Journal of Organometallic Chemistry, 56 (1973) 261–267

COMPLEXES OF DITERTIARY STIBINES: GROUP VIB METAL CARBONYL DERIVATIVES OF BIS(DIPHENYLSTIBINO)METHANE

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(Received November 20th, 1972)

SUMMARY

The potentially bidentate antimony ligand $(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$ (Dpsm) has been allowed to react with the Group VIB metal carbonyls and some of their derivatives under a variety of synthetic conditions. Molecular structures and bonding behavior of the substituted complexes $M(CO)_5$(Dpsm), $M(CO)_4$(Dpsm), $[M(CO)_4$(Dpsm)$]_2$, and $Mo(CO)_3$(Dpsm)$_2$ are based upon NMR and infrared spectral studies and molecular weight measurements.

INTRODUCTION

In contrast to the numerous transition metal carbonyl derivatives of amine, phosphine, and arsine ligands very few organostibine complexes have been reported[1–5]. Moreover, except for one article that describes some monosubstituted iron, chromium, molybdenum, and tungsten compounds*, no metal carbonyl complexes containing potentially bidentate antimony chelating agents are known. Since the transition metal carbonyl chemistry of bis(diphenylphosphino)methane and bis(diphenylarsino)methane has received considerable attention[7–16], and since the synthesis of molecules of the type $R_2SbCH_2SbR_2$ (R=Cl[17], CH_3[17,18], C_6H_5[19], p-$CH_3C_6H_4$[6]) has been described recently, an opportunity to extend these studies in the Group VA ligand series is afforded.

This paper describes the interaction of the Group VIB metal carbonyls with $(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$ (Dpsm) under a variety of preparative conditions.

EXPERIMENTAL

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany and M–H–W Laboratory, Garden City, Michigan. Molecular weights (M–H–W) were determined by osmometry at 37° in $CHCl_3$ or benzene. Infrared spectra were recorded in methylcyclohexane and methylene chloride solutions on a Model 621 Perkin–Elmer spectrometer. Proton NMR spectra were taken in chloroform-*d* on a Varian Associates Model T-60 instrument with tetramethylsilane

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* This article appeared as our work was nearing completion[6].

as an internal standard. Melting points were taken in open capillaries and are uncorrected. Chemicals were obtained from the following sources: triphenylstibine (M and T Chemical Co.); metal hexacarbonyls (Pressure Chemical Co.); 2,5-norbornadiene (Nbd), 1,3-tetramethylpropylenediamine (Tmpa), and cycloheptatriene (Cht) (Aldrich Chemical Co.). Florisil (60–100 mesh) used for column chromatography was obtained from Fisher Scientific Co. The starting materials $Cr(CO)_4$-(Nbd)[20], $Mo(CO)_4(Nbd)$[21], $Mo(CO)_3(Cht)$[22], $W(CO)_4(Tmpa)$[23] and Dpsm[19] were prepared from literature methods. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels.

$M(CO)_5(Dpsm)$. Synthesis of pentacarbonyl complexes discussed in this paper involved refluxing equal molar amounts of the metal hexacarbonyl and the distibine ligand in methylcyclohexane (100 ml) for three hours to give ($Mo(CO)_5(Dpsm)$), three days ($Cr(CO)_5(Dpsm)$), and five days ($W(CO)_5(Dpsm)$). Evaporation of the solvent (25°/0.1 mm) yielded light yellow solids which were purified by dissolution in CH_2Cl_2, elution from a Florisil column in 25/75 benzene–hexane and subsequent recrystallization from $CHCl_3$–hexane to give white crystals. Yields: 50–83%. $Mo(CO)_5(Dpsm)$ was also prepared by ultraviolet irradiation for thirty minutes of a 50/50 tetrahydrofuran–hexane solution of equal molar amounts of $Mo(CO)_6$ and Dpsm. Anal. Found: C, 47.43; H, 2.91; Sb, 32.49; Cr, 6.71; Mol. wt., 780 (m.p. 148–149°). $C_{30}H_{22}CrO_5Sb_2$ calcd.: C, 47.53; H, 2.93; Sb, 32.13; Cr, 6.86%; Mol. wt., 758.0. Found: C, 44.72; H, 2.72; Sb, 30.36; Mo, 11.83; Mol. wt., 830 (m.p. 132–133°). $C_{30}H_{22}MoO_5Sb_2$ calcd.: C, 44.93; H, 2.77; Sb, 30.37; Mo, 11.96%; Mol. wt., 801.9. Found: C, 40.83; H, 2.31; Sb+W, 47.43; Mol. 930 (m.p. 128–130°) $C_{30}H_{22}WO_5Sb_2$ calcd.: C, 40.49; H, 2.49; Sb+W, 48.03%; Mol. wt., 889.9.

$[M(CO)_4(Dpsm)]_2$. The dimeric tetracarbonyl compounds were prepared by stirring a solution of equimolar quantities of Dpsm and a reactive intermediate ($Cr(CO)_4(Nbd)$, $Mo(CO)_4(Nbd)$, or $W(CO)_4(Tmpa)$) until the maximum quantity of product was obtained as indicated by monitoring the carbonyl stretching frequencies in the infrared spectrum (2200–1700 cm^{-1}). Reaction conditions were as follows: $Cr(CO)_4(Dpsm)$, 250 ml methylcyclohexane at 38° for four days; $Mo(CO)_4(Dpsm)$, 250 ml methylcyclohexane at 26° for twenty-four hours; and $W(CO)_4(Dpsm)$, 100 ml CH_2Cl_2 at 40° for fifteen days. The molybdenum and chromium products precipitated from solution and were recrystallized from $CHCl_3$–hexane to yield white (Mo) and pale yellow (Cr) solids. The tungsten complex was purified by evaporating the CH_2Cl_2 (25°/30 mm), stirring the residue in methylcyclohexane to dissolve $W(CO)_5(Dpsm)$, and recrystallizing the solid from $CHCl_3$–hexane to yield a white product. Yields: 10–27%. Anal. Found: C, 47.77; H, 3.04; Sb, 33.27; Cr, 6.97; O, 8.36; Mol. wt., 1450 (m.p. 169–171° dec). $C_{58}H_{44}Cr_2O_8Sb_4$ calcd.: C, 47.71; H, 3.04; Sb, 33.36; Cr, 7.12; O, 8.77%; Mol. wt., 1460. Found: C, 44.95; H, 2.80; Sb, 31.29; Mo, 12.36; Mol. wt., 1430, 1660 (run in benzene at 37°) (m.p. 177–179° dec.). $C_{58}H_{44}Mo_2O_8Sb_4$ calcd.: C, 45.00; H, 2.87; Sb, 31.47; Mo, 12.40%; Mol. wt., 1548. Found: C, 41.43; H, 2.83; Sb, 27.63; O, 7.48 (m.p. 250°). $C_{58}H_{44}W_2O_8Sb_4$ calcd.: C, 40.41; H, 2.57; Sb, 28.26; O, 7.44%.

$M(CO)_4(Dpsm)$. Monomeric $Mo(CO)_4(Dpsm)$ was prepared by ultraviolet irradiation of a 1-liter hexane solution of $Mo(CO)_6$ (1.0 g) and Dpsm (2.0 g) for four days. The filtered solution was evaporated (25°/30 mm) and the residue was placed on

a Florisil column in 90/10 hexane–benzene and eluted with benzene. Eluant evaporation followed by recrystallization from $CHCl_3$–hexane yielded 40 mg (5%) of white solid. Anal. Found: C, 45.65; H, 3.12; Sb, 32.00; Mol. wt., 940. $C_{29}H_{22}MoO_4Sb_2$ calcd.: C, 45.00; H, 2.87; Sb, 31.47%. Mol. wt., 774. $Cr(CO)_4$(Dpsm) and $W(CO)_4$(Dpsm) were obtained in quantities sufficient only for IR and NMR spectral measurements.

$Mo(CO)_3(Dpsm)_2$. The tricarbonyl $Mo(CO)_3(Dpsm)_2$ was synthesized by allowing a 1/3 mixture of $Mo(CO)_3$(Cht) and Dpsm to react at 80° in 200 ml benzene for twelve hours. Evaporation of the solvent and recrystallization of the residue from CH_2Cl_2–hexane yielded white crystals in 79% yield. Anal. Found: C, 48.29; H, 3.61; Sb, 36.85; Mol. wt., 1220, 1260 (m.p. 169–171° dec.). $C_{53}H_{44}MoO_3Sb_4$ calcd.: C, 48.52; H, 3.38; Sb, 37.12%. Mol. wt., 1312. There was no evidence of chromium or tungsten tricarbonyl formation using the above procedure.

RESULTS AND DISCUSSION

When allowed to react with $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ under a variety of thermal synthetic conditions the potentially bidentate ligand bis(diphenylstibino)methane (Dpsm) yielded at least three different types of products. The initial evolution of carbon monoxide produced a pentacarbonyl derivative with Dpsm functioning as a monodentate ligand

$$M(CO)_6 + Dpsm \rightarrow M(CO)_5(Dpsm) + CO$$

Invariably, a small amount of the more highly substituted tetracarbonyl derivative formed during the preparation necessitating column chromatographic purification of the pentacarbonyls.

More drastic conditions such as high temperatures and/or extended reaction periods led to additional carbonyl replacement and the production of tetracarbonyl dimers.

$$2M(CO)_5(Dpsm) \rightarrow [M(CO)_4(Dpsm)]_2 + 2\,CO$$

However, because of slow concurrent disproportionation to pentacarbonyl, tricarbonyl, and decomposition products, chromatographic techniques were again necessary to achieve purification of the tetracarbonyl derivatives. Larger yields of these complexes were obtained by taking advantage of the facile replacement of 2,5-norbornadiene (Nbd) or 1,3-tetramethylpropylenediamine (Tmpa) from their metal carbonyls.

$$2Cr(CO)_4(Nbd) + 2Dpsm \rightarrow [Cr(CO)_4(Dpsm)]_2 + 2Nbd$$

$$2Mo(CO)_4(Nbd) + 2Dpsm \rightarrow [Mo(CO)_4(Dpsm)]_2 + 2Nbd$$

$$2W(CO)_4(Tmpa) + 2Dpsm \rightarrow [W(CO)_4(Dpsm)]_2 + 2Tmpa$$

Upon heating $Mo(CO)_5$(Dpsm) with additional ligand at 130° for thirteen days a tricarbonyl complex with the molecular formula $Mo(CO)_3(Dpsm)_2$ was produced. The same compound formed more efficiently by utilizing a reactive intermediate with an excess of Dpsm.

$$Mo(CO)_3(Cht) + Dpsm(excess) \rightarrow Mo(CO)_3(Dpsm)_2 + Cht$$

No evidence of analogous chromium or tungsten tricarbonyl derivatives was observed by either of the above procedures.

Several reaction parameters such as different metal carbonyl–ligand ratios; the use of polar, nonpolar, aromatic and saturated solvents; a range of temperatures from 25–160°; and times up to three weeks were varied in attempts to optimize product formation and to obtain conditions amenable to the synthesis of different derivatives. The qualitative trend in reactivity of the ligands $(C_6H_5)_2ECH_2E(C_6H_5)_2$ toward the Group VIB metal carbonyls is apparently $E = P > As > Sb$[24]. Further, the tendency to achieve chelation with metals in these systems decreases markedly in the same order. Decomposition of the ligand and products, sometimes extensively, accompanied each of the above reactions and tended to increase with elevated temperatures and longer reaction times. Also, because of disproportionation and other competing pathways, except for the $Mo(CO)_3$(Cht)–Dpsm interaction, mixtures comprised of the penta-, tetra-, and tricarbonyl derivatives were often obtained. In contrast to the thermally induced reactions ultraviolet irradiation of $Mo(CO)_6$ and Dpsm in hexane yielded a mixture of not only pentacarbonyl and tricarbonyl derivatives along with copious decomposition but a monomeric tetracarbonyl complex.

Solubility of the new complexes in hydrocarbon solvents range from slightly soluble (pentacarbonyls) to very slightly soluble (tetracarbonyls) to virtually in-

TABLE 1

INFRARED AND NMR SPECTRA OF Dpsm METAL CARBONYLS AND RELATED COMPOUNDS

Compound	$\nu(CO)^a (cm^{-1})$				*Proton NMR Spectra*[b] *(ppm)*	
					$\tau(CH_2)$	$\tau(C_6H_5)$
Dpsm[19]					7.96	2.74
$Cr(CO)_5(Dpsm)$		2067 m	1943 vs		7.65	2.72 2.62
$Mo(CO)_5(Dpsm)$		2079 m	1952 vs		7.64	2.69 2.59
$W(CO)_5(Dpsm)$		2078 m	1947 vs		7.56	2.70 2.62
cis-$[Cr(CO)_4(Dpsm)]_2$	2008 m	1919 m	1898 s, (br)		7.45	2.67
cis-$[Mo(CO)_4(Dpsm)]_2$	2028 m	1931 m	1914 s	1903 (sh)	7.61	2.72
cis-$[W(CO)_4(Dpsm)]_2$	2024 m	1927 m	1905 s (br)		7.42	2.67
cis-$Cr(CO)_4(Dpsm)$[c]		2010 m	1895 vs (br)		8.01	2.80
cis-$Mo(CO)_4(Dpsm)$[c]	2028 m	1918 vs	1895 (sh)		8.00	2.80
cis-$W(CO)_4(Dpsm)$[c]	2022 m	1921 (sh)	1899 vs (br)		7.97	2.83
cis-$Mo(CO)_3(Dpsm)_2$[c]		1945 s	1852 s (br)		8.07	2.99 2.79
$Mo(CO)_5[Sb(C_6H_5)_3]$[d,27]		2073 m	1954 vs			
$Mo(CO)_5[As(C_6H_5)_3]$[d,28]		2074 m	1951 vs			
$Mo(CO)_5[P(C_6H_5)_3]$[d,29]	2073 m	1984 w	1952 vs			
cis-$Mo(CO)_4[Sb(C_6H_5)_3]_2$[d,27]	2024 m	1935 m	1921 s	1909 (sh)		
cis-$Mo(CO)_3(Diphos)[Sb(C_6H_5)_3]$[e,25]		1945 s	1857 s (br)			

[a] Recorded in methylcyclohexane unless otherwise noted. Intensities: weak (w), medium (m), strong (s), very strong (vs), shoulder (sh), broad (br). [b] Recorded in chloroform-*d* with TMS as internal standard. $\tau(CH_2)$ is a singlet, $\tau(C_6H_5)$ is a multiplet with a predominant center band(s). [c] Infrared recorded in methylene chloride. [d] Recorded in saturated hydrocarbon solution. [e] Recorded in chloroform; Diphos = 1,2-bis-(diphenylphosphino)ethane.

soluble (the tricarbonyl). All are moderately soluble in chlorinated solvents and acetone.

Molecular structures of the various products have been assigned based on a comparison of the infrared spectra in the metal carbonyl stretching region with "model" compounds (Table 1) along with elemental analyses, molecular weight determinations, and NMR spectra. The pentacarbonyl derivatives adopt the pseudooctahedral configuration shown in Fig. 1 and exhibit two phenyl resonances—one each for those on the bound and unbounded antimony atoms*. Owing to accidental degeneracy of the A_1 and E modes only two ν(CO) stretching frequencies were observed**.

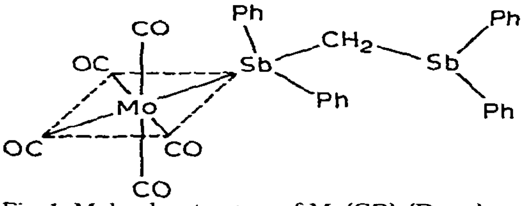

Fig. 1. Molecular structure of $Mo(CO)_5(Dpsm)$.

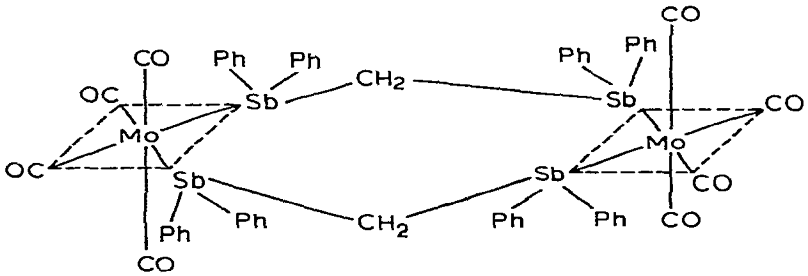

Fig. 2. Molecular structure of $[Mo(CO)_4(Dpsm)]_2$.

The thermally prepared tetracarbonyl compounds were established to be bridged dimers as shown in Fig. 2. Although the four expected ν(CO) stretching frequencies were seen for $[Mo(CO)_4(Dpsm)]_2$ in a methylcyclohexane solution, only three were resolved for the chromium and tungsten analogues. Due to broadening effects only three bands were resolved in chlorinated solvents even for the molybdenum derivative.

The *cis* configuration for the tricarbonyl complex (Fig. 3) was derived from the positions and intensities of the two ν(CO) bands displayed in the infrared spectrum[25]. The monomeric tetracarbonyls produced in very low yields from ultraviolet reactions contain the distibine ligand functioning as a chelate similar to the known diphosphine[8] and diarsine[7] metal tetracarbonyls (Fig. 4).

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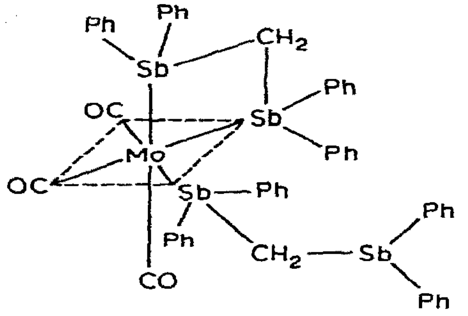
* The two phenyl resonances may arise from different chemical shifts of the *ortho*, *meta*, and *para* protons. The authors are indebted to a referee for pointing out this possibility.

** Since pure samples of $M(CO)_5(Dpsm)$ display only two ν(CO) bands even in $CHCl_3$, we suggest that the two additional frequencies reported in ref. 6 are due to the presence of $M(CO)_6$ (~1980 cm^{-1}) and $[M(CO)_4(Dpsm)]_2$ (~2015 cm^{-1}). Other bands between 1900–1930 cm^{-1} for the dimers were probably buried under the very strong band at ~1950 cm^{-1}. The darker colors of the previously reported pentacarbonyls are also consistent with the presence of impurities.



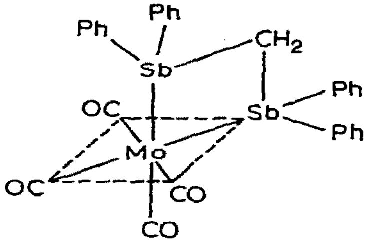


Fig. 3. Molecular structure of $Mo(CO)_3(Dpsm)_2$.

Fig. 4. Molecular structure of $Mo(CO)_4(Dpsm)$.

Whereas in the pentacarbonyl and dimeric tetracarbonyl derivatives the methylene and phenyl proton resonances suffer net deshielding which results in a downfield shift (0.02–0.54 ppm) from the free ligand values, the chelated tetracarbonyls and the molybdenum tricarbonyl complex experience a slight upfield shift from the free ligand. Apparently a delicate balance exists between the amount of charge removal from the ligand upon bond formation (which should decrease with substitution in metal carbonyl derivatives) and the degree of ligand interaction in the coordination sphere which may increase the proton shielding. Similar effects in proton shifts have been noted in tritolylphosphine substituted metal carbonyl compounds[26].

ACKNOWLEDGEMENT

We are indebted to the Memphis State University Research Foundation for partial support of this work and to the M and T Chemical Company, Inc., Rahway, N.J., for a gift of triphenylstibine.

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