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SOME COBALT CARBONYL COMPLEXES OF LIGANDS CONTAINING THE ECH_2E (E = Sb, As, P) MOIETY

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Summary

Complexes of the type, $Co_2(CO)_6[(R_2E)_2CH_2]$ ($R = CH_3$, C_2H_5, $p\text{-}CH_3C_6H_4$; E = Sb. $R = C_6H_5$; E = Sb, As, P) were prepared by the reaction of dicobalt octacarbonyl with the corresponding ligands in benzene at room temperature. Treatment of these complexes with a diarylacetylene in refluxing benzene displaced two bridging carbonyl groups to give complexes of the type, $Co_2(CO)_4(R'_2C_2)[(R_2E)_2CH_2]$ ($R' = C_6H_5$, $p\text{-}CH_3C_6H_4$), which also were obtained from the reaction between $Co_2(CO)_6(R'_2C_2)$ and $(R_2E)_2CH_2$. The structures of these derivatives are discussed on the basis of their infrared spectra.

It was found from the PMR spectra in CH_2Cl_2 at room temperature that the coordinated stibine ligand in these complexes can be easily replaced by either a free phosphine or arsine ligand, while the coordinated arsine ligand is replaced only by a free phosphine.

Introduction

We have reported [1,2] recently concerning the behavior of $(R_2Sb)_2CH_2$ in substitution reactions with mononuclear metal carbonyls. These di-tertiary stibines tend to bridge between two metal carbonyls. Although tertiary stibine derivatives of dicobalt octacarbonyl, $[Co(CO)_3(SbR_3)]_2$ ($R = C_2H_5$, $i\text{-}C_3H_7$, C_6H_5) and $\{Co(CO)_3[Sb(C_6H_5)_3]_2\}\{Co(CO)_4\}$ have been briefly reported [3, 4], the reaction of $Co_2(CO)_8$ with di-tertiary stibines has not yet been described.

In this paper, we report the preparation and properties of new bis(diorganostibino)methane derivatives of cobalt carbonyls, together with the phosphine and arsine analogs. The replacement reactions of the coordinated stibine, arsine or phosphine in these complexes by free ligands, $[(C_6H_5)_2E]_2CH_2$ (E = Sb, As, P) as observed by means of the PMR spectra will be also described.

Experimental

All the reactions and subsequent manipulations were carried out under a nitrogen atmosphere. Solvents were purified by standard methods, and nitrogen was bubbled through prior to use.

IR spectra were recorded on a Hitachi 225 spectrophotometer, equipped with gratings. The PMR spectra were measured on JEOL model 3H-60 and PS-100 spectrometers operating at 60 and 100 MHz, respectively, using TMS as an internal standard. Mass spectra were obtained on a JEOL model JPS-1S mass spectrometer.

The compounds $Co_2(CO)_8$ [5], $(R_2Sb)_2CH_2$ ($R = CH_3$ [6], C_6H_5 [7], p-$CH_3C_6H_4$ [1]) and $[(C_6H_5)_2P]_2CH_2$ [8] were prepared by literature methods, and $[(C_6H_5)_2As]_2CH_2$ was prepared similarly to $[(C_6H_5)_2P]_2CH_2$. We have synthesized colorless bis(diethylstibino)methane in a manner similar to the preparation of bis(di-p-tolylstibino)methane [1]: $[(C_2H_5)_2Sb]_2CH_2$ [b.p. 93—95°/ 1.5 mmHg (lit. [9] b.p. 103—105°/0.8 mmHg), PMR (neat); $\delta(SbCH_2Sb)$ 1.05 s, $\delta(SbC_2H_5)$ 1.14—1.50 m ppm]; the derivative $[Br_2(C_2H_5)_2Sb]_2CH_2$ [m.p. 84—85°, (Found: C, 15.59; H, 3.25. $C_9H_{22}Sb_2Br_4$ calcd.: C, 15.59; H, 3.20%), PMR ($CHCl_3$); $\delta(SbCH_2Sb)$ 4.17 (s, 2H), $\delta(SbCH_2CH_3)$ 3.19 (q, J 8 Hz, 8H), $\delta(SbCH_2CH_3)$ 1.64 (t, J 8 Hz, 12H) ppm].

Preparation of $Co_2(CO)_6[(R_2E)_2CH_2]$ *(*$R = CH_3$, C_2H_5; p-$CH_3C_6H_4$; $E = Sb$. $R = C_6H_5$; $E = Sb, As, P$*)*

A mixture of $Co_2(CO)_8$ (1.6 g; 4.7 mmole) and $[(CH_3)_2Sb]_2CH_2$ (1.5 g; 4.7 mmole) in benzene (80 ml) was stirred at room temperature until the evolution of carbon monoxide had stopped (ca. 2 h). The solvent was removed under reduced pressure. The residue was dissolved in a small amount of dichloromethane and chromatographed on an alumina column. The major red-brown band was eluted from the column with dichloromethane/petroleum ether. The solvent was removed under reduced pressure, and the residual solid was recrystallized from dichloromethane/n-hexane to give red crystals of $Co_2(CO)_6\{[(CH_3)_2Sb]_2CH_2\}$ (2.1 g; 75% yield). The other stibine and phosphine complexes, and the arsine complex (I) were prepared in a similar manner. In the arsine complexes, the column chromatography and recrystallization from benzene/n-hexane gave complex (II) shown in Table 1. The complexes (I) and (II) exhibit different IR spectra as Nujol mulls, but their PMR spectra and solution IR spectra were found to be identical as shown in Tables 1 and 2.

Preparation of $Co_2(CO)_4(R'_2C_2)[(R_2E)_2CH_2]$ *(*$R = CH_3$, C_6H_5; $E = Sb$; $R' = C_6H_5$, p-$CH_3C_6H_4$. $R = C_2H_5$, p-$CH_3C_6H_4$; $E = Sb$; $R' = C_6H_5$. $R = C_6H_5$; $E = As, P$; $R' = C_6H_5$*)*

A mixture of $Co_2(CO)_6\{[(CH_3)_2Sb]_2CH_2\}$ (1.1 g; 1.9 mmole) and $C_6H_5C{\equiv}CC_6H_5$ (0.35 g; 2.0 mmole) was heated in refluxing benzene (40 ml) for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and chromatographed on an alumina column using dichloromethane/n-hexane as the eluent. The black solid obtained by the removal of the solvent was recrystallized from dichloromethane/n-hexane to give black crystals of $Co_2(CO)_4[(C_6H_5)_2C_2]\{[(CH_3)_2Sb]_2CH_2\}$ (0.87 g; 67%

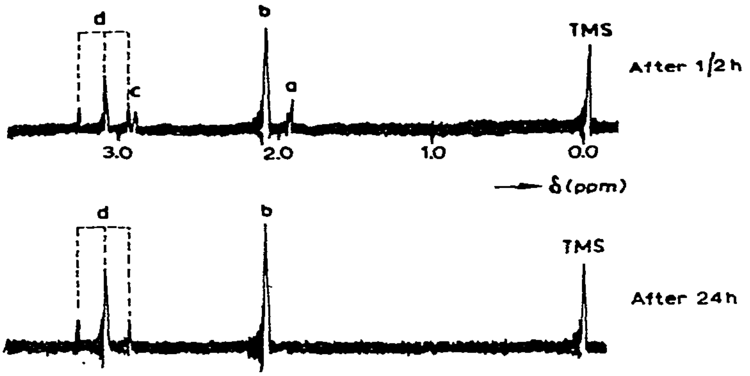


Fig. 1. The PMR spectra in the region of methylene protons for the reaction of $Co_2(CO)_6$-$\{[(C_6H_5)_2Sb]_2CH_2\}$ (0.1 mmole) with $[(C_6H_5)_2P]_2CH_2$ (0.1 mmole) in CH_2Cl_2 (0.3 ml) at room temperature after 1/2 and 24 h. (a) $Co_2(CO)_6\{[(C_6H_5)_2Sb]_2CH_2\}$, (b) $[(C_6H_5)_2Sb]_2CH_2$, (c) $[(C_6H_5)_2P]_2CH_2$, (d) $Co_2(CO)_6\{[(C_6H_5)_2P]_2CH_2\}$.

yield). The same compound also was obtained by heating the mixture of $[(CH_3)_2Sb]_2CH_2$ and $Co_2(CO)_6[(C_6H_5)_2C_2]$ in refluxing n-hexane. The other complexes were prepared in a similar fashion.

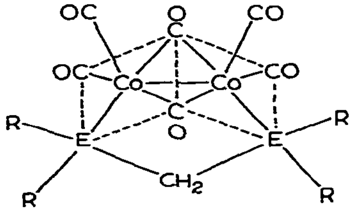
Properties and yields of all the new cobalt carbonyl complexes thus obtained are summarized in Table 1. These complexes are stable in air as solids but they decompose slowly in solution. IR data are listed in Table 2.

The ligand substitution reactions of the complexes

The progress of the reactions was followed by measuring the PMR spectra in the region of the methylene protons of the ligands. Typical spectra are shown in Fig. 1. The other substitution reactions were similarly carried out.

Results and discussion

All the complexes shown in Table 1 are monomeric in dichloromethane. The solution infrared spectra (Table 2) of the complexes $Co_2(CO)_6[(R_2E)_2CH_2]$ exhibit three very strong terminal, and two strong bridging carbonyl stretching bands with fairly large separation. The compounds are assigned structure [A] on the basis of their infrared spectra which are similar to that of $Co_2(CO)_6$-$[(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2]$ [10] which is known from X-ray studies [11] to be of that structural type.



[A]

E = Sb, R = CH_3, C_2H_5, C_6H_5, p-$CH_3C_6H_4$
E = P or As, R = C_6H_5.

(continued on p. 443)

TABLE 1

PROPERTIES AND YIELDS FOR $Co_2(CO)_6[(R_2E)_2CH_2]$ AND $Co_2(CO)_4(R'_2C_2)[(R_2E)_2CH_2]$

Compound		Yield (%)	Color	M.p. (decomp.) (°C)	Analysis Found (calcd.) (%)		Mol. wt. Found[c] (calcd.)	PMR (ppm)[d] $\delta(ECH_2E)$
					C	H		
$Co_2(CO)_6[(R_2E)_2CH_2]$								
E = Sb	R = CH_3[a]	75	red	129-130	21.85 (21.89)	2.38 (2.34)	624 (604)	1.42[e]
Sb	C_2H_5	47	red	104-105	27.11 (27.31)	3.53 (3.36)	683 (660)	1.02[f]
Sb	C_6H_5	86	red-brown	121-123	43.67 (43.71)	2.59 (2.60)	851 (852)	1.92
Sb	p-$CH_3C_6H_4$[b]	72	red-brown	114-116	45.50 (45.34)	3.57 (3.30)	944 (936)	1.78[g]
As	C_6H_5(I)	67	red	138-140	48.85 (49.11)	2.83 (2.93)	751 (758)	2.61
As	C_6H_5(II)	71	orange	143-145	49.16 (49.11)	2.90 (2.93)	749 (758)	2.61
P	C_6H_5	50	orange	158-160	55.41 (55.55)	3.32 (3.31)	657 (670)	3.06[h]

$Co_2(CO)_4(R'_2C_2)[(R_2E)_2CH_2]$									
E = Sb	R = CH_3	R' = C_6H_5[a]	67	black	179-180	37.94 (38.06)	3.44 (3.33)	732 (726)	1.53[i]
Sb	CH_3	p-$CH_3C_6H_4$	81	black	162-163	39.53 (39.83)	3.64 (3.74)	741 (754)	1.50[j]
Sb	C_2H_5	C_6H_5	37	black	113-114	41.24 (41.47)	4.22 (4.13)	781 (782)	[k]
Sb	C_6H_5	C_6H_5	65	black	162-164	52.76 (53.02)	3.36 (3.31)	974 (974)	2.20
Sb	C_6H_5	p-$CH_3C_6H_4$	75	black	194-195	53.31 (53.93)	3.66 (3.62)	953 (1016)	2.22[l]
Sb	p-$CH_3C_6H_4$	C_6H_5	72	black-purple	195-197	54.34 (54.80)	4.04 (3.91)	1047 (1030)	2.09[m]
As	C_6H_5	C_6H_5	80	brown	177-179	58.65 (58.66)	3.62 (3.66)	879 (880)	2.87
P	C_6H_5	C_6H_5	84	brown	205-207	65.37 (65.17)	4.34 (4.07)	818 (793)	3.22[h]

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[a] The molecular ion followed by successive loss of six and four carbonyl groups was observed from the mass spectra, respectively. [b] 1/3 CH_2Cl_2 solvate. [c] Measured using a vapor pressure osmometer in CH_2Cl_2 at 25° (concn. 0.5—1.0 wt%). [d] Measured in CH_2Cl_2 unless otherwise stated, $[(C_6H_5)_2Sb]_2CH_2$: $\delta(SbCH_2Sb)$ 2.07, $[(R_2Sb)_2CH_2]$ (R = CH_3, p-$CH_3C_6H_4$): see ref. 1, $[(C_6H_5)_2As]_2CH_2$: $\delta(AsCH_2As)$ 2.62, $[(C_6H_5)_2P]_2CH_2$: $\delta(PCH_2P)$ 2.85 (t, J(P—H) 1 Hz), $(p\text{-}CH_3C_6H_4)_2C_2$: $\delta(C{-}CH_3)$ 2.35 ppm. [e] In CD_3COCD_3, $\delta(SbCH_3)$ 1.36. [f] $\delta(SbC\underline{H}_2CH_3)$ 1.32 (q, J 7 Hz, 8H), $\delta(SbCH_2C\underline{H}_3)$ 1.84 (t, J 7 Hz, 12H). [g] In $CDCl_3$, $\delta(C{-}CH_3)$ 2.35. [h] Triplet (J(P—H) 10 Hz). [i] $\delta(SbCH_3)$ 1.04. [j] $\delta(SbCH_3)$ 1.04, $\delta(C{-}CH_3)$ 2.26. [k] 1.05-1.77 m, masked by $\delta(SbC_2H_5)$. [l] $\delta(C{-}CH_3)$ 2.28. [m] In $CDCl_3$, $\delta(C{-}CH_3)$ 2.30.

TABLE 2

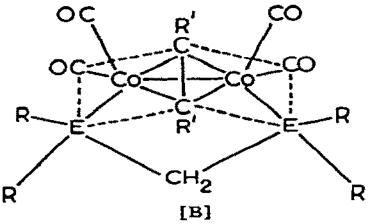
CARBONYL STRETCHING FREQUENCIES FOR $Co_2(CO)_6[(R_2E)_2CH_2]$ AND $Co_2(CO)_4(R'_2C_2)[(R_2E)_2CH_2]$[a]

Compound				Terminal	ν(CO)		Bridge	ν(CO)
$Co_2(CO)_6[(R_2E)_2CH_2]$								
E = Sb	R = CH_3		Nujol	2034(10)	2000(10),1989(9)	1969(10),1947(9)	1805(9)	1764(9)
			$CHCl_3$	2041(9)	2008(10)	1983(10)	1821(5)	1765(6)
Sb	C_2H_5		Nujol	2029(10)	1998(9),1989(9)	1976(10),1950(8)	1804(9)	1764(9)
			$CHCl_3$	2039(8)	2006(9)	1980(10)	1819(4)	1765(5)
Sb	C_6H_5		Nujol	2040(8)	2014(9)	1976(10)	1831(7)	1766(8)
			n-hexane	2048(8)	2017(9)	1995(10)	1844(6)	1783(4)
Sb	p-$CH_3C_6H_4$		Nujol	2039(9)	2010(10)	1979(10)	1819(7)	1774(8)
			n-hexane	2046(10)	2016(10)	1993(10)	1844(7)	1784(5)
As	C_6H_5 (I)		Nujol	2050(9)	2016(10),2004(10)	1969(10)	1832(9)	1770(9)
			Cyclohexane	2049(9)	2017(10)	1992(10)	1841(7)	1789(4)
As	C_6H_5 (II)		Nujol	2047(7),2043(8)	2005(10),2000(10)	1985(9),1975(9)	1810(8)	1795(10)
			Cyclohexane	2049(9)	2017(10)	1992(10)	1842(7)	1790(4)
P	C_6H_5		Nujol	2047(7),2042(8)	2005(10),2000(10)	1985(9),1974(9)	1810(7)	1799(10)
			Cyclohexane	2049(8)	2017(10)	1991(9)	1842(6)	1793(4)
$Co_2(CO)_4(R'_2C_2)[(R_2E)_2CH_2]$								
E = Sb	R = CH_3	R′ = C_6H_5	$CHCl_3$	2021(8)	1992(10)	1965(7)		
Sb	CH_3	p-$CH_3C_6H_4$	$CHCl_3$	2020(8)	1990(10)	1963(7)		
Sb	C_2H_5	C_6H_5	$CHCl_3$	2018(8)	1988(10)	1963(7)		
Sb	C_6H_5	C_6H_5	$CHCl_3$	2026(8)	1999(10)	1973(7)		
Sb	C_6H_5	p-$CH_3C_6H_4$	$CHCl_3$	2024(8)	1996(10)	1970(7)		
Sb	p-$CH_3C_6H_4$	C_6H_5	$CHCl_3$	2024(8)	1997(10)	1970(7)		
As	C_6H_5	C_6H_5	$CHCl_3$	2025(9)	1999(10)	1970(10)		
P	C_6H_5	C_6H_5	$CHCl_3$	2025(9)	1999(10)	1972(10)		

[a] Values are listed in cm^{-1} and relative intensities are given in parentheses.

In the solid state, all stibine complexes and the arsine complex (I) would have the same structure [A] as that in solution, since the pattern of carbonyl stretching bands is similar to that in solution and a difference in frequencies for the two bridging carbonyls is still large. However, for the arsine complex (II) and the phosphine complex, whose solid IR spectra exhibit a much smaller frequency separation of the bridging carbonyl bands, a possibility that the ligand $[(C_6H_5)_2E]_2CH_2$ (E = As, P) is chelating to one cobalt atom or bridging intermolecularly to form either a dimeric or polymeric structure may not be excluded.

In the infrared spectra (Table 2) of the complexes $Co_2(CO)_4(R'_2C_2)$-$[(R_2E)_2CH_2]$, only terminal carbonyl stretching frequencies were observed. These spectra resemble those of disubstituted phosphine derivatives of the type $Co_2(CO)_6$ (acetylene) such as $Co_2(CO)_4[(C_6H_5)_2C_2]\{[(C_6H_5)_3P]_2\}$ [12] and $Co_2(CO)_4[(C_6H_5)_2C_2]\{[(C_6H_5)_2PC_2CH_3]_2\}$ [13]. Thus structure [B] containing both $(R_2E)_2CH_2$ and R'_2C_2 bridging may be proposed for our complexes Co_2-$(CO)_4(R'_2C_2)[(R_2E)_2CH_2]$, as shown below.



[B]

E = Sb, RR' = CH_3, C_6H_5 or p-$CH_3C_6H_4$; C_2H_5, C_6H_5; C_6H_5, C_6H_5 or p-$CH_3C_6H_4$; p-$CH_3C_6H_4$, C_6H_5.
E = P or As, RR' = C_6H_5.

The position of the bands for the carbonyl stretching frequencies of the phenyl stibine complexes of the type [A] and [B] is very similar to that for the arsine or phosphine analogs. In a series of the stibine complexes, the position of the carbonyl stretching bands shows the slight higher shift with the decrease of the σ-donor property of the organic groups attached to the antimony atom. The carbonyl stretching bands of the complexes $Co_2(CO)_4(R'_2C_2)$-$[(R_2E)_2CH_2]$ are shifted to lower frequencies (ca. 20 cm^{-1}) than those of the complexes $Co_2(CO)_6[(R_2E)_2CH_2]$. This may be due to the weaker π-acceptor property of the acetylene groups in comparison with the carbonyl groups.

The methylene protons ($EC\underline{H}_2E$; E = Sb, As) and the methyl protons [$(C\underline{H}_3)_2Sb$, (p-$C\underline{H}_3C_6H_4)_2Sb$ or (p-$C\underline{H}_3C_6H_4$)C] of the complexes described in this paper are expected to be stereochemically nonequivalent in the proposed structures [A] and [B], but the PMR spectra of their protons show only a single resonance as shown in Table 1. The PMR spectrum of $Co_2(CO)_4$-$[(p\text{-}CH_3C_6H_4)_2C_2]\{[(CH_3)_2Sb]_2CH_2\}$ is unchanged even at temperatures down to —50°. This would suggest that these complexes are non-rigid in solution on the PMR time scale.

From the PMR spectra in CH_2Cl_2 at room temperature, it was found that the coordinated stibine in the complexes can be easily replaced by either the free phosphine or the arsine, while the coordinated arsine can be replaced by the free phosphine, as shown below and in Fig. 1.

$$Co_2(CO)_6\{[(C_6H_5)_2E]_2CH_2\} + [(C_6H_5)_2E']_2CH_2 \rightarrow Co_2(CO)_6\{[(C_6H_5)_2E']_2CH_2\} + [(C_6H_5)_2E]_2CH_2$$

(E = Sb; E' = As or P. E = As; E' = P)

Substitution by the free phosphine proceeded to completion in 24 h. Similar substitutions also were observed for the complexes $Co_2(CO)_4[(C_6H_5)_2C_2]$-$\{[(C_6H_5)_2E]_2CH_2\}$ (E = Sb or As). These facts suggest that the nucleophilicities of the ligands to the cobalt atoms decrease in the following sequence: $[(C_6H_5)_2P]_2CH_2 > [(C_6H_5)_2As]_2CH_2 > [(C_6H_5)_2Sb]_2CH_2$. This trend is consistent with the usually observed order of nucleophilicities of the Group VB elements.

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