Structure and Reactions of Bis[tricarbonyl(π-cyclopentadienyl)chromium]

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$[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ is extremely reactive. It readily undergoes reactions which involve homolytic or heterolytic scission of the Cr–Cr bond, or the insertion of another atom into it. These observations are rationalized in terms of the structure of the dimer, and this is discussed in detail. Some facile CO substitution reactions of $[(\pi\text{-}C_5H_5Cr(CO)_3]_2$ and $(\pi\text{-}C_5H_5)Cr(CO)_3I$ with phosphorus(III) ligands are described.

ALTHOUGH the chemistry of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ has been studied in detail,[1] much less attention has been paid to its relatively inaccessible chromium analogue $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$. As this last compound reacts more readily with tin(II) halides than does its molybdenum and tungsten counterparts,[2] we have investigated its structure and chemistry. The results are reported here.

EXPERIMENTAL

Literature methods or extensions of them were used to prepare $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$,[1,3] $[(\pi\text{-}MeC_5H_4)Cr(CO)_3]_2$,[1,3] and the hexaorganodilead compounds.[4] Other chemicals were purchased from the usual sources.

All reactions were carried out under an atmosphere of nitrogen at room temperature (unless stated otherwise) using purified solvents. They were monitored by i.r. spectroscopy.

$[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ (0·4 g) in tetrahydrofuran or toluene (*ca.* 25 ml) was stirred with zinc powder (2 g), cadmium powder (2 g), or mercury (1 ml) for 30 min. The solvents were removed and the residues recrystallized from ethanol to give $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2M$ (M = Cd [5] or Hg [6]) in *ca.* 80% yields. No pure products could be isolated with zinc. High yields of $(C_4H_8O)_2Cd[Co(CO)_4]_2$,[5] $Hg[Co(CO)_4]_2$,[7] $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$,[6] and $[(\pi\text{-}C_5H_5)W(CO)_3]_2Hg$ [6] were obtained by similar reactions. These were complete within 10 min using $Co_2(CO)_8$ in tetrahydrofuran at room temperature, but they required 4 and 12 days respectively for $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ in refluxing dioxan.

$[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ (*ca.* 0·5 g) and thallium(I) acetate (*ca.* 0·5 g) were refluxed in ethanol for 10 min. On cooling the hot filtered reaction mixture, crystals of $Tl[(\pi\text{-}C_5H_5)Cr(CO)_3]_3$ were deposited (yield *ca.* 40%). $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ gave a similar product [8] after *ca.* 1 h in refluxing butanol.

$[(\pi\text{-}C_5H_5)Cr(CO)_3]_2Hg$ [6] was the sole product, after 30 min, from the reaction of equimolar amounts of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ (0·5 g) and mercury(I) chloride in tetrahydrofuran (25 ml) (yield, 55%). Under the same conditions, mercury(II) chloride gave only $(\pi\text{-}C_5H_5)Cr(CO)_3HgCl$ (yield 29%).[9]

Although $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ did not react with Ph_4Pb or Ph_3PbMe in refluxing butanol, Ph_3MCl, Ph_2MCl_2, R_6Pb_2, or Me_3PbOAc gave $(\pi\text{-}C_5H_5)Cr(CO)_3MPh_3$,[10] $(\pi\text{-}C_5H_5)Cr(CO)_3MClPh_2$, $(\pi\text{-}C_5H_5)Cr(CO)_3PbR_3$, or $(\pi\text{-}C_5H_5)Cr(CO)_3PbMe_3$ within 5 min (reactant mole ratio = 1 : 1; M = Sn or Pb; R = Ph, $p\text{-}MeC_6H_4$, $p\text{-}MeOC_6H_9$, or cyclohexyl). The products were isolated by allowing the hot filtered reaction mixtures to cool. The precipitated crystals were filtered off (yields, 40—85%).

$[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ (1 g) was heated to reflux in toluene (25 ml) for 2½ h. The solvent was removed, and the residue crystallized from toluene–petrol to give $[(\pi\text{-}C_5H_5)Cr(CO)_2]_2$ in *ca.* 90% yield. $[(\pi\text{-}MeC_5H_4)Cr(CO)_2]_2$ and $[(\pi\text{-}PhCH_2C_5H_4)Cr(CO)_2]_2$ were prepared similarly.

Equimolar amounts of Ph_3P and $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ (1 g) in ethanol (50 ml) were heated on a steam-bath for 1 h. The hot solution was filtered, and on cooling deposited bright yellow crystals of $[(\pi\text{-}C_5H_5)Cr(CO)_2PPh_3]_2$. Other phosphines gave similar though less stable products which could not be isolated, but $(MeO)_3P$ in warm tetrahydrofuran solution gave a low yield of yellow *trans*-$(\pi\text{-}C_5H_5)Cr(CO)_3\{P(OMe)_3\}P(O)(OMe)_2$.

$[(\pi\text{-}C_5H_5)Cr(CO)_3I]$ [9] was prepared by the reaction of equimolar amounts of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ and iodine in carbon tetrachloride solution. When it (1 g) was refluxed in pentane solution with monodentate tertiary phosphines and phosphites (L) for 5—60 min, and the filtered reaction mixtures cooled, $[(\pi\text{-}C_5H_5)Cr(CO)_2(L)I]$ were obtained as purple crystals. With $Ph_2PCH_2CH_2PPh_2$, in ether, yellow $(\pi\text{-}C_5H_5)Cr(CO)_2(Ph_2PCH_2CH_2PPh_2)I$ was the product.

When stirred with mercury metal in tetrahydrofuran solution for *ca.* 1 h, $[(\pi\text{-}C_5H_5)Cr(CO)_3Br]$ [9] and $(\pi\text{-}C_5H_5)Cr(CO)_3I$ [9] gave $(\pi\text{-}C_5H_5)Cr(CO)_3HgX$ [9] (X = Br or I). These were purified by crystallization from ethanol.

The various products were identified by analyses, m.p.s, and spectra. The data for new compounds are given in Table 1. I.r. spectra were obtained as described previously.[11] N.m.r. spectra were run on a Perkin-Elmer R12 spectrometer.

RESULTS AND DISCUSSION

The i.r. spectra of various $(\pi\text{-}C_5H_5)Cr(CO)_3X$ compounds are very similar to those of their molybdenum counterparts in the C–O stretching region (*e.g.* ref. 1 where X = Ph_3Sn). Thus it is probable that the distribution of the ligands about the Cr atom is similar

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[10] H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1401.

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to that found in, *e.g.*, $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$,[12] and that in $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ where two such polyhedra are joined by a Cr–Cr bond. $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ has a similar structure and adopts a centrosymmetric *trans* configuration in the solid state.[13] In solution, this isomer is in equilibrium with a gauche species.[14] A similar equilibrium is observed for $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ (Table 2), but here the gauche form is important even in non-polar solvents. However, the absence of any absorption band with a frequency greater than *ca.* 1960 cm^{-1} due to ν(CO) modes in the i.r. spectra of solid samples of this compound implies that it adopts a *trans* structure in the solid state.

TABLE 1

Melting points, analyses, and i.r. spectra of some complexes described in the text

		Analyses						
		Found (%)			Required (%)			
	M.p.[a] (t/°C)	C	H	X	C	H	X	I.r. spectra[b]
$(C_5H_5)Cr(CO)_3Pb(C_6H_4Me\text{-}p)_3$	152—154	51·1	3·9		51·1	3·8		1901(6·8), 1922(3·3), 1982(10)
$(C_5H_5)Cr(CO)_3Pb(C_6H_4OMe\text{-}p)_3$	100—101	48·2	3·7		47·7	3·6		1901(6·5), 1922(3·5), 1981(10)
$(C_5H_5)Cr(CO)_3Pb(C_6H_{11})_3$	dec. 185	47·8	6·7		47·5	5·9		1879(7·3), 1900(2·9), 1964(10)
$(C_5H_5)Cr(CO)_3Pb(Cl)Ph_2$ [c]	134—136	40·1	2·6	5·8	40·2	2·5	6·0	1917(4·6), 1949(4·0), 1999(10)
$(C_5H_5)Cr(CO)_3Sn(Cl)Ph_2$ [c]	138—140	47·0	2·8	7·1	47·1	3·0	7·0	1905(6·1), 1941(4·0), 1998(10)
$[(C_5H_5)Cr(CO)_3]_3Tl$	220—222	35·1	1·9		35·7	1·9		1899(7·0), 1948(10), 1973(1·1)
$[(C_5H_5)Cr(CO)_2]_2$ [d]	205—206	48·2	2·9	30·6	48·6	2·9	30·1	1881(10), 1904(9·0)
$[(MeC_5H_4)Cr(CO)_2]_2$	128—129	51·3	3·9		51·2	3·8		1875(10), 1897(8·5)
$[(PhCH_2C_5H_4)Cr(CO)_2]_2$	162—164	64·2	4·3		63·8	4·2		1875(10), 1900(8·5)
$[(C_5H_5)Cr(CO)_2(PPh_3)]_2$	176—179	68·6	4·8		69·0	4·6		1808(6·3), 1956(10)
$(C_5H_5)Cr(CO)_2\{P(OMe)_3\}P(O)(OMe)_2$	112—114	35·2	5·1		35·4	4·9		1902(10), 1969(2·9)
$(C_5H_5)Cr(CO)_2(PPh_3)I$	dec. 130	53·4	3·6		53·4	3·6		1906(10), 1974(3·5)
$(C_5H_5)Cr(CO)_2(PBu_3)I$	82—84	45·8	6·3		45·4	6·2		1888(7·5), 1959(10)
$(C_5H_5)Cr(CO)_2\{P(OPh)_3\}I$	110—111	50·2	3·1		49·2	3·3		1922(5·7), 1979(10)
$(C_5H_5)Cr(CO)_2\{P(OMe)_3\}I$ [e]	85—86	27·8	3·1	28·6	28·3	3·3	28·0	1914(10), 1972(3·6)
$(C_5H_5)Cr(CO)_2(Ph_2PCH_2CH_2PPh_2)I$	dec. 160	57·0	4·6		56·6	4·2		1910(5·2), 1964(10)

[a] Determined in sealed tubes, dec. = decomposes without melting. [b] Absorption bands due to ν(CO) vibrations. Peak positions (cm^{-1}) with relative peak heights in parentheses determined in CS_2 solution. [c] X = Cl. [d] X = Cr. [e] X = I.

TABLE 2

The effect of solvent on the i.r. spectrum of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$

Solvent[a]	Absorption bands[b]				
Heptane	1920(3·9)	1932(5·5)	1957(10)		2005(2·8)
CS_2	1898(sh)	1911(4·1)	1922(7·7)	1946(10)	2011(2·3)
$CHCl_3$	1890 (sh)	1913 (sh)	1925(8·3)	1948(10)	2012(3·9)
Xylene	1905 (sh)	1912(3·9)	1922(7·7)	1945(10)	2008(1·3)
THF	1895 (sh)	1911(4·4)	1924(8·9)	1948(10)	2005(4·2)
DMSO	1769(10)	1890(8·9)	1949(2·5)	1976(4·7)	2036(2·5)
DMF	1772(10)	1891(9·2)	1952(2·2)	1977(5·3)	2039(2·7)

[a] THF = tetrahydrofuran, DMSO = dimethyl sulphoxide, and DMF = dimethylformamide. [b] Peak positions with relative peak heights in parentheses.

When it is dissolved in very polar solvents such as dimethylformamide or dimethyl sulphoxide, $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ ionizes completely to $[(\pi\text{-}C_5H_5)Cr(CO)_3S]^+[(\pi\text{-}C_5H_5)Cr(CO)_3]^-$. The presence of the anion is confirmed unequivocally by the two absorption bands at *ca.* 1770 and 1880 cm^{-1} due to its ν(CO) vibrations,* whilst the frequencies and relative intensities of the three absorption bands at *ca.* 1950, 1977, and 2038 cm^{-1} are consistent with the presence of the cation where the ligand S is a co-ordinated solvent molecule. Neither $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ nor $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ ionize in these solvents.

We have previously reported that $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ reacts more readily than its Mo and W counterparts with tin(II) halides.[2] A similar difference in reactivity is observed in the insertion of metallic cadmium or mercury into the metal–metal bond. Furthermore, of the dimeric carbonyls or cyclopentadienyl carbonyls of Mo, W, Mn, Re, Fe, and Co, only $Co_2(CO)_8$ gives $Hg[Co(CO)_4]_2$ or its cadmium counterpart at room temperature, and is actually somewhat more reactive than the chromium dimer. In all other instances more vigorous conditions were necessary (*e.g.* ref. 15). In view of this high reactivity the formation of $Tl[Cr(CO)_3(\pi\text{-}C_5H_5)]_3$ was not surprising.

Although the scission of the Cr–Cr bond by iodine, Ph_3MCl, Ph_2MCl_2, and Me_3PbOAc (M = Sn or Pb) was expected (*cf.* ref. 16), the reaction with R_6Pb_2 (R = Ph, p-MeC_6H_9, p-$MeOC_6H_4$, or *cyclo*-hexyl) to give $(\pi\text{-}C_5H_5)Cr(CO)_3PbR_3$ was not. Comparable reactions are those of Pt^0 complexes with Ph_6Pb_2 to give $(Ph_3P)_2Pt(PbPh_3)_2$,[17] and of Me_6Sn_2 with various metal carbonyl derivatives to give compounds containing transition metal–tin bonds.[18] $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ decomposed before it reacted with Me_6Sn_2 in boiling butanol.

We have found that many dimeric metal carbonyl complexes give products analogous to $(\pi\text{-}C_5H_5)Cr(CO)_3$-

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* For $[Et_4N][(\pi\text{-}C_5H_5)Cr(CO)_3]$ in dimethyl sulphoxide solution ν(CO) = 1768 and 1878 cm^{-1}.

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[16] P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1972, 1467.

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[18] E. W. Abel and S. Moorehouse, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 905.

HgCl on reaction with mercury(II) chloride.[19] However, we are unable to account for the different product, $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2Hg$, obtained with mercury(I) chloride.

The decomposition of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ to $[(\pi\text{-}C_5H_5)Cr(CO)_2]_2$ in refluxing toluene is unusual. In most instances, cyclopentadienylmetal carbonyls give cluster complexes under such conditions, *e.g.* $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ is converted to $[(\pi\text{-}C_5H_5)Fe(CO)]_4$.[20] The i.r. spectrum of $[(\pi\text{-}C_5H_5)Cr(CO)_2]_2$ is similar to that of $[(\pi\text{-}C_5Me_5)Cr(CO)_2]_2$,[21] and so it is probable that the first has a structure similar to that found for the second.[22] It is possible that in the preparation of $[(\pi\text{-}C_5Me_5)Cr(CO)_2]_2$, $[(\pi\text{-}C_5Me_5)Cr(CO)_3]_2$ was formed but decarbonylated under the conditions of the experiment.[21]

$[(\pi\text{-}C_5H_5)Cr(CO)_2]_2$ reacted with phosphines, but no products could be isolated. With iodine, only a very low yield of $(\pi\text{-}C_5H_5)Cr(CO)_3I$ could be isolated.

The mode of reaction of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ with triphenylphosphine differs from that of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$. Even under the mild conditions employed, $[(\pi\text{-}C_5H_5)Cr(CO)_2PPh_3]_2$ was the only product. There was no evidence for the monosubstituted or ionic compounds {*cf.* $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and tertiary phosphines [23,24]}. The product is cleaved by iodine to $(\pi\text{-}C_5H_5)Cr(CO)_2(PPh_3)I$, and with mercury at room temperature it gives $[(\pi\text{-}C_5H_5)Cr(CO)_2(PPh_3)]_2Hg$.[9] Other phosphines and triphenyl phosphite form similar, but less stable, compounds to those given by Ph_3P. However, with $(MeO)_3P$, the only isolated product was *trans*-$(\pi\text{-}C_5H_5)Cr(CO)_2\{P(OMe)_3\}P(O)(OMe)_2$ {*cf.* $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $(MeO)_3P$ [25]}.

In view of the ease with which Ph_3P replaced CO in the dimer, we also investigated the substitution reactions of the most stable halide $(\pi\text{-}C_5H_5)Cr(CO)_3I$. They took place under milder conditions than had been required for the molybdenum counterpart,[1,11] and various $(\pi\text{-}C_5H_5)Cr(CO)_2(L)I$ complexes were formed. These gave rise to two absorption bands in the i.r. spectra which may be assigned to their $\nu(CO)$ vibrations. Their relative intensities indicate that when $L = (MeO)_3P$ or Ph_3P, the complexes exist in solution solely or predominately as *trans* isomers, when $L = (PhO)_3P$ as *cis* isomers, and when $L = Bu^n{}_3P$ as a mixture of the two. ^1H N.m.r. spectra were difficult to obtain, but those in $CDCl_3$ solution show that when $L = (MeO)_3P$, the cyclopentadienyl protons give rise to a doublet resonance at τ 5·02 with J(P-H) *ca.* 5 c.p.s., when $L = (PhO)_3P$ a broad singlet at τ 5·13, and when $L = Bu^n{}_3P$ an asymmetric singlet at τ 4·99. These observations are consistent with those reported for $(\pi\text{-}C_5H_5)Mo(CO)_2(L)I$ and related complexes.[1,11] Although the yellow product obtained from $(\pi\text{-}C_5H_5)Cr(CO)_3I$ and $Ph_2PCH_2CH_2PPh_2$ appears to be $(\pi\text{-}C_5H_5)Cr(CO)_2(Ph_2PCH_2CH_2PPh_2)I$, its solubility in carbon disulphide implies that, unlike its yellow molybdenum counterpart,[26] it is not ionic. Its low stability prevented further study.

Both $(\pi\text{-}C_5H_5)Cr(CO)_3I$ and its bromo-analogue react very readily with mercury to give $(\pi\text{-}C_5H_5)Cr(CO)_3HgX$ (X = Br or I). A similar reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ requires drastic conditions.[27]

Many of the reactions of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ imply that the Cr–Cr bond is weak relative to the metal–metal bonds in its Mo and W counterparts. The strength of a metal–metal bond and the bond lengths observed are the results of a balance of attractive, bonding, forces between the metal atoms, and repulsive forces between 'adjacent' ligands co-ordinated to the different metal atoms. As $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ has a structure similar to that of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, it is unlikely that the 'adjacent' interactions would allow the Cr–Cr bond to be markedly shorter than the already long Mo–Mo bond of length 3·22 Å.[13] Thus the constraints imposed by the structure prevent the optimum overlap of orbitals, and so a weak Cr–Cr bond results.[*]

The consequences of the 'adjacent' interactions may be eliminated by cleavage of the metal–metal bond either homolytically *e.g.* in the reaction with hexaphenyldilead, or heterolytically *e.g.* in the ionization in dimethyl sulphoxide solution. Alternatively, they may be reduced by the insertion of another atom such as mercury between the two $(\pi\text{-}C_5H_5)Cr(CO)_3$ moieties. Therefore, such reactions take place much more readily than with $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$. The thermal decomposition of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ to $[(\pi\text{-}C_5H_5)Cr(CO)_2]_2$ also results in a reduction of the 'adjacent' interactions by the loss of two carbonyl ligands and the adoption of a *trans* structure.

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[*] *Added in proof:* A recent *X*-ray diffraction study (R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1974, **96**, 749) has confirmed that the Cr–Cr bond in $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ is unusually long, and these authors also suggest that adjacent interactions are responsible for this.

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