

New transition-metal derivatives of the fullerene C₆₀

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The new compounds [M(NO)(PPh₃)₂(η²-C₆₀)] (M = Co **1** or Rh **2**), [RuX(NO)(PPh₃)₂(η²-C₆₀)] (X = Cl **3** or H **4**), [Re₂H₈(PMe₃)₄(η²: η²-C₆₀)] **5** and [TaH(η-C₅H₅)₂(η²-C₆₀)] have been prepared and characterised. Crystal structures have been determined for **3** and **5** and show typical η² co-ordination of C₆₀ in the former, but a rare example of η⁴ co-ordination in the latter. The soluble adducts **1**, **2**, **4**, **5** and [M(CO)₄(η²-C₆₀)] (M = Ru **7** or Fe **8**) have been electrochemically reversibly reduced up to the dianion and to the trianion for **4**. The E° values are shifted to slightly less negative values than for C₆₀ itself in consonance with the reduction in the number of fullerene double bonds. Addition of the electrophiles I₂, maleic anhydride or PPh₃ to **1** or **2** easily regenerated free C₆₀. The presence of an isobenzofuran side chain in C₆₀(C₂₀H₁₄O) prevents attack by the incoming metal centre Fe(CO)₄ at adjacent double bonds and results in inequivalency of the remaining double bonds and a mixture of regioisomeric products. However, the isobenzofuran side chain may be displaced by Pd(PPh₃)₂ or [Co(η-C₅H₅)₂] resulting in the formation of [Pd(PPh₃)₂(η²-C₆₀)] or [Co(η-C₅H₅)₂]⁺[C₆₀]⁻.

There are relatively few transition-metal fullerene derivatives in comparison with the plethora of organic derivatives.¹⁻³ This paper describes the preparation and characterisation of a number of new metallo-C₆₀ derivatives. Many of the complexes display extensive and interesting dynamical behaviour on the ¹³C NMR time-scale. A preliminary report of this behaviour has been published, and a fuller account, including details of the C₇₀ analogues, will appear shortly.¹

The fullerene C₆₀, being an electron-deficient (E_A ≈ 2.65 eV; 1 eV ≈ 1.60 × 10⁻¹⁹ J) π-acidic alkene, forms most stable adducts with electron-rich metal fragments.¹ Previously prepared adducts have centred upon Pt(PR₃)₂ and IrCl(CO)(PR₃)₂ (R = alkyl group) fragments bound to the fullerene at one of its 30 equivalent double bonds, which occur at the fusions of two six-membered rings.^{4,5} The fullerene electron affinity is slightly reduced by metal complexation and the moiety can be displaced by other ligands. Partly because of their low solubility in most common organic solvents, many transition-metal fullerene complexes have often only been characterised by X-ray crystallography, IR spectroscopy and elemental analysis.

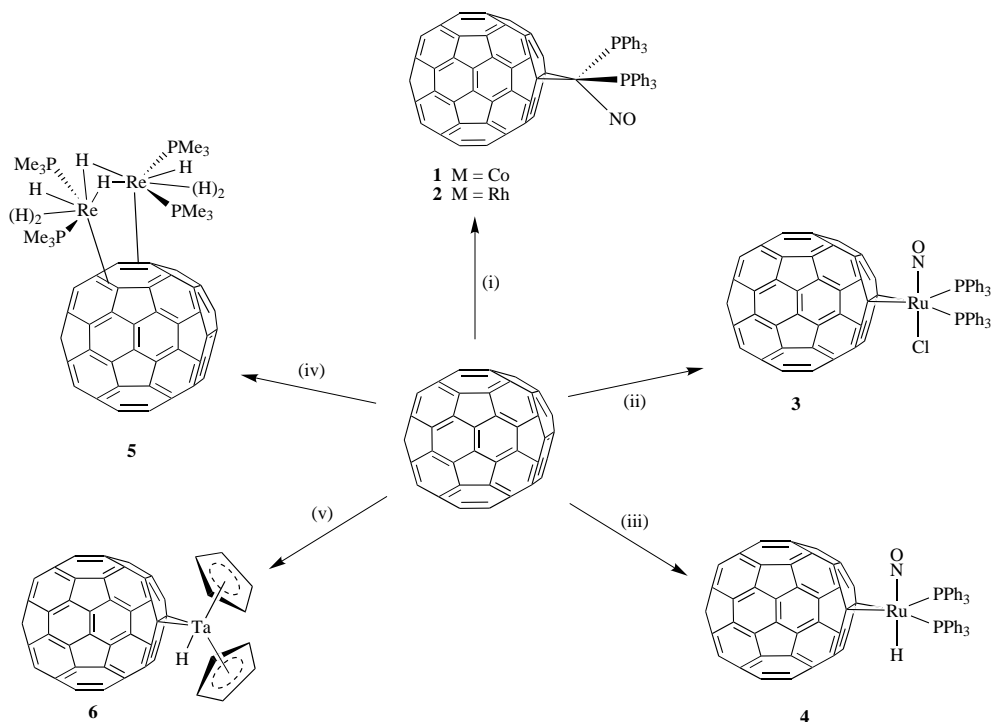
Initial experiments focused on the reaction of C₆₀ with the catalyst precursors [RuCl₂(PPh₃)₃], [RuH(Cl)(PPh₃)₃] and [RhCl(PPh₃)₃].⁶⁻⁸ These reagents are known to form adducts with alkenes and in an analogous study Balch and Green both found that C₆₀ reacts with the hydroformylation catalyst [RhH(CO)(PPh₃)₃] to produce [RhH(CO)(PPh₃)₂(η²-C₆₀)] in high yields.⁹⁻¹⁰ However, even after heating a solution containing equimolar amounts of either [RuH(Cl)(PPh₃)₃] or [RhCl(PPh₃)₃] and C₆₀ in toluene at 50 °C for 1 week, no reaction occurred; C₆₀ was also found to be unreactive towards [RuH₂(CO)(PPh₃)₃] and [Ru(NO)₂(PPh₃)₂].

Results and Discussion

Synthesis and characterisation

Treatment of a thf suspension of C₆₀ with [M(NO)(PPh₃)₃] (M = Co, Rh or Ir) allowed the successful isolation of [M(NO)(PPh₃)₂(η²-C₆₀)] (M = Co **1** or Rh **2**) in high yields (Scheme 1). The compound [Ir(NO)(PPh₃)₃] was found to react only very slowly with C₆₀ and no tractable product could be isolated. Similar difficulties have been previously noted for the preparation of other [Ir(NO)(PPh₃)₂(alkene)] complexes.¹¹ The preparations could also be successfully performed in benzene although a longer reaction time was required. Attempts to

decrease the reaction time and increase the yield by addition of either stoichiometric or excess amounts of B(C₆F₅)₃ to sequester the PPh₃ gave only a slight increase in the yield and no significant increase in the reaction rate. The compounds **1** and **2** have very similar properties, a high solubility only in aromatic solvents and thf, and thermal stability at room temperature, although only solutions of **2** are stable in air for more than 5 min. Characterising data for the new compounds described in this paper are summarised in Table 1 and will not be further discussed except where assignments are not straightforward. The IR spectra of **1** and **2** contained, in addition to C₆₀ bands at 522 and 580 cm⁻¹, ν(NO) stretches at 1687 and 1611 cm⁻¹ respectively, typical of a linear MNO system. These values were slightly higher than for other [M(NO)(PPh₃)₂(alkene)] complexes and confirm that C₆₀ is only a weakly electron-withdrawing alkene.¹¹ The UV/VIS spectra contain three intense bands at ≈220, 256 and 329 nm, a weak shoulder at 404 nm and a weak and broad band at 530–750 nm exhibiting considerably less fine structure than for unco-ordinated C₆₀. These features are typical of a fullerene cage which has been modified only slightly by complexation.^{12,13} The spectrum also showed a weak and broad band at ≈440 nm (Fig. 1) diagnostic of closed organic 6,6 fullerene C₆₀ complexes.^{14,15} Its presence in the spectra of **4** and **5**, and those of all the other adducts described in this paper, suggests a useful diagnostic rule. The ³¹P-¹H NMR spectrum of **1** contained a very broad resonance at δ 47.4 consistent with coupling to the large quadrupole moment of the ⁵⁹Co nucleus. That of **2** contained a sharp doublet at δ 29.8 [¹J(RhP) = 193 Hz] with a value typical of such one-bond couplings {for [Ru(NO)(PPh₃)₃] ¹J(RhP) 176 Hz}.¹⁶ The presence of only one signal in the ³¹P-¹H NMR spectra of **1** and **2** indicates that the P atoms are equivalent in each molecule; no significant change occurred on cooling to 183 K. The ¹³C-¹H NMR spectra of **1** and **2** showed distinct signals for the *ipso*, *ortho*, *para* and *meta* PPh₃ carbon atoms and a very broad peak at δ 144 (Δν_i ≈ 2 ppm) due to the fullerene carbon atoms. The geometry of the ligands around the metal cannot be rigorously defined on the basis of the spectroscopic evidence presented. However, for the other known [M(NO)(PPh₃)₂(alkene)] (M = Co, Rh or Ir) complexes an approximate tetrahedral arrangement of ligands around the metal atom with a linear nitrosyl group was proposed on the basis of spectroscopic evidence. Furthermore various MO studies of four-co-ordinate [M(NO)L₃] d¹⁰ systems have shown that two limiting co-ordination geometries exist; tetrahedral with essentially linear



Scheme 1 Reagents: (i) $[M(\text{NO})(\text{PPh}_3)_3]$ ($M = \text{Co}$ or Rh); (ii) $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$; (iii) $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$; (iv) $[\text{Re}_2\text{H}_8(\text{PMe}_3)_4]$; (v) $[\text{TaH}_3(\eta\text{-C}_5\text{H}_5)_2]$

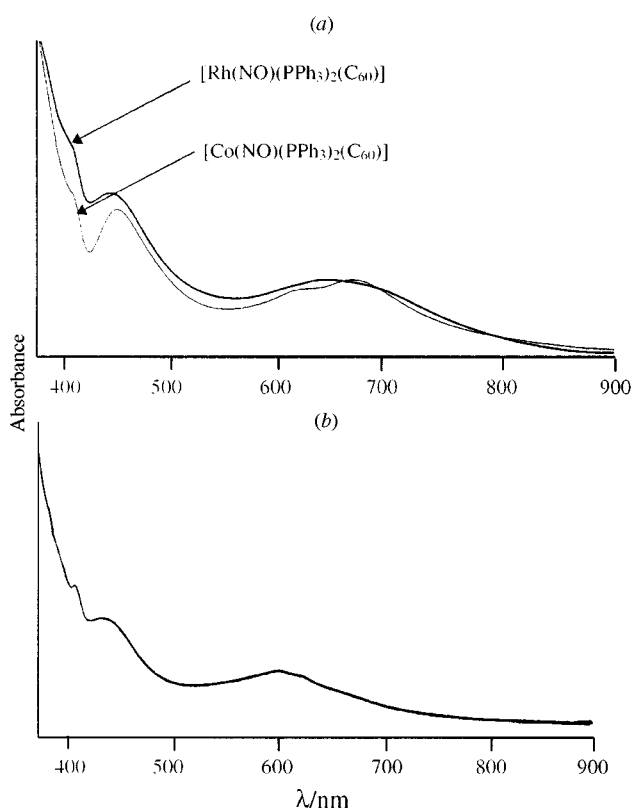


Fig. 1 The UV/VIS spectrum of compounds **1**, **2** (a) and **3** (b) in thf

MNO groups or square planar with strongly bent MNO units.^{17,18} The former is slightly favoured thermodynamically and has been exclusively observed for all such structurally characterised compounds. Unfortunately crystals of **1** or **2** suitable for X-ray diffraction could not be successfully grown using the standard methods of vapour diffusion and low-temperature crystallisation. Attempted co-crystallisations with ferrocene, triphenylphosphine oxide or naphthalene were also unsuccessful.

Both compounds **1** and **2** were found to show considerable

fluxionality on the ¹³C NMR time-scale, because of this other nitrosyl-containing species were prepared. Treatment of C₆₀ with $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$, a complex known to form stable 1:1 adducts with alkenes, resulted in the formation of $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2(\eta^2\text{-C}_{60})]$ **3** in high yields.^{19,20} Complex **3** is air and thermally stable, unlike most other fullerene organometallics, and only sparingly soluble in all common organic solvents. Its IR spectrum showed a typically strong $\nu(\text{NO})$ stretch at 1785 cm^{-1} , comparable with those of other $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2(\text{alkene})]$ complexes, and also bands assignable to the C₆₀ moiety at 527, 577 and 1183 cm^{-1} .^{19,20} Although bands at 588, 519 and 513 cm^{-1} were observed these were not assigned to the reduced symmetry splitting of the C₆₀ modes as they were all present for $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$. The UV/VIS spectrum of **3** was similar to those of **1** and **2** and included the weak band diagnostic of closed 6,6 monoadducts at 435 nm (Fig. 1). Judicious use of the high-boiling aromatic solvents *o*-xylene and 1-methylnaphthalene, in which fullerenes and their derivatives are often relatively soluble, allowed us successfully to record ¹H and ³¹P-¹H NMR spectra. The latter consisted of a broad singlet at δ 27 indicating two equivalent phosphorus atoms. Crystals suitable for structure determination were grown by allowing equimolar benzene solutions of C₆₀ and $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$ to diffuse together slowly. Selected interatomic distances and bond angles are listed in Table 2. The crystal is isomorphous with that of $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-C}_{60})] \cdot 5\text{C}_6\text{H}_6$ which is to be expected as **3** is isoelectronic with $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-C}_{60})]$. The structure (Fig. 2) shows the now well documented features of a fullerene organometallic including η^2 co-ordination of a 6,6 fullerene fusion to the metal centre with alternating short (6,6 fusions) and long (6,5 fusions) fullerene C–C bonds, and is entirely consistent with the spectroscopic data detailed above.¹ The co-ordination geometry around the Ru atom can best be described as pseudo-octahedral with coplanar P(1), P(2), Ru, C(1) and C(2) atoms. The transannular 6,6 bond bound to the metal centre is much longer (1.489 Å) than the remaining double bonds (average 1.392 Å), and suggests that the interaction can best be described as metallacyclopropane rather than metal-alkene. Nevertheless, this bond is shorter than in many other fullerene organometallics, such as those listed in Table 3, and is indicative of a weaker fullerene–metal interaction. The

Table 1 Analytical, mass, UV, infrared and NMR spectral data for compounds 1–6

Compound	Analysis (%) ^a and <i>m/z</i> ^b	Spectroscopic data ^c
1 [Co(NO)(PPh ₃) ₂ (η ² -C ₆₀)] Green powder Air sensitive	C, 86.1 (86.4); H, 2.6 (2.3); Co, 4.1 (4.4); N, 1.0 (1.0); 720 ([C ₆₀] ⁺), 614 {[Co(NO)-(PPh ₃) ₂] ⁺ }, 583 {[Co(PPh ₃) ₂] ⁺ }, 321 {[Co(PPh ₃)] ⁺ }	¹ H NMR (300 MHz, C ₆ D ₆ , 25 °C): 7.50 (m, 2 H, PPh ₃ , H _o), 6.93 (m, 3 H, PPh ₃ , H _m and H _p) ³¹ P-{ ¹ H} NMR (121 MHz, C ₆ D ₆ , 25 °C): 47.4 (vbr, s) ¹³ C-{ ¹ H} NMR (75 MHz, C ₄ D ₈ O, 50 °C): 145–143 (br, C ₆₀), 135.2 [d, ¹ J(PC) 35, PPh ₃ , C _{ipso}], 134.9 [d, ² J(PC) 11, PPh ₃ , C _o], 130.2 (s, PPh ₃ , C _p), 130 [d, ³ J(PC) 11, PPh ₃ , C _m] IR: 1687s [ν(NO)], 1184m, 1156w, 1092s, 1021m, 801m, 738m, 696s, 580w [ν(C ₆₀)], 542w, 528m [ν(C ₆₀)], 519s, 494w, 486w UV/VIS (C ₄ H ₈ O): 220, 257, 329, 405 (sh), 444, 615, 659
2 [Rh(NO)(PPh ₃) ₂ (η ² -C ₆₀)] Green powder Air sensitive	C, 82.6 (82.8); H, 2.4 (2.6); N, 1.0 (1.0); 824 ([C ₆₀ Rh] ⁺), 720 ([C ₆₀] ⁺), 655 {[Rh(NO)-(PPh ₃) ₂] ⁺ }	¹ H NMR (300 MHz, C ₆ D ₆ , 25 °C): 7.39 (m, 2 H, PPh ₃ , H _o), 6.94 (m, 3 H, PPh ₃ , H _m and H _p) ³¹ P-{ ¹ H} NMR (121 MHz, C ₆ D ₆ , 25 °C): 29.8 [d, J(PRh) 193, PPh ₃] ¹³ C-{ ¹ H} NMR (75 MHz, C ₄ D ₈ O, 25 °C): 145–143 (br, C ₆₀), 134.5 [d, ² J(PC) 13, PPh ₃ , C _o], 130.6 (s, PPh ₃ , C _p), 129.2 [d, ³ J(PC) 8, PPh ₃ , C _m] IR: 1611s [ν(NO)], 1437s, 1186s, 1121m, 741m, 696s, 580w [ν(C ₆₀)], 540s, 522s [ν(C ₆₀)] UV/VIS (C ₄ H ₈ O): 217, 256, 329, 404 (sh), 438, 633
3 [RuCl(NO)(PPh ₃) ₂ (η ² -C ₆₀)] Green microcrystalline solid Air stable	C, 81.9 (81.6); H, 1.9 (2.1); Cl, 3.0 (2.5); N, 1.0 (1.0); 1072 {[C ₆₀ RuCl(NO)PPh ₂] ⁺ }, 919 {[C ₆₀ RuCl(NO)P] ⁺ }, 873 ([C ₆₀ RuClO] ⁺), 856 ([C ₆₀ RuCl] ⁺), 720 ([C ₆₀] ⁺), 691 {[RuCl(NO)(PPh ₃) ₂] ⁺ }	¹ H NMR [300 MHz, C ₆ D ₄ (CD ₃) ₂ , 25 °C]: 7.76 (br s, 2 H, PPh ₃), 7.03 (m, 3 H, PPh ₃) ³¹ P-{ ¹ H} NMR (121 MHz, 1-methylnaphthalene + C ₆ D ₆ , 25 °C): 27.3s IR: 1785s [ν(NO)], 1461s, 1435s, 1356w, 1339w, 1183m, 1092s, 1027s, 801m, 740s, 693s, 588m, 577m, 527s [ν(C ₆₀)], 519s, 513s, 487s UV/VIS (C ₄ H ₈ O): 229, 255, 329, 405, 435, 604
4 [RuH(NO)(PPh ₃) ₂ (η ² -C ₆₀)] Green powder Air stable	C, 82.8 (83.7); H, 2.3 (2.3); N, 1.0 (1.0); P, 3.6 (4.5)	¹ H NMR (300 MHz, C ₄ D ₈ O, 25 °C): 7.5–7.3 (br m, 30 H, PPh ₃), -4.73 [t, 1 H, ² J(PH) 31, RuH] ³¹ P-{ ¹ H} NMR (202 MHz, C ₄ D ₈ O, 25 °C): 45.5s ¹³ C-{ ¹ H} NMR (125 MHz, C ₄ D ₈ O, 50 °C): 164.9 (s, 4 C, C ₆₀), 148.6 (s, 4 C, C ₆₀), 147.2 (s, 2 C, C ₆₀), 146.2 (s, 4 C, C ₆₀), 145.7 (s, 2 C, C ₆₀), 145.6 (s, 8 C, C ₆₀), 145.4 (s, 4 C, C ₆₀), 145.3 (s, 4 C, C ₆₀), 145.0 (s, 2 C, C ₆₀), 144.6 (s, 4 C, C ₆₀), 144.4 (s, 4 C, C ₆₀), 144.0 (s, 4 C, C ₆₀), 143.4 (s, 4C, C ₆₀), 143.0 (s, 4C, C ₆₀), 141.4 (s, 4 C, C ₆₀), 134.4 (s, PPh ₃ , C _o), 131.3 (s, PPh ₃ , C _p), 130.0 (d, PPh ₃ , C _m), 79.4 (s, 2 C, C ₆₀) IR: 1724s [ν(NO)], 1184m, 1092s, 1020s, 800s, 742s, 692s, 578m, 526s [ν(C ₆₀)], 516s
5 [Re ₂ H ₈ (PMe ₃) ₄ (η ² -C ₆₀)] Brown microcrystalline solid	C, 61.6 (61.5); H, 3.1 (3.1); P, 5.2 (8.8); 1402 ([M - 2H] ⁺), 1324 ([M - PMe ₃ - 4H] ⁺), 1246 ([M - 2PMe ₃ - 6H] ⁺), 720 ([C ₆₀] ⁺)	¹ H NMR (500 MHz, C ₄ D ₈ O, -10 °C): 1.95 [d, 18 H, ² J(PH) 10, PMe ₃], 1.80 [d, 18 H, ² J(PH) 10, PMe ₃], -2.63 (br s, 2 H, ReH _{bridging}), -5.95 [ddd, 4 H, ² J(PH) 68, ² J(PH) 27, ⁴ J(PH) 5, ReH _{terminal}], -6.18 (br s, 2 H, ReH _{terminal}) ³¹ P-{ ¹ H} NMR (202 MHz, C ₄ D ₈ O, 25 °C): -19.9s, -26.6s ¹³ C-{ ¹ H} NMR (125 MHz, C ₄ D ₈ O, 25 °C): 171.7 (s, 2 C, C ₆₀), 167.2 (s, 2 C, C ₆₀), 163.3 (s, 2 C, C ₆₀), 154.2 (s, 1 C, C ₆₀), 153.3 (s, 2 C, C ₆₀), 148.5 (s, 2 C, C ₆₀), 147.3 (s, 2 C, C ₆₀), 147.2 (s, 2 C, C ₆₀), 147.1 (s, 2 C, C ₆₀), 146.9 (s, 2 C, C ₆₀), 146.8 (s, 2 C, C ₆₀), 146.6 (s, 2 C, C ₆₀), 145.8 (s, 2 C, C ₆₀), 145.7 (s, 2 C, C ₆₀), 145.6 (s, 2 C, C ₆₀), 145.4 (s, 2 C, C ₆₀), 145.1 (s, 2 C, C ₆₀), 145.0 (s, 4 C, C ₆₀), 144.8 (s, 2 C, C ₆₀), 144.7 (s, 3 C, C ₆₀), 144.3 (s, 2 C, C ₆₀), 143.8 (s, 2 C, C ₆₀), 142.8 (s, 1 C, C ₆₀), 142.5 (s, 2 C, C ₆₀), 141.6 (s, 1 C, C ₆₀), 141.1 (s, 2 C, C ₆₀), 137.8 (s, 2 C, C ₆₀), 137.1 (s, 2 C, C ₆₀), 84.0 (s, 2 C, sp ³ C of C ₆₀), 31.0 [d, ² J(PC) 40, PMe ₃], 26.0 [d, ² J(PC) 35, PMe ₃] IR: 1948s [ν(ReH)], 1600w (br), 1412s, 1300m, 1279s, 1095s, 1020s, 957s, 943s, 855m, 800s, 677m, 579w [ν(C ₆₀)], 524s [ν(C ₆₀)] ¹³ C-{ ¹ H} NMR (62.5 MHz, CPMAS, 25 °C): 146 (br, C ₆₀), 99 (br s, C ₅ H ₅) IR: ^d 3113w, 2949w, 2918w, 2851w, 1791m [ν(TaH)], 1566s, 1549s, 1453s, 1436s, 1185m, 1072s, 1024s, 842s, 815s, 572w [ν(C ₆₀)], 562w, 529s [ν(C ₆₀)], 518s
6 [TaH(η-C ₅ H ₅) ₂ (η ² -C ₆₀)] Brown microcrystalline solid	C, 82.1 (82.1); H, 1.7 (1.5)	

^a Analytical data are given as found (calculated) in %. ^b Fast atom bombardment with 3-nitrobenzyl alcohol as matrix, given as *M*⁺ assignment. ^c NMR data given as: chemical shift (δ) [multiplicity, relative intensity, *J*/Hz, assignment]. Where necessary assignments were confirmed using ¹H–¹H and ¹H–¹³C shift correlation experiments. IR data (cm⁻¹) determined for Nujol mulls. UV/VIS data given in λ/nm. ^d Infrared data (cm⁻¹) determined for KBr disc.

C(1)–C(9), C(1)–C(6), C(2)–C(12) and C(2)–C(3) bond lengths are all comparable with normal C(sp³)–C(sp²) single bonds. Excluding bonds to C(1) and C(2), the average 6,6 fusion (C=C) bond length is 1.392 Å and for the 6,5 fusions (C–C) 1.450 Å. These values are little altered from the corresponding values for C₆₀, 1.383 and 1.453 Å respectively, and provide further evidence that metal complexation little affects the remainder of the fullerene cage. The C(59)–C(60) bond which is the double

bond diametrically opposite, and therefore furthest away from the site of metal complexation, has a length of 1.37(1) Å compared to 1.383 Å for C₆₀, and is consistent with the fact that it should be the least affected of all C–C bonds by complexation.

Owing to the low solubility of compound **3** in all common organic solvents, synthesis of the hydride analogue was undertaken by reaction of [RuH(NO)(PPh₃)₃] with C₆₀ and gave [RuH(NO)(PPh₃)₂(η²-C₆₀)] **4** in high yields. Unusually for a

Table 2 Selected interatomic distances (Å) and angles (°) for [RuCl(NO)(PPh₃)₂(η²-C₆₀)]·5C₆H₆ **3** and [Re₂H₈(PMe₃)₄(η²:η²-C₆₀)]·1.5C₆H₆ **5**

Compound 3			
C(1)–C(2)	1.489(7)	C(59)–C(60)	1.37(1)
C(1)–C(9)	1.478(7)	Ru–P(1)	2.459(1)
C(1)–C(6)	1.482(7)	Ru–P(2)	2.449(2)
C(2)–C(12)	1.479(7)	Ru–N*	1.747(3)
C(2)–C(3)	1.480(7)	Ru–Cl*	2.349(2)
C(9)–C(10)	1.375(7)	6,6-Fusion	1.392 _(average)
C(11)–C(12)	1.380(7)	6,5-Fusion	1.450 _(average)
C(1)–Ru–C(2)	39.3(2)	C(1)–Ru–Cl	88.6(1)
P(1)–Ru–P(2)	113.22(5)	Cl–Ru–N*	179.2(1)
P(1)–Ru–Cl	91.93(6)		
Compound 5			
Re(1)–Re(2)	2.8945(5)	Re(2)–Re(1)–P(1)	121.85(7)
Re(1)–P(1)	2.299(2)	Re(2)–Re(1)–P(2)	126.90(6)
Re(1)–P(2)	2.335(3)	P(1)–Re(1)–P(2)	98.92(9)
Re(1)–C(1)	2.230(8)	Re(2)–Re(1)–C(1)	91.2(2)
Re(1)–C(2)	2.189(8)	P(1)–Re(1)–C(1)	128.0(2)
C(1)–C(2)	1.48(1)	P(2)–Re(1)–C(1)	88.1(2)
C(1)–C(6)	1.48(1)	Re(2)–Re(1)–C(2)	70.6(2)
C(1)–C(19)	1.48(1)	P(1)–Re(1)–C(2)	111.2(2)
C(2)–C(3)	1.50(1)	P(2)–Re(1)–C(2)	127.2(2)
C(5)–C(6)	1.35(1)	C(1)–Re(1)–C(2)	39.2(3)

* Refers to 80% occupancy form.

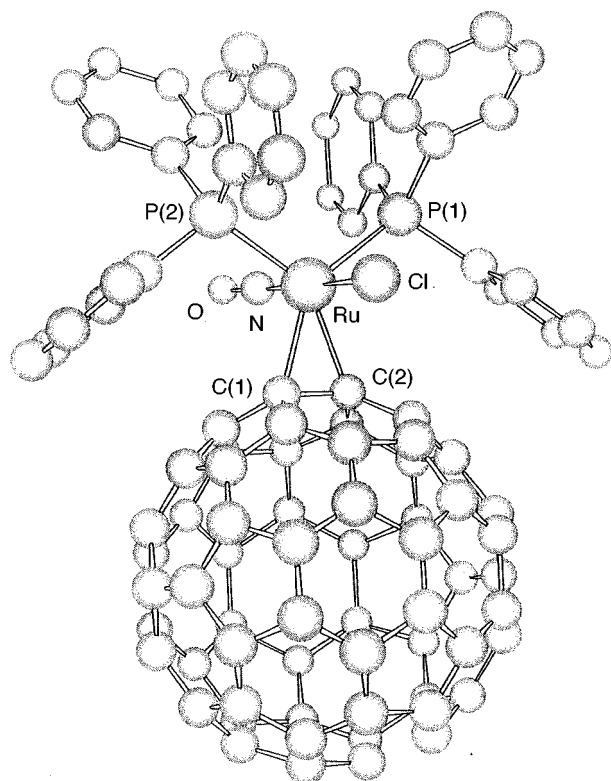


Fig. 2 The molecular structure of [RuCl(NO)(PPh₃)₂(η²-C₆₀)] **3**

fullerene organometallic, the solid and its solutions were found, like **3**, to be air stable. Compound **4** was soluble in aromatic solvents, thf and CH₂Cl₂, and insoluble in non-aromatic hydrocarbon solvents. Its IR spectrum included a weak band at 1949 cm⁻¹ and an intense band at 1724 cm⁻¹ assignable to the ν(RuH) and ν(NO) stretches respectively. The ¹H, ³¹P-¹H and ¹³C-¹H NMR spectra are in accord with the proposed structure.

The lack of reactivity of C₆₀ with the fragments mentioned in the introduction is intriguing, and may be a function of their electron richness. Other fragments are currently under investigation.

Table 3 Metal-bound fullerene C–C bond distances in some fullerene organometallics

Compound	C(sp ³)–C(sp ³)/Å	Ref.
[OsO ₄ (4-Bu ^t C ₅ H ₄ N) ₂ C ₆₀]	1.62(4)	22
[IrCl(CO)(PPh ₃) ₂ (η ² -C ₆₀)]	1.53(3)	4
[Pt(PPh ₃) ₂ (η ² -C ₆₀)]	1.502(30)	5
[C ₆₀ {Pt(PEt ₃) ₂ } ₆]	1.497(7)	23
3 [RuCl(NO)(PPh ₃) ₂ (η ² -C ₆₀)]	1.489(7)	This work
5 [Re ₂ H ₈ (PMe ₃) ₄ (η ² :η ² -C ₆₀)]	1.48(1)	This work
[RhH(CO)(PPh ₃) ₂ (η ² -C ₆₀)]	1.479(11)	9
[{Ir ₂ (μ-Cl) ₂ (1,5-C ₈ H ₁₂) ₂ } ₂ (η ² :η ² -C ₆₀)]	1.491(10), 1.454(12)	21
[Pd(PPh ₃) ₂ (η ² -C ₆₀)]	1.447(25)	15
C ₆₀	1.383(4)*	24

* Corresponds to the 6,6 ring fusion (C=C) bond length.

The reaction of fullerenes with polyhydrido-containing species was also investigated as a possible route to fullerene hydrides *via* metal-hydride insertion into a fullerene double bond. Reaction of C₆₀ with [Re₂H₈(PMe₃)₄] produced brown air-stable microcrystals of [Re₂H₈(PMe₃)₄(η²:η²-C₆₀)] **5** in high yields. Compound **5** is very soluble in thf, moderately soluble in CS₂, aromatic solvents and CH₂Cl₂, and insoluble in diethyl ether and acetone. Almost uniquely amongst fullerene organometallics, the FAB mass spectrum of **5** included a peak corresponding to [M – 2H]⁺. The IR spectrum included a strong ν(ReH) stretch at 1948 cm⁻¹ in addition to ν(C₆₀) bands at 524 and 579 cm⁻¹ which showed no splitting.²⁵ Although there were bands at 1600 and 800 cm⁻¹, it is not possible unambiguously to assign them to the ν(ReHRe) and δ(ReH) vibrations which generally occur near to these wavenumbers. The ¹H, ³¹P-¹H and ¹³C-¹H NMR spectra of **5** are all fully consistent with the proposed structure. The ¹H NMR spectrum, in addition to signals corresponding to two chemically inequivalent types of PMe₃ groups, also showed three sets of hydride signals in the ratio 1:2:1 which varied with temperature. At 203 K the hydride resonances comprise of broad singlets at δ –2.6 and –6.1 and a doublet of doublets at δ –5.95. The latter signal is split by coupling to two inequivalent P atoms and has values [²J(PH) 68, 27 Hz] consistent with a terminal hydride coupling to P atoms that are approximately *trans* and *cis* to the hydride ligand respectively.²⁶ As the temperature is raised the signals sharpen slightly and above 20 °C the two higher-field resonances coalesce into a single broad peak. Although it is not possible to locate unambiguously the relative positions of the hydride atoms, by analogy with known Re₂H₈L₄ (L = PMe₃, PEt₃Ph or PPh₃) systems, some structural inferences can be drawn. The hydrides shown in Scheme 1 are present merely to illustrate the different chemical shift environments and are not meant to infer a particular geometry. The unique lower-field signal (δ –2.6) is likely to be due to two bridging hydrides with the remaining resonances due to terminal hydrides, which undergo exchange at elevated temperatures. The latter two chemical shift values are comparable with those for [ReH₂L₂(C₂H₄)] [L = PPhPr¹₂ or P(C₂H₉)₃] (δ –6.1 and –6.9 respectively).²⁷ This stereochemical non-rigidity of hydride groups is commonly observed for organometallic polyhydride complexes. In the case of **5** fullerene complexation has significantly increased the activation energy barrier for the exchange process as by comparison only the high-temperature limiting spectrum has ever been observed for the Re₂H₈L₄ systems [L = PEt₃Ph, PMe₂Ph, PMePh₂ or PR₃ (R = Me, Et, Prⁿ or Ph)].²⁵ By contrast, both the ³¹P and ¹³C NMR spectra show no change with temperature (183–353 K). The former spectrum contained two singlets assignable to the two different PMe₃ environments whilst the latter contained (Fig. 3), in addition to two doublets for PMe₃ groups, 29 fullerene resonances consistent with a C_s symmetry complex. Although 32 signals, comprising 28 with I = 2 and 4 with I = 1, are expected for a complex possessing C_s symmetry, the commonly occurring accidental coincidence of

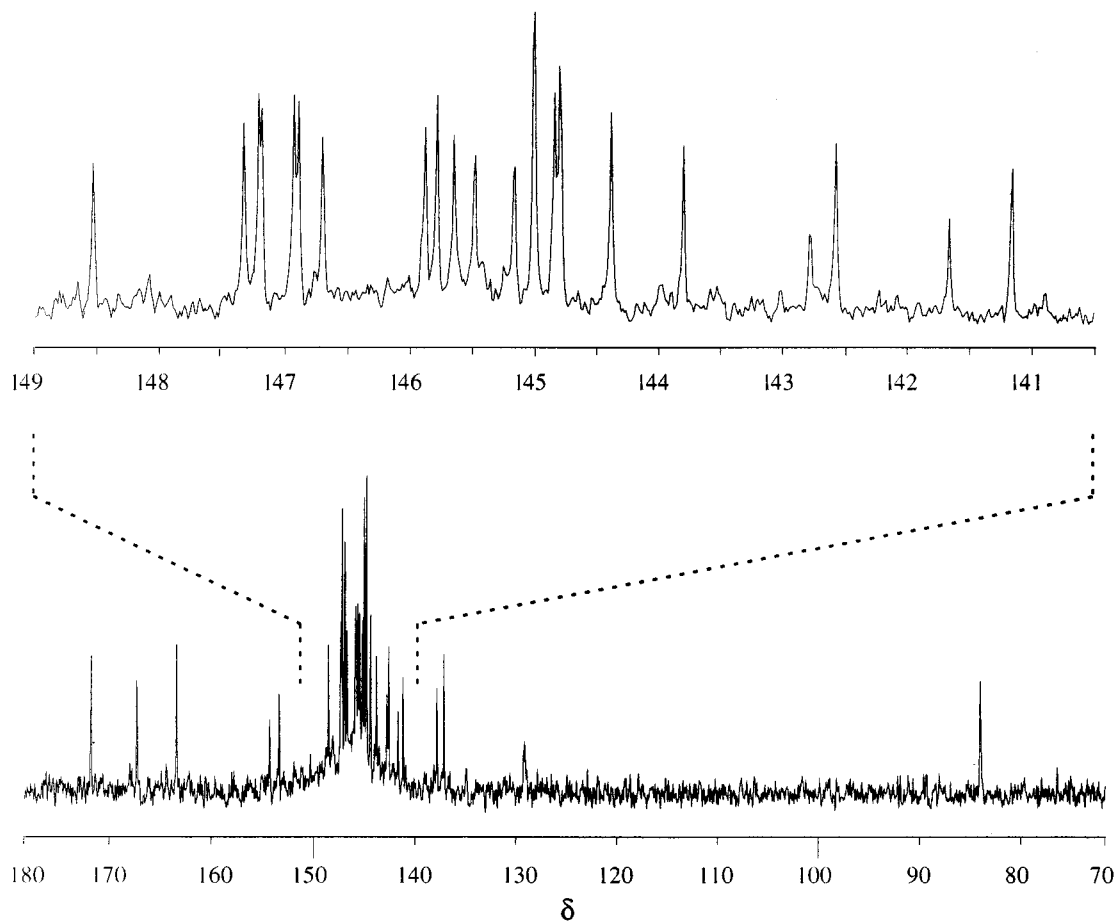


Fig. 3 The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of $[\text{Re}_2\text{H}_8(\text{PMe}_3)_4(\eta^2:\eta^2\text{-C}_{60})]$ **5** in $\text{C}_4\text{D}_8\text{O}$

resonances accounts for 31 out of the expected 32. The highest-field signal, a partially resolved triplet (δ 84), can be assigned to one pair of carbon atoms bound to rhenium which couple to two P atoms. The other metal-bound fullerene carbon atoms cannot be distinguished in the spectrum, their resonances overlapping with solvent resonances or are broadened due to unresolved coupling to P and Re atoms. Further confirmation of the proposed structure comes from the observation of three resonances at especially low field (δ 172, 167 and 163) which can generally be assigned to fullerene sp^2 carbon atoms adjacent to the metal-bound ones and only the structure outlined above contains three such environments.¹ Crystals suitable for structure determination were grown by allowing a reaction solution to stand undisturbed for several months. Selected interatomic distances and angles are listed in Table 2. The structure (Fig. 4) is unusual in that it does not involve simple η^2 binding of the fullerene but instead contains the unconventional $\eta^2:\eta^2$ mode of co-ordination. After $[\{\text{Ir}_2(\mu\text{-Cl})_2(1,5\text{-C}_8\text{H}_{12})_2\}_2(\eta^2:\eta^2\text{-C}_{60})]$ and $[\{\text{Ru}_2(\mu\text{-Cl})(\mu\text{-X})(\eta\text{-C}_5\text{Me}_5)_2\}(\eta^2:\eta^2\text{-C}_{60})]$ ($\text{X} = \text{H}$ or Cl), **5** is only the fourth such example.^{21,28} The Re–Re distance of 2.89 Å is comparable with the single-bond distances found in $[\text{Re}_2\text{H}_8(\text{dppm})_2]$ (2.93 Å) and $[\text{Re}_2(\text{CO})_{10}]$ (3.04 Å), suggesting that the formal bond order is one, which is consistent with electron-counting arguments.²⁵ As observed in the structure of **3**, the fullerene C–C bonds show similar changes on complexation. Thus the metal-bound C–C bonds are elongated to 1.48 Å, compared with 1.383 Å for an uncomplexed C_{60} C=C bond and 1.453 Å for the C–C bond. As for $[\{\text{Ir}_2(\mu\text{-Cl})_2(1,5\text{-C}_8\text{H}_{12})_2\}_2(\eta^2:\eta^2\text{-C}_{60})]$ and $[\{\text{Ru}_2(\mu\text{-Cl})(\mu\text{-X})(\eta\text{-C}_5\text{Me}_5)_2\}(\eta^2:\eta^2\text{-C}_{60})]$ ($\text{X} = \text{H}$ or Cl), the C–C bond is intermediate between the two metal-bound ones [C(2)–C(3) shows the longest length in the fullerene cage (1.50 Å)]. Those C–C bonds removed from the site of complexation show very little change from the values for uncomplexed C_{60} . It was not possible to locate the positions

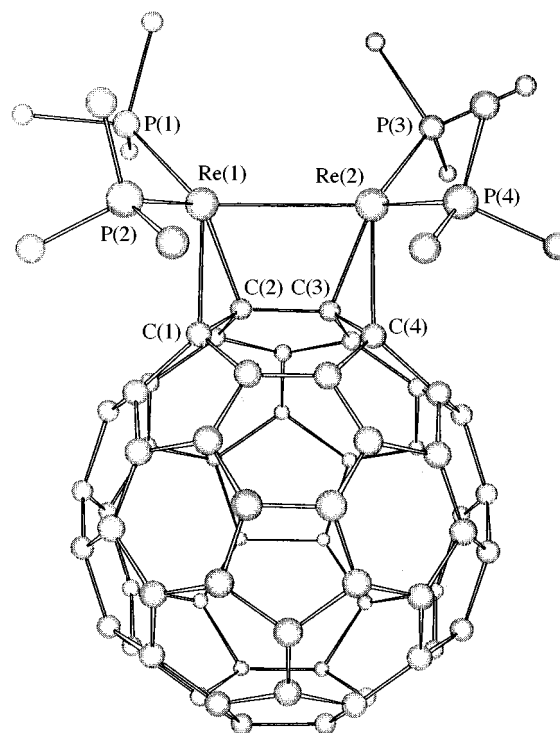


Fig. 4 Molecular structure of $[\text{Re}_2\text{H}_8(\text{PMe}_3)_4(\eta^2:\eta^2\text{-C}_{60})]$ **5**

of the metal hydride atoms. The absence of Re–H insertion into a double bond or hydrogenation in the reaction of C_{60} with $[\text{Re}_2\text{H}_8(\text{PM}_3)]$ to form **5** (90% yield) is to be noted. For such reactions to occur a double bond and a Re–H bond must be parallel and as this does not occur in **5** may account for its

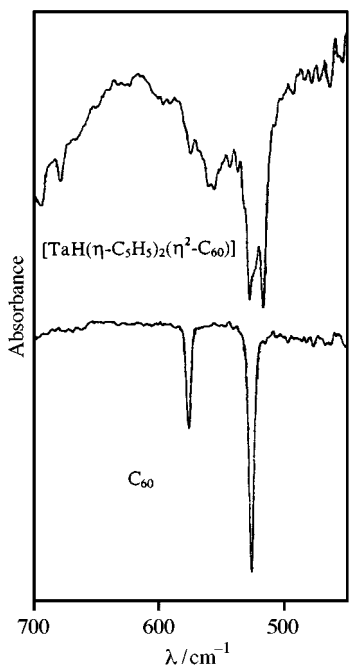
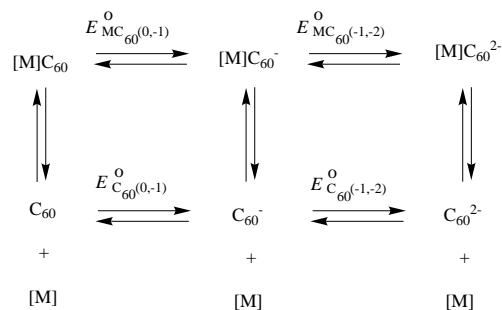


Fig. 5 Partial IR spectra of $[\text{TaH}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_{60})]$ **6** and C_{60} in Nujol mull

stability. Similar explanations have been invoked to explain the stability of the structurally related $[\text{ReH}_3(\text{PPh}_3)_2(\text{diene})]$ systems.

Treatment of a solution of C_{60} with $[\text{TaH}_3(\eta\text{-C}_5\text{H}_5)_2]$ resulted in the precipitation of $[\text{TaH}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_{60})]$ **6** over 12 h in high yield. Compound **6** is an air-stable brown microcrystalline solid practically insoluble in C_6H_6 , CH_2Cl_2 , CS_2 , acetone, and only sparingly soluble in high-boiling aromatic solvents such as $\text{C}_6\text{H}_4\text{Cl}_2$, $\text{C}_6\text{H}_4\text{Me}_2$, or 1-methylnaphthalene. Thus it was not possible successfully to obtain a ^1H or ^{13}C NMR spectrum and, furthermore, attempts to acquire a solution ^1H NMR spectrum by performing the reaction *in situ* also failed. The IR spectrum of **6** contained a broad $\nu(\text{Ta-H})$ stretch at 1791 cm^{-1} , a similar value to that observed for other $[\text{TaH}(\eta\text{-C}_5\text{H}_5)_2(\text{alkene})]$ complexes.^{29,30} The spectrum is also unusual in that $\nu(\text{C}_{60})$ bands are clearly split (Fig. 5) as a result of the reduced symmetry (C_s as opposed to I_h for C_{60}) which permits a greater number of IR-active vibrational modes.^{14,15} Although this behaviour is expected for most C_{60} adducts, only a few fullerene complexes such as $\text{C}_{60}\text{H}(\text{Et})$ or $[\text{Os}_3(\text{CO})_{11}(\eta^2\text{-C}_{60})]$ actually show it, and of the complexes described in this paper only **6** exhibits such an effect.^{14,31} The solid-state ^{13}C NMR (CP MAS) spectrum contained two sets of signals with large spinning side-band envelopes centred at δ 146, due to the fullerene carbon atoms, and a sharper one at δ 99, due to the 10 equivalent carbon atoms of the C_5H_5 ligand. The broadness of the fullerene signal is most likely due to a combination of overlapping resonances (31 signals are expected in the sp^2 region for C_s symmetry) and restricted tumbling. In addition there was a low intensity signal at δ 30 which could not be unambiguously assigned, although it is to be noted that for other $[\text{TaH}(\eta\text{-C}_5\text{H}_5)_2(\text{alkene})]$ complexes studied by solution ^{13}C NMR spectroscopy the metal-bound alkene carbons characteristically resonate at $\delta \approx 20$.^{29,32} The proposed structure of **6** can be compared with that of the related molybdenum complex $[\text{Mo}(\eta\text{-Bu}^t\text{C}_5\text{H}_4)_2(\eta^2\text{-C}_{60})]$, prepared by reaction of $[\text{MoH}_2(\eta\text{-Bu}^t\text{C}_5\text{H}_4)_2]$ with C_{60} .³³ Like the main products of the reaction of C_{60} with $[\text{MH}(\text{CO})(\text{PPh}_3)_3]$ ($\text{M} = \text{Rh}$ or Ir), $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$ or $[\text{Re}_2\text{H}_8(\text{PMe}_3)_4]$, no metal-hydride insertion into the fullerene $\text{C}=\text{C}$ bond was observed for **6**. One of the only examples of such an insertion is the reaction of $[\text{ZrH}(\text{Cl})(\eta\text{-C}_5\text{H}_5)_2]$ with C_{60} which yielded, after acidic work-up, C_{60}H_2 .³⁴ Attempts by the current authors to isolate the intermediate σ -bound zirconium complex



Scheme 2 Electrochemical equilibria present in the cyclic voltammograms of compounds **1**, **2**, **4**, **5** and **7**. $[\text{M}] = \text{Co}(\text{NO})(\text{PPh}_3)_2$ (**1**), $\text{Rh}(\text{NO})(\text{PPh}_3)_2$ (**2**), $\text{RuH}(\text{NO})(\text{PPh}_3)_2$ (**4**), $\text{Re}_2\text{H}_8(\text{PMe}_3)_4$ (**5**) or $\text{Ru}(\text{CO})_4$ (**7**)

failed. Similar attempts to prepare the niobium analogue of **6**, namely $[\text{NbH}(\eta\text{-C}_5\text{H}_5)_2\text{C}_{60}]$, produced a highly air-sensitive product characterised by a $\nu(\text{Nb-H})$ stretch at 1715 cm^{-1} in its IR spectrum.

Electrochemical studies

Cyclic voltammetry (CV) and square wave voltammetry (SWV) studies were performed on the thf-soluble adducts **1**, **2**, **4**, **5** and the previously prepared CH_2Cl_2 -soluble adducts $[\text{M}(\text{CO})_4(\eta^2\text{-C}_{60})]$ ($\text{M} = \text{Ru}$ **7** or Fe **8**) and show that they may be reversibly electrochemically reduced (Scheme 2) to the dianions and irreversibly oxidised to unknown species. Cyclic voltammograms were recorded at low temperatures to suppress dissociation and to extend the potential limit.

The cyclic voltammogram of compound **1** at $-20\text{ }^\circ\text{C}$ in thf (Fig. 6) contained four reduction and corresponding oxidation waves. By comparison with authentic samples of C_{60} , run under identical conditions, it is possible to assign the first and third reduction and oxidation waves to the couples $\text{C}_{60} - \text{C}_{60}^{-}$ and $\text{C}_{60}^{-} - \text{C}_{60}^{2-}$. Similar reduction couples corresponding to formation of the trianion C_{60}^{3-} were observed for **4** and up to the dianion for **2**, **5** and **7**. Although no free C_{60} was observed in any of the ^{13}C NMR studies previously described for **1**, **2**, **4** and **5**, it is possible that the presence of an electrolyte significantly alters the equilibrium concentrations between bound and uncomplexed fullerene. Additionally, small amounts of C_{60} may be present due to decomposition of **1** caused by impurities in the electrochemical cell. This is not totally unexpected as **1** was only present in very low concentrations ($\approx 0.3\text{ mM}$). The amount of free C_{60} varied from sample to sample in an ill defined manner. The cyclic voltammogram of **8**, run under identical conditions to those for **7**, showed only four quasi-reversible reduction waves attributable to uncomplexed C_{60} and an irreversible oxidation at -0.539 V . The previously noted decreased thermal stability of **8** relative to **7** may be partly responsible for the failure to observe any couples for **8**.

For compound **1** the remaining two reduction waves and corresponding oxidations were assigned to the couples $\mathbf{1} - \mathbf{1}^{-}$ and $\mathbf{1}^{-} - \mathbf{1}^{2-}$. The relative areas of the four reduction waves are approximately equal whereas the oxidation waves of the $\mathbf{1}^{-}$ species are considerably smaller and those of the free C_{60} species are relatively large. It can be concluded that $\mathbf{1}^{-}$ and $\mathbf{1}^{2-}$ are unstable with respect to dissociation of the metal fragment and give rise to C_{60}^{-} and C_{60}^{2-} respectively. Attempts to depress the kinetic and thermodynamic driving force for this dissociation by carrying out the cyclic voltammogram at lower temperatures had no noticeable effect. However, the use of scan rates of up to 100 mV s^{-1} , which resulted in a decrease in metal dissociation, caused the relative area of the peaks for **1** to increase and scans reversed after only the second and third reduction wave qualitatively showed increased amounts of **1** species. Although not shown in Fig. 6, there was an additional reduction couple for **1** that could be attributed to formation of

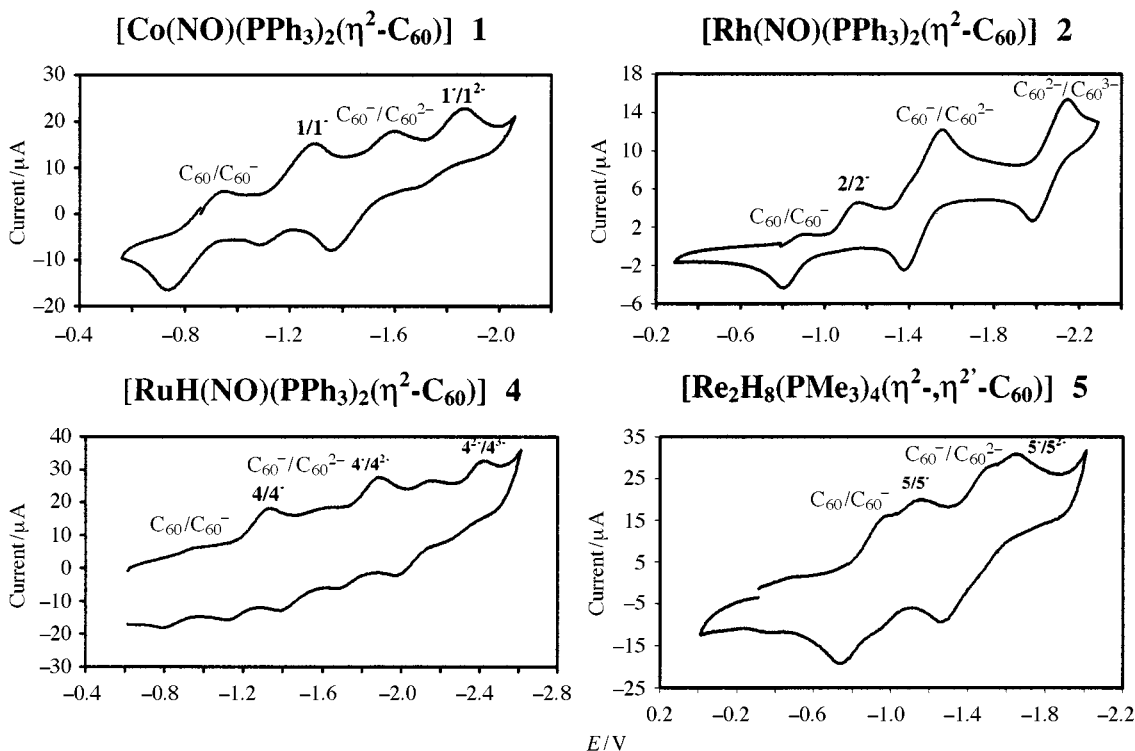


Fig. 6 Cyclic voltammograms in thf-0.1 M NBu₄PF₆ at -20 °C (scan rate 500 mV s⁻¹). Initial scan direction 0 to -2.0 V

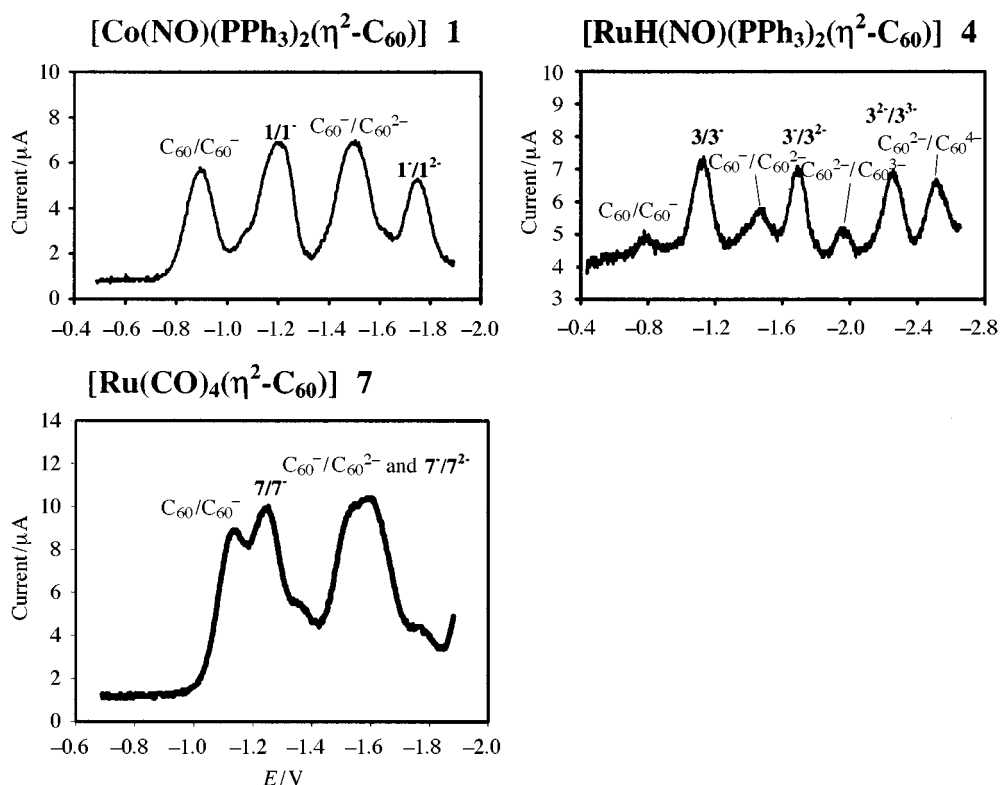


Fig. 7 Square-wave voltammograms in thf-0.1 M NBu₄PF₆ at -20 °C (1, 4) and in CH₂Cl₂-0.1 M NBu₄PF₆ at -30 °C (7)

1³⁻ with an area smaller than those for the 1⁻/1²⁻ couples indicating that 1³⁻ is even less stable than 1⁻ and 1²⁻. The electrochemical behaviour of 2 is similar to that of 1, except that the area of the couples of the former species are very much smaller than those of C₆₀, indicating that anions of 2 are considerably less stable than those of 1. The C₆₀ to C₆₀⁻ reduction wave is also quite small, in consonance with the fact that 2 is considerably less sensitive to air than 1. For 4 up to three reversible reductions, with large area, are observable, indicating enhanced stability for 4ⁿ⁻ (n = 0-3). For 5 only two quasi-

reversible reductions couples are observed. For 7 only the couple 7⁻/7²⁻ could be easily observed. However, by careful choice of sweep width and rate, the third peak in the square-wave voltammogram (Fig. 7) in the case of 7 may be resolved into two overlapping peaks (-1.45 and -1.50 V) which can be provisionally assigned to the C₆₀⁻-C₆₀²⁻ and 7⁻-7²⁻ couples. The values of the various couples are listed in Table 4.

All the reduction couples are thought to be C₆₀⁻ rather than metal-based owing to their very similar values. Fagan and co-workers³⁵ reached a similar conclusion when studying the

Table 4 Electrochemical half-wave potential^a for various fullerene organometallic complexes

Complex	$E^{\circ}_{(ox)}/V$	$E^{\circ}_{(0,-1)}/V$	$E^{\circ}_{(-1,-2)}/V$	$E^{\circ}_{(-2,-3)}/V$	Ref.
C_{60}		-0.86	-1.48	-2.08	35
1 [Co(NO)(PPh ₃) ₂ (η^2 -C ₆₀)]	-0.29	-1.17	-1.72	-2.25	This work
2 [Rh(NO)(PPh ₃) ₂ (η^2 -C ₆₀)]	+0.35	-1.14			This work
4 [Ru(NO)(PPh ₃) ₂ (η^2 -C ₆₀)H]		-1.12	-1.70	-2.29	This work
5 [Re ₂ (PMe ₃) ₄ H ₈ (η^2 : η^2 -C ₆₀)]	-0.34	-1.05	-1.53		This work
[Ni(PEt ₃) ₂ (η^2 -C ₆₀)]	+0.08	-1.20	-1.74	-2.32	35
[Pd(PEt ₃) ₂ (η^2 -C ₆₀)]	+0.20	-1.18	-1.69	-2.23	35
[Pt(PEt ₃) ₂ (η^2 -C ₆₀)]	+0.33	-1.20	-1.73	-2.27	35
[Pt(PPh ₃) ₂ (η^2 -C ₆₀)]	+0.42	-1.21	-1.75	-2.23	35
C_{60}^b		-1.00	-1.39	-1.81	36
7 [Ru(CO) ₄ (η^2 -C ₆₀)] ^b		-1.13	-1.50		This work
[Ir(η^5 -C ₉ H ₇)(CO)(η^2 -C ₆₀)] ^b	+0.72	-1.08	-1.43	-1.94	36

^a All couples are quoted relative to the ferrocene-ferrocenium couple with $E^{\circ}_{(+1,0)} = 0.00$ V and are recorded in thf-0.1 or -0.2 M NBu₄PF₆.

^b Recorded in CH₂Cl₂-0.1 M NBu₄PF₆.

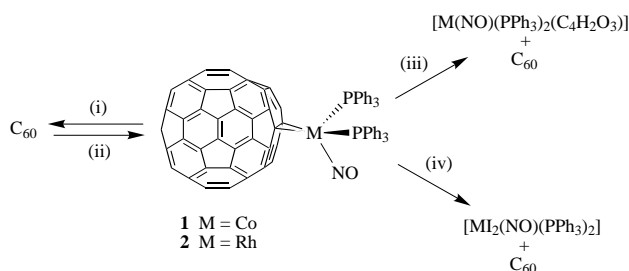
complexes [M(PEt₃)₂C₆₀] (M = Ni, Pd or Pt). The metal complexes are harder to reduce than free C₆₀ (by ≈ -0.2 V) due to perturbations in the electron affinity of the fullerene cage caused by metal complexation. Metal complexation effectively removes one double bond from the fullerene π system thus raising the energy of the LUMO and decreasing the electron affinity of the cage. Nevertheless, it does not always fully 'decouple' this double bond and instead allows some residual interaction between the metal centre and the fullerene π system. Thus, changes in the metal fragment electronegativity may account for the slight differences in the E° . In the reduced species the additional electrons are accommodated in this LUMO, which is derived from the remaining 29 double bonds of C₆₀ as well as a component of the metal-C₆₀ antibonding character. With increased occupancy of the LUMO for the more highly reduced anions, the metal-fullerene bonding will become weaker thus favouring metal dissociation and accounting for the smaller areas of successive couples in CV. The much smaller area of the reduction couples for **2** and **5** relative to those for **1** and **4** is presumably because the LUMO in the former species have a larger component of metal-C₆₀ antibonding character which on being populated with electrons causes relatively more metal fragment dissociation.

In addition to these reductions, compounds **1** and **2** also show one irreversible oxidation wave at -0.29 and +0.35 V respectively, with the ease of oxidation being Rh > Co. Since these values are so different from one another and uncomplexed C₆₀ shows no corresponding oxidation wave at similar potentials, it is postulated that the oxidation is metal centred. Compound **5** shows a weak reversible oxidation couple at -0.34 V which is comparable with the one-electron oxidations found for [Re₂H₈(PR₃)₄] between -0.4 and -1.1 V.²⁵ The $E^{\circ}_{(0,+1)}$ values follow the basicity of the phosphine and suggest that **5** is relatively difficult to oxidise with a value comparable to that of [Re₂H₈(Ph₂PC₂H₄PPh₂)₂] ($E^{\circ}_{(0,+1)}$ -0.49 V) and considerably different from that of [Re₂H₈(PMe₃)₄] ($E^{\circ}_{(0,+1)}$ -0.81 V). Withdrawal of electron density by C₆₀ at the metal centre may account for the ordering.

Chemical reactivity

For all the compounds described the fullerene moiety was only weakly bound to metal centres and could be easily displaced by other ligands such as more π -acidic alkenes. Hence **1** and **2** were found to react with maleic anhydride leading to displacement of the C₆₀ ligand and addition of an excess of PPh₃ to **1** or **2** resulted in reformation of [M(NO)(PPh₃)₃] (Scheme 3). Iodine was also shown oxidatively to displace C₆₀ from **1** or **2**. Compound **1** was generally found to be more reactive and, unlike **2**, reacted with halogenated solvents such as CH₂Cl₂ to generate [CoCl₂(NO)(PPh₃)₂].

All these reactions, in which the products were identified by



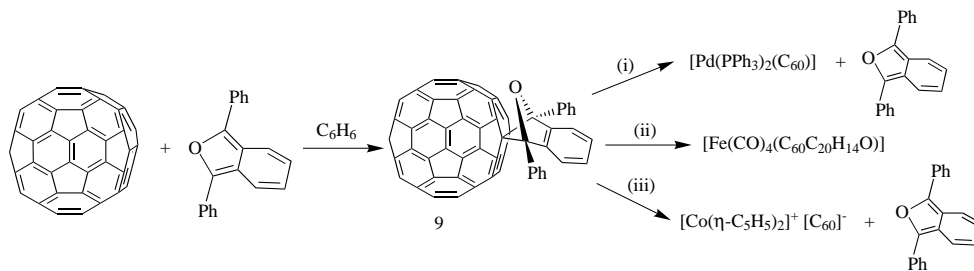
Scheme 3 Reagents: (i) (PPh₃); (ii) [M(NO)(PPh₃)₃] (M = Co or Rh); (iii) maleic anhydride; (iv) I₂

IR spectroscopy, were conveniently followed by observing colour changes of the reaction solution. Complexes **1** and **2** are intensely green, but on addition of the ligand the solution rapidly became the characteristic mauve colour of C₆₀ with the other products tending to be relatively colourless.

These reactions demonstrate that compounds **1** and **2** behave in a similar fashion to [M(NO)(PPh₃)(alkene)] (M = Co, Rh or Ir) and [M(PR₃)₂(alkene)] (M = Ni, Pd or Pt), which are all formally d¹⁰ metal systems, whose alkene ligand is easily displaced and which readily undergo oxidative additions.¹¹ The reactivity patterns of fullerene organometallics have not been widely investigated although **1** and **2** behave in a similar fashion to complexes such as [Ir(η^5 -C₉H₇)(CO)(η^2 -C₆₀)] and **8**, where the C₆₀ ligand can be readily displaced by donor groups such as CO, P(OMe)₃ or PPh₃.³⁶

Attempts to prepare multimetallic adducts of compounds **1**, **2**, **3** and **4** by addition of an excess of starting metal complex to C₆₀ failed. Only **1**, **2**, **3** or **4** were ever isolated and it seems likely that the bulky nature of the metal fragment may be partly responsible. Fagan and co-workers³⁵ reported that for the system [C₆₀{Pt(PR₃)₂}_n] when R = Ph only the monoadduct may be successfully isolated whereas when R = Et up to six metal fragments can complex to one C₆₀. Electronic differences for the phosphines do not seem to be the determining factor as the cyclic voltammograms of [Pt(PPh₃)₂(η^2 -C₆₀)] and [Pt(PEt₃)₂(η^2 -C₆₀)] are almost identical.

Investigations were also undertaken to see how the presence of a bulky organic side chain affected the regiochemistry of metal fragment addition. The reaction of the previously reported C₆₀(C₂₀H₁₄O) with [Pd(PPh₃)₄], [Fe₂(CO)₉] and [Co(η -C₅H₅)₂], all known to form isolable adducts with C₆₀, was therefore investigated (Scheme 4).^{15,33,37} Treatment of a benzene solution of C₆₀(C₂₀H₁₄O) with 1 equivalent of [Pd(PPh₃)₄] caused the solution to turn green immediately and upon concentration, followed by addition of an excess of pentane, a flocculent green precipitate and a pale yellow mother-liquor were obtained. These were identified as [Pd(PPh₃)₂(η^2 -C₆₀)] and 1,3-diphenylisobenzofuran respectively using ³¹P and ¹H NMR spectroscopy by comparison with authentic samples and seem to



Scheme 4 Reagents: (i) $[\text{Pd}(\text{PPh}_3)_4]$; (ii) $[\text{Fe}_2(\text{CO})_9]$; (iii) $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]$

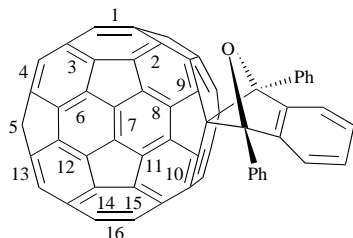


Fig. 8 The 16 possible sites of addition of an $\text{Fe}(\text{CO})_4$ unit to $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$

suggest that the bonds joining C_{60} to the isobenzofuran moiety are easily broken.¹⁵

However, treatment of a benzene solution of $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$ with 1 mol equivalent of $[\text{Fe}_2(\text{CO})_9]$ produced a deep red solid upon work-up that was preliminarily identified on the basis of IR and NMR spectroscopic data as the $\text{Fe}(\text{CO})_4$ adduct, *i.e.* $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_{60}\text{C}_{20}\text{H}_{14}\text{O})]$. Like $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$, the adduct showed enhanced solubility over its corresponding C_{60} analogue (**8**) and was also considerably more thermally stable than **8**. The IR spectrum contained features very similar to those of $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$ and **8** and included three strong $\nu(\text{CO})$ stretches at 2090, 2029 and 1993 cm^{-1} . These values, little shifted from those observed for **8** at 2092, 2030 and 1997 cm^{-1} , suggest that the benzofuran side chain has negligible electronic effect on the remainder of the fullerene cage which is in consonance with the conclusions drawn from the electrochemical studies performed on $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$. The $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum contained groups of resonances in the regions δ 207–206 [$\text{Fe}(\text{CO})_4$ moieties], 160–135 (fullerene sp^2 carbons), 132–120 (isobenzofuran side chain sp^2 carbons), 97–93 (isobenzofuran sp^3 carbons) and 83–78 (fullerene sp^3 carbons). The large number of resonances indicates that the adduct exists in solution as a mixture of the up to 16 possible regioisomers (Fig. 8). By analogy with **8**, it seems likely that the signals between δ 206 and 207, totalling 12, represent the $\text{Fe}(\text{CO})_4$ moieties of 12 different regioisomers. It is postulated that the absent isomers correspond to $\text{Fe}(\text{CO})_4$ complexing to the four $\text{C}=\text{C}$ bonds closest to the isobenzofuran side chain and indicate that the latter is only partially successful at shielding the fullerene double bonds from further reaction. Attempts to separate the regioisomers by column chromatography were not successful. Similar kinetic regioselectivity has been found in the reaction of $\text{C}_{60}\text{C}(\text{CO}_2\text{Et})_2$ with carbene: $\text{C}(\text{CO}_2\text{Et})_2$.³⁸

The different reactivity of $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$ towards $[\text{Pd}(\text{PPh}_3)_4]$ and $[\text{Fe}_2(\text{CO})_9]$ may result from the different sizes of the $\text{Pd}(\text{PPh}_3)_2$ and $\text{Fe}(\text{CO})_4$ units. Only in the case of the former, which is even more bulky than C_{60} , a product results which is unstable with respect to loss of the isobenzofuran side chain.

Attempts were also made to prepare anionic $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$ by reaction with $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]$ which readily forms $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]^+[\text{C}_{60}]^-$ on addition to C_{60} .³⁸ Mixing together equimolar benzene solutions of $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$ and $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]$ caused the instantaneous formation of a flocculent red precipitate which became a fine red-brown precipitate within

minutes and the mother-liquor developed the characteristic dichroic blue-yellow colour of 1,3-diphenylisobenzofuran. An ^1H NMR spectrum confirmed that the mother-liquor contained solely 1,3-diphenylisobenzofuran and elemental analysis of the red solid was consistent with the formulation $[\text{Co}(\text{C}_5\text{H}_5)_2\text{C}_{60}]$. This result is consistent with electrochemical studies performed on $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$ which showed that the anion was very unstable with respect to decomposition into C_{60}^- and it therefore seems likely that the initially formed flocculent red precipitate may be $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]^+[\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})]^-$.

In conclusion these reactions indicate that the bonds joining the isobenzofuran side chain to C_{60} are weak and on addition of an organometallic precursor the former moiety is often lost to yield C_{60} , rather than a complex of $\text{C}_{60}(\text{C}_{20}\text{H}_{14}\text{O})$. This is unusual for a Diels–Alder adduct in which a new aromatic system is created and may well be a result of the presence of bulky phenyl side groups.

Conclusion

The fullerene C_{60} shows a chemical reactivity very similar to those of bulky, electron-deficient alkenes. It readily reacts with a variety of electron-rich metal complexes to form stable π complexes. The lack of reactivity with certain fragments investigated may be related to their lower electron richness. Reaction with $[\text{Re}_2\text{H}_8(\text{PMe}_3)]$ resulted in a rare example of complexation involving adjacent fullerene double bonds. In all the systems studied the metal centre could be easily removed from the fullerene surface either by electrochemical reduction or electrophilic attack. The presence of an organic side chain on the fullerene limits the sites of complexation available to the metal centre but results in the double bonds becoming inequivalent which hinders separation and characterisation.

Experimental

General

All manipulations of air- and/or moisture-sensitive materials were performed in an inert atmosphere using either a dual vacuum/nitrogen line and standard Schlenk techniques, or in an inert-atmosphere dry-box containing nitrogen. In each case the nitrogen was purified by passage over 4 Å molecular sieves, and either BASF catalyst for the dry-box or MnO for the Schlenk line. Solvents and solutions were transferred through stainless-steel cannulae using a positive pressure of nitrogen. Filtrations were generally performed using modified stainless-steel cannulae which had been fitted with glass-fibre filter discs. All glassware and cannulae were dried overnight at $150\text{ }^\circ\text{C}$ before use.

Physical measurements

The ^1H , ^{31}P and ^{13}C NMR spectra were recorded using either Brüker AM300 (^1H 300 MHz; ^{13}C , 75.5 MHz; ^{31}P , 121.6 MHz), AMX500 (^{13}C , 125 MHz) or Varian UNITY plus (^{13}C , 125

MHz) spectrometers at room temperature unless otherwise stated. They were referenced internally using the residual proton solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ 0) or externally using orthophosphoric acid in D_2O (^{31}P). For ^{13}C NMR spectra a relaxation delay of ≈ 2 s was generally used. Owing to the tendency of fullerene compounds to precipitate over time, all samples were prepared immediately prior to acquisition. This is especially important for low-temperature studies. Samples used more than once were stored in liquid N_2 between experiments. The IR spectra were recorded on either a Mattson-Polaris or a Perkin-Elmer 1710 FT interferometer or, in the region below 400 cm^{-1} , on a Perkin-Elmer grating spectrometer. Mass spectra (FAB) were obtained by the SERC Mass Spectrometry Service at Swansea. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford. The UV/VIS spectra were recorded on a Perkin-Elmer lambda 3 spectrometer (190–900 nm); samples were contained in quartz cuvettes of 1 mm path length sealed with a Teflon stopper. Electrochemical studies were performed using the standard three-electrode system consisting of a silver-wire reference electrode, a platinum-gauze counter electrode and a silver-wire working electrode in thf, 0.1 M NBu_4PF_6 . All couples quoted have been referenced internally to ferrocene–ferrocenium.

Materials

Solvents were pre-dried by standing over 4 Å Linde molecular sieves and then refluxed and distilled under a nitrogen atmosphere from phosphorus pentoxide or calcium hydride (dichloromethane, CS_2), potassium thf, sodium (toluene) or sodium–potassium alloy (1:3 w/w) [light petroleum (b.p. 40–60 °C), diethyl ether, pentane]. Deuteriated solvents (Aldrich) for NMR studied were stored in Young's ampoules over 4 Å molecular sieves under nitrogen [$(\text{CD}_3)_2\text{C}_6\text{D}_4$, $\text{C}_6\text{D}_4\text{Cl}_2$], refluxed with potassium metal and stored in Young's ampoules over a potassium film (C_6D_6 , $\text{CD}_3\text{C}_6\text{D}_5$, $\text{C}_4\text{D}_8\text{O}$), or refluxed with calcium hydride (CD_2Cl_2). The NMR solvents were transferred using a teat pipette in an inert-atmosphere dry-box. The compound $[\text{Cr}(\text{acac})_3]$ was used as supplied. Fullerene soot was produced using a slight modification of the standard contact-arc DC generator of Hauffler *et al.*,³⁹ C_{60} was purified using the standard Soxhlet/chromatography column method as devised by Chatterjee *et al.*,⁴⁰ and Wudl and co-workers.⁴¹ The following materials were prepared following standard literature methods: $[\text{Co}(\text{NO})(\text{PPh}_3)_3]$,⁴² $[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$,⁴³ $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$,⁴⁴ $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$ ⁴⁵ and $[\text{Ru}(\text{CO})_4\{\text{H}_2\text{CC}(\text{H})\text{CO}_2\text{Me}\}]$.⁴⁶

General comments on the manipulation of fullerene adducts

Although fullerene organometallics possess many of the physical and chemical properties typical of other air-sensitive compounds, they additionally show some other special characteristics. These often cause problems for the successful isolation of a pure fullerene complex. All fullerene adducts tenaciously retain solvent molecules and this can prove troublesome for elemental analyses. Furthermore some fullerene resonances are often obscured in ^{13}C NMR spectra. To circumvent these problems the following procedure is thoroughly recommended. (1) With the aid of sonication, a concentrated solution of the impure compound was prepared using an appropriate solvent. (2) A large excess (≈ 5 –10 volumes) of pentane was added and the resulting precipitate allowed to settle. Sometimes it is necessary to filter using either glass or Whatman 50 filter-papers as natural settling takes too long. Ordinary Whatman 1 filter-paper allows through many of the finer particles of product. (3) The precipitate was then washed with pentane, aided by sonication for ≈ 30 s periods which breaks down the particle size. (4) Step 3 was repeated a further two times. (5) The solid was dried *in vacuo* for at least 4 h.

Preparations

[Co(NO)(PPh₃)₂(η^2 -C₆₀)] 1. A suspension of C_{60} (100 mg, 0.14 mmol) in thf (20 cm^3) was placed in an ampoule and a solution of $[\text{Co}(\text{NO})(\text{PPh}_3)_3]$ (114 mg, 0.13 mmol) dissolved in thf (70 cm^3) added. The resulting mixture was left to stir for 5 h to produce a deep green solution. The volatiles were removed under reduced pressure and the solid obtained was extracted with thf (100 cm^3 , $2 \times 30\text{ cm}^3$). The thf extracts were reduced in volume to 5 cm^3 , methanol (50 cm^3) was added and the precipitate allowed to settle. The product was isolated as a green solid by washing with methanol (25 cm^3) and pentane ($5 \times 15\text{ cm}^3$) and drying *in vacuo*. Yield 160 mg, 86%.

[Rh(NO)(PPh₃)₂(η^2 -C₆₀)] 2. A solution of C_{60} (105 mg, 0.15 mmol) in toluene (50 cm^3) was placed in an ampoule and a solution of $[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$ (133 mg, 0.14 mmol) in toluene (30 cm^3) added to produce a deep emerald-green solution which was stirred for 5 h. The volatiles were removed under reduced pressure and the solid extracted with thf ($3 \times 25\text{ cm}^3$). The thf extracts were reduced in volume to 10 cm^3 and pentane (50 cm^3) was added to cause the precipitation of a green solid. After washing with pentane (30 cm^3), methanol ($2 \times 30\text{ cm}^3$) and pentane ($3 \times 30\text{ cm}^3$), the product was isolated as a green powder. Yield 170 mg, 85%.

[RuCl(NO)(PPh₃)₂(η^2 -C₆₀)] 3. Solutions of C_{60} (111 mg, 0.15 mmol) in benzene (100 cm^3) and $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$ (104 mg, 0.15 mmol) in benzene (30 cm^3) were mixed and left to stand for 24 h during which time green microcrystals of product formed. This solid was washed with pentane (15 cm^3), ethanol ($2 \times 25\text{ cm}^3$) and pentane ($3 \times 15\text{ cm}^3$), and dried *in vacuo*. Yield 170 mg, 78%. Crystals suitable for X-ray diffraction were grown by allowing benzene solutions of C_{60} and $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$ slowly to diffuse together over 1 week. The glass apparatus used consisted of two bulbs (capacity 15 cm^3) joined by a narrow tube in the shape of the letter H.

[RuH(NO)(PPh₃)₂(η^2 -C₆₀)] 4. Solutions of C_{60} (52 mg, 0.07 mmol) in benzene (50 cm^3) and $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$ (62 mg, 0.07 mmol) in benzene (10 cm^3) were mixed to yield a green solution which was left to stand for 8 h. The volume was reduced to 15 cm^3 and the product precipitated as a green solid by addition of methanol (100 cm^3). The solid was washed with methanol (20 cm^3) and pentane ($3 \times 20\text{ cm}^3$) and dried *in vacuo*. Yield 82 mg, 85%.

[Re₂H₈(PMe₃)₄(η^2 : η^2 -C₆₀)] 5. A solution of $[\text{Re}_2\text{H}_8(\text{PMe}_3)_4]$ (95 mg, 0.14 mmol) in benzene (10 cm^3) was added to a solution of C_{60} (100 mg, 0.14 mmol) in benzene (100 cm^3) and the resulting mixture left to stand for 24 h. The mother-liquor was decanted off and the solid dissolved in the minimum volume of thf (15 cm^3) and precipitated by addition of an excess of pentane (50 cm^3). The product was isolated as a brown powder by washing with pentane ($3 \times 30\text{ cm}^3$) and drying *in vacuo*. Yield 176 mg, 90%.

[TaH(η -C₅H₅)₂(η^2 -C₆₀)] 6. A solution of $[\text{TaH}_3(\eta\text{-C}_5\text{H}_5)_2]$ (63 mg, 0.20 mmol) in benzene (30 cm^3) was added to a solution of C_{60} (146 mg, 0.21 mmol) in benzene (150 cm^3) and the resulting mixture left to stand for 24 h at room temperature. The mother-liquor was decanted off and the solid washed with benzene (10 cm^3) and pentane ($3 \times 30\text{ cm}^3$) and dried *in vacuo* to yield the product as brown microcrystals. Yield 80 mg, 88%.

Reaction of C₆₀ with [NbH₃(η -C₅H₅)₂]. A solution of $[\text{NbH}_3(\eta\text{-C}_5\text{H}_5)_2]$ (33 mg, 0.15 mmol) in benzene (15 cm^3) was added to a solution of C_{60} (106 mg, 0.15 mmol) in benzene (130 cm^3) and the resulting mixture left to stand for 24 h. The mother-liquor was decanted off and the fine brown powder

washed with benzene (10 cm³) and pentane (3 × 30 cm³) and dried *in vacuo*.

[Ru(CO)₄(η²-C₆₀)] 7. A solution of C₆₀ (95 mg, 0.13 mmol) in toluene (50 cm³) cooled to -10 °C was added to a similarly cooled standard solution of [Ru(CO)₄{H₂CC(H)CO₂Me}] (0.12 mmol) in toluene (10 cm³) and the resulting mixture stirred at room temperature for 12 h to produce a deep red solution. The volume was reduced to 10 cm³, ice-cooled pentane (50 cm³) added and the precipitate allowed to settle over 12 h at -80 °C. The product was isolated as a red-brown powder after washing with ice-cooled pentane (5 × 30 cm³) and drying *in vacuo* for at least 1 h. Yield 110 mg, 89%.

[Fe(CO)₄(η²-C₆₀)] 8. A solution of C₆₀ (120 mg, 0.17 mmol) in toluene (75 cm³) cooled to 0 °C was added to a mixture of [Fe₂(CO)₉] (55 mg, 0.15 mmol) in toluene (20 cm³) at 0 °C. The suspension was stirred and occasionally sonicated until all [Fe₂(CO)₉] had dissolved (approximately 1 h). The resulting deep red solution was reduced in volume under reduced pressure to 10 cm³ at 10 °C; pentane (75 cm³) was added and the resulting precipitate allowed to settle at -80 °C overnight. After washing with ice-cold pentane (3 × 30 cm³) and drying *in vacuo* for at least 1 h, the product was isolated as a dark red powder. Yield 130 mg, 88%.

Reactions with maleic anhydride. [Co(NO)(PPh₃)₂(η²-C₆₀)] **1**. Solutions of [Co(NO)(PPh₃)₂(η²-C₆₀)] **1** (22 mg, 0.02 mmol) in benzene (20 cm³) and maleic anhydride (2 mg, 0.02 mmol) in thf (10 cm³) were mixed resulting in the solution instantaneously turning red. The volatiles were removed under reduced pressure and the solid was identified as a mixture of C₆₀ and [Co(NO)(PPh₃)₂(C₄H₂O₃)] by IR spectroscopy.

[Rh(NO)(PPh₃)₂(η²-C₆₀)] **2**. Solutions of [Rh(NO)(PPh₃)₂(η²-C₆₀)] **2** (10 mg, 0.08 mmol) in benzene (20 cm³) and maleic anhydride (2 mg, 0.02 mmol) in thf (10 cm³) were mixed and the resulting solution instantaneously turned red. The volatiles were removed under reduced pressure and the solid was identified as a mixture of C₆₀ and [Rh(NO)(PPh₃)₂(C₄H₂O₃)] by IR spectroscopy.

Reactions of [Co(NO)(PPh₃)₂(η²-C₆₀)] 1. *With an excess of PPh₃.* Solutions of [Co(NO)(PPh₃)₂(η²-C₆₀)] **1** (10 mg, 0.01 mmol) in benzene (20 cm³) and PPh₃ (100 mg, 0.3 mmol) in benzene (25 cm³) were mixed and the mixture immediately changed from green to red. The volatiles were removed under reduced pressure and the solid was identified as a mixture of C₆₀ and [Co(NO)(PPh₃)₃] by IR spectroscopy.

With I₂. Iodine (20 mg, 0.10 mmol) dissolved in benzene (10 cm³) was added to a solution of [Co(NO)(PPh₃)₂(η²-C₆₀)] **1** (10 mg, 0.08 mmol) in benzene (10 cm³) and the resulting solution instantaneously turned red. The mixture was left to stand for 10 min and the volatiles were removed under reduced pressure. The presence of C₆₀ and [CoI₂(NO)(PPh₃)₂] in the residual solid was confirmed by IR spectroscopy (KBr disc).

Reaction of [Rh(NO)(PPh₃)₂(η²-C₆₀)] 2 with I₂. Iodine (20 mg, 0.10 mmol) dissolved in benzene (10 cm³) was added to a solution of [Rh(NO)(PPh₃)₂(η²-C₆₀)] **2** (10 mg, 0.08 mmol) in benzene (10 cm³) and the mixture immediately turned from green to red. It was left to stand for 5 min and the volatiles were removed under reduced pressure. The presence of C₆₀ and [RhI₂(NO)(PPh₃)₂] in the residual solid was confirmed by IR spectroscopy (KBr disc).

C₆₀(C₂₀H₁₄O). An ampoule was charged with a solution of C₆₀ (105 mg, 0.15 mmol) in benzene (100 cm³) and a solution of 1,3-diphenylisobenzofuran C₂₀H₁₄O (39 mg, 0.14 mmol) in benzene (20 cm³) was added dropwise over 30 min with stirring.

The mixture was left to stand for 36 h at room temperature and then reduced in volume to 5 cm³ under reduced pressure and pentane (50 cm³) was added. The resulting precipitate was washed with pentane (4 × 30 cm³) and dried *in vacuo* and the product isolated as an orange solid.⁴⁷

Reactions of C₆₀(C₂₀H₁₄O). *With [Pd(PPh₃)₄].* A solution of C₆₀(C₂₀H₁₄O) (22 mg, 0.02 mmol) in benzene (10 cm³) was added to a solution of [Pd(PPh₃)₄] (26 mg, 0.02 mmol) in benzene (10 cm³). The resulting green solution was stirred for 1 h, reduced in volume to 5 cm³ under reduced pressure and pentane (60 cm³) added. The flocculent green precipitate was washed with pentane (2 × 50 cm³), dried *in vacuo* and identified as [Pd(PPh₃)₂(η²-C₆₀)] by ¹H and ³¹P NMR spectroscopy (C₆D₆). The mother-liquor and pentane washings were combined and pumped to dryness under reduced pressure to yield a yellow solid that was identified as 1,3-diphenylisobenzofuran by ¹H NMR spectroscopy (CD₂Cl₂).

With [Fe₂(CO)₉]. A solution of C₆₀(C₂₀H₁₄O) (78 mg, 0.08 mmol) in benzene (15 cm³) was added to a suspension of [Fe₂(CO)₉] (29 mg, 0.08 mmol) in benzene (15 cm³). The resulting red solution was stirred for 1 h and after removal of the volatiles under reduced pressure the product was isolated as a red solid.

With [Co(η-C₅H₅)₂]. A solution of [Co(η-C₅H₅)₂] (8 mg, 0.04 mmol) in benzene (5 cm³) was added to a solution of C₆₀(C₂₀H₁₄O) (43 mg, 0.04 mmol) in benzene (15 cm³). The initially flocculent red precipitate was allowed to settle over 30 min during which time it became a fine red solid. The mother-liquor was decanted off, the volatiles were removed under reduced pressure and the residue was identified as 1,3-diphenylisobenzofuran by ¹H NMR spectroscopy (C₆D₆). The fine red solid was washed with benzene (3 × 5 cm³) and pentane (3 × 5 cm³) and identified as [Co(η-C₅H₅)₂][C₆₀]-C₆H₆ by elemental analysis.

X-Ray crystallography

All crystals were mounted in Lindemann glass capillaries under nitrogen. Crystal data, data collection and refinement parameters for both compounds are given in Table 5. Data for **3** were collected on a Rigaku R-axis IIC image-plate detector diffractometer at room temperature at the EPSRC crystallographic facility and for **5** on an Enraf-Nonius FAST area-detector diffractometer at 150 K. All data were corrected for Lorentz-polarisation effects. The data for **3** were corrected for the effects of absorption using DIFABS.⁴⁸

The structures were solved by direct methods giving non-hydrogen atom positions.⁴⁹ For compound **3** the structure suffers from two-fold disorder between the Cl, N and O atoms which was modelled using partial occupancy [Cl(1), N(1), O(1) have 80% occupancy and Cl(2), N(2), O(2) have 20% occupancy]. All non-hydrogen atoms were refined with anisotropic thermal parameters except for the disordered Cl and NO group and the carbon atoms of the solvent molecules which were all refined with isotropic thermal parameters. Throughout refinement the phenyl rings of the triphenylphosphine groups were restrained to their idealised geometries and the bond lengths and angles associated with the disordered chlorine and NO groups were restrained to their mean values. The benzene solvent molecules were refined as rigid groups. For **5** the C atoms of the C₆₀ were refined with isotropic thermal parameters and all other non-hydrogen atoms with anisotropic thermal parameters. For both **3** and **5** the hydrogen atoms were placed in calculated positions and included in the final refinement with the fixed positional and thermal parameters. Three-parameter Chebyshev weighting schemes and corrections for anomalous dispersion were applied to all data. Crystallographic calculations were carried out using the CRYSTALS program on a MicroVAX 3800 computer for **3** and

Table 5 Crystal data and details of data collection and structure refinement for compounds **3** and **5**

	3	5
Empirical formula	C ₁₂₆ H ₆₀ CINOP ₂ Ru	C ₇₂ H ₄₄ P ₂ Re ₂ ·1.5C ₆ H ₆
Crystal size/mm	0.15 × 0.15 × 0.30	0.07 × 0.07 × 0.36
<i>M_r</i>	1802.3	1522.60
Space group	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> /Å	14.9349(8)	29.017(7)
<i>b</i> /Å	20.025(1)	17.410(1)
<i>c</i> /Å	28.431(2)	24.444(2)
β/°	100.567(4)	116.35(1)
<i>U</i> /Å ³	8358.6	11 065.1
<i>Z</i>	4	8
<i>D_c</i> /g cm ⁻³	1.43	1.83
<i>h, k, l</i> Ranges	0, 15; -23, 23; -33, 33	- <i>h, h</i> ; - <i>k, k</i> ; - <i>l, l</i>
μ/mm ⁻¹	0.312	4.597
<i>F</i> (000)	3688	5992
<i>T</i> /K	298	150
No. reflections collected	28 974	23 632
No. independent reflections	14 131	8444
No. observed reflections [<i>I</i> > 3σ(<i>I</i>)]	8556	4033
No. parameters refined	949	484
Merging <i>R</i> factor	0.091	0.195
Absorption correction (minimum, maximum)	0.75, 1.00	
Ratio data: parameters	9.5:1	8.3:1
Minimum, maximum residual peaks/e Å ⁻³	-1.04, 0.87	-1.00, 1.48
<i>R</i>	0.061	0.035
<i>R'</i>	0.062	0.034

* Details in common: monoclinic; Mo-Kα radiation (λ 0.710 69 Å); θ_{min}, θ_{max} 2, 25°.

on a PC/AT-486 computer for **5**.⁵⁰ Neutral atom scattering factors were taken from ref. 51.

CCDC reference number 186/855.

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