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OCTAHEDRAL METAL CARBONYLS

XLVIII *. KINETICS AND MECHANISM OF REACTIONS OF HEXACARBONYLTUNGSTEN(0) WITH BIS(TRIPHENYLPHOSPHINE)IMMINIUM PSEUDO HALIDES

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Summary

Hexacarbonyltungsten(0) reacts with $[(Ph_3P)_2N]^+[X]^-([PPN]^+[X]^-)$ salts (X^- = CN^-, OCN^-, SCN^-) in chlorobenzene at 90—120°C to afford $[PPN]^+[W(CO)_5(X)]^-$ (X^- = OCN^-, SCN^-) and $[PPN]^+_2[cis\text{-}W(CO)_4(CN)_2]^{2-}$ products. Rate data taken over this temperature range support a rate-law,

$$-d[W(CO)_6]/dt = k_2[W(CO)_6][PPN^+X^-]$$

The data are consistent with a mechanism involving initial attack of the anionic nucleophiles (which exist in chlorobenzene as contact ion pairs) at a carbonyl carbon of the substrate. Additional studies of reactions of $[PPN]^+[SCN]^-$ reveal that at no time is a coordinatively-unsaturated species formed during the substitution process. It is likely that the same is true for the other pseudo-halides as well.

It appears probable that most reactions of anionic nucleophiles with $M(CO)_6$ species (M = Cr, Mo, W) involve interaction at carbon, in contrast to results for uncharged Lewis bases (L) such as phosphines and phosphites, for which the bimolecular path is best described as a dissociative interchange. The pseudohalides are "labilizing" ligands, and thus $[cis\text{-}W(CO)_4(L)(X)]^-$ species are formed from $[W(CO)_5(X)]^-$ substrates under mild conditions (ca. 60°C) via an unimolecular process. The inability to produce $[W(CO)_4(X)_2]^{2-}$ products (X^- = OCN^-, SCN^-) thus results from thermodynamic considerations.

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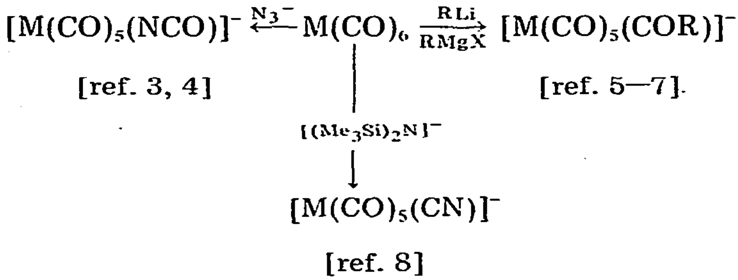
* Part XLVII see ref. 22.

Introduction

Two distinct bimolecular paths in ligand-exchange have been documented for reactions of the group VIB metal carbonyls (M = Cr, Mo, W) with nucleophiles [1]. For molecular Lewis bases such as amines, phosphines and phosphites, extensive evidence suggests that the bimolecular path is a dissociative interchange (I_d) process [2]. For the displacement of CO from metal hexacarbonyl by anionic nucleophiles, however, the identity of the reaction products in several instances suggests interaction at a carbonyl carbon:



$$\begin{tikzcd}
{[M(CO)_5(NCO)]^-} & M(CO)_6 \arrow[l, "N_3^-"'] \arrow[r, "RLi", "RMgX"'] \arrow[d, "{[(Me_3Si)_2N]^-}"] & {[M(CO)_5(COR)]^-} \\
 & {[M(CO)_5(CN)]^-} &
\end{tikzcd} \qquad (1)$$

[ref. 3, 4] [ref. 5—7]. [ref. 8]

For other anionic nucleophiles such as halides (Cl^-, Br^-, I^-) [9,10] and pseudohalides (CN^-, OCN^-, SCN^-), [3,11,12] simple substitution products are obtained:

$$M(CO)_6 \xrightarrow{X^-} [M(CO)_5(X)]^- + CO \qquad (2)$$

Thus, in these systems, product identity provides no clue as to the nature of the CO-exchange process. Kinetics studies of reactions of $M(CO)_6$ with halides [10] have revealed a bimolecular reaction path to be accessible. Based upon the relative rates of nucleophilic attack as a function of the identity of the metal atom in $M(CO)_6$ and of the halide ion, it was proposed that both the CO-interchange and carbonyl-attack paths were operative in these systems.

In order to investigate further the question of the site of attack in bimolecular reactions of anionic nucleophiles with metal hexacarbonyls, a study of the $W(CO)_6$-pseudo-halide reactions, according to eq. 2, was initiated. The results of that investigation are the subject of this report.

Experimental

General

Infrared spectra were obtained emploing a Perkin—Elmer Model 621 grating spectrophotometer, and were calibrated against a band of water vapor at 1869.4 cm^{-1} [13]. Elemental analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Preparation and purification of reagents

Bis(triphenylphosphine)imminium chloride was obtained from Strem Chemical Co., The potassium salts of the pseudo halides (CN^-, OCN^-, SCN^-) were purchased from the J.T. Baker Chemical Co., Triphenylphosphine was obtained from Cincinnati Milachron, and was recrystallized from absolute ethanol and dried in vacuo. Triisopropyl phosphite (Aldrich) was distilled over sodium (60—68°C/10 torr, N_2 bleed). The chlorobenzene (Fisher) was distilled from P_2O_5 and was stored over molecular sieves. Hexacarbonyltungsten(0) (Pressure Chemical) was used as obtained.

The $[PPN]^+[X]^-$ salts were prepared employing the method of Ruff [12].

Preparation and identification of reaction products.

The $[PPN]^+[W(CO)_5(X)]^-$ products ($X^- = NCO^-, NCS^-$) were prepared by thermal methods reported by Ruff [12]; the final reaction products, $[PPN]^+$-$[W(CO)_5(X)]^-$ ($X^- = OCN^-, SCN^-$) and $[PPN]_2^+[cis\text{-}W(CO)_4(CN)_2]^{2-}$ were prepared by thermal methods reported previously for the preparation of similar compounds [3,11]. Infrared spectral data for the complexes are presented in Table 1; they support W—NCO^-, W—NCS^- and W—CN^- bonding in these products [3,12]. An elemental analysis for the previously-unreported $[PPN]^+$-$[W(CO)_5(NCO)]^-$ was also obtained. Anal.: Found: C, 55.67; H, 3.43; N, 2.93. $C_{42}H_{30}O_6P_2N_2W$ calcd.: C, 55.77; H, 3.34; N, 3.10%.

Preparation of disubstituted anionic species.

$[PPN]_2^+[W(CO)_4(CN)_2]^{2-}$

$[PPN]^+[CN]^-$ (5.6 g; 10 mmol) and $W(CO)_6$ (1.76 g; 5 mmol) in chlorobenzene were allowed to react under N_2 at 95°C for 3 h. The solution was cooled, whereupon the product precipitated as yellow crystals. The latter were collected by suction filtration, washed with n-hexane, and dried in vacuo at 50°C. The carbonyl stretching bands for this complex (Table 1) were similar to those reported for the same complex, prepared photochemically.

$[PPN]^+[W(CO)_4(NCS)(L)]^-$ ($L = PPh_3, P(OPr\text{-}i)_3$)

A mixture of $[PPN]^+[W(CO)_5(NCS)]^-$ and a three-fold excess of L was stirred in chlorobenzene under N_2 at 60°C for 3 h. The resulting solution was filtered, and the yellow crystalline product was precipitated through addition of petroleum ether to the filtrate. It was dried in vacuo. Anal.: ($L = PPh_3$): Found:

TABLE 1

INFRARED SPECTRA OF THE ANIONS

Anion	ν(CN)	ν(CO) ^{d}	Ref.
$[W(CO)_5(NCS)]^{-\,a}$	2100w	2063vw, 1965(sh), 1920vs 1870m	[12] and this work
$[W(CO)_5(NCO)]^{-\,b}$	2230m	2060w, 1956(sh), 1910vs 1850m	[3] and this work
$[W(CO)_4(CN)_2]^{2-\,c}$	2088vw, 2082vw	1982w, 1862s, 1843(sh) 1798m	[12] and this work
$[W(CO)_4(NCS)(PPh_3)]^{-\,b}$	2095w	2003w, 1885(sh), 1870s 1822m	This work
$[W(CO)_4(NCS)(P(OPr\text{-}i)_3)]^{-\,b}$	2095w	2005w, 1890(sh), 1868s, 1825m	
$[W(CO)_4(NCO)(P(OPr\text{-}i)_3)]^{-\,b}$	2226m	1999w, 1872s, 1860s 1805m	This work

^{a} THF solvent. ^{b} Chlorobenzene solvent. ^{c} $C_2H_4Cl_2$ solvent. ^{d} Relative intensities: s, strong; m, medium; w, weak; (sh), shoulder; v, very.

TABLE 2a

RATES OF REACTION OF $W(CO)_6$ WITH $[PPN]^+[X]^-$ IN CHLOROBENZENE AT VARIOUS TEMPERATURES

X^-, T (°C)	$[X^-]$ (M)	$10^4\ k_{obsd}$ (s^{-1})	X^-	T, (°C)	$[X^-]$ (M)	$10^4\ k_{obsd}$ (s^{-1})	X^-, T(°C)	$[X^-]$ (M)	$10^4\ k_{obsd}$ (s^{-1})
NCO^-, 90.00(5)	0.0265	0.99(1)	CN^-	95	0.0223	1.17(1)	NCS^-, 100	0.0289	1.31(2)
	0.0293	1.09(1)			0.0313	1.63(2)		0.0315	1.55(1)
	0.0355	1.33(1)			0.0361	1.80(2)		0.0335	1.65(3)
	0.0383	1.43(1)			0.0401	2.00(2)		0.0363	1.74(2)
	0.0487	1.80(2)			0.0555	3.00(7)		0.0400	1.99(5)
	0.0580	2.15(3)			0.0609	3.29(8)		0.0465	2.33(2)
	0.0669	2.54(2)			0.0874	4.43(7)		0.0564	2.80(4)
	0.0828	3.07(2)						0.0687	3.33(8)
				105	0.0133	1.73(2)		0.0846	4.18(5)
100.00(5)	0.0201	1.61(2)			0.0170	2.02(4)			
	0.0263	2.16(2)			0.0214	2.63(3)	105	0.0230	1.52(2)
	0.0297	2.45(3)			0.0233	2.84(5)		0.0267	1.76(2)
	0.0332	2.75(3)			0.0236	2.99(3)		0.0334	2.18(2)
	0.0352	2.86(2)			0.0273	3.43(4)		0.0405	2.66(2)
					0.0312	3.90(6)		0.0573	3.86(4)
110.00(5)	0.0160	2.91(2)			0.0359	4.49(4)			
	0.0197	3.56(3)					110	0.0254	2.22(2)
	0.0220	3.91(5)	11	115	0.0129	3.36(3)		0.0302	2.65(2)
	0.0273	4.88(4)			0.0147	3.89(3)		0.0384	3.38(3)
					0.0161	4.34(5)		0.0409	3.61(3)
					0.0186	4.76(10)			
					0.0209	5.47(11)	120	0.0299	4.56(7)
								0.0353	5.42(5)
								0.0389	5.92(5)
								0.0497	7.66(9)

TABLE 2b

REACTION OF $[PPN]^+[W(CO)_5(NCS)]^-$ WITH $P(OPr\text{-}i)_3$ IN CHLOROBENZENE

T (°C)	$[P(OPr\text{-}i)_3]$ (M)	$10^4\ k_{obsd}$	k
60.2	0.2228	2.36(3)	
	0.2970	2.19(2)	
	0.37135	2.25(2)	2.26(3)
	0.51980	2.22(5)	
	0.7426	2.26(2)	

C, 61.32; H, 4.20; N, 2.28. $C_{59}H_{45}N_2O_4P_3SW$ calcd.: C, 61.36; H, 3.93; N, 2.43%. (L = $P(OPr\text{-}i)_3$): Found: C, 54.77; H, 4.79; N, 2.28. $C_{50}H_{51}N_2O_7P_3SW$ calcd.: C, 54.56; H, 4.67; N, 2.55%. The carbonyl stretching spectra are given in Table 1.

$[PPN]^+[W(CO)_4(NCO)(P(OPr\text{-}i)_3]^-$

This complex was prepared through a method identical to that for the corresponding isothiocyanato species at 50°C for 2 h. Anal.: Found: C, 55.68; H, 4.70; N, 2.76. $C_{50}H_{51}N_2O_8P_3W$ calcd.: C, 55.37; H, 4.74; N, 2.58%.

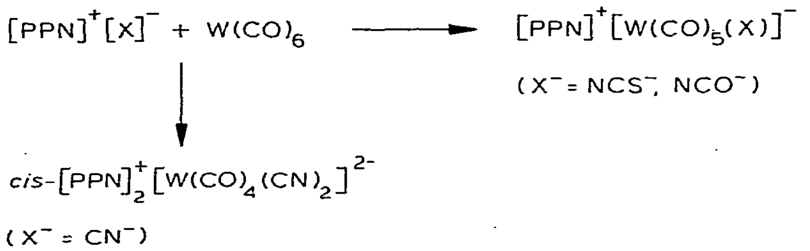
Determination of rates of reaction

Reaction rates ($W(CO)_6$ + $[PPN]^+[X]^-$) were monitored in chlorobenzene solvent employing a Perkin—Elmer model 621 grating spectrophotometer as described in earlier works [10,14]. For reactions of $[PPN]^+[CN]^-$, for which the disubstituted product was obtained, that product precipitated from solution during the kinetics runs. It was removed from the reaction solution prior to monitoring through use of a millipore filter. The products exhibited no absorbance at the wavelength monitored (T_{1u} band of the $W(CO)_6$ substrate), and thus a solvent-ligand blank was employed in place of a t_∞ reading. Plots of $\ln(A_t - A_{bl})$ vs. time (A_t and A_{bl} are the absorbance values at time t, and of the solvent-ligand blank, respectively) were linear to two or three half-lives.

Reactions of $[PPN]^+[W(CO)_5(NCS)]^-$ with triisopropyl phosphite were studied through observation of the disappearance of the carbonyl stretching band (E symmetry) of the substrate at 1918 cm^{-1}; values of A_∞ were determined for this system. Plots of $\ln(A_t - A_\infty)$ vs. time were linear to about four half-lives. Rate data for all systems are presented in Tables 2a and 2b. Limits of error determined through use of a non-linear least-squares computer program (IBM 360 Model 50 computer) are one standard deviation, and are given in parentheses.

Results and discussion

Identification of reaction products through infrared spectroscopy and elemental analysis reveals that reactions of hexacarbonyltungsten(0) with $[PPN]^+[X]^-$ in chlorobenzene solvent proceed cleanly according to eq. 3.



(3)

These reactions have been carried out both photochemically and thermally employing both PPN^+ and other cations in other laboratories [11,12]. The PPN^+ cation was employed in studies of the kinetics and mechanism of the reactions (3) because of the solubility of both the pseudo-halide salts and

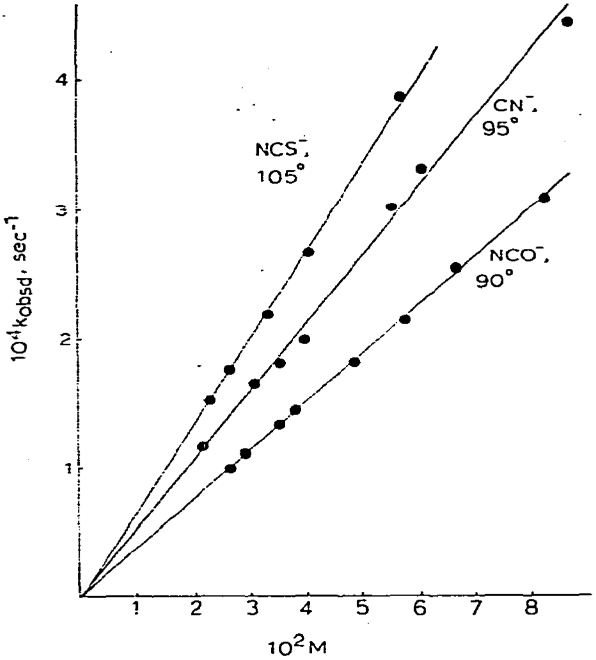


Fig. 1. Plots of k_{obsd} vs. $[X]^-$ for reaction of $W(CO)_6$ with $[PPN]^+[X]^-$ salts (X^- = SCN^-, OCN^-, CN^-) in chlorobenzene at various temperatures.

TABLE 3

FIRST AND SECOND ORDER RATE CONSTANT FOR REACTIONS OF $[PPN]^+[X]^-$ (X^- = NCS^-, NCO^-, CN^-) WITH $W(CO)_6$ AT VARIOUS TEMPERATURES

X^-	T (°C)	$10^4\ k_1$ (s^{-1})	$10^4\ k_2$ ($M^{-1}\ s^{-1}$)
NCS^-	100.00(5)	0.005(13)	49.2(6)
	105.00(5)	—0.06(5)	68.1(1)
	110.00(5)	—0.07(4)	89.7(1)
	120.00(5)	0.12(1)	156.(2)
NCO^-	90.00(5)	0.021(8)	36.7(2)
	100.00(5)	—0.4(8)	83.(3)
	110.00(5)	0.12(8)	174.0(4)
CN^-	95.00(5)	0.008(100)	52.0(2)
	105.00(5)	—0.3(8)	125.0(3)
	115.00(5)	0.1(3)	254.0(15)

ACTIVATION PARAMETERS FOR REACTIONS OF $[PPN^+][X^-]$ WITH $W(CO)_6$ IN CHLOROBENZENE

X^-	$\Delta H^{\neq}$, (kcal/mol)	$\Delta S^{\neq}$, (cal/deg-mol)
NCS^-	16.0(7)	—26.7(17)
NCO^-	20.7(9)	—13.0(25)
CN^-	21.8(18)	—9.9(48)

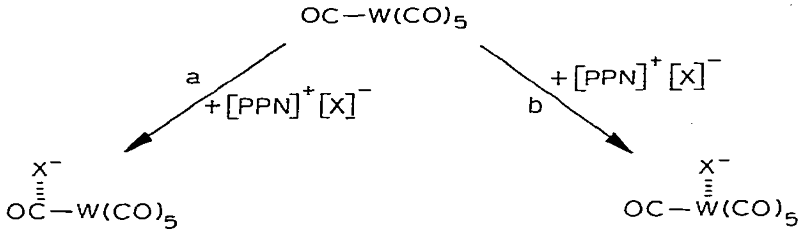
reaction products in chlorobenzene. Rate data for the reactions were obtained over a temperature range of 90—120°C, and are presented in Tables 2a and 2b. Representative plots of k_{obsd} vs. $[PPN^+X^-]$ are presented in Fig. 1.

The results support a rate law (eq. 4) for all systems. Second-order rate

$$-d[W(CO)_6]/dt = k_2[W(CO)_6][PPN^+X^-] \qquad (4)$$

constants, and activation parameters from data at several temperature are presented in Table 3.

The data support a bimolecular reaction path, which conceivably could involve either attack at a carbonyl carbon (eq. 5a), or at the metal atom (eq. 5b) by the pseudo-halide salt.



(5)

Evidence in other systems indicates that where attack at the metal atom is involved, reaction conditions are such that both a ligand-independent and ligand-dependent term in the rate law are observed [1]. This observation has been taken to indicate that the ligand dependent term is ascribable to a dissociative interchange (I_d) path, since the factors which influence the ligand-independent path (D) also affect the ligand-depenedent path; there thus is no credible evidence for operation of a true associative path involving nucleophilic attack at the metal atom in octahedral metal carbonyl systems.

It is worth noting that the present reactions proceed under much milder conditions than those for which the D and I_d paths are observed (Table 4). Thus it is reasonable to assume that initial attack is at a carbonyl carbon, and that in a subsequent step the CO is lost.

Presuming attack at carbon, the nature of that attack, particularly for the ambident NCS^- and NCO^-, is of interest. In the relatively non-polar solvent chlorobenzene, it is probable that the $[PPN]^+[X]^-$ salts exist as contact ion pairs. However, under the kinetics conditions employed, it is also probable that the N-bonded and O- or S-bonded species co-exist in solution. For the $[PPN]^+$-$[OCN]^-$ salt, in particular, the presence of two cyanide stretching bands, at 2138 and 2150 cm^{-1}, indicates the presence of both linkage isomers in solution; The relative intensities of the two bands vary with temperature, with the 2138 cm^{-1} band, presumably due to the $[PPN]^+[NCO]^-$ isomer, predominant at 100—110°C.

Infrared data (Table 1) suggest the identities of the reaction products to be N-bonded for NCO^- and NCS^-, and C-bonded for CN^-. The spectra obtained in this investigation agree closely with those given in previous reports [4,11,12] for which those assignments had been given.

Given the identity of the reaction products it is pertinent to inquire whether the substitution of an anion for a carbonyl proceeds in a concerted manner, as

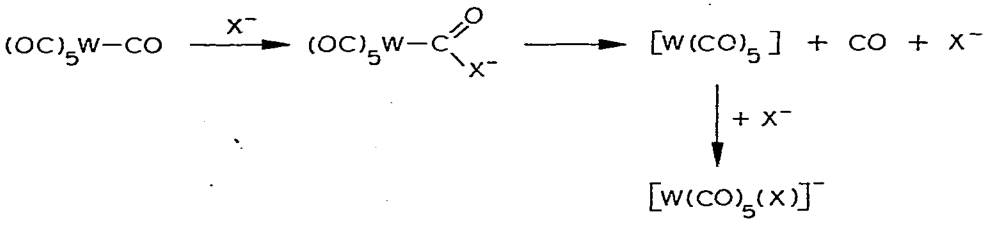
TABLE 4

RATES OF REACTION OF GROUP VI-B METAL HEXACARBONYLS WITH VARIOUS NUCLEOPHILES

Substrate	Nucleophile	T (°C)	$10^4 k_1$ (s^{-1})	$10^4 k_2$ ($M^{-1} s^{-1}$)	Solvent	Reference
$Cr(CO)_6$	MeLi	25.0		72,900	Et_2O	7
	$PhCH_2MgBrCl$	27.0		5300	THF	6
	N_3^-	30.0		97	acetone	4
	Br^-	120.0	0.60	28.9 [a]	C_6H_5Cl	10
	I^-	125.0	1.19	22.0 [a]	C_6H_5Cl	10
	$PBu\text{-}n_3$	130.7	1.38	0.854 [a]	decalin	15
	$PhCH_2NH_2$	130.7	1.24	0.79 [a]	decalin	16
	PPh_3	130.7	1.38	0.431 [a]	decalin	15
$Mo(CO)_6$	MeLi	25.0		86,700	Et_2O	7
	$PhCH_2MgBrCl$	27.0		914	THF	6
	N_3^-	28.5		380	acetone	4
	Br^-	55.0		32.4	C_6H_5Cl	10
	$PBu\text{-}n_3$	112.0	2.13	20.5 [a]	decalin	15
	$C_6H_{11}CH_2NH_2$	112.0	2.38	4.2 [a]	decalin	16
	PPh_3	112.0	2.13	1.77 [a]	decalin	16
	$AsPh_3$	112.0	2.13	1.03 [a]	decalin	16
$W(CO)_6$	MeLi	25.0		149,500	Et_2O	7
	$PhCH_2MgCl$	27.0		1080	THF	6
	N_3^-	30.0		1070	acetone	4
	CN^-	95.0		51.8	C_6H_5Cl	This work
	Cl^-	95.0		41.4	C_6H_5Cl	10
	NCO^-	100.0		83.3	C_6H_5Cl	this work
	NCS^-	100.0		49.2	C_6H_5Cl	this work
	Br^-	100.0		20.0	C_6H_5Cl	10
	I^-	120.0		32.0	C_6H_5Cl	10
	$PBu\text{-}n_3$	165.7	1.15	7.10 [a]	decalin	15
	$P(OEt)_3$	165.7	1.15	1.70 [a]	decalin	15
	PPh_3	165.7	1.15	0.888 [a]	decalin	15
	$C_6H_5CH_2NH_2$	150.0	0.33	0.248 [a]	decalin	16

[a] I_d path probable.

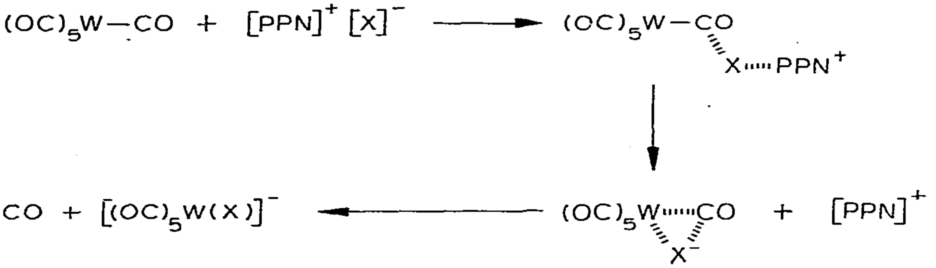
has been proposed for the reaction of the azide ion with the metal hexacarbonyls (via a Curtius-Type rearrangement) [4], or whether, alternatively, the substitution proceeds via a five-coordinate intermediate produced, for example, through loss of COX^- [17]:



(6)

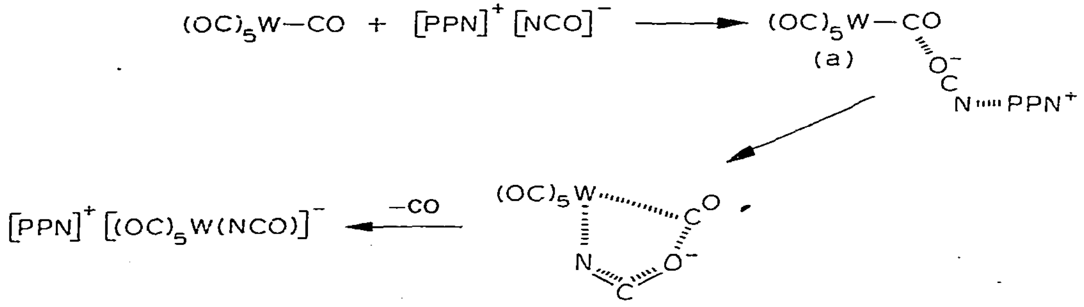
That the latter path was not, in fact, operative, was deduced through experiments in which such a five-coordinate species, if formed, would be trapped. Thus, $W(CO)_6$, $[PPN]^+[NCS]^-$ and a twenty-fold excess of triphenylphosphine were allowed to react under kinetics conditions. The sole product observed was [*cis*-$W(CO)_4(PPh_3)(NCS)]^-$. Under these conditions a separate study of the reaction of $W(CO)_5(PPh_3)$ with NCS^- showed the metal carbonyl to be inert; thus $[cis\text{-}W(CO)_4(PPh_3)(NCS)]^-$ could not have been formed via the mono-triphenylphosphine species; the latter complex should have been produced from $[W(CO)_5]$, if present *.

Thus a concerted rearrangement with extrusion of CO is envisioned to be the probable mechanism:



(7)

Given the *N*-bonded products obtained through reaction of the OCN^- and SCN^- salts, it is reasonable to assume that initial interaction at carbon would involve O or S. Given further that the salt exists in chlorobenzene as contact ion pairs, the $[PPN]^+[NCO]^-$ and $[PPN]^+[NCS]^-$ forms of the salts would appear to be the reactive species. Thus, for $[PPN]^+[NCO]^-$, an overall mechanism such as (8) is proposed:



(8)

An analogous mechanism is envisioned for the $[PPN]^+[NCS]^-$ salt.

A mechanism in which CO from $W(CO)_6$ is incorporated into NCO^-, e.g.,

(9)

has been found not to be operative in the reaction of $(\eta\text{-Cp})Fe(CO)_3^+$ with NCO^- [19].

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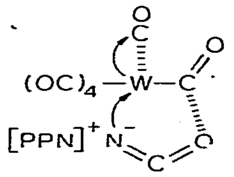
* Evidence has been presented that the sixteen electron, five-coordinate $M(CO)_5$ species is relatively non-discriminating in it's reactivity with a variety of nucleophiles, e.g. ref. [18].

An alternative path involving (8a) could involve loss of a CO *cis* to $C(O)OCN^-$ under the labilizing influence of the latter [20].



(10)

It is of interest to note that $[PPN]^+[W(CO)_5(NCS)]^-$ does not react further with $[PPN]^+[NCS]^-$ to afford a disubstituted complex, but does react with triphenylphosphine to afford $[PPN]^+[\textit{cis}\text{-}W(CO)_4(PPh_3)(NCS)]^-$. This observation prompted a brief kinetics investigation of the latter reaction; rate data are presented in Tabel 2b. The first-order rate law observation at 60.2° supports unimolecular W—CO bond fission in the rate-determining step. Thus NCS^-, as are halides [21], is a labilizing ligand relative to CO. The observed formation of $[W(CO)_4(PPh_3)(NCS)]^-$, but not $[W(CO)_4(NCS)_2]^{2-}$ suggests that the latter complex is not formed to a significant extent because the equilibrium,

$$[PPN]^+[W(CO)_5(NCS)]^- + [PPN]^+[NCS]^- \rightleftharpoons [PPN]_2^+[W(CO)_4(NCS)_2]^{2-} + CO \qquad (11)$$

lies far to the left. In contrast, however, the observed product for the reaction of $[PPN]^+[CN]^-$ with $W(CO)_6$ is the *cis*-disubstituted species.

Activation parameters for the reactions are presented in Table 3. Entropies of activation, while varying significantly among the pseudo halides, are negative, as would be expected for an associative process, in which there is more bond-making than bond-breaking leading to formation of the transition state. Given the likelihood that a pre-equilibrium between the $[PPN]^+[X]^-$ linkage isomers may exist, it would be unwise to interpret further the activation parameters, or to comment on the order of rates as a function of the identity of the pseudo halide ion; given similar $\Delta G^{\neq}$ values at the reaction temperature, but the significantly difering $\Delta H^{\neq}$ values, this order will be highly dependent on temperature.

The results of this study, together with other rate data compiled in Table 4 indicate that reactions of the Group VI-B metal carbonyls with anionic nucleophiles, whether they form acylate products, rearrangement products or proceed via simple ligand-exchange, involve attack at carbon. The only possible exceptions would appear to be those for which rates closely approximate those observed for the dissociative process, possibly those of $Cr(CO)_6$ with halides [10].

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