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SOME CHEMICAL PROPERTIES OF (ARENE)NONACARBONYLTETRACOBALT COMPLEXES AND THE PREPARATION OF (ARENE)OCTACARBONYLTETRACOBALT TRIALKYLPHOSPHITES

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Summary

In reactions of $Co_4(CO)_9$(arene) with carbon monoxide, phosphines and acetylenes, displacement of the arene takes place and known derivatives of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ are formed. With phosphites, however, displacement of one carbon monoxide can be achieved, to give $Co_4(CO)_8$(arene)$P(OR)_3$. The same type of complexes can also be prepared by treatment of $Co_4(CO)_{11}$-$P(OR)_3$ with arenes.

Introduction

The first arene derivatives of cobalt clusters were perpared by Robinson et al. [1, 2] by heating (methylidine)nonacarbonyltricobalt complexes in aromatic solvents. Pauson et al. [3, 4] described the preparation of arene derivatives of $Co_4(CO)_{12}$ using (alkyne)hexacarbonyldicobalt, octacarbonyldicobalt and dodecacarbonyltetracobalt as starting compounds. Infrared spectroscopic data and some further details of preparation were given by Bor et al. [5]. The X-ray structure of two derivatives was determined recently [6].

Kitamura and Joh [7] reported recently the replacement of *p*-xylene in $Co_4(CO)_9[p\text{-}(CH_3)_2C_6H_4]$ by cycloheptatriene and cyclooctatriene. We describe below some reactions involving replacement of the arene of $Co_4(CO)_9$-(arene).

Results and discussion

At temperatures above 70° the arene of the complex $Co_4(CO)_9$(arene) was replaced in solution by carbon monoxide and $Co_4(CO)_{12}$ was formed. The rate and extent of this reaction increased in the following order: iso-durene ~ mesitylene $\ll$ *m*-xylene < *p*-xylene ~ *o*-xylene < toluene < anisole < biphenyl < fluorene < phenanthrene < benzene. The order is also that of the decreasing thermal stability of the arene complexes.

The replacement of one arene by another took place at 100-120°; this reaction is similar to that described by Robinson and Spencer [2]. Reaction with alkynes took place above 90°, to give $Co_2(CO)_6(alkyne)$ and $Co_4(CO)_{10}$-(alkyne).

Alkyl- and aryl-phosphines displaced the arene molecule in either carbon monoxide or argon atmosphere, the products being mono- and di-substituted cobalt carbonyl derivatives:

$$\begin{aligned} Co_4(CO)_9(\text{arene}) + PR_3 \xrightarrow[\text{CO}]{20\text{-}65^\circ} & [Co(CO)_3(PR_3)_2][Co(CO)_4] + \\ & Co_2(CO)_6(PR_3)_2 + Co_2(CO)_7PR_3 + \\ & Co_4(CO)_{10}(PR_3)_2 \end{aligned}$$

With alkylphosphites at room temperature mono-, di- and tri-substituted dodecacarbonyltetracobalt derivatives were formed. At 65° when the phosphite/arene complex ratio was ⩾ 5/1, $Co_4(CO)_8(arene)P(OR)_3$ complexes were formed, together with substituted octacarbonyldicobalt derivatives:

$$Co_4(CO)_9(\text{arene}) + P(OR)_3 \left\{ \begin{array}{l} \xrightarrow[\text{CO}]{20^\circ} Co_4(CO)_{11}P(OR)_3 + Co_4(CO)_{10}\text{-}(P(OR)_3)_2 + Co_4(CO)_9(P(OR)_3)_3 \\ \\ \xrightarrow[\text{CO}]{65^\circ} Co_4(CO)_8(\text{arene})P(OR)_3 + Co_2(CO)_6\text{-}(P(OR)_3)_2 + \text{uncharacterised product(s)} \end{array} \right.$$

Triphenylphosphite did not react at room temperature, but did so above 60°, to give $Co_4(CO)_8(arene)P(OPh)_3$ complexes together with $Co_2(CO)_6$-$(P(OPh)_3)_2$. The triphenylphosphite-substituted (arene)carbonylcobalt species are less stable under carbon monoxide than the analogous trialkylphosphite compounds. In the course of three days in heptane most of the complexes are converted into $Co_4(CO)_{11}P(OPh)_3$.

The phosphite-substituted (arene)carbonylcobalts were also prepared by the reaction of $Co_4(CO)_{11}P(OR)_3$ with arenes:

$$Co_4(CO)_{11}P(OR)_3 + \text{arene} \xrightarrow{130^\circ} Co_4(CO)_8(\text{arene})P(OR)_3$$

Spectra and structures

The ^1H NMR spectra of the new phosphite-substituted (arene)carbonylcobalt compounds are shown along with those of $Co_4(CO)_9(arene)$ complexes [4] in Table 1. The chemical shifts of the ring protons in substituted arene complexes are at higher field than those in $Co_4(CO)_9(arene)$ compounds. This effect was also observed by Strohmeier and Hellmann in the case of $Cr(CO)_2$-(arene)L complexes (L = PPh_3, etc.) [8].

High resolution IR spectra of $Co_4(CO)_9(arene)$ complexes were reported only for arene = toluene, tetraline and mesitylene derivatives [5]. The features of the spectra of some further complexes of this type are listed in Table 2. The spectrum of the biphenyl derivative, showing special features in the terminal ν(C—O) region, is shown in Fig. 1.

TABLE 1

^{1}H NMR SPECTRA OF SOME ARENE-SUBSTITUTED COBALT CARBONYLS
CS_2 solution

Compound	δ(ring protons)	δ(Me)(phosphite)	δ(Me)(arene)	Ref.
$Co_4(CO)_9[m\text{-}(CH_3)_2\text{-}C_6H_4]$	5.92 m	—	2.47 s	4
$Co_4(CO)_8[m\text{-}(CH_3)_2\text{-}C_6H_4]P(OMe)_3$	5.83 m	3.42 d [J(PH) 11.5 Hz]	2.40 s	
$Co_4(CO)_9[(CH_3)_3\text{-}C_6H_3]$	5.93 s	—	2.54 s	4
$Co_4(CO)_8[(CH_3)_3\text{-}C_6H_3]P(OMe)_3$	5.83 s	3.47 d [J(PH) 10.5 Hz]	2.43 s	

The broadening or splitting of the *E* band in the bridging carbonyl region accompanied by appearance of a band of low intensity at higher wave numbers was observed for most $Co_4(CO)_9$(arene) compounds, in which the symmetry of the arene deviates from the threefold one of the $Co_4(CO)_9$ skeleton. (This is in accordance with observations made by Bor et al. [5].)

Using some more asymmetric arene ligands, the splitting of the $\nu_3(E)$ and $\nu_4(E)$ bands in the terminal ν(C—O) region was also observed (see Table 2). This splitting provides experimental support for the assignments by Bor et al. [5] based on theoretical considerations.

Details of the IR spectra of the new $Co_4(CO)_8(\text{arene})P(OR)_3$ complexes and some $Co_4(CO)_{12-n}[P(OR)_3]_n$ derivatives (R = Me and Ph; n = 1, 2) are listed in Table 3.

$Co_4(CO)_8[(CH_3)_3C_6H_3]P(OMe)_3$ most probably has the structure shown in Fig. 2. This means that the Co(1)Co(2)$(CO)_4$ moiety has C_{2v} symmetry perturbed by the asymmetry in the bridging "ligands". If negligible CO_t—CO_t interaction is assumed between the four CO ligands of this unit and the carbonyl group on Co(3) (a rough approximation), the spectrum can be tentatively assigned as follows:

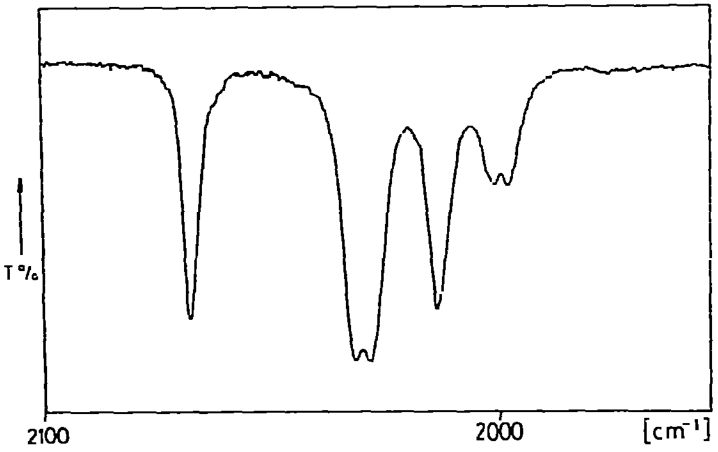

Fig. 1. IR spectrum of (biphenyl)nonacarbonyltetracobalt in the terminal ν(C—O) region (heptane solution).

TABLE 2

ν(C—O) ABSORPTIONS OF $Co_4(CO)_9$(arene) COMPLEXES
Heptane solution, DCl calibration; assignments on the basis of ref. 5

Arene	Terminal ν(C—O) frequencies				Bridging ν(C—O) frequencies	
	$\nu_1(A_1)$	$\nu_3(E)$	$\nu_2(A_2)$	$\nu_4(E)$	A_1	E
Benzene	2076.3 s	2033.0 vs	2014.6 s	2001.3 m	—	1831.8 m
p-Xylene	2074.9 s	2030.9 vs	2013.4 s	1999.8 m	—	1827.0 m
o-Xylene	2074.4 s	2030.8 vs	2013.1 s	1999.8 m	1856 vw	1820.5 m 1810 m (br)
m-Xylene	2074.0 s	2030.7 vs	2012.4 s	1999.3 m	—	1820.5 m (br)
iso-Durene	2072.2 s	2027.6 vs	2011.3 s	1996.6 m	1853 vw	1826 m 1819 m
Anisole	2074.7 s	2033 vs (br)	2014.7 s	2001.6 m 1998.7 m	1858 vw	1828 m (br) 1824 (sh)
Biphenyl	2075.0 s	2035.1 vs 2030.5 vs	2015.6 s	2002.8 m 1998.4 m	1860 vw	1832 m (br) 1827 (sh)
Fluorene	2073.7 s	2032 vs (br)	2014.2 s	2000 m (br) 1997 (sh)	1853 vw	1820 m 1818 (sh)
Phenanthrene	2074.3 s	2031 vs (br)	2013.1 s	2003.4 m 1996 (sh)	1852 vw	1820 m (br) 1820 (sh)

TABLE 3

ν(C—O) ABSORPTIONS OF SOME PHOSPHITE-SUBSTITUTED COBALT CARBONYL DERIVATIVES
Heptane solution

$Co_4(CO)_{11}P(OMe)_3$	2087.5 m, 2048.7 vs, 2044.0 vs, 2029.2 s 2024 (sh), 2012.2 w, 1999.2 w, 1880 vw, 1850 m, 1836 m
$Co_4(CO)_{11}P(OPh)_3$	2088.7 m, 2050.3 vs, 2043.9 vs, 2032.9 s 2027 (sh), 2011 m (br), 1885 vw, 1856 m, 1842 m
$Co_4(CO)_{10}[P(OPh)_3]_2$ [a]	2074.2 m, 2040 s, 2034 (sh), 2024.5 s, 2012 (sh) 1999 w (br), 1857 (sh), 1841 m (br), 1828 (sh)
$Co_4(CO)_8[(CH_3)_3C_6H_3]P(OMe)_3$	2052.2 s, 2019.6 s, 1995.1 s, 1985.6 m, 1975.1 s 1842 vw, 1814 m, 1801 m
$Co_4(CO)_8[m\text{-}(CH_3)_2C_6H_4]P(OMe)_3$	2053.5 s, 2020.5 s, 1996.6 s, 1987 m, 1977.5 s 1845 vw, 1813 m, 1801 m
$Co_4(CO)_8[(CH_3)_3C_6H_3]P(OPh)_3$	2052.3 m, 2019.1 s, 1996.7 s, 1987 s 1845 vw, 1819.5 m, 1808 m (br)

[a] In CCl_4.

(a) The (lowest) band at 1975.1 cm^{-1} can be attributed primarily to the stretching vibration of the carbonyl group on Co(3)* as influenced by the electron donating effect of the P-ligand.

(b) The rest of the spectrum may be attributed to a bent square planar ("roof") $M_2(CO)_4(bridge)_2$ structure of approximate C_{2v} symmetry; the assignments (cf. Lewis et al. [10]**) using the notation of C_{2v} modes, are: A_1 2052.2; B_1 2019.6; B_2 1995.1; A_2 (inactive if strict C_{2v} selection rules operate) 1985.6 cm^{-1}.

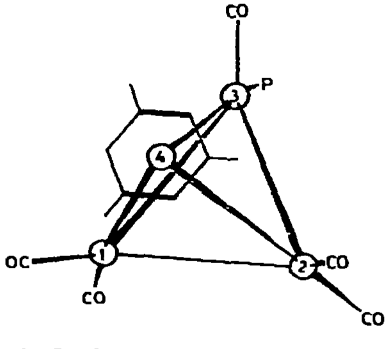

Fig. 2. The supposed structure of (mesitylene)octacarbonyltetracobalt trimethylphosphite. (Bridges between 1, 2 and 3 are omitted.)

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* Similar behaviour of the ν(C—O) vibration was postulated for $(AsEt_3)_2COCo(CO)_2Co(CO)_3$ [9].

** These authors assigned the ν(C—O) bands of $Rh_2(CO)_4X_2$ (X = Cl, Br, I, SEt, SPh) compounds by means of isotopic studies. They also determined the approximate position of the A_2 (IR inactive) band. The results seem to be applicable to several similar compounds [11] even with unequal ligands in the bridges [12].

This picture becomes more convincing when the spectrum of $Co_4(CO)_8$-$[(CH_3)_3C_6H_3]P(OMe)_3$ is compared with that of its $P(OPh)_3$ analogue: in the spectrum of this latter compound the part attributed to the $Co(1)Co(2)(CO)_4$ moiety is almost unchanged, whereas the lowest band is shifted by about 12 cm^{-1} towards higher wave numbers and fuses with the lowest of the bands attributed to the $Co(1)Co(2)(CO)_4$ part of the molecule. The "mobility" of the lowest band, the direction of its shift, the constancy of the rest of the terminal ν(C—O) spectrum, as well as a moderate upward shift in the average bridge CO frequency ($\Delta\tilde{\nu}_{bridge}$ = +5 cm^{-1}) are all in good agreement with the rough assignment made above.

It is of interest to compare the spectra of $Co_4(CO)_{11}P(OMe)_3$ [13] and $Co_4(CO)_{11}P(OPh)_3$, since similar behaviour of bands is observed for this pair of compounds. Upon changing from $P(OMe)_3$ to $P(OPh)_3$ the lowest band is shifted 12 cm^{-1} upwards, fuses with the band which was at this position in the spectrum of the $P(OMe)_3$ derivative, and the relative intensity of the new band agrees with the sum of that of its components; the rest of the terminal spectrum changes in this cases also only by 2-3 cm^{-1}, and the average bridge CO frequency is increased by 5-6 cm^{-1}. This analogous behaviour confirms that in the monophosphite derivatives of $Co_4(CO)_{12}$ the phosphorus ligand has replaced a terminal CO in the "basal plane" (containing the bridges), and, for steric reasons, this is most probably an axial one.

Experimental

Preparation of $Co_4(CO)_9$(arene) compounds

$Co_4(CO)_9$(arene) complexes were prepared from $Co_4(CO)_{12}$ and arenes, as described by Bor and his co-workers [5]. To suppress decomposition to metallic cobalt, the heating of the $Co_4(CO)_{12}$ arene mixtures was performed in a 5 m long glass coil-tube under argon with 1-3 min residence time. Reaction temperatures generally corresponded to the boiling point of the arene used, but did not exceed 165°. The following yields were achieved after chromatography, evaporation of the heptane/benzene eluent and recrystallization: for $Co_4(CO)_9$(arene): arene = mesitylene, 35%; iso-durene, 33%; *m*-xylene, 30%; *o*-xylene, 25%; *p*-xylene, 22%; anisole, 20%; toluene, 20%; biphenyl, 16%; benzene, 10%; fluorene, 8%; phenanthrene, 2%.

Reaction of $Co_4(CO)_9[(CH_3)_3C_6H_3]$ with CO

Experiments were carried out in a thermostatted flask. $Co_4(CO)_9$-$[(CH_3)_3C_6H_3]$ (10^{-4} mol) was dissolved in 50 ml heptane and CO was bubbled through the solution at 100° for 1 h. The reaction mixture was separated by chromatography on activated silica gel with 2/1 heptane/benzene as eluent. The yield of $Co_4(CO)_{12}$ was 20%.

Preparation of $Co_4(CO)_{11}P(OR)_3$ ($R = CH_3, C_6H_5$)

$Co_4(CO)_{11}P(OMe)_3$ was prepared by Labroue and Poilblanc's method [14] from $Co_4(CO)_{12}$ and $P(OMe)_3$ in heptane at 0°.

$Co_4(CO)_{11}P(OPh)_3$ was obtained by adding to the stirred solution of 5×10^{-3} mol of $Co_4(CO)_{12}$ in 500 ml heptane 5×10^{-3} mol of $P(OPh)_3$ in 100 ml heptane dropwise at 50° under argon. After 30 min the products were separated by chromatography on silica gel with 1/1 heptane/benzene as eluent. Complexes were obtained after recrystallization from heptane as black crystals, soluble in most organic solvents to give dark red solutions, though the disubstituted compound dissolved only slowly in aliphatic hydrocarbons. The first fraction gave 2.56 g (59%) $Co_4(CO)_{11}P(OPh)_3$. (Analysis found: Co, 28.1; P, 3.94. $C_{29}H_{15}Co_4O_{14}P$ calcd.: Co, 27.6; P, 3.63%.)

From the second fraction was obtained 0.85 g (15%) $Co_4(CO)_{10}$-$(P(OPh)_3)_2$. (Analysis found: Co, 20.9; P, 6.10. $C_{46}H_{30}Co_4O_{16}P_2$ calcd.: Co, 20.5; P, 5.45%.)

Preparation of $Co_4(CO)_8(arene)P(OR)_3$ *(R =* CH_3, C_6H_5*)*

Method A. A solution of 10^{-3} mol of $Co_4(CO)_9[(CH_3)_3C_6H_3]$ in 100 ml heptane and 5 × 10^{-3} mol of $P(OMe)_3$ was stirred at 65° for 30 min. Chromatography on silica gel gave a dark yellow-brown fraction. After evaporation in high vacuum [removing $P(OMe)_3$] and recrystallization from heptane, Co_4-$(CO)_8[(CH_3)_3C_6H_3]P(OMe)_3$ was obtained as black crystals, which were soluble in most organic solvents. Yield 0.11 g (16%). (Analysis found: Co, 33.7; P, 4.62; mol. wt. 681. $C_{20}H_{21}Co_4O_{11}P$ calcd.: Co, 33.5; P, 4.11%; mol. wt., 704.)

In the case of $P(OPh)_3$ 80° and 60 min were used. The by-product $Co_2(CO)_6[P(OPh)_3]_2$ was filtered off. We could not completely remove the residual of $P(OPh)_3$ from $Co_4(CO)_8[(CH_3)_3C_6H_3]P(OPh)_3$ because the complex decomposed on chromatography.

Method B. A solution of 10^{-3} mol $Co_4(CO)_{11}P(OMe)_3$ in *m*-xylene was heated 4-5 times to 140° in the coil-tube apparatus. Products were separated on non-activated silica gel with 1/1 heptane/benzene as eluent. Evaporation of the fraction containing $Co_4(CO)_8[m\text{-}(CH_3)_2C_6H_5]P(OMe)_3$ and recrystallization from heptane gave 0.07 g (10%) of complex. (Analysis found: Co, 34.8; P, 4.49. $C_{19}H_{19}Co_4O_{11}P$ calcd.: Co, 34.2; P, 3.92%.)

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