 g, 0.70 mmol) was added. The solution was stirred for 1 hr. Under reduced pressure solvent was removed until precipitation occurred. Infrared analysis of the yellow solid showed no reaction.
III. RESULTS OF THE EPOXIDE REACTIONS

The reactions of epoxides with some iridium(I), rhodium(I), palladium(0), and platinum(0) substrates have produced a number of new complexes containing epoxides and fragments of epoxides. The complexes of tetracyanoethylene oxide are stable to air in the solid state, crystalline and range in color from white to light brown. The crystalline platinum complex Pt(Ph₃P)₂[C₂(CN)₄O] was obtained from the reaction of tetracyanoethylene with Pt(Ph₃P)₄, Pt(Ph₃P)₃ and Pt(CO)₂(Ph₃P)₂. The isolated iridium and rhodium complexes MX(CO)(Ph₃P)₂[C₂(CN)₄O] (M = Ir, X = Cl, Br; M = Rh, X = Cl) were formed by the reaction of the coordinatively unsaturated MX(CO)(Ph₃P)₂ with tetracyanoethylene oxide. The rhodium, iridium, nickel, and palladium compounds which reacted with tetracyanoethylene oxide but did not afford well characterized products are IrH(CO)(Ph₃P)₃, IrH(CO)(Ph₃P)₂, [Ir(diphos)₂]Cl, RhOl(Ph₃P)₃, Ni(CO)₂(Ph₃P)₂, and Pd(Ph₃P)₄.

Two other epoxides were used in this study with little success. Trans-1-cyano-1,2-diphenyloxirane and trans-stilbene oxide reacted with Pt(Ph₃P)₄ to give products which were characterized as [Pt(Ph₃P)₂]₂ (substituted oxirane). No reaction was observed to occur between these substituted oxiranes and iridium(I) and palladium(0) complexes.

The reactivity of the epoxides is determined by
the substituents on the carbon atoms of the oxirane ring. Tetracyanoethylene oxide reacted with every low valent transition metal complex tested. The trans-l-cyano-1,2-ciphenyloxirane and trans-stilbene oxide reacted only with Pt(Ph₃P)₄. Reactivity of the epoxide is increased when the epoxide is activated by the presence of electronegative cyanide groups rather than by the presence of the phenyl groups. No differentiation between the stilbene- and cyano-substituted stilbene oxides was observed as to reactivity.
IV. DISCUSSION OF EPOXIDE REACTIONS

A. Tetracyanoethylene Oxide Chemistry

Reactions described in the Experimental section II of this Dissertation show that tetracyanoethylene oxide reacts with unsaturated noble metal complexes by oxidative addition to give saturated metallocycles, eq. 13. Tetra-

\[
\begin{align*}
M + & \text{NC}_3H_3O \rightarrow M(O)(\text{NC})_3 \quad (13)
\end{align*}
\]

cyanocyclopropane has been shown to react with Pt(Ph\(_3\)P)\(_4\) by replacing two of the triphenylphosphine groups and incorporating the substituted platinum atom into a metallo-

cyclobutane ring.\(^{45,96}\) Addition of an equimolar amount of tetracyanoethylene oxide to a benzene solution of Pt(Ph\(_3\)P)\(_4\) caused a yellow color of the solution to change to a golden brown. Methanol was added to the solution and solvent was removed under reduced pressure until precipitation occurred. The light yellow crystals which formed are stable to 210°C (dec). Infrared spectral data of this solid provided some indication of the possible structure of this complex, Figure 1. A Nujol mull of these yellow crystals revealed two absorptions which could not be attributed to the triphenylphosphine ligands. The higher
Selected Infrared Absorptions of the Complex

\[ \text{Pt(Ph}_3\text{P)}_2\text{[C}_2\text{(CN)}_4\text{O]} \]

(Nujol Mull)
energy absorption at 2218 cm$^{-1}$ is attributed to a $\nu_{\text{CN}}$ nitrile absorption. The cyanide ligand could be bound to the metal in a variety of ways. A list of some platinum complexes with various CN infrared absorptions is given in Table I. The absorption at 2218 cm$^{-1}$ is attributed to a -CN bonded to an organic portion of the complex rather than bonded to the metal directly or $\sigma$-bonded through the nitrogen of the nitrile to the metal. Another possibility is the $\pi$-bonding to the metal of the carbon-nitrogen triple bond. However, an example of this mode of bonding has yet to be verified. The second absorption of interest was recorded at 1080 cm$^{-1}$ and is attributed to a possible linkage in the metallo-cyclobutane ring. Bellamy has reported that cyclic four membered rings exhibit an absorption in this region which is attributed to the C-O-C linkage.

It would be reasonable to consider this reaction as the attack of a nucleophilic reagent on the oxirane ring. It has been shown that in solution platinum(0) complexes of the type $\text{ML}_4$ will dissociate as described in eq. 14

$$\text{ML}_4 \rightarrow \text{ML}_3 \rightarrow \text{ML}_2$$

(14)

providing the nucleophilic species $\text{Pt(Ph}_3\text{P)}_2$. Parker and Isaacs have formulated what appears to be the most acceptable model to account for the large number of nucleophilic reactions which ethylene oxides undergo. Initial attack of the nucleophilic species on
TABLE I
CN STRETCHING FREQUENCIES OF SOME PLATINUM COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{CN}$ (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-PtH(CN)(Ph$_3$P)$_2$</td>
<td>2142</td>
<td>100</td>
</tr>
<tr>
<td>cis-Pt(CN)$_2$(Ph$_3$P)$_2$</td>
<td>2148, 2142</td>
<td>101</td>
</tr>
<tr>
<td>trans-PtH(NCS)(Ph$_3$P)$_2$</td>
<td>2092</td>
<td>100</td>
</tr>
<tr>
<td>Pt(NCS)$_2$(Ph$_3$P)$_2$</td>
<td>2097</td>
<td>102</td>
</tr>
<tr>
<td>PtH(TCM)(Ph$_3$P)$_2^a$</td>
<td>2025, 2175</td>
<td>103</td>
</tr>
<tr>
<td>Pt(NCCH$_3$)$_2$Cl$_2$</td>
<td>2320</td>
<td>104</td>
</tr>
<tr>
<td>Pt(TCNE)(Ph$_3$P)$_2$</td>
<td>2220</td>
<td>105</td>
</tr>
</tbody>
</table>

a) TCM is the tricyanomethanide anion
one of the ring carbon atoms of the oxirane ring and breaking of the \(-\) bond between the carbon attacked by the nucleophile and the oxygen atom comprise the essence of these reactions, eq. 15. Following this line of thought

\[
\begin{align*}
\text{\includegraphics{diagram.png}}
\end{align*}
\]

concerning the reaction between the platinum metal complex and tetracyanoethylene oxide, one would have to conclude that \(\text{Pt(Ph}_3\text{P)}_2\) acts as the nucleophilic species and attacks the ring carbon and causes the opening of the C-O bond. Since the platinum complex is still unsaturated at this point, it is reasonable that the alkoxide end of the open oxirane structure would attach itself to the platinum atom to complete the metallocyclopropyl ether.

Originally this complex was reported and formulated as the insertion product of \(\text{PtL}_2\) into the carbon-carbon bond of the oxirane ring.\(^{45,106}\) This formulation was by analogy to the reaction of \(\text{PtL}_4\) with 1,1,2,2-tetracyano-cyclopropane, eq. 16.\(^{107}\)
These reaction products were formulated in the same manner as the previous platinum complexes with cyclopropanes as metallocyclobutanes. These investigators assumed that the carbon-carbon bond between the cyano-substituted carbons had been broken and the metal included in the symmetrical metallocyclooxabutane. The tetracyanoethylene oxide-platinum complex was analogously formulated.

In a subsequent study Schlodder, Ibers, Lenarda, and Graziani reported the crystal and molecular structure from three-dimensional X-ray data of $\text{Pt}(\text{Ph}_3\text{As})_2[\text{C}_2(\text{CN})_4\text{O}]$. This structural data showed that the tetracyanoethylene oxide was bonded to the platinum as a metallaoxacyclobutane. The $\text{Pt}(\text{Ph}_3\text{As})_2$ fragment was included in the ring between a carbon and an oxygen atom. Chatt and Davidson described a similar oxidative addition process in the reaction of $\text{IrCl(CO)}(\text{Ph}_3\text{P})_2$ with hydrogen in which they formulated the mechanism of the reaction as insertion of the iridium atom into the H-H bond. Chock and Halpern carried out the first kinetic study of oxidative addition to the compound $\text{IrCl(CO)}(\text{Ph}_3\text{P})_2$ with $\text{H}_2$ an addendum A-B. It was suggested
that the alkylation of the iridium complex be considered as a bimolecular displacement (S_N^2) reaction at the carbon atom. The iridium atom acts as a nucleophile in the reaction on the carbon atom.

In the light of these previous studies one can readily formulate a mechanism, eq. 17, for this reaction

\[
\text{in which the nucleophile is the } \text{Pt} (\text{Ph}_3\text{P})_2 \text{ species. Attack on the ring carbon by the nucleophilic platinum atom would cause a weakening of the C-O bond on the same carbon. This reaction could not be considered a "true" } S_N^2 \text{ type in that the transition state does not allow the linear allignment of the incoming nucleophile, the carbon atom and the leaving oxygen atom due to the geometry of the epoxide ring. However, this process is very similar to the } S_N^2 \text{ mechanism.}

\text{Tris(triphenyolphosphine)platinum(0) and tetracyanoethylene oxide react readily to form the same light yellow crystals as had the tetrakis(triphenyolphosphine)-platinum(0) complex on reaction with the tetracyanoethylene oxide. This reaction must be kept more rigorously oxygen free due to the extreme reactivity of } \text{Pt} (\text{Ph}_3\text{P})_3 \text{ with oxygen. This complex has exactly the same infrared spectral}
data, analytical data, and melting point as did the product of the \( \text{Pt(Ph}_3\text{P)}_4 \) and tetracyanoethylene oxide reaction.

The reaction of \( \text{Pt(CO)}_2(\text{Ph}_3\text{P})_2 \) with tetracyanoethylene oxide also gave the same product as the two previous reactions. The platinacyclopentyl ether, or platinoaocyclobutane as one prefers, is produced in each case by nucleophilic attack of the \( \text{Pt(Ph}_3\text{P)}_2 \) on the epoxide ring at the carbon atom causing cleavage of the C-O bond. Closure of the ring by attachment of the alkoxide formed to the platinum atom results in a saturated metalloccyclic complex.

New complexes of \( \text{MX(CO)(Ph}_3\text{P)}_2[C_2(\text{CN})_4\text{O}] \) \( M = \text{Ir}, X = \text{Cl, Br}; M = \text{Rh}; X = \text{Cl} \) were prepared by allowing trans- \( \text{MX(CO)(Ph}_3\text{P)}_2 \) and tetracyanoethylene oxide to react in benzene at reflux under an inert atmosphere. Infrared spectral data, Figures 2, 3 and 4, show a strong absorption in the range of 2040-2080 cm\(^{-1}\) which is attributed to a M(III)-carbonyl stretching frequency. Table II lists some comparative stretching frequencies of iridium complexes with one carbonyl incorporated. Complexes with electron withdrawing substituents form six coordinate complexes whose carbonyl stretching frequencies are shown to range from 2040-2080 cm\(^{-1}\). One must consider the 2045 cm\(^{-1}\) absorption for the Vaska’s compound addition product to indicate a six coordinate iridium(III) structure. An absorption at 2218 cm\(^{-1}\) again is attributed to a nitrile
FIGURE 2

Selected Infrared Absorptions of the Complex

$\text{IrCl(CO)(Ph}_3\text{P)}_2[\text{C}_2(\text{CN})_0]$

(Nujol Mull)
FIGURE 3

Selected Infrared Absorptions of the Complex

\[ \text{IrBr(CO)(Ph}_3\text{P)}_2[C_2(CN)_4O] \]

(Nujol Mull)
FIGURE 4

Selected Infrared Absorptions of the Complex

\[ \text{RhCl(CO)(Ph}_3\text{P)}_2[\text{C}_2(\text{CN})_4\text{O}] \]

(Nujol Mull)
TABLE II

CARBONYL STRETCHING FREQUENCIES OF SOME IRIDIUM(I) AND (III) COMPLEXES

<table>
<thead>
<tr>
<th>Complexes</th>
<th>CO cm⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Four-Coordinate Complexes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrCl(CO)(Ph₃P)₂</td>
<td>1960</td>
<td>112</td>
</tr>
<tr>
<td>Ir(TCM)(CO)(Ph₃P)₂</td>
<td>2005</td>
<td>113</td>
</tr>
<tr>
<td><strong>Five-coordinate Complexes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrH(CO)(Ph₃P)₃</td>
<td>1930</td>
<td>77</td>
</tr>
<tr>
<td>IrCl(CO)(SO₂)(Ph₃P)₂</td>
<td>2020</td>
<td>114</td>
</tr>
<tr>
<td><strong>Six-coordinate Complexes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrCl₃(CO)(Ph₃P)₂</td>
<td>2078</td>
<td>114</td>
</tr>
<tr>
<td>IrCl(CO)(Ph₃P)₂(TCNE)</td>
<td>2075</td>
<td>115</td>
</tr>
<tr>
<td>IrCl(CO)(Ph₃P)₂(C₂F₄)</td>
<td>2040</td>
<td>116</td>
</tr>
<tr>
<td>IrClII(CF₃)(CO)(Ph₃P)₂</td>
<td>2060</td>
<td>117</td>
</tr>
</tbody>
</table>
bonded to a carbon atom in the addendum following arguments above. The absorption at 1072-1075 cm\(^{-1}\) is attributed to the metal-oxygen-carbon stretch of an alkoxy substitution similar to a cyclic four membered ether linkage which Bellamy reports has an absorption for the C-O-C stretch between 1100 and 1050 cm\(^{-1}\).\(^{111}\)

Chock's and Halpern's description of the alkylation of iridium complexes in which a nucleophilic attack of the iridium atom on the carbon atom takes place, eq. 18, is

\[
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{CO} \quad \text{RX} \quad \left[\text{Ph}_3\text{P}\right]_2\text{Y(CO)Ir---R---X}\]

\[
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{CO} \quad \left[\text{Ph}_3\text{P}\right]_2\text{Y(CO)Ir---R---X}\]

\[
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{CO} \quad \left[\text{Ph}_3\text{P}\right]_2\text{Y(CO)Ir---R---X}\]

(18)

applicable to the iridacycle complex formation from \(\text{IrX(CO)(Ph}_3\text{P)}_2\) and tetracyanoethylene oxide.

The reaction of \(\text{RhCl(CO)(Ph}_3\text{P)}_2\) with tetracyanoethylene oxide proceeded as did the analogous iridium reaction. The four-coordinate rhodium(I) complex oxidatively added tetracyanoethylene oxide to form a six-coordinate \(\text{Rh(III)}\) complex. The infrared spectrum, Figure 4, of the brown crystals shows the carbonyl stretching frequency after addition of the oxirane was recorded at 2070-2080 cm\(^{-1}\) indicating a six coordinate structure. The medium strength
absorption at 2220 cm\(^{-1}\) again corresponds to a nitrile bonded to an organic part of the complex. The 1080 cm\(^{-1}\) absorption indicates the M-O-C linkage.\(^{111}\) The formation of complex III is considered to be the same as for the platinum and iridium complexes.

A toluene solution of hydridocarbonylytris(triphenylphosphine)iridium(I) was mixed with an equimolar amount of tetracyanoethylene oxide at -78\(^\circ\)C with no visible change. The solution was allowed to warm slowly to room temperature and the solution changed from a bright yellow to a rich almond color. Absolute ethanol was added to cause precipitation and a small amount of a dark brown solid was removed by filtration and placed under vacuum for 2 hr. After this period of time the solid changed to a dark brown tar. An infrared spectrum of the tar showed no characteristic absorptions of the starting materials or any which could be attributed to a new complex. All solids isolated from the reaction of this iridium hydride and tetracyanoethylene oxide decomposed so rapidly that characterization was not possible.

A toluene solution of hydridodicarbonylbis(triphenylphosphine)iridium(I) was mixed with an equimolar
amount of tetracyanoethylene oxide and allowed to react in
the same manner. Again there was no reaction at -78°C and
the temperature was allowed to rise to room temperature.
A light yellow solid precipitated. This solid was filtered
and dried under vacuum. The infrared analysis of a Nujol
mull of the yellow powder showed eight significant absorp­
tions between 2220 and 2000 cm\(^{-1}\). This supposed mixture
was chromatographed on a column of silica gel to give three
fractions all of which had the same infrared spectral
absorption pattern. No absorption between 2200 and 2000
cm\(^{-1}\) was observed. The reaction was attempted again in
dichloromethane at room temperature. Solvent was removed
from the flask under reduced pressure and ether added
causing precipitation. The solid was filtered and dried
under vacuum. The infrared pattern of this yellow-brown
solid was much simpler, as shown in Figure 5. A medium
strength doublet at 2220-2195 cm\(^{-1}\) is in the range to be
assigned to nitrile bonded to an organic part of the molecule.
A medium strength band at 2080 cm\(^{-1}\) is suggestive of a
carbonyl group coordinated to an Ir(III) atom. A medium
strength band at 1984 cm\(^{-1}\) and a strong band at 1610 cm\(^{-1}\)
are not easily assigned. The 1984 cm\(^{-1}\) band is in the range
of some five coordinate iridium(I) complexes containing at
least one carbonyl. The 1610 cm\(^{-1}\) absorption is in the
range to be considered the C=\(\equiv\)C absorption of the tricyano­
ethenolate ion\(^{118}\) Chromatography of this product on a
silica gel column gave a solid which showed only two weak,
FIGURE 5

Selected Infrared Absorptions of the Yellow Crystalline Product Formed in the Reaction of Tetracyanoethylene Oxide and IrH(CO)$_2$(Ph$_3$P)$_2$

(Nujol Mull)
broad bands at 2200 and 1670 cm\(^{-1}\) when analyzed by infrared spectrophotometry. Recrystallization of the original yellow brown product from dichloromethane/ether gave a solid which had the same infrared spectral absorptions as the initial product but different analytical data. The proton nmr signals of a CDCl\(_3\) solution of the yellow-brown solid showed two absorptions. A broad multiplet at 7.5 ppm is assigned to phenyl protons of the phosphine ligands. The origin of a small doublet at 1.23 ppm is unknown. The ratio of these absorptions is approximately 30:1. There was no absorption to indicate that the iridium-hydride bond was still intact. No assignment of a possible structure can be made at this time.

The reactions of tetracyanoethylene oxide with [Ir(diphos)\(_2\)]Cl, Ni(CO)\(_2\)(Ph\(_3\)P)\(_2\), and RhCl(Ph\(_3\)P)\(_3\) are similar to the above reaction. In each case 1:1 molar reaction ratios were allowed to react in dichloromethane at room temperature. Each reaction produced a dark brown solid which was soluble in organic solvents and insoluble in alcohols. The infrared spectral data, Figures 6, 7, and 8, of Nujol mulls of the products were very similar in the positions and strengths of absorptions to each other and also to the spectra of tetraethylammonium tricyanoethenolate, Figure 9. As previously mentioned, reactions of certain nucleophiles, I\(^-\), with tetracyanoethylene oxide produces the tricyanoethenolate ion and the cyanide ion.\(^{71}\) Also
FIGURE 6

Selected Infrared Absorptions of the Brown Solid Product Formed in the Reaction of Tetracyanoethylene Oxide and $[\text{Ir(diphos)}_2]\text{Cl}$ (Nujol Mull)
FIGURE 7

Selected Infrared Absorptions of the Brown Solid Product Formed in the Reaction of Tetracyanoethylene Oxide and Ni(CO)₂(Ph₃P)₂ (Nujol Mull)
FIGURE 8

Selected Infrared Absorptions of the Brown Solid Product Formed in the Reaction of Tetracyanoethylene Oxide and RhCl(Ph₃P)₃ (Nujol Mull)
FIGURE 9

Selected Infrared Absorptions of Tetraethylammonium Tricyanoethenolate (Nujol Mull)
discussed above was the fact that transition metal atoms often act as nucleophiles in reactions with tetracyano-
ethylene oxide. In all cases analytical data was low for carbon percentages and high for nitrogen percentages when compared with calculated 1:1 values. Purification techniques caused further deviation from 1:1 calculated values in the directions indicated.

The reaction of $[\text{Ir(diphos)}_2]\text{Cl}$ with tetracyano-
ethylene oxide produced a dark oil upon cooling of the reaction solution. This oil was crystallized from chloroform/ether to give a dark brown solid. The infrared spectrum of a Nujol mull of this solid, Figure 5, showed two strong absorptions at $2198$ and $1612$ cm$^{-1}$ and a shoulder at $2170$ cm$^{-1}$. Since the solid was soluble in organic solvents it is probably not a salt. The analytical data for the brown solid show low values for carbon and hydrogen percentages as compared to the calculated percentages for a 1:1 formulation. Attempted purification by chromatography or recrystallization resulted in the isolation of tar-like solids which lost spectral absorptions mentioned above. A logical conclusion to draw from this evidence is that the reaction of tetracyanoethylene oxide with the iridium salt forms a complex like those formed with the platinum and iridium complexes reported above. This complex must not be stable due to the basicity of the iridium-diphos complex and the metallocyclobutane degrades to a tricyano-
ethenolate containing species. At ambient conditions further degradation seems to occur. No structural projection will be made. The reaction of RhCl(Ph₃P)₃ with tetracyanoethylene oxide in dichloromethane produced an orange-brown solid which was not fully characterized. A three band absorption pattern, Figure 8, of the infrared spectrum of the solid could be due to the presence of tricyanoethenolate ion in a new rhodium complex. Attack of the nucleophilic rhodium ion on one of the electron-deficient carbon atoms in the cyano-substituted epoxide ring could cause generation of the tricyanovinyl alcoholate ion as well as formation of a Rh-CN moiety. Due to lack of confirming analytical and molecular weight data, no structural proposal may be made.

The reaction of Ni(CO)₂(Ph₃P)₂ with tetracyanoethylene oxide produced initially a yellow solid at temperatures below 0°C. Isolation of this solid and attempts to characterize at ambient conditions resulted in a darkening of the solid to brown. Infrared analysis of a Nujol mull spectrum of the product, Figure 7, revealed a three band pattern again similar to the absorptions of the tricyanoethenolate ion. The spectra also reveals very weak absorptions in the characteristic ranges for triphenylphosphine. Analytical data for these brown solids are closest to agreement with a nickel-tricyanoethenolate compound which contains no phosphine ligands. There can be
no structural proposal made for this reaction product.

The reaction of \( \text{Pd(Ph}_3\text{P)}_4 \) with tetracyanoethylene oxide at 80°C in benzene produced a yellow solid which was not fully characterized. Figure 10 shows a portion of the infrared absorption pattern of the solid. The positions and strengths of the bands of interest lead to an interesting formulation for the product. A medium band found at 2185-2167 cm\(^{-1}\) could be assigned to a nitrile absorption bonded to an organic portion of the molecule. The shift of the absorption from the 2220-2200 cm\(^{-1}\) range of the nitrile bands in the metalloccycle complexes to lower energy values indicates a different environment in this complex. A weak band at 2135 cm\(^{-1}\) could represent a nitrile bonded directly to the transition metal. The strong, sharp band at 1590 cm\(^{-1}\) is in the range for the carbon-carbon double bond stretching frequency of the tricyanoethenolate moiety. These pieces of information would lead to the speculation of the formation of a palladium(II) complex containing two triphenylphosphine ligands, a metal-bonded cyanide ligand, and a metal-bonded tricyanoethenolate ligand. However, the analytical data for this yellow solid does not correspond to the calculated values for a 1:1 \( \text{Pd(Ph}_3\text{P)}_2 \) to tetracyanoethylene oxide ratio. The experimental data is consistent with a 1:1 \( \text{Pd(Ph}_3\text{P)}_2 \) to tricyanoethenolate ion ratio. The presence of the weak 2135 cm\(^{-1}\) band can not be explained without the metal-nitrile linkage being included in the
FIGURE 10

Selected Infrared Absorptions of the Yellow Solid Product formed in the Reaction of Tetracyanoethylene Oxide and Pd(Ph$_3$P)$_4$
(Nujol Mull)
structural considerations. Resolution of the structural verdict cannot be made without further data.

The reaction of Pt(Ph₃P)₄ with 1-cyano-1,2-diphenyloxirane at room temperature in benzene yielded a complex for which the analytical data indicate a 2:1 ratio of Pt(Ph₃P)₂ to oxirane. Infrared spectral analysis of the yellow solid reveal a weak band at 2183 cm⁻¹ assigned to a C-CN stretch and a strong band at 1606 cm⁻¹ which could arise from the C=C stretch of an ethenolate ion. These absorptions indicate possible formation of a cyanodiphenylethenolate ion on reaction of this oxirane with the Pt(Ph₃)₂ fragment. No proposal concerning structure will be made.

Reaction of 1-cyano-1,2-diphenyloxirane with IrCl(CO)(Ph₃P)₂ at room temperature was attempted, but it did not proceed. Attempted reaction of 1-cyano-1,2-diphenyloxirane with Pd(Ph₃P)₄ was also unsuccessful.

There was a reaction between Pt(Ph₃P)₄ and trans-stilbene oxide at room temperature. Two different compounds were isolated. A solution of equimolar amounts of the reactants in dichloromethane was stirred for 48 hr. Methanol was added and gold crystals precipitated and was removed by filtration. Under reduced pressure most of the dichloromethane was removed from the filtrate and methanol was added. A white solid precipitated and was isolated. Analysis of the gold crystals showed a 2:1 ratio of
Pt(Ph\textsubscript{j}P\textsubscript{2}) to stilbene oxide. Again there were no infrared absorptions which might give an indication of possible modes of bonding.

**Trans**-stilbene oxide was stirred in solution with IrCl(CO)(Ph\textsubscript{j}P\textsubscript{2})\textsubscript{2} and with Pd(Ph\textsubscript{j}P\textsubscript{2})\textsubscript{4}. No reaction was found with either of these coordinatively unsaturated complexes and the phenyl-substituted oxirane.

Relative reactivities of the various oxiranes tested with transition metal substrates are seen as a function of the substituents of the carbon atoms in the ring. The presence of electron-withdrawing or electron-donating groups on the oxirane ring is the most obvious determining factor to judge reactivity in the epoxides considered in this work. Tetracyanoethylene oxide containing the greatest number of electron-withdrawing groups has shown the highest degree of reactivity. As electrons are pulled from the ring to the nitrile groups, the ring is left more susceptible to attack. Tetracyanoethylene oxide reacted with every metal substrate which was examined.

The 1-cyano-1,2-diphenyloxirane and **trans**-stilbene oxide members of the epoxide family were tested to determine if any difference could be seen in the reactivities due to the presence of the cyanide group on the diphenyl-substituted compound. No difference was observed for these two epoxides with regard to reactivity.
V. INTRODUCTION - METAL-OLEFIN COMPLEXES

A. Review of Metal Complexes with Olefins

The first metal-olefin complex was prepared when Zeise in 1827 isolated a crystalline compound from the reaction of platinum(IV) chloride and ethanol.\textsuperscript{119,120} The compound was formulated as $\text{KCl}\cdot\text{PtCl}_2\cdot\text{C}_2\text{H}_4\cdot\text{H}_2\text{O}$. A large number of complexes with olefins were prepared but it was almost a century before the nature of the bonding was understood. There was much debate concerning the composition of the ethylene-platinum halide complexes.\textsuperscript{121-123} Birnbaum prepared by an independent method the same complex, $\text{K}[(\text{C}_2\text{H}_4)\text{PtCl}_3]\cdot\text{H}_2\text{O}$ in 1868 to substantiate the belief that ethylene had been bound to the metal.\textsuperscript{124}

Discussions of possible modes of bonding of olefinic hydrocarbons to metals have proceeded almost as far back as the initial discovery of metal-olefin complexes. Problems arose because it was necessary to explain how an olefin could become bonded to a metal since olefinic carbons do not possess a lone pair of electrons. A completely satisfactory explanation of the bonding between the olefinic ligand and the metal was not given until 1951 when Dewar showed the importance of the simultaneous donor and acceptor functions of both the metal and the olefin.\textsuperscript{125} Dewar introduced the thought that the interplay between molecular antibonding orbitals on the olefin and hybrid
orbitals on the metal could account for the surprising stability of silver-olefin complexes. Chatt and Duncanson in discussing Zeise's salt, used Dewar's description to explain the bonding between ethylene and the platinum atom atom. Overlap between the filled ethylene \( \pi \)-molecular orbital and one of the vacant platinum hybrid orbitals forms a bond with directional characteristics of electron flow from the ligand to the metal. There is also overlap between a vacant olefinic antibonding \( \pi^* \)-molecular orbital and a filled platinum hybrid atomic orbital which results in the formation of another bond with directional characteristics of electron flow from the metal to the ligand. This bonding back to the ligand from the metal gives the stability to metal-olefin \( \pi \)-complexes. X-ray crystallography confirmed the spatial arrangement of atoms required by the orbital overlap.

Ethylene and substituted ethylenes appear to form \( \pi \)-complexes only with transition metals and usually these metals are in the low oxidation states. Therefore more electrons are available for bonding from the metal to the olefin, and the stability of the metal-olefin complex is thereby increased. When olefins react with main group elements, \( \sigma \)-bonds are formed due to the fact that the energies of the metal orbitals required for possible back-bonding (usually \( d \)) are incompatible with those on the ligand. In the same manner alkyl-transition metal compounds
are σ-bonded since alkyl groups lack the necessary empty low lying antibonding π*-orbitals necessary for back-bonding from metal to ligand.

Reports in the literature of complexes of olefins with transition metals which show novel reactions are of interest. A five-coordinate iridium(I) ethylene compound, IrCl(C₂H₄)₄ has been isolated from a suspension of [IrCl(C₆H₁₄)₂]₂ in heptane after treatment with ethylene.¹²⁹ The most likely structure is the trigonal bipyramid with little or no molecular exchange between the ethylene molecules.

Ethylene reacts with Ru₃(CO)₁₂ and Os₃(CO)₁₂ to give two isomers which provide some information about a system which is analogous to the reaction of olefins with metal surfaces.¹³⁰ X-ray crystal structure of one of these isomers, VIII, revealed a transfer of two hydrogen atoms from the ethylene to the metal cluster and the concurrent
formation of two metal-carbon σ-bonds.

It has been reported that molybdenum and tungsten complexes of ethylene and cyclopentadienes are very easily protonated by weak acids to give the metal hydrides with the ethylene still complexed to the metal.\textsuperscript{131}

Reaction of IrCl(CO)(PhMe\textsubscript{2}P)\textsubscript{2} with ethylene in a methanol solution of tetraphenylborate resulted in the absorption of two molecules of ethylene per iridium and the compound [Ir(CO)(PhMe\textsubscript{2}P)\textsubscript{2}(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}]BPh\textsubscript{4} precipitated.\textsuperscript{132} The ethylene ligands can be displaced from the complex by diphenylacetylene or 2,3-dimethylbutadiene.

B. Review of Metal Complexes with Cyclic Olefinic Ketones

Interest in complexes of cyclopropenones with transition metals was first mentioned in the literature in connection with a study of the carbonylation of acetylenes to acrylic acids. C. W. Bird and J. Hudec studied the reaction of diphenylcyclopropenone with nickel carbonyl in benzene under the same conditions which were used in the reaction of diphenylacetylene with nickel carbonyl.\textsuperscript{133} The products of these two reactions were found to be the same, trans-α-phenylcinnamic acid and its ethyl ester. These workers concluded that diphenylcyclopropenone was not an intermediate in this conversion.

Later Bird and Hollins reexamined this reaction
and reported that under suitable conditions: diphenylcyclopropenone reacted with nickel carbonyl to give small amounts of a tris(diphenylcyclopropenone)nickel(0) carbonyl complex in addition to diphenylacetylene and tetracyclone. Reported infrared, analytical, and magnetic data led these workers to formulate the complex with the three diphenylcyclopropenone molecules complexed to the nickel through the double bond and a carbonyl in the fourth coordination site.\(^{134}\)

In 1967, Bird and Briggs reported the reactions of various metal salts with diphenylcyclopropenone.\(^{135}\) Zinc(II), cobalt(II), nickel(II), copper(II), ruthenium(II), rhodium(III), palladium(II), and platinum(II) and (IV) salts reacted with diphenylcyclopropenone to give complexes formulated as having two, three, or six molecules of diphenylcyclopropenone complexed to the metal atom through the carbonyl oxygen atom of the cyclic ketone. In this formulation the diphenylcyclopropenone molecule is considered to be in a dipolar form, eq. 19, due to the high dipole moment and basicity of the molecule. The dipolar structure would be very similar to well known ligands such
as N-pyridine oxides, phosphine oxides, and sulfoxides which are known to coordinate through the oxygen. These formulations, however, were made almost entirely on infrared spectral data. Very little analytical data were reported and therefore the metal to diphenylcyclopropenone ratios were determined by the ratios of the reactants used in the reactions.

In a further study of the possibility of isolating intermediates in the process of carbonylation of acetylene, Bird, Briggs, and Hudec reported the reactions of cyclopropenones with iron and cobalt carbonyls. Reactions of diphenyl- and dibutylcyclopropenone and cycloheptenocyclopropenone with dicobalt octacarbonyl gave complexes whose infrared spectra indicated the formation of the \([\text{(cyclopropenone)}_6\text{Co}][\text{Co(CO)}_4]_4\). Only the diphenylcyclopropenone complex was isolated in a purified form. The reaction of diphenylcyclopropenone with tri-iron dodecacarbonyl gave the same products as the reaction of diphenylacetylene with this iron carbonyl. There were no complexes isolated from this reaction which contained a ketone as a ligand. The reaction of diphenylcyclopropenone with di-iron nonacarbonyl yielded an acetylenic-diiron complex and two complexes which contained cyclic unsaturated ketones. Also in the product mixture was found a five membered unsaturated ring which included an iron atom and two ketone functions, V. This complex was presumably formed by a carbonyl
insertion in the proposed intermediate, VI. The carbon monoxide probably came from decarbonylation of the cyclopropenone.

Reaction of cycloheptenocyclopropenone with di-iron nonacarbonyl gave only one product, VII, and it was
speculated that carbonyl insertion was involved in forming the metallocyclopentendione.

Fichteman, Schmidt and Orchin also reported the \([\text{hexakis}(\text{diphenylcyclopropenone})\text{cobalt}][\text{tetracarbonyl-cobaltate}]\) as the reaction product of diphenylcyclopropenone and dicobalt octacarbonyl\(^{137}\) as did Bird and Briggs.\(^{135}\) This report\(^{137}\) in addition described the preparation of square planar complexes, trans-\(\text{PtCl}_2\) (diphenylcyclopropenone)(L) [L = ethylene, cis-2-butene, carbon monoxide, and tri-n-butylphosphine]. The diphenyl-cyclopropenone ligand was considered to be coordinated through the carbonyl oxygen to the platinum atom.

After some of the cyclopropenone work described in this Dissertation was published, Visser and Ramakers-Blom reported the reactions of cyclopropenones with platinum(0) phosphine complexes.\(^{138}\) Further comment will be held until this topic is considered in the appropriate Discussion section of this work.

The objective of this work is to determine the mode of bonding of cyclic ketones with metal substrates in low oxidation states and to isolate, if possible, any complexes which could shed some light on the homogeneous processed of carbonylation, decarbonylation, and carboxylation.
C. Review of Metal Complexes with Amine-Substituted Olefins

Initial attempts to prepare complexes of olefins substituted with amine groups were reported in 1883 by Liegermann and Paal.\textsuperscript{139} Reactions were conducted with boiling solutions of hexachloroplatinate(IV) salt and allyl amine. Compounds with the empirical formula (amine-H)PtCl\textsubscript{3} were isolated and reported.

Reaction between diallylamine and ammonium tetra-chloroplatinate(II) revealed two compounds, monomer and dimer, which were proposed to be complexes containing the diallylamine complexed by the two unsaturated carbon-carbon bonds to the platinum atoms.\textsuperscript{140}

Experiments to determine reaction products at different pH values were reported by Gelman and Essen in 1951.\textsuperscript{141} Treatment of potassium tetrachloroplatinate(II) with allyl amine in neutral solution resulted in the isolation of a compound for which two molecules of allylamine were complexed through participation of the double bond.

Cramer has reported the exchange of an ethylene molecule from the complex (acac)Rh(C\textsubscript{2}H\textsubscript{4})\textsubscript{2} in solution with \(N,N\)-bis(trifluoromethyl)vinylamine.\textsuperscript{142} However, the mixed complex (acac)Rh(C\textsubscript{2}H\textsubscript{4})[CH\textsubscript{2}=CHN(CF\textsubscript{3})\textsubscript{2}] was not isolated.

Unsaturated amines when in acid solution, tend to function as monodentate ligands due to the formation of the ammonium cation by addition of the proton to the
nitrogen atom. Formation of the monodentate complexes occurs between platinum(II) halides and the zwitterion $R_2N^+-(CH_2)_nCH=CH_2$ in dilute hydrochloric acid solution. Unsaturated amines have been reported to serve as bridging ligands of mono- and polynuclear complexes. By careful neutralization of the zwitterion complexes below $0^\circ C$, the $\pi$-bonded olefinic ammonium ions are converted to amines. The amine group then serves as a donor group to another complex molecule through its nitrogen atom. The chain like compounds are very insoluble and have the general formula $[R_NH(CH_2)_nCH=CH_2\text{PtCl}_2]_x$.

Copper halide complexes of allylamine have been reported in which a 3:1 ratio of reactants is observed. These complexes are very air-sensitive and easily lose two moles of allyl amine at room temperature to give colorless, air stable 1:1 complexes. From heats of formation and infrared spectra of the complexes it was concluded that the allylamine functions as a bidentate ligand, being coordinated to copper both through the amine and the C=C double bond. In the initially formed complex two of the allyl amines appear to be coordinated only through the amine group as indicated by infrared data of two additional allylamine absorptions.

Venanzi and workers reported that tertiary allylic amines react with palladium(II) halides in alcoholic solutions to give complexes bonded by a $\sigma$-aminoalkyl link-
age and the $\sigma$-amino-donor bond.\textsuperscript{146,147} Venanzi also showed by physicochemical measurements that the zwitterion complexes are true $\pi$-olefin complexes of the type discovered by Ziese, $\text{(olefin)}\text{PtCl}_3^-$, with no bonding to the ammonium cation.

There have been several major reviews concerning the reactions of ethylene and substituted ethylenes in the last few years.\textsuperscript{128,151-154} The most complete of these is a monograph by Heberhold which provides a complete literature survey on mono-olefin $\pi$-complexes of transition metals up to 1970.\textsuperscript{155} Since the area of organometallic chemistry is so large, this review has been concerned only with the reactions of metals with olefins similar to those studied as subjects of this Dissertation.

It was of interest to us to attempt the preparation of amino-olefin complexes in which the amino-function was bonded to the olefinic carbon atom. Such compounds are not known. In view of the electron donating ability of the amino-group, it might seem that the olefin-metal $\sigma$-bond strength would be enhanced. But of course, at the same time the metal-olefin $\pi$-bond would be expected to be less stable. Just what the net effect would be, it was hoped, could be learned from experimentation. This work is described in Sections VI and VII.
D. Review of Metal Nitrosyl Complexes with Activated Olefins

The chemistry of transition metal nitrosyls has been studied for many years and continues to be a subject of much interest. This study has to some extent followed the rise in attention devoted to organometallic chemistry especially the study of metal carbonyl complexes. Just as metal carbonyl complexes have shown catalytic activity, some metal nitrosyls are useful as selective homogeneous catalysts. Other nitrosyl complexes undergo reactions at the coordinated nitric oxide to give N-bonded organic compounds.156

Several excellent, comprehensive reviews on transition metal nitrosyl chemistry have been published in the past 10 years which provided the majority of the information for this overview.156-160 For many years prior to 1960 the principle interest in the chemistry of nitric oxide was the synthesizing of nitrosyl complexes. The bonding of nitric oxide to transition metals was initially described as involving either NO+ or NO- by Sidgwick in 1934.161 Lewis structures, IX and X, were used to picture these two methods the nitrosyl bonded to the metal atom. The linear and bent modes of bonding are still
used by some in discussing the chemistry of these complexes. These designations arise from the formalism used in coordination chemistry in which the electron pair in the metal-ligand σ-bond is associated entirely with the ligand for the purpose of assigning ligand charge and metal oxidation state. The existence metal-ligand π-bonding is ignored in the assignment of formal oxidation state, but since π-bonding is essential to the linear mode of nitrosyl coordination IX, these formalisms have been criticized due to the fact that these labels do not describe the physical realities of charge distributions, bond strengths, and bond angles.162 However, formalisms of this type are not meant to act as substitutes for detailed bonding descriptions but only as tools to aid in the conceptualization of the problem.

The older bonding concepts are of value in considering changes in the thinking concerning the bonding of nitric oxide. As well as acting as a doubly- or triply-bridging ligand, nitric oxide has been regarded as bonding to a metal in one of the following modes: by donation of one electron from an anti-bonding nitric oxide orbital to the metal followed by an additional electron-pair donation from NO⁺; by donation of two electrons to the metal from neutral NO; and by acceptance of one electron from the metal followed by electron pair donation from NO⁻. In these three cases nitric oxide functions as a three-electron donor, a two electron-donor, and a one electron-donor respectively.
Analogous to metal-carbonyl bonding, coordination of NO$^+$ to the metal center involves both σ and π bonding. Sidgwick proposed that the NO$^-$ moiety was analogous to the halide ion and structurally similar to the organic nitroso-compounds. The most frequently expressed view prior to 1960 was that the vast majority of nitrosyl complexes were linear in structural arrangement. There were no definite evidence available to confirm any other structural arrangement for metal-NO bonding.

Kettle had suggested that in M(CO)$_3$ systems that the metal would donate to different extents to the carbonyls due to the two π* orbitals of each of the carbonyl ligands. This will cause the M-C-O angle to deviate from linearity. Similarly, Enemark has shown that even in mononitrosyl species the M-N-O bond angle will deviate from linearity as long as the overall symmetry is less than C$_3$. Using these reasonings there may be reasons for the M-N-O relationship to deviate from the predicted angle due to other effects than the charge assigned to the nitrosyl ligand.

Infrared absorptions of the nitrosyl stretching frequency were used to infer the specific mode of bonding of the nitrosyl to the metal. NO$^+$ complexes were said to absorb in the range of 1700-1900 cm$^{-1}$ while NO$^-$ complexes were said to absorb in the region of 1500-1700 cm$^{-1}$. Neutral NO complexes were assumed to have bonds in either
of these regions.

In 1967 Ibers and Hodgson reported the first structurally documented bent nitrosyl complex. This report confirmed the bent model which had been suggested years earlier. The complex was a product of NO$^+$ and IrCl(CO)(Ph$_3$P)$_2$ in which the iridium complex served as an electron-pair donor to the nitrosyl in the product complex XI. This report also established that NO$^+$ could function as either an electron-pair acceptor or an electron-pair donor with the necessary $\pi$-backbonding. The infrared spectroscopy nitrosyl stretching frequency of the complex at 1680 cm$^{-1}$ fits very well the method of inferring the geometry of metal-nitrosyl angle from the nitrosyl absorption ranges quoted above. A summary of representative nitrosyl complexes and the appropriate structural and infrared data show very quickly that the method is not completely inclusive. Data for four, five, and six coordinate mono-nitrosyl transition metal complexes is given in Table III.

It is also easily seen from Table III that the two bonding modes of nitric oxide not only result in different
TABLE III
SELECTED STRUCTURAL AND INFRARED ABSORPTION DATA FOR
REPRESENTATIVE METAL NITROSYL COMPLEXES

<table>
<thead>
<tr>
<th>Complexes</th>
<th>M-N-O angle (deg)</th>
<th>$\nu_{NO}$ (cm$^{-1}$)</th>
<th>M-N (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Four-Coordinate Complexes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(NO)(CO)$_2$L</td>
<td>178.5 (6)</td>
<td>1756 (169)</td>
<td>1.74 (1)</td>
</tr>
<tr>
<td>Ir(NO)L$_3$</td>
<td>180 (0)</td>
<td>1615 (170)</td>
<td>1.67 (2)</td>
</tr>
<tr>
<td>Ni(NO)(N$_3$)L$_2$</td>
<td>153 (1)</td>
<td>1710 (172)</td>
<td>1.69 (1)</td>
</tr>
<tr>
<td><strong>Five-Coordinate Complexes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrCl(NO)(CO)L$_2$+</td>
<td>124 (1)</td>
<td>1680 (173)</td>
<td>1.97 (1)</td>
</tr>
<tr>
<td>Ru(NO)(diphos)$_2$+</td>
<td>176 (1)</td>
<td>1673 (174)</td>
<td>1.76 (1)</td>
</tr>
<tr>
<td>IrH(NO)L$_3$+</td>
<td>175 (3)</td>
<td>1715 (175)</td>
<td>1.68 (3)</td>
</tr>
<tr>
<td><strong>Six-Coordinate Complexes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(CN)$_5$(NO)$_3$-</td>
<td>176 (1)</td>
<td>1660 (176)</td>
<td>1.71 (1)</td>
</tr>
<tr>
<td>Fe(CN)$_5$(NO)$_2$-</td>
<td>178 (1)</td>
<td>1939 (178)</td>
<td>1.63 (2)</td>
</tr>
<tr>
<td>Fe(das)$_2$(NO)Cl+</td>
<td>148 (2)</td>
<td>1620 (180)</td>
<td>1.7</td>
</tr>
</tbody>
</table>

L = Ph$_3$P
M-N-O' angles but in different M-N bond lengths. The linear mode of bonding very often represented as NO\(^+\) allows the metal to back-donate electrons to the \(n^*_{NO}\) orbitals causing the M-N bond to gain considerable multiple-bond character. The M-N bond length will therefore be much shorter than that of a single M-N bond. However, the bent mode of bonding of NO\(^-\) prohibits the metal back-donation of electrons and causes the M-N bond lengths not to be as short as those in linear bonded nitrosyls. Connelly in his recent review has observed ranges for metal-nitrogen bond lengths in linear and bent modes\(^{156}\). The M-N bond lengths for the linear five-coordinate nitrosyls fall in the range 1.78-1.57 Å. Bent nitrosyls which are five-coordinate lie between 1.98-1.86 Å.

Eisenberg reported that the reaction of chloro-nitrosylbis(triphenylphosphine)ruthenium(0) with nitrosonium tetrafluoroborate produced a complex which contained two nitrosyl stretches in the infrared absorption pattern separated by approximately 200 cm\(^{-1}\).\(^{167}\) On the basis of the fact that there were two absorptions which could be attributed to nitrosyl stretching absorptions and the fact that the complex would not obey the "18 electron rule" if two nitrosyl ligands were counted as three-electron donors, the presence of both NO\(^+\) and NO\(^-\) was postulated. Structural studies showed this postulate to be confirmed. Each molecule was found to be square pyramidal with a bent
nitrosyl ligand in the apical position and a linear nitrosyl in one of the basal positions, XII. Collman, Farnham and

\[
\begin{array}{c}
\text{Cl} \\
\text{Ru} \\
\text{L} \\
\text{N} \\
\text{O} \\
\text{L} \\
\text{N} \\
\text{O}
\end{array}
\]

XII

and Dolcetti reported indirect evidence for the reversible interconversion of linear and bent nitrosyls in stereochemically non-rigid molecules. The reaction of \([\text{Ru}(^{15}\text{NO})\text{ClL}_2]\) with \(^{14}\text{NO}^+\text{BF}_4^-\) yielded \([\text{Ru(NO)Cl}_2]^+\) where the labeled nitrogen atoms were completely scrambled, implying rapid equilibrium between the modes of nitrosyl bonding. Pierpoint and Eisenberg have proposed a mechanism, eq. 20, for this interconversion.

\[
\begin{array}{c}
\text{Cl} \\
\text{Ru} \\
\text{L} \\
\text{N} \\
\text{O} \\
\text{L} \\
\text{N} \\
\text{O}
\end{array} \overset{\text{CL}}{\longrightarrow} \begin{array}{c}
\text{Cl} \\
\text{Ru} \\
\text{L} \\
\text{N} \\
\text{O} \\
\text{L} \\
\text{N} \\
\text{O}
\end{array} \overset{\text{CL}}{\longrightarrow} \begin{array}{c}
\text{Cl} \\
\text{Ru} \\
\text{L} \\
\text{N} \\
\text{O} \\
\text{L} \\
\text{N} \\
\text{O}
\end{array}
\]

The conversion of \(\text{NO}^+\) to \(\text{NO}^-\) has also been demonstrated by Enemark and Feltham with the addition of a coordinating anion to the coordinatively saturated \(\text{Co(NO)}-(\text{diars})_2^{2+}\) \([\text{diars} = \sigma\text{-phenylenedis(dimethylarsine)}]\). Transfer of an electron pair from the metal to the nitrosyl, giving the bent nitrosyl and a coordination site to which the anion may bond. The product \([\text{Co}^{III}(\text{NO})(\text{diars})_2X]^+\) \([\text{X} = \text{Cl}^-, \text{Br}^-, \text{NCS}^-]\) is more easily rationalized than the product
of the reaction of CO with IrCl(NO)L$_2$\(^+\) to give IrCl(NO)-(CO)L$_2$\(^+\), III, where the nitrosyl is also bent.\(^{165}\)

Basolo and Morris first suggested that the interconversion of NO\(^+\) to NO\(^-\) could play a role in the bimolecular reaction process of Fe(NO)$_2$(CO)$_2$ being substituted by a ligand L.\(^{184}\) Comparison of this system with the isoelectronic Ni(CO)$_4$ system which reacts by a first order process was thought to be the presence of nitric oxide as NO\(^+\). The reaction involves a bimolecular displacement which is assumed to go through a five-coordinate active intermediate. In this intermediate the nitric oxide is postulated to be in the NO\(^-\) form. This makes available a vacant orbital of low energy on the metal which can readily accept a pair of electrons from the entering nucleophile. This unique method of a metal center acquiring coordinative unsaturation open the possibility of metal nitrosyl complexes having catalytic activity. Several metal nitrosyl complexes have been found which catalyze reactions such as hydrogenation isomerization, diolefin dimerization, polymerization, and oligomerization.\(^{185-195}\) However, none of the catalytic nitrosyl complexes discovered so far has any definite link between catalytic activity and the NO bending to create a site needed for catalytic coordination.\(^{162}\)

There have been a few reports in the recent literature concerning the reactions between transition metal nitrosyl complexes and activated olefins. Brunner and
Laskot reported a very interesting reaction in which $[\pi-C_5H_5Co(CO)_2]$, NO, and certain alkenes are allowed to react. With norbornene a crystalline stable species is isolated.\textsuperscript{196} Infrared, nmr, and mass spectral data are reported and it is suggested that the complex has a structure with a five membered ring that included the cobalt atom and two bridging nitrosyls, XIII. The dimer $[\pi-C_5H_5Co(NO)]_2$ is postulated to be the complex which reacts with norbornene to form the isolated species. This reaction holds forth many possibilities in the formation of nitrogen containing organic compounds.

During the course of the work described in this portion of the Dissertation, several reports of reactions of transition metal nitrosyls with activated olefins have been published.

Clemens \textit{et al.} have reported the reactions of hexafluorobut-2-yne and tetrafluoroethylene with tris(tri-phenylphosphine)nitrosyl iridium(-1).\textsuperscript{197} The acetylene molecule reacted with the iridium nitrosyl complex to form a complex whose identity was established by X-ray crystallography as di-$\mu$-hexafluorobut-2-ylene-bis-(cis-tri-
phenylphosphine)nitrosyliridium(1). Tetrafluoroethylene reacts with the same iridium-nitrosyl complex to give a 1:1 complex which loses one molecule of triphenylphosphine. La Monica, Navazio, and Sandrini reported the reaction of M(NO)(Ph,P)₃ [M = Co, Rh, and Ir] with quinones and some activated olefins to give products of formula M(NO)(Ph,P)-L where L is the activated olefin or quinone. Fitzgerald and Lin reported the reaction of a nitrosyl analogue of Vasks's compound [IrCl(NO)(Ph,P)₂]⁺ with tetracyanoethylene to give a 1:1 complex. Each of those reactions with activated olefins is very similar to reactions of iridium nitrosyls with tetracyanoethylene which is included in the work described in this Dissertation and therefore, further comment on these reactions will be held until the discussion section of this portion of the work.

Previous studies in this laboratory have dealt with the reactions of activated olefins such as tetracyanoethylene and fumaronitrile with various transition metal substrates, and especially, with metal carbonyl complexes. It was therefore of interest, in view of the similarity of metal carbonyls and metal nitrosyls to examine the behavior of activated olefins such as these toward metal nitrosyls.
VI. EXPERIMENTAL - UNSATURATED COMPOUNDS REACTIONS

A. Reactions with Cyclic, Phenyl-Substituted Aromatic Ketones

1. Preparation and Characterization of Pt(Ph3P)2-
   \[C_3(C_6H_5)_2O]\]
   
   To a 30 ml solution of tetrakis(triphenylphosphine)platinum(0) (0.62 g, 0.50 mmol) in dichloromethane at room temperature was added a 2:1 molar excess of diphenylcyclopropenone (0.21 g, 1.0 mmol). The reaction solution was stirred for 10 min. Methanol was added and under reduced pressure solvent was removed until precipitation occurred. Yellow-orange crystals were removed by filtration and dried in air: [0.28 g, 60%; mp, 158-160°C (dec)].

   Anal. Calcd for C_{51}H_{40}OP_2Pt: C, 66.29; H, 4.36. Found: C, 65.85; H, 4.75.

   Infrared (Nujol): 1652 s (C=C).

   The complex was dissolved in toluene and heated to reflux for 0.5 hr with no change in the 1652 cm\(^{-1}\) absorption in an effort to decarbonylate the complex. The solution darkened until the complex decomposed completely. There was no spectral evidence of decarbonylation of the complexed ketone.

   A mixture of the new complex and excess diphenylcyclopropenone in dichloromethane produced a deep purple
solution. An infrared spectrum of the solution mixture was identical to a superposition of spectra of the two components. Attempts to isolate a new complex from the mixture were not successful.

A dichloromethane solution of the new complex was saturated with carbon monoxide in an attempt to carbonylate the complex. After an hour there was no change in the infrared spectrum of the complex to indicate carbonylation.

2. Reaction of $[\text{Ir}(\text{diphos})_2]\text{Cl}$ with Diphenylcyclopropenone

Orange crystals of bis(1,2-diphenylphosphinoethane)iridium(I) chloride (0.26 g, 0.25 mmol) dissolved in 25 ml of dichloromethane were mixed with a 10 ml dichloromethane solution of diphenylcyclopropenone (0.051 g, 0.25 mmol). The reaction solution was stirred for 1 hr and toluene added. Under reduced pressure solvent was removed from the flask and the dry residue recovered.

**Anal.** Calcd for $C_{67}H_{58}ClIrOP_4$: C, 65.30; H, 4.74. Found: C, 60.69; H, 5.06.

Infrared (Nujol): 1622 m br.

The analytical data are very close to that required for the initial iridium complex before reaction, however, thin layer chromatography showed the product to be a different compound.

3. Attempted reaction of $\text{IrH(CO)(Ph}_3\text{P}_3$ and Diphenyl-
cyclopropenone

Yellow crystals of hydridocarbonyltris(triphenylphosphine)iridium(I) (0.50 g, 0.50 mmol) were dissolved in dichloromethane and solid diphenylcyclopropenone (0.20 g, 1.0 mmol) was added with stirring. The temperature of the reaction was raised to 45°C for 1 hr. All solvent was removed under reduced pressure. Infrared analysis of the residue in a Nujol mull showed only evidence for the presence of the two reactants and no new complexes.

4. Attempted Reaction of IrCl(CO)(Ph₃P)₂ and Diphenylcyclopropenone

Vaska's compound (0.39 g, 0.50 mmol) was dissolved in a minimum amount of benzene (80 ml) under nitrogen. Diphenylcyclopropenone (0.1 g, 0.5 mmol) was added to the solution and the mixture stirred overnight. Infrared analysis of the benzene solution showed that there had been no reaction. The mixture stirred in an ultraviolet exposure chamber for 4 hr and again an infrared analysis of the solution was recorded which showed that no reaction had occurred.

5. Reaction of Pd(Ph₃P)₂ with Diphenylcyclopropenone

Tetrakis(triphenylphosphine)palladium(0) (0.625 g, 0.50 mmol) was dissolved in a minimum amount of dichloromethane (40 ml) under nitrogen. Solid diphenylcyclopropenone (0.10 g, 0.50 mmol) was added with stirring. The solution was left overnight. Methanol was added and under
reduced pressure solvent removed until a yellow solid precipitated [0.2 g, mp. 255-275°C (dec)].

**Anal.** Calcd for C_{51}H_{40}OP_{2}Pd: C, 73.12; H, 4.33. Found: C, 55.70; H, 4.43.

Infrared (Nujol): 1650 m br.

On stirring these compounds for 1 hr under the same conditions, a light yellow solid precipitated. This was filtered and dried under vacuum. The infrared spectrum of a Nujol mull of this solid showed no band in the 1600-1700 cm\(^{-1}\) region indicative of reaction with the cyclic ketone. The product was not characterized.

6. Attempted Reaction of IrH(CO)\(_2\)(Ph\(_3\)P)\(_2\) with Diphenylcyclopropenone

Yellow crystals of hydridocicarbonyl bis(triphenylphosphine)iridium(I) (0.78 g, 1.0 mmol) was dissolved in 100 ml of benzene and diphenylcyclopropenone (0.30 g, 1.5 mmol) was added. The reaction mixture was stirred for 0.5 hr at 60°C. Under reduced pressure all solvent was removed and the residue redissolved in dichloromethane. Methanol was added and again under reduced pressure solvent was removed until precipitation occurred. The yellow-brown solid when analyzed in a Nujol mull by infrared spectroscopy was identified as a mixture of the two reactants. There was no reaction.
7. Attempted Reaction of Pt(Ph₃P)₄ with Tetraphenylcyclopentadienone

To a 60 ml solution of tetrakis(triphenylphosphine)platinum(0) (1.2 g, 1.0 mmol) in dichloromethane was added solid tetraphenylcyclopentadienone (0.76 g, 2.0 mmol). The solution was stirred for 1 hr. Methanol was added and under reduced pressure all solvent was removed. The residue was collected when dry and analyzed by infrared spectroscopy as a Nujol mull. The spectrum showed the absorptions of the reactants with no new or different peaks. There was no reaction.

8. Attempted Reaction of Pt(Ph₃P)₄ with 2,5-Dimethyl-3,4-diphenylcyclopentadienone

Tetrakis triphenylphosphine)platinum(0) (1.2 g, 1.0 mmol) was dissolved in 60 ml of dichloromethane and solid 2,5-dimethyl-3,4 diphenylcyclopentadienone (0.50 g, 2.0 mmol). The solution was stirred for 0.5 hr and methanol was added. Under reduced pressure all solvent was removed. The residue was analyzed by infrared spectroscopy and the spectrum showed only the absorptions of the reactants. There was no reaction.

9. Attempted Reaction of Pt(Ph₃P)₄ with Cycloheptatrienone

A 30 ml solution of tetrakis(triphenylphosphine)-platinum(0) (0.62 g, 0.50 mmol) in dichloromethane was
added to cycloheptatrienone (0.65 g, 6.1 mmol). The solution was stirred for 0.5 hr. Methanol was added and under reduced pressure solvent was removed until precipitation occurred. The yellow solid was analyzed as a Nujol mull and the filtrate as a solution spectrally by infrared spectroscopy. The solid was identified as the starting platinum complex and the solution spectrum was that of the reactant cyclic ketone. There was no reaction.

10. Attempted Reaction of Pt(Ph₃P)₄ and N-acetyl-diphenylcyclopropenoxime

Tetrakis(triphenylphosphine)platinum(0) (0.62 g, 0.50 mmol) was dissolved in a minimum amount of dichloromethane (40 ml) under nitrogen. N-acetyl diphenylcyclopropenoxime (0.25 g, 1.0 mmol) was added with stirring. The solution was stirred for 1 hr. Under reduced pressure all solvent was removed and the residue was recrystallized from dichloromethane/methanol/cyclohexane to give white crystals.


The infrared spectra of the white solid showed no bands which could not be accounted for by the presence of triphenylphosphine. There was no nitrogen found in the elemental analysis and a very low carbon percentage. The percentages are for a platinum-phosphine complex reported recently. 200
B. Reactions with Amino-Ethylenes

1. Reaction of Pt(C₂H₄)(Ph₃P)₂ with 1,1-Diamino-2,2-dicyanoethylene

The white solid bis(triphenylphosphine)ethylene-platinum(0) (0.186 g, 0.25 mmol) was dissolved in 30 ml of benzene under nitrogen. Solid crystals of 1,1-diamino-2,2-dicyanoethylene (0.27 g, 0.25 mmol) were added with stirring. Acetone (5 ml) was added to effect solution of the substituted ethylene compound. After 1 hr solvent was removed under reduced pressure until a precipitate formed in solution. The off-white solid was filtered and washed with hexane and dried [0.08 g, 40%; mp, 190-194°C (dec)].

**Anal.** Calcd for C₄₆H₄₀N₄P₂Pt: C, 60.99; H, 4.45; N, 6.19. Found: C, 60.41; H, 4.14; N, 6.83.

Infrared (Nujol): 3325 w (N-H), 2193 m (CN), 2170 s (CN), 2154 w sh, 1638 s, 1535 s.

NMR (CDCl₃): 7.35 br multiplet, 2.68 w, 1.45 w.

Recrystallization of the off-white solid from dichloromethane/methanol yielded a yellow solid, mp, 190-195°C.

**Anal.** Found: C, 52.82; H, 3.92; N, 6.03.

Infrared (Nujol): 3352 w, 2190 s, 2170 s, 2160 sh, 1620 m, 1595 s, 1538 m.

The identical reaction was repeated except that
methanol was added to dissolve the ethylene compound. A yellow solid very similar to the recrystallized product above was isolated, mp, 165-174°C.

Anal. Found: C, 52.93; H, 3.18; N, 5.54.
Infrared (Nujol): 3322 w, 2185 m, 2160 s, 1610 m, 1532 s.

2. Reaction of Pt(Ph₃P)₄ with 1,1-Diamino-2,2-dicyanoethylene

Tetrakis(triphenylphosphine)platinum(0) (0.62 g, 0.50 mmol) was dissolved in a minimum amount of benzene (50 ml) under nitrogen. White needles of 1,1-diamino-2,2-dicyanoethylene (0.054 g, 0.50 mmol) were added in 5 ml of dichloromethane. The solution was stirred for 1 hr. Under reduced pressure solvent was removed until precipitation occurred. A yellow-brown solid (0.1 g, mp, 250-300°C) was filtered and dried under vacuum for 0.5 hr.

Anal. C, 36.84; H, 3.65; N, 6126.
Infrared (Nujol): 3335 w br, 3325 w br, 2175 s, 1630 s, 1590 s.

3. Attempted Reaction of trans-\text{MX(CO)}(\text{Ph₃P})₂ [M = Ir; X = Cl, P; M = Rh; X = Cl] with 1,1-Diamino-2,2-dicyanoethylene

Trans- chlorocarbonyl bis(triphenylphosphine)-iridium(I) (0.39 g, 0.50 mmol) was dissolved in 60 ml of
benzene under nitrogen. Solid 1,1-diamino-2,2-dicyanoethylene (0.108 g, 1.0 mmol) was added with 5 ml of dichloromethane to effect solution of the ethylene compound. The reaction solution was stirred for 1 hr. Under reduced pressure solvent was removed until precipitation occurred. The yellow solid was analyzed by infrared spectroscopy and was shown to be a mixture of the reactants. There was no reaction.

Solid trans-fluorocarbonylbis(triphenylphosphine)-iridium(I) (0.382 g, 0.50 mmol) was dissolved in 80 ml of benzene under nitrogen. A solution of 1,1-diamino-2,2-dicyanoethylene (0.54 g, 0.50 mmol) in dichloromethane was added with stirring. After 1 hr solvent was removed under reduced pressure until precipitation occurred. An infrared spectrum showed this solid to be a mixture of the reactants. There was no reaction.

A 50 ml solution of chlorocarbonylbis(triphenylphosphine)rhodium(I) (0.172 g, 0.25 mmol) in benzene was mixed with a 10 ml dichloromethane solution of 1,1-diamino-2,2-dicyanoethylene (0.108 g, 1 mmol) under nitrogen. The reaction solution was heated to 80°C and stirred for 1 hr. Hexane was added and under reduced pressure solvent was removed until precipitation occurred. An infrared spectrum of the yellow solid revealed it to be a mixture of the reactants. There was no reaction.
4. Reaction of RhCl(Ph₃P)₃ with 1,1-Diamino-2,2-dicyanoethylene

Burgandy crystals of chlorotris(triphenylphosphine)-rhodium(I) (0.23 g, 0.25 mmol) were dissolved in 60 ml of benzene under nitrogen. White crystals of 1,1-diamino-2,2-dicyanoethylene (0.027 g, 0.25 mmol) were dissolved in 5 ml of dichloromethane and added with stirring to the rhodium complex solution. After 1 hr hexane was added to initiate precipitation. A light orange solid [0.07 g; mp, 140-240°C (dec)] was collected by filtration and dried under vacuum for 1 hr.


   Infrared (Nujol): 3330 w, 2204 sh, 2180 s, 1615 m, 1530 m.

5. Reaction of Pt(Ph₃P)₄ with Diaminomaleonitrile

Yellow crystals of tetrakis(triphenylphosphine)-platinum(0) (1.13 g, 0.85 mmol) were dissolved in a minimum amount (60 ml) of benzene under nitrogen. Diaminomaleonitrile (0.90 g, 0.85 mmol) was dissolved in 5 ml of ethanol and this solution added to the metal complex solution. After 1 hr of stirring solvent was removed under reduced pressure and a bright orange precipitate isolated [0.3 g; 36%; mp, 250-300°C (dec)] and dried.
6. Reaction of Pt(C$_2$H$_4$)(Ph$_3$P)$_2$ with Diaminomaleonitrile

Bis(triphenylphosphine)ethyleneplatinum(0) (0.187 g, 0.25 mmol) was dissolved in a minimum amount (30 ml) of benzene under nitrogen. A 5 ml ethanol solution of diaminomaleonitrile (0.027 g, 0.25 mmol) was added. After 0.5 hr of stirring, the solvent was removed under reduced pressure and an orange solid precipitated. The solid [0.06 g, mp, 122-124°C (dec)] was filtered and dried under vacuum for 0.5 hr.

Anal. Calcd for C$_{40}$H$_{34}$N$_2$P$_2$Pt: C, 58.04; H, 4.04; N, 6.77. Found: C, 51.83; H, 3.64; N, 5.07.

Infrared (Nujol): 3390 w, 2198-2177 s, 1635 w, 1558 m.

Recrystallization resulted in solids which gave the same infrared data but different analytical data indicating partial loss of the coordinated ethylene ligand.

7. Reaction of Pt(CO)(Ph$_3$P)$_2$ with Diaminomaleonitrile

Bis(triphenylphosphine)dicarbonylplatinum(0) (0.195 g, 0.25 mmol) was dissolved in a minimum amount (25 ml) of dichloromethane under nitrogen. Diaminomaleonitrile (0.027
g, 0.25 mmol) was dissolved in 5 ml of ethanol and the solutions were mixed at room temperature. The solution turned a dark brown on addition of the ethylene ligand. After 1 hr solvent was removed under reduced pressure and a red-brown solid [0.04 g; mp, 250-300°C (dec)] was isolated.

Anal. Found: C, 52.75; H, 3.64; N, 4.50.

Infrared (Nujol): 3385 w, 2189-2178 s, 1640s br, 1558 m.

Recrystallization from dichloromethane/methanol yielded a brown amorphous solid which exhibited different physical characteristics.

Anal. Found: 54.22; H, 3.72; N, 3.28.

Infrared (Nujol): 2257 s, 2130 w.

8. Reaction of IrX(CO)(Ph3P)2 [X = Cl, Br, I] with Diaminomaleonitrile

To a 50 ml solution of trans-chlorocarbonylbis-(triphenylphosphine)iridium(I) (0.195 g, 0.25 mmol) was added a 5 ml ethanol solution of diaminomaleonitrile (0.027 g, 0.25 mmol). The solution was stirred for 0.5 hr at 80°C under nitrogen. The original bright yellow solution had changed after addition of the ethylene ligand to a dark brown. Under reduced pressure a black tar was recovered. Dichloromethane was added to dissolve the tar and petroleum ether was added to cause precipitation. A brown-black solid (0.09 g) was filtered and dried.
Infrared (Nujol): 3848 w, 2214 m, 2171 m, 2050 w, 1945 s, 1624 s, 1560 sh, 312 w.

Recrystallization of the black solid with dichloromethane/petroleum ether yielded the two starting materials but no new complex.

This reaction was repeated with the bromo-and iodo-analogues to Vaska's compound with the same reaction conditions and time. There was no evidence of any reaction with these metal complexes.

9. Attempted Reaction of IrH(CO)(Ph₃P)₃ with Diamino-maleonitrile

Bright yellow crystals of hydridocarbonyltris-(triphenylphosphine)iridium(I) (0.25 g, 0.25 mmol) were dissolved in a minimum amount of dichloromethane (40 ml). Excess diaminomaleonitrile (0.135 g, 1.25 mmol) was dissolved in 15 ml of methanol and added to the yellow iridium solution. The mixture was stirred for 1 hr at 50°C. Under red reduced pressure a solid was obtained which when analyzed by infrared spectroscopy was shown to be a mixture of the reactants. There was no reaction.

10. Attempted Reaction of RhCl(CO)(Ph₃P)₂ with Diamino-maleonitrile

Chlorocarbonylbis(triphenylphosphine)rhodium(I)
(0.17 g, 0.25 mmol) was dissolved in 40 ml of benzene and added to a 10 ml solution of diaminomaleonitrile (0.135 g, 1.25 mmol) in ethanol. The solution was stirred for 1 hr at 60°C. Under reduced pressure solvent was removed until a precipitate was formed. The yellow-brown solid was shown to be a mixture of the reactants by infrared spectroscopy. There was no reaction.

11. Reaction of RhCl(Ph₃P)₃ with Diaminomaleonitrile

Chlorotris(triphenylphosphine)rhodium(I) (0.23 g, 0.25 mmol) was dissolved in a minimum amount (30 ml) of dichloromethane. Diaminomaleonitrile (0.027 g, 0.25 mmol) was dissolved in a minimum amount (5 ml) of methanol. The solutions were mixed for 1 hr. Under reduced pressure solvent was slowly removed to give shiny green crystals [0.2 g, mp, 118-120°C (dec)].

Anal. Calcd for C₄₀H₃₄ClN₄P₂Rh: C, 62.33; H, 4.41; N, 7.27. Found: C, 62.67; H, 4.44; N, 5.33.

Infrared (Nujol): 3220 w, 2204 m, 1610-1588 w.

12. Attempted Reaction of Pt(C₂H₄)(Ph₃P)₂ with 1,1-Bis-(dimethylamino)-2,2-dicyanoethylene

Bis(triphenylphosphine)ethyleneplatinum(0) (0.186 g, 0.25 mmol) was dissolved in 40 ml of benzene at room
temperature. An equimolar amount of 1,1-bis(dimethylamino)-2,2-dicyanoethylene (0.041 g, 0.025 mmol) was added in a 5 ml solution of ethanol and the mixture stirred for 1 hr. Under reduced pressure all solvent was removed leaving a light brown residue. Analysis by infrared spectroscopy revealed only evidences of the original starting materials. There was no reaction.

13. Attempted Reaction of \textit{trans}-IrCl(CO)(Ph$_3$P)$_2$ with 1,1-Bis(dimethylamino)-2,2-dicyanoethylene

Yellow crystals of \textit{trans}-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.098 g, 0.126 mmol) were dissolved in 20 ml of benzene and mixed with a 1 ml solution of 1,1-bis(dimethylamino)-2,2-dicyanoethylene (0.22 g, 1.3 mmol) in methanol. The solution was stirred for 1 hr at room temperature. Solvent was removed under reduced pressure. The residue was analyzed by infrared spectroscopy to reveal that no reaction had taken place.

14. Reaction of RhCl(Ph$_3$P)$_3$ with 1,1-Bis(dimethylamino)-2,2-dicyanoethylene

To a burgundy solution of chlorotris(triphenylphosphine)rhodium(I) (0.23 g, 0.25 mmol) in dichloromethane was added a colorless 5 ml ethanol solution of 1,1-bis(dimethylamino)-2,2-dicyanoethylene. Under reduced pressure all solvent was removed leaving a light brown residue. Analysis by infrared spectroscopy revealed only evidences of the original starting materials. There was no reaction.
methylamino)-2,2-dicyanoethylene (0.041 g, 0.25 mmol).
A brown solution developed and was stirred for 1 hr. All solvent was removed under reduced pressure leaving a light brown solid (0.25 g; mp, >300°C).

**Anal.** Found: C, 57.90; H, 4.43; N, 3.03.
Infrared (Nujol): 3430 w, 2220 m br, 2198 m, 1565 s, 1535 s.

C. Reactions of Metal Nitrosyls with Tetracyanoethylene

1. Reaction of Ir(NO)(CO)(Ph₃P)₂ with Tetracyanoethylene

The yellow crystals of nitrosylcarbonylbis(triphenylphosphine)iridium(-I) (0.39 g, 0.50 mmol) were dissolved in a minimum amount of benzene (50 ml) producing a dark red-brown solution. Tetracyanoethylene (0.32 g, 2.5 mmol) in five molar excess was added to the solution and the solution was stirred for 1 hr at room temperature. As the solution was stirring green crystals precipitated on the walls of the flask. The green-brown solid [0.1 g, 20%; mp, >300°C] was filtered and dried in the air.

**Anal.** Calcd for C₄₉H₃₀IrN₉O₂P₂: C, 57.03; H, 2.93; N, 12.22, mol wt, 1031. Found: C, 56.53; H, 2.85; N, 10.83; mol wt, 1050 (chloroform).

Infrared (Nujol): 2220 w, 2165 m, 2080 s.
An equimolar mixture of nitrosylcarbonylbis(tri-
phenylphosphine)iridium(-I) (0.39 g, 0.50 mmol) and tetracyanoethylene (0.065 g, 0.50 mmol) were dissolved in a minimum amount of benzene (60 ml) and stirred for 1 hr at room temperature. A green solid (0.13 g) which precipitated from the solution was filtered and dried. This green solid on analysis by infrared spectroscopy showed the same three band pattern as the product of the carbonylnitrosyliridium species with excess tetracyanoethylene. This solid was recrystallized from chloroform/ethanol to give a green solid [0.1 g, 20%; mp, + 300°C].

Anal. Calcd for C_{43}H_{30}IrN_{5}O_{2}P_{2}: C, 57.14; H, 3.30; N, 7.75; mol wt, 903. Found: C, 56.97; H, 3.30; N, 7.47; mol wt, 835 (chloroform).

Infrared (Nujol): 2225 w, 2080 s.

2. Reaction of Ir(NO)(Ph_{3}P)_{3} with Tetracyanoethylene

Nitrosyltris(triphenylphosphine)iridium(-I) (0.50 g, 0.50 mmol) was dissolved in a minimum amount (50 ml) of benzene at room temperature. An equimolar amount of tetracyanoethylene (0.064 g, 0.50 mmol) was added with stirring. After 1 hr a purple-brown solid which had precipitated was filtered and dried in air 0.16 g, 37%; mp, 200-210°C (dec)].

Anal. Calcd for C_{42}H_{30}IrN_{5}OP_{2}: C, 58.71; 3.42; N, 7.99; mol wt, 875. Found: C, 58.31; H, 3.99; N, 6.45;
mol wt, 973 (chloroform).

Infrared((Nujol): 2225 w, 1615 s.

3. Reaction of $[\text{IrH(NO)(Ph}_3\text{P)}_3]\text{ClO}_4$ and Tetracyanoethylene

Excess tetracyanoethylene (0.16 g, 1.25 mmol) was mixed with hydridonitrosyltris(triphenylphosphine)iridium(I) perchlorate (0.28 g, 0.25 mmol) in 40 ml of dichloromethane under nitrogen. Hexane was added to the solution slowly to cause precipitation in the solution. A red-purple solid [0.1 g; mp, 203-207°C (dec)] was filtered and dried in air.

Anal. Calcd for $\text{C}_{42}\text{H}_{31}\text{IrN}_5\text{O}_5\text{P}_2$: C, 51.67; H, 3.20; N, 7.17. Found: C, 54.50; H, 3.45; N, 7.22.

Infrared((Nujol): 2210 w, 2168 w.

$(\text{CH}_2\text{Cl}_2)$: 2224 m, 2060 w, 1607 m.

Recrystallization attempts or other purification methods yielded small amounts of a bright orange solid.

Anal. Calcd for $\text{C}_{36}\text{H}_{31}\text{ClIrNO}_2\text{P}_2$: C, 50.04; H, 3.64; N, 1.62. Found: C, 48.10; H, 3.44; N, 1.56.

Infrared (Nujol): 1863 s.

4. Reaction of $\text{IrCl}_2(\text{NO})(\text{Ph}_3\text{P})_2$ with Tetracyanoethylene

Excess tetracyanoethylene (0.20 g, 1.57 mmol) was mixed with dichloronitrosylbis(triphenylphosphine)iridium(I) (0.20 g, 0.25 mmol) in 40 ml of dichloromethane. This
solution was heated to reflux for 1 hr. Ethanol was added and under reduced pressure solvent was removed until precipitation occurred. Infrared analysis of a Nujol mull of this solid revealed that there was no change in the absorption pattern of the nitrosyl complex. There was no reaction.

5. Reaction of \([\text{IrCl(NO)(CO)(Ph_3P)_2}]\text{BF}_4\) with Tetracyanoethylene

Chloronitrosylcarbonylbis(triphenylphosphine)-iridium(III) tetrafluoroborate (0.46 g, 0.50 mmol) was dissolved in 50 ml of dichloromethane and tetracyanoethylene (0.064 g, 0.50 mmol) was added. The dark-red-violet solution did not change color upon addition of the tetracyanoethylene. Addition of benzene and removal of some of the dichloromethane under reduced pressure precipitated the reactant metal complex. Addition of ethanol to cause precipitation yielded a green solid which when analyzed by infrared spectroscopy showed very weak absorptions in the cyanide region of the spectrum. There was no identifiable absorption which could be attributed to the nitrosyl group.

However when this reaction was monitored by infrared spectroscopy, the reaction solution revealed absorptions which indicated that a new complex was formed. All efforts to isolate the complex were unsuccessful.
Infrared (chloroform): 2225 w, 2165 w, 2080 m, 2055 sh, 1675 s.

6. Attempted Reaction of Ir(NO)(CO)(Ph₃P)₂ with Fumaronitrile

Fumaronitrile (0.20 g, 2.5 mmol) was added to a 50 ml benzene solution of nitrosylcarbonylbis(triphenylphosphine)iridium(-1) (0.39 g, 0.50 mmol) at room temperature. The reaction solution was heated to reflux for 2 hr. and the solution darkened. Under reduced pressure solvent was removed and ethanol added until precipitation occurred. Infrared analysis of a Nujol mull of the solid reveal it to be the initial starting complex. There was no reaction.

7. Attempted Reaction of Ir(NO)(Ph₃P)₂ with Fumaronitrile

Nitrosyltris(triphenylphosphine)iridium(-1) (0.50 g, 0.5 mmol) was dissolved in 50 ml of benzene and fumaronitrile (0.20 g, 2.5 mmol) was added. The reaction solution was heated at reflux for 1 hr with no visible change. Under reduced pressure solvent was removed and ethanol added to cause precipitation. Infrared analysis of the solid revealed that no reaction had taken place. The initial complex reactant was recovered.

8. Attempted Reaction of Ir(NO)(Ph₃P)₃ with Cinnamo-
nitrile

Excess cinnamonic nitride (0.32 g, 2.5 mmol) was refluxed with nitrosyltris(triphenylphosphine)iridium(-I) (0.50 g, 0.50 mmol) in 50 ml of benzene for 1 hr. Under reduced pressure solvent was removed and ethanol was added to cause precipitation. The solid isolated was identified by infrared spectroscopy as the starting iridium complex. There was no reaction.

9. Attempted Reaction of Ir(NO)(Ph₃P)₃ with Dimethyl-acetylene Dicarboxylate

Nitrosyltris(triphenylphosphine)iridium(-I) (0.25 g, 0.25 mmol) was dissolved in 30 ml of benzene. Excess dimethylacetylene dicarboxylate (0.71 g, 5.0 mmol) was added and the temperature of the reaction solution raised to 50°C for 1.5 hr. Under reduced pressure all solvent was removed and the residue examined by infrared spectroscopy. A mixture of the reactants was revealed. No reaction had taken place.
VII. RESULTS OF METAL-OLEFIN REACTIONS

The platinum complex $\text{Pt}(\text{Ph}_3\text{P})_2(dpcp)$ [$dpcp = \text{diphenylcyclopropenone}$] was prepared and characterized from the reaction of the coordinatively unsaturated $\text{Pt}(\text{Ph}_3\text{P})_2$ with diphenylcyclopropenone. The reactions of $[\text{Ir}(\text{diphos})_2]^-$-Cl and $\text{Pd}(\text{Ph}_3\text{C})_{4}$ with diphenylcyclopropenone also gave evidence of the formation of 1:1 complexes but did not afford well characterized crystals. Coordinatively unsaturated iridium(I) complexes which showed no reaction with diphenylcyclopropenone were $\text{IrH(CO)(Ph}_3\text{P})_2$, $\text{IrH(CO)}_2-(\text{Ph}_3\text{P})_2$, and $\text{IrCl(CO)(Ph}_3\text{P})_2$. Other unsaturated ketone substituted rings which showed no reaction with $\text{Pt}(\text{Ph}_3\text{P})_4$ were tetraphenylcyclopentadienone, 2,5-dimethyl-3,4-diphenylcyclopentadienone, cycloheptatrienone, and N-acetyl diphenylcyclopropenoxime.

The reactions of several diamine-substituted ethylenes with noble metal complexes revealed that only the most reactive complexes react to form stable new compounds with these ligands. The reaction of $\text{Pt}(\text{C}_2\text{H}_4)(\text{Ph}_3\text{P})_2$ with 1,1-diamino-2,2-dicyanoethylene resulted in a 1:1 complex. A complex which reacts with this ligand but does not afford a well characterized product is $\text{RhCl(Ph}_3\text{P})_3$. No reaction was observed between $\text{MX(CO)(Ph}_3\text{P})_2$ [$M = \text{Ir}; X = \text{Cl}, F; M = \text{Rh}; X = \text{Cl}$] with 1,1-diamino-2,2-dicyanoethylene. A 1:1 complex was formed by the reaction of $\text{Pt(PhP)}_4$ with diamino-
maleonitrile. The complex RhCl(Ph₃P)₃ again reacts with diaminomaleonitrile but does not afford a well characterized product. No reaction was observed in the case of diaminomaleonitrile and MX(CO)(Ph₃P)₂ [M = Ir; X = Cl, Br, I; M = Rh; X = Cl] and IrH(CO)(Ph₃P)₃. Reaction occurred between RhCl(Ph₃P)₃ and 1,1-bis(dimethylamino)-2,2-dicyanoethylene but no well characterized product was isolated. No reaction was observed with 1,1-bis(dimethylamino)-2,2-dicyanoethylene and PtfCgH^)(Ph^P)² or IrCl(CO)(Ph^P)g.

Reaction of tetracyanoethylene with various iridium complex substrates produced a new complex in all but one case. Reaction of an excess of tetracyanoethylene with nitrosylcarbonylbis(triphenylphosphine)iridium(−I) at room temperature yielded a complex with a 2:1 ligand to metal ratio. A second product was isolated from this reaction which was shown to be a 1:1 complex. This 1:1 complex was also obtained by reacting equimolar amounts of the reactants. Reactions of Ir(NO)(Ph₃P)₃ with tetracyanoethylene gives a 1:1 complex. Tetracyanoethylene reacts with hydrido-nitrosyltris(triphenylphosphine)iridium(I) perchlorate and chloronitrosylcarbonylbis(triphenylphosphine)iridium(I)-tetrafluoroborate but no well characterized products were isolated. There was no reaction between dichloronitrosyl-bis(triphenylphosphine)iridium(I) and tetracyanoethylene. Other activated olefins which showed no reactivity with the iridium-nitrosyl complexes Ir(NO)(CO)(Ph₃P)₂ and Ir(NO)-(Ph₃P)₃ were fumaronitrile and cinnamonicitrile.
A. Reactions of Olefinic Ketones

Tetrakis(triphenylphosphine)platinum(0) reacted with diphenylcyclopropenone in dichloromethane at room temperature to give a 1:1 complex. Three possible structures, XIV-XVI, should be considered. Coordination of diphenylcyclopropenone through the oxygen atom would be similar to coordination of N-pyridine oxides through the oxygen atom to noble metal substrates.\textsuperscript{201} Table IV gives the absorptions of the diphenylcyclopropenone ligand coordinated through the oxygen atom or its polar form as described by Orchin.\textsuperscript{137} Selected infrared spectral data of the complex from Figure 11 shows no absorptions in the 1900-1800 cm\textsuperscript{-1} range eliminating this structure as a possibility. Structure XV depicts coordination of diphenylcyclo- through the double bond in the ring to the metal atom. This mode of coordination is typical of ethylene molecules to transition metals. Various unsaturated rings have been shown to coordinate to platinum(0) through the carbon-carbon double bond. Even unsaturated cyclic three membered rings
<table>
<thead>
<tr>
<th>Complex</th>
<th>Infrared Absorption Frequencies</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dpcp)CoCl₂</td>
<td>1870, 1860, 1840, 1830, 1600, 1590, 1580</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₂CoBr₂</td>
<td>1870, 1850 sh, 1830, 1605, 1590, 1580, 1575 sh</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₆Co(ClO₄)₂</td>
<td>1870, 1850, 1830, 1605, 1590, 1580, 1575 sh</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₂NiBr₂</td>
<td>1880, 1860, 1820, 1600, 1585, 1570 sh, 1560</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₆Ni(ClO₄)₂</td>
<td>1870, 1850 sh, 1830, 1605, 1590, 1580, 1575 sh</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₂CuCl₂</td>
<td>1880, 1865, 1825, 1605, 1590, 1570, 1560</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₂RuCl₂</td>
<td>1880, 1850, 1820, 1600, 1580, 1550, 1540</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₃RuCl₃</td>
<td>1880 sh, 1850, 1820 sh, 1600, 1580, 1565, 1555, 1530</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₂PtCl₄</td>
<td>1880, 1840, 1810, 1600, 1580, 1570 sh, 1550, 1540</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)₂Pt₂Cl₄</td>
<td>1855, 1830 sh, 1600, 1580, 1550, 1530, 1510 br</td>
<td>122</td>
</tr>
<tr>
<td>(dpcp)(C₂H₄)PtCl₂</td>
<td>1838, 1593, 1572, 1543, 1517</td>
<td>124</td>
</tr>
<tr>
<td>(dpcp)(CO)PtCl₂</td>
<td>1845, 1590, 1574, 1540, 1521</td>
<td>124</td>
</tr>
<tr>
<td>(dpcp)₂PdCl₂</td>
<td>1880, 1860, 1820, 1600, 1580, 1550, 1530</td>
<td>122</td>
</tr>
</tbody>
</table>
FIGURE 11

Selected Infrared Absorptions of the Complex \( \text{Pt(Ph}_3\text{P)}_2\text{(dpcp)} \)
(Benzene Solution)
cyclopropene and its derivatives\textsuperscript{202,203} and thiiren 1,1-di-oxides\textsuperscript{204} have been shown to coordinate through the carbon-carbon double bond to unsaturated platinum(0) complexes. Hendra and Powell have reported evidence that the carbon-carbon double bond stretching frequency of olefins is lowered by 140 cm\textsuperscript{-1} on coordination to a platinum atom.\textsuperscript{205}

In the infrared absorption spectrum of uncomplexes diphenylcyclopropenone, Figure 12, bands at 1830 and 1620 cm\textsuperscript{-1} are thought to be involved with C=C and C=O stretching vibrations. Fichtman, Schmidt, and Orchin report that in diphenylcyclopropenone complexed through the oxygen atom to the metal, the 1620 cm\textsuperscript{-1} band is lowered indicating that the C=C vibration dominates the 1830 cm\textsuperscript{-1} absorption.\textsuperscript{137}

In a platinum complex having a structure XV, one would expect a bond around 1700 cm\textsuperscript{-1} indicating a lowering of the C=C stretching frequency on coordination of the double bond to the metal. Absence of such a band in Figure 11 lessens the possibility of the complex having this structure. Bird and Briggs first suggested the possibility of a metal complex of type XVI in reports of studies of carbonylation of acetylenes with metal carbonyl complexes as catalysts. Intermediates suggested for iron,\textsuperscript{136} VI, and nickel,\textsuperscript{206} XVII, reactions with acetylenes were postulated as being

\[\text{(XVII)}\]
FIGURE 12

Selected Infrared Absorptions of Diphenylcyclopropenone (Benzene Solution)
formed by carbonyl insertion into acetylene-metal carbonyl complexes. Reaction of diphenylcyclopropenone with di-iron nonacarbonyl in benzene at ambient temperature in the absence of light gave as one of the products V, presumably formed by carbonyl insertion to a compound of type VI. A similar complex, VII was isolated from the reaction of cycloheptenocyclopropenone with di-iron nanacarbonyl. Carbonyl insertion should be favored over dicarbonylation of the propenone due to the formation of the highly strained cycloheptyne if decarbonylation occurs.

An X-ray structural determination of the product $\left[\left(C_{6}H_{5}\right)_{2}P\right]_{2}Pt\left[C_{3}\left(C_{6}H_{5}\right)_{2}O\right]$ has shown that the diphenylcyclopropenone has indeed opened and that platinum insertion has afforded a metallocyclobutenone, Figure 13. The metallocycle is nearly coplanar with the P-Pt-P portion. Both single and double bonds remain in the metallocycle as identifiable parts of the ring.

An attempt to decarbonylate the platinacyclobutenone by heating a toluene solution of the complex to reflux for 0.5 hr was unsuccessful. Monitoring of the infrared spectrum of the solution showed no change in the strong absorption at 1663 cm$^{-1}$ over this time period. Further heating caused complete decomposition of the complex in solution. No platinum complex could be isolated after decomposition.

An attempt to carbonylate diphenylcyclopropenone
FIGURE 13

Molecular Structure and X-Ray Crystallographic Results for
\[(\text{c}_{6}\text{H}_{5})_3\text{P}]_2\text{Pt}[\text{OC}_3(\text{c}_{6}\text{H}_{5})_2]\]
complexed to the platinum metal to form a compound analogous to structure VI or VII was made at ambient temperature by bubbling carbon monoxide through a solution of the metallocycle. There was no evidence of carbon monoxide uptake or any change in the complex as recorded in the infrared spectral absorptions of the solution or by spectrum of the isolated solid after exposure to carbon monoxide.

A mixture of the yellow platinocyclobutenone complex dissolved in dichloromethane and a clear dichloromethane solution of excess diphenylcyclopropenone produced a deep purple solution. An infrared spectrum of the solution showed each absorption of the reactants with no new bands. Evaporation of the solvent left only the reactants. The deep color may possibly be explained by a charge-transfer interaction between the platinum-diphenylcyclopropenone complex and free diphenylcyclopropenone.

After some of this work was published, Visser and Ramakers-Blom reported the reaction of methyl-, dimethyl- and diphenylcyclopropenone with bis(triphenylphosphine)-ethyleneplatinum(0). The results reported are in accord with those reported here. Reaction of methylcyclopropenone with the platinum-ethylene complex at -65°C in CDCl$_3$ yielded a complex with structure XV, eq. 23, 24. Coordination of

\[ \text{L}_2\text{Pt} - \text{Me} + \text{Me} \xrightarrow{-65^\circ} \text{L}_2\text{Pt} - \text{Me} \] (23)
methylcyclopropenone to the metal was initially through the double bond as indicated by the chemical shifts and the $^{195}$Pt-H and P-H spin-spin coupling constants in the nmr spectrum. In solution at -30°C the coordinated olefin was changed into the metallocyclobutenone complex. No indication of the olefin coordinated complex was found with the dimethyl- or diphenylcyclopropenone reactions with the platinum complex.

The most reasonable mechanism by which this reaction could take place is by the initial fleeting complexation of the double bond in the three membered ring to the unsaturated Pt(Ph$_3$P)$_2$ species. The metal atom then inserts into the carbon-carbon single bond forming the metallocyclobutenone. Insertion of the platinum atom into the carbon-carbon bond relieves the strain in the three membered ring and also saturates the platinum atom coordinatively.

Bis(1,2-diphenylphosphinoethane)iridium(I) chloride and an equimolar amount of diphenylcyclopropenone were stirred together in dichloromethane at room temperature. After 1 hr toluene was added. Under reduced pressure all solvent was removed slowly and a light brown solid was
recovered which was shown to be homogenous by TLC. One medium infrared absorption (Figure 14) at 1622 cm\(^{-1}\) is in the same region as the band in the complex \(\text{Pt(Ph}_3\text{P)}_2(\text{C}_3\text{Ph}_2\text{O})\) at 1660 cm\(^{-1}\). The analytical data for this product was consistently low for carbon percentages even after recrystallization from dichloromethane/toluene when compared with calculated values for a 1:1 ratio of reactants.

Tetrakis(triphenylphosphine)palladium(0) and diphenylcyclopropenone in dichloromethane were stirred together overnight. Methanol was added and under reduced pressure solvent was slowly removed, causing the separation of a yellow amorphous solid. As in the case of the \([\text{Ir(diphos)}_2]\text{Cl}\) reaction product with the cyclopropenone, an infrared absorption at 1650 cm\(^{-1}\), Figure 15, of medium strength was found. Again analytical data for the yellow solid was low in carbon percentage as compared to calculated percentages for a 1:1 ratio of \(\text{Pd(Ph}_3\text{P)}_2\) to the cyclopropenone. Visser and Ramakers-Blom reported that they did not find evidence of reaction of \(\text{Pd(Ph}_3\text{P)}_4\) with cyclopropenones.\(^{138}\)

The similarity of the reactions of \(\text{Pt(Ph}_3\text{P)}_4\), \([\text{Ir(diphos)}_2]\text{Cl}\), and \(\text{Pd(Ph}_3\text{P)}_4\) with diphenylcyclopropenone are indicated by the absorptions between 1663 and 1622 cm\(^{-1}\) in the infrared spectral absorption patterns. Analytical data for the iridium and palladium compounds are close to the 1:1 ratio of unsaturated metal complex to ligand which
Figure 14

Selected Infrared Absorptions of the Product of the Reaction of $[\text{Ir(diphos)}_2]\text{Cl}$ with Diphenylcyclopropenone (Nujol Mull)
FIGURE 15

Selected Infrared Absorptions of the Product of the Reaction of Pd(Ph₃P)₄ with Diphenylcyclopropenone (Nujol Mull)
was found for the platinum complex. Without analytical data or other data which support the presumed metallocycles, no further comment can be made concerning their structure.

The attempted reactions of IrH(CO)(Ph₃)₃ and IrH(CO)₂(Ph₃P)₂ with diphenylcyclopropenone in benzene at 50-60°C yielded only a mixture of the reactants. The attempted reaction of IrCl(CO)(Ph₃P)₂ with diphenylcyclopropenone in benzene at room temperature for 24 hr resulted in the return of the reactants. Even the attempted reaction of Vaska's compound with diphenylcyclopropenone in benzene in an ultraviolet exposure chamber at 50-60°C was not successful after a period of 2 hr.

Other unsaturated cyclic ketones which were mixed with tetrakis(triphenylphosphine)platinum(0) in solution were tetraphenylcyclopentadienone, 2,5-dimethyl-3,4-diphenylcyclopentadienone, cycloheptatrienone, and N-acetyldiphenylcyclopropenoxime. None of these compounds reacted with the platinum species. Only the three membered unsaturated ketone system reacted under these conditions. The difference in reactivity of the three membered ring and the larger rings could be the increased steric effect as the ligand approaches the metal atom, hindering formation of the olefin complex with the metal. Another consideration: must be the lessening of ring strain as the ring size increases which would decrease the reactivity of the cyclic ketones especially opening of the ring.
B. Reactions of Diaminodicyanoethylene

Tetrakis(triphenylphosphine)platinum(0) reacted with diaminomaleonitrile in benzene at room temperature to give a 1:1 adduct of Pt(Ph₃P)₂ with the substituted olefin. Possible structures for the complexation of this symmetrically substituted olefin to the metal atom are the π-bonded olefin complex, XVII, the σ-bonded amine complex, XVIII,

\[ \text{XVII} \]

the nitrogen of the nitrile σ-bonded to the metal, XIX,

\[ \text{XIX} \]

and the π-bonded carbon-nitrogen multiple bond complexed to the metal, XX. In the most common mode of bonding between olefins and transition metals, i.e. XVII, the infrared spectrum shows a lowering of the C=C stretching frequency relative to the uncoordinated olefin.¹³⁷ The orange crystals of the 1:1 complex showed a lowering of the C=C stretching frequency on coordination of the olefin to the
metal form 1615 cm\(^{-1}\) in the uncoordinated diaminomaleonitrile, Figure 16, to 1570 cm\(^{-1}\) in the coordinated olefin, Figure 17. Other absorptions of interest are seen at 3395 cm\(^{-1}\) attributed to an N-H stretching vibration and a strong band at 2195-2185 cm\(^{-1}\) attributed to a C=\(\equiv\)N stretching frequency.

Reaction of \(\text{Pt}(\text{C}_2\text{H}_4)(\text{Ph}_3\text{P})_2\) with diaminomaleonitrile in benzene at room temperature gave an orange solid. An infrared spectrum of the solid showed the same absorptions as did the product of \(\text{Pt}(\text{Ph}_3\text{P})_4\) with diaminomaleonitrile, however, a broad weak band at 1635 cm\(^{-1}\) was observed which was not in the previous product. Analytical data for the product showed low percentages of carbon and nitrogen compared to calculated values for \(\text{Pt}(\text{Ph}_3\text{P})_2\) (diaminomaleonitrile). Recrystallization of the solid from dichloromethane/hexane did not remove the weak band at 1635 cm\(^{-1}\) from the spectrum of the recrystallized product. Analytical percentages were also low.

Reaction of \(\text{Pt}(\text{CO})_2(\text{Ph}_3\text{P})_2\) with diaminomaleonitrile in dichloromethane at room temperature produced a dark-orange solid. This product was very similar to the product of the platinum-ethylene complex with this ligand. Low analytical data and a strong absorption at 1640 cm\(^{-1}\) were again observed.

The reaction of \(\text{RhCl}(\text{Ph}_3\text{P})_3\) with diaminomaleonitrile yielded shiny green crystals which analytical data
FIGURE 16

Selected Infrared Absorptions of Diaminomaleonitrile
(Nujol Mull)
FIGURE 17

Selected Infrared Absorptions of
Pt(Ph₃P)₂(diaminomaleonitrile)
(Nujol Mull)
showed to be very close to the calculated values for RhCl-(Ph$_3$P)$_2$[(NH$_2$)C=C(NH$_2$)(CN)]. Loss of a cyano-group from the ligand and a triphenylphosphine from the metal gives a possible formulation of this product. The infrared spectrum of the green crystals, Figure 18, revealed two weak bands at 3330 and 3230 cm$^{-1}$ attributed to N-H stretching frequencies, a strong band at 2204 cm$^{-1}$ attributed to the CN stretching mode, and weak bands at 1610 and 1588 cm$^{-1}$ attributed to C=C and N-H vibrations. Except for the analytical data, evidence indicates a similar reaction product to the Pt(Ph$_3$P)$_2$(diaminomaleonitrile) product is formed.

The reaction of MX(CO)(Ph$_3$P)$_2$ [M = Ir; X = Cl, Br, I; M = Rh; X = Cl] with diaminomaleonitrile produced no oxidative addition products at room temperature in benzene. Only the reactants were isolated. However, the reaction of IrCl(CO)(Ph$_3$P)$_2$ with diaminomaleonitrile in benzene at reflux produced a brown solution. Under reduced pressure solvent was removed and a black tar recovered. An infrared spectrum of the solid showed at 1945 cm$^{-1}$ a strong absorption corresponding to the carbonyl stretch of Vaska's compound. Also seen in the spectrum were small bands at 3398, 2177, 2050, and 1568 cm$^{-1}$. These bands indicate the possible oxidative addition to the iridium(I) complex by the olefin. After separation of the Vaska's compound from the black tar, no other metal containing species could
FIGURE 18

Selected Infrared Absorptions of the Product of the Reaction of $\text{RhCl(Ph}_3\text{P)}_3$ with Diaminomaleonitrile (Nujol Mull)
be found. A very small amount of organic material was recovered but not characterized. Unreacted diaminomaleonitrile was also recovered. Possible reaction of the Ir(I) complex with the olefin with subsequent decomposition is evidenced by the presence of a 2050 cm$^{-1}$ absorption which could indicate an Ir(III) carbonyl stretching frequency. It is possible that the metal atom serves as the site for some catalytic degradation of the olefin with the subsequent regeneration of the starting metal complex.

Thermal stabilities of complexes of Pt(Ph$_3$P)$_2$ with various cyano-substituted olefins have been correlated with the number of cyano-groups substituted on the olefin. Table V lists the thermal stabilities of various olefins complexed to Pt(Ph$_3$P)$_2$. The presence of electron-donating amine substituents causes the Pt(Ph$_3$P)$_2$(diaminomaleonitrile) complex to be less thermally stable.

A definite structural formulation when diaminomaleonitrile complexes to Pt(0) and Rh(I) substrates cannot be made at this time. The lack of reactivity with Vaska's compound and analogous complexes must be attributed to the presence of the electron-donating amine-groups on the olefin. Olefin-IrCl(CO)(Ph$_3$P)$_2$ complex stability varies directly with the electron affinity of the substituents on the olefin. For cyano-olefin complexes of these metals the order of stability has been given in the order: TCNE $>$ fumaronitrile $>$ acrylonitrile. Loss of electronegativity
<table>
<thead>
<tr>
<th>Olefin</th>
<th>Decomposition °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCNE</td>
<td>268-270</td>
<td>105</td>
</tr>
<tr>
<td>Fumaronitrile</td>
<td>208-210</td>
<td>208</td>
</tr>
<tr>
<td>Diphenylmethylene maleonitrile</td>
<td>162-164</td>
<td>208</td>
</tr>
<tr>
<td>Cinnamonicitrile</td>
<td>153-158</td>
<td>208</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>126-129</td>
<td>208</td>
</tr>
<tr>
<td>Diaminomaleonitrile</td>
<td>122-124</td>
<td>a</td>
</tr>
<tr>
<td>1,1-Diamino-2,2-dicyanoethylene</td>
<td>165-170</td>
<td>a</td>
</tr>
</tbody>
</table>

a refers to this work
on the olefin either by removal of electronegative groups or by the presence of electron-donating groups would be expected to lower the thermal stability of the complexes.

The reactions of an isomer of diaminomaleonitrile, 1,1-diamino-2,2-dicyanoethylene, with coordinatively unsaturated noble metal substrates were studied to determine the mode of reaction, if any, and similarities or differences to its symmetrical isomer. The reaction of Pt(Ph₃P)₂⁻(C₂H₄) with 1,1-diamino-2,2-dicyanoethylene in benzene at room temperature produced a 1:1 solid product. An infrared spectrum of the off-white solid, Figure 19, showed absorptions very similar to those of the diaminomaleonitrile complex with Pt(Ph₃P)₄. The infrared spectrum of the uncoordinated 1,1-diamino-2,2-dicyanoethylene, Figure 20, when compared to the spectrum of diaminomaleonitrile, Figure 15, shows similar absorptions except for two bands below 1635 cm⁻¹. The spectrum of the symmetrically substituted olefin shows a band at 1615 cm⁻¹ while the polar isomer has a band at 1535 cm⁻¹. Coordination of 1,1-diamino-2,2-dicyanoethylene to the Pt(Ph₃P)₂ moiety caused a decrease in the frequency of the band at 1632 to 1612 cm⁻¹ indicating coordination through the double bond of the olefin to the metal. Analytical data for this off-white solid showed low percentage values for carbon and nitrogen compared to calculated percentages of a 1:1 complex of Pt(Ph₃P)₂ and
FIGURE 19

Selected Infrared Absorptions of the Product of the Reaction of Pt(C₂H₄)(Ph₃P)₂ with 1,1-Diamino-2,2-dicyanoethylene (Nujol Mull)
FIGURE 20

Selected Infrared Absorptions of 1,1-Diamino-2,2-dicyanoethylene (Nujol Mull)
1,1-diamino-2,2-dicyanoethylene. Recrystallization of this solid from benzene/ethanol gave a yellow solid which analytically revealed lower values for carbon and nitrogen percentages than the initially isolated product. No firm structural proposal will be made at this time.

The reaction of Pt(Ph₃P)₄ with 1,1-diamino-2,2-dicyanoethylene in benzene at room temperature gave a yellow solid. A similar absorption pattern was found in the infrared spectral data for this product, Figure 21, as was in the spectrum of the ethylene-platinum complex with this olefin. Analytical data showed an extremely low percentage of carbon in this solid. Recrystallization of the solid from dichloromethane/hexane gave a solid with the same spectral features and the same analytical data within 2%.

Reaction occurred upon mixing equimolar amounts of RhCl(Ph₃P)₃ with 1,1-diamino-2,2-dicyanoethylene in benzene at room temperature. Upon addition of hexane, a light orange precipitate was isolated. Infrared spectral absorptions (Figure 22) of the solid were similar to those of the platinum phosphine complex reported above. Analytical data correspond to a 1:1 complex of RhCl(Ph₃P) with the olefin percent of nitrogen and hydrogen which are within limits but low carbon percentage. Comparison of the experimental data for this complex with calculated values for RhCl(Ph₃P)₂(olefin) revealed carbon and hydrogen percentages which were within 0.5% but the nitrogen was lower than this.
FIGURE 21

Selected Infrared Absorptions of the Product of the Reaction of \( \text{Pt(Ph}_3\text{P)}_4 \) with 1,1-Diamino-2,2-dicyanoethylene (Nujol Mull)
FIGURE 22

Selected Infrared Absorptions of the Product of the Reaction of $\text{RhCl(Ph}_3\text{P)}_3$ with 1,1-Diamino-2,2-dicyanoethylene

(Nujol Mull)
Attempted reactions of $\text{MX(CO)(Ph}_3\text{P)}_2$ $[\text{M} = \text{Ir}; \text{X} = \text{Cl}, \text{F}; \text{M} = \text{Rh}; \text{X} = \text{Cl}]$ with 1,1-diamino-2,2-dicyanoethylene gave no evidence of any interaction.

Another amine-substituted cyano-olefin with which attempts were made to determine its reactivity with transition metals of low valence was 1,1-bis(dimethylamino)-2,2-dicyanoethylene. The reaction of RhCl(Ph$_3$P)$_3$ with this olefin in dichloromethane at room temperature produced a brown solid. Thin layer chromatography showed the solid to be homogeneous and different from the reactants and triphenylphosphine. Low values for carbon and nitrogen percentages were noted when analytical determinations were made and compared to calculated values for RhCl(Ph$_3$P)$_2$(olefin).

Figures 23 and 24 show the infrared spectra of the olefin and the reaction product with the rhodium(I) complex respectively. The brown crystals show a very similar pattern of absorptions compared to the platinum complexes with diaminomaleonitrile and 1,1-diamino-2,2-dicyanoethylene. There is some indication of the presence of N-H bonds in the product as seen by a broad weak band at 3430 cm$^{-1}$.

The complexes Pt(C$_2$H$_4$)(Ph$_3$P)$_2$ and IrCl(CO)(Ph$_3$P)$_2$ show no reactivity with 1,1-bis(dimethylamino)-2,2-dicyanoethylene in benzene at room temperature. This was confirmed by TLC and the infrared spectra of the recovered reactants.

The reactivity of these amine-substituted cyanoethylenes was found to be consistent in that only the
FIGURE 23

Selected Infrared Absorptions of
1,1-Bis(dimethylamino)-2,2-dicyanoethylene
(Nujol Mull)
Selected Infrared Absorptions of the Product of the Reaction of RhCl(Ph₃P)₃ with 1,1-Bis(dimethylamino)-2,2-dicyanoethylene (Nujol Mull)
platinum(0) and rhodium(I) complexes formed products. In each reaction the most likely mode of bonding of the olefin to the metal is by complexation of the double bond of the olefin to the metal atom. A lowering of the absorption attributed to the C=C stretching vibration was observed in the infrared spectrum for each reaction. The fact that no product was evidenced in the mixing of Pt(C$_2$H$_4$)(Ph$_3$P)$_2$ with 1,1-bis(dimethylamino)-2,2-dicyanoethylene is not understood at this time. The platinum species is expected to be more reactive than the rhodium complex. The fact that the platinum-olefin complexes were more easily characterized than the rhodium-olefin complexes also indicates the greater reactive potential of the rhodium species.

C. Reactions of Metal-Nitrosyl Complexes with Tetracyanoethylene

The reaction of nitrosylcarbonylbis(triphenylphosphine)iridium(-I) with either an equimolar or excess of tetracyanoethylene in benzene at room temperature produced a green solid which was shown analytically to have a ratio of 2:1 for tetracyanoethylene to iridium. Figure 25 shows the infrared spectral pattern of this solid. When this product is recrystallized from chloroform/ethanol another green solid is obtained which shows some differences.
FIGURE 25

Selected Infrared Absorptions of the Product of the Reaction of \textit{Ir(NO)(CO)(Ph}_3\textit{P)}_2 \textit{with Tetracyanoethylene and this Product Recrystallized (Nujol Mull)
Figure 25 also shows the infrared spectra of the recrystallized product. Analytical data for the recrystallized solid revealed a 1:1 tetracyanoethylene to iridium ratio. The initial green product shows a three band pattern in the range from 1500-2300 cm$^{-1}$ with bands at 2220-2210, 2160, and 2080 cm$^{-1}$. The weak bands above 2200 cm$^{-1}$ are easily attributed to the carbon-nitrogen triple bond absorptions of nitriles bonded to carbon atoms. The strong bond at 2080 cm$^{-1}$ fits in very well with the expected product of oxidative addition of the iridium atom to Ir(III) carbon monoxide absorption. The interesting medium intensity band at 2160 cm$^{-1}$ is less easily assigned. The reaction of IrH(CO)(Ph$_3$P)$_3$ with tetracyanoethylene was reported and produced a complex which had a ratio of 2:1 for tetracyanoethylene to iridium analytically. The infrared spectrum of this complex showed a similar three band pattern in the range of interest. However, a band at 1360 cm$^{-1}$ was present in the product of the iridium hydride-tetracyanoethylene reaction but not found in the iridium nitrosyl-tetracyanoethylene reaction product. Also the intensity of the 2164 cm$^{-1}$ band in the iridium-hydride-tetracyanoethylene product was judged to be very strong. Formulation of the structure of the product was proved to be coordination of one tetracyanoethylene molecule as a π-bonded olefin and coordination of the other tetracyanoethylene by a 1,4-addition of the hydride to the tetracyanoethylene attached to the metal as a keteniminato
ligand. The bands at 2164 cm\(^{-1}\) and 1360 cm\(^{-1}\) were attributed to the \(\nu_{\text{N=C=C}}\) asymmetric and symmetric absorptions, respectively. Due to the difference in the strength of the higher energy keteniminatō absorption and the 2160 cm\(^{-1}\) band in the iridium-nitrosyl product with tetracyanoethylene and the absence of the lower keteniminatō band in the iridium-nitrosyl product, one cannot suggest a possible analogy to the iridium-hydride reaction to tetracyanoethylene. The analytical data of this compound are closest to an 8:1 nitrogen to iridium ratio. If two tetracyanoethylene molecules are considered to be bonded to the metal then the nitrosyl ligand would have to be eliminated. There is no infrared absorption which could be easily assigned to a nitrosyl vibration with certainty. No structural formulation can be made for this product without further data.

The recrystallized product showed infrared absorptions which indicated one tetracyanoethylene molecule was bonded as a \(\pi\)-olefin to the metal atom. Analytical data indicate a 5:1 ratio of nitrogen to iridium which would allow for the retention of the nitrosyl ligand on the metal as the olefin adds oxidatively. The absorptions are assigned to \(\nu_{\text{CN}}\) absorption at 2220 cm\(^{-1}\) and \(\nu_{\text{CO}}\) absorption for Ir(III) at 2080 cm\(^{-1}\). Again however, there is no easily assignable band to account for the nitrosyl ligand. Bellamy has reported for organic nitrosyls that there is no absorp-
tion for nitrosyl vibration due to the fact that organic nitrosyls dimerize removing the vibration. Both the initial product and the recrystallized product give molecular weights which correspond to monomeric units. Both products are very stable thermally. A possible structure for the recrystallized product could be the six-coordinate Ir(III) oxidative addition product which would be analogous to the Vaska's compound product with tetracyanoethylene. Structure XXI represents this speculation.

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\begin{array}{c}
\text{XXI} \\
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\text{The reaction of } \text{Ir(NO)(Ph}_3P)_3 \text{ with tetracyanoethylene gave a purple-brown solid which was stable in air. Figure 26 shows the infrared absorptions which are seen in the 2300-1500 cm}^{-1} \text{ range. These absorptions are consistent with other complexes of activated olefins with this metal complex. A band at 2225 cm}^{-1} \text{ is attributed to the nitrile vibration bonded to a carbon atom and the band at 1615 cm}^{-1} \text{ is attributed to the nitrosyl ligand. Reaction of this complex with maleic anhydride, tetrafluoroethylene, and 3,4,5,6-tetrachloro-1,2-benzoquinone produced complexes with the formula Ir(NO)(Ph}_3P)_2(olefin). In each}
\end{array}
\end{array}
\]
FIGURE 26

Selected Infrared Absorptions of
Ir(NO)(Ph₃P)₂(TCNE)
(Nujol Mull)
of these complexes a nitrosyl absorption was assigned at 1672, 1630, and 1592 cm\(^{-1}\) respectively. The complex Rh(NO)\((\text{Ph}_3\text{P})_3\) has been reacted with tetracyanoethylene and a similar complex was formed.\(^{198}\) The nitrosyl assigned infrared absorption was seen at 1650 cm\(^{-1}\) for the rhodium complex. The analytical data for the iridium for the iridium-nitrosyl-tetracyanoethylene product was approximately 0.26\% below the 0.5\% limit on the nitrogen percentage with the carbon and hydrogen values within the limit. Molecular weight data support a monomeric formulation. The most consistent formulation for this product is \(\text{Ir(NO)}(\text{Ph}_3\text{P})_2\)\-(TCNE), XXII. The proposed structural formulation includes a bent \(\text{M-N-O}\) linkage analogous to proven square pyramidal structures \(^{165,167}\) with an apical nitrosyl ligand.

Excess tetracyanoethylene was mixed with hydrido-nitrosyltris(triphenylphosphine)iridium(I) perchloroate in dichloromethane solution. Addition of hexane produced a dark red-purple solid. The infrared spectral absorptions of interest are reproduced in Figure 27. The broad medium band at 2224 cm\(^{-1}\) is attributed to carbon-nitrogen triple bond
FIGURE 27

Selected Infrared Absorptions of the Product of the Reaction of \([\text{IrH(NO)(Ph}_3P)_3\]ClO_4\) with Tetracyanoethylene (Nujol Mull)
of the nitrile bonded to a carbon atom. The band at 1607 cm\(^{-1}\) is attributed to the nitrosyl absorption as in the iridium-nitrosyl-phosphine reaction product above. The weak band at 2060 cm\(^{-1}\) is not easily assigned. The initial Ir-H absorption of the reactant complex was observed at 2168 cm\(^{-1}\). A lowering of the Ir-H absorption energy would be difficult to rationalize on oxidative addition to the metal atom. The analytical data for the new compound show values close to a 1:1 ratio of [IrH(NO)(Ph\(_3\)P)]ClO\(_4\) to tetracyanoethylene. Recrystallization of this product from dichloromethane/hexane gave a bright orange solid which was shown to be [Ir(OH)(NO)(Ph\(_3\)P)]ClO\(_4\) by infrared and analytical data. Structure XXIII is a possibility of the formulation

![Structure XXIII](image)

of the reaction product if the Ir-H is intact.

The reaction of IrCl\(_2\)(NO)(Ph\(_3\)P)\(_2\) was stirred with excess tetracyanoethylene at room temperature in dichloromethane solution and at reflux for 1 hr. No reaction occurred.

The reaction of [IrCl(NO)(CO)(Ph\(_3\)P)\(_2\)]BF\(_4\) with tetracyanoethylene in dichloromethane produced a green solid
when ethanol was added. This solid showed very weak absorptions in the cyanide and Ir(III)-CO vibration regions. There was no absorption in the 1600-1900 cm$^{-1}$ range which could be a nitrile absorption. A chloroform solution of the reactants revealed that reaction had taken place when monitored with infrared spectroscopy. Figure 28 shows absorptions of interest from the solution spectrum. The strong band at 1675 cm$^{-1}$ is attributed to the nitrosyl ligand in the reaction product is shifted down in energy from the initial metal complex. There is no strong absorption in the 2100-2000 range as was seen in the spectrum of the initial complex assigned to Ir(III)-CO vibration at 2065 cm$^{-1}$. All efforts to isolate a stable solid product which retained some of these infrared absorptions were unsuccessful.

Other activated olefins which were tested for reactivity with iridium-nitrosyl complexes did not proceed. The complex Ir(NO)(CO)(Ph$_3$P)$_2$ was added to fumaronitrile and no reaction occurred. Ir(NO)(Ph$_3$P)$_3$ was mixed with fumaronitrile and cinnamonic acid. There was no reaction in either case.

The reactions of tetracyanoethylene with various iridium-nitrosyls yielded some interesting products. The most straightforward reaction was the Ir(NO)(Ph$_3$P)$_3$ with tetracyanoethylene which yielded a complex analogous to the complexes of other activated olefins with this complex. The
FIGURE 28

Selected Infrared Absorptions of the Reaction Solution of $[\text{IrCl}(\text{NO})(\text{CO})(\text{Ph}_3\text{P})_2]\text{BF}_4$

with Tetracyanoethylene

(Chloroform Solution)
value of the absorption assigned to the nitrosyl vibration cannot be used to comment on the deviation from linearity of the M-N-O angle. The other complexes which reacted with the cyano-olefin gave products which are not yet understood. The fate of the nitrosyl in the Ir(NO)(CO)(Ph₃P)₂-tetracyanoethylene reaction products deserves structural study. The reactions of [IrH(NO)(Ph₃P)₃]ClO₄ and [IrCl(NO)-(CO)(Ph₃P)₂]BF₄ with tetracyanoethylene produced products which could not be isolated. The fact that only the tetracyano-substituted olefin reacted with the iridium nitrosyls tested indicates the lower reactivity of the olefins with fewer electron-withdrawing nitriles attached.

In comparing the reactions of metal nitrosyls with tetracyanoethylene to the reactions of metal carbonyls with tetracyanoethylene the most direct comparison of reactivity would be to consider the complexes IrCl(CO)(Ph₃P)₂ and [IrCl(NO)(Ph₃P)₂]ClO₄ with tetracyanoethylene. Both metal complexes form Ir(III) six-coordinate oxidative addition products with tetracyanoethylene. Reactions were attempted with both the iridium-carbonyl and the iridium-nitrosyl complexes with fumaronitrile. The carbonyl complex reacted to form a stable complex while the nitrosyl complex did not react with this less activated olefin.

Another example of the lower reactivity of iridium nitrosyl complexes compared with iridium carbonyl complexes is the complexes IrH(CO)(Ph₃P)₃ and [IrH(NO)(Ph₃P)₂]ClO₄ with.
tetracyanoethylene. The carbonyl complex reacts with two molecules of tetracyanoethylene when reacted with excess olefin,\textsuperscript{209} while the nitrosyl reacted with only one molecule of the olefin. Another difference in the effect of reaction of metal nitrosyls and metal carbonyls is the effect oxidative addition, for example, has on the vibrations of the ligands. The complexes IrCl(CO)(Ph\textsubscript{3}P)\textsubscript{2} reacts with tetracyanoethylene and the $\nu_{CO}$ absorption increases in energy, whereas the analogous nitrosyl complex, [IrCl(NO)(Ph\textsubscript{3}P)\textsubscript{2}]ClO\textsubscript{4} reacts with tetracyanoethylene and the $\nu_{NO}$ absorption decreases.\textsuperscript{199,144}
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