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SOME CARBONYL HALIDE COMPLEXES OF MANGANESE(I) AND RHENIUM(I) CONTAINING TRITHIOPHOSPHITE LIGANDS

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Summary

The reaction of trithiophosphites, $P(SR)_3$ ($R = CH_3$, C_2H_5 and C_6H_5), with $M(CO)_5X$ (M = Mn, Re, X = Cl, Br) yields complexes of the general formula $M(CO)_4P(SR)_3X$ and $M(CO)_3[P(SR)_3]_2X$. The geometry of the disubstituted complexes is established from infrared and PMR spectroscopy to be *fac*-Re$(CO)_3[P(SR)_3]_2X$ and *mer*-[*trans*-$\{P(SR)_3\}_2Mn(CO)_3X$] while all $M(CO)_4P(SR)_3X$ compounds are found to be *cis*. From a comparison of the ν(CO) absorptions of the trithiophosphite complexes with analogous compounds containing phosphites, phosphines and aminophosphines, the order $P(SR)_3 > P(OR)_3 > P(NR_2)_3 > PR_3$ is obtained.

Introduction

Although transition metal complexes of phosphines [1,2], phosphites [3] and aminophosphines [3] number well into the tens of thousands, less than two dozen complexes which contain trithiophosphites, $P(SR)_3$, have been reported [3,4]. Of these few compounds, only about one quarter have been adequately characterized [5,6]. This is somewhat surprising in view of the facile methods of synthesis for an extensive number of trithiophosphites and the reported applicability of these ligands as stabilizers for lubricating oils and polyolefins [4]. In the light of this and the lack of data from which an evaluation of the influence of the SR moiety on the bonding properties of a tricovalent phosphorus may be made, we have prepared and characterized several complexes of Mn^I and Re^I carbonyl halides which contain $P(SCH_3)_3$, $P(SC_2H_5)_3$ and $P(SC_6H_6)_3$.

Results and discussion

A major difficulty encountered in the preparation of many metal complexes of trithiophosphites is their relatively rapid decomposition, particularly in solution, to yield stable metal sulfides. The diamagnetic complexes reported herein are stable as solids for up to two weeks. However, in $CHCl_3$ or CCl_4 solution they decompose completely within a few hours. Table 1 contains the infrared and PMR data for 15 new complexes, four of which have been characterized only from their infrared spectra. Attempts to obtain these materials in the pure state employing column chromatography were thwarted by decomposition.

The infrared spectra of the $M(CO)_4LX$ complexes exhibit the four absorptions of appropriate intensity in the $\nu(CO)$ region expected for a *cis*-configuration (C_s symmetry) which is most common when L is a phosphine, phosphite or an aminophosphine [7-10]. For the $M(CO)_3L_2X$ complexes there are three possible geometries: *fac* (C_s symmetry), *mer* with *trans* L's (C_{2v} symmetry), *mer* with *cis* L's (C_s symmetry). The rhenium complexes exhibit the three strong $\nu(CO)$ absorptions reported for numerous complexes possessing the *fac*-configuration [11-13]. The three CO absorptions of weak, strong and medium intensity observed for the manganese compounds are characteristic of a *mer* complex having a *trans* ligand arrangement [7,14,15]. The *mer* compound $(C_6H_5)Mn(CO)_3$-(diphos), which of necessity contains *cis*-phosphorus atoms, is reported to show only two $\nu(CO)$ absorptions [16].

The *trans*-directing ability of the trithiophosphite ligands favors the formation of *fac*-$Mn(CO)_3L_2X$. However, compounds of this type when L = phosphite or phosphine have been shown to isomerize rapidly to yield the sterically less hindered *trans*-$Mn(CO)_3L_2X$ [7,14]. Thus with $P(SR)_3$, which is more bulky than corresponding phosphites, and at the temperature used in preparation, the isolation of *trans*-$Mn(CO)_3[P(SR)_3]_2X$ is expected. The preference of $Re(CO)_3L_2X$ complexes for the *fac* form may, in part, be attributed to the decrease in steric interaction between ligands bound to the large Re atom [12].

From Table 1 it can be seen that for similar complexes wherein only the R group of the trithiophosphite is varied, the positions of the $\nu(CO)$ absorptions follow the order $P(SC_6H_5)_3 > P(SCH_3)_3 > P(SC_2H_5)_3$. A similar trend was observed in numerous complexes containing phosphites and phosphines and may be correlated with the electronic effect of the R group [5]. A comparison of the $\nu(CO)$ positions of the trithiophosphite complexes with analogous ones containing phosphines [7,9,12,14,15,17,19], aminophosphine [10] and phosphites [7,12,14,18] yields the following frequency order: $P(SR)_3 > P(OR)_3 > P(NR_2)_3 > PR_3$. The arguments concerning the implication of this order with respect to the σ and π bonding abilities of ligands have been adequately discussed elsewhere [5,20]. Previously it has been shown that the π and σ bonding capacity of $P(SCH_2)_3CC_5H_{11}$ is greater than $P(OCH_2)_3CC_5H_{11}$, using the treatment of Graham [5]. The $\nu(CO)$ absorptions of $Mo(CO)_5P(SCH_3)_3$ [6] occur at higher energy than for $Mo(CO)_4P(OCH_3)_3$. Our data and those of Keiter and Verkade [5] support the idea that in bonding ability towards metals in low oxidation states, $P(SR)_3 > P(OR)_3$ where R is the same moiety.

Further evidence in support of the assigned geometries is obtained from the PMR spectra. The occurrence of a large amount of virtual spin—spin coupling when two phosphorus ligands are *trans* across a metal center is well established [21-23]. The observance of a sharp 1/2/1 triplet for the $Mn(CO)_3[P(SCH_3)_3]_2X$ complexes supports the proposed *trans* ligand arrangement. For the *fac*-$Re(CO)_3[P(SCH_3)_3]_2X$ compounds a multiplet of several lines with the outer two being of greatest intensity ($1/{\approx}0.8/1$) is detected. This pattern, which indi-

TABLE 1

INFRARED AND PMR DATA[a]

Compound	$\nu(CO)$ (cm^{-1})				Chemical shifts (δ)			Coupling constants (Hz)	
	A_1'	A_2'	A''	A_3'	α	β	γ	J(PSCH)	J(HH)
$Mn(CO)_4P(SC_2H_5)_3Cl$	2102w	2040(sh)	2022s	1964(br)	2.39			12.0	7.5
$Re(CO)_4P(SC_2H_5)_3Cl$	2111w	2047(sh)	2021s	1960(br)					
$Re(CO)_4P(SC_6H_5)_3Cl$	2114w		2033s	1951(br)	7.62	7.33	7.38		
$Re(CO)_4P(SC_6H_5)_3Br$	2112w	2047(sh)	2033s	1958(br)	7.66	7.33	7.38		
	A_1'	A_2'	A''						
$Re(CO)_3[P(SCH_3)_3]_2Cl$	2048s	1981s	1924s		2.43[c]			12.0	
$Re(CO)_3[P(SCH_3)_3]_2Br$	2048s	1980s	1925s		2.43[c]			12.5	
$Re(CO)_3[P(SC_2H_5)_3]_2Cl$	2044s	1972s	1918s		3.08[c]	1.38		*d*	7.5
$Re(CO)_3[P(SC_2H_5)_3]_2Br$	2045s	1974s	1923s		3.07[c]	1.38		*d*	7.5
$Re(CO)_3[P(SC_{12}H_{25})_3]_2Cl$	2043s	1956s	1917s						
	A_1''	B_1	A_1'						
$Mn(CO)_3[P(SCH_3)_3]_2Cl$	2060w	1983s	1923m		2.45[b]			12.0	
$Mn(CO)_3[P(SCH_3)_3]_2Br$	2057w	1980s	1936m		2.45[b]			12.0	
$Mn(CO)_3[P(SC_2H_5)_3]_2Cl$	2059w	1981s	1930m		3.05[c]	1.38		*d*	7.5
$Mn(CO)_3[P(SC_2H_5)_3]_2Br$	2060w	1980s	1932m		3.04[c]	1.38		*d*	7.5
$Mn(CO)_3[P(SC_6H_5)_3]_2Cl$	2078w	2002s	1956m						
$P(SCH_3)_3$					2.26			10.2	
$P(SC_2H_5)_3$					2.80	1.35		8.0	7.5
$P(SC_6H_5)_3$					7.44	7.24	7.28		

[a] Infrared data from $CHCl_3$ solutions, PMR data from $CDCl_3$ solutions containing TMS [b] 1/2/1 triplet. [c] Broad multiplet. [d] Not determined due to complication by virtual coupling.

TABLE 2

PREPARATIVE AND ANALYTICAL DATA

Compound	Preparative data				Analytical data found (calcd.) (%)		Color
	Mole ratio $P(SR)_3/M(CO)_5X$	Solvent	Reaction time (h)	Precipitating solvent	C	H	
$Mn(CO)_4P(SC_2H_5)_3Cl$	1/1	CCl_4	7	$CHCl_3$—hexane	28.92 (28.79)	3.57 (3.63)	Orange
$Re(CO)_4P(SC_2H_5)_3Cl$	1/1	CCl_4	1	pet. ether[a]	[b]		White
$Re(CO)_4P(SC_6H_5)_3Cl$	2/1	CCl_4	2	pet. ether—hexane	38.40 (38.17)	2.30 (2.18)	Cream
$Re(CO)_4P(SC_6H_5)_3Br$	2/1	CCl_4	2	pet. ether—hexane	35.69 (35.86)	2.04 (2.05)	Cream
$Re(CO)_3[P(SCH_3)_3]_2Cl$	5/1	CCl_4	12	ether	16.88 (16.74)	2.80 (2.79)	White
$Re(CO)_3[P(SCH_3)_3]_2Br$	5/1	CCl_4	2	ether	15.07 (15.67)	2.65 (2.61)	White
$Re(CO)_3[P(SC_2H_5)_3]_2Cl$	10/1	CCl_4	2	pet. ether	24.63 (24.53)	4.13 (4.12)	White
$Re(CO)_3[P(SC_2H_5)_3]_2Br$	10/1	CCl_4	2	pet. ether	23.20 (23.13)	3.82 (3.89)	White
$Re(CO)_3[P(SC_{12}H_{25})_3]_2Cl$	3/1	CCl_4	24	ether	[b]		White
$Mn(CO)_3[P(SCH_3)_3]_2Cl$	5/1	CCl_4	2	pentane	20.72 (20.83)	3.46 (3.49)	Orange
$Mn(CO)_3[P(SCH_3)_3]_2Br$	5/1	CCl_4	1	pentane	19.32 (19.68)	3.16 (3.19)	Orange
$Mn(CO)_3[P(SC_2H_5)_3]_2Cl$	5/1	C_6H_6	2	$CHCl_3$—hexane	29.65 (29.87)	5.00 (5.02)	Orange
$Mn(CO)_3[P(SC_2H_5)_3]_2Br$	5/1	CCl_4	24	pet. ether	28.01 (27.82)	4.64 (4.67)	Orange
$Mn(CO)_3[P(SC_6H_5)_3]_2Cl$	2/1	CCl_4	2	pet. ether—hexane	[b]		Cream

[a] B.p 20-40°C. [b] Not isolated in a pure form.

cates a small degree of P—P coupling, is typical of *cis*-phosphorus ligands and thus substantiates the geometry assigned on the basis of ν(CO) data. For the *trans*-$Mn(CO)_3[P(SC_2H_5)_3]_2X$ complexes the CH_2 or α-proton resonance which occurs as a quintuplet for the free ligand has coalesced to yield a broad single absorption. The PMR spectra of the *fac*-$Re(CO)_3[P(SC_2H_5)_3]_2X$ compounds exhibit a quintuplet with measurable absorbance between the peaks, similar to that reported for $Ni[P(OC_2H_5)_3]_4$ [21]. The deshielding of the α-protons of $P(SC_2H_5)_3$ and $P(CH_3)_3$ on complex formation and the increase in J(PSCH) is typical of other phosphorus donor ligands [3].

Experimental

Infrared spectra were recorded for chloroform solutions contained in a 0.2 mm NaCl cell using a Perkin—Elmer Model 621 spectrophotometer and were calibrated against polystyrene film. The PMR spectra were recorded for saturated deuteriochloroform solution which contained tetramethylsilane as an internal reference using a Varian HA-100 spectrometer. Mass spectra were recorded using a Hitachi—Perkin—Elmer RMU6E spectrometer operating at an ionization voltage of 80 eV. Carbon and hydrogen compositions were ascertained by combustion employing a F and M C-H-N Analyzer Model 185.

Published methods were followed for the preparation of the $M(CO)_5X$ compounds where M = Mn, Re; X = Cl, Br [24,25]. Trimethyl and triethyl trithiophosphite were prepared by heating to 50°C an acetone solution which contained the appropriate dialkyl disulfide (0.8 mol), yellow phosphorus (0.5 mol) and 1 ml of 15 *N* KOH [26]. Triphenyl trithiophosphite was obtained from the reaction of phosphorus trichloride (0.2 mol) with an excess of thiophenol (0.8 mol) at 65°C [27]. The purity of the ligands was verified by their boiling or melting points, PMR spectra, mass spectra and carbon, hydrogen analysis (Table 2). Since the ligands are noxious and their toxicity levels have not been established, appropriate caution should be observed when handling these materials or their complexes.

For the preparation of the complexes, a procedure similar to the one given below was used. Any variation in detail of the preparations is given, along with the analytical data for the compounds, in Table 2.

fac-Bromotricarbonylbis(trimethyltrithiophosphite)rhenium(I)

To 0.41 g (1.0 mmol) of bromopentacarbonylrhenium(I) in 25 ml of carbon tetrachloride was added 1 ml (5.0 mmol) of trimethyl trithiophosphite. After the solution was refluxed for 2 h under a helium atmosphere, it was cooled to room temperature and reduced to one-fifth of its original volume by vacuum evaporation. The addition of 10 ml of diethyl ether to this solution caused the formation of a white precipitate which was collected on a filter, washed with 5 ml of cold diethyl ether and dried in vacuo for 24 h.

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