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OCTAHEDRAL METAL CARBONYLS: REACTIONS AND BONDING—VIII [1]

METAL CARBONYL DERIVATIVES OF 1-DIPHENYLPHOSPHINO-2-(METHYLTHIO)ETHANE

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Abstract—The synthesis of the "mixed" bidentate phosphorus-sulfur ligand, 1-diphenylphosphino-2-(methylthio)ethane (SPE), and its reactions with $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn(CO)_5Br$ and (*o*-phenanthroline)$Mo(CO)_4$ are reported. SPE functions as a monodentate ligand bonded through phosphorus, or as a chelating or bridging ligand. The mode of coordination of SPE in these metal carbonyl complexes is inferred primarily through comparison of their spectra in the carbonyl stretching region of the infrared to those of "model" complexes.

INTRODUCTION

DERIVATIVES of metal carbonyls containing bidentate ligands have been extensively investigated[2]; particular attention has been paid to the phosphorus-containing 1,2-bis(diphenylphosphino)ethane (diphos)[3] and the sulfur-containing 2,5-dithiahexane (DTH [4] for which recent kinetic[1] and preparative [1,5] investigations have been reported. Herein is reported the synthesis of the "mixed" phosphorus-sulfur analogue of these two bidentate ligands, 1-diphenylphosphino-2-(methylthio)ethane (SPE), $(C_6H_5)_2PC_2H_4SCH_3$, and an investigation of some of its reactions with octahedral metal carbonyls and derivatives. Two other "mixed" phosphorus-sulfur ligands, 1-diethylphosphino-2-(ethylthio)-ethane[6] and diphenyl(*o*-methylthiophenyl)phosphine[7] have been reported. In each case, however, complexes with divalent Ni or Pd rather than metal carbonyl derivatives were investigated.

EXPERIMENTAL

Infrared spectra (Table 1) were obtained using Perkin Elmer Model 421 or Model 237B spectrophotometers and were calibrated against the known bands of polystyrene. Microanalyses and the molecular weight determination were made by Midwest Microlab., Inc., Indianapolis, Indiana.

1-Diphenylphosphino-2-(methylthio)ethane. To 300 ml of dry tetrahydrofuran in a 1-liter three necked flask equipped with a nitrogen inlet, pressure-equalized dropping funnel, mechanical stirrer and condenser was added 2·78 g (0·4 mole) shaved Li metal and 52·4 g (0·2 mole)triphenyl-phosphine.

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1. Part VII: G. C. Faber and G. R. Dobson, *Inorg. Chem.* 7, 584 (1968).
2. For a recent review, See T. A. Manuel, *Adv. organomet. Chem.* **3**, 181 (1965).
3. J. Chatt and H. R. Watson, *J. chem. Soc.* 4980 (1961).
4. H. C. E. Mannerskantz and G. Wilkinson, *J. chem. Soc.* 4454 (1962).
5. L. W. Houk and G. R. Dobson, *Inorg. chim. Acta* **1**, 287 (1967); S. O. Grim, D. A. Wheatland and R. R. McAllister, *Inorg. Chem.* **7**, 161 (1968).
6. J. F. Sieckhaus and T. Layloff, *Inorg. Chem.* **6**, 2185 (1967).
7. M. O. Workman, G. Dyer and D. W. Meek, *Inorg. Chem.* **6**, 1543 (1967).

The mixture was stirred until the Li had dissolved (approx. 2 hr), the temperature being maintained between 45° and 55°C; 18·5 g (0·2 mole) of *tert*-butyl chloride was then added dropwise. The solution was then stirred at room temperature for 0·5 hr after the addition was complete, and a solution of 22·1 g freshly distilled 2-chloroethyl methyl sulfide in tetrahydrofuran was then added dropwise. The red-orange color of the reaction mixture was discharged upon this addition, and the reaction mixture was stirred at room temperature for an additional hour. Precipitated LiCl was removed by filtration, and the THF removed employing an aspirator vacuum. The oily residue was then vacuum distilled until a fraction consisting mainly of diphenylphosphine (b.p. 112–14°/1 mm) had distilled. The residue, which solidified with difficulty, was then recrystallized from methanol to give 19·9 g (38%) of white crystalline product (m.p. 49–51°). *Anal. Calc.* for $C_{15}H_{17}PS$: C, 69·20; H, 6·60; P, 11·90; S, 12·31. Found: C, 68·88; H, 6·49; P, 11·45; S, 12·08.

SPE was also prepared via a Grignard synthesis similar to that employed by Mann and Millar in the preparation of a mixed nitrogen-phosphorus ligand [8]:

$$C_2H_5Br + Mg \xrightarrow{\text{dry ether}} C_2H_5MgBr$$

$$(C_6H_5)_2PH + C_2H_5MgBr \xrightarrow[\text{benzene}]{\text{dry ether}} (C_6H_5)_2PMgBr + C_2H_6$$

$$(C_6H_5)_2PMgBr + ClC_2H_4SCH_3 \xrightarrow{\text{benzene}} SPE + MgBrCl.$$

(SPE)CR(CO)$_4$. 0·5 g $Cr(CO)_6$ and 0·59 g SPE (equimolar amounts) were refluxed under nitrogen in 30 ml of 2,2,5-trimethylpentane for 24 hr. During this time a yellow crystalline product precipitated from the solution. The solution was cooled, the crude $(SPE)Cr(CO)_4$ was collected by suction filtration, and was recrystallized from a petroleum ether-1,2-dichloroethane mixture. *Anal. Calc.* for $C_{19}H_{17}O_4PSCr$: C, 53·77; H, 4·08. Found: C, 54·00; H, 4·09.

(SPE)Mo(CO)$_4$. 0·5 g $Mo(CO)_6$ and 0·49 g SPE (equimolar amounts) were refluxed under nitrogen in methylcyclohexane for 10 hr. The workup of the yellow crystalline product was similar to that of $(SPE)Cr(CO)_4$. *Anal. Calc.* for $C_{19}H_{17}O_4PSMo$: C, 48·72; H, 3·66. Found: C, 48·84; H, 3·89. Molecular weight: Calc. 468. Found 480.

(SPE)W(CO)$_4$. 0·5 g $W(CO)_6$ and 0·37 g SPE(equimolar amounts) were refluxed under nitrogen in xylene for 36 hr. The solvent was removed *in vacuo* and the residue was recrystallized from hot *n*-hexane to give the yellow product. *Anal. Calc.* for $C_{19}H_{17}O_4PSW$: C, 41·02; H, 3·09. Found: C, 40·83; H, 2·77.

(SPE)$_2$Mo(CO)$_2$. 1·5 g $(SPE)Mo(CO)_4$ and 0·833 g SPE (equimolar amounts) were refluxed under nitrogen in mesitylene for seven hours. Upon cooling of the reaction mixture, a precipitate formed, which was collected by suction filtration and recrystallized from toluene to give the yellow product. *Anal. Calc.* for $C_{32}H_{34}P_2S_2O_2Mo$: C, 57·13; H, 5·11. Found: c, 57·69; H, 5·24.

(SPE)Mn(CO)$_3$Br. 0·2 g $Mn(CO)_5Br$ and 0·235 g SPE (equimolar amounts) were heated dry under nitrogen at 120°C for 25 min. The resulting mixture was cooled, and 15 ml of chloroform was added. The solution was filtered by suction, and the yellow orange product obtained through addition of 10 ml of *n*-hexane to the filtrate. It was then recrystallized from methanol. *Anal. Calc.* for $C_{18}H_{17}BrO_3PSMn$: C, 45·11; H, 3·58. Found: C, 46·05; H, 3·76.

(o-phenanthroline)(SPE)Mo(CO)$_3$. 0·55 g $(phen)Mo(CO)_4$ and 0·372 g SPE (equimolar amounts) were refluxed under nitrogen in xylene for 3 hr. The maroon product was obtained by suction filtration after cooling the reaction mixture, and was washed with petroleum ether, *Anal. Calc.* for $C_{30}H_{25}N_2O_3PSMo$: C, 58·04; H, 4·07. Found: C, 57·77: H, 4·28.

Other reactions. 0·2472 g of $(phen)(SPE)Mo(CO)_3$ and 0·1729 g of $(phen)Mo(CO)_4$ (equimolar amounts) were refluxed under nitrogen in xylene for 24 hr. Upon cooling of the reaction mixture a purple-brown precipitate formed, which was collected by suction filtration, washed with petroleum ether, and was dried *in vacuo*. A satisfactory analysis for the product, $[(phen)Mo(CO)_3]_2(SPE)$ was not obtained, but its presence was inferred through the disappearance of carbonyl stretching bands attributable to $(phen)Mo(CO)_4$. Attempts to prepare the analogous bridged derivative of 2,5-dithiahexane were unsuccessful. $[(Phen)Mo(CO)_3]_2$(diphos) was prepared by refluxing diphos and (phen) $Mo(CO)_4$ in a 1 : 2 mole ratio in xylene under nitrogen for 1 hr. Upon cooling of the reaction mixture, red crystals of the product were obtained. The crystals were collected by suction filtration, washed

8. F. G. Mann and I. T. Millar, *J. chem. Soc.* 3039 (1952).

with petroleum ether, and dried *in vacuo*. *Anal.* Calc. for $C_{56}H_{42}N_4O_6P_2Mo_2$: C, 0·24; H, 3·58. Found: C, 60·21; H, 3·82. $(Diphos)_2Mo(CO)_2$, analogous to $(SPE)_2Mo(CO)_2$ is a known compound [3]. Attempts were made to synthesize $(DTH)_2Mo(CO)_2$, but no evidence was ever obtained for its existance; carbonyl stretching bands corresponding to those expected for a DTH derivative in which three carbonyls had been replaced were observed in solution, but no product was isolated either through direct reaction, or through attempts at its preparation through replacement of 1,3,5-cycloheptatriene from $(cycloheptatriene)Mo(CO)_3$[9] by DTH.

Reaction of triethyl phosphite with $(SPE)Mo(CO)_4$ at 60° in 1,2-dichloroethane resulted in the formation of *cis*-$[P(OC_2H_5)_3]_2Mo(CO)_4$, as shown by its i.r. spectrum in the carbonyl stretching region[10].

RESULTS AND DISCUSSION

Derivatives of diphos and DTH may be utilized in comparisons of carbonyl stretching spectra so that the mode of attachment of SPE to the metal in the synthesized derivatives may be inferred. The results suggest that SPE can function as a chelating, bridging or monodentate ligand. For derivatives of the type $(SPE)M(CO)_4$ ($M = Cr, Mo, W$) and for $(SPE)Mn(CO)_3Br$, carbonyl stretching frequencies are roughly the mean of those reported for the corresponding diphos and DTH complexes (Table 1). $(SPE)Mo(CO)_4$ reacts under forcing conditions with an additional molecule of SPE to form $(SPE)_2Mo(CO)_2$. Although $(diphos)_2$ $Mo(CO)_2$ is a known compound[3], all attempts to prepare the analogous $(DTH)_2$ $Mo(CO)_2$ failed. These observations suggest that the primary bonding function

Table 1. Carbonyl stretching data for derivatives

Compound	Carbonyl stretching frequencies* (cm^{-1})				
$(SPE)Cr(CO)_4$†	2017 (m)	1915(s),	1895(s),	1970(ms)	
$(SPE)Mo(CO)_4$†	2027(m),	1923(s),	1905(s),	1874(ms)	
$(SPE)W(CO)_4$†	2023(m),	1914(s),	1897(s),	1871(ms)	
$(diphos)Mo(CO)_4$[3]	2020	1919	1907	1881	
$(DTH)Mo(CO)_4$[4]	2030	1919	1905	1868	
$(SPE)_2Mo(CO)_2$‡	1830(s),	1750(s)			
$(diphos)_2Mo(CO)_2$[3]	1852	1786			
$(SPE)Mn(CO)_3Br$‡	2035(vs),	1960(s),	1920(s)		
$(diphos)Mn(CO)_3Br$§	2022	1959	1918		
$(DTH)Mn(CO)_3Br$[3]	2052	1970	1922		
$(SPE)(phen)Mo(CO)_3$‡	1920(vs),	1825(s),	1785(s)		
$(diphos)[(phen)Mo(CO)_3]_2$†	1916(vs),	1820(s),	1787(s)		
$(SPE)[(phen)Mo(CO)_3]_2$‡‖	1900(vs),	1810(s),	1795(s),	1785(s)	1760(s)

*Spectra taken in chloroform solution unless otherwise noted; relative band intensities: s = strong; m = medium; v = very.

†Spectrum recorded on Perkin Elmer Model 421 spectrophotometer.

‡Spectrum recorded on Perkin Elmer Model 237B spectrophotometer.

§A. G. Osborne and M. H. B. Stiddard, *J. chem. Soc.* 4715 (1962).

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10. R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. Fr.* 1301 (1962).

in DTH is σ-bonding, and that π-bonding, which might stabilize the formation of a tetrasubstituted derivative, is of relatively minor importance.

It has been shown that carbonyl stretching frequencies in (L)(phen)M$(CO)_3$ complexes are sensitive to the electronic nature of the monodentate ligand (L)[11]. The fact that carbonyl stretching frequencies for diphos and DTH also differ (Table) suggests that carbonyl stretching frequencies may be employed to infer the mode of attachment of SPE in (SPE)(phen)Mo$(CO)_3$. So that a valid comparison could be made, the bridged binuclear [(phen)Mo$(CO)_3]_2$(diphos) was synthesized; attempts to prepare the analogous complex of DTH were unsuccessful. The carbonyl stretching frequencies (Table 1) for (SPE)(phen) Mo$(CO)_3$ and [(phen)Mo$(CO)_3]_2$(diphos) are virtually identical; both SPE and diphos contain the -$C_2H_4P(C_6H_5)_2$ moiety, and thus it is strongly suggested that the ligand coordinates through P in (SPE)(phen)Mo$(CO)_3$.

Reaction of (SPE)(phen)Mo$(CO)_3$ with an equimolar quantity of (phen) Mo$(CO)_4$ results in the disappearance of carbonyl stretching bands attributable to the latter, and thus the formation of the asymmetric bridged, dimeric complex, [(phen)Mo$(CO)_3]_2$(SPE) may be inferred. Although mull spectra may often be unreliable due to crystal effects, the infrared spectrum obtained for the reaction product is consistent with this formulation. Five terminal carbonyl absorptions are noted (Table 1); the four bands of lower energy are the number expected ($2A' + 2A''$) on the basis of the local symmetry of the carbonyls in each half of the molecule (C_s). The failure to observe the expected two higher energy bands ($2A'$) may be attributable to accidental degeneracy. The failure to obtain a satisfactory analysis for the compound is not surprising in light of the known weak bonding properties of sulfur in Group VIB metal carbonyl derivatives[12], and the failure to prepare the corresponding bridged complex of DTH.

Reaction of (SPE)Mo$(CO)_4$ with triethyl phosphite shows that the SPE ligand is replaced to give the *cis*-(phosphite)Mo$(CO)_4$ complex. For (DTH)Mo$(CO)_4$ replacement of DTH by phosphites is also noted[5], while for (diphos)Mo$(CO)_4$ a carbonyl is instead lost under drastic conditions to give a "mixed" trisubstituted derivative[5]. Thus whether or not the bidentate can be replaced in these systems would appear to be influenced by the relative ease of breaking of the first metal-bidentate ligand bond.

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