

equivalent step are disfavored since further oxidation of $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ results in irreversible decomposition, whereas it has been shown here that the expected yield of ferricenium ion is obtained quantitatively. Furthermore, the chronopotentiometric oxidation of ferrocene is a one-equivalent reversible conversion to ferricenium ion; even potentials as high as +1.4 V vs. sce did not produce a second oxidation wave.⁷

The effect of the product, $\text{Fe}(\text{C}_5\text{H}_5)_2^+$, was studied in two experiments as shown in Table II. Its concentration was increased considerably compared to the other runs and no retarding effect was found, supporting eq 7 and not eq 8 or 9 as the rate determining step. This is in agreement with the mechanism in other instances where the reducing agent is not a complex which undergoes rapid ligand substitution.^{5,8}

If $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ exerts any effect at these high concentrations it is to increase the rate of reaction by a small amount. This phenomenon might be rationalized by a product-catalysis term,⁹ but the effect was not explored in detail. In any event the possible existence of this term is not sufficient to cause us to question the conclusion from the present work that the oxidation of ferrocene by chromium(VI) occurs in a sequence of one-equivalent steps with the first such step the slowest.

(7) T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Amer. Chem. Soc.*, **82**, 5811 (1960).

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Cyanophosphine Complexes of Nitrosylcobalt Carbonyl

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It is well understood that the C–O antibond orbitals in a metal carbonyl can accept metal d electrons, causing lower C–O stretching frequencies than would occur without such metal→carbon back-bonding. However, since the CO ligands are competing for the back-bonding d electrons, some replacement of CO by a weaker acceptor ligand leads to better acceptor action by the remaining CO ligands, further decreasing their stretching frequencies.¹ For example, aminophosphines or alkylphosphines are dramatically effective as replacement ligands which lower the C–O frequencies. Stronger π -acceptor ligands such as PF_3 or trifluoromethylphosphines are less effective for lowering the C–O frequencies,² but the rule has been that some significant decrease always results from replacement of CO by any phosphine.

We now have tried three cyanophosphines as ligands for single replacement of CO in $\text{NOCo}(\text{CO})_3$, finding

(1) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970), and the extensive bibliography there cited.

(2) A. B. Burg and G. B. Street, *Inorg. Chem.*, **5**, 1532 (1966).

that the resulting $\text{LCoNO}(\text{CO})_2$ complexes have some of the highest C–O stretching frequencies yet observed for such compounds—in one mode even higher than in pure $\text{NOCo}(\text{CO})_3$. It appears that these ligands are more effective than any previously used, for attracting metal 3d electrons and so minimizing the interaction of such electrons with the CO antibonding orbitals. The significant infrared frequencies (cm^{-1} , vapor phase) are compared in Table I.

TABLE I
COMPARISON OF PERTINENT INFRARED FREQUENCIES (cm^{-1}) OF
 $\text{LCoNO}(\text{CO})_2$ COMPOUNDS

	L					
	CO	PF_3^a	$(\text{CF}_3)_3\text{P}$	$(\text{CF}_3)_2\text{P-CN}$	$\text{CF}_3\text{P}(\text{CN})_2$	$\text{P}(\text{CN})_3$
C–N str				2192 (2194) ^b	2198 (2197) ^b	2200 (2179) ^b
C–O in-phase str	2108	2087	2088	2095	2098	2102
C–O out-of-phase str	2047	2044	2043	2055	2058	2064
N–O str	1822	1825	1832	1833	1833	1833

^a I. H. Sabherwal and A. B. Burg, *Chem. Commun.*, 854 (1969).

^b The parenthetical numbers refer to the free ligands.

The nearly unchanged C–N stretching frequencies show that the ligand action is through P rather than CN in all cases. It also seems that the positive and negative effects of ligand action, upon the C–N frequencies, are fairly well balanced.

One such effect would be delocalization of the metal 3d electrons across phosphorus into the σ - and π -antibonding orbitals of the CN group. This would account for the extreme electron-withdrawing effect, indicated by the high C–O stretching frequencies, while the effect upon the C–N stretching frequency would be negative. A compensating positive effect concerns the phosphorus lone-pair electrons. In the free cyanophosphine, these are expected to interact with the C–N antibond orbitals; hence their reemployment for σ bonding to the metal would lead to higher C–N stretching frequencies. Ostensibly, these two effects nearly balance each other except in the case of $\text{P}(\text{CN})_3$. However, the cogency of this argument is diminished by a third variable: one cannot be sure about how much the C–N stretching frequency is affected by tetrahedral rehybridization of phosphorus. In sum, there is no good argument against the idea of delocalization of metal electrons into the C–N antibonding orbitals, a hypothesis which is needed to explain the present results.

Ligand Synthesis and Characterization.—The iodo-phosphines $(\text{CF}_3)_2\text{PI}$ and CF_3PI_2 were converted by $\text{Hg}(\text{CN})_2$ (moderate excess, sealed tubes, 8 hr, 40–60°) to $(\text{CF}_3)_2\text{PCN}$ and $\text{CF}_3\text{P}(\text{CN})_2$ in 99–100% yields. The end of each process was indicated by decolorization of the liquid. Our attempts to use AgCN for the same conversion³ gave unaccountably erratic results. For the conversion of PCl_3 to $\text{P}(\text{CN})_3$, however, the AgCN method⁴ was chosen to avoid contamination by HgCl_2 . We employed excess PCl_3 in a sealed tube (28 hr, 180°), obtaining a 57% yield of $\text{P}(\text{CN})_3$, which was isolated by high-vacuum sublimation at bath temperatures up to 90°.

(3) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1570 (1953).

(4) H. Hübner and G. Wehrane, *Justus Liebig's Ann. Chem.*, **128**, 259 (1863).

An alternative synthesis of $(CF_3)_2PCN$ is by the action of ICN upon $P_2(CF_3)_4$, first performed in our laboratories by Dr. H. W. Birnkraut.⁵ The reaction of the nearly equimolar mixture was slow at 25°, but complete after 5 hr at 80°, giving $(CF_3)_2PI$ and a 43% yield of $(CF_3)_2PCN$. Accurate vapor-tension measurements on the purified product gave the equation $\log P = 5.2225 + 1.75 \log T - 0.00366T - 1773/T$ (bp, 46.1°; Trouton constant, 23.5 eu; examples, 5.37 mm at -45.4°, 99.0 mm at 0°, and 255.4 mm at 19.4°). Somewhat later, Birnkraut made also the previously unknown compound $CF_3P(CN)_2$ from CF_3PI_2 and $AgCN$, sometimes obtaining almost quantitative yields, but often far less. Its volatility conformed to the equation $\log P = 8.5207 + 1.75 \log T - 0.0073T - 2830/T$ (bp, 111°; Trouton constant, 24.4 eu; examples, 9.9 mm at 18.25°, 106.7 mm at 60.95°). The new compound was confirmed by its vapor-phase molecular weight and analysis by basic hydrolysis, giving the expected yields of HCF_3 and CN^- .⁶ Birnkraut's data were used to prove the purity of our new samples of $(CF_3)_2PCN$ and $CF_3P(CN)_2$.

The infrared frequencies (cm^{-1} , vapor phase) which we observed for these compounds were as follows. $(CF_3)_2PCN$: 2194 (w), 1214 (vs), 1181 (vs), 1144 (vs), 1125 (vs), 826 (m), 732 (m, complex), 650 (w, br), 515 (w), 466 (w, br). $CF_3P(CN)_2$: 2197 (m), 1196 (vs), 1174 (vs), 1148 (vs), 750 (m, br), 647 (ms), 540 (w, br), 459 (m).

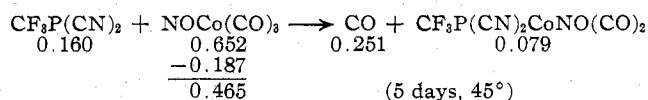
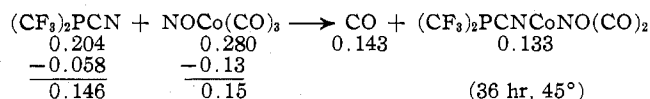
The nmr spectra recorded for the most volatile ligands and their $LCoNO(CO)_2$ complexes are shown in Table II.

TABLE II
FLUORINE AND PHOSPHORUS NMR SPECTRA^a

	δ_F	J_{FCP}^c	δ_P	J_{PCF}
$(CF_3)_2PCN^b$	51.4	86.2	41.2	86.4 septet
$(CF_3)_2PCNCoNO(CO)_2$	61.0	95		(Not observable) ^d
$CF_3P(CN)_2$	52.2	78.7	80.1	79.2 quartet
$CF_3P(CN)_2CoNO(CO)_2$	62.7	102		(Not observable) ^d

^a δ in ppm from Cl_3CF or H_3PO_4 ; J in sec^{-1} . ^b Substantially agreeing with K. J. Packer, *J. Chem. Soc.*, 960 (1963). ^c All doublets. ^d We never have been able to observe ³¹P signals for P-Co complexes, probably because the cobalt quadrupole blurred and spread out the weak multiplet patterns.

Synthesis of the Complexes.—The formation of $LCoNO(CO)_2$ compounds from $NOCO(CO)_3$ was nearly quantitative with $(CF_3)_2PCN$, much less efficient with $CF_3P(CN)_2$, and very poor with $P(CN)_3$. Polymer formation and instability of the desired products seemed to govern the trend. With $(CF_3)_2PCN$, equimolar $NOCO(CO)_3$ gave only a 60% yield, whereas a fivefold excess of $NOCO(CO)_3$ led to nearly quantitative utilization of the ligand to make the complex. The following equations with millimole stoichiometry represent experiments performed in sealed tubes without solvent, with quantitative high-vacuum methods for measuring reactants and products. The negative numbers represent recovered reactants.



In the latter case, complete consumption of the ligand was required, for it could not have been separated from the complex. The excess formation of CO and the even more excessive use of $NOCO(CO)_3$ could be ascribed to formation of copolymers with CO bridging.

The reaction of $P(CN)_3$ with $NOCO(CO)_3$ in large excess was successful only in dry chloroform, with only 5% yields of the desired $P(CN)_3CoNO(CO)_2$. The product was so difficultly volatile that its infrared spectrum (Table I) could be recorded for the vapor only by placing the cell in a heated box.

The formulas of all three $LCoNO(CO)_2$ complexes were confirmed by mass spectrometry. Each parent ion showed rather weakly, as expected in view of the easy detachment of CO or L, but the assignments were not ambiguous. Prominent significant peaks were assignable to L^+ , $NOCO(CO)_2^+$, $NOCOCo^+$, $NOCO^+$, Co^+ , $LCoNOCO^+$, $LCoNO^+$, NO^+ , CO^+ , and CN^+ . The fragmentation pattern of the ligand in the complex was in each case almost perfectly superposable upon that of the free ligand, confirming that each ligand remained intact in the complex. The infrared spectra also demonstrated that the ligands were undamaged; and the nmr results in Table II further confirm this.

The relatively volatile complexes $(CF_3)_2PCNCoNO(CO)_2$ and $CF_3P(CN)_2CoNO(CO)_2$ were isolated by high-vacuum fractional condensation, passing traps at 0° and condensing at -10°. As liquids in the dark, they could be stored for weeks at 25° without serious decomposition, but they proved to be decidedly unstable in sunlight. Their infrared spectra could be recorded for the vapors at 1 mm pressure, at moderate scanning speeds, but decomposition became troublesome during longer runs. For example, the vapor of $(CF_3)_2PCNCoNO(CO)_2$ was 30% decomposed during 2 hr in the infrared cell, showing increasing intensity of free-ligand peaks and formation of CO; and under similar conditions $CF_3P(CN)_2CoNO(CO)_2$ was 80% decomposed, again giving CO and the free-phosphine ligand.

Polymeric By-Products.—The nonvolatile by-products of the synthesis of the $(CF_3)_2PCN$ and $CF_3P(CN)_2$ complexes were very similar: both seemed stable *in vacuo* at 300° or higher, giving neither CO nor other volatile products and showing no detectable mass spectrum. Their terminal C-N stretching frequencies (2160 and 2165 cm^{-1} , respectively, in Nujol mulls) showed relatively low intensity, suggesting that they represented only the end groups of polymer chains. Far stronger was absorption at 1795 and 1801 cm^{-1} , respectively, quite distinct from the N-O terminal stretching peaks at 1870 cm^{-1} for both products; polymerization through CN (or CO?) thus was indicated. Both products proved to be slightly soluble in tetrahydrofuran, suggesting only moderate degrees of polymerization.

(5) WADC Technical Report 57-126, to Directorate of Materials and Processes, Wright-Patterson Air Force Base, Ohio, 1961, Part VI, p 177.

(6) Same Report, Part VII, 1963, pp 87-88. The fuller details given in Parts VI and VII of this report are not essential. For example, the reactions of diborane with $(CF_3)_2PCN$ or $CF_3P(CN)_2$ gave only unintelligible polymeric materials, and the evidence for the formation of $CF_3P(CN)_2$ from HCl and $CF_3P(CN)_2$ was incomplete.

Other observed infrared spectral peaks for these polymers were as follows (cm^{-1}). $(\text{CF}_3)_2\text{PCN}$ product: 2043 (m), 1995 (m), 1137 (br, poorly resolved), 726 (m, br), 620 (vw). $\text{CF}_3\text{P}(\text{CN})_2$ product: 2047 (m), 1995 (m), 1135 (s, br), 725 (m, br), 621 (w).

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Diamagnetic Anisotropy Induced by Metal-Metal Multiple Bonds^{1a}

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The most compelling criterion for the existence of a metal-metal bond has been, and remains, the metal-metal bond distance as determined by crystallographic techniques. Recently metal-metal double,² triple,^{3,4} and quadruple⁵ bonds have been proposed to exist in a number of compounds. These proposals have been based primarily on the exceptionally short metal-metal distances in these compounds. Undoubtedly, the length of a bond of a given multiplicity between a given pair of metal atoms is a sensitive function of a variety of parameters, including oxidation states, nature of additional ligands, and other aspects of molecular structure. It is apparent, therefore, that the use of interatomic distances to infer the multiplicity of metal-metal bonds requires caution. Indeed, the question of whether a multiple metal-metal bond actually exists rests squarely on the interpretation of metal-metal bond distances, the precise validity of which remains unclear.

Our interest in the general area of metal-metal bonds has prompted us to examine the question of multiplicity in such systems. Here we wish to report the results of an investigation that uses a noncrystallographic technique for probing the presence of certain multiple metal-metal centers.

Experimental Section

General.—All solvents were spectro quality and were degassed prior to use. Phosphine and phosphites were purchased from Strem Chemicals and used without further purification. Nmr samples were prepared and sealed under nitrogen. Nmr spectra were determined on a Varian HA-100 spectrometer. Optical spectra were recorded on sealed samples using a Cary Model 14 spectrophotometer. The infrared spectra of all new complexes were determined as chloroform solutions in sealed sodium chloride

cells on a Perkin-Elmer Model 337 grating spectrophotometer and were essentially equivalent to the spectrum observed for the uncomplexed ligand. Analyses and molecular weights were determined in the microanalytical laboratories of Stanford University and Galbraith Laboratories, Knoxville, Tenn.

Hexachlorobis(triethylphosphine)dirhenium(III), $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$, was prepared by the procedure of Cotton and Foxman.⁶ **trans-Dichlorobis(tri-*n*-butylphosphine)platinum(II)** was prepared by the procedure of Grim, *et al.*⁸

Preparation of Dinuclear Rhenium(III) Complexes.—The procedure outlined below for the preparation of hexachlorobis(tri-*n*-butylphosphine)dirhenium(III) is typical of the general method used.

Tetra-*n*-butylammonium octachlorodirhenium,⁷ $[\text{Re}_2\text{Cl}_8][\text{N}(\text{C}_4\text{H}_9)_4]_2$ (1.0 g, 0.88 mmol), was suspended in 25 ml of methanol containing 1 ml of concentrated hydrochloric acid and tri-*n*-propylphosphine (1.0 g, 6.2 mmol) was added. The solution turned green immediately. After stirring for an additional 30 min, the solution was chilled to -20° and the green crystals collected by suction filtration. The isolated yield was 93%.

Preparation of Dinuclear Molybdenum(II) Complexes.—A typical procedure used to prepare the desired dinuclear molybdenum(II) complexes is presented below.

Tetrachlorotetrakis(triethylphosphine)dimolybdenum(II), $\text{Mo}_2\text{Cl}_4[\text{P}(\text{C}_2\text{H}_5)_3]_4$.—Pentaammonium nonachlorodimolybdenum(II) monohydrate,⁸ $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ (2.0 g, 3.2 mmol), was placed in a 40-ml centrifuge tube containing a Teflon-coated stirrer bar. The tube was capped with a rubber septum stopper and flushed with prepurified nitrogen. Oxygen-free methanol (30 ml) was added, followed by 2.0 g (17 mmol) of triethylphosphine. The solution turned blue immediately. The resulting mixture was stirred for 1 hr, chilled to -78° , and centrifuged. The supernatant solution was removed through a cannula employing a positive pressure of nitrogen. Fresh oxygen-free methanol was again added and the tube was shaken, cooled, and again centrifuged. The solid was washed a total of five times. The remaining solid was suspended in 20 ml of oxygen-free methanol, chilled to -78° , and then filtered under a positive pressure of nitrogen. The isolated solid was obtained in 85% yield. Tetrachlorotetrakis(triethylphosphine)dimolybdenum(II) is stable indefinitely at ambient temperatures in the absence of oxygen; it is oxidized slowly on exposure to room atmosphere, but solutions decompose rapidly in presence of oxygen.

Results and Discussion

It has been recognized for some time that the anomalous shielding observed in the ^1H nmr spectra of certain organic compounds which contain a hydrogen nucleus in the vicinity of a carbon-carbon multiple bond is a direct consequence of the diamagnetic anisotropy that results when the circulating electrons within this multiple bond are subjected to an external field. The theoretical aspects of such long range shielding have been treated by McConnell,⁹ the approximate relationship for an axially symmetrical group of electrons being

$$\sigma_{\text{av}} = \frac{(3 \cos^2 \theta - 1)(X_L - X_T)}{3r^3}$$

where r is the distance between the proton and the electrical center of gravity of the multiple bond, θ is the acute angle between r and the symmetry axis, and X_L and X_T are respectively the longitudinal and transverse magnetic susceptibilities of the bond in question. The subscript "av" is included to indicate that the shielding, σ , has been averaged over all orientations of the system. From the angular dependence of this relationship it is noted that the value of the function

(1) (a) Supported by ARPA Contract No. N00014-67-A-0112-0056 and by the Petroleum Research Fund, administered by the American Chemical Society. (b) Address correspondence to author at Rutgers University.

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