Some Chemistry of Ethyltetramethylcyclopentadienylcobalt: Arene, Ethylene, Butadiene, Ammine, Tertiary Phosphine, and Chloro-derivatives

By **Malcolm L. H. Green** * and **Richard B. A. Pardy**, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

Tri-n-butyl(ethyltetramethylcyclopentadienyl)tin, Sn(etmcp)Bu$^n_3$, reacts with cobalt(II) chloride to give, after treatment with chlorine, [{Co(etmcp)Cl(μ-Cl)}$_2$] and [Co$_3$(etmcp)$_2$Cl$_6$]. Using these compounds as precursors, many derivatives of the Co(η-etmcp) system have been prepared; examples are [(η-etmcp)Co(μ-Cl)$_3$Co(η-etmcp)][FeCl$_4$], [Co(η-etmcp)(PPh$_3$)Cl$_2$], [Co(η-etmcp)L$_2$Cl][PF$_6$] [L$_2$ = Ph$_2$P(CH$_2$)$_2$PPh$_2$, or (PMe$_2$Ph)$_2$], [Co(η-etmcp)L$_3$][PF$_6$] [L$_3$ = (NH$_3$)$_3$, (MeCN)$_3$, (MeCN)$_2$(Me$_2$C=NH), (CH$_2$=CHCN)$_3$, η-benzene, or η-toluene], and [Co(η-etmcp)L$_2$][L$_2$ = (η-C$_2$H$_4$)$_2$, butadiene, or 1,5-C$_8$H$_{12}$].

IT has been demonstrated that the chemistry of pentamethylcyclopentadienyl derivatives of Group 4 transition metals can differ markedly from that of the unsubstituted cyclopentadienyl compounds of these metals.[1] Apart from these studies, the most extensively explored pentamethylcyclopentadienyl derivatives are those arising from the work of Maitlis especially on rhodium, iridium, palladium, and platinum.[2] There are also a few reports of pentamethylcyclopentadienyl carbonyl derivatives of Fe,[3] Co,[4] Mn,[5] Re,[6] and Group 6 metals.[5-7] We have recently shown that cyclopentadienyltin trialkyl derivatives are convenient reagents for the synthesis of cyclopentadienylmetal halide complexes, one of the advantages of these reagents being their solubility in non-polar solvents.[8] We were interested to explore the utility of the cyclopentadienyltin reagents and, in particular, to examine the extent to which peralkylation of the cyclopentadienyl ring led to interesting differences compared with the unsubstituted η-cyclopentadienyl metal analogues. Here we describe the results of our studies on some ethyltetramethylcyclopentadienylcobalt compounds. The ligand ethyltetramethylcyclopentadienyl (etmcp) was chosen in preference to pentamethylcyclopentadienyl since, at the time this work was begun, it seemed that the former was much more readily accessible.[9] However, attention has recently been drawn to an improved route to pentamethylcyclopentadienyl salts.[10]

RESULTS

Chemical Studies.—Treatment of anhydrous cobalt(II) chloride with tri-n-butyl(ethyltetramethylcyclopentadienyl)tin gives a red-brown, volatile, air-sensitive oil which after treatment with chlorine gas gives a green powder. Crystallisation of the green powder gave green crystals of [{Co(etmcp)Cl$_2$}$_2$] (1) and blue microcrystals of [Co$_3$(etmcp)$_2$Cl$_6$] (2). The stoicheiometry of (1) was established by total analysis, and determination of the molecular weight in chloroform. Compound (1) is diamagnetic and the ^{1}H n.m.r. spectrum clearly shows the presence of the etmcp group.

Compound (2) appeared to decompose in air. The ^{1}H n.m.r. spectrum showed a series of broad bands. No e.s.r. spectrum could be obtained. The compound dissolved in water, concentrated hydrochloric acid, liquid sulphur dioxide, dichloromethane, and 1,4-dichlorobutane; solutions were intensely blue. Crystals obtained from 1,4-dichlorobutane solutions were of excellent appearance but *X*-ray diffraction studies showed them to be twinned. The molar conductance in dichloromethane was low (0.140 S cm^2 mol^{-1}). The electronic spectrum of (2) in dichloromethane shows a broad band centred at 638 nm (ε 4.32 × 10^5 dm^3 mol^{-1} m^{-1}. The mass spectrum of (2) shows a highest band at *m/e* corresponding to an ion of stoicheiometry [Co$_2$(etmcp)$_2$Cl$_2$]$^+$. Addition of iron(II) chloride to a solution of (2) in concentrated hydrochloric acid followed by exposure to air gave turquoise crystals of the compound [Co$_2$(etmcp)$_2$(μ-Cl)$_3$][FeCl$_4$] (3). The crystal structure of (3) has been determined [11] and is shown in the Scheme. Further data characterising (3) are given in the Table.

When the blue dichloromethane solutions of (2) are treated with water the aqueous phase becomes blue and the dichloromethane layer becomes green owing to the presence of (1). Indeed, it was possible to convert aqueous solutions of (2) into (1) by extraction with chlorobenzene. From the above observations we conclude that (2) probably has a structure closely related to that of (3) including a binuclear [Co$_2$(etmcp)$_2$Cl$_3$] unit. There is no clear evidence for the presence of the [CoCl$_4$]$^{2-}$ ion in (2).

Treatment of (1) with triphenylphosphine gives the air-stable blue compound [Co(etmcp)(PPh$_3$)Cl$_2$] (4) which crystallises from dichloromethane–toluene as the toluene solvate. The crystal structure of (4) [11] is given in the Scheme. The closely related compound [Co(η-C$_5$Me$_5$)(PPh$_3$)I$_2$] has been described.[12] Addition of dimethylphenylphosphine to (1) gave a blue oil presumably analogous to (4). The oil dissolved in water giving red solutions from which the red-brown compound [Co(η-etmcp)(PMe$_2$Ph)$_2$Cl][PF$_6$] (5) was readily crystallised. The related compound [Co(etmcp)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Cl][PF$_6$] (6) was obtained from (1) and 1,2-bis(diphenylphosphino)ethane in the same way.

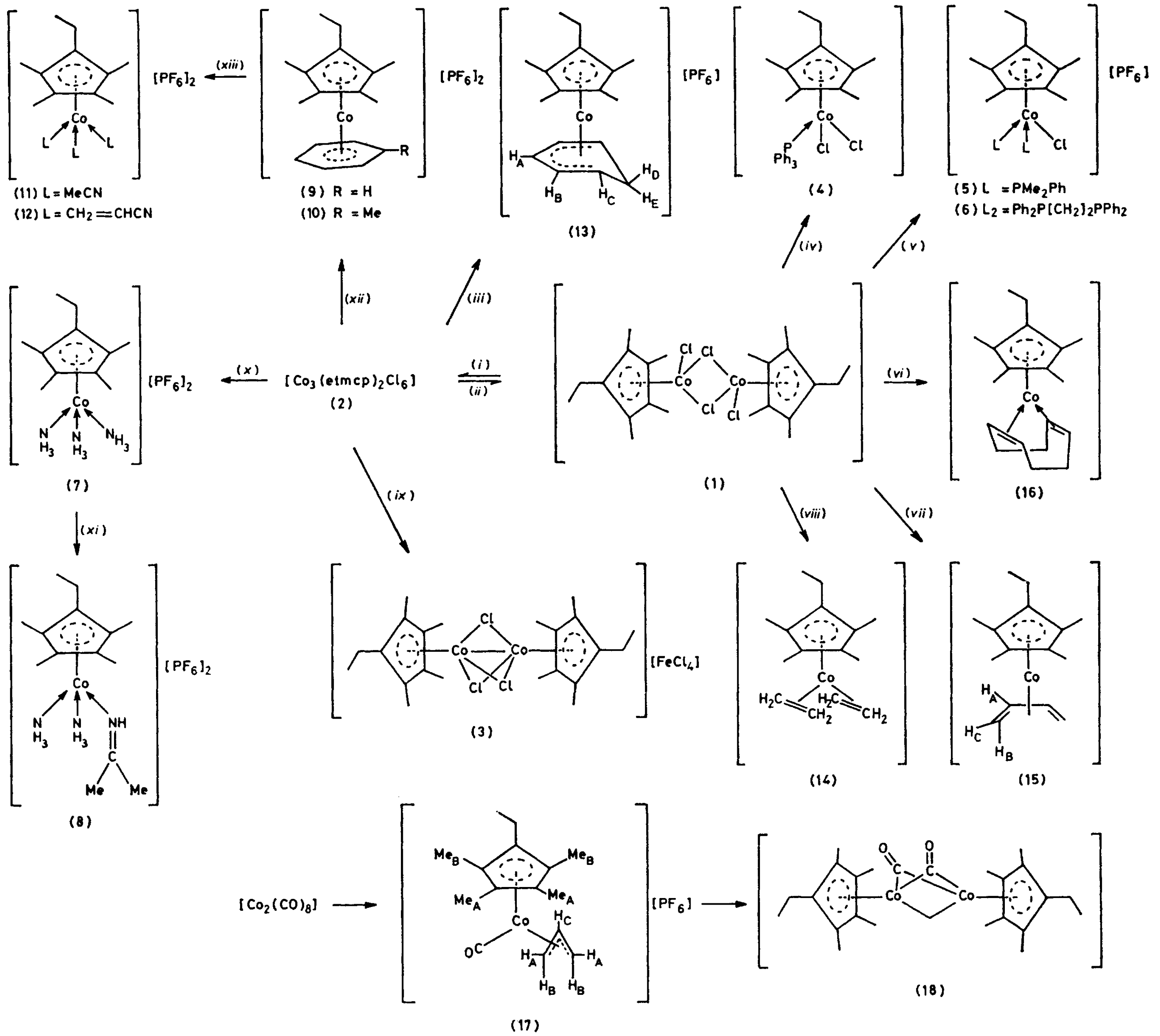
Compounds (1) and (2) dissolve readily in aqueous ammonia giving red air-stable solutions, from which the compound [Co(η-etmcp)(NH$_3$)$_3$][PF$_6$]$_2$ (7) may be isolated. This compound is very soluble in acetonitrile and acetone and reacts with the latter giving red prisms which the data in the Table suggest to be [Co(etmcp)(NH$_3$)$_2$(HN=CMe$_2$)][PF$_6$]$_2$·0.5Me$_2$CO (8).

Treatment of (2) with dichloro(ethyl)aluminium in benzene gives a yellow oil which dissolves in water. Addition of hexafluorophosphate gives [Co(η-etmcp)(η-C$_6$H$_6$)][PF$_6$]$_2$ (9) in high yield. The toluene analogue [Co(η-etmcp)(η-C$_6$H$_5$Me)][PF$_6$]$_2$ (10) is similarly prepared using toluene solutions of (AlEtCl$_2$)$_2$. The arene ligands in (9) and (10) are quite readily displaced. For example, these compounds in warm acetonitrile or acrylonitrile give

Analytical and spectroscopic data

	Compound	Colour	Analysis (%) [a]				^{1}H N.m.r. [b]
			C	H	Cl or N	Co	
(1)	$[\{Co(etmcp)Cl(\mu\text{-}Cl)\}_2]$	Green	46.8 (47.3)	6.1 (6.1)	24.4 (25.4)	20.7 (21.2) [e]	7.3, **2** q (*J* 7.5), CH_2 of Et; 8.35, **12**, *s*, 4 Me (A and B); 8.6, **3**, *t* (*J* 7.5), Me of Et [d]
(2)	$[Co_3(etmcp)_2Cl_6]$	Deep blue	38.3 (38.4)	5.1 (4.9)	31.2 (31.0)	25.7 (25.7) [e]	6.6, vbr; 7.2, vbr, rel. intensity 1 : 2
(3)	$[(etmcp)Co(\mu\text{-}Cl)_3Co(etmcp)][FeCl_4]$	Turquoise	36.9 (36.6)	5.0 (4.7)	34.6 (34.4)	16.1 (16.4)	
(4)	$[Co(etmcp)(PPh_3)Cl_2]\cdot C_6H_5Me$	Deep blue	68.5 (68.4)	6.7 (6.3) [f]			2.1, 2.5, 2.65, **20**, *c*, 4 Ph; 7.5, **3**, *s*, Me of C_6H_5Me; 7.9, **2**, *q*, (*J* 7), CH_2; 8.6, **6**, *s*, 2 Me (A or B); 8.7, **6**, *s*, 2 Me (B or A); 9.0, **3**, *t* (*J* 7), Me of Et [d]
(5)	$[Co(etmcp)(PMe_2Ph)_2Cl][PF_6]\cdot 0.5CH_2Cl_2$	Red	46.1 (46.6)	5.7 (5.7)	11.5 (10.0)	8.2 (8.3)	2.2, 2.5, **10**, *c*, 2 Ph; 4.5, **1**, *s*, 0.5 CH_2Cl; 8.0, **6**, *c*, Me_AP; 8.1, **2**, *q* (*J* 7.0), CH_2 of Et; 8.25, **6**, *c*, Me_BP; 8.65, **6**, *t* (*J* 1.65), 2 Me (A or B); 8.68, **6**, *t* (*J* 1.55), 2 Me (B or A); 9.1, **3**, *t* (*J* 7.0), Me of Et [g]
(6)	$[Co(etmcp)(Ph_2PCH_2CH_2PPh_2)Cl][PF_6]$	Deep red	57.0 (56.5)	5.6 (5.2)	5.0 (4.5)	7.8 (7.5)	2.0—2.6, **20**, *c*, 4 Ph; 6.9—7.5, **4**, *c*, CH_2CH_2; 7.9, **2**, *q* (*J* 7.5), CH_2 of Et; 8.45, **6**, *s*, 2 Me (A or B); 8.55, **6**, *s*, 2 Me (B or A), 8.8, **3**, *t* (*J* 7.5), Me of Et [d]
(7)	$[Co(etmcp)(NH_3)_3][PF_6]_2$	Red	24.5 (24.1)	5.0 (4.8)	7.2 (7.6)	10.8 (10.8)	7.1, **9**, br *s*, 3 NH_3; 7.58, **2**, *q* (*J* 8), CH_2 of Et; 8.4, **6**, *s*, 2 Me (A or B); 8.5, **6**, *s*, 2 Me (B or A); 8.9, **3**, *t*, Me of Et [g]
(8)	$[Co(etmcp)(NH_3)_2(HN{=}CMe_2)][PF_6]_2\cdot 0.5Me_2CO$	Red	29.8 (29.9)	5.7 (5.7)	6.75 (6.8)	9.6 (9.5)	6.25, **1**, br *s*, NH of $Me_2C{=}NH$; 7.05, **6**, br *s*, 2 NH_3; 7.50, **3**, *s*, Me of Me_2C; 7.54, **3**, *s*, Me of Me_2C; 7.9, **3**, *s*, 0.5 Me_2CO; 8.40, 8.42, **12**, *d*, 4 Me (A and B); 8.9, **3**, *t*, Me of Et [g]
(9)	$[Co(etmcp)(\eta\text{-}C_6H_6)][PF_6]_2$	Yellow	35.2 (35.4)	4.7 (4.0)		10.5 (10.2)	2.4, **6**, *s*, C_6H_6; 7.1, **2**, *q*, (*J* 9), CH_2 of Et; 7.6, 7.63, **12**, *d*, 4 Me (A and B); 8.8, **3**, *t*, (*J* 9), Me of Et [g]
(10)	$[Co(etmcp)(\eta\text{-}C_6H_5Me)][PF_6]_2$	Yellow	36.9 (36.6)	4.5 (4.2)		10.2 (10.0)	2.6, **5**, *c*, Ph; 7.15, **2**, *q* (*J* 9), CH_2 of Et; 7.25, **3**, *s*, Me of C_6H_5Me; 7.75, 7.77, **12**, d, 4 Me (A and B); 8.85, **3**, *t* (*J* 9), Me of Et [h]
(11)	$[Co(etmcp)(NCMe)_3][PF_6]_2$	Red	33.3 (32.9)	4.4 (4.2)	6.7 (6.7)	9.6 (9.5) [i]	7.6, **2**, *q* (*J* 9), CH_2 of Et; 7.9, **9**, *s*, 3 MeCN; 8.50, 8.52, **12**, *d*, 4 Me (A and B); 8.8, **3**, *t* (*J* 9), Me of Et [i]
(12)	$[Co(etmcp)(NCCH{=}CH_2)_3][PF_6]_2$	Red	37.4 (37.6)	4.2 (4.0)	6.3 (6.4)	9.0 (9.0) [j]	3.9, **9**, *c*, 3 $CH_2{=}CHCN$; 7.55, **2**, *q* (*J* 8), CH_2 of Et; 8.45, 8.47, **12**, *d*, 4 Me (A and B); 8.8, **3**, *t* (*J* 8), Me of Et [i]
(13)	$[Co(etmcp)(\eta\text{-}C_6H_7)][PF_6]$	Red-brown	46.8 (47.1)	6.1 (5.6)		13.8 (13.7) [k]	3.1, **1**, *t of d*, H_A; 4.73, **2**, *t of d*, H_B; 6.44, **2**, *t of t*, H_C; 7.0, **1**, *d of t*, H_D; 7.34, **2**, *q* (*J* 8), CH_2 of Et; 7.9, **12**, *s*, 4 Me (A and B); 8.55, **1**, *d of m*, H_E; 8.85, **3**, *t*, (*J* 8), Me of Et [g]
(14)	$[Co(etmcp)(\eta\text{-}C_2H_4)_2]$	Brown oil	68.0 (68.2)	9.4 (9.5)			7.72, **2**, *q* (*J* 7.9), CH_2 of Et; 8.4, **6**, *s*, 2 Me (A or B); 8.48, **6**, *s*, 2 Me (B or A); 8.95, **3**, *t* (*J* 7.9) Me of Et, 8.65 (centre), **8**, complex AA′BB′ *m*, 2 C_2H_4 [l]
(15)	$[Co(etmcp)(1,3\text{-}C_4H_6)]$	Red oil	68.5 (68.7)	8.9 (8.8) [n]			5.4, **2**, *c*, H_A; 7.49, **2**, *q* (*J* 7.3), CH_2 of Et; 8.02, 8.03, **12**, *d*, 4 Me (A and B); 8.5, **2**, *c*, H_B; 8.72, **3**, *t* (*J* 7.3), Me of Et; 9.85, **2**, *d* (*J* 8), H_C [l]
(16)	$[Co(etmcp)(1,5\text{-}C_8H_{12})]$	Orange wax	72.0 (72.1)	9.1 (9.2) [m]			7.2, **8**, br *c*, 4 CH_2 of C_8H_{12}; 7.7, **2**, *q* (*J* 7.7), CH_2 of Et; 7.85, **4**, *c*, 4 CH of C_8H_{12}; 8.28, **6**, *s*, 2 Me (A or B); 8.75, **6**, *s*, 2 Me (B or A); 8.75, **3**, *t* (*J* 7.7), Me of Et.[l] ^{13}C N.m.r.: 97.4, 91.8, 90.7, 69.8, 32.0, 17.5, 14.2, 8.1, 7.9 [l]
(17)	$[Co(etmcp)(\eta\text{-}C_3H_5)(CO)][PF_6]$	Orange-yellow	43.0 (42.6)	5.3 (5.2) [p]		14.2 (14.0)	5.2, **1**, *t of t* [*J*(H_AH_C)7, *J*(H_BH_C)12], H_C; 6.3, **2**, *d of t* [*J*(H_AH_C) 7, *J*(H_AH_B)1], H_A; 7.32, **2**, *d of t* [*J*(H_BH_C) 12, *J*(H_AH_B) 1], H_B; 7.4, **2**, *q* (*J* 9), CH_2 of Et; 7.9, 7.92, **12**, *d*, 4 Me (A and B); 8.8, **3**, *t* (*J* 9), Me of Et [g]
(18)	$[\{Co(etmcp)(\mu\text{-}CO)\}_2]$	Black	60.7 (61.0)	7.1 (7.2) [o]			7.9, **2**, *q* (*J* 9), CH_2 of Et; 8.1, **6**, *s*, 2 Me (A or B); 8.4, **6**, *s*, 2 Me (B or A); 9.2, **3**, *t* (*J* 9), Me of Et [l]

$[Co(\eta\text{-etmcp})(NCMe)_3][PF_6]_2$ (11) and $[Co(\eta\text{-etmcp})(NCCH{=}CH_2)_3][PF_6]_2$ (12) respectively. The acetonitrile ligands in (11) seem to be labile since, for example the ^1H n.m.r. spectrum of (11) in CD_3CN shows a singlet due to free MeCN.



SCHEME (*i*) C_6H_5Cl solution 50 °C, 2 h; (*ii*) $CaCl_2{\cdot}H_2O$ in C_6H_5Cl, r.t., 1 min; (*iii*) $AlEt_2Cl$ in C_6H_{12} then 1,3-C_6H_8, $[PF_6]^-$(aq) ; (*iv*) PPh_3 in CH_2Cl_2; (*v*) excess of ligand in CH_2Cl_2 or C_6H_5Cl, $[PF_6]^-$(aq); (*vi*) Na-Hg in C_6H_5Me, 1,5-C_8H_{12}, 110 °C; (*vii*) Na-Hg in C_6H_5Me, C_4H_6, 110 °C; (*viii*) Na-Hg in C_6H_5Me, C_2H_4, 110 °C; (*ix*) $FeCl_2$ in HCl(aq), O_2; (*x*) NH_3(aq), $[PF_6]^-$(aq); (*xi*) Me_2CO, 1 week, r.t.; (*xii*) $AlEtCl_2$ in C_6H_{12}; benzene or toluene; $[PF_6]^-$(aq); (*xiii*) MeCN or $CH_2{=}CHCN$, reflux

Treatment of (2) with chlorodiethylaluminium in cyclohexane gives a brown oil. On addition of cyclohexa-1,3-diene, followed by aqueous hexafluorophosphate, orange $[Co(\eta\text{-etmcp})(\eta^5\text{-}C_6H_7)][PF_6]$ (13) is formed.

Reduction of (1) with sodium amalgam in the presence of excess of olefin gives neutral monovalent cobalt derivatives of stoicheiometry $[Co(\eta\text{-etmcp})(\text{olefin})_2]$. For example, ethylene, butadiene, and cyclo-octa-1,5-diene give $[Co(\eta\text{-etmcp})(\eta\text{-}C_2H_4)_2]$ (14), $[Co(\eta\text{-etmcp})(\eta\text{-}C_4H_6)]$ (15), and

---

Notes to Table:

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (τ), **relative intensity**, *multiplicity* (*J* in Hz), assignment, *etc.* Assignments as in the Scheme. [c] *M* in $CHCl_3$ (by osmometry) = 457 (calc.: 558). [d] In $CDCl_3$. [e] In CH_2Cl_2 (1.6×10^{-3} mol dm^{-3}, 20 °C), Λ = 0.140 S cm^2 mol^{-1}. Electronic spectrum in CH_2Cl_2 (370—700 nm); 638 (4.32×10^5), 440 (sh) (9.95×10^4 dm^3 mol^{-1} cm^{-1}), 370 nm high absorption edge. Mass spectrum at 200 °C: *m/e* 488 (9), 486 (13) $[Co_2(etmcp)_2Cl_2]^+$; 245 (14), 243 (41) $[Co(etmcp)Cl]^+$. [f] *M* in $CHCl_3$ (by osmometry) = 452 (calc.: 632); *M* in C_6H_6 (by cryoscopy) of benzene solvate = 590 ± 5 (calc.: 618). [g] In $(CD_3)_2CO$. [h] In CD_3CN. [i] ν(CN) at 2 330 and 2 305 cm^{-1}. [j] ν(CN) at 2 315 and 2 280 cm^{-1}. [k] ν[CH(*exo*)] at 2 815 cm^{-1}. [l] In C_6D_6. [m] Mass spectrum at 61 °C: *m/e* 316 (100) $[Co(etmcp)(C_8H_{12})]^+$. [n] Mass spectrum at 35 °C: *m/e* 262 (100) $[Co(etmcp)(C_4H_6)]^+$. [o] ν(CO) at 1 753 cm^{-1}. Mass spectrum at 60 °C: *m/e* 472 (50) $[Co(etmcp)(CO)]^+$. [p] ν(CO) at 2 055 cm^{-1}.

[Co(η-etmcp)(η-1,5-C_8H_{12})] (16) respectively. Compounds (14)—(16) are volatile and air sensitive and they were purified by vacuum distillation; (14) slowly decomposes at room temperature.

Treatment of octacarbonyldicobalt with Sn(etmcp)-Bu^n_3 gives a volatile red oil, presumably [Co(η-etmcp)$(CO)_2$], which is analogous to the previously described [Co(η-C_5Me_5)$(CO)_2$].[5,6] The red oil reacts readily with allyl bromide and after aqueous work up the orange compound [Co(η-etmcp)(η-C_3H_5)(CO)][PF_6] [17) was isolated in high yield. The ^1H n.m.r. spectrum of (17) shows only one set of bands assignable to the η-C_3H_5 group. Thus we are unable to tell whether (17) is present as only one isomer or whether there is a rapid equilibrium between isomers analogous to those found by Faller in other related η-C_3H_5 metal compounds.[13] Treatment of (17) with triphenylphosphine gives [$PPh_3(C_3H_5)$][PF_6] and a volatile dark green compound which the data show to be the dimer [{Co(η-etmcp)(μ-CO)}$_2$] (18).

DISCUSSION

The reactions described above and the structures proposed for the new compounds are shown in the Scheme. It is clear that there is an extensive chemistry of the peralkylcyclopentadienylcobalt system where the cobalt may occur in both the uni- and tri-valent state. Comparison of the chemistry of the Co(η-etmcp) system with that of unsubstituted Rh(η-C_5H_5) and especially Rh(η-C_5Me_5) [2] shows that there is a great deal of similarity, as would be expected. There are, however, some noticeable differences between the chemistry of unsubstituted Co(η-C_5H_5) derivatives and the Co(η-etmcp) compounds. For example, compound (1) is stable in solution at room temperature whilst [{Co(η-C_5H_5)$_2$Cl(μ-Cl)}$_2$] readily disproportionates to [Co(η-C_5H_5)$_2$]$^+$. It has been previously noted that [{Co(η-C_5Me_5)I(μ-I)}$_2$] is also very stable.[12] Also, compounds of the type [Co(η-etmcp)L_3]$^{2+}$ (L = NH_3 or MeCN) are unknown for the unsubstituted Co(η-C_5H_5) system. Similarly, whilst the bis(ethylene) compounds [M(η-C_5H_5)$(C_2H_4)_2$] (M = Rh or Ir) are well known [14] the cobalt analogue has not been described. The compound [Co(η-etmcp)$(C_2H_4)_2$] (14), however, may be prepared, as described above.

These observations lead to the general inference that peralkylation of the cyclopentadienyl ring makes the cobalt chemistry more closely resemble that of rhodium and iridium. Presumably, this tendency arises principally from the greater electron-donating ability of the peralkylated cyclopentadienyl ring compared with that of the unsubstituted analogue. Thus the cobalt centre would be more electron-rich and the 3*d* orbitals more expanded when bonded to peralkylcyclopentadienyl ligands than when bonded to the unsubstituted cyclopentadienyl ring.

EXPERIMENTAL

All the preparations and manipulations were carried out under dinitrogen or *in vacuo* unless otherwise stated. Solvents were dried and distilled before use. Microanalyses were by A. Bernhardt Microanalytical laboratory or by the analytical laboratory of this department. Infrared spectra were recorded using mulls on a Perkin-Elmer 457 spectrometer and were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were obtained at 90 or 100 MHz on Perkin-Elmer R14 or R32 instruments; ^1H, ^{13}C, and ^{31}P Fourier-transform n.m.r. spectra were determined on a Bruker WH90 instrument. Phosphorus-31 spectra were calibrated using external trimethyl phosphate, ^{13}C spectra against solvent as internal standard. Mass spectra were recorded on an A.E.I. MS9 spectrometer. E.s.r. spectra were obtained on a JEOL *X*-band instrument using 100-MHz modulation and were calibrated using a Mullard cell and a Wayne-Kerr bridge. Electronic spectra were recorded at room temperature (r.t.) on Unicam SP 800 and Cary 17 instruments.

Tri-n-butyl(ethyltetramethylcyclopentadienyl)tin(IV).—Tri-n-butylchlorotin (34.8 g, 0.107 mol) in tetrahydrofuran (thf) (50 cm^3) was treated with lithium ethyltetramethylcyclopentadienide (16.6 g, 0.106 mol) in thf (50 cm^3). The mixture was stirred at r.t. for 20 h. The solvent was then removed under reduced pressure and the residue was extracted with light petroleum (b.p. 30—40 °C, 50 cm^3 then 2 × 20 cm^3). The combined extracts were concentrated under reduced pressure giving a pale yellow oil. This was distilled (115—120 °C, 0.05 mmHg).* The yield was 87% based on Li(etmcp). The pale yellow oil was moderately sensitive to air and water and was stored under dinitrogen (Found: C, 44.6; H, 8.5. Calc.: C, 44.3; H, 8.3%).

The Compound [$Co_3(etmcp)_2Cl_6$] (2).—Anhydrous cobalt(II) chloride (7.35 g, 56.6 mmol) suspended in dry thf (100 cm^3) was treated with Sn(etmcp)Bu^n_3 (25.4 g, 58 mmol) and the mixture was stirred at 65 °C for 2 h. The initially blue solution turned red-black and the cobalt(II) chloride dissolved. The solvent was removed under reduced pressure leaving an air-sensitive brown oil. This was extracted with light petroleum (100 cm^3) and the extract was filtered leaving a small quantity of a blue material. Dry chlorine was passed through the filtrate which had been previously cooled to −20 °C. A green solid precipitated and the passage of chlorine was stopped when the petroleum layer became essentially colourless. The green solid was separated and washed with light petroleum (2 × 50 cm^3).

It was then extracted with dichloromethane and the extract was filtered into chlorobenzene. Concentration of the mixture under reduced pressure gave dark blue microcrystals of [$Co_3(etmcp)_2Cl_6$]. These were collected, washed with light petroleum, and dried, yield 9.8 g (84%). The mother liquors from the above were treated with a large excess of light petroleum (b.p. 100—120 °C) and the solution was cooled to −30 °C. Large green crystals slowly separated. These were collected, washed with light petroleum, and dried *in vacuo*. They were recrystallised from chlorobenzene–light petroleum at −30°, yield 2.4 g (15%). The green crystals were the compound [{Co(etmcp)Cl(μ-Cl)}$_2$] (1). (see below).

Di-μ-chloro-bis[chloro(ethyltetramethylcyclopentadienyl)-cobalt(III)] (1).—Compound (2) (1.23 g, 1.79 mmol) and calcium dichloride (1.5 g) were treated with chlorobenzene (50 cm^3) and water (1 cm^3). The mixture was vigorously shaken at r.t. for 15 min. The deep green chlorobenzene layer was separated and the blue residue was further extracted with chlorobenzene (20 cm^3). The combined

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

filtrates were treated with light petroleum (b.p. 100—120 °C, 200 cm^3) and the solution was cooled to -30 °C for 2 h giving green crystals of (1). These were separated, washed with light petroleum, and dried *in vacuo*, yield 0.79 g (80%).

Tri-μ-chloro-bis[(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*(III)] *Tetrachloroferrate*(III), (3).—Compound (2) (0.4 g, 0.582 mmol) in concentrated hydrochloric acid (10 cm^3) was treated with iron(II) chloride (0.55 g, 4.3 mmol) in concentrated HCl (10 cm^3). The resulting deep blue solution was filtered and the filtrate was exposed to air. A turquoise precipitate formed steadily. This was collected, washed with hydrochloric acid (3 × 10 cm^3), and dried *in vacuo* for 3 h at 90 °C. The compound was recrystallised from dichloromethane–light petroleum giving air-stable crystals (0.37 g, 98%) suitable for *X*-ray diffraction studies.

Dichloro(*η-ethyltetramethylcyclopentadienyl*)(*triphenylphosphine*)*cobalt*(III)–*Toluene* (1/1), (4).—Compound (1) (0.4 g, 0.7 mmol) in dichloromethane (30 cm^3) was treated with triphenylphosphine (1.0 g, 3.8 mmol). Toluene (50 cm^3) was added to the deep blue solution and, after filtration, the solvent was slowly removed under reduced pressure. When the volume had been reduced to *ca.* 30 cm^3 light petroleum (b.p. 100—120 °C, 30 cm^3) was added. Large blue prisms separated over 4 h and were recrystallised from toluene–dichloromethane, yield 0.92 g (95%). Recrystallisation from dichloromethane–benzene–light petroleum gave the benzene solvate [Co(etmcp)(PPh$_3$)-Cl$_2$]·C$_6$H$_6$ [Found: C, 68.2; H, 6.9%; *M* (cryoscopic in benzene) 590. Calc.: C, 68.0; H, 6.1%; *M* 618].

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*chloro*(*η-ethyltetramethylcyclopentadienyl*)*cobalt*(III) *Hexafluorophosphate*, (6).—Compound (2) (1.31 g, 1.91 mmol) in chlorobenzene (40 cm^3) was treated with 1,2-bis(diphenylphosphino)ethane (1.87 g, 4.7 mmol) at 110 °C for 2 h. The solvent was removed from the resulting deep red solution under reduced pressure and the residue was extracted with water (100 cm^3) and dichloromethane (20 cm^3). The red organic layer was separated, washed with water, and the solvent was removed under reduced pressure. The residue was then extracted into water (100 cm^3) leaving the excess of the phosphine undissolved. The red aqueous solution was filtered and then treated with excess of aqueous ammonium hexafluorophosphate (3 g in 10 cm^3) giving a deep red precipitate. This was collected, washed with water (10 cm^3), and dried *in vacuo*. It was then recrystallised from dichloromethane–ethanol as deep red crystals. These were collected, washed with ethanol then light petroleum, and dried *in vacuo*, yield 1.85 g (62%).

Chlorobis(*dimethylphenylphosphine*)(*η-ethyltetramethylcyclopentadienyl*)*cobalt*(III) *Hexafluorophosphate*, (5).—Compound (1) (0.22 g, 0.38 mmol) in dichloromethane (20 cm^3) was treated with dimethylphenylphosphine (0.1 cm^3). The initially green solution became purple. The solvent was removed under reduced pressure and the oily residue was extracted with water (20 cm^3) and acetone (2 cm^3). The red extract was filtered into an excess of aqueous [NH$_4$][PF$_6$] giving a red precipitate. This was collected, washed with water, and then extracted into dichloromethane (20 cm^3). Ethanol (20 cm^3) was added to the separated dichloromethane layer and the solution was concentrated under reduced pressure giving red needles after 2 h. These were collected, washed with ethanol, and dried *in vacuo*, yield 0.23 g (42%).

Triammine(*η-ethyltetramethylcyclopentadienyl*)*cobalt*(III) *Bis*(*hexafluorophosphate*), (7).—Compound (2) (0.5 g, 0.72 mmol) was dissolved in 0.880 s.g. aqueous ammonia (10 cm^3) giving a red solution. This was filtered into an excess of [NH$_4$][PF$_6$] dissolved in 0.880 s.g. ammonia (10 cm^3). On cooling red crystals separated. These were collected, washed with cold water (3 × 5 cm^3 at 0 °C), and then dried *in vacuo* for 2 h, yield *ca.* 70%. The compound could be recrystallised rapidly (3 h) from acetone–ethanol at -30 °C, yield *ca.* 70%.

Diammine(*η-ethyltetramethylcyclopentadienyl*)(*isopropylideneamine*)*cobalt*(III) *Bis*(*hexafluorophosphate*), (8).—Compound (7) (0.47 g, 0.86 mmol) was dissolved in acetone (20 cm^3) and ethanol (20 cm^3) in air. The solution was allowed to stand for 1 week and then cooled to give red crystals which were collected, washed with ethanol, and dried *in vacuo*, yield 0.36 g (67%).

η-Benzene(*η-ethyltetramethylcyclopentadienyl*)*cobalt*(III) *Bis*(*hexafluorophosphate*), (9).—A suspension of (2) (1.65 g, 2.4 mmol) in benzene was treated with dichloro(ethyl)-aluminium [50 cm^3 of a solution (41.7 mmol) in cyclohexane]. The mixture was shaken for 25 min giving a yellow precipitate and a pale green supernatant liquor. The supernatant liquor was discarded and the yellow solid was washed with light petroleum (2 × 10 cm^3) and dried *in vacuo*. The residue was dissolved in water (50 cm^3) and the extract was filtered into aqueous [NH$_4$][PF$_6$] [2 g in water (10 cm^3)]. The resulting yellow precipitate was washed with water and crystallised from acetone–ethanol, yield 2 g (75%).

(*η-Ethyltetramethylcyclopentadienyl*)(*toluene*)*cobalt*(III) *bis*(*hexafluorophosphate*), (10), was prepared in the same way in similar yield, using toluene instead of benzene.

Tris(*acetonitrile*)(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*(III) *Bis*(*hexafluorophosphate*), (11).—Compound (9) (0.21 g, 0.36 mmol) in acetonitrile (20 cm^3) was warmed to 95 °C for 3 h. The solution became deep red after 1 h. The solvent was removed under reduced pressure until the volume reached 5 cm^3 and ethanol (20 cm^3) was added. After 1 week large red crystals separated which were collected. Further concentration of the mother liquor yielded more red microcrystals. The product was washed with ethanol then light petroleum, and finally dried *in vacuo*, yield 0.22 g (95%).

Tris(*acrylonitrile*)(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*(III) *bis*(*hexafluorophosphate*), (12), was prepared in the same manner in similar yield using acrylonitrile instead of acetonitrile.

η-Cyclohexadienyl(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*(III) *Hexafluorophosphate*, (13).—Compound (2) (0.62 g, 0.9 mmol) was suspended in cyclohexane (10 cm^3) and treated with freshly distilled cyclohexa-1,3-diene (2 cm^3) and then chlorodiethylaluminium (1.57 g). The mixture was shaken for 5 min and a brown oil separated. The pale yellow supernatant was decanted and the residual oil was washed with light petroleum. The residue was cooled and treated cautiously with water (10 cm^3). Gases were evolved and an orange aqueous solution was formed, together with a small amount of a black precipitate. The aqueous layer was filtered into an excess of aqueous [NH$_4$]-[PF$_6$] giving an orange precipitate. This was collected, washed with water, dried *in vacuo*, and crystallised from dichloromethane–ethanol, yield 0.19 g (24%).

Bis(*η-ethylene*)(*η-ethyltetramethylcyclopentadienyl*)*cobalt*, (14).—Compound (1) (0.77 g, 1.35 mmol) in toluene (20 cm^3) was treated with sodium amalgam (13.3 g of 3%). The mixture under an atmosphere of ethylene was stirred on an oil-bath at 110 °C for 30 min. The initially green solution became brown after 10 min. The reaction mixture was filtered into a distillation apparatus and the solvent was removed under reduced pressure, leaving a dark brown oil. This was distilled (0.05 mmHg, 130 °C) leaving a black residue. The distillate was collected; it was very air sensitive, and was stored under at atmosphere of ethylene, yield *ca.* 25%.

*η-Cyclo-*1,5-*octadiene*(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*, (16).—Compound (1) (0.38 g, 0.67 mmol) was treated with sodium amalgam (9.54 g of 3%), freshly distilled cyclo-1,5-octadiene (5 cm^3), and toluene (10 cm^3). The mixture was stirred at 95 °C for 1.5 h giving an orange-yellow solution. This was separated and filtered into a distillation apparatus. The solvent was removed under reduced pressure and the orange oil was distilled (125 °C, 0.05 mmHg). The distillate was a waxy solid, m.p. *ca.* 50 °C, yield 0.25 g (60%).

*η-Buta-*1,3-*diene*(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*, (15).—Compound (1) (0.17 g, 0.32 mmol) and sodium amalgam (7.0 g, 3%) were treated with toluene (10 cm^3). The mixture, under an atmosphere of butadiene, was stirred at 110 °C for 30 min giving a red solution. This was handled in the manner described for the cyclo-octa-1,5-diene analogue. Distillation (at 120 °C, 0.1 mmHg) gave a red oil which was very air sensitive, *ca.* 50%.

η-Allyl(*carbonyl*)(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*(III) *Hexafluorophosphate*, (17).—Octacarbonyldicobalt (0.8 g, 2.35 mmol) in light petroleum (10 cm^3, b.p. 100—120 °C) was treated with Sn(etmcp)Bu$^n_3$ (1.655 g., 3.78 mmol). The mixture was heated at 125 °C for 1.5 h with stirring. Gases were evolved and the solution changed from red to green then to red-brown. At this point allyl bromide (4 cm^3) was added. Further gases were evolved and the solution was stirred at 80 °C for 30 min. A green solid separated leaving a red-brown liquor. The green solid was isolated, washed with light petroleum, and dried *in vacuo*, yield 1.22 g. The residue was then extracted with water giving an orange solution which was filtered into [NH$_4$][PF$_6$] (1.5 g in 10 cm^3 of water). The resulting orange precipitate was collected, washed with water, and recrystallised twice from hot ethanol, yield 0.729 (69% based on tin).

Di-μ-carbonyl-bis[(*η-ethyltetramethylcyclopentadienyl*)-*cobalt*], (18).—Compound (17) (0.43 g, 1.0 mmol) in chlorobenzene was treated with triphenylphosphine (0.027 g, 1.05 mmol) and the mixture was stirred at 130 °C for 1 h. The initially orange solution became deep green, and very sensitive to oxidation. The solvent was removed under reduced pressure and the residue was extracted with light petroleum (3 × 10 cm^3). The extract was transferred to a distillation apparatus and the solvent was removed under reduced pressure giving deep green-black fern-like crystals. These were sublimed at 140 °C (0.05 mmHg), yield 0.13 g (54%). The residue from the light petroleum extract was shown to contain [PPh$_3$(C$_3$H$_5$)][PF$_6$] by comparison of the i.r. spectrum with that of an authentic sample.

We thank the S.R.C. for support (to R. B. A. P.).

[8/760 *Received*, 24*th April*, 1978]

REFERENCES

[1] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1971, **93**, 2054; J. E. Bercaw, R. R. Marvick, L. G. Bell, and H. H. Brintzinger, *ibid.*, 1974, **96**, 612; J. E. Bercaw, *ibid.*, p. 5087; A. N. Nesmeyanov, O. V. Nogina, and V. A. Dudovitsky, *Izvest. Akad. Nauk S.S.S.R., Ser. khim. Eng. Edn.*, 1968, 514; J. E. Bercaw and J. M. Manriquez, *J. Amer. Chem. Soc.*, 1974, **96**, 6229.

[2] P. M. Maitlis, *Ann. New York Acad. Sci.*, 1971, **172**, 523; *Trans. New York Acad. Sci.*, 1971, **33**, 87; S. J. Thompson, P. M. Bailey, C. White, and P. M. Maitlis, *Angew. Chem. Internat. Edn.* 1976, **15**, 490; H. B. Lee and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2316; D. S. Gill and P. M. Maitlis, *J. Organometallic Chem.*, 1975, **87**, 359; T. A. Stephenson and D. R. Robertson, *ibid.*, 1976, **107**, C46; C. White, A. J. Oliver, and P. M. Maitlis, *J.C.S. Dalton*, 1973, 1901; A. K. Smith and P. M. Maitlis, *ibid.*, 1976, 1773; J. Muller, H. O. Stuhler, and W. Gall, *Chem. Ber.*, 1975, **108**, 1074; P. Diversi, G. Ingrosso, and A. Luckerini, *J.C.S. Chem. Comm.*, 1974, 52; K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

[3] S. McVey and P. L. Pauson, *J. Chem. Soc.*, 1965, 4312.

[4] R. B. King, A. Efraty, and W. M. Douglas, *J. Organometallic Chem.*, 1975, **56**, 345.

[5] R. B. King and A. E. Efraty, *J. Amer. Chem. Soc.*, 1972, **94**, 3773.

[6] R. B. King and M. B. Bisnette, *J. Organometallic Chem.*, 1967, **8**, 28.

[7] J. L. Thomas, *J. Amer. Chem. Soc.*, 1973, **95**, 1838.

[8] M. J. Bunker, A. DeCian, and M. L. H. Green, *J.C.S. Chem. Comm.*, 1977, 59; J. C. Daran, K. Prout, A. DeCain, M. L. H. Green, and N. Siganporia, *J. Organometallic Chem.*, 1977, **136**, C4.

[9] D. Feitler and G. M. Whitesides, *Inorg. Chem.*, 1976, **15**, 466.

[10] R. S. Threlkel and J. E. Bercaw, *J. Organometallic Chem.*, 1977, **136**, 1.

[11] C. Couldwell and J. Hussain, *Acta Cryst.*, 1978, **B34**, 2444.

[12] D. M. Roe and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1971, 3173.

[13] J. W. Faller, C.-C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organometallic Chem.*, 1973, **52**, 361.

[14] R. Cramer, *J. Amer. Chem. Soc.*, 1972, **94**, 5681.