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Equilibrium Studies of Phosphine and Amine Substitution Reactions of Tungsten Carbonyl

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Equilibrium constants, K, have been determined for the reaction $(Am)W(CO)_5 + L \rightleftharpoons (L)W(CO)_5 + Am$. For a given L group, K values increase for different amines, Am, in the order: $p\text{-}CH_3OC_6H_4NH_2 < p\text{-}CH_3C_6H_4NH_2 < C_6H_5NH_2 < p\text{-}BrC_6H_4NH_2$. This trend is interpreted to mean that the strength of the W–Am bond decreases with decreasing basicity of the amine. For a given Am group, K decreases with different L groups as follows: $P(n\text{-}C_4H_9)_3 \sim P(C_6H_{11})_3 \geq P(OCH_2)_3CC_2H_5 > P(SCH_2)_3CCH_3 \geq P(O\text{-}n\text{-}C_4H_9)_3 > P(C_6H_5)_3 > As(C_6H_5)_3 > Sb(C_6H_5)_3 \sim P(OC_6H_5)_3 \sim p\text{-}CH_3OC_6H_4NC > Bi(C_6H_5)_3$. Since this is essentially the order of decreasing basicity of the phosphorus donor ligands, the results suggest that σ bonding, not π bonding, is largely responsible for the strength of the W–L bond. Enthalpies and entropies have been determined for some of these reactions, and they support the above conclusions.

The nature of M–L bonding in substituted transition metal carbonyl complexes of the type $M(CO)_xL_y$, where L is a phosphine or phosphite, has frequently, been inferred from the observed C–O stretching frequencies of these compounds. It has been observed that, in general, complexes containing $P(OR)_3$ ligands exhibit higher C–O stretching frequencies than those which contain PR_3 ligands.[1] This is usually interpreted to mean that $P(OR)_3$ groups π-bond more strongly with metals than do PR_3 ligands. Nuclear magnetic resonance studies of $^{183}W\text{–}^{31}P$ coupling constants in $R_3PW(CO)_5$ complexes have also been interpreted in terms of the importance of W–P π bonding.[2] If π bonding does make a substantial contribution to the M–L bond, those ligands which are capable of forming strong π bonds would be expected to form strong M–L bonds. Therefore, $M\text{–}P(OR)_3$ bonds should be stronger, with respect to dissociation to M and $P(OR)_3$, than $M\text{–}PR_3$ bonds.

On the other hand, recent infrared studies[3–6] of substituted metal carbonyls suggest that M–L σ bonding contributes significantly to determining the C–O stretching frequencies and presumably also to the strength of the M–L bond. If σ bonding predominates, the more basic PR_3 should form stronger M–L bonds than $P(OR)_3$. To be sure, the relative importance of σ and π bonding in such complexes is not well established.

In an attempt to provide more direct evidence of M–L bond strengths, we have measured the equilibrium constants for the reaction

$$(Am)W(CO)_5 + L \overset{K}{\rightleftharpoons} (L)W(CO)_5 + Am \qquad (1)$$

In these studies, Am is $p\text{-}CH_3OC_6H_4NH_2$, $p\text{-}CH_3C_6H_4NH_2$, $C_6H_5NH_2$, or $p\text{-}BrC_6H_4NH_2$, and L is any of a variety of potentially π-bonding ligands.

Experimental Section

Materials.—Commercially available tributylphosphine and tributyl phosphite were purified by distillation at reduced pressures and stored under a nitrogen atmosphere. The caged phosphite, $P(OCH_2)_3CC_2H_5$, was prepared according to the method of Stetter and Steinacker.[7] The caged thiophosphite, $P(SCH_2)_3CCH_3$, was a gift of Dr. R. L. Keiter. The method of Hertler and Corey[8] was used in the preparation of $p\text{-}CH_3OC_6H_4NC$. All other ligands were obtained from commercial sources and were used without further purification. The solvents—decahydronaphthalene (decalin, mixture of *cis* and *trans* isomers), toluene, chlorobenzene, and *o*-dichlorobenzene—were reagent grade and were not purified further.

Preparation of $(Am)W(CO)_5$.—The aniline complexes were prepared by irradiating solutions of $W(CO)_6$ and the aniline with ultraviolet light according to the general method of Strohmeier.[9] The complexes used in this study have been prepared previously[3] and were identified by their infrared spectra. Satisfactory analyses for $(C_6H_5NH_2)W(CO)_5$ and $(p\text{-}CH_3C_6H_4NH_2)W(CO)_5$ were obtained. Although the infrared spectra in the C–O stretching region indicated the presence of $(p\text{-}CH_3OC_6H_4NH_2)W(CO)_5$ and $(p\text{-}BrC_6H_4NH_2)W(CO)_5$, analyses of these samples as well as their infrared spectra in the N–H stretching region indicated the presence of free $p\text{-}CH_3OC_6H_4NH_2$ and $p\text{-}BrC_6H_4NH_2$ in the respective samples. As will be seen, the presence of excess amine introduces a negligible error into the equilibrium measurements which were obtained in the presence of much larger amounts of aniline of known concentration.

Equilibrium Measurements.—The yellow $(Am)W(CO)_5$ complexes exhibit maxima at 410 mμ in decalin and toluene solvents, at 406 mμ in chlorobenzene, and at 405 mμ in *o*-dichlorobenzene. Since the anilines, L, and $LW(CO)_5$ are colorless and have essentially no absorption at these wavelengths, it was possible to determine the concentration of $(Am)W(CO)_5$ present at equilibrium. In practice, these other species contributed slightly to the absorbance, but the necessary correction was very small. That the product was indeed $(L)W(CO)_5$ was established from the known uv–visible spectra of the products. Also the infrared spectra of many reaction solutions showed that $(L)W(CO)_5$ was the only carbonyl-containing product. There was no evidence of complexes formed from the displacement of CO by L.

The equilibrium constants, K, were calculated from the measured absorbances, A, at equilibrium of a series of solutions initially containing $\sim 1.5 \times 10^{-4}$ M $(Am)W(CO)_5$, $(100\text{–}1600) \times 10^{-4}$ M Am, and $(2\text{–}100) \times 10^{-4}$ M L. This absorbance results

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[1] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 745.

[2] S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967).

[3] R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

[4] G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967).

[5] W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

[6] D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

[7] H. Stetter and K. H. Steinacker, *Chem. Ber.*, **85**, 451 (1952).

[8] W. R. Hertler and E. J. Corey, *J. Org. Chem.*, **23**, 1221 (1958).

[9] (a) W. Strohmeier, K. Gerlach, and G. Matthias, *Z. Naturforsch.*, **15b**, 621 (1960); (b) W. Strohmeier, K. Gerlach, and D. von Hobe, *Chem. Ber.*, **94**, 164 (1961).

TABLE I

EQUILIBRIUM CONSTANTS FOR REACTION 1 IN TOLUENE AT 35.4°

	Am			
L	p-$CH_3OC_6H_4NH_2$ (5.3[a])	p-$CH_3C_6H_4NH_2$ (5.1[a])	$C_6H_5NH_2$[d] (4.6[a])	p-$BrC_6H_4NH_2$ (3.9[a])
$P(n\text{-}C_4H_9)_3$, 131[c]	8.91	48.1	225 (345, 359)[b]	164–826
$P(OCH_2)_3CC_2H_5$, 665[c]	8.47	37.0	180–360	254
$P(O\text{-}n\text{-}C_4H_9)_3$, 530[c]	3.77	16.5	31.2 (63.3, 65.9)[b]	80.7
$P(C_6H_5)_3$, 573[c]	3.12	6.55	17.1 (49.2, 65.7)[b]	25.9
$As(C_6H_5)_3$, . . .	1.42	1.58	11.2 (15.4, 30.9)[b]	47.8
$P(OC_6H_5)_3$, 875[c]	0.25	1.16	6.6 (12.4, 25.4)[b]	29.1

[a] pK_a. From D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth and Co. Ltd., London, 1965. [b] K values at 40.5 and 45.4°, respectively. [c] ΔHNP values (see text).[10,11] [d] Equilibrium constants for other L groups with $(C_6H_5NH_2)W(CO)_5$ in toluene at 35.4°: $P(C_6H_{11})_3$, 198; $P(SCH_2)_3CCH_3$, 45.3; $Sb(C_6H_5)_3$, 7.54; $Bi(C_6H_5)_3$, 1.08; p-$CH_3OC_6H_4NC$, 33.2 (in decalin solvent).

TABLE II

SOLVENT DEPENDENCE OF THE EQUILIBRIUM CONSTANTS FOR THE REACTION OF $(C_6H_5NH_2)W(CO)_5$ WITH L ACCORDING TO EQ 1 AT 35.4°

	Solvent					
L	Toluene	75% toluene–25% decalin	50% toluene–50% decalin	Decalin	C_6H_5Cl	o-$Cl_2C_6H_4$
$P(n\text{-}C_4H_9)_3$	225	109	450	871–1258	. . .	. . .
$P(OCH_2)_3CC_2H_5$	180–360	92.6	451	577–973	300–450	208
$P(O\text{-}n\text{-}C_4H_9)_3$	31.2	27.1	148	301–695	80–140	84.5
$P(C_6H_5)_3$	17.1	17.9	61.4	101	59.5	. . .
$As(C_6H_5)_3$	11.2	9.26	19.6	47.7	31.9	29.6
$P(OC_6H_5)_3$	6.6	5.07	15.3	35.3	11–29	13.7

primarily from $(Am)W(CO)_5$ and a small contribution from $(L)W(CO)_5$. Thus

$$A = A_0X + A_\infty(1 - X) \qquad (2)$$

where X is the fraction of the original $(Am)W(CO)_5$ which is present at equilibrium, A_0 is the absorbance before reaction or the initial absorbance of $(Am)W(CO)_5$, and A_∞ is the absorbance under conditions where reaction 1 was forced to completion and represents the absorbance of $(L)W(CO)_5$ which was always very nearly zero. In any series of equilibrium studies involving several solutions of the same concentration of $(Am)W(CO)_5$ but varying concentrations of Am and L, A_0 was determined from a solution containing no L. Over the 2-day equilibration period A_0 did not change, indicating that no decomposition of the complex occurred. In the absence of added Am, however, $(Am)W(CO)_5$ does decompose. The value of A_∞ was determined in solutions containing no added Am but a large excess of L.

Rearranging eq 2 gives $X = (A - A_\infty)/(A_0 - A)$. From the value of X and the concentrations of added Am and L, the equilibrium constants were calculated.

$$K = \frac{(1 - X)[\mathrm{Am}]}{X[\mathrm{L}]} = \frac{[(\mathrm{L})\mathrm{W(CO)_5}][\mathrm{Am}]}{[(\mathrm{Am})\mathrm{W(CO)_5}][\mathrm{L}]}$$

A typical equilibrium constant determination was conducted as follows. Into a culture tube were pipetted 2-ml solutions each of Am and L and 5 ml of a freshly prepared solution of $(Am)W(CO)_5$. The system was purged with N_2, sealed with a septum, and allowed to equilibrate in a constant-temperature bath for 2 days. Several such tubes of different L and Am concentrations were run simultaneously. Kinetic studies indicated that this was more than enough time for the system to come to equilibrium. At the end of this period, samples of the solution were withdrawn and the absorbances were measured in 1-cm quartz cells on a Beckman DB-G grating uv–visible spectrophotometer. The kinetic studies also showed that the rate of reaction was so slow that any shift in the position of the equilibrium which might occur during the spectral measurements was negligible.

The only reaction which was not studied by the uv–visible method was that of $(C_6H_5NH_2)W(CO)_5$ with p-$CH_3OC_6H_4NC$. In this case the concentrations of $(C_6H_5NH_2)W(CO)_5$ initially and at equilibrium were determined from the intensity of its C–O stretching absorption at 1922 cm^{-1}. The infrared spectrum of the product of the reaction was virtually identical with that of the known $(p\text{-}CH_3OC_6H_4NC)Mo(CO)_5$.[10] These measurements were made on a Beckman IR-8 spectrophotometer. Solution concentrations of all reactants were increased by 10-fold to provide sufficient absorption for measurement.

Results

Table I presents the equilibrium constants for reaction 1 measured in toluene solvent at 35.4°. These values are reproducible to with ±15% and each represents an average of about five determinations. In a few of the reactions, K varied greatly with the concentration of Am or L added. Despite many attempts to locate the source of the problem, no reason for this behavior can be offered. In these cases, the ranges of values that were obtained are given in the tables. Values given in parentheses in Table I are equilibrium constants determined at other temperatures for the reaction of $(C_6H_5NH_2)W(CO)_5$ with various L groups.

Table II shows the dependence on the solvent of the equilibrium constants, K, for the reaction of $(C_6H_5NH_2)W(CO)_5$ with L. The values of $\Delta H°$ and $\Delta S°$ (Table III) for the reaction of $(C_6H_5NH_2)W(CO)_5$ with L were calculated from values of K determined at different temperatures (Table I). The limits of error associated with these values in the tables are one standard deviation.

Discussion

The values of K presented in Table I for the reaction of various $(Am)W(CO)_5$ complexes with any given L increase with the nature of Am in the order: p-$CH_3OC_6H_4NH_2$ < p-$CH_3C_6H_4NH_2$ < $C_6H_5NH_2$ < p-$BrC_6H_4NH_2$. This is also the order of decreasing

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(10) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

TABLE III

ΔH° AND ΔS° VALUES FOR THE REACTION OF $(C_6H_5NH_2)W(CO)_5$ WITH L IN TOLUENE

L	ΔH°, kcal/mol	ΔS°, eu
$P(n\text{-}C_4H_9)_3$	7.6 ± 2.6^a	36 ± 8^a
$P(n\text{-}OC_4H_9)_3$	14.2 ± 1.8	53 ± 6
$P(C_6H_5)_3$	24.8 ± 1.6	86 ± 5
$As(C_6H_5)_3$	19.1 ± 1.8	67 ± 6
$P(OC_6H_5)_3$	26.2 ± 0.5	89 ± 2

[a] Limits of error are one standard deviation.

basicity, as measured by pK_a (Table I), which suggests that the most basic anilines form the strongest bonds to the $W(CO)_5$ moiety. Since the $W\text{-}NH_2R$ bond must depend virtually solely upon the σ-bonding ability of the amine, it is not surprising that this trend in K's is observed. Free energy plots of log K *vs.* pK_a of Am are, however, not linear but show considerable curvature.

For the reaction of $(C_6H_5NH_2)W(CO)_5$ in toluene at 35.4° with a variety of L groups, the value of K decreases with the nature of L as follows: $P(n\text{-}C_4H_9)_3 \sim P(C_6H_{11})_3 \geq P(OCH_2)_3CC_2H_5 > P(SCH_2)_3CCH_3 \geq P(O\text{-}n\text{-}C_4H_9)_3 > P(C_6H_5)_3 > As(C_6H_5)_3 > Sb(C_6H_5)_3 \sim P(OC_6H_5)_3 > Bi(C_6H_5)_3$. Since it was not possible to examine the reaction with $p\text{-}CH_3OC_6H_4NC$ in the same solvent, toluene, its position in the above series can only be approximated. In decalin solvent its K value is essentially the same as that for $P(OC_6H_5)_3$ in the same solvent. Thus it is reasonable to place $p\text{-}CH_3OC_6H_4NC$ near $P(OC_6H_5)_3$ in the above series for the reactions in toluene as well. It should be noted that the above trend is also valid in the other solvent systems (Table II).

The basicities toward H^+ of several of the phosphorus donors in the series have been determined[11,12] and are given as half-neutralization potentials, ΔHNP, in Table I. High values of ΔHNP indicate weak bases, and there is an inverse relationship between the ΔHNP and pK_a of the ligand. For those phosphorus ligands whose ΔHNP values are known, it is clear that the more basic L groups yield the highest equilibrium constants. With the exception of the caged phosphite, $P(OCH_2)_3CC_2H_5$, which forms more stable complexes than predicted from its ΔHNP, the most basic L groups presumably form the strongest W–L bonds. A related observation is that $p\text{-}CH_3OC_6H_4NC$, a potentially strongly π-bonding ligand, forms one of the least stable complexes of those examined. The available evidence thus strongly indicates that the σ-bonding ability of L dominates the trend in equilibrium constants. Although these data may be interpreted as indicating an insignificant amount of W–L π bonding, it is possible that the extent of W–L π-bonding may be nearly constant for the different L groups, and π bonding would therefore have no effect on the values of K. This, however, seems unlikely in view of our current concepts of metal–ligand π bonding.[1] At present, the simplest yet most reasonable interpretation of the equilibrium constants trend is that σ bonding is significantly more important in the W–L bond than is π bonding. A similar conclusion[3] was derived from an infrared study of these same compounds. While W–L σ bonding appears to supersede π bonding, the $(L)W(CO)_5$ complexes represent a very favorable σ-bonding situation. In other complexes containing fewer π-accepting CO groups, phosphines and phosphites will perhaps participate significantly in π bonding with the metal.

Those phosphorus-donor L groups which form the most stable $(L)W(CO)_5$ complexes are also those which have the highest nucleophilicity in CO displacement reactions of metal carbonyls.[12,13] In general, an excellent correlation exists between the ΔHNP of the attacking ligand and its nucleophilicity. The one ligand which exhibits a much lower nucleophilicity than would be anticipated from its basicity is tricyclohexylphosphine, $P(C_6H_{11})_3$. The bulkiness of the cyclohexyl groups is presumed to be responsible for its reduced nucleophilicity. It should be noted, however, that in this study K is very close to that predicted from the basicity of the ligand. Perhaps the larger W atom reduces steric crowding around the metal as compared to that in the kinetic studies which involved first-row transition elements.

Other conclusions from this equilibrium study are that the thiophosphite, $P(SCH_2)_3CCH_3$, forms a slightly less stable complex than its oxygen analog and K decreases with different donor atoms as: $P(C_6H_5)_3 > As(C_6H_5)_3 > Sb(C_6H_5)_3 > Bi(C_6H_5)_3 \sim C_6H_5NH_2$.

The effect of different solvents on the equilibrium constants is small as would be expected since none of the species involved is ionic. The values of K are, however, approximately 5 times higher in decalin solvent than toluene. That chlorobenzene and *o*-dichlorobenzene yield equilibrium constants between those of toluene and decalin suggests that the dielectric constant of the solvent is not of primary importance in determining the solvent effect.

The ΔH° values (Table III) for the reactions of $(C_6H_5NH_2)W(CO)_5$ are positive. The trend in these values suggests that the W–L bond strength decreases in the order: $P(n\text{-}C_4H_9)_3 > P(O\text{-}n\text{-}C_4H_9)_3 > As(C_6H_5)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$. Except for the reversal of $As(C_6H_5)_3$ and $P(C_6H_5)_3$, this is the same order as observed for the equilibrium constants. Because of difficulty in measuring precise equilibrium constants, the standard deviations for ΔH° are rather large. Nevertheless, these ΔH's do tend to support the conclusions based on K values only. That the ΔH°'s are all positive indicates that the $W\text{-}NH_2C_6H_5$ bond is stronger than the W–L bonds which is contrary to the conclusion obtained from the equilibrium constants. The high values for K result from the exceedingly high positive values of ΔS°. Reaction 1 would be expected to give ΔS° values very close to zero. The observed values which range from +36 to +90 eu

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(11) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

(12) D. E. Morris and F. Basolo, *J. Am. Chem. Soc.*, **90**, 2531 (1968).

(13) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

are simply not understood. Another unusual aspect is that plots of ΔH° *vs.* ΔS° are linear according to $\Delta S^\circ = (2.9 \times 10^{-3})\Delta H^\circ + 13$. The equation $\Delta G^\circ = \Delta H^\circ - T\Delta S$, upon substituting $\Delta G^\circ = -RT \ln K$, may be arranged into the same form: $\Delta S^\circ = (\Delta H^\circ/T) + R \ln K$. The constants in the experimental equation are therefore related to $1/T$ and $R \ln K$. Thus $T = 344°K$ or 71°C and $K = 660$. This means that all of the reactions will have the same equilibrium constant (660) at 71°. This unusual relationship between ΔH° and ΔS° has also been observed in a few other quite different systems[14,15] and has been discussed from a theoretical standpoint.[16]

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(14) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **77**, 2164 (1955).

(15) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.

(16) W. B. Person, *J. Am. Chem. Soc.*, **84**, 536 (1962). We thank a referee for calling this reference to our attention.

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The Chemistry of Dinuclear Carbonyl Anions. IV.[1] Thiocyanate- and Cyanide-Bridged Complexes

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The reaction of either cyanide or thiocyanate ions with $M(CO)_6$ (where M = Cr or W) produced, in addition to the mononuclear anions $M(CO)_5X^-$, dinuclear anions of the type $M_2(CO)_{10}X^-$. Extension of this reaction to $Fe(CO)_5$ resulted in the preparation of the anions $Fe(CO)_4NCS^-$, $Fe(CO)_4CN^-$, and $Fe_2(CO)_8CN^-$. The spectra of these materials are discussed in relation to their structure.

The previous paper in this series[1] described the preparation of halogen-containing dinuclear carbonyl anions of the type $M_2(CO)_{10}X^-$ (where X = I, Br, or Cl). Their preparation was believed to occur in the stepwise manner

$$M(CO)_6 + X^- \longrightarrow M(CO)_5X^- + CO$$

$$M(CO)_5X^- + M(CO)_6 \longrightarrow M_2(CO)_{10}X^-$$

These reactions have now been extended to include the pseudohalides, CN^- and SCN^-. Both the mononuclear and the dinuclear species could be isolated when either chromium or tungsten hexacarbonyl was employed. Furthermore, treatment of iron pentacarbonyl under the same conditions led to the formation of the new anions $Fe(CO)_4CN^-$, $Fe_2(CO)_8CN^-$, and $Fe(CO)_4NCS^-$. The reaction of cyanide ion with iron pentacarbonyl appeared to be unique since no dinuclear iron carbonyl thiocyanate derivative could be isolated.

Experimental Section

The analytical data for the compounds prepared are summarized in Table I.

Materials.—The cyanide and thiocyanate salts of the bis(triphenylphosphine)imminium cation (hereafter abbreviated as PPN) were prepared by reaction of the chloride with a large (50 times) excess of potassium cyanide or thiocyanate in aqueous solution. The metal carbonyls were obtained from commercial sources.

Preparation of (PPN)$Fe(CO)_4NCS$.—A mixture of 0.6 ml of $Fe(CO)_5$ and 1.19 g of (PPN)SCN in 50 ml of CH_2Cl_2 was irradiated with a uv flood lamp until 75 cm^3 of gas (STP) was evolved. The solvent was removed from the mixture at room temperature. The residue was dissolved in 20 ml of CH_2Cl_2, and 120 ml of ether was added. The mixture was filtered, and pentane was added to the filtrate. A 0.55-g sample of product was obtained.

Preparation of (PPN)$Fe(CO)_4CN$ and (PPN)$Fe_2(CO)_8CN$.—A mixture of 1.17 g of (PPN)CN and 0.6 ml of $Fe(CO)_5$ in 50 ml of CH_2Cl_2 was treated as described above. After irradiation was complete, the solvent was removed under vacuum. The residue was extracted three times with 50 ml of ether. Pentane was added to the combined extracts and a 0.21-g sample of (PPN)$Fe_2(CO)_8CN$ was obtained. The residue from the extraction was dissolved in 10 ml of CH_2Cl_2 and 75 ml of ether was added. The mixture was filtered, and pentane was added to the filtrate. A 0.29-g sample of (PPN)$Fe(CO)_4CN$ was obtained.

Preparation of (PPN)$M(CO)_5NCS$ (Where M = Cr or W).—The preparations of both the chromium and tungsten derivatives were performed in analogous manners. A mixture of 1.0 g of $Cr(CO)_6$ and 1.25 g of (PPN)SCN in 30 ml of CH_2Cl_2 was irradiated with a uv flood lamp until 50 cm^3 of gas (STP) was evolved. The solvent was removed from the mixture and the excess metal carbonyl was sublimed away. The residue was dissolved in 15 ml of CH_2Cl_2, and 50 ml of ether was added. The mixture was filtered, and pentane was added to the filtrate. The product crystallized on cooling.

Preparation of (PPN)$M_2(CO)_{10}SCN$ (Where M = Cr or W).—The preparations of both the chromium and tungsten derivatives were carried out in analogous manners. A mixture of 0.69 g of (PPN)SCN and 1.0 g of $Cr(CO)_6$ in 50 ml of THF was irradiated until approximately 80 cm^3 of gas had been evolved. The solvent was removed under vacuum. The residue was extracted with 25 ml of ether. Another 25-ml portion of ether was added to the extract, followed by pentane. The product crystallized on cooling and was recrystallized from ether and pentane.

The Preparation of (PPN)$_2M(CO)_4(CN)_2$ and (PPN)$M(CO)_5CN$ (Where M = Cr or W).—The reaction was performed similarly for both the metal carbonyl derivatives. A mixture of 0.52 g of $Cr(CO)_6$ and 1.03 g of (PPN)CN in 50 ml of CH_2Cl_2

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(1) Part III: J. K. Ruff, *Inorg. Chem.*, **7**, 1821 (1968).