# Synthesis and Characterisation of Permethylindenyl Complexes of Cobalt and Chromium: Crystal Structures of $[Cr(\eta^5\text{-}C_9Me_7)_2]$, $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ and $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$†

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Treatment of lithium heptamethylindenide with either anhydrous $[Co(acac)_2]$ (acac = acetylacetonate) or $CrCl_2$ in tetrahydrofuran (thf) gave $[Co(\eta^5\text{-}C_9Me_7)_2]$ and $[Cr(\eta^5\text{-}C_9Me_7)_2]$ respectively. Single-crystal X-ray studies showed that $[Cr(\eta^5\text{-}C_9Me_7)_2]$ belongs to the centrosymmetric space group *Pbca* with $a$ = 19.333(10), $b$ = 14.586(9), $c$ = 9.241(2) Å, $Z$ = 4, $R$ = 0.043 and $R'$ = 0.047. The metal centre lies on a crystallographic inversion centre and the permethylindenyl rings adopt a staggered conformation with a M–$C_9Me_7$ ($C_5$-centroid) distance of 1.81(2) Å. Gas-phase UV photoelectron spectroscopy experiments on $[Cr(\eta^5\text{-}C_9Me_7)_2]$ yield a first ionisation potential of 4.67 eV. The complexes $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ and $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ were isolated by treatment of the neutral complexes with $NH_4PF_6$ in thf. Single-crystal X-ray studies show that both of these complexes belong to the centrosymmetric space group $P\bar{1}$. For $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$, $a$ = 14.332(15), $b$ = 16.661(11), $c$ = 14.426(15) Å, $\alpha$ = 109.55(10), $\beta$ = 89.99(10), $\gamma$ = 112.75(9), $Z$ = 2, $R$ = 0.064 and $R'$ = 0.071, average M–$C_9Me_7$ ($C_5$-centroid) distance = 1.68(2) Å. For $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$, $a$ = 14.297(8), $b$ = 16.842(9), $c$ = 14.169(9) Å, $\alpha$ = 109.10(5), $\beta$ = 90.06(5), $\gamma$ = 111.49(4)°, $Z$ = 2, $R$ = 0.075, $R'$ = 0.095, average M–$C_9Me_7$ ($C_5$-centroid) distance = 1.84(1) Å. The cyclic voltammogram of $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ in MeCN indicates that this complex is redox active with a one-electron reduction at $E_{\frac{1}{2}} = -1.15$ V *vs.* saturated calomel electrode (SCE). The solid-state magnetic susceptibility data for $[Co(\eta^5\text{-}C_9Me_7)_2]$, $[Cr(\eta^5\text{-}C_9Me_7)_2]$ and $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ can be modelled by the Curie law ($\chi_M = C/T$) in the temperature range 4–300 K with $\mu_{eff}$ = 1.65, 2.67 and 3.47 for the three complexes respectively. The latter exhibits an axially symmetric EPR signal at 6 K with $g_{\parallel} = 1.99$ ($m_s = -\frac{3}{2} \longrightarrow m_s = -\frac{1}{2}$) and the double quantum transition $g_{\perp} = 4.33$ ($m_s = -\frac{3}{2} \longrightarrow m_s = \frac{1}{2}$), $[Cr(\eta^5\text{-}C_9Me_7)_2]$ also exhibits an axially symmetric powder line-shape at 11 K with $g_{\parallel} = 2.04$ and $g_{\perp} = 2.06$.

Transition-metal indenyl complexes have been found to display enhanced reactivity in both $S_N1$[1–3] and $S_N2$[2–6] substitution reactions compared to their cyclopentadienyl analogues. This observation has been attributed to the relative ease of slippage of the indenyl ring from $\eta^5$ to $\eta^3$ co-ordination ('the indenyl effect').[7] In addition, enhanced catalytic activity has been demonstrated for $[ML_2(\eta^5\text{-indenyl})]$ complexes (M = Co or Rh, L = alkene) in intermolecular hydroacylation reactions,[8] cyclotrimerisation of alkynes to benzenes,[9] and cyclotrimerisation of alkynes and nitriles to pyridines.[10]

In particular, we have been interested in recent years in developing the organometallic chemistry of transition-metal complexes containing the permethylindenyl ligand in contrast to the pentamethylcyclopentadienyl ligand.[11,12] We have recently published an account of the synthesis of the heptamethylindenyl complexes $[M(\eta^5\text{-}C_9Me_7)_2]^{+/0}$ (M = Fe or Co).[11]

In this paper we report the synthesis of the permethylindenyl complexes of $[M(\eta^5\text{-}C_9Me_7)_2]^{+/0}$ (M = Co or Cr) and a detailed study of their electronic structures using gas-phase photoelectron spectroscopy, cyclic voltammetry, magnetic susceptibility and electron paramagnetic resonance where appropriate. We also report the crystal structures of $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$, $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ and $[Cr(\eta^5\text{-}C_9Me_7)_2]$. Comparisons are made with the solid-state structures of other indenyl and permethylindenyl complexes.

## Results and Discussion

*Synthesis and Characterisation of* $[M(\eta^5\text{-}C_9Me_7)_2]^{+/0}$ (M = Cr *or* Co).—*Synthesis.* Treatment of freshly sublimed $[Co(acac)_2]$ (acac = acetylacetonate) with $Li(C_9Me_7)$ in tetrahydrofuran (thf) gave $[Co(\eta^5\text{-}C_9Me_7)_2]$ **1**. Although it was not possible to isolate an analytically pure sample of **1** from this reaction, oxidation of the reaction mixture with $NH_4PF_6$ gave a red precipitate of $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **2**. Dark red single crystals of **2** were formed by slow diethyl ether diffusion into acetone. Analytically pure samples of **1** can be formed by reduction of **2** with 1% sodium amalgam in thf (Scheme 1).

Treatment of anhydrous $CrCl_2$ with $Li(C_9Me_7)$ in thf gave $[Cr(\eta^5\text{-}C_9Me_7)_2]$ **3**. Dark green air-sensitive crystals of **3** were obtained by slow recrystallisation from toluene. Compound **3** can be readily oxidised to the 15-electron radical cation species $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **4** by the addition of $NH_4PF_6$ in thf. Compound **4** forms dark red, air-sensitive, single crystals on slow diffusion of diethyl ether into an acetone solution.

*Crystal Structures of Compounds* **2**, **3** *and* **4**.—The X-ray crystal structures of compounds **2**, **3** and **4** have been determined. A summary of the crystallographic data is shown in Table 1. Compounds **2** and **4** crystallise in the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit contains two independent cation molecules. The molecular structures together with atomic labelling schemes are shown in Figs. 1–4. Selected bond lengths and angles are given in Tables 2–4 and positional parameters in Tables 5 and 6. Compound **3** crystallises in the centrosymmetric orthorhombic space group *Pbca*. The molecular structure together with atomic labelling

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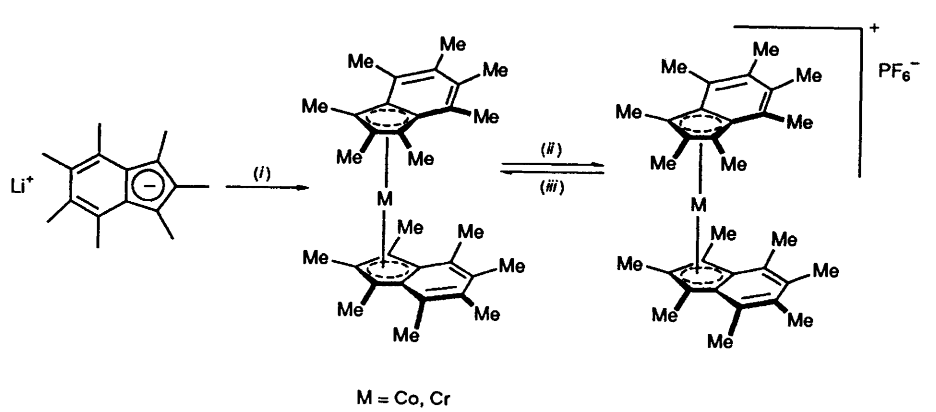
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

*Non-SI unit employed:* eV ≈ 1.6 × $10^{-19}$ J.



**Scheme 1** (*i*) For **1**, [Co(acac)$_2$] in thf, yield 43%; for **3**, CrCl$_2$ in thf, yield 70%. (*ii*) For **2** and **4** in NH$_4$PF$_6$, yields 47 and 50%. (*iii*) For **1**, 1% sodium amalgam in thf

**Table 1** Crystallographic details

| | [Co(C$_9$Me$_7$)$_2$][PF$_6$] | [Cr(C$_9$Me$_7$)$_2$][PF$_6$] | [Cr(C$_9$Me$_7$)$_2$] |
|---|---|---|---|
| Formula | C$_{32}$H$_{42}$CoF$_6$P | C$_{32}$H$_{42}$CrF$_6$P | C$_{32}$H$_{42}$Cr |
| *M* | 630.57 | 623.64 | 478.68 |
| Crystal size/mm | 0.32 × 0.32 × 0.10 | 0.68 × 0.32 × 0.22 | 0.54 × 0.32 × 0.20 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | *Pbca* |
| *a*/Å | 14.332(15) | 14.297(8) | 19.333(10) |
| *b*/Å | 16.661(11) | 16.842(9) | 14.586(9) |
| *c*/Å | 14.246(15) | 14.169(9) | 9.241(2) |
| α/° | 109.55(10) | 109.10(5) | 90 |
| β/° | 89.99(10) | 90.06(5) | 90 |
| γ/° | 112.75(9) | 111.49(4) | 90 |
| *U*/Å$^3$ | 2923 | 2971 | 2606 |
| *Z* | 2 | 2 | 4 |
| $D_c$/g cm$^{-3}$ | 1.43 | 1.39 | 1.22 |
| μ/cm$^{-1}$ | 6.96 | 4.85 | 4.44 |
| *F*(000) | 1320 | 1308 | 1032 |
| θ Limits/° | 1.00–23.0 | 1.00–22.5 | 1.00–22.5 |
| Total data collected | 9711 | 11 011 | 2715 |
| Total unique data | 8129 | 9297 | 1693 |
| No. of observations [$I > 3\sigma(I)$] | 5400 | 6281 | 841 |
| No. of variables | 651 | 651 | 153 |
| Largest residual/e Å$^{-3}$ | 0.78 near Co(1) | 0.94 near Cr(1) | 0.24 near Cr |
| *R*[a] | 0.064 | 0.075 | 0.043 |
| *R'*[b] | 0.071 | 0.095 | 0.047 |

Details in common: ω-scan width (1.0 + 0.35 tanθ)°, Chebyshev weighting scheme.

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

scheme is shown in Figs. 5 and 6, selected bond lengths and angles are given in Table 7 and the positional parameters are given in Table 8. The results of the X-ray analyses on **2**, **3** and **4** confirm the molecular compositions proposed on the basis of the elemental analyses. The average distances from the metal to the centroid of the five membered rings are: 1.68(2), 1.81(2) and 1.84(1) Å for **2**, **3** and **4** respectively. The average angle between the planes of the C$_5$ rings are 1.1 and 0.6° for **2** and **4** respectively.

Several parameters have been previously defined to estimate the degree of slip-fold distortion in indenyl complexes.[13,14] The slip parameter ($\Delta_{M-C}$), is defined as the difference in the average bond lengths of the metal to the ring-junction carbons C(1), C(5) and the metal to adjacent carbon atoms of the five-membered ring, C(2), C(4). The hinge angle (h.a.), is defined as the angle between the planes [C(2), C(3), C(4)] and [C(1), C(2), C(3), C(4)]. The fold angle (f.a.), is defined as the angle between the planes [C(2), C(3), C(4)] and [C(1), C(5), C(6), C(7), C(8), C(9)]. The hinge angle represents bending at C(2), C(4) whereas the fold angle represents bending at C(1), C(5).

We define the rotation angle (r.a.), as the angle formed by the intersection of the two planes determined by the centroids of the five- and six-membered rings. A rotation angle of 0° would indicate a completely eclipsed geometry whereas an angle of 180° corresponds to the fully staggered arrangement of the two rings.

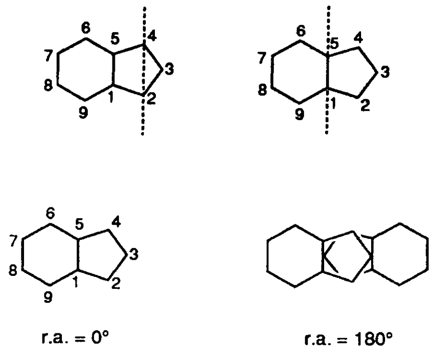


Table 9 reports the values of $\Delta_{M-C}$, h.a., f.a. and r.a. for compounds **2**, **3** and **4**, together with other indenyl complexes for comparison. The values of $\Delta_{M-C}$, h.a. and f.a. for the two independent molecules in the asymmetric units of **2** and **4** suggest almost undistorted η$^5$-co-ordination of the permethylindenyl rings. Both of these compounds have a rotation angle of 89°.

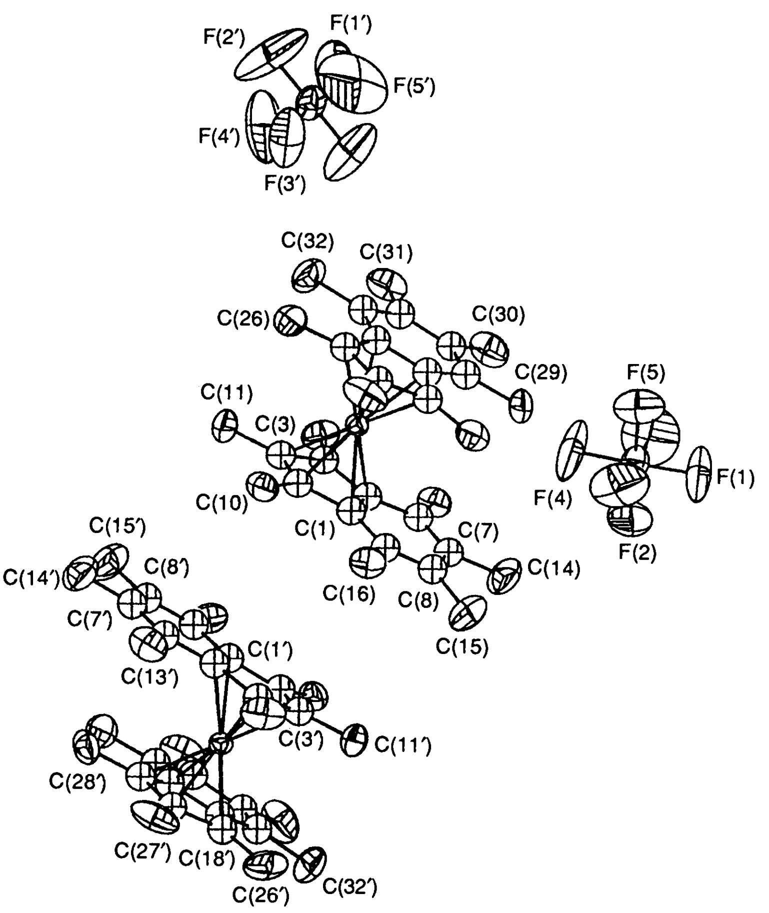


**Fig. 1** Molecular structure together with atomic labelling system for $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **2** showing the two independent molecules in the asymmetric unit. Hydrogen atoms have been omitted for clarity. Atoms are displayed with 50% ellipsoids. Primes indicate second independent molecule

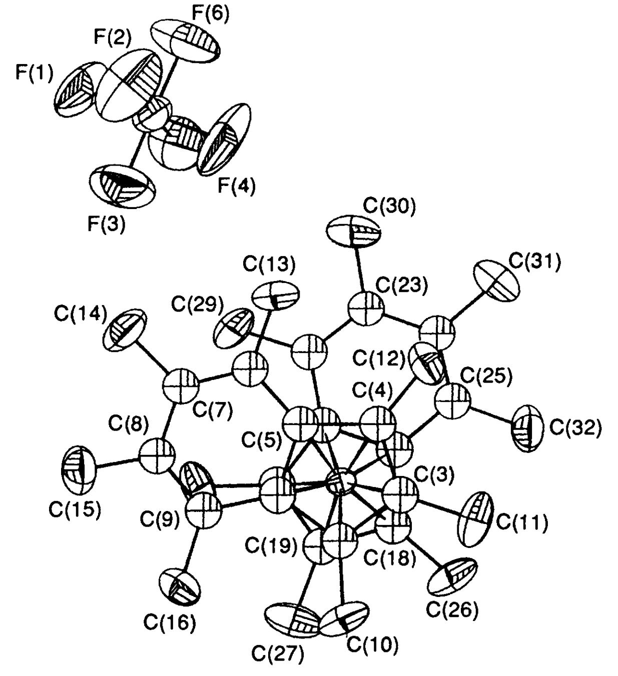


**Fig. 2** Molecular structure of $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **2** showing the view orthogonal to the permethylindenyl rings. Hydrogen atoms have been omitted for clarity. Atoms are displayed with 50% ellipsoids

The values of $\Delta_{M-C}$ and h.a. for compound **3** are similar to those reported for $[Co(\eta^5\text{-}C_9H_7)_2]$.[2] Compound **3** may be regarded as having 'distorted $\eta^5$-' co-ordination of the two permethylindenyl rings. This distortion can be seen to some extent in Fig. 5. It is interesting that the r.a. parameter of 180° is significantly different from that of compound **4**. In general it appears that this parameter falls broadly into two regions, 90° for the cations and 180° for the neutral complexes.

*Photoelectron Spectroscopy.*—The He I and He II photoelectron (PE) spectra of $[Cr(\eta^5\text{-}C_9Me_7)_2]$ are presented in Fig. 7. Ionisation energy (i.e.) data for $[Cr(\eta^5\text{-}C_9Me_7)_2]$ are given in Table 10.

*General bonding model.* The bonding in indenyl compounds is known to resemble that of the analogous cyclopentadienyl compounds.[15,16] The He I and He II PE spectra of $[Fe(\eta^5\text{-}C_9Me_7)_2]$ and $[Co(\eta^5\text{-}C_9Me_7)_2]$ and their interpretation in terms of a molecular orbital (MO) scheme have been discussed.[11] The permethylindenyl ring possesses nine $\pi$ orbitals, five of which are filled in the anion, and these are discussed in detail elsewhere.[11,17] The three highest lying occupied $\pi$ MOs, $\pi_5$, $\pi_4$ and $\pi_3$ resemble the degenerate $e_1$ highest occupied molecular orbital (HOMO) of the cyclopentadienyl anion and might therefore be expected to interact with the d orbitals at the metal centre.

X-Ray studies reveal that $[Cr(\eta^5\text{-}C_9Me_7)_2]$ possesses $C_{2h}$ symmetry. We therefore expect mixing of the $d_{xz}$,$d_{yz}$ orbitals, transforming as $b_g$ in the $C_{2h}$ point group, with the $b_g$ symmetry combination of the two $\pi_5$ orbitals ($\pi_5$–$\pi_5$). The ($\pi_4$–$\pi_4$) ligand combination can interact with metal d orbitals of $a_g$ symmetry ($d_{z^2}$, $d_{x^2-y^2}$ or $d_{xy}$). Fig. 8 presents the qualitative MO scheme for $[Cr(\eta^5\text{-}C_9Me_7)_2]$ with orbital labellings corresponding to the PE spectra, shown in Fig. 7.

*Assignment of the PE spectra.* Since $[Cr(\eta^5\text{-}C_9Me_7)_2]$ is an

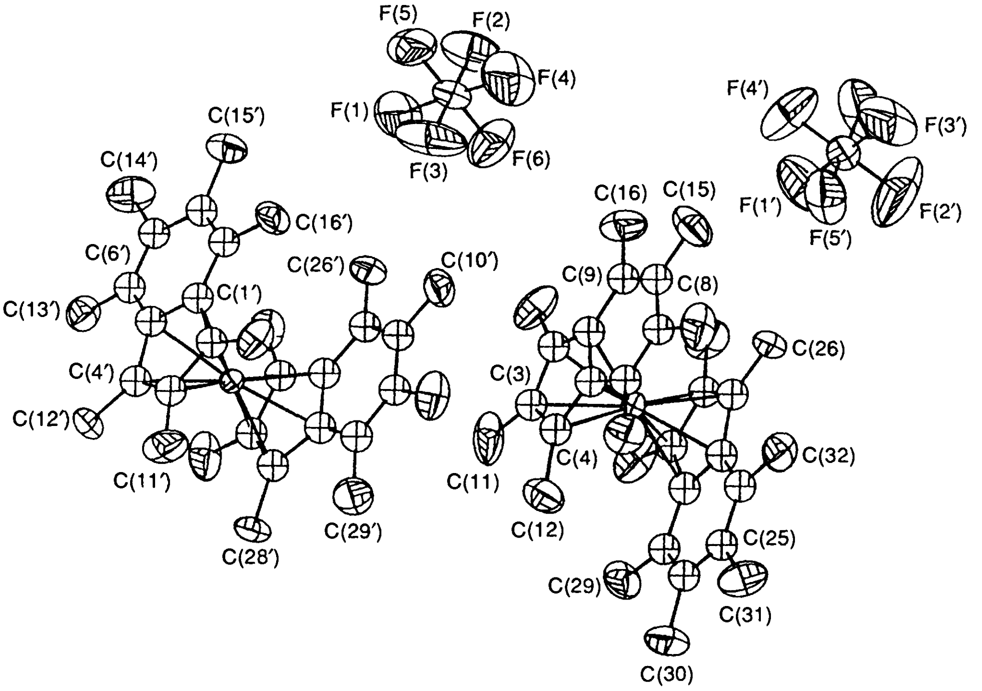


Fig. 3 Molecular structure together with atomic labelling system for $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ 4 showing the two independent molecules in the asymmetric unit. Hydrogen atoms have been omitted for clarity. Atoms are displayed with 50% ellipsoids. Primes indicate second independent molecule

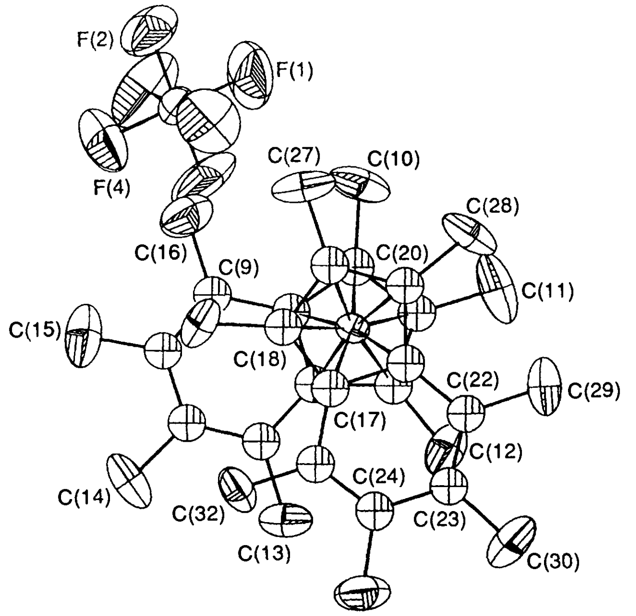


Fig. 4 Molecular structure of $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ 4 showing the view orthogonal to the permethylindenyl rings. Hydrogen atoms have been omitted for clarity. Atoms are displayed with 50% ellipsoids

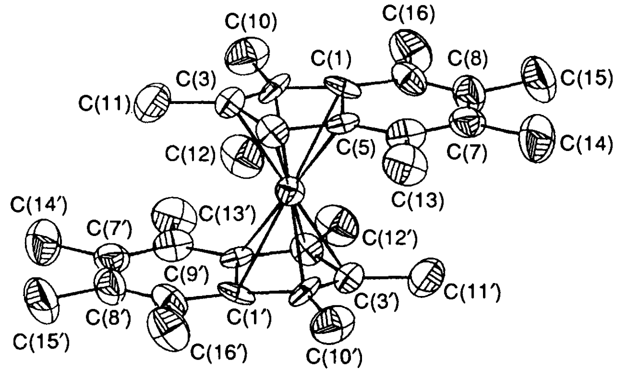


Fig. 5 Molecular structure together with atomic labelling system for $[Cr(\eta^5\text{-}C_9Me_7)_2]$ 3. Hydrogen atoms have been omitted for clarity. Atoms are displayed with 50% ellipsoids. Primed atoms related to unprimed equivalents by $-x, -y, -z$

open shell molecule, correlation between a single band in the PE spectrum and ionisation from one MO does not apply. A variety of ion states may be produced upon ionisation of a single MO; in $[Cr(C_5Me_5)_2]$, for example, ionisation from the predominately d-based MOs leads to the formation of five ion states[15] (one quartet and four doublet states). Ligand-field calculations reveal that ionisation to quartet states requires lower energy than that to doublet states and that the energies of ionisation to certain doublet states will be close to those of ligand-based ionisations. In $[Cr(C_5H_5)_2]$ and $[Cr(C_5Me_5)_2]$, four of the five expected d bands are resolved.

By analogy with $[Cr(C_5H_5)_2]$ and $[Cr(C_5Me_5)_2]$, the lowest i.e. band of $[Cr(\eta^5\text{-}C_9Me_7)_2]$ (band $A_1$) is assigned to the quartet molecular-ion ground state. Between ionisation energies of 5.5 and 10 eV (bands A–D) the spectrum is not well resolved for the reasons outlined above and precise assignment of the bands A, B, C and D is therefore problematic. Meaningful $R_{2/1}$ (He II/He I intensity ratio) values are also difficult to obtain due to the unresolved nature of the spectrum in this region, but the He II spectrum shows that bands A–C all increase in intensity relative to band D, suggesting a metal contribution to the ionising MOs. Band D may be assigned in a manner analogous to that of $[Fe(\eta^5\text{-}C_9Me_7)_2]$ and $[Co(\eta^5\text{-}C_9Me_7)_2]$, *i.e.* to the ligand-based $\pi_3$ orbitals.[11,17] Therefore bands A–C must be assigned to the MOs derived from the $\pi_5$ and $\pi_4$ orbitals of the indenyl rings (interacting with the Cr 3d orbitals as explained above), together with the doublet states of the molecular ion produced upon ionisation of the metal d orbitals. Simple relative energy considerations suggest that band C is due to the $\pi_4$ based orbitals, while band B is produced upon ionisation of $\pi_5$ based orbitals. Band A is attributed to one or

**Table 2** Selected intramolecular distances for $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **2** with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| Co(1)–C(1) | 2.115(8) | Co(1′)–C(1′) | 2.155(8) |
| Co(1)–C(2) | 2.051(9) | Co(1′)–C(2′) | 2.051(8) |
| Co(1)–C(3) | 2.068(9) | Co(1′)–C(3′) | 2.054(9) |
| Co(1)–C(4) | 2.066(8) | Co(1′)–C(4′) | 2.051(9) |
| Co(1)–C(5) | 2.120(8) | Co(1′)–C(5′) | 2.105(8) |
| Co(1)–C(17) | 2.109(8) | Co(1′)–C(17′) | 2.103(8) |
| Co(1)–C(18) | 2.056(9) | Co(1′)–C(18′) | 2.051(9) |
| Co(1)–C(19) | 2.061(9) | Co(1′)–C(19′) | 2.067(9) |
| Co(1)–C(20) | 2.045(8) | Co(1′)–C(20′) | 2.053(8) |
| Co(1)–C(21) | 2.106(7) | Co(1′)–C(21′) | 2.098(8) |
| C(1)–C(2) | 1.467(11) | C(1′)–C(2′) | 1.428(11) |
| C(1)–C(5) | 1.429(11) | C(1′)–C(5′) | 1.448(11) |
| C(1)–C(9) | 1.433(11) | C(1′)–C(9′) | 1.431(11) |
| C(2)–C(3) | 1.437(12) | C(2′)–C(3′) | 1.426(12) |
| C(2)–C(10) | 1.496(12) | C(2′)–C(10′) | 1.497(12) |
| C(3)–C(4) | 1.422(12) | C(3′)–C(4′) | 1.421(12) |
| C(3)–C(11) | 1.508(13) | C(3′)–C(11′) | 1.501(12) |
| C(4)–C(5) | 1.465(11) | C(4′)–C(5′) | 1.450(12) |
| C(4)–C(12) | 1.489(12) | C(4′)–C(12′) | 1.507(12) |
| C(5)–C(6) | 1.436(11) | C(5′)–C(6′) | 1.444(11) |
| C(6)–C(7) | 1.349(12) | C(6′)–C(7′) | 1.353(12) |
| C(6)–C(13) | 1.510(12) | C(6′)–C(13′) | 1.514(12) |
| C(7)–C(8) | 1.423(12) | C(7′)–C(8′) | 1.444(12) |
| C(7)–C(14) | 1.527(13) | C(7′)–C(14′) | 1.503(13) |
| C(8)–C(9) | 1.361(12) | C(8′)–C(9′) | 1.370(12) |
| C(8)–C(15) | 1.510(13) | C(8′)–C(15′) | 1.505(13) |
| C(9)–C(16) | 1.523(12) | C(9′)–C(16′) | 1.501(12) |
| C(17)–C(18) | 1.451(11) | C(17′)–C(18′) | 1.457(12) |
| C(17)–C(21) | 1.437(11) | C(17′)–C(21′) | 1.426(11) |
| C(17)–C(25) | 1.442(11) | C(17′)–C(25′) | 1.432(11) |
| C(18)–C(19) | 1.421(12) | C(18′)–C(19′) | 1.432(13) |
| C(18)–C(26) | 1.485(12) | C(18′)–C(26′) | 1.498(13) |
| C(19)–C(20) | 1.429(12) | C(19′)–C(20′) | 1.415(12) |
| C(19)–C(27) | 1.497(12) | C(19′)–C(27′) | 1.488(13) |
| C(20)–C(21) | 1.446(11) | C(20′)–C(21′) | 1.458(11) |
| C(20)–C(28) | 1.499(12) | C(20′)–C(28′) | 1.494(12) |
| C(21)–C(22) | 1.440(11) | C(21′)–C(22′) | 1.433(11) |
| C(22)–C(23) | 1.372(12) | C(22′)–C(23′) | 1.373(11) |
| C(22)–C(29) | 1.509(12) | C(22′)–C(29′) | 1.499(12) |
| C(23)–C(24) | 1.427(12) | C(23′)–C(24′) | 1.434(12) |
| C(23)–C(30) | 1.515(12) | C(23′)–C(30′) | 1.517(12) |
| C(24)–C(25) | 1.349(11) | C(24′)–C(25′) | 1.361(12) |
| C(24)–C(31) | 1.524(12) | C(24′)–C(31′) | 1.518(13) |
| C(25)–C(32) | 1.512(12) | C(25′)–C(32′) | 1.507(13) |

The second independent molecule is denoted by (′).

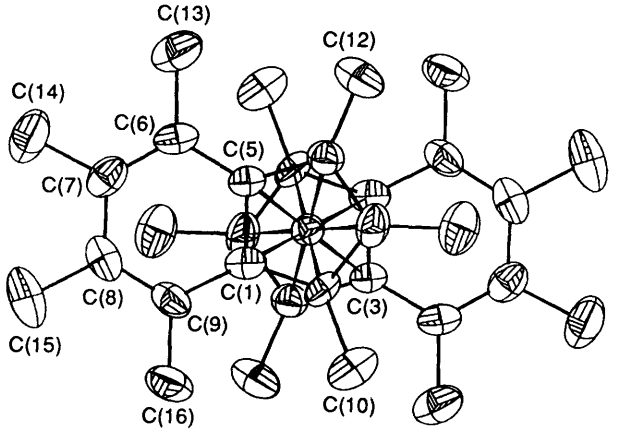


**Fig. 6** Molecular structure together with atomic labelling system for $[Cr(\eta^5\text{-}C_9Me_7)_2]$ **3** showing the view orthogonal to the permethylindenyl rings. Hydrogen atoms have been omitted for clarity. Atoms are displayed with 50% ellipsoids

more Cr 3d orbital derived doublet states, which may also contribute to bands B and C.

**Table 3** Selected intramolecular distances for $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **4** with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Cr(1)–C(1) | 2.202(6) | Cr(1′)–C(1′) | 2.232(6) |
| Cr(1)–C(2) | 2.193(7) | Cr(1′)–C(2′) | 2.197(6) |
| Cr(1)–C(3) | 2.222(7) | Cr(1′)–C(3′) | 2.219(7) |
| Cr(1)–C(4) | 2.189(6) | Cr(1′)–C(4′) | 2.192(6) |
| Cr(1)–C(5) | 2.200(5) | Cr(1′)–C(5′) | 2.227(5) |
| Cr(1)–C(17) | 2.225(5) | Cr(1′)–C(17′) | 2.208(5) |
| Cr(1)–C(18) | 2.198(6) | Cr(1′)–C(18′) | 2.192(6) |
| Cr(1)–C(19) | 2.219(7) | Cr(1′)–C(19′) | 2.217(7) |
| Cr(1)–C(20) | 2.199(7) | Cr(1′)–C(20′) | 2.193(6) |
| Cr(1)–C(21) | 2.222(6) | Cr(1′)–C(21′) | 2.216(6) |
| C(1)–C(2) | 1.433(9) | C(1′)–C(2′) | 1.446(9) |
| C(1)–C(5) | 1.410(8) | C(1′)–C(5′) | 1.438(8) |
| C(1)–C(9) | 1.465(9) | C(1′)–C(9′) | 1.423(8) |
| C(2)–C(3) | 1.404(10) | C(2′)–C(3′) | 1.422(9) |
| C(2)–C(10) | 1.523(10) | C(2′)–C(10′) | 1.495(9) |
| C(3)–C(4) | 1.422(10) | C(3′)–C(4′) | 1.408(9) |
| C(3)–C(11) | 1.520(10) | C(3′)–C(11′) | 1.509(10) |
| C(4)–C(5) | 1.444(8) | C(4′)–C(5′) | 1.467(8) |
| C(4)–C(12) | 1.521(10) | C(4′)–C(12′) | 1.497(9) |
| C(5)–C(6) | 1.444(8) | C(5′)–C(6′) | 1.443(8) |
| C(6)–C(7) | 1.385(9) | C(6′)–C(7′) | 1.360(9) |
| C(6)–C(13) | 1.506(10) | C(6′)–C(13′) | 1.501(9) |
| C(7)–C(8) | 1.407(10) | C(7′)–C(8′) | 1.434(9) |
| C(7)–C(14) | 1.510(10) | C(7′)–C(14′) | 1.518(10) |
| C(8)–C(9) | 1.382(9) | C(8′)–C(9′) | 1.366(9) |
| C(8)–C(15) | 1.482(10) | C(8′)–C(15′) | 1.526(10) |
| C(9)–C(16) | 1.514(11) | C(9′)–C(16′) | 1.509(9) |
| C(17)–C(18) | 1.430(8) | C(17′)–C(18′) | 1.422(8) |
| C(17)–C(21) | 1.435(8) | C(17′)–C(21′) | 1.429(8) |
| C(17)–C(25) | 1.431(8) | C(17′)–C(25′) | 1.451(8) |
| C(18)–C(19) | 1.430(9) | C(18′)–C(19′) | 1.432(9) |
| C(18)–C(26) | 1.507(9) | C(18′)–C(26′) | 1.498(10) |
| C(19)–C(20) | 1.411(9) | C(19′)–C(20′) | 1.413(10) |
| C(19)–C(27) | 1.515(10) | C(19′)–C(27′) | 1.506(10) |
| C(20)–C(21) | 1.455(9) | C(20′)–C(21′) | 1.447(8) |
| C(20)–C(28) | 1.503(10) | C(20′)–C(28′) | 1.503(10) |
| C(21)–C(22) | 1.432(9) | C(21′)–C(22′) | 1.436(9) |
| C(22)–C(23) | 1.378(9) | C(22′)–C(23′) | 1.367(9) |
| C(22)–C(29) | 1.506(10) | C(22′)–C(29′) | 1.513(10) |
| C(23)–C(24) | 1.420(9) | C(23′)–C(24′) | 1.436(9) |
| C(23)–C(30) | 1.512(10) | C(23′)–C(30′) | 1.510(10) |
| C(24)–C(25) | 1.374(9) | C(24′)–C(25′) | 1.365(9) |
| C(24)–C(31) | 1.506(11) | C(24′)–C(31′) | 1.501(9) |
| C(25)–C(32) | 1.503(9) | C(25′)–C(32′) | 1.505(9) |

The second independent molecule is denoted by (′).

*Magnetic Susceptibility and EPR studies.*—The magnetic properties of metallocenes have been studied extensively from both an experimental and theoretical viewpoint.[17–24] The simplest behaviour is found for systems with orbitally non-degenerate ground states, *i.e.* compounds with 15-electron $^4A_{1g}$ $\{[Cr(\eta^5\text{-}C_5H_5)_2]^+\}$ or 20-electron $^3A_{2g}$ $\{[Ni(\eta^5\text{-}C_5H_5)_2]\}$ configurations. In these complexes the magnetic moments are close to their spin-only values since no orbital contributions are expected. In contrast, magnetic studies have established that 16- and 19-electron metallocenes possess orbitally degenerate ground state configurations. Theoretical considerations are therefore more complex and $g$ values are very sensitive to ring substitution and changes in the diamagnetic host.

The EPR spectrum of a randomly-oriented single crystal of **4** at 6 K exhibits an axially symmetric pattern characterised by $g_{\parallel} = 1.99$ ($m_s = -\frac{3}{2} \longrightarrow m_s = -\frac{1}{2}$) and the double quantum transition with $g_{\perp} = 4.33$ ($m_s = -\frac{3}{2} \longrightarrow m_s = \frac{1}{2}$). These values are comparable to those obtained for $[Cr(\eta^5\text{-}C_5H_5)_2]^+$ and $[Cr(\eta^5\text{-}C_5Me_5)_2]^+$.[13] The lowest energy ionisation from photoelectron spectroscopy is entirely consistent with these EPR measurements which suggest an orbitally non-degenerate quartet ground state for the cation. The EPR spectrum of a freshly sublimed microcrystalline sample of **3** at 11 K exhibits an axially symmetric pattern characterised by $g_{\parallel} = 2.04$ and

**Table 4** Selected bond angles (°) for $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **2** and $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **4** with e.s.d.s in parentheses

| | **2** | **4** |
|---|---|---|
| C(5)–C(1)–C(2) | 108.1(7) | 108.3(5) |
| C(1)–C(2)–C(3) | 106.4(7) | 106.9(6) |
| C(2)–C(3)–C(4) | 110.1(8) | 110.2(6) |
| C(3)–C(4)–C(5) | 106.8(7) | 105.8(6) |
| C(4)–C(5)–C(1) | 108.3(7) | 108.5(5) |
| C(1)–C(5)–C(6) | 120.1(7) | 120.6(5) |
| C(5)–C(6)–C(7) | 117.2(8) | 117.9(6) |
| C(6)–C(7)–C(8) | 117.2(9) | 122.1(9) |
| C(7)–C(8)–C(9) | 119.3(9) | 121.7(9) |
| C(8)–C(9)–C(1) | 118.0(6) | 118.0(6) |
| C(9)–C(1)–C(5) | 120.2(7) | 119.7(5) |
| C(21)–C(17)–C(18) | 107.9(7) | 108.7(5) |
| C(17)–C(18)–C(19) | 107.3(7) | 106.2(5) |
| C(18)–C(19)–C(20) | 109.4(8) | 110.9(6) |
| C(19)–C(20)–C(21) | 107.4(7) | 106.1(6) |
| C(20)–C(21)–C(17) | 107.8(7) | 107.9(5) |
| C(17)–C(21)–C(22) | 119.6(7) | 121.1(5) |
| C(21)–C(22)–C(23) | 118.1(8) | 117.3(6) |
| C(22)–C(23)–C(24) | 121.3(8) | 121.8(6) |
| C(23)–C(24)–C(25) | 123.2(8) | 122.3(6) |
| C(24)–C(25)–C(17) | 117.5(8) | 118.0(6) |
| C(5′)–C(1′)–C(2′) | 108.1(7) | 108.0(5) |
| C(1′)–C(2′)–C(3′) | 107.9(9) | 106.9(5) |
| C(2′)–C(3′)–C(4′) | 109.1(8) | 110.7(6) |
| C(3′)–C(4′)–C(5′) | 107.6(8) | 106.6(5) |
| C(4′)–C(5′)–C(1′) | 107.2(7) | 107.6(5) |
| C(1′)–C(5′)–C(6′) | 120.3(7) | 120.9(5) |
| C(5′)–C(6′)–C(7′) | 118.4(8) | 117.2(6) |
| C(6′)–C(7′)–C(8′) | 121.4(8) | 121.7(6) |
| C(7′)–C(8′)–C(9′) | 122.1(8) | 122.5(6) |
| C(8′)–C(9′)–C(1′) | 118.3(8) | 117.9(6) |
| C(9′)–C(1′)–C(5′) | 119.5(7) | 119.7(5) |
| C(21′)–C(17′)–C(18′) | 107.4(7) | 109.2(5) |
| C(17′)–C(18′)–C(19′) | 107.7(8) | 106.3(6) |
| C(18′)–C(19′)–C(20′) | 109.0(8) | 110.0(6) |
| C(19′)–C(20′)–C(21′) | 107.5(7) | 106.8(5) |
| C(20′)–C(21′)–C(17′) | 108.3(7) | 107.4(5) |
| C(17′)–C(21′)–C(22′) | 120.6(7) | 121.1(5) |
| C(21′)–C(22′)–C(23′) | 117.1(8) | 117.9(6) |
| C(22′)–C(23′)–C(24′) | 121.8(8) | 121.9(6) |
| C(23′)–C(24′)–C(25′) | 122.6(8) | 121.5(6) |
| C(24′)–C(25′)–C(17′) | 117.0(8) | 118.7(6) |
| C(25′)–C(17′)–C(21′) | 120.8(7) | 118.9(5) |

The second independent molecule is denoted by (′).

$g_\perp = 2.06$. It is surprising that a signal is observed from compound **3** since no signal has been seen for $[Cr(\eta^5\text{-}C_5H_5)_2]$, $[Cr(\eta^5\text{-}C_5Me_5)_2]$[12] or $[Cr(\eta^5\text{-}C_5HPh_4)_2]$.[25] The variable-temperature EPR spectra for **1** in the temperature range 4.3–298 K exhibit characteristic anisotropic powder line-shapes with measured $g$-tensors $g_x = 2.1381$, $g_y = 2.0419$ and $g_z = 1.9429$

Solid-state magnetic susceptibility measurements have been performed on compounds **1**, **3** and **4** in the temperature range 4.3–290 K. Results indicate simple Curie behaviour. The magnetic susceptibilities of compounds **1**, **3** and **4** can be fitted to the Curie law $\chi_M = C/T$. For compound **1** $\mu_{eff} = 1.65 \pm 0.05$ (5–290 K).[10] For compound **3** $\mu_{eff} = 2.67 \pm 0.05$ (5–235 K), consistent with a ground triplet ($S = 1$) state and for compound **4** $\mu_{eff} = 3.47 \pm 0.05$ (5–190 K), consistent with a ground quartet ($S = \frac{3}{2}$) state. No evidence of zero-field splitting or spin-crossover was observed in these complexes. The magnetic data also showed no evidence for short range intermolecular interactions. The data are entirely consistent with the electronic structure suggested by the gas-phase photoelectron experiments.

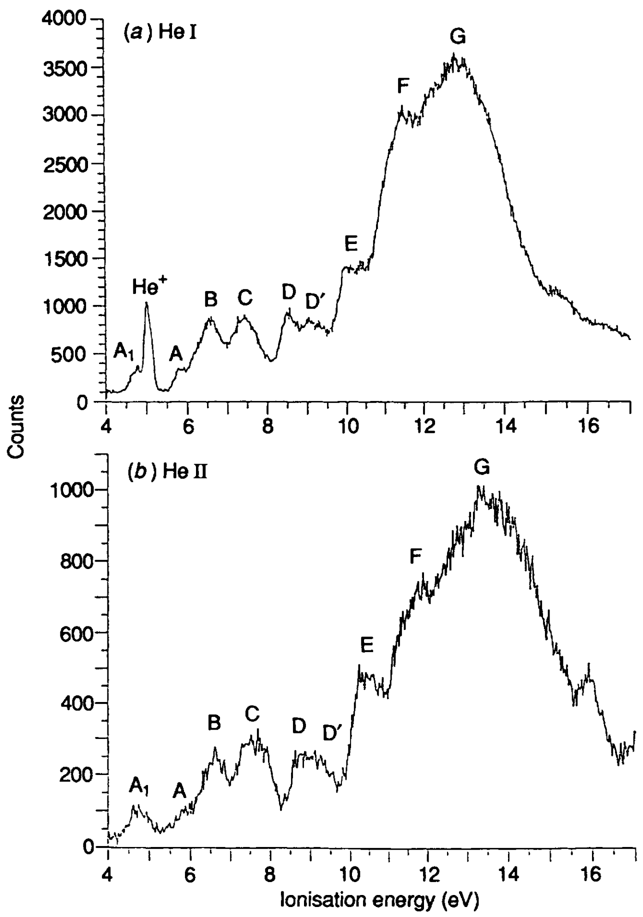


**Fig. 7** Helium-I and -II photoelectron spectra of $[Cr(\eta^5\text{-}C_9Me_7)_2]$

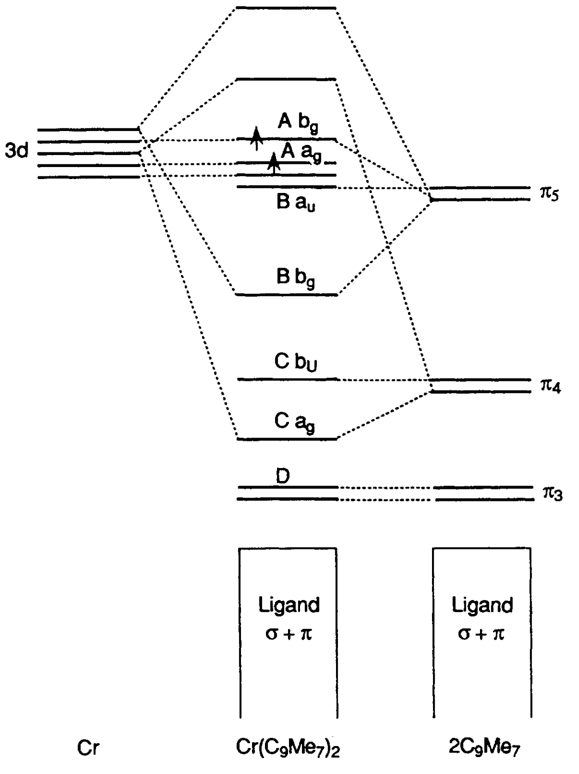


**Fig. 8** Qualitative molecular orbital scheme for $[Cr(\eta^5\text{-}C_9Me_7)_2]$

*Electrochemistry*.—The cyclic voltammogram of **4** in dry, oxygen-free acetonitrile shows a reversible redox wave at −1.15 V (*vs.* a saturated calomel electrode),[26] with a peak separation of 60 mV. Table 11 reports this half-wave potential together with other metallocene compounds for comparison.

**Table 5** Fractional atomic coordinates for $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **2** with e.s.d.s in parentheses

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Co(1) | 0.2005(1) | 0.0077(1) | 0.2559(1) |
| Co(1′) | −0.2541(1) | −0.5034(1) | 0.3014(1) |
| C(1) | 0.1444(6) | −0.1273(5) | 0.2632(6) |
| C(2) | 0.0638(6) | −0.1060(6) | 0.2276(6) |
| C(3) | 0.0891(7) | −0.0910(6) | 0.1355(7) |
| C(4) | 0.1858(6) | −0.0933(6) | 0.1176(6) |
| C(5) | 0.2188(6) | −0.1193(5) | 0.1962(6) |
| C(6) | 0.3077(6) | −0.1351(6) | 0.2141(6) |
| C(7) | 0.3145(7) | −0.1612(6) | 0.2930(7) |
| C(8) | 0.2395(7) | −0.1723(6) | 0.3585(7) |
| C(9) | 0.1562(6) | −0.1544(6) | 0.3463(6) |
| C(10) | −0.0328(7) | −0.1084(7) | 0.2687(9) |
| C(11) | 0.0210(8) | −0.0772(8) | 0.0673(8) |
| C(12) | 0.2359(9) | −0.0794(7) | 0.0294(7) |
| C(13) | 0.3854(7) | −0.1278(7) | 0.1422(8) |
| C(14) | 0.4078(8) | −0.1783(9) | 0.3160(9) |
| C(15) | 0.2510(9) | −0.2072(9) | 0.4411(8) |
| C(16) | 0.0761(8) | −0.1616(7) | 0.4170(7) |
| C(17) | 0.2840(6) | 0.1400(6) | 0.2473(6) |
| C(18) | 0.1921(6) | 0.1348(6) | 0.2925(6) |
| C(19) | 0.2012(7) | 0.1155(6) | 0.3811(6) |
| C(20) | 0.2925(6) | 0.1011(6) | 0.3887(6) |
| C(21) | 0.3460(6) | 0.1194(5) | 0.3070(6) |
| C(22) | 0.4411(6) | 0.1167(6) | 0.2770(6) |
| C(23) | 0.4682(7) | 0.1329(6) | 0.1906(7) |
| C(24) | 0.4055(6) | 0.1535(6) | 0.1327(6) |
| C(25) | 0.3164(6) | 0.1579(6) | 0.1578(6) |
| C(26) | 0.1056(7) | 0.1537(7) | 0.2627(9) |
| C(27) | 0.1287(8) | 0.1123(7) | 0.4569(8) |
| C(28) | 0.3265(8) | 0.0775(7) | 0.4716(7) |
| C(29) | 0.5072(7) | 0.0991(8) | 0.3434(8) |
| C(30) | 0.5653(8) | 0.1265(8) | 0.1540(9) |
| C(31) | 0.4410(9) | 0.1681(7) | 0.0365(7) |
| C(32) | 0.2501(9) | 0.1807(8) | 0.0973(8) |
| C(1′) | −0.1835(6) | −0.3776(5) | 0.2743(6) |
| C(2′) | −0.1110(6) | −0.4025(6) | 0.3128(6) |
| C(3′) | −0.1323(7) | −0.4048(7) | 0.4099(7) |
| C(4′) | −0.2218(7) | −0.3884(6) | 0.4299(7) |
| C(5′) | −0.2540(6) | −0.3695(5) | 0.3461(6) |
| C(6′) | −0.3359(7) | −0.3445(6) | 0.3267(6) |
| C(7′) | −0.3445(7) | −0.3286(6) | 0.2407(7) |
| C(8′) | −0.2742(7) | −0.3365(6) | 0.1690(7) |
| C(9′) | −0.1960(6) | −0.3610(6) | 0.1838(6) |
| C(10′) | −0.0219(7) | −0.4174(7) | 0.2679(8) |
| C(11′) | −0.0671(9) | −0.4165(8) | 0.4824(8) |
| C(12′) | −0.2670(9) | −0.3846(8) | 0.5260(7) |
| C(13′) | −0.4110(8) | −0.3408(7) | 0.4011(9) |
| C(14′) | −0.4280(8) | −0.3010(9) | 0.2190(9) |
| C(15′) | −0.2900(9) | −0.3165(9) | 0.0761(9) |
| C(16′) | −0.1219(8) | −0.3676(7) | 0.1102(7) |
| C(17′) | −0.2513(6) | −0.6347(6) | 0.2276(6) |
| C(18′) | −0.2993(7) | −0.6300(6) | 0.3182(7) |
| C(19′) | −0.3870(7) | −0.6114(7) | 0.3048(7) |
| C(20′) | −0.3909(6) | −0.5980(6) | 0.2121(6) |
| C(21′) | −0.3078(6) | −0.6150(5) | 0.1624(6) |
| C(22′) | −0.2782(6) | −0.6135(6) | 0.0667(6) |
| C(23′) | −0.1932(7) | −0.6303(6) | 0.0422(7) |
| C(24′) | −0.1388(7) | −0.6529(6) | 0.1068(7) |
| C(25′) | −0.1647(7) | −0.6546(6) | 0.1983(7) |
| C(26′) | −0.2710(9) | −0.6492(8) | 0.4073(8) |
| C(27′) | −0.4635(9) | −0.6166(7) | 0.3755(9) |
| C(28′) | −0.4719(7) | −0.5757(7) | 0.1749(8) |
| C(29′) | −0.3401(8) | −0.5972(8) | −0.0041(7) |
| C(30′) | −0.1545(9) | −0.6251(7) | −0.0557(8) |
| C(31′) | −0.0475(8) | −0.6727(8) | 0.0711(9) |
| C(32′) | −0.1061(9) | −0.6768(9) | 0.2666(9) |
| P(1) | 0.7627(2) | 0.0111(2) | 0.2575(2) |
| P(1′) | 0.2564(2) | 0.4907(2) | 0.2520(2) |
| F(1) | 0.848(1) | 0.031(1) | 0.341(1) |
| F(2) | 0.751(1) | −0.089(1) | 0.211(1) |
| F(3) | 0.685(1) | −0.007(1) | 0.328(2) |
| F(4) | 0.678(1) | −0.005(2) | 0.178(1) |
| F(5) | 0.775(1) | 0.114(1) | 0.305(1) |
| F(6) | 0.843(2) | 0.039(2) | 0.190(2) |
| F(1′) | 0.349(1) | 0.537(2) | 0.202(2) |
| F(2′) | 0.206(2) | 0.551(2) | 0.234(2) |
| F(3′) | 0.164(1) | 0.445(2) | 0.302(1) |
| F(4′) | 0.202(2) | 0.413(2) | 0.147(1) |
| F(5′) | 0.299(3) | 0.559(2) | 0.356(2) |
| F(6′) | 0.306(2) | 0.428(2) | 0.271(2) |

## Experimental

*General.*—All reactions were performed by using standard Schlenk techniques or in a Vacuum Atmospheres Dri-Box under a nitrogen atmosphere. Solvents were pre-dried over molecular sieves (type 4 Å) and refluxed with the appropriate drying agents under a continuous stream of nitrogen. Tetrahydrofuran and diethyl ether were refluxed over sodium–potassium alloy, and MeCN was refluxed over $CaH_2$. Solvents were distilled prior to use and stored over molecular sieves in flame-dried ampoules under nitrogen. The heptamethylindenyl ligand, $C_9Me_7$, was synthesised by the multistep procedure described in detail elsewhere.[11]

*Equipment.*—Cyclic voltammograms were recorded in the three-electrode configuration with a platinum disc working electrode, platinum gauze auxiliary electrode, and a silver wire pseudo-reference in MeCN–0.1 mol dm$^{-3}$ $[NBu^n{}_4][PF_6]$. All potentials were referenced to the saturated calomel electrode (SCE) by measuring the ferrocene–ferrocenium couple ($E_{\frac{1}{2}}$ = 0.355 V *vs.* SCE) under identical conditions. The gas-phase ultraviolet photoelectron spectra were measured using a PES Laboratories 0078 spectrometer interfaced with a Research Machines 380Z microcomputer. Both He I and He II radiation were used for spectral acquisition. Data were collected by repeated scans and the spectra calibrated with He, Xe and $N_2$. Solid-state magnetic susceptibility measurements were carried out on microcrystalline samples using a Cryogenics Consultants SCU500 superconducting quantum interference device (SQUID) susceptometer. The susceptibilities have been corrected for the intrinsic diamagnetism of the sample container and the diamagnetism of the electronic cores of the constituent atoms. The EPR spectra were obtained using the X-band of a Bruker ESP-300 spectrometer. The samples were prepared under an atmosphere of nitrogen as single crystals or microcrystalline solids, and recorded in 4 mm high-purity Spectrosil quartz tubes fitted with a Young's Teflon stopcock. Infrared spectra were recorded on a Mattison Instruments Polaris Fourier transform spectrometer as Nujol mulls between KBr plates. Crystallographic calculations were performed on a Microvax computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system.[27–32]

Elemental microanalyses were performed by the Analytical Services of the Inorganic Chemistry Laboratory.

*Syntheses.*—*Bis*($\eta^5$-*heptamethylindenyl*)*cobalt*(II), $[Co(\eta^5\text{-}C_9Me_7)_2]$ **1**. An analytically pure sample of **1** was prepared by reduction of $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$. To a suspension of $[Co(acac)_2]$ (1.05 g, 4.09 mmol) in thf (50 cm$^3$) was added a solution of lithium heptamethylindenide (1.82 g, 8.18 mmol) in thf (40 cm$^3$). The resultant light brown mixture was stirred for 2 h at room temperature. The volatiles were then removed under reduced pressure, and the resulting black residue was extracted with light petroleum (b.p. 40–60 °C, 2 × 50 cm$^3$), giving a dark red solution. The solution was filtered through a bed of Celite. A saturated solution of $NH_4PF_6$ in thf (*ca.* 10 cm$^3$) was added to the light petroleum solution. A bright red flocculant precipitate

**Table 6** Fractional atomic coordinates for $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **4** with e.s.d.s in parentheses

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Cr(1) | 0.2433(1) | 0.4936(1) | 0.2993(1) |
| Cr(1′) | −0.3001(1) | 0.0052(1) | 0.2550(1) |
| C(1) | 0.2371(4) | 0.3544(4) | 0.2246(4) |
| C(2) | 0.1880(5) | 0.3586(5) | 0.3132(5) |
| C(3) | 0.1028(5) | 0.3777(5) | 0.2974(5) |
| C(4) | 0.1008(5) | 0.3933(4) | 0.2048(5) |
| C(5) | 0.1842(4) | 0.3751(4) | 0.1583(4) |
| C(6) | 0.2194(5) | 0.3798(4) | 0.0640(5) |
| C(7) | 0.3079(5) | 0.3661(4) | 0.0428(5) |
| C(8) | 0.3609(5) | 0.3440(4) | 0.1076(5) |
| C(9) | 0.3921(5) | 0.3379(4) | 0.1979(5) |
| C(10) | 0.2130(9) | 0.3374(6) | 0.4044(6) |
| C(11) | 0.0250(7) | 0.3831(6) | 0.3696(8) |
| C(12) | 0.0212(6) | 0.4193(6) | 0.1658(7) |
| C(13) | 0.1609(7) | 0.3991(6) | −0.0082(6) |
| C(14) | 0.3512(7) | 0.3754(6) | −0.052(6) |
| C(15) | 0.4537(6) | 0.3281(7) | 0.0781(8) |
| C(16) | 0.3879(8) | 0.3170(7) | 0.2689(8) |
| C(17) | 0.3201(4) | 0.6255(4) | 0.2757(4) |
| C(18) | 0.3937(5) | 0.6009(4) | 0.3144(5) |
| C(19) | 0.3721(5) | 0.6017(5) | 0.4131(5) |
| C(20) | 0.2827(5) | 0.6175(4) | 0.4337(5) |
| C(21) | 0.2511(4) | 0.6356(4) | 0.3478(4) |
| C(22) | 0.1661(5) | 0.6561(4) | 0.3271(5) |
| C(23) | 0.1562(5) | 0.6694(4) | 0.2374(5) |
| C(24) | 0.2254(5) | 0.6610(5) | 0.1665(5) |
| C(25) | 0.3048(4) | 0.6373(4) | 0.1822(4) |
| C(26) | 0.4829(5) | 0.5836(5) | 0.2693(7) |
| C(27) | 0.4341(8) | 0.5854(7) | 0.4863(7) |
| C(28) | 0.2360(8) | 0.6204(6) | 0.5292(6) |
| C(29) | 0.0915(6) | 0.6611(6) | 0.4016(7) |
| C(30) | 0.0705(7) | 0.6957(7) | 0.2149(9) |
| C(31) | 0.2098(8) | 0.6796(7) | 0.0719(7) |
| C(32) | 0.3779(6) | 0.6278(6) | 0.1072(6) |
| C(1′) | −0.2836(4) | −0.1278(4) | 0.1865(4) |
| C(2′) | −0.3164(5) | −0.1016(4) | 0.1090(5) |
| C(3′) | −0.4141(5) | −0.1008(4) | 0.1257(5) |
| C(4′) | −0.4407(5) | −0.1171(4) | 0.2153(5) |
| C(5′) | −0.3597(4) | −0.1376(4) | 0.2529(4) |
| C(6′) | −0.3458(4) | −0.1593(4) | 0.3409(5) |
| C(7′) | −0.2606(5) | −0.1744(4) | 0.3553(5) |
| C(8′) | −0.1840(5) | −0.1629(5) | 0.2900(5) |
| C(9′) | −0.1932(5) | −0.1395(4) | 0.2079(5) |
| C(10′) | −0.2649(7) | −0.0859(5) | 0.0211(5) |
| C(11′) | −0.4801(7) | −0.0833(6) | 0.0582(7) |
| C(12′) | −0.5383(5) | −0.1199(5) | 0.2554(8) |
| C(13′) | −0.4231(6) | −0.1638(5) | 0.4129(6) |
| C(14′) | −0.2451(8) | −0.2022(7) | 0.4439(7) |
| C(15′) | −0.0893(6) | −0.1776(7) | 0.3159(8) |
| C(16′) | −0.1138(6) | −0.1303(5) | 0.1375(6) |
| C(17′) | −0.1549(4) | 0.1241(4) | 0.3147(4) |
| C(18′) | −0.2051(5) | 0.1054(4) | 0.3963(5) |
| C(19′) | −0.2970(5) | 0.1201(5) | 0.3899(5) |
| C(20′) | −0.3084(5) | 0.1399(4) | 0.3021(5) |
| C(21′) | −0.2171(4) | 0.1454(4) | 0.2558(4) |
| C(22′) | −0.1881(5) | 0.1608(4) | 0.1643(5) |
| C(23′) | −0.0996(5) | 0.1537(4) | 0.1349(5) |
| C(24′) | −0.0368(5) | 0.1311(4) | 0.1922(5) |
| C(25′) | −0.0613(4) | 0.1180(4) | 0.2806(5) |
| C(26′) | −0.1720(7) | 0.0802(6) | 0.4789(6) |
| C(27′) | −0.3708(7) | 0.1131(6) | 0.4656(7) |
| C(28′) | −0.3971(6) | 0.1586(6) | 0.2727(8) |
| C(29′) | −0.2542(7) | 0.1837(7) | 0.1027(7) |
| C(30′) | −0.0675(7) | 0.1663(6) | 0.0376(6) |
| C(31′) | 0.0563(6) | 0.1221(6) | 0.1495(7) |
| C(32′) | 0.0031(6) | 0.0954(6) | 0.3435(7) |
| P(1) | 0.2636(1) | 0.0081(1) | 0.2573(1) |
| P(1′) | 0.7563(1) | 0.4978(1) | 0.2576(1) |
| F(1) | 0.180(1) | −0.0124(9) | 0.321(1) |
| F(2) | 0.3446(9) | 0.0226(8) | 0.3392(8) |
| F(3) | 0.1832(9) | −0.0063(8) | 0.1757(8) |
| F(4) | 0.348(1) | 0.034(2) | 0.190(1) |
| F(5) | 0.2450(8) | −0.0937(7) | 0.2131(9) |
| F(6) | 0.2822(8) | 0.1100(7) | 0.3015(9) |
| F(1′) | 0.6858(9) | 0.5075(8) | 0.337(1) |
| F(2′) | 0.799(1) | 0.600(1) | 0.2821(9) |
| F(3′) | 0.834(1) | 0.4935(9) | 0.1831(9) |
| F(4′) | 0.714(1) | 0.3954(7) | 0.2333(9) |
| F(5′) | 0.6797(7) | 0.486(1) | 0.1741(9) |
| F(6′) | 0.8345(7) | 0.510(1) | 0.343(1) |

**Table 7** Bond lengths (Å) and angles (°) for $[Cr(\eta^5\text{-}C_9Me_7)_2]$ **3** with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Cr(1)–C(1) | 2.266(9) | C(3)–C(11) | 1.509(8) |
| Cr(1)–C(2) | 2.132(9) | C(4)–C(5) | 1.435(9) |
| Cr(1)–C(3) | 2.152(8) | C(4)–C(12) | 1.516(7) |
| Cr(1)–C(4) | 2.149(7) | C(5)–C(6) | 1.435(9) |
| Cr(1)–C(5) | 2.209(8) | C(6)–C(7) | 1.365(8) |
| C(1)–C(2) | 1.422(9) | C(6)–C(13) | 1.526(8) |
| C(1)–C(5) | 1.453(8) | C(7)–C(8) | 1.438(8) |
| C(1)–C(9) | 1.434(8) | C(7)–C(14) | 1.514(8) |
| C(2)–C(3) | 1.423(9) | C(8)–C(9) | 1.370(9) |
| C(2)–C(10) | 1.522(8) | C(8)–C(15) | 1.512(9) |
| C(3)–C(4) | 1.430(8) | C(9)–C(16) | 1.512(8) |
| C(2)–C(1)–C(5) | 107.4(6) | C(5)–C(6)–C(7) | 119.6(5) |
| C(1)–C(2)–C(3) | 107.7(5) | C(6)–C(7)–C(8) | 121.0(6) |
| C(2)–C(3)–C(4) | 109.4(4) | C(7)–C(8)–C(9) | 121.1(6) |
| C(3)–C(4)–C(5) | 106.6(5) | C(8)–C(9)–C(1) | 119.9(5) |
| C(4)–C(5)–C(1) | 108.2(6) | C(9)–C(1)–C(5) | 118.5(5) |
| C(1)–C(5)–C(6) | 119.7(6) | | |

**Table 8** Fractional atomic coordinates for $[Cr(\eta^5\text{-}C_9Me_7)_2]$ with e.s.d.s in parentheses

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Cr(1) | 0.5 | 0.5 | 0.5 |
| C(1) | 0.4543(3) | 0.3684(7) | 0.5885(6) |
| C(2) | 0.5273(3) | 0.3748(6) | 0.6045(7) |
| C(3) | 0.5568(3) | 0.3753(6) | 0.4635(7) |
| C(4) | 0.5030(4) | 0.3834(5) | 0.3581(5) |
| C(5) | 0.4388(3) | 0.3788(6) | 0.4356(6) |
| C(6) | 0.3681(4) | 0.3812(6) | 0.3882(6) |
| C(7) | 0.3162(3) | 0.3775(4) | 0.4881(8) |
| C(8) | 0.3312(3) | 0.3716(5) | 0.6402(7) |
| C(9) | 0.3980(3) | 0.3690(5) | 0.6896(7) |
| C(10) | 0.5709(3) | 0.3660(5) | 0.7410(8) |
| C(11) | 0.6334(3) | 0.3729(6) | 0.4315(8) |
| C(12) | 0.5153(4) | 0.3846(5) | 0.1960(6) |
| C(13) | 0.3513(4) | 0.3838(5) | 0.2270(7) |
| C(14) | 0.2406(3) | 0.3824(6) | 0.4464(9) |
| C(15) | 0.2722(4) | 0.3670(6) | 0.7474(9) |
| C(16) | 0.4143(4) | 0.3656(6) | 0.8495(6) |

of $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ formed immediately, which was collected on a frit and washed with degassed water (2 × 10 cm$^3$) to remove the unreacted $NH_4PF_6$. A suspension of the red precipitate (0.26 g, 0.41 mmol) in thf (30 cm$^3$) was added to a 1% sodium amalgam (*ca.* 100 g), and the reaction mixture was stirred for 3 h. A clear dark red solution was obtained. The unreacted sodium amalgam was removed by filtering the reaction mixture through a bed of Celite. Removal of the solvent under reduced pressure gave a dark red residue, which was extracted with toluene (2 × 50 cm$^3$). The solution was concentrated to *ca.* 30 cm$^3$, and on slow cooling to −20 °C gave bright red crystals of $[Co(\eta^5\text{-}C_9Me_7)_2]$ in 43% yield (0.085 g, 0.17 mmol) [Found (Calc.) for $C_{32}H_{42}Co$: C, 79.10 (79.15); H, 8.60 (8.70)%]. IR(Nujol): 2931, 2855, 1463, 1377 and 1019 cm$^{-1}$.

*Bis*($\eta^5$*-heptamethylindenyl*)*cobalt*(III) *hexafluorophosphate*, $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **2**. To a suspension of $[Co(acac)_2]$

**Table 9** Comparison of the solid-state structures of indenyl complexes

| Compound | M–C(av)/Å | $\Delta_{M-C}$/Å | h.a./° | f.a./° | r.a./° | Ref. |
|---|---|---|---|---|---|---|
| $[Co(\eta\text{-}C_9Me_7)_2]^+$ | 2.077(8) | 0.079(9) 0.087(9) | 5.4 4.7 | 5.5 5.4 | 89 | This work |
| | | 0.079(9) 0.049(9) | 3.9 4.0 | 4.8 3.4 | | |
| $[Co(\eta\text{-}C_9H_7)_2]$ | 2.121(4) | 0.114 0.124 | 7.3 7.8 | 6.0 5.9 | — | 2 |
| $[Cr(\eta\text{-}C_9Me_7)_2]^+$ | 2.208(6) | 0.010(9) 0.025(8) | 5.0 5.3 | 1.5 4.3 | 89 | This work |
| | | 0.035(8) 0.020(7) | 5.4 4.8 | 3.8 0.2 | | |
| $[Cr(\eta\text{-}C_9Me_7)_2]$ | 2.182(8) | 0.097(9) | 7.2 | 3.6 | 180 | This work |
| $[Fe(\eta\text{-}C_9Me_7)_2]$ | 2.074(4) | 0.030(14) | 2.5 | 4.4 | 151 | 2 |
| $[Fe(\eta\text{-}C_9Me_2H_5)_2]^+$ | 2.103(4) | 0.074(4) | — | — | — | 10 |
| $[Fe(\eta\text{-}C_9H_7)_2]$ | 2.065(4) | 0.050 0.050 | 2.6 2.6 | 0.4 1.6 | — | 2 |
| | | 0.034 0.039 | 2.1 1.6 | 0.9 0.9 | | |
| $[Ni(\eta\text{-}C_9H_7)_2]$ | 2.204(6) | 0.419 0.416 | 13.7 14.1 | 12.7 13.4 | 175 | 2 |

**Table 10** Ionisation energies for $[Cr(\eta^5\text{-}C_9Me_7)_2]$

| Band | i.e./eV |
|---|---|
| $A_1$ | 4.67 |
| A | 5.84 |
| B | 6.63 |
| C | 7.35 |
| D | 7.70 |

**Table 11** Electrochemical potentials of selected metallocenes *vs.* SCE

| Compound | $E_{\frac{1}{2}}$/V | Ref. |
|---|---|---|
| $[Co(\eta\text{-}C_5H_5)_2]^{+/0}$ | −0.91 | 3 |
| $[Co(\eta\text{-}C_5Me_5)_2]^{+/0}$ | −1.47 | 3 |
| $[Co(\eta\text{-}C_9Me_7)_2]^{+/0}$ | −1.05 | 1 |
| $[Cr(\eta\text{-}C_5H_5)_2]^{+/0}$ | −0.55 | 3 |
| $[Cr(\eta\text{-}C_5Me_5)_2]^{+/0}$ | −1.04 | 3 |
| $[Cr(\eta\text{-}C_9Me_7)_2]^{+/0}$ | −1.15 | This work |

(1.05 g, 4.09 mmol) in thf (50 cm$^3$) was added a solution of lithium heptamethylindenide (1.82 g, 8.18 mmol) in thf (40 cm$^3$). The resultant light brown mixture was stirred for 2 h at room temperature. The volatiles were then removed under reduced pressure, and the resulting black residue was extracted with light petroleum (b.p. 40–60 °C, 2 × 50 cm$^3$), giving a dark red solution. The solution was filtered through a bed of Celite. A saturated solution of $NH_4PF_6$ in thf (*ca.* 10 cm$^3$) was added to the light petroleum solution. A bright red flocculant precipitate formed immediately, which was collected on a frit and washed with degassed water (2 × 10 cm$^3$) to remove the unreacted $NH_4PF_6$. The precipitate was dried *in vacuo* for *ca.* 12 h and recrystallised from 1:1 acetone–diethyl ether at −20 °C yielding dark red crystals of $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$, yield 47% (1.2 g, 1.09 mmol). Crystals for X-ray analysis were obtained by ether diffusion into acetone [Found (Calc.) for $C_{32}H_{42}CoF_6P$: C, 60.45 (60.95); H, 6.75 (6.70); Co, 9.55 (9.35)%]. IR(Nujol): 2924, 2854, 1463, 1378, 1201 and 801 cm$^{-1}$.

*Bis*($\eta^5$-*heptamethylindenyl*)*chromium*(II), $[Cr(\eta^5\text{-}C_9Me_7)_2]$ **3**. To a suspension of $CrCl_2$ (0.61 g, 5.00 mmol) in thf (50 cm$^3$) was added a solution of lithium heptamethylindenide (2.20 g, 10.0 mmol) in thf (40 cm$^3$). The resultant green solution was stirred for 4 h at room temperature. The volatiles were then removed under reduced pressure, and the resulting dark green residue was extracted with toluene giving a dark green solution. The solution was concentrated to *ca.* 30 cm$^3$, and slow cooling to −80 °C gave dark green crystals of $[Cr(\eta^5\text{-}C_9Me_7)_2]$ in 70% yield (1.68 g, 3.50 mmol) [Found (Calc.) for $C_{32}H_{42}Cr$: C, 79.95 (80.30); H, 9.35 (8.85); Cr, 10.85 (10.85)%]. IR(Nujol): 2928, 2851, 1457, 1377 and 1008 cm$^{-1}$.

*Bis*($\eta^5$-*heptamethylindenyl*)*chromium*(III) *hexafluorophosphate*, $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ **4**. To a solution of **3** (0.60 g, 1.25 mmol) in toluene (*ca.* 40 cm$^3$) was added a saturated solution of $NH_4PF_6$ in thf (*ca.* 10 cm$^3$). A bright red flocculant precipitate formed immediately, which was collected on a frit and washed with diethyl ether (2 × 10 cm$^3$). The precipitate was dried *in vacuo* for *ca.* 12 h and recrystallised from 1:1 acetone–diethyl ether at −20 °C yielding dark red crystals of $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$, yield 50% (0.39 g, 0.63 mmol). Crystals for X-ray analysis were obtained by ether diffusion into acetone [Found (Calc.) for $C_{32}H_{42}CrF_6P$: C, 61.55 (61.65); H, 7.00 (6.80); Cr, 8.70 (8.35)%]. IR(Nujol): 2926, 2857, 1458, 1377 and 841 cm$^{-1}$.

*Crystal Structure Determinations.*—Crystallographic details for compounds **2**, **3** and **4** are presented in Table 1. The crystals were sealed under nitrogen in Lindemann glass capillaries and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer interfaced to a PDP 11/23 mini computer. Unit-cell parameters were calculated from the setting angles of 25 carefully-centred reflections. Three reflections were chosen as intensity standards and measured every 3600s of X-ray exposure time, and four orientation controls were measured every 250 reflections. The data were measured using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.710 69 Å) and an $\omega$–2$\theta$ scan mode.

For **2** 8129 unique reflections were measured ($1.00 \leqslant \theta \leqslant 23°$, $+h, \pm k, \pm l$, merging $R = 0.013$ after absorption correction), giving 5400 with $I \geqslant 3\sigma(I)$. Linear and approximately isotropic crystal decay of *ca.* 1%, corrected during processing. Corrections were made for Lorentz and polarisation effects.

For **4** 9297 unique reflections were measured ($1.00 \leqslant \theta \leqslant 22.5°$, $+h, \pm k, \pm l$, merging $R = 0.010$ after absorption correction), giving 6281 with $I \geqslant 3\sigma(I)$. Linear and approximately isotopic crystal decay of *ca.* 1%, corrected during processing. Corrections were made for Lorentz and polarisation effects.

For **3** 1693 unique reflections were measured ($1.00 \leqslant \theta \leqslant 22.5°$, $+h, +k, +l$, merging $R = 0.029$ after absorption correction), giving 841 with $I \geqslant 3\sigma(I)$. Linear and approximately isotopic crystal decay of *ca.* 4%, corrected during processing. Corrections were made for Lorentz and polarisation effects.

*Structure analysis and refinement.* Heavy-metal atom positions were revealed by direct methods. Subsequent Fourier synthesis revealed the positions of the other non-hydrogen atoms. The structures were refined using least-squares procedures. For **2** and **4** the metal atoms, methyl carbons, phosphorus and fluorine atoms were refined with anisotropic thermal parameters. The indenyl-ring carbons were refined with isotropic thermal parameters due to the relatively low ratio of observations to least squares parameters. The $PF_6^-$ anion is disordered over two sites for which refinement gave disordered occupancy factors of 0.5 per site. Non-crystallographic chemical restraints were included in the least-squares refinement to preserve $O_h$ symmetry of the anion. Internal bond lengths and angles were equivalenced to their arithmetic mean. A four-term Chebyshev[30] weighting scheme was applied (coefficients: for **2**, 11.1, 3.13, 9.46, 1.30; for **4**, 16.1, 5.05, 12.7, −0.09). Final $R$ and $R'$ values were: for **2**, 0.064 and 0.071; for **4**, 0.075 and 0.095.

For **3** all non-hydrogen atoms were refined with anisotropic thermal parameters. A three-term Chebyshev weighting scheme was applied (coefficients: 7.72, −1.57, 5.87). The final $R$ and $R'$ values were 0.043 and 0.047.

All hydrogens were placed in calculated positions (C–H 1.0 Å) and allowed to ride on their attached carbons. Corrections were made for the effects of anomalous dispersion and isotropic extinction[29] in the final stages of refinement. Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 31.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

## Conclusion

A convenient synthesis of permethylindenyl complexes of cobalt and chromium has been described. These complexes have been shown to exhibit very low first ionisation energies and redox potentials, as measured by gas-phase photoelectron spectroscopy and cyclic voltammetry. The permethylindenyl ligand appears to be more electron donating than the pentamethylcyclopentadienyl ligand when complexed to chromium while the reverse is true for the cobalt analogues. Both neutral complexes can be reversibly oxidised to the monocation. The crystal structures of $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$, $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ and $[Cr(\eta^5\text{-}C_9Me_7)_2]$ have been reported. The latter adopts a staggered conformation and the metal atom lies on a crystallographic inversion centre. In $[Co(\eta^5\text{-}C_9Me_7)_2][PF_6]$ and $[Cr(\eta^5\text{-}C_9Me_7)_2][PF_6]$ the permethylindenyl rings are rotated through an angle of 89° with respect to each other resulting in a partially staggered conformation. Extended Hückel molecular orbital calculations are currently in progress to attempt to probe the causes of these differences and the results will be reported in due course.

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