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PREPARATION AND PROPERTIES OF BIS(DIORGANOSTIBINO)-METHANE SUBSTITUTED METAL CARBONYL COMPLEXES

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SUMMARY

The reactions of a bis(diarylstibino)methane, $(R_2Sb)_2CH_2$, with metal carbonyls, $M(CO)_n$, gave the monosubstituted complexes, $M(CO)_{n-1}(R_2Sb)_2CH_2$ ($n=6$; $M=Cr$, Mo, W; $R=C_6H_5$, p-$CH_3C_6H_4$. $n=5$; $M=Fe$; $R=C_6H_5$), while those of bis(dimethylstibino)methane gave the complexes $[M(CO)_{n-1}]_2[(CH_3)_2Sb]_2CH_2$ ($n=6$; $M=Mo$, W . $n=5$; $M=Fe$). From molecular weight, PMR and IR data, it was concluded that a bis(diarylstibino)methane behaves as a monodentate ligand and bis(dimethylstibino)methane as a bridging ligand in these complexes.

INTRODUCTION

Bis(diphenylphosphino)methane and bis(diphenylarsino)methane have been widely used in transition metal chemistry and are reported to act as either bidentate *i.e.*, bridging or chelating, or monodentate ligands[1]. However, in the case of transition metal complexes containing a bis(diorganostibino)methane, only platinum and palladium complexes of bis(dimethylstibino)methane have been briefly reported[2].

This paper describes the properties of ten new complexes obtained by the reactions of the Group VI metal hexacarbonyls and iron pentacarbonyl with a bis-(diorganostibino)methane.

EXPERIMENTAL

General comment

All the reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard methods, and nitrogen was bubbled through each just before use. The volume of liberated carbon monoxide was measured by displacement of water. Since essentially the same procedure was used to prepare all of the complexes, only typical procedures will be described.

Preparation of bis(diorganostibino)methane

The preparation of bis(diphenylstibino)methane (Dpsm) and bis(dimethylstibino)methane (Dmsm) have already been described[3–4] and that of bis(di-*p*-tolylstibino)methane (Dtsm) was as follows. An ether solution of bis(dichlorostibino)-

methane[4] (8.0 g, 20 mmoles) was added to *p*-tolylmagnesium bromide (≈84 mmoles) in ether in the presence of 2.0 g (84 mmoles) of *N,N,N′,N′*-tetramethylethylenediamine. After refluxing of this mixture for about 1½ h and treating with water saturated with ammonium chloride, the ether layer was separated and the solvent was removed. The viscous oily residue thus obtained (which was used without further purification in the reactions with metal carbonyls) was identified as its reaction product with bromine, $[Br_2(p\text{-}CH_3C_6H_4)_2Sb]_2CH_2$; m.p. 168.5–169.5°. (Found: C, 37.10; H, 3.28. $C_{29}H_{30}Br_4Sb_2$ calcd.: C, 36.99; H, 3.21%.) NMR ($CDCl_3$): $\delta(CH_3)$ 2.38 (12H) and $\delta(CH_2)$ 5.51 (2H) ppm.

Preparation of the bis(diarylstibino)methane complexes

$Cr(CO)_6$ (1.1 g, 5 mmoles) and Dpsm (2.4 g, 4 mmoles) were heated in diglyme (40 ml) at 140–150° for 7 h with stirring. After the evolution of carbon monoxide had

TABLE 1

PROPERTIES OF BIS(DIORGANOSTIBINO)METHANE SUBSTITUTED METAL CARBONYL COMPLEXES

Compound[a]	*Color*	*M.p.* (°C)	*Analysis (%) found (calcd.)*		*Mol.wt. found*[b] *(calcd.)*	*Mass* (m/e^+)[d]	*PMR (ppm)*	
			C	*H*			$\delta(CH_2)$[f]	$\delta(CH_3)$[f]
Dtsm							1.97	2.29
$Cr(CO)_5$Dtsm	Light	120.5–121.5	50.67	3.90	837			2.30
	yellow		(50.16)	(3.71)	(814)			2.34
$Mo(CO)_5$Dtsm	Pale	115.5–116.5	48.04	3.77	832			2.30
	yellow		(47.59)	(3.52)	(858)			2.34
$W(CO)_5$Dtsm	Pale	133–134	43.52	3.19	898			2.30
	yellow		(43.17)	(3.20)	(946)			2.34
Dpsm							2.04	
$Cr(CO)_5$Dpsm	Yellow	142–143	47.44	2.91	722[c]	758	2.35	
			(47.54)	(2.93)	(758)			
$Mo(CO)_5$Dpsm	Pale	126–127	45.06	2.73	770[c]	774[e]	2.33	
	yellow		(44.93)	(2.77)	(802)		2.44	
$W(CO)_5$Dpsm	Yellow	138–139	40.74	2.34	917	890		
			(40.49)	(2.49)	(890)			
$Fe(CO)_4$Dpsm	Orange	100–101	47.37	2.97	724		2.45	
	red		(47.47)	(3.02)	(734)			
Dmsm							1.20	0.80
$[Mo(CO)_5]_2$Dmsm	Light	98–99	22.68	1.87	766[c]		1.85	1.35
	yellow		(22.80)	(1.79)	(789)			
$[W(CO)_5]_2$Dmsm	Light	107–108	18.90	1.52	936		2.04	1.47
	yellow		(18.66)	(1.46)	(965)			
$[Fe(CO)_4]_2$Dmsm	Orange	74–75	23.86	2.17	585[c]		2.10	1.55
			(23.90)	(2.16)	(653)			

[a] Dtsm = $[(p\text{-}CH_3C_6H_4)_2Sb]_2CH_2$; Dpsm = $[(C_6H_5)_2Sb]_2CH_2$; Dmsm = $[(CH_3)_2Sb]_2CH_2$.
[b] Measured using a vapor pressure osmometer in C_6H_6 solution at 25°.
[c] Cryoscopically in C_6H_6 solution.
[d] Parent peak with the strongest intensity of isotope.
[e] Parent peak was not observed.
[f] In $CDCl_3$ solution (internal reference TMS).

stopped, the solvent and excess $Cr(CO)_6$ were removed under reduced pressure. The residual yellow crystalline solid was recrystallized from dichloromethane/hexane to give 1.8 g (63%) of $Cr(CO)_5$Dpsm. The yields of $Mo(CO)_5$Dpsm and $W(CO)_5$Dpsm were almost identical to that of $Cr(CO)_5$Dpsm. $M(CO)_5$Dtsm (M = Cr, Mo, W) were prepared in a manner similar to the above method in diglyme (about 10–15% yields). $Fe(CO)_4$Dpsm (38%) was obtained from the reaction of $Fe(CO)_5$ with Dpsm in n-heptane (reflux for 2 h).

Further substitution of CO by the treatement of $Cr(CO)_5$Dpsm with Dpsm did not occur even on refluxing in diglyme for 3 h.

Preparation of the bis(dimethylstibino)methane complexes

$Mo(CO)_6$ (5.2 g, 20 mmoles) and Dmsm (2.8 g, 9 mmoles) in n-heptane (50 ml) were refluxed for 5 h with stirring. After the evolution of carbon monoxide had stopped, the light-yellow crystals, obtained by the removal of the solvent and excess $Mo(CO)_6$, were recrystallized from dichloromethane/hexane to give 4.5 g (63%) of $[Mo(CO)_5]_2$Dmsm. The reactions of $W(CO)_6$ and $Fe(CO)_5$ with Dmsm were carried out in diglyme and in n-heptane, giving $[W(CO)_5]_2$Dmsm and $[Fe(CO)_4]_2$Dmsm (28 and 40% yields), respectively.

Properties of all the new complexes thus obtained are summarized in Table 1. The solid complexes shown in Table 1 are stable in air and fairly stable even in solution except for $[Fe(CO)_4]_2$Dmsm. They are very soluble in acetone, chloroform or dichloromethane, soluble in benzene and sparingly soluble in saturated hydrocarbons or alcohols.

Physical measurements

The PMR spectra were measured using Japan Electron Optics JNM-3H-60 or HNM-MH-60 spectrometers at 60 MHz and 20°. The IR spectra were recorded using a Hitachi 225 spectrophotometer, equipped with grating. Mass spectra were run on a Niphondenshi Type JPS-1S mass spectrometer. Molecular weights were determined using a Mechrolab vapor pressure osmometer Model 302.

PMR and mass spectral data are listed in Table 1, and IR data in Table 2.

TABLE 2

CO STRETCHING FREQUENCIES FOR BIS(DIORGANOSTIBINO)METHANE SUBSTITUTED METAL CARBONYL COMPLEXES IN $CHCl_3$ SOLUTION (in cm^{-1})

$Cr(CO)_5$Dtsm	2057 s		1976 m(sh)	1928 vs
$Mo(CO)_5$Dtsm	2070 s	2021 w	1985 m(sh)	1942 vs
$W(CO)_5$Dtsm	2067 s		1975 m(sh)	1927 vs
$Cr(CO)_5$Dpsm	2059 s	2002 w(sh)	1980 m(sh)	1940 vs
$Mo(CO)_5$Dpsm	2073 s	2022 w	1990 m(sh)	1950 vs
$W(CO)_5$Dpsm	2070 s	2015 w	1982 m(sh)	1940 vs
$Fe(CO)_4$Dpsm[a]	2044 s		1970 s(sh)	1935 vs
$[Mo(CO)_5]_2$Dmsm	2070 s	2017 w	1988 m(sh)	1950 vs
$[W(CO)_5]_2$Dmsm	2069 s	2014 w	1980 m(sh)	1942 vs
$[Fe(CO)_4]_2$Dmsm[a]	2044 s		1975 s(sh)	1932 vs

[a] In n-hexane solution.

RESULTS AND DISCUSSION

In the PMR spectra (Table 1) of the bis(di-*p*-tolylstibino)methane complexes in $CDCl_3$ solution, the methyl protons of the four tolyl groups attached to the antimony atoms show a two-line resonance at δ 2.30 and δ 2.34 ppm with almost the same intensity*. The methyl protons of the free ligand in $CDCl_3$ solution show only a single resonance at δ 2.29 ppm. These facts suggest that nonequivalent antimony atoms exist in the complexes, and we associate the low-field resonance to an antimony atom coordinated to the transition metal and the high-field resonance to an uncoordinated antimony atom.

As shown in Table 2, a characteristic feature of the CO stretching frequencies of the bis(diarylstibino)methane complexes of chromium, molybdenum and tungsten is the appearance of three strong bands and one additional weak band near 2015 cm^{-1}, and in some cases the disappearance of this weak band. The position of the three strong bands is similar to that of $M(CO)_5E(C_6H_5)_3$, having C_{4v} symmetry (M=Cr; E=Sb)[5] (M=Cr, Mo, W; E=P)[6]. The appearance of the additional weak band seems to be due to some lowering of the C_{4v} symmetry of the molecule by the ligand. Similar results have been reported for some amine[7-8] and phosphine[9-10] substituted Group VI metal pentacarbonyl complexes. $Fe(CO)_4$Dpsm shows three CO stretching bands, and hence probably has a structure with C_{3v} symmetry in which bis(diphenylstibino)methane replaces one carbonyl group at an axial position of iron pentacarbonyl, as in $Fe(CO)_4P(C_6H_5)_3$[11] (Fig. 1).

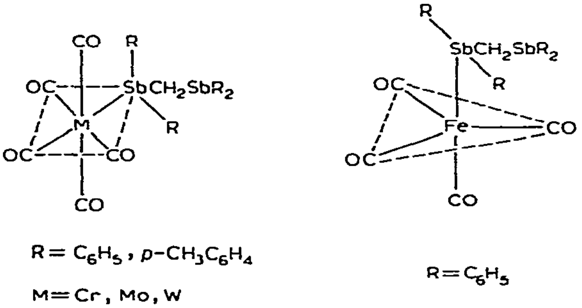

Fig. 1. Bis(diarylstibino)methane complexes.

As shown in Table 1, in the PMR spectra of the three bis(dimethylstibino)methane complexes, both the methylene and the methyl proton resonances were observed as a one-line peak at a lower magnetic field than those of the free ligand. These facts, together with the molecular weight data in benzene, suggest that bis(dimethylstibino)methane coordinates to the metal as a bridging ligand.

The molybdenum and tungsten complexes show four CO stretching bands analogous to those of the bis(diphenylstibino)methane complexes, and the iron complex shows three bands similar to the bis(diphenylstibino)methane analogue.

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* The methylene protons were masked by the methyl protons. However, in C_6H_6 solution these signals are observed at $\delta(CH_2)$ 2.32, $\delta(CH_3)$ 2.05 and 1.98 for the Cr and W complexes, and at $\delta(CH_2)$ 2.28, $\delta(CH_3)$ 2.05 and 1.98 ppm for the Mo complex.

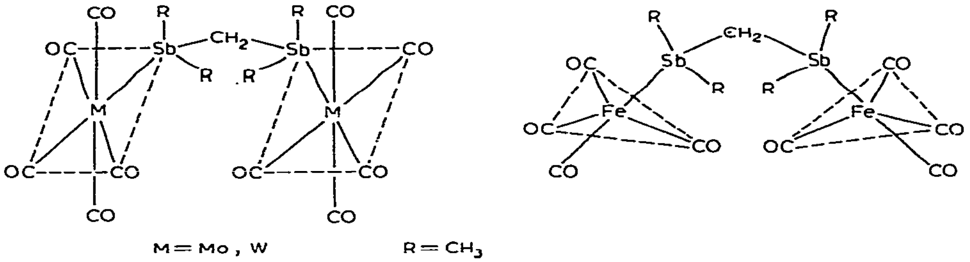

Fig. 2. Bis(dimethylstibino)methane complexes.

Therefore, the structures as shown in Fig. 2 can be proposed*.

It is noteworthy that bis(di-*p*-tolylstibino)methane and bis(diphenylstibino)methane behave as monodentate ligands and bis(dimethylstibino)methane as bridging ligands in our complexes. In contrast it has been reported that bis(diphenylphosphino)methane acts as a chelating ligand in $Mo(CO)_4[(C_6H_5)_2P]_2CH_2$[13].

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* $[Fe(CO)_4]_2P_2(CH_3)_4$ has been reported to have a similar configuration[12].