Reactions of Tetracyanoethylene and Other Cyano-Substituted Ethylenes with Iridium(I) Complexes[1]

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Abstract: Reactions of the cyanocarbon, tetracyanoethylene (TCNE), with iridium(I) complexes of the type $IrX(CO)(Ph_3E)_2$ (E = P, X = Cl, Br, I, NCS, NCO; E = As, X = Cl) have been studied under preparative conditions, and a number of new, very stable compounds, $IrX(CO)(Ph_3E)_2TCNE$, have been isolated and characterized. Attempts were also made to prepare complexes containing coordinated acrylonitrile, cinnamonitrile, crotononitrile, fumaronitrile, and diphenylmethylenemalononitrile, but only with acrylonitrile and fumaronitrile were solid complexes isolated, and these are less stable than the tetracyanoethylene compounds. Infrared spectral data suggest that the cyanoolefins are bonded to iridium *via* the olefinic bond, and it has been inferred that substantial electron density on the metal has been transferred to the olefin in the tetracyanoethylene complexes.

Reactions of olefins with transitional metal complexes have been a subject of much investigation since the first metal-olefin complex was prepared in 1827 by Zeise.[2] Experimentalists have been aided greatly in their studies by the theoretical contributions of Dewar[3] and Chatt and Duncanson,[4] who have explained metal-olefin bonding in terms of combined σ (olefin$\rightarrow$metal) and π (metal$\rightarrow$olefin) bonding effects. For a given metal ion, the stabilities of complexes containing acyclic monooelfins must be viewed in terms of both steric and electronic factors. Insofar as electronic factors are concerned, the effect of various substituents attached to the olefin on the stability of the metal-olefin bond is somewhat ambiguous. This ambiguity arises because, in the context of the Dewar-Chatt-Duncanson model of the metal-olefin bond, stability will be dependent on the relative importance of the two components of the M-olefin bond, *i.e.*, the M$\rightarrow$olefin π bond and the olefin$\rightarrow$M σ bond. If the σ component is the more important, then electron-donating substituents will enhance the stability and electron-withdrawing substituents will lower the stability. On the other hand, if the π component is more important in the over-all bonding scheme, effects opposite to those mentioned above would be anticipated. In the case of silver(I)-olefin complexes, the σ component of the bond appears to be the more important, as evidenced by equilibrium studies where it has been found that alkyl substituents on the olefin give rise to more stable complexes than do hydroxyl and carboxyl substituents.[5] For platinum(II) complexes, however, measurements of stability constants indicate that the π acceptor capacity of the olefin is more important than its σ donor capacity for the formation of stable platinum-olefin bonds.[6] Cramer recently reported equilibrium studies of rhodium(I)-olefin complexes and showed that coordination was enhanced when fluorine and chlorine were attached to the olefin.[7]

From a preparative point of view, inadequate attention has been given to the reactions of highly activated olefins with transitional metal substrates. In 1959 Watterson and Wilkinson[8] attempted the preparation of complexes using tetrafluoroethylene. This approach was based on the premise that activated olefins might be bonded to a metal *via* a "pure π-bond," since the donor properties of the C=C bond in such an olefin would be negligible whereas the acceptor properties would be enhanced by strongly electron-withdrawing substituents. Their expectations were not immediately realized, but more recently a number of tetrafluoroethylene complexes have been reported.[9] The nature of the bonding in these tetrafluoroethylene complexes is still of a speculative nature.

In part I of this series, we reported the first complexes containing the activated olefin, tetracyanoethylene, covalently bonded to a transitional metal.[10] Particularly noteworthy of these platinum complexes is their high thermal stability relative to analogous hydrocarbon complexes. For example, the hydrocarbon complex, $Pt(Ph_3P)_2$(ethylene), decomposes[11] at 122-125°, whereas the cyanocarbon complex, $Pt(Ph_3P)_2$(tetracyanoethylene), decomposes at 268-270°. The propensity of certain d^8 square-planar complexes of iridium(I) to undergo oxidative addition reactions with various molecules, including olefinic hydrocarbons[12] and fluorocarbons,[9a,b] suggests that olefinic cyanocarbons might form adducts. This paper reports preparative studies of the reactions of a number of cyano-substituted ethylenes (acrylonitrile, cinnamonitrile, crotononitrile, fumaronitrile, diphenylmethylenemalononitrile, and tetracyanoethylene) with iridium substrates of the type $IrX(CO)(Ph_3E)$ (E = P, X = Cl, Br, I, NCO, NCS; E = As, X = Cl). Some of the results

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[1] Paper III of the series, Metal Complexes of Cyanocarbons; part II: W. H. Baddley, *J. Am. Chem. Soc.*, **88**, 4545 (1966).

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described herein have been previously communicated.[1] Reactions of several cyanoolefins with some four-, five-, and six-coordinate hydridoiridium complexes are currently under study, and these results and their relevance to homogeneous catalysis will be reported in a later paper in this series.

Experimental Section

I. Materials. Tetracyanoethylene was purchased from Columbia Organic Chemicals Co., Inc., and was sublimed prior to use. Acrylonitrile was an Eastman Organic Chemicals product. Cinnomonitrile, crotononitrile, and 1,1-dicyano-2,2-diphenylethylene (diphenylmethylenemalononitrile) were purchased from Aldrich Chemical Co. Inc., and were used without further purification. Fumaronitrile was obtained from K and K Laboratories, Inc.

Iridium-containing starting materials were prepared from either $Na_3IrCl_6 \cdot 12H_2O$ or $IrCl_3 \cdot 3H_2O$, both of which were purchased from Alfa Inorganics, Inc. Vaska's compound, $IrCl(CO)(Ph_3P)_2$, was prepared by literature methods.[13,14] The triphenylarsine analog of Vaska's compound was prepared from $Na_3IrCl_6 \cdot 12H_2O$ by a procedure similar to that used in preparing $IrCl(CO)(Ph_3P)_2$.[13] Compounds of the type $IrX(CO)(Ph_3P)_2$ (X = Br, I, NCS, NCO) were synthesized *via* metathetical reactions of $IrCl(CO)(Ph_3P)_2$ and NaX or LiX in acetone. Preparations of $IrX(CO)(Ph_3P)_2$ (X = NCS and NCO) do not seem to have been described previously in the literature. From the metathetical reaction of $IrCl(CO)(Ph_3P)_2$ with a tenfold excess of NaSCN in acetone at 50° for 30 min, a yellow solid was obtained. The infrared spectrum[15] of this compound in Nujol mull included bands at 1973 (vs, sp) and 2079 (vs, sp) cm^{-1} which are the C≡O and C≡N stretching frequencies, respectively. In the 650–900-cm^{-1} region of the spectrum, the absorptions of $IrCl(CO)(Ph_3P)_2$ and $Ir(NCS)CO(Ph_3P)_2$ were quite similar except for a weak, broad band at 856 cm^{-1} in the latter compound. For X = NCO, bright yellow crystals were obtained after recrystallization from benzene–methanol. The infrared spectrum of this compound in hexachlorobutadiene (hereafter abbreviated as HCBD) mull included bands at 1958 (vs, sp) and 2245 cm^{-1} (vs, sp).

Thiophene-free benzene was dried over sodium wire.

All reactions were carried out in a nitrogen atmosphere, but work-up of reaction mixtures was usually done in the open atmosphere.

II. Preparation and Characterization of Tetracyanoethylene Complexes of Iridium. The preparation of these compounds was quite simple. Generally, the iridium(I) substrate, $IrX(CO)(Ph_3E)_2$ (E = P, X = Cl, Br, I, NCO, NCS; E = As, X = Cl) was dissolved or suspended in a small volume of benzene at room temperature or slightly above (50–70°), and either solid tetracyanoethylene or a benzene solution was added in an equimolar amount, or up to a fivefold excess. The mixture was stirred with a magnetic stirring bar and within a few minutes complete precipitation of the product had occurred. The white or pale yellow solid was collected on a filter, washed with benzene and hexane, and recrystallized from a suitable solvent mixture. The yields were essentially quantitative.

A. **Chloro(carbonyl)bis(triphenylphosphine)(tetracyanoethylene)iridium,** $IrCl(CO)(Ph_3P)_2TCNE$, was recrystallized from $CHCl_3$–EtOH to give small, pale yellow crystals. *Anal.* Calcd for $IrC_{43}H_{30}OClP_2N_4$: C, 56.85; H, 3.33; Cl, 3.91; P, 6.82; N, 6.17; mol wt, 908. Found: C, 56.85; H, 3.27; Cl, 4.20; P, 6.93; N, 6.30; mol wt, 896 (osmometry in $CHCl_3$). The compound is insoluble in methanol, ethanol, and hexane, sparingly soluble in benzene, and very soluble in dichloromethane and chloroform.

A pyrolysis experiment was carried out with $IrCl(CO)(Ph_3P)_2$-TCNE in which a weighed amount of the compound, 0.1078 g, was placed in a glass spoon inside a sublimation apparatus. The apparatus was placed in an oil bath and heated at 210° for 9 hr, the pressure being reduced to 0.1 mm with a vacuum pump during the process. The sample had not lost weight after the heating was terminated, and there was no visible change in its appearance. The infrared spectrum after heating was identical with that of an unheated sample of $IrCl(CO(Ph_3P)_2TCNE$.

B. **Chloro(carbonyl)bis(triphenylarsine)(tetracyanoethylene)iridium,** $IrCl(CO)(Ph_3As)_2TCNE$, was obtained as pale yellow crystals after recrystallization from CH_2Cl_2–hexane. *Anal.* Calcd for $IrC_{43}H_{30}OClAs_2N_4$: C, 51.82; H, 3.03; As, 15.04; N, 5.62; mol wt, 996. Found: C, 52.41; H, 3.26; As, 14.68; N, 5.77; mol wt, 1005.

C. **Bromo(carbonyl)bis(triphenylphosphine)(tetracyanoethylene)iridium,** $IrBr(CO)(Ph_3P)_2TCNE$, precipated as a cream-colored solid when $IrBr(CO)(Ph_3P)_2$ and TCNE were allowed to react in benzene at room temperature. Recrystallization of reaction product from CH_2Cl_2–MeOH afforded pale yellow crystals. *Anal.* Calcd for $IrC_{43}H_{30}OBrP_2N_4$: C, 54.19; H, 3.17; mol wt, 952. Found: C, 54.31; H, 3.47; mol wt, 972.

D. When TCNE was added to a benzene solution of $IrI(CO)(Ph_3P)_2$ at room temperature, the color of the solution changed immediately to dark red. After the mixture was stirred for 2 min, a buff-colored solid precipitated. This amorphous solid was collected on a filter and washed with ethanol. **Iodo(carbonyl)bis(triphenylphosphine)(tetracyanoethylene)iridium,** $IrI(CO)(Ph_3P)_2TCNE$, was not obtained analytically pure. *Anal.* Calcd for $IrC_{43}H_{30}OIP_2N_4$: C, 51.66; H, 3.02. Found: C, 53.83; H, 3.39.

E. **Isothiocyanato(carbonyl)bis(triphenylphosphine)(tetracyanoethylene)iridium,** $Ir(NCS)CO(Ph_3P)_2TCNE$, was isolated as an off-white solid. *Anal.* Calcd for $IrC_{44}H_{30}P_2ON_5S$: C, 56.75; H, 3.25; P, 6.65; N, 7.52; S, 3.44; mol wt, 930. Found: C, 56.90; H, 3.53; P, 5.80; N, 7.64; S, 4.21; mol wt, 963.

F. **Isocyanato(carbonyl)bis(triphenylphosphine)(tetracyanoethylene)iridium,** $Ir(NCO)CO(Ph_3P)_2TCNE$, was prepared by dissolving $Ir(NCO)CO(Ph_3P)_2$ (0.39 g, 0.5 mmole) in 30 ml of boiling benzene and adding 0.12 g of TCNE (1 mmole). A white solid precipitated immediately and was collected on a filter after the mixture was stirred for 0.5 hr. The yield was 0.4 g. A portion of the solid was recrystallized from CH_2Cl_2–hexane, affording pale yellow crystals. *Anal.* Calcd for $IrC_{44}H_{30}O_2N_5P_2$: C, 57.75; H, 3.30; mol wt, 914. Found: C, 57.77; H, 3.46; mol wt, 935.

III. Reactions of Other Cyanoolefins with Iridium(I) Substrates. A. Acrylonitrile, $H_2C{=}CHCN$ (10 ml, 150 mmoles), was poured into a flask containing $IrCl(CO)(Ph_3P)_2$ (0.4 g, 0.5 mmole), and the bright yellow mixture was stirred at room temperature. After 2 min, the color of the mixture began to lighten, and in 10 min the color was snow-white. A white powder settled. The mixture was allowed to stand overnight under a stream of nitrogen and the supernatant liquid evaporated, leaving a bright yellow residue. The ir spectrum of a Nujol mull of this residue in the 1900–2300-cm^{-1} region showed a strong band at 1955 cm^{-1} indicating that the substance was $IrCl(CO)(Ph_3P)_2$. Acrylonitrile (10 ml) was added to the reaction vessel containing the yellow residue, and again the color reverted to white. Hexane (10 ml) was added, and the white powder was collected on a filter. An infrared spectrum of this material in a Nujol mull was recorded immediately, and bands were observed at 1955 (w), 2017 (vs, sp), 2210 (m, sp), and 2230 cm^{-1} (w). A spectrum was also recorded by mulling the white product with a few drops of acrylonitrile in Nujol, bands being observed in this case at 2017 (vs, sp), 2210 (m), and 2230 cm^{-1} (m). The white product of the reaction is presumably **chloro(carbonyl)bis(triphenylphosphine)(acrylonitrile)iridium,** $IrCl(CO)(Ph_3P)_2(H_2C{=}CHCN)$, but it was not analyzed. On sitting in air the white solid began to change color to pale yellow and in 24 hr had attained a bright yellow color. The ir spectrum of the yellow material showed it to be $IrCl(CO)(Ph_3P)_2$.

B. Crotononitrile, $CH_3CH{=}CHCN$ (10 ml, 123 mmoles), was poured onto $IrCl(CO)(Ph_3P)_2$ (0.4 g, 0.5 mmole), and the mixture was stirred at 70–80° for 1 hr. The solution, which originally was bright yellow, did not change color. Addition of hexane caused yellow crystals to form, which were identified as $IrCl(CO)(Ph_3P)_2$ *via* infrared.

C. Results similar to the above were obtained when a large excess of cinnamonitrile ($PhCH{=}CHCN$) was mixed with $IrCl(CO)(Ph_3P)_2$. No reaction occurred after heating the mixture at 70–80° for 1 hr.

D. Diphenylmethylenemalononitrile, $Ph_2C{=}C(CN)_2$ (1.15 g, 5 mmoles), was added to 20 ml of benzene containing 0.4 g (0.5 mmole) of $IrCl(CO)(Ph_3P)_2$, and the mixture was stirred at room temperature for 18 hr. There was no reaction. In another experiment, $IrCl(CO)(Ph_3P)_2$ and a 20-fold excess of $Ph_2C{=}C(CN)_2$ were refluxed in benzene for 1 hr, and again there was no reaction.

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(15) Abbreviations used in this paper to describe infrared band intensities and widths are: s, strong; vs, very strong; m, medium; w, weak; sp, sharp; and br, broad. All infrared band positions are given in cm^{-1}

Table I. Properties of Cyanoolefin Complexes of Iridium

Compound	Color	Mp, °C dec	Molecular weight Exptl	Molecular weight Theoret	Selected infrared bands ν_{CO}[a]	Selected infrared bands ν_{CN}[b]	Selected infrared bands Other
$IrCl(CO)(Ph_3P)_2TCNE$	White	265–270	896	908	2060	2235	
$IrCl(CO)(Ph_3As)_2TCNE$	Pale yellow	295–300	1005	996	2055	2235	
$IrBr(CO)(Ph_3P)_2TCNE$	Pale yellow	224–230	972	952	2056	2233	
$IrI(CO)(Ph_3P)_2TCNE$	Buff	210–218	*c*	1000	2060[d]	2230[d]	
$Ir(NCO)(CO)(Ph_3P)_2TCNE$	Pale yellow	285–289	935	914	2061	2232	ν_{CN}, 2271;[e] ν_{CO}, 1320[f]
$Ir(NCS)(CO)(Ph_3P)_2TCNE$	Pale yellow	240–250	963	930	2067	2230	ν_{CN}, 2105;[g] ν_{CS}, 880[h]
$IrCl(CO)(Ph_3P)_2(H_2C{=}CHCN)$	White	*i*	*j*	833	2017[k]		
$IrCl(CO)(Ph_3P)_2(NCCH{=}CHCN)$	White	268–270	793	853	2029	2212, 2223	
$IrBr(CO)(Ph_3P)_2(NCCH{=}CHCN)$	White	264–266	795	902	2030	2218, 2224	

[a] In CH_2Cl_2 solution; solid-state spectra are more complicated (see Experimental Section and Discussion). [b] In CH_2Cl_2 solution; solid-state spectra in Nujol or HCBD are similar. [c] Decomposition is extensive in solution and molecular weight was not measured. [d] Nujol mull spectrum. [e] C–N stretch of coordinated NCO in CH_2Cl_2 solution. [f] C–O stretch of coordinated NCO in Nujol mull. [g] C–N stretch of coordinated NCS in CH_2Cl_2 solution. [h] C–S stretch of coordinated NCS in Nujol mull. [i] Complex loses acrylonitrile on standing in air at room temperature. [j] Extensive dissociation in solution; molecular weight was not measured. [k] Nujol mull spectrum.

E. To a benzene solution (20 ml) of $IrCl(CO)(Ph_3P)_2$ (0.4 g, 0.5 mmole) was added 0.78 g (10 mmoles) of fumaronitrile (*trans*-1,2-dicyanoethylene). The color of the solution lightened immediately, and in 1 min a white solid began to form. The mixture was stirred for 0.5 hr, and the snow-white solid was collected on a filter, yielding 0.35 g of **chloro(carbonyl)bis(triphenylphosphine)(fumaronitrile)iridium,** $IrCl(CO)(Ph_3P)_2(NCCH{=}CHCN)$, after having been washed with benzene and hexane. A portion of the solid was dissolved in hot benzene to give a yellow solution which deposited small, white crystals after hexane was added and the solution was allowed to cool. *Anal.* Calcd for $IrC_{41}H_{32}OClP_2N_2$: C, 57.35; H, 3.77; mol wt, 858. Found: C, 57.24; H, 4.07; mol wt, 793. Solutions of $IrCl(CO)(Ph_3P)_2(NCCH{=}CHCN)$ in CH_2Cl_2 are pale yellow, and the ir spectrum of such a solution includes bands at 1966 (m), 2029 (vs, sp), 2212 (m, sp), and 2223 cm^{-1} (m, sp). Addition of excess fumaronitrile to a CH_2Cl_2 solution of $IrCl(CO)(Ph_3P)_2(NCCH{=}CHCN)$ causes an immediate disappearance of the yellow color, and the resulting solution is colorless. This change in color is accompanied by a complete loss of the 1966-cm^{-1} band in the infrared spectrum, the spectrum otherwise remaining the same in the 1900–2300-cm^{-1} region, except for the appearance of bands at 2244 (vs, sp) and 2268 cm^{-1} (w) due to the excess uncoordinated fumaronitrile.

F. **Bromo(carbonyl)bis(triphenylphosphine)(fumaronitrile)iridium,** $IrBr(CO)(Ph_3P)_2(NCCH{=}CHCN)$, was prepared from $IrBr(CO)(Ph_3P)_2$ and fumaronitrile by a procedure analogous to that described above for the chloro derivative. *Anal.* Calcd for $IrC_{41}H_{32}ON_2P_2Br$: C, 54.53; H, 3.58; mol wt, 902. Found: C, 54.11; H, 3.89; mol wt, 795.

IV. **Analyses and Instrumentation.** Analyses for carbon and hydrogen were carried out by Mr. R. Seab of the Department of Chemistry, Louisiana State University. Nitrogen, phosphorus, sulfur, and halogen analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Infrared spectra in the NaCl region were measured on a Beckman IR-7 spectrophotometer in Nujol or hexachlorobutadiene mulls, KBr pellets, and dichloromethane solutions.

Molecular weights were measured using a Mechrolab osmometer, Model 302, with a 37° probe. Chloroform was used as the solvent in all measurements, and the concentrations of the solutions were in the 5–15 × 10^{-3} *m* range.

Decomposition temperatures were measured on a Fisher-Johns melting point apparatus.

Results

A number of new complexes containing tetracyanoethylene covalently bonded to iridium have been prepared. These compounds are white or pale yellow in color, well crystallized, and stable to air indefinitely in the solid state. Solutions of $IrX(CO)(Ph_3P)_2TCNE$ (X = Cl, NCS, NCO) are stable for days, but, for X = I, solutions deteriorate rapidly, whereas solutions of $IrBr(CO)(Ph_3P)_2TCNE$ are stable for only about 1 day. The complexes show high thermal stability and decompose in the 200–300° range. Attempts to prepare several other cyanoolefin complexes were less successful than for tetracyanoethylene. Fumaronitrile and acrylonitrile reacted with $IrCl(CO)(Ph_3P)_2$ to yield isolable complexes. The acrylonitrile complex, $IrCl(CO)(Ph_3P)_2(H_3C{=}CHCN)$, loses acrylonitrile on standing in air and reverts to $IrCl(CO)(Ph_3P)_2$. The fumaronitrile complexes appear to be stable indefinitely in the solid state, but in solution there is partial dissociation to $IrX(CO)(Ph_3P)_2$ and fumaronitrile. In the case of crotononitrile, cinnamonitrile, and 1,1-diphenylmethylenemalononitrile, no reaction was observed to occur between these olefins and $IrCl(CO)(Ph_3P)_2$. Pertinent data for the new complexes are summarized in Table I.

Discussion

The new cyanoolefin complexes will be discussed from three points of view: structure, stability, and bonding.

I. **Structures of $IrX(CO)(Ph_3P)_2$(cyanoolefin).** The compound $IrBr(CO)(Ph_3P)TCNE$ has been examined crystallographically,[16] and the TCNE is known to be coordinated to iridium *via* the olefinic bond. The X-ray results also disclose that the molecular structure is essentially trigonal bipyramidal (if the TCNE is assumed to occupy one coordination position) with the two phosphine ligands *cis* to one another in the trigonal plane. The Br and CO groups are *trans* to one another in the apical positions. For such a structure, only one $C{\equiv}O$ stretching frequency would be expected in the infrared spectrum. In CH_2Cl_2 solutions, only one band is observed. However, in hexachlorobutadiene or Nujol mull spectra, two bands were found in the 2000–2100-cm^{-1} region for most of the complexes. This observation could be explained perhaps as being due to solid-state splitting effects in the mulls and is ostensibly corroborated by the fact that three recrystallizations of $IrCl(CO)(Ph_3P)_2TCNE$ did not change the relative intensities of the bands at 2041 and 2055 cm^{-1}. This behavior of $IrCl(CO)(Ph_3P)_2TCNE$ is atypical for these complexes, however, because recrystallization did in fact change the relative intensities of the ν_{CO} bands for most of the compounds, and it is therefore suggested that geometrical isomerism is the cause. Changes in spectra on recrystallization are illustrated in Figure 1 for

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(16) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

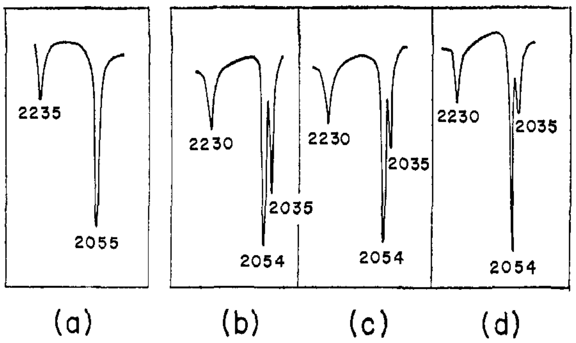

Figure 1. Infrared spectra of $IrCl(CO)(Ph_3As)_2TCNE$ in the 2000–2300-cm^{-1} region: (a) dichloromethane solution spectrum of the initial product of the reaction; (b) HCBD mull spectrum of the initial product of the reaction; (c) HCBD mull spectrum of the recrystallized material; (d) HCBD mull spectrum of the material which separated in the mother liquor from the recrystallization.

$IrCl(CO)(Ph_3As)_2TCNE$. The dichloromethane solution spectra of all the complexes exhibit only one band due to ν_{CO}, and, since spectra were recorded immediately (<5 min) after preparation of the solutions, isomerization to the more stable isomer must be fairly rapid in solution. Attempts were made to ascertain if isomerization occurs in the solid state by thermal means. For example, a solid sample of $IrBr(CO)(Ph_3P)_2TCNE$ was heated to 205°, and the HCBD mull spectrum was recorded, but there was no change from the spectrum of the unheated sample. There is some evidence that isomerization occurred under the conditions used to prepare KBr pellets for spectral examination, since the KBr pellet spectrum of $IrCl(CO)(Ph_3P)_2TCNE$ shows only one ν_{CO}.

II. Stabilities of $IrX(CO)(Ph_3P)_2$(cyanoolefin). The stabilities of $IrCl(CO)(Ph_3P)_2$(cyanoolefin), as deduced from the preparative experiments, melting point data, and solution behavior depend on the nature of the cyanoolefin and decrease in the order: tetracyanoethylene > fumaronitrile ≫ acrylonitrile ≫ crotononitrile, cinnamonitrile, and diphenylmethylenemalononitrile. From the preparative point of view, the bright yellow color of benzene solutions of $IrCl(CO)(Ph_3P)_2$ faded rapidly (<2 min) to pale yellow or colorless when either tetracyanoethylene, fumaronitrile, or acrylonitrile was added at 25°, and the solid complex precipitated subsequently. In contrast, no color change was observed at 25° when large excesses of either crotonitrile, cinnamonitrile, or diphenylmethylenemalononitrile were added to solutions of $IrCl(CO)(Ph_3P)_2$, nor did color changes occur when the reaction mixtures were refluxed for an hour or so. For the complexes $IrCl(CO)(Ph_3P)_2$(cyanoolefin) which were isolated as solids (cyanoolefin = tetracyanoethylene, fumaronitrile, and acrylonitrile), the tetracyanoethylene and fumaronitrile complexes appear to be stable indefinitely in the solid state. A sample of $IrCl(CO)(Ph_3P)_2TCNE$ has not changed over a 24-month period. However, the white compound $IrCl(CO)(Ph_3P)_2$(acrylonitrile) loses acryonitrile in a day or so on standing in air and reverts to bright yellow $IrCl(CO)(Ph_3P)_2$. In benzene, CH_2Cl_2, or $CHCl_3$ solutions, the complexes $IrX(CO)(Ph_3P)_2TCNE$ (X = Cl, Br, NCS, NCO) are quite stable as evidenced by the fact that no visible signs of decomposition were observed during recrystallization procedures, and also by the fact that molecular weight measurements gave normal values (see Table I). An exception to the above statement concerning solution stability is the iodo complex, $IrI(CO)(Ph_3P)_2TCNE$, whose benzene solutions darkened when recrystallization was attempted. Since tetracyanoethylene is a good oxidizing agent,[17] it is not surprising that decomposition resulted in the presence of iodide ion. In fact, a convenient laboratory synthesis[17] of potassium tetracyanoethylenide involves the reaction of TCNE with KI.

In contrast to the behavior of iridium–TCNE complexes in solution, the complexes of fumaronitrile and acrylonitrile undergo dissociation in solution.

$$IrCl(CO)(Ph_3P)_2(\text{cyanoolefin}) \rightleftharpoons IrCl(CO)(Ph_3P)_2 + \text{cyanoolefin}$$

$$\text{cyanoolefin} = \text{acrylonitrile, fumaronitrile}$$

Solutions of these complexes are bright yellow in color (indicative of $IrCl(CO)(Ph_3P)_2$) but change immediately to colorless if an excess of the olefin is added. Additionally, molecular weight measurements of the fumaronitrile complexes gave low values. Thus, of the cyanoolefin complexes isolated, those of tetracyanoethylene are the most stable, and stabilities generally increase as the number of electron-withdrawing cyano groups attached to the olefin increase. It was somewhat surprising that complexes of cinnamonitrile or diphenylmethylenemalononitrile could not be isolated, because it would seem that, with electron-withdrawing phenyl groups as well as cyano groups present in the system, the coordinating abilities would be enhanced relative to, say, acrylonitrile. Molecular models do not seem to suggest severe steric constrictions. However, in terms of the structure of a possible transition state in which the olefin approaches the square substrate from above or below the square plane, it is quite evident from molecular models that there will be, in fact, strong steric interactions between the phenyl groups attached to the olefin and the triphenylphosphine groups on the substrate. Hence, it is supposed that a kinetic factor is primarily responsible for the failure of cinnamonitrile and diphenylmethylenemalononitrile to react with $IrCl(CO)(Ph_3P)_2$.

The C≡O stretching frequencies in the complexes $IrCl(CO)(Ph_3P)_2$(cyanoolefin) show an interesting parallel with the stabilities; *i.e.*, the more stable the complex is, the higher ν_{CO} is. The increases in ν_{CO} for $IrCl(CO)(Ph_3P)_2$(cyanoolefin) relative to ν_{CO} in $IrCl(CO)(Ph_3P)_2$ are 100, 70, and 62 cm^{-1} respectively for tetracyanoethylene, fumaronitrile, and acrylonitrile. As noted in the introductory section, the over-all stability of a metal–olefin complex may be considered to be related to the relative importance of the olefin→metal σ bond as compared to the metal→olefin π bond in the context of the Dewar–Chatt–Duncanson model of metal–olefin bonding. It is tempting to regard the ν_{CO} values as being an experimental basis for believing that the π bond is more important than the σ bond in determining the stabilities of these iridium–olefin complexes, since a higher ν_{CO} implies greater transfer of electronic charge from metal to olefin and not *vice versa.* However, the situation is somewhat beclouded by the fact that the stereochemistries of the molecules

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[17] O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

are not known, and a change in ν_{CO} could certainly be due to a change in stereochemistry of the molecule as well as being due to a change in π acidity of the olefin.

Tetracyanoethylene complexes of iridium are much more stable than the analogous hydrocarbon or fluorocarbon complexes. It was noted by Vaska and Rhodes[18] that $IrI(CO)(Ph_3P)_2$ reacted reversibly with ethylene at 26° and 700 mm in toluene, but owing to rapid dissociation the complex was not isolated. The chloro complex $IrCl(CO)(Ph_3P)_2$ was less reactive toward ethylene. Tetrafluoroethylene was reported[9a] to react with $IrCl(CO)(Ph_3P)_2$ at 25° and 3 atm to give pale yellow $IrCl(CO)(Ph_3P)_2(C_2F_4)$, a complex which is completely (97%) dissociated[9b] into $IrCl(CO)(Ph_3P)_2$ and C_2F_4 at 130°. In striking contrast, a sample of $IrCl(CO)(Ph_3P)_2TCNE$, as described in the Experimental Section, was recovered unchanged after being heated at 210° for 9 hr at *ca.* 0.1 mm.

III. Bonding in $IrX(CO)(Ph_3P)_2$(cyanoolefin). A number of metal complexes containing monounsaturated moieties have been prepared in recent years in which certain ambiguities develop when an attempt is made to describe the stereochemistry of the complex, the oxidation of the central metal, and the manner in which the unsaturated moiety is bonded to the transitional metal.

The bonding in these cyanoolefin complexes of iridium presents a similar dilemma to that in some olefin and acetylene complexes previously reported.[19] Thus, in the context of valence-bond theory, structures as shown in Figure 2 may be drawn for $IrX(CO)(Ph_3P)_2$(cyanoolefin). Structure A of Figure 2 implies a trigonal bipyramid with the iridium in a +1 formal oxidation state such that the olefin is very little distorted from the structure of the free olefin. In structure B, however, the implication is that the complex has an octahedral structure with the iridium being formally +3, and the organic moiety is bonded to the iridium *via* two σ bonds in an "iridacyclopropane" ring structure such that it more closely approximates an alkane structure than an alkene one. Unfortunately, carbon–carbon stretching frequencies are not observed in these complexes, and hence this probe cannot be used to judge the carbon–carbon bond order. Nevertheless, a clue as to the charge on the metal can be obtained from the carbon monoxide stretching frequencies, even though the stereochemical reservation (*vide supra*) must be kept in mind. A tabulation of ν_{CO} values is shown in Table II for complexes of the type $IrCl(CO)(Ph_3P)_2$(ligand), where "ligand" may represent two halide ions, BF_3, oxygen, olefin, acetylenes, etc. From Table II it is seen that ν_{CO} for the *bona fide* iridium(I) complex, $IrCl(CO)(Ph_3P)_2$, occurs at 1955 cm⁻¹, whereas ν_{CO} for the *bona fide* iridium(III) complex, $IrCl_3(CO)(Ph_3P)_2$, is found at 2080 cm⁻¹. This increase of ν_{CO} with increasing formal oxidation state of the metal is, of course, the usual thing observed in carbonyl-containing complexes, and presumably arises because of weaker "back-donation" from the metal to carbon monoxide in the complex where the metal is in a more positive formal oxidation state. To the extent that this criterion is valid as an assessment of the positive charge on the metal, it would appear from the data in Table II that the fumaronitrile complex, and particularly the tetracyanoethylene complex, should be regarded as derivatives of iridium(III), and that structure B of Figure 2 would be a better valence-bond description of these molecules than structure A. It is to be noted that ν_{CO} for the oxygen complex, $IrCl(CO)(Ph_3P)_2O_2$, occurs at 2000 cm⁻¹, and that a crystallographic study of this compound[20] has shown the oxygen–oxygen bond distance to be 1.30 Å, which is about the same length of the O–O bond in the superoxide anion (1.28 Å). The O–O bond distance is consistent with one electron having been donated to the oxygen from the iridium; *i.e.*, the oxidation state of the iridium is formally +2. These data for the oxygen complex, in conjunction with the ν_{CO} values for the acrylonitrile, fumaronitrile, and tetracyanoethylene complexes, which are 17, 29, and 60 cm⁻¹ higher, respectively, than ν_{CO} of $IrCl(CO)(Ph_3P)_2O_2$, are certainly more suggestive of structure B in Figure 2 if one is attempting to describe these molecules *via* a valence-bond approach.

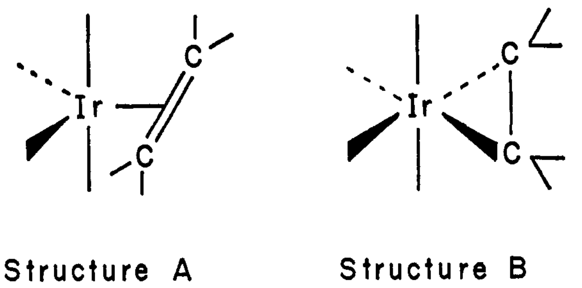

Figure 2. Valence-bond formulations for cyanoolefin mode of bonding in $IrX(CO)(Ph_3P)_2$(cyanoolefin).

Table II. Carbonyl Stretching Frequencies in Complexes of the Type $IrCl(CO)(Ph_3P)_2$(ligand)

Ligand	ν_{CO}, cm⁻¹	Type of spectrum	Ref
No ligand	1964	C_6H_6	*a*
$CH_3OOCC{\equiv}CCOOCH_3$	1980	KBr	*b*
O_2	2000	Nujol	*c*
$H_2C{=}CHCN$	2017	Nujol	*d*
$NCC{\equiv}CCN$	2018	CH_2Cl_2	*e*
$CF_3C{\equiv}CCF_3$	2025	Nujol	9b
$NCCH{=}CHCN$	2029	CH_2Cl_2	*d*
$F_2C{=}CF_2$	2040	KBr	9b
$(NC)_2C{=}C(CN)_2$	2060	CH_2Cl_2	*d*
BF_3	2067	C_6D_6	*f*
Cl, Cl	2080		*g*

[a] J. Chatt, N. P. Johnson, and D. L. Shaw, *J. Chem. Soc., A*, 604 (1967). [b] J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **89,** 844 (1967). [c] L. Vaska, *Science*, **140,** 809 (1963). [d] This work. [e] W. H. Baddley and G. L. McClure, unpublished work. [f] D. F. Shriver, private communication. [g] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84,** 679 (1962).

Notwithstanding the discussion of the preceding paragraph, our view is that it is not profitable to quibble as to whether the iridium is univalent or tervalent, or as to whether the structure is trigonal bipyramidal or octahedral, or as to whether an "iridacyclopropane" ring structure is extant in these compounds. These

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(18) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, 87, 4970 (1965).

(19) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957); J. Chatt, B. L. Shaw, and A. A. Williams, *J. Chem. Soc.*, 3269 (1962); J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.* (Amsterdam), 7, P9 (1967).

(20) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, 87, 2581 (1965).

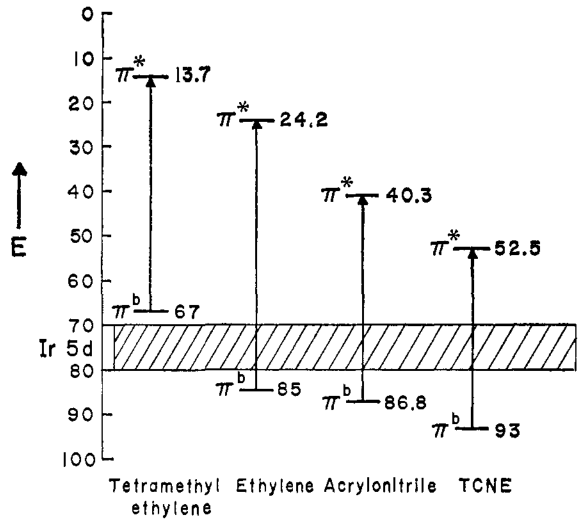

Figure 3. Energies of the highest filled π molecular orbitals and the lowest, vacant π* molecular orbitals of several olefins. Energies are given in thousands of wave numbers. The energy of the 5d orbitals of iridium(0) is expected to be in the dashed area.

particular labels of oxidation state, stereochemistry, and chemical bonding are inherent in valence-bond descriptions of molecules essentially because two-center bonding is invoked. A more realistic appraisal of the bonding situation may be couched in molecular orbital verbiage, the important point being that gradations in various features, *i.e.*, structural, of these cyanoolefin complexes (or any metal–olefin complexes) can be anticipated, depending on the extent to which the metal d orbitals mix with the π and/or π* orbitals of the olefin.

The essential point to be gotten from the data of Table II is that in these cyanoolefin complexes of iridium, a substantial but unknown amount of electron density which originally was on the metal has been transferred to the olefin. A qualitative indication as to why this occurs can be obtained by comparing the energies of the pertinent molecular orbitals in the olefins with the Coulombic energies of the metal valence d orbitals. A schematic representation of the energies of the π^b and π* molecular orbitals of several olefins is shown[21] in Figure 3. From the diagram, it is evident that, in going from an olefin containing four electron-donating substituents (tetramethylethylene) to an olefin containing four electron-withdrawing substituents (tetracyanoethylene), there is a progressive stabilization of the π and π* orbitals as well as a decrease in the $\pi \rightarrow \pi^*$ energy difference. For purposes of this qualitative discussion, the Coulombic energy of the iridium 5d orbitals is considered[22] to be in the 70,000–80,000-cm^{-1} range, as denoted by the dashed area in Figure 3. It is apparent from this diagram that mixing of the iridium valence d orbitals and the π^b orbital of the olefin to form a σ-bonding molecular orbital in the complex will progressively decrease as the number of cyano groups attached to the olefin increases. Likewise, it is clear that mixing of the iridium d orbitals with the π* orbitals of the olefin to form a π^b molecular orbital in the complex increases progressively as the number of cyano groups attached to the olefin increases. Since the stabilities of $\text{IrX(CO)(Ph}_3\text{P)}_2\text{(olefin)}$ increase progressively as the olefin is changed from ethylene to acrylonitrile to fumaronitrile to tetracyanoethylene, the stabilizing effect due to metal→olefin π-bond formation must considerably overcompensate for the destabilizing effect due to decreasing olefin→metal σ-bond formation as the olefin is changed in the order mentioned. From the structural point of view, one can anticipate in this series of complexes that the coordinated olefin will gradually lose double-bond character and take on an alkane nature as the electrons in the π^b molecular orbital of the complex become more localized on the organic moiety. In the limiting case, one can say that a "pure π bond" exists. This is completely equivalent to the valence-bond conception of two σ bonds. The molecular orbital approach would seem to be preferable because of its ability to describe intermediate situations, which probably are the ones of greatest chemical interest. Also, the MO approach is more unified in that a fundamental difference in electronic structures is not implied, whereas the valence-bond model does imply such a difference. In using the MO description, however, one does sacrifice the tidy concepts of oxidation states, coordination numbers, and stereochemical descriptions.

Acknowledgment. This research was supported by the National Science Foundation, Grant GP-6769.

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(21) The data for tetramethylethylene, ethylene, and acrylonitrile were taken from a paper by G. N. Schrauzer (*Chem. Ber.*, **94**, 642 (1961)). The energy of the π* molecular orbital of tetracyanoethylene was considered to be equal in magnitude to the electron affinity of TCNE, which has been measured (F. M. Page and J. Kay, *Nature*, **199**, 485 (1963)). The energy of the highest filled bonding molecular orbital of TCNE was placed 40,520 cm^{-1} below the π* orbital on the basis of the band in the absorption spectrum of TCNE at this position, which has been assigned as a $\pi \rightarrow \pi^*$ transition (J. Halper, W. D. Closson, and H. B. Gray, *Theoret. Chim. Acta*, 4, 174 (1966)).

(22) For the ionization, $\text{Co} \rightarrow \text{Co}^+ + e^-$, where the processes considered were $d^9 \rightarrow d^8$ and $d^8s \rightarrow d^7s$, a recently published value is 58,000 cm^{-1} (M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, 4, 44 (1966)). We arbitrarily suppose that the 5d orbitals in iridium are *ca.* 10,000–20,000 cm^{-1} more stable than the 3d orbitals in cobalt. The first ionization potential of iridium is 72,594 cm^{-1}.