Table III

Thermodynamic Data for the Formation of Various Co(II) Complexes of Neutral Ligands (ΔG, kcal mol^{-1} at 25°; ΔH, kcal mol^{-1}; ΔS, cal deg^{-1} mol^{-1})

$$Co^{2+} + L = CoL^{2+}$$

$$CoL^{2+} + L = CoL_2^{2+}$$

	L				
	3NH$_3$[c]	den[d]	terpy[b]	en[e]	bipy[f]
$-\Delta G_1$	6.16	10.9	12.95 ± 0.04 (11.5)[a]	8.1	8.1
$-\Delta G_2$	6.08	8.0	12.42 ± 0.01 (13.5)[a]	6.4	7.2
$-\Delta G_3$	...	...	...	4.1	6.4
$-\Delta H_1$	5.26	8.15	22 ± 0.9 (10.7)[a]	6.9	8.2
$-\Delta H_2$	7.74	10.25	12.2 ± 0.3	7.1	7.0
$-\Delta H_3$	...	...	...	8.2	6.1
ΔS_1	2.9	9.0	−30 ± 3	+4.0	−0.35
ΔS_2	−5.54	−7.5	0 ± 1	−2.0	0.7
ΔS_3	...	...	...	−13.8	1.05

[a] From kinetic data of Holyer, *et al.*;[6] ΔG_2 given at 5°. [b] Computed from data in Table I (this work) and terpy data.[8] [c] M. Chatelet, *J. Chim Phys.*, **59,** 2365 (1937); J. Bjerrum, "Metal Ammine Formation in Solution," Thesis, 1941, reprinted by P. Haase and Son, Copenhagen, Denmark, 1957, p 187. [d] den = diethylenetriamine: M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 2994 (1961). [e] en = ethylenediamine: M. Ciampolini, P. Paoletti, and L. Sacconi, *Nature*, **186,** 880 (1960); *J. Chem. Soc.*, 4553 (1958). [f] bipy = 2,2′-bipyridine: G. Anderegg, *Helv. Chim. Acta*, **46,** 2397, 2813 (1963).

The large differences in ΔH for the two steps are almost completely compensated by changes in ΔS, as observed in a number of other systems.[13]

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Novel Complexes of Rhodium and Iridium with Electronegative Olefins

By PAOLO UGUAGLIATI, GIULIO DEGANELLO, LUIGI BUSETTO, and UMBERTO BELLUCO

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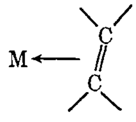
$[Rh(CO)_2Cl]_2$ undergoes halogen bridge splitting by triphenylphosphine to give *trans*-$RhCl(CO)_2(P(C_6H_5)_3)$. Tetracyanoethylene (TCNE) forms a 1:1 adduct with this substrate, of the formula $RhCl(CO)_2(P(C_6H_5)_3)(TCNE)$ (*cis*-dicarbonyl). *cis*-$RhCl(CO)_2(L)$ (L = pyridine, *p*-toluidine) forms adducts with TCNE and fumaronitrile (FMN) of the type $RhCl(CO)_2(L)$(TCNE or FMN) (*trans*-dicarbonyl). $IrCl(N_2)(P(C_6H_5)_3)_2$ reacts with TCNE to give $[IrCl(P(C_6H_5)_3)_2(TCNE)]$ and with FMN to give both $IrCl(N_2)(P(C_6H_5)_3)_2(FMN)$ and $IrCl(P(C_6H_5)_3)_2(FMN)$. In all these adducts the cyanoolefins are bonded to the metal through the olefinic bond. By the action of 1,2-bis(diphenylphosphino)ethane (diphos), $RhCl(CO)_2(L)(TCNE)$ is converted to [Rh(L)(diphos)(TCNE)]Cl whereas $RhCl(CO)_2(L)(FMN)$ gives $[Rh(diphos)(CO)_2]Cl$. Infrared spectra, bonding modes, and reactivity are discussed.

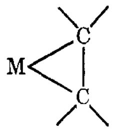
Introduction

Cyanoolefins display a remarkable electrophilic character[1,2] which also manifests itself when the cyanoolefin is coordinated to a transition metal ion.[3-5] The extent of such electron-withdrawing ability, as is deduced from the carbonyl stretching frequency in adducts of the type $IrCl(CO)(P(C_6H_5)_3)_2$(Lewis acid),[5] is intermediate between the SO_2 and BF_3 groups for tetracyanoethylene and fumaronitrile. This peculiar property has recently provoked speculations as to the modes of bonding of cyanoolefins in a metal complex.[6-9] The arguments center around the following alternative configurations for these complexes; M is (initially) a d^8 metal ion. The origin of this dual interpretation lies in the fact that it is impossible to define a coordination number for the central metal even when the



I

conventional metal–olefin structure



II

three-membered, metallocyclopropane ring

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(1) T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73,** 520 (1961).

(2) K. Vasudevan and V. Ramakrishnan, *Rev. Pure Appl. Chem.*, **17,** 95 (1967).

(3) W. H. Baddley, *J. Am. Chem. Soc.*, **88,** 4545 (1966).

(4) W. H. Baddley, *ibid.*, **90,** 3705 (1968).

(5) R. N. Scott, D. F. Shriver, and L. Vaska, *ibid.*, **90,** 1079 (1968).

(6) P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).

(7) W. H. Baddley, *Inorg. Chim. Acta Rev.*, **2,** 5 (1968).

(8) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **89,** 844 (1967).

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

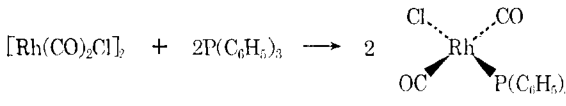
crystal structures of complexes are known.[9-11] Further, the absence of a diagnostic band in the electronic spectra of these complexes prevents an assessment of the oxidation state of the metal. In this regard the cyanoolefins might be classified as "suspect" ligands in Jørgensen's notation. The two alternative formulations, however, should lead to a different chemical behavior of these compounds, so that a choice between them would not be merely formal. Although we do not intend to oversimplify the matter, we shall draw the structures of the new cyanoolefin complexes of rhodium and iridium reported in this paper in accord with the Chatt–Duncanson type of structure (I).

We have prepared and characterized a number of novel complexes of rhodium and iridium with tetracyanoethylene (TCNE) and *trans*-1,2-dicyanoethylene (fumaronitrile, FMN), focusing on the reactivity of these complexes with mono- and bidentate π-acceptor ligands. Our aim was (i) to ascertain the factors which promote the cyanoolefin–d^8 metal ion bonding interaction and (ii) to formulate these compounds in a manner more consistent with chemical behavior.

Results and Discussion

Substrates.—As is known the halogen bridge in rhodium carbonyl chloride dimer, $[Rh(CO)_2Cl]_2$, is readily split by aromatic amines to give mononuclear amine complexes of the type *cis*-$RhCl(CO)_2$(amine).[12] Analogous complexes have been obtained recently by bridge splitting with enimines.[13] By contrast, 4 mol of tertiary phosphines, arsines, or stibines reacts easily with 1 mol of rhodium carbonyl chloride to give mononuclear complexes of type *trans*-$RhCl(CO)L_2$ with evolution of carbon monoxide.[14-16] By using chelating diphosphines with an excess of $[Rh(CO)_2Cl]_2$ at low temperature, the complex (diphosphine)$[Rh(CO)_2Cl]_2$ could be isolated but it appeared contaminated by a product having less carbon monoxide per metal atom.[17]

We have reconsidered the bridge-splitting reactions of $[Rh(CO)_2Cl]_2$ with tertiary phosphines in hopes of isolating the intermediate *cis*-$RhCl(CO)_2(P(C_6H_5)_3)$. By the reaction of 2 mol of triphenylphosphine and 1 mol of rhodium carbonyl chloride in benzene at room temperature we have instead obtained the *trans* isomer (1) in high yield. Analytical data and physical properties for this as well as for other complexes described in this work are reported in Table I. The configuration of 1 is suggested by the presence of only one infrared band in the terminal carbonyl stretching region at 1980 cm^{-1} (in Nujol, see Table II). As far as we know this is one of the very few examples of *trans*-dicarbonylphosphinerhodium complexes yet reported. Another instance is the cation *trans*-$Rh(CO)_2(P(C_6H_5)_3)_2^{+}$ [18] (the anion $Rh(CO)_2(P(C_6H_5)_3)_2^{-}$ [19] is, of course, tetrahedral). The far-infrared spectrum of 1 in the 400-200-cm^{-1} region shows the Rh–Cl stretching frequency at 295 cm^{-1}, a value in agreement with a chloride *trans* to a tertiary arylphosphine in a Rh^{I} complex.[20]



1

The conditions required for carrying out the preparation of 1 are critical since even a small excess of $P(C_6H_5)_3$ reacts further with 1 to give $RhCl(CO)(P(C_6H_5)_3)_2$, which is also formed through disproportionation of 1 in a warmed benzene solution. It appears therefore that the *trans*-dicarbonyl configuration is rather labile, although thermodynamically more stable than the *cis* configuration. Isomer 1 may be expected to be a very interesting intermediate for many oxidative addition reactions as are its now famous analogs $MCl(CO)(P(C_6H_5)_3)_2$ (M = Rh, Ir). Work is now in progress in this regard and results will be reported later.

The substrates that we employed in the reactions with cyanoolefins to be described below were *cis*-$RhCl(CO)_2(L)$ (L = pyridine, *p*-toluidine) and *trans*-$RhCl(CO)_2(P(C_6H_5)_3)$. The recent discovery of the nitrogen complex $IrCl(N_2)(P(C_6H_5)_3)_2$, described by Collman, *et al.*,[21] prompted us also to use this derivative as a reactive substrate, on account of the lability of coordinated nitrogen.

Reactions with Cyanoolefins. a. Rhodium Compounds.—Tetracyanoethylene and fumaronitrile react smoothly at room temperature with *cis*-$RhCl(CO)_2(L)$ to give stable 1:1 adducts of the formula $RhCl(CO)_2(L)$(cyanoolefin)

cis-$RhCl(CO)_2(L)$ + cyanoolefin $\longrightarrow$
$RhCl(CO)_2(L)$(cyanoolefin)

TCNE	FMN
2a, L = pyridine	**3a**, L = pyridine
2b, L = *p*-toluidine	**3b**, L = *p*-toluidine

For reactions with TCNE an equimolar amount of cyanoolefin is sufficient to obtain high product yields, whereas an excess of cyanocarbon is required when using FMN. Formation of the adduct **3b** is incomplete even with a large excess of FMN and the product isolated appears to be contaminated with significant amounts of starting carbonyl complex; repeated attempts to purify it were unsuccessful. The infrared spectra of 2 and 3 as Nujol mulls in the CN–CO stretching region show a medium strong, sharp band at 2210–2225 cm^{-1} due to ν(CN) of coordinated cyanoolefin, like similar adducts $MX(CO)(E(C_6H_5)_3)_2$(cyanoolefin) (M = Rh, Ir; X = halide or pseudohalide; E = P, As) reported previously.[3,4] A single strong band in the range

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(10) C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Am. Chem. Soc.*, **90**, 798 (1968).

(11) R. Graziani, C. Panattoni, U. Belluco, and W. H. Baddley, submitted for publication.

(12) D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965).

(13) J. W. Kang and P. M. Maitlis, *Can. J. Chem.*, **46**, 897 (1968).

(14) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

(15) W. Hieber, H. Heusinger, and O. Vohler, *Ber.*, **90**, 2425 (1957).

(16) J. Chatt and B. L. Shaw, *J. Chem. Soc., A*, 1437 (1966).

(17) W. Hieber and F. Volker, *Ber.*, **100**, 148 (1967).

(18) W. Hieber and F. Volker, *ibid.*, **99**, 2614 (1966).

(19) J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 5035 (1966).

(20) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(21) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Am. Chem. Soc.*, **90**, 5430 (1968).

TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF COMPLEXES

Complex	Color	Recrystn solvent	% calcd C	% calcd H	% calcd N	% calcd Cl	% found C	% found H	% found N	% found Cl	Λ_M[a]
trans-$RhCl(CO)_2[P(C_6H_5)_3]$	Orange-yellow	CH_2Cl_2–pentane	52.6	3.3	...	7.8	52.8	3.2	...	7.6	...
$RhCl(CO)_2[P(C_6H_5)_3](C_6N_4)$[b]	Golden	C_6H_6–pentane	53.4	2.6	9.6	6.1	53.6	2.8	9.2	6.4	...
$RhCl(CO)_2(C_5H_5N)(C_6N_4)$	Yellow	CH_2Cl_2–C_6H_6	38.9	1.3	17.4	8.8	38.7	1.4	17.4	9.0	...
$RhCl(CO)_2(CH_3C_6H_4NH_2)(C_6N_4)$	Golden	CH_2Cl_2–C_6H_6	41.9	2.1	16.3	8.3	41.8	2.3	16.4	8.6	...
$IrCl[P(C_6H_5)_3]_2(C_6N_4)$	Brown	CH_2Cl_2–C_6H_6	57.0	3.4	6.4	4.0	57.6	3.7	6.3	3.6	...
$RhCl(CO)_2(C_5H_5N)(C_4H_2N_2)$[c]	Yellow	C_6H_6–pentane	37.6	2.0	11.9	10.1	37.2	2.1	12.3	10.4	...
$RhCl(CO)_2(CH_3C_6H_4NH_2)(C_4H_2N_2)$[d]	Orange-yellow	...	...	...	...	...	...	...	...	...	...
$IrCl(N_2)[P(C_6H_5)_3]_2(C_4H_2N_2)$	Pale rose	CH_2Cl_2–C_6H_6	55.9	3.8	6.5	4.1	56.0	3.9	6.6	4.1	...
$IrCl[P(C_6H_5)_3]_2(C_4H_2N_2)$	Orange	C_6H_6–pentane	57.8	3.9	3.4	4.3	57.7	3.9	3.3	4.2	
$\{Rh[(C_6H_5)_2PCH_2]_2(C_5H_5N)(C_6N_4)\}Cl$	Buff	CH_2Cl_2–pentane	59.7	3.9	9.4	4.8	59.0	4.1	9.0	4.8	22.1
$\{Rh[(C_6H_5)_2PCH_2]_2(CH_3C_6H_4NH_2)(C_6N_4)\}Cl$	Creamy	CH_2Cl_2–pentane	60.7	4.3	9.1	4.6	60.1	4.4	9.1	4.7	20.3
$\{Rh(CO)_2[(C_6H_5)_2PCH_2]_2\}Cl$	Yellow	CH_2Cl_2–pentane	56.7	4.1	...	6.0	56.6	4.2	...	6.1	26.8

[a] Units: $ohm^{-1}\ cm^2\ mol^{-1}$; 10^{-3} *M* in dichloromethane at 25°. [b] C_6N_4 = tetracyanoethylene. [c] $C_4H_2N_2$ = fumaronitrile. [d] Contaminated by starting material. Characterized only by ir spectrum (see text).

TABLE II

SELECTED INFRARED BANDS (CM^{-1}, NUJOL)[a]

Complex	ν(CN)	ν(CO)	ν(M–X)	Other bands
trans-$RhCl(CO)_2(P(C_6H_5)_3)$	...	1980 vs	295 ms	
$RhCl(CO)_2(P(C_6H_5)_3)$(TCNE)	2221 ms, sp	2082 vs, sp 2020 vs, sp	330 m, br	
$RhCl(CO)_2$(py)(TCNE)	2225 m	2118 vs, sp	266 m, br	
$RhCl(CO)_2(p\text{-}CH_3C_6H_4NH_2)$(TCNE)	2223 ms	2092 s	270 w, br	
$IrCl(P(C_6H_5)_3)_2$(TCNE)	2211 s, sp	...	335 w, br	
$RhCl(CO)_2$(py)(FMN)	2212 s, sp	2055 vs, sp	251 ms	
$RhCl(CO)_2(p\text{-}CH_3C_6H_4NH_2)$(FMN)	2221 ms, sp	2056 vs, sp	260 m	
$IrCl(N_2)(P(C_6H_5)_3)_2$(FMN)	2210 ms, sp 2203 s, sp	...	333 w, br	2182 vs, sp (N≡N)
$IrCl(P(C_6H_5)_3)_2$(FMN)	2213 ms	...	320 w, br	
[Rh(diphos)(py)(TCNE)]Cl	2220 s, sp 2200 ms	...	...	
[Rh(diphos)(p-$CH_3C_6H_4NH_2$)(TCNE)]Cl	2222 s	...	...	
$[Rh(CO)_2$(diphos)]Cl	...	2062 vs, sp 1982 vs	...	

[a] Abbreviations used to describe infrared band intensities and widths are: s, strong; vs, very strong; ms, medium strong; m, medium w, weak; sp, sharp; br, broad.

2050–2120 cm^{-1} is assigned to ν(CO) for a *trans*-dicarbonyl configuration (see Table II). The carbonyl stretching frequencies for the TCNE adducts are much higher than those for the FMN adducts, implying a weaker "back-donation" of electron charge from the metal to carbon monoxide in the former adducts. This reflects a trend in synergic acceptor–donor abilities of FMN (weaker acceptor, stronger donor) and TCNE (stronger acceptor, weaker donor). Increasing substitution of hydrogen by electronegative groups in the olefin causes a decrease of basicity of the central metal. Since coordination of the electronegatively substituted olefin to the metal atom brings about a significant drift of d-electron density from the metal to the unsaturated ligand, the cyanoolefins behave as effective bond-weakening ligands[22] so that the metal complex might be expected to be sensitive toward nucleophilic attack (see below). The rather low ν(Rh–Cl) (250–270 cm^{-1}) for **2** and **3** indicates a decreased metal–halide bond strength; based on this infrared evidence cyanoolefins should have greater bond-weakening properties than tertiary phosphines.[20,23]

The new rhodium carbonyl derivative, *trans*-$RhCl(CO)_2P(C_6H_5)_3$, reacts rapidly at room temperature with TCNE to give the 1:1 adduct **4** in high yield

$$trans\text{-}RhCl(CO)_2(P(C_6H_5)_3) + TCNE \xrightarrow{\text{benzene}} \underset{\mathbf{4}}{RhCl(CO)_2(P(C_6H_5)_3)(TCNE)}$$

No reaction occurs with fumaronitrile. The presence of two strong, sharp bands in the terminal carbonyl stretching region of the infrared spectrum of **4** both as a Nujol mull and in CH_2Cl_2 solution (2082, 2020 cm^{-1}) suggests a *cis*-dicarbonyl configuration.

Interestingly, $[Rh(CO)_2Cl]_2$ does not react with either TCNE or FMN. It is worth recalling in this regard that complexes of the type $IrX(CO)(olefin)_2$[24] undergo oxidative additions less readily than $IrCl(CO)(P(C_6H_5)_3)_2$ and that carbon monoxide and olefin ligands have comparable donor–acceptor capacities.

There appears to be a decreasing affinity of fumaronitrile for the substrates $RhCl(CO)_2(L)$ in the order of L: pyridine > *p*-toluidine ≫ triphenylphosphine. If this is also the order of increasing basicity of the central metal as determined by the σ-donor ability of the ligand L, it may be suggested that the donor capacity of this cyanoolefin is more important than the π-acceptor properties in forming the metal–olefin bond. With

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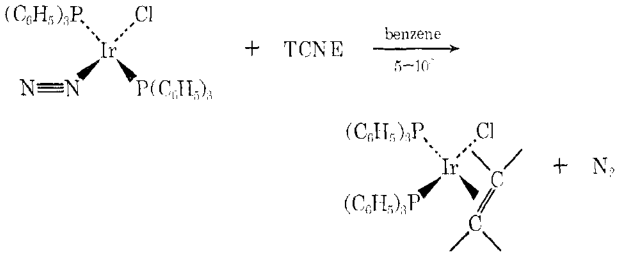
[22] P. Uguagliati and W. H. Baddley, *J. Am. Chem. Soc.*, **90**, 5446 (1968).

[23] D. M. Adams, "Metal–Ligand and Related Vibrations," Edward Arnold (Publishers)., London, 1967.

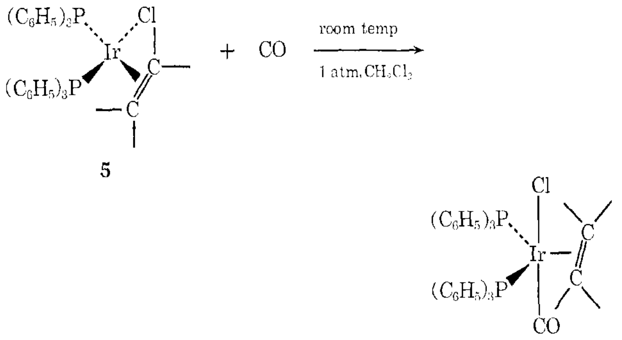
[24] B. L. Shaw and E. Singleton, *J. Chem. Soc., A*, 1683 (1967).

tetracyanoethylene the π-acceptor ability is so overwhelming that no discrimination among the different L's is observed.

b. Iridium Compounds.—The labile nitrogen complex $IrCl(N_2)(P(C_6H_5)_3)_2$[21] reacts with TCNE to give the coordinatively unsaturated adduct **5** with evolution of molecular nitrogen. Although isomers are possible we have no evidence to suggest the formation of more than one species, for which we propose the structure depicted above. The unsaturated nature of **5** is demonstrated by the easy absorption of carbon monoxide under ambient conditions to give nearly quantitatively the known[4] $IrCl(CO)(P(C_6H_5)_3)_2(TCNE)$.

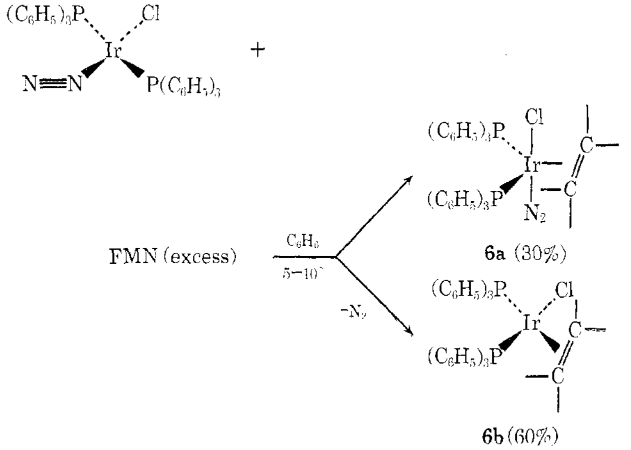


5



5

The reaction of the nitrogen–iridium complex with unsaturated ligands with liberation of nitrogen has been recently described by Collman, *et al.*[8] Since molecular nitrogen as a ligand seems to be a more powerful π acid than CO[21] we anticipated that fumaronitrile, as a weaker π acceptor than TCNE, would react with the nitrogen complex to give detectable yields of an adduct still having nitrogen coordinated to the metal. As a matter of fact, such reaction gives a mixture of complexes **6a** and **6b** which can be separated on account of their different solubility in the reaction medium. Compound **6a** remains unchanged over prolonged periods of time in the solid even in the open atmosphere but decomposes slowly in solution to give unknown, tarry materials. Its infrared spectrum shows, besides the bands due to ν(CN), a very strong, sharp band at 2182 cm^{-1} assigned to $\nu(N{\equiv}N)$. The increase of $\nu(N{\equiv}N)$ of *ca.* 80 cm^{-1} from the value in the starting $IrCl(N_2)(P(C_6H_5)_3)_2$ indicates a reduced back-donation to coordinated nitrogen caused by the olefin competing with N_2 for d-electron density. We feel that a *trans* Cl–N$_2$ configuration best explains the high ν(Ir—Cl) (333 cm^{-1}).



6a (30%)

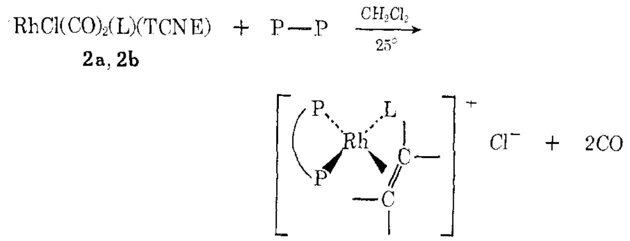
6b (60%)

In agreement with its coordinatively unsaturated character, **6b** adds carbon monoxide under ambient conditions in dichloromethane solution to give the known[4] $IrCl(CO)(P(C_6H_5)_3)_2(FMN)$ which dissociates in solution into the free olefin and Vaska's compound

$$\mathbf{6b} + CO \xrightarrow{CH_2Cl_2} IrCl(CO)(P(C_6H_5)_3)_2 + FMN$$

It is worth mentioning that $IrCl(CO)(P(C_6H_5)_3)_2$ gives only a nitrogen-containing adduct when reacting with diethyl maleate.[21] These results suggest a trend of π acidity for electronegatively substituted olefins in the order: diethyl maleate $\leqslant$ fumaronitrile $<$ tetracyanoethylene and probably the same order of metal–olefin bond strength.

Reactivity of Cyanoolefin Complexes.—The adducts **2a** and **2b** react rapidly with 1,2-bis(diphenylphosphino)ethane (P–P) in dichloromethane at room temperature to give salts of the formula [Rh(P–P)(L)(TCNE)]Cl, with carbon monoxide being liberated

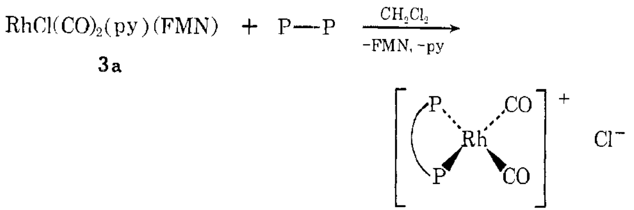


2a, 2b

7a, L = pyridine
7b, L = *p*-toluidine

The salts **7a** and **7b** are very stable compounds, soluble in chlorinated solvents, slightly soluble in alcohol, and insoluble in hydrocarbons. In dichloromethane they behave as uni-univalent electrolytes. Their conductivities fall in the range expected for such conducting species in poorly ionizing solvents (20–22 ohm^{-1} cm^2 mol^{-1} at 25°, 10^{-3} *M* in CH_2Cl_2). The far-infrared spectrum shows that the bands (ν(M–Cl)) at *ca.* 270 cm^{-1} of the original Cl complexes had disappeared. The carbonyl stretching bands also have vanished (Table II). The course of the reaction involving **2a** was monitored by following the changes in conductivity of a dichloromethane solution of the starting compound caused by addition of a concentrated solution of bidentate ligand P–P. The conductivity increased linearly until 1 mol of P–P per metal atom had been added, after which it remained constant. Identical results were obtained starting from **2b**. The cations **7a** and **7b** are the first positively charged complexes of transitional metals with cyanoolefins to be reported.

A quite different behavior toward nucleophilic agents is displayed by the fumaronitrile adduct **3a**. This reacts with diphosphine losing the cyanoolefin and pyridine to give a salt in which both carbonyl groups of the original complex are retained



8

The salt **8** is very soluble in dichloromethane and insoluble in alcohol and hydrocarbons. In chlorinated solvents it behaves as a 1:1 electrolyte ($\Lambda = 27$ ohm^{-1} cm^2 mol^{-1} at 25°, 10^{-3} M in CH_2Cl_2). The infrared spectrum shows that bands due to coordinated FMN, pyridine, and chloride have vanished. The strong carbonyl stretching band at 2055 cm^{-1} of the original complex **3a** has been replaced by two equally intense bands at 2062 and 1982 cm^{-1} assignable to the carbonyl absorptions of the *cis*-dicarbonyl species **8**.

Finally, the adduct $RhCl(CO)_2(P(C_6H_5)_3)(TCNE)$ (**4**) loses 1 mol of carbon monoxide when reacting with triphenylphosphine in benzene leading to the known[3] $RhCl(CO)(P(C_6H_5)_3)_2(TCNE)$

$$RhCl(CO)_2(P(C_6H_5)_3)(TCNE) \xrightarrow[-CO]{+P(C_6H_5)_3} RhCl(CO)(P(C_6H_5)_3)_2(TCNE)$$

The easy replacement of carbon monoxide leading to **7a** and **7b** may be accounted for in terms of a more effective competition for d-electron density by TCNE relative to CO which results in weakening of the M–CO bond. In the event that the cyanoolefin is removed, as is FMN in the reaction leading to **8**, carbon monoxide is not so easily displaced by the entering diphosphine.

Formation of the adducts of cyanoolefins with square-planar Rh^I and Ir^I complexes is related to the general problem of the occurrence of five-coordination in d^8 systems and to the relative stability of π ligands coordinated to such metals. Even though the question as to under which conditions pentacoordination is to be expected is still a matter of controversy, it may be stated that this type of coordination is more likely with strong-field ligands, whatever the particular configuration that ensues (whether the more frequent trigonal bipyramid or the square pyramid). In fact such ligands are less sensitive to displacement by the entering fifth ligand while they afford a greater stabilization through extensive π delocalization of electronic charge. In this way formation of a dative bond with the additional ligand is also made more facile. These conditions prevail in all of the adducts of d^8 metal ions with cyanoolefins yet reported. In other words the cyanoolefins would add to d^8 metal substrates bearing soft ligands coordinated. We are therefore inclined to consider the adducts $RhCl(CO)_2(L)$(cyanoolefin) (**2**–**4**) and $IrCl(N_2)(P(C_6H_5)_3)_2(FMN)$ (**6a**) as conventional π-olefinic derivatives of M^I with the strongly electron-withdrawing cyanoolefin occupying one coordination site. The complexes $IrCl(P(C_6H_5)_3)_2$(cyanoolefin) (**5**, **6b**) would then be looked upon as four-coordinate Ir^I–olefin complexes, in agreement with their coordinatively unsaturated character. The infrared spectral data discussed above are consistent with, although they do not prove, these views.

Experimental Section

I. Materials.—Tetracyanoethylene was purchased from Fluka. The yellow, crude commercial material was purified by sublimation to give white crystals melting at 201–202°. Fumaronitrile (Fluka) was used without further purification. All other chemicals used were reagent grade materials.

The following rhodium and iridium complexes were synthesized by previously described procedures: $[Rh(CO)_2Cl]_2$,[25] *cis*-$RhCl(CO)_2(py)$,[12] *cis*-$RhCl(CO)_2(p\text{-}CH_3C_6H_4NH_2)$,[12] $RhCl(CO)(P(C_6H_5)_3)_2$,[14] $IrCl(N_2)(P(C_6H_5)_3)_2$ (from $IrCl(CO)(P(C_6H_5)_3)_2$ and benzoyl azide[26]).[21]

All reactions were carried out at room temperature (unless otherwise stated) in a nitrogen atmosphere, but work-up of reaction mixtures was usually done in the open atmosphere. Analytical data, physical properties, and recrystallization methods of new complexes are reported in Table I.

***trans*-Chlorodicarbonyltriphenylphosphinerhodium, $RhCl(CO)_2(P(C_6H_5)_3)$.**—$[Rh(CO)_2Cl]_2$ (0.39 g, 1 mmol) in 20 ml of benzene was treated slowly dropwise with triphenylphosphine (0.524 g, 2 mmol) in 20 ml of benzene with vigorous stirring. The resulting orange solution was concentrated to a small volume on a rotating evaporator. Addition of pentane gave the orange-yellow *product* which was filtered off, washed with pentane, and dried *in vacuo* (yield 85%).

II. Reactions of Tetracyanoethylene with Rh^I and Ir^I Complexes. A. Chlorodicarbonyl(triphenylphosphine)(tetracyanoethylene)rhodium, $RhCl(CO)_2(P(C_6H_5)_3)(TCNE)$.—$RhCl(CO)_2(P(C_6H_5)_3)$ (0.228 g, 0.5 mmol) suspended in 50 ml of a benzene–dichloromethane mixture (1:1 v/v) was treated dropwise with a benzene solution of TCNE (0.07 g, 0.5 mmol in 10 ml). Upon addition the orange-yellow suspension turned into an orange solution. After stirring for 15 min the solution was evaporated to a small volume under reduced pressure and pentane was added. The golden *product* which separated was filtered off, washed with pentane, and dried under vacuum (yield 73%).

The complex could also have been prepared *in situ* with analogous work-up by adding a benzene solution of triphenylphosphine (2 mmol) to a mixture of $[Rh(CO)_2Cl]_2$ (1 mmol) and TCNE (2 mmol) in benzene.

B. Chlorodicarbonyl(pyridine)(tetracyanoethylene)rhodium, $RhCl(CO)_2(py)(TCNE)$.—$RhCl(CO)_2(py)$ (0.274 g, 1 mmol) in 20 ml of benzene was treated with TCNE (0.130 g, 1 mmol) in 10 ml of benzene. The deep yellow *product* precipitated slowly. Precipitation was completed by adding 50 ml of pentane. The solid was filtered off, washed with pentane, and dried (yield 91%).

C. Chlorodicarbonyl(*p*-toluidine)(tetracyanoethylene)rhodium, $RhCl(CO)_2(p\text{-}CH_3C_6H_4NH_2)(TCNE)$.—$RhCl(CO)_2(p\text{-}CH_3C_6H_4NH_2)$ (0.226 g, 0.75 mmol) dissolved in benzene–dichloromethane (15 ml/5 ml) was treated dropwise with TCNE (0.098 g, 0.75 mmol) in 10 ml of benzene. In the course of the addition the golden *product* precipitated. After the mixture was stirred for 0.5 hr, pentane was added to complete the precipitation. Fil-

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[25] J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 211 (1966).

[26] E. W. Barrett and C. W. Porter, *J. Am. Chem. Soc.*, **63**, 3434 (1941).

tration and washing with pentane gave the solid in an almost quantitative yield.

D. Chlorobis(triphenylphosphine)(tetracyanoethylene)iridium, $\mathrm{IrCl(P(C_6H_5)_3)_2(TCNE)}$.—As soon as isolated, $\mathrm{IrCl(N_2)(P(C_6H_5)_3)_2}$ (0.3 g, *ca.* 0.4 mmol) in 20 ml of benzene was treated with TCNE (0.08 g, *ca.* 0.6 mmol) in 10 ml of benzene at 5–10° with vigorous stirring. Over a period of 20 min a brown precipitate separated. Filtration and washing with a small amount of benzene to remove the excess TCNE gave the brown *product* (yield 60%).

III. Reactions of Fumaronitrile with $\mathrm{Rh^I}$ and $\mathrm{Ir^I}$ Complexes. A. Chlorodicarbonyl(pyridine)(fumaronitrile)rhodium, $\mathrm{RhCl(CO)_2(py)(FMN)}$.—$\mathrm{RhCl(CO)_2(py)}$ (0.180 g, 0.75 mmol) in 20 ml of benzene was treated with an excess of fumaronitrile (5 mmol). The solution turned yellow-green. After being stirred for 1 hr, the reaction mixture was filtered and concentrated to *ca.* half its volume under reduced pressure and pentane was added. On cooling, the yellow product separated as a fine powder. It was filtered off, washed with cold benzene and ether, and dried (yield 59%).

B. Chlorodicarbonyl(*p*-toluidine)(fumaronitrile)rhodium, $\mathrm{RhCl(CO)_2(\textit{p}\text{-}CH_3C_6H_4NH_2)(FMN)}$.—$\mathrm{RhCl(CO)_2(\textit{p}\text{-}CH_3C_6H_4NH_2)}$ (0.15 g, 0.5 mmol) dissolved in benzene–dichloromethane (15 ml/5 ml) was treated with excess fumaronitrile (10 mmol). The reaction mixture was stirred for 2 days and then concentrated to a small volume. The orange-yellow *product* was separated by adding pentane, filtering, and washing with cold benzene to remove the excess fumaronitrile. The material was contaminated with the starting, unreacted rhodium complex (see text). Attempts to purify the product by repeated recrystallizations from various solvent mixtures were unsuccessful.

C. Reaction of *trans*-Chloronitrogenbis(triphenylphosphine)iridium(I) with Fumaronitrile.—As soon as isolated, $\mathrm{IrCl(N_2)(P(C_6H_5)_3)_2}$ (0.3 g, *ca.* 0.4 mmol) in 20 ml of benzene was treated with FMN (0.160 g, 2 mmol) in 10 ml of benzene at 5–10° with stirring. On addition, the yellow solution turned orange and after a few minutes a pale rose solid began to precipitate. The reaction mixture was allowed to stand for 0.5 hr at room temperature, after which the rose chloronitrogenbis(triphenylphosphine)(fumaronitrile)iridium, $\mathrm{IrCl(N_2)(P(C_6H_5)_3)_2(FMN)}$, was filtered off, washed with a little benzene, and dried (yield *ca.* 30%).

To the orange filtrate was added pentane dropwise with vigorous stirring whereupon **chlorobis(triphenylphosphine)(fumaronitrile)iridium,** $\mathrm{IrCl(P(C_6H_5)_3)_2(FMN)}$, precipitated as a finely divided orange powder. This was filtered off, washed with ethyl ether to remove any excess fumaronitrile, and dried (yield *ca.* 60%).

IV. Reactions of Cyanocarbon Complexes of Rhodium and Iridium. A. $\mathrm{RhCl(CO)_2(P(C_6H_5)_3)(TCNE)}$ and Triphenylphosphine.—$\mathrm{RhCl(CO)_2(P(C_6H_5)_3)(TCNE)}$ (0.180 g, 0.3 mmol) in 20 ml of benzene was treated with $\mathrm{P(C_6H_5)_3}$ (0.082 g, 0.3 mmol) in 5 ml of benzene dropwise with stirring. In the course of the addition, a golden solid precipitated. Once the reaction was complete, the solid was filtered off, washed with pentane, dried, and identified as **chloro(carbonyl)bis(triphenylphosphine)(tetracyanoethylene)rhodium**[3] by elemental analysis and ir spectrum (nearly quantitative yield).

B. Reactions of 1,2-Bis(diphenylphosphino)ethane (diphos). i. With $\mathrm{RhCl(CO)_2(py)(TCNE)}$.—$\mathrm{RhCl(CO)_2(py)(TCNE)}$ (0.2 g, 0.5 mmol) in 20 ml of dichloromethane was treated dropwise with diphos (0.2 g, 0.5 mmol) in 10 ml of dichloromethane. The yellow solution turned orange-brown at once. The resulting reaction mixture was concentrated under reduced pressure and pentane was added to give the buff-colored **1,2-bis(diphenylphosphino)ethane(pyridine)(tetracyanoethylene)rhodium chloride.** [Rh(diphos)(py)(TCNE)]Cl, as a powdery precipitate (yield *ca.* 94%).

ii. With $\mathrm{RhCl(CO)_2(\textit{p}\text{-}CH_3C_6H_4NH_2)(TCNE)}$.—The reaction was carried out in the same way as the above (Rh:P = 1:2) and gave almost quantitatively the cream-colored **1,2-bis(diphenylphosphino)ethane(*p*-toluidine)(tetracyanoethylene)rhodium chloride,** $\mathrm{[Rh(diphos)(\textit{p}\text{-}CH_3C_6H_4NH_2)(TCNE)]Cl}$.

iii. With $\mathrm{RhCl(CO)_2(py)(FMN)}$.—$\mathrm{RhCl(CO)_2(py)(FMN)}$ (0.176 g, 0.5 mmol) suspended in 20 ml of dichloromethane was treated dropwise with diphos (0.200 g, 0.5 mmol) in 5 ml of dichloromethane. The solid dissolved to give an orange-yellow solution. After being stirred for 15 min, the solution was concentrated and then poured into pentane. The yellow **1,2-bis(diphenylphosphino)ethanedicarbonylrhodium chloride,** $\mathrm{[Rh(diphos)(CO)_2]Cl}$, which precipitated was filtered off, washed with ether, and dried (yield 80%).

C. Absorption of Carbon Monoxide. i. By $\mathrm{IrCl(P(C_6H_5)_3)_2(TCNE)}$.—$\mathrm{IrCl(P(C_6H_5)_3)_2(TCNE)}$ was dissolved in dichloromethane and carbon monoxide was bubbled through the solution for 2 days. The solution turned slowly colorless. Concentration and addition of pentane gave a white precipitate which was filtered off, washed with pentane, and identified as chlorocarbonylbis(triphenylphosphine)(tetracyanoethylene)iridium by elemental analysis and ir spectrum[4] (almost quantitative yield).

ii. By $\mathrm{IrCl(P(C_6H_5)_3)_2(FMN)}$.—The reaction was carried out in the same way as above. After *ca.* 1 day, the solution had turned pale yellow. Concentration and addition of hexane gave a white solid identified as chlorocarbonylbis(triphenylphosphine)(fumaronitrile)iridium by elemental analysis and ir spectra in solid and in solution.[4]

V. Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer 621 double-beam spectrophotometer in Nujol mulls or dichloromethane solutions. Conductivity measurements were carried out with a conductivity bridge, Model KLM.

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