Transition Metal-carbonyl, -hydrido and -η-Cyclopentadienyl Derivatives of the Fullerene C_{60}

Richard E. Douthwaite, Malcolm L. H. Green,* Adam H. H. Stephens and John F. C. Turner
Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

Monoadduct derivatives of the fullerene C_{60}, namely $[\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{C_{60}})]$, $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4R})_2(\eta^2\text{-}\mathrm{C_{60}})]$ (R = H, Bu^n), $[\mathrm{Ta}(\eta^2\text{-}\mathrm{C_5H_5})_2(\eta^2\text{-}\mathrm{C_{60}})\mathrm{H}]$ and $[\mathrm{Rh(Ph_3P)_2(CO)}(\eta^2\text{-}\mathrm{C_{60}})\mathrm{H}]$, are described.

The recent availability of gram quantities of the fullerene C_{60} has facilitated the study of the reactivity of this intriguing molecule.[1] We have set out to develop the organometallic chemistry of fullerenes. The organometallic compounds $[\mathrm{C_{60}\{M(PEt_3)_2\}}_n]$ (n = 1 or 6, and M = Ni, Pd, Pt),[2] $[\mathrm{M(PPh_3)_2}(\eta^2\text{-}\mathrm{C_{60}})]$ (M = Ni, Pd, Pt),[3] $[\mathrm{Ir(CO)(PPh_3)_2}(\eta^2\text{-}\mathrm{C_{60}})\mathrm{Cl}]$,[4] $[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CO})(\eta^2\text{-}\mathrm{C_{60}})]$,[5] $[\mathrm{C_{60}\{OsO_4(4\text{-}Bu^tC_5H_4N)_2\}}n]$ (n = 1 or 2)[6,7] have been described previously. Here we report new organometallic C_{60} derivatives of iron, molybdenum, tantalum and rhodium.

Addition of a deep-purple solution of C_{60} in benzene to a suspension of $[\mathrm{Fe_2(CO)_9}]$ in benzene at room temp. for 1 h causes a steady colour change to deep red. After removal of the solvent and washing with pentane, a dark-red microcrystalline compound $[\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{C_{60}})]$ **1** was isolated in high yield. The compound **1** is soluble in toluene, benzene, CS_2 and CH_2Cl_2. These solutions are thermally unstable at room temp. and liberate C_{60} over periods of up to 24 h. Compound **1** and all the other new compounds described in this work were fully characterized by spectroscopic and analytical data.† The ^{13}C NMR spectrum of **1** is given in Fig. 1 and shows one resonance assignable to the carbonyl groups and a further 17 peaks assignable to the C_{60} moiety. The solution IR spectrum of **1**

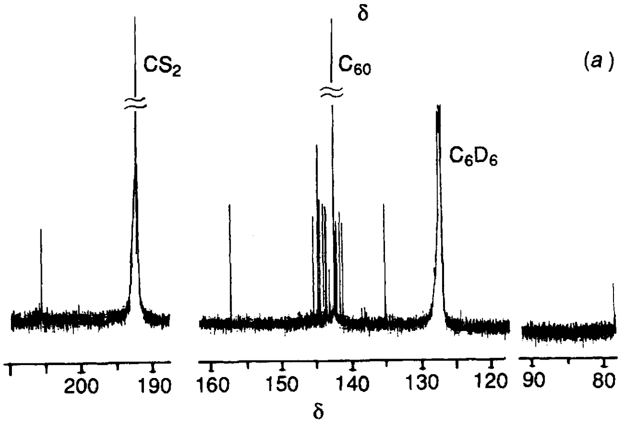

Fig. 1 (a) ^{13}C NMR spectrum of **1** in CS_2 + C_6D_6 with Cr(acac)$_3$ (Hacac = pentane-2,4-dione) added as a relaxant; (b) expansion in the region δ 141–147

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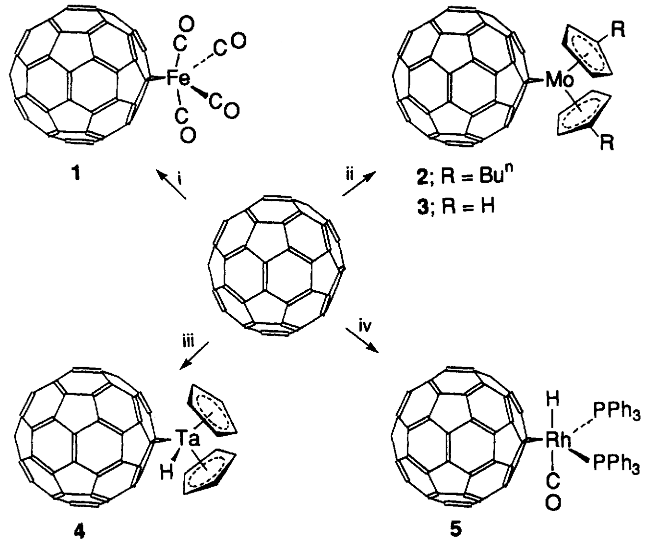
† *Selected spectroscopic and analytical data*: Satisfactory elemental analysis has been obtained for all the new compounds. **1**, IR (CS_2) ν_{CO}/cm^{-1} 2096, 2033, 2005, 1974; ^{13}C NMR (CS_2 + C_6D_6) δ 136–158 (s, 16 C_{60} signals), 79 (s, sp^3 carbons C_{60}), 206 (s, Fe(CO)$_4$).

2, ^{1}H NMR (CS_2 + C_6D_6) δ 0.9 (t, 3 H, $\mathrm{CH_2CH_2CH_2C}H_3$), 1.4 (m, 2 H, $\mathrm{CH_2CH_2C}H_2\mathrm{CH_3}$), 1.6 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$), 2.3 (t, 2 H, $\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$), 4.7 (apparent t, 2 H, $\mathrm{Bu^nC_5}H_4$), 5.2 (apparent t, 2 H, $\mathrm{Bu^nC_5}H_4$); ^{13}C NMR (CS_2 + C_6D_6) δ 15 (s, $\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$), 24 (s, $\mathrm{CH_2CH_2}C\mathrm{H_2CH_3}$), 31 (s, $\mathrm{CH_2}C\mathrm{H_2CH_2CH_3}$), 35 (s, $C\mathrm{H_2CH_2CH_2CH_3}$), 93, 94 (s, $\mathrm{Bu^nC}C_4\mathrm{H_4}$), 105 ($\mathrm{Bu^n}C\mathrm{C_4H_4}$), 135–170 (s, 17 C_{60} signals).

5, IR (nujol mull) ν/cm^{-1} 1986 (CO), 2056 (RhH); ^{1}H NMR (C_6D_6) δ 7.6, 6.9 (br, 30 H, PPh$_3$), −9.1 (t, 1 H, RhH); ^{13}C NMR (C_6D_6) δ 128, 129, 130, 133 (s, PPh$_3$) 141–145 (br, C_{60}); ^{31}P NMR (C_6D_6) δ 36 (d, PPh$_3$).



Scheme 1 *Reagents and conditions*: i, $Fe_2(CO)_9$ (1 equiv.) in benzene, room temp., (>80%); ii, $[Mo(\eta\text{-}RC_5H_4)_2H_2]$ (1 equiv.) in toluene, room temp., (>80%); iii, $[Ta(\eta\text{-}C_5H_5)_2H_3]$ (1 equiv.) in benzene, room temp., (>90%); iv, $Rh(PPh_3)_3(CO)H$ (1 equiv.) in toluene, room temp., (>95%)

shows four bands in the carbonyl stretching region. These data are entirely consistent with a molecule possessing C_{2v} symmetry, with C_{60} occupying an equatorial position at the iron centre and with the carbonyls undergoing rapid exchange on the NMR timescale between axial and equatorial positions. The C_{60} moiety in **1** is easily displaced and addition of YPh_3 (Y = P, As, Sb) to **1** gives C_{60}, $Fe(CO)_4YPh_3$ and $Fe(CO)_3(YPh_3)_2$ over a period of approximately 2 h.

Treatment of a solution of C_{60} in toluene at room temp. with the dihydride $[Mo(\eta\text{-}C_5H_4Bu^n)_2H_2]$ for 24 h gives a deep emerald-green solution from which the green compound $[Mo(\eta\text{-}C_5H_4Bu^n)_2(C_{60})]$ **2** may be isolated in near quantitative yield. The data of **2**† are entirely consistent with the structure proposed in Scheme 1. Thus, the ^{13}C NMR spectrum of **2** shows 17 resonances assignable to the C_{60} moiety and a further 7 resonances due to the $C_5H_4Bu^n$ ligands. The compound **2** is slightly soluble in hexane, moderately soluble in benzene and toluene and very soluble in CS_2. Solutions in tetrahydrofuran decompose with release of C_{60} over a period of hours. Treatment of C_{60} with $[Mo(\eta\text{-}C_5H_5)_2H_2]$ gives the analogue of **2**, namely $[Mo(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_{60})]$ **3**, which is markedly less soluble than **2** and dissolves only very slightly in toluene.

Treatment of C_{60} with a solution of $[Ta(\eta\text{-}C_5H_5)_2H_3]$ in benzene at room temp. over 12 h causes the precipitation of $[Ta(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_{60})H]$ **4** as a brown microcrystalline solid in near quantitative yield. The IR spectrum of **4** shows a band (1791 cm^{-1}) assignable to the tantalum–hydrogen stretch and the band characteristic for C_{60} at 527 cm^{-1} becomes a doublet in **4** (518 and 529 cm^{-1}) as expected for a lower symmetry C_{60} group. Compound **4** is only slightly soluble in benzene and toluene. The solid state ^{13}C NMR of **4** shows a broad featureless band centred at δ 146 assignable to the C_{60} fragment and a peak at δ 99 assignable to the cyclopentadienyl ligands. Hydrogen was presumed to be liberated as H_2, although no gas evolution was observed during the formation of **2**, **3** or **4**.

On addition of 1 equiv. of $[Rh(PPh_3)_3(CO)H]$ in toluene to C_{60}, also in toluene, an emerald-green solution develops instantaneously. Subsequent removal of solvent, extraction with tetrahydrofuran and precipitation with diethyl ether yields a dark-green powder of $[Rh(PPh_3)_2(CO)(\eta^2\text{-}C_{60})H]$ **5** in high yield. The IR spectrum of **5** exhibits one carbonyl stretch (1986 cm^{-1}) and one rhodium–hydride stretch (2056 cm^{-1}), both of which are shifted to higher wavenumbers in comparison with the corresponding bands in $[Rh(PPh_3)_3(CO)H]$. The bands characteristic for C_{60} are observed at 516 and 525 cm^{-1}. The ^1H NMR spectrum of **5** shows 2 broad peaks assignable to the phenyl groups at δ 6.95 and 7.61 and a triplet at δ −9.09 $[^2J(^{31}P\text{–}^1H) = 9\ Hz]$ assigned to the hydride ligand. The value of this coupling constant is indicative of a *cis* arrangement of the tertiary phosphine and hydride ligands around the rhodium. No resolvable coupling between the hydride ligand and the rhodium was observed. The ^{31}P NMR spectrum of **5** shows a doublet at δ 36 $[^1J(^{103}Rh\text{–}^{31}P) = 140\ Hz]$. The ^{13}C NMR spectrum of **5** shows bands characteristic for the triphenyl phosphine ligands and a broad signal at δ 141–145, which may be assigned to a fluxional C_{60} group. No signal was observed for the CO ligand. It is interesting that the C_{60} molecule does not insert into the Rh–H bond. Also, we have found that **5** is an effective catalyst for the hydroformylation of ethene and propene.[8]

In conclusion, we have demonstrated that C_{60} is a highly reactive molecule towards a variety of organometallic reagents and have reported the first examples of C_{60} derivatives of a simple transition metal carbonyl, metallocenes and transition metal hydrido derivatives. The reactions and proposed structures are shown in Scheme 1.

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