

## Transition Metal-carbonyl, -hydrido and - $\eta$ -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  $[\text{Fe}(\text{CO})_4(\eta^2\text{-}C_{60})]$ ,  $[\text{Mo}(\eta\text{-}C_5H_4R)_2(\eta^2\text{-}C_{60})]$  ( $R = \text{H}, \text{Bu}^n$ ),  $[\text{Ta}(\eta^2\text{-}C_5H_5)_2(\eta^2\text{-}C_{60})\text{H}]$  and  $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})(\eta^2\text{-}C_{60})\text{H}]$ , are described.

The recent availability of gram quantities of the fullerene  $C_{60}$  has facilitated the study of the reactivity of this intriguing molecule.<sup>1</sup> We have set out to develop the organometallic chemistry of fullerenes. The organometallic compounds  $[\text{C}_{60}\{\text{M}(\text{PEt}_3)_2\}_n]$  ( $n = 1$  or  $6$ , and  $M = \text{Ni}, \text{Pd}, \text{Pt}$ ),<sup>2</sup>  $[\text{M}(\text{PPh}_3)_2(\eta^2\text{-}C_{60})]$  ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ ),<sup>3</sup>  $[\text{Ir}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-}C_{60})\text{Cl}]$ ,<sup>4</sup>  $[\text{Ir}(\eta^5\text{-}C_9H_7)(\text{CO})(\eta^2\text{-}C_{60})]$ ,<sup>5</sup>  $[\text{C}_{60}\{\text{OsO}_4(4\text{-Bu}^n\text{C}_5\text{H}_4\text{N})_2\}_n]$  ( $n = 1$  or  $2$ )<sup>6,7</sup> 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  $[\text{Fe}_2(\text{CO})_9]$  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  $[\text{Fe}(\text{CO})_4(\eta^2\text{-}C_{60})]$  **1** was isolated in high yield. The compound **1** is soluble in toluene, benzene,  $\text{CS}_2$  and  $\text{CH}_2\text{Cl}_2$ . 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.<sup>†</sup> The  $^{13}\text{C}$

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**

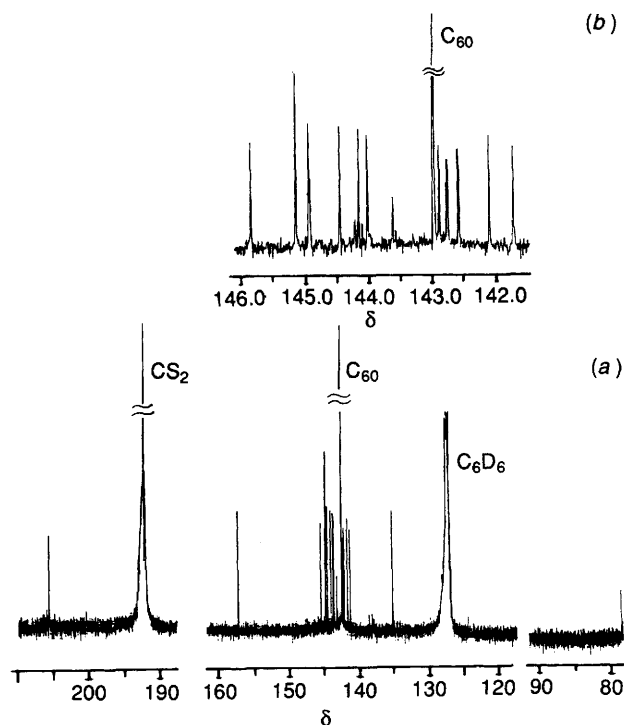
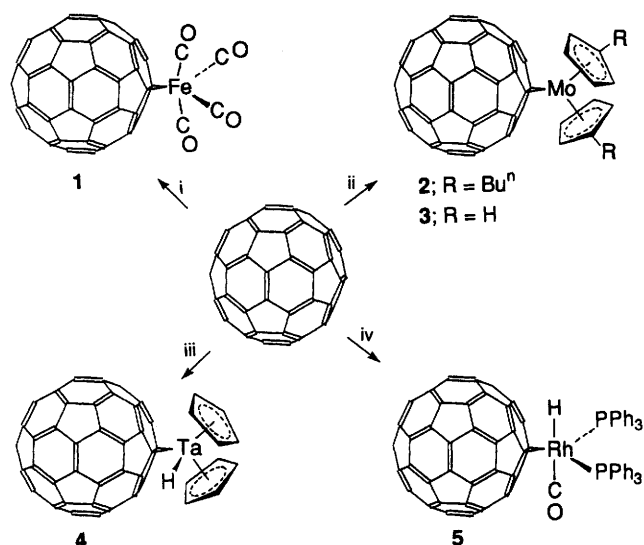


Fig. 1 (a)  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{CS}_2 + \text{C}_6\text{D}_6$  with  $\text{Cr}(\text{acac})_3$  (Hacac = pentane-2,4-dione) added as a relaxant; (b) expansion in the region  $\delta$  141–147

<sup>†</sup> Selected spectroscopic and analytical data: Satisfactory elemental analysis has been obtained for all the new compounds. **1**, IR ( $\text{CS}_2$ )  $\nu_{\text{CO}}/\text{cm}^{-1}$  2096, 2033, 2005, 1974;  $^{13}\text{C}$  NMR ( $\text{CS}_2 + \text{C}_6\text{D}_6$ )  $\delta$  136–158 (s, 16  $\text{C}_{60}$  signals), 79 (s,  $\text{sp}^3$  carbons  $\text{C}_{60}$ ), 206 (s,  $\text{Fe}(\text{CO})_4$ ).

**2**,  $^1\text{H}$  NMR ( $\text{CS}_2 + \text{C}_6\text{D}_6$ )  $\delta$  0.9 (t, 3 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.4 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.6 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.3 (t, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.7 (apparent t, 2 H,  $\text{Bu}^n\text{C}_5\text{H}_4$ ), 5.2 (apparent t, 2 H,  $\text{Bu}^n\text{C}_5\text{H}_4$ );  $^{13}\text{C}$  NMR ( $\text{CS}_2 + \text{C}_6\text{D}_6$ )  $\delta$  15 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 24 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 31 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 35 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 93, 94 (s,  $\text{Bu}^n\text{CC}_4\text{H}_4$ ), 105 ( $\text{Bu}^n\text{CC}_4\text{H}_4$ ), 135–170 (s, 17  $\text{C}_{60}$  signals).

**5**, IR (nujol mull)  $\nu/\text{cm}^{-1}$  1986 (CO), 2056 (RhH);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.6, 6.9 (br, 30 H,  $\text{PPh}_3$ ),  $-9.1$  (t, 1 H, RhH);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  128, 129, 130, 133 (s,  $\text{PPh}_3$ ) 141–145 (br,  $\text{C}_{60}$ );  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  36 (d,  $\text{PPh}_3$ ).



**Scheme 1** Reagents and conditions: i,  $\text{Fe}_2(\text{CO})_9$  (1 equiv.) in benzene, room temp., (>80%); ii,  $[\text{Mo}(\eta\text{-C}_5\text{H}_4)_2\text{H}_2]$  (1 equiv.) in toluene, room temp., (>80%); iii,  $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$  (1 equiv.) in benzene, room temp., (>90%); iv,  $\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{H}$  (1 equiv.) in toluene, room temp., (>95%)

shows four bands in the carbonyl stretching region. These data are entirely consistent with a molecule possessing  $\text{C}_{2v}$  symmetry, with  $\text{C}_{60}$  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  $\text{C}_{60}$  moiety in **1** is easily displaced and addition of  $\text{YPh}_3$  ( $\text{Y} = \text{P}, \text{As}, \text{Sb}$ ) to **1** gives  $\text{C}_{60}$ ,  $\text{Fe}(\text{CO})_4\text{YPh}_3$  and  $\text{Fe}(\text{CO})_3(\text{YPh}_3)_2$  over a period of approximately 2 h.

Treatment of a solution of  $\text{C}_{60}$  in toluene at room temp. with the dihydride  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Bu}^n)_2\text{H}_2]$  for 24 h gives a deep emerald-green solution from which the green compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Bu}^n)_2(\text{C}_{60})]$  **2** may be isolated in near quantitative yield. The data of **2**† are entirely consistent with the structure proposed in Scheme 1. Thus, the  $^{13}\text{C}$  NMR spectrum of **2** shows 17 resonances assignable to the  $\text{C}_{60}$  moiety and a further 7 resonances due to the  $\text{C}_5\text{H}_4\text{Bu}^n$  ligands. The compound **2** is slightly soluble in hexane, moderately soluble in benzene and toluene and very soluble in  $\text{CS}_2$ . Solutions in tetrahydrofuran decompose with release of  $\text{C}_{60}$  over a period of hours. Treatment of  $\text{C}_{60}$  with  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  gives the analogue of **2**, namely  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_{60})]$  **3**, which is markedly less soluble than **2** and dissolves only very slightly in toluene.

Treatment of  $\text{C}_{60}$  with a solution of  $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$  in benzene at room temp. over 12 h causes the precipitation of  $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_{60})\text{H}]$  **4** as a brown microcrystalline solid in near quantitative yield. The IR spectrum of **4** shows a band ( $1791\text{ cm}^{-1}$ ) assignable to the tantalum-hydrogen stretch and the band characteristic for  $\text{C}_{60}$  at  $527\text{ cm}^{-1}$  becomes a doublet in **4** ( $518$  and  $529\text{ cm}^{-1}$ ) as expected for a lower symmetry  $\text{C}_{60}$  group. Compound **4** is only slightly soluble in benzene and toluene. The solid state  $^{13}\text{C}$  NMR of **4** shows a broad featureless band centred at  $\delta$  146 assignable to the  $\text{C}_{60}$  fragment and a peak at  $\delta$  99 assignable to the cyclopentadienyl ligands. Hydrogen was presumed to be liberated as  $\text{H}_2$ , although no gas evolution was observed during the formation of **2**, **3** or **4**.

On addition of 1 equiv. of  $[\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{H}]$  in toluene to  $\text{C}_{60}$ , 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  $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\eta^2\text{-C}_{60})\text{H}]$  **5** in high yield. The IR spectrum of **5** exhibits one carbonyl stretch ( $1986\text{ cm}^{-1}$ ) and one rhodium-hydride stretch ( $2056\text{ cm}^{-1}$ ), both of which are shifted to higher wavenumbers in comparison with the corresponding bands in  $[\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{H}]$ . The bands characteristic for  $\text{C}_{60}$  are observed at  $516$  and  $525\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of **5** shows 2 broad peaks assignable to the phenyl groups at  $\delta$  6.95 and 7.61 and a triplet at  $\delta$  -9.09 [ $^2J(^{31}\text{P}\text{-}^1\text{H}) = 9\text{ Hz}$ ] 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  $^{31}\text{P}$  NMR spectrum of **5** shows a doublet at  $\delta$  36 [ $^1J(^{103}\text{Rh}\text{-}^{31}\text{P}) = 140\text{ Hz}$ ]. The  $^{13}\text{C}$  NMR spectrum of **5** shows bands characteristic for the triphenyl phosphine ligands and a broad signal at  $\delta$  141–145, which may be assigned to a fluxional  $\text{C}_{60}$  group. No signal was observed for the CO ligand. It is interesting that the  $\text{C}_{60}$  molecule does not insert into the  $\text{Rh}\text{-H}$  bond. Also, we have found that **5** is an effective catalyst for the hydroformylation of ethene and propene.<sup>8</sup>

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

We are grateful to Dr R. Claridge for help in acquiring the  $^{13}\text{C}$  NMR spectrum of **1**. We also wish to thank the SERC for studentships to R. E. D., A. H. H. S. and J. F. C. T.

Received, 21st June 1993; Com., 3/03574C

## References

- 1 R. Taylor, J. P. Hare, A. K. Abdul-Sada and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1990, 1423; W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Muffman, *Nature*, 1990, **347**, 354.
- 2 P. J. Fagan, J. C. Calabrese and B. Malone, *Acc. Chem. Res.*, 1992, **25**, 134.
- 3 P. J. Fagan, J. C. Calabrese and B. Malone, *Science*, 1991, **252**, 1160.
- 4 A. L. Balch, V. J. Catalano and J. W. Lee, *Inorg. Chem.*, 1991, **30**, 3980.
- 5 R. S. Koefed, M. F. Hudgens and J. R. Shapley, *J. Am. Chem. Soc.*, 1991, **113**, 8957.
- 6 J. M. Hawkins, A. Meyer, T. A. Lewis, S. Loren and F. J. Hollander, *Science*, 1991, **252**, 312.
- 7 J. M. Hawkins, A. Meyer, T. A. Lewis, U. Bunz, R. Nunlist, G. E. Ball, T. W. Ebbesen and K. Tanigaki, *J. Am. Chem. Soc.*, 1992, **114**, 7954.
- 8 J. B. Claridge, R. E. Douthwaite, M. L. H. Green, R. M. Lago, S. C. Tsang and A. P. E. York, presented in part at the Fullerenes 1993 Colloquium, Santa Barbara, USA and submitted to *J. Mol. Catal.*