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Synthesis and Characterization of Organochromium Complexes *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$, *fac*/*mer*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ and *fac*-$Cr(CO)_3(L)(dppe)$ ($L = PPh_3$, $4\text{-}MeC_5H_4N$)†

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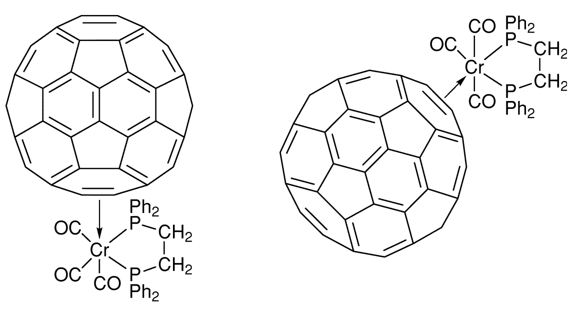
Reaction of *fac*-$Cr(CO)_3(MeCN)(dppe)$ [dppe = 1,2-bis(diphenylphosphino)ethane] or $Cr(CO)_4(dppe)$ with fullerene C_{60} afforded a single isomer *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ and an isomeric mixture of *fac*/*mer*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$, whereas the isomer *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ reacted with Ph_3P or 4-methylpyridine to give single isomers *fac*-$Cr(CO)_3(Ph_3P)(dppe)$ and *fac*-$Cr(CO)_3(4\text{-}MeC_5H_4N)(dppe)$, respectively.

Since the discovery of a method for gram-scale isolation of fullerene C_{60},[1] numerous organotransition metal fullerene C_{60} derivatives containing a direct metal-to-C_{60} bond have been prepared and characterized, such as those of Pt,[2] Ir,[3] Ru,[4] Mo[5] and W.[5] However, up to now, no report regarding the synthesis and characterization of chromium complexes of this type has appeared. Herein we report the synthesis and characterization of the first such chromium η^2-C_{60} complexes, the single isomer *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ and the isomer mixture of *fac*- and *mer*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$, as well as of two organochromium complexes without C_{60} ligands derived from ligand displacement reactions of *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ with Ph_3P or 4-methylpyridine.

One equivalent of fullerene C_{60} reacted with *fac*-$Cr(CO)_3(MeCN)(dppe)$ in chlorobenzene at about 95 °C, through a ligand displacement reaction between C_{60} and MeCN to give a single isomer *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (Scheme 1) in 17% yield.



fac-isomer *mer*-isomer

Scheme 1

In principle, the product formed from the above reaction might exist as another isomer, *i.e.* the *mer* isomer, or as a mixture of the *fac* and *mer* isomers (Scheme 1). However, since the ^{31}P NMR spectrum of the product shows only one singlet at δ 77.22, the product should be the *fac* isomer. This is because this isomer has two identical P atoms in the same chemical environment.

As seen in Fig. 1, the ^{13}C NMR spectrum of the C_{60} core of the *fac* isomer displays 29 resonance peaks, in which the 4 peaks at δ 150.02, 145.12, 143.40 and 141.43 could be each assigned to each carbon atom (altogether 4 × 1C) on the C_s symmetry plane, whereas the 3 peaks with about triple intensity at δ 152.12, 147.61 and 143.71, as well as the other 22 peaks with about double intensity, might be each assigned to each of four carbon atoms (altogether 3 × 4C) and each of two carbon atoms (altogether 22 × 2C) on two sides of the symmetry plane, respectively. This is consistent with the C_s symmetry and the C_{60} core having 60 sp^2-C atoms.[6] No sp^3-C signal observed for the C_{60} core of this isomer may mean that the fullerene C_{60} is co-ordinated to chromium through a 6:6 bond mainly in an η^2,π-olefin fashion and thus the metal is not involved in a three-membered ring.[7]

We further found that the η^2-C_{60} ligand of *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ could also be replaced with *fac*-configuration retention by Ph_3P or 4-methylpyridine in chlorobenzene at reflux to give *fac*-$Cr(CO)_3(Ph_3P)(dppe)$ and *fac*-$Cr(CO)_3(4\text{-}MeC_5H_4N)(dppe)$ in 63 and 72% yield, respectively.

The combustion analysis and spectroscopic data of these two *fac* isomers are in accord with their structures. For example, the ^{31}P NMR spectrum of *fac*-$Cr(CO)_3(Ph_3P)(dppe)$ shows one singlet at δ 55.73 for the P atom in Ph_3P and one singlet at δ 74.76 for two identical P atoms in dppe, whereas that of *fac*-$Cr(CO)_3(4\text{-}MeC_5H_4N)(dppe)$ exhibits only one singlet at δ 75.68 for two identical P atoms in dppe. No coupling observed in the ^{31}P NMR between the different P atoms of dppe and Ph_3P in *fac*-$Cr(CO)_3(Ph_3P)(dppe)$ is obviously due to their similarity in chemical environment.[8]

It is noteworthy that the reaction of $Cr(CO)_4(dppe)$ with C_{60}, different from that of *fac*-$Cr(CO)_3(MeCN)(dppe)$ in refluxing chlorobenzene, afforded a mixture of two isomers *fac*- and *mer*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (Scheme 1) in 15% yield. The two isomers are very close in polarity and thus could not be separated by conventional chromatography and recrystallization methods. The mixture was charac-

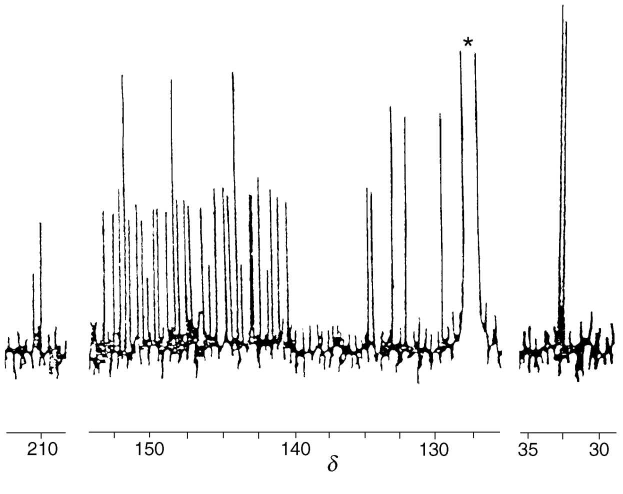


Fig. 1 The ^{13}C NMR spectrum of *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (* peaks due to solvent)

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

terized by elemental analysis, IR, UV-vis and NMR (^{1}H and ^{31}P) spectroscopy. The ^{31}P NMR spectrum shows three singlets at δ 76.38, 77.39 and 77.69. Apparently, the singlet at δ 77.39 should be assigned to two identical P atoms of the *fac* isomer, whereas the two singlets at δ 76.38 and 77.69 should be assigned to two different P atoms of the *mer* isomer. Although coupling between the two different P atoms of dppe in the *mer* isomer could take place through the chromium atom, it is not observed since they have very similar chemical environments.[8] In view of C_{60} being electron-withdrawing, the downfield singlet for the *mer* isomer should be assigned to the P atom *cis* to the C_{60} ligand and the upfield singlet to the P atom *trans* to C_{60}.

The IR spectrum of this isomer mixture, similar to that of the *fac* isomer, shows four absorption bands characteristic of the C_{60} ligand. However, in contrast to the *fac* isomer which shows three absorption bands for its terminal carbonyls, the isomer mixture exhibits four absorption bands for its terminal carbonyls. This is consistent with the observation that the number of IR active bands cannot exceed but may be less than the number of CO ligands in the complexes.[7]

Experimental

All reactions were carried out under a nitrogen atmosphere. Silica gel (300–400 mesh) for column chromatography (15 × 2 cm) was activated for 1 h at 120 °C. Toluene and light petroleum (bp 60–90 °C) were dried and deoxygenated by distillation from sodium–benzophenone. Chlorobenzene and chloroform were dried by distillation from P_2O_5. Triphenylphosphine, 4-methylpyridine and fullerene C_{60} (99.9%) were of commercial origin. The complexes $Cr(CO)_4(dppe)$[8] and *fac*-$Cr(CO)_3(MeCN)(dppe)$[9] were prepared according to the literature. The IR and UV-vis spectra were recorded on a Nicolet 170 SX FTIR and a Shimadzu UV-240 spectrometer respectively, NMR spectra on a JEOL 90Q, Bruker AC-P 200 or UNITY plus-400 spectrometer. Elemental analysis, MS and melting points were determined using a Yanaco CHN Corder MT-3 analyzer, a Zabspec spectrometer and a Yanaco MP-500 apparatus, respectively.

fac-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$.—A 100 ml two-necked flask was charged with *fac*-$Cr(CO)_3(MeCN)(dppe)$ (58 mg, 0.10 mmol), C_{60} (72 mg, 0.10 mmol) and chlorobenzene (30 ml). The reaction mixture was heated to about 95 °C and stirred at this temperature for 18 h. After removal of the solvent under reduced pressure, the residue was separated by column chromatography using 1:4 (v/v) toluene–light petroleum as eluent under anaerobic conditions. From the first purple band we obtained 8.5 mg of unchanged C_{60} and from the second light green band 19 mg (17% based on consumed C_{60}) of *fac*–$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ as a greenish solid; mp 110–112 °C. $\tilde{\nu}_{max}/cm^{-1}$ 1929, 1861, 1843 (C≡O), 1427, 1182, 576, 527 (C_{60}). δ_H ($CDCl_3$) 2.59 (d, $J = 16$ Hz, 4 H, $2CH_2$), 7.24–7.56 (m, 20 H, $4C_6H_5$). δ(^{31}P) ($CDCl_3$) 77.22. δ(^{13}C) [100.6 MHz, C_6D_6, 0.006 M,$Cr(acac)_3$] 210.30, 210.95 (s, s, CO); 153.75, 153.11, 152.60, 152.12, 151.82, 150.75, 150.36, 150.02, 149.50, 149.21, 148.53, 147.61, 147.26, 146.54, 146.06, 145.31, 145.12, 144.86, 14436, 144.02, 143.71, 143.40, 142.43, 142.32, 141.86, 141.43, 141.12, 140.62, 140.03 (s, 29 resonances for C_{60}); 135.25, 134.91, 133.53, 132.03, 130.07 (5 resonances for C_6H_5); 33.00 (d, $J = 27.2$ Hz, $2CH_2$) UV-vis(toluene, 1.5×10^{-3} M): $\lambda_{max}(\log \varepsilon)$ 283.7 (2.97), 333.5 (2.75), 406.5 (1.94), 431.9 nm (1.79). *m/z* 720 (C_{60}^+), 1254 (M^+) (Found: C, 84.90; H, 2.03. $C_{89}H_{24}CrO_3P_2$ requires C, 85.17; H, 1.93%).

fac-$Cr(CO)_3(Ph_3P)(dppe)$.—A 50 ml two-necked flask was charged with *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (13 mg, 0.01 mmol), Ph_3P (3 mg, 0.01 mmol) and chlorobenzene (20 ml). The reaction mixture was refluxed for 8 h. Removal of the solvent under vacuum gave a yellow-brown residue, which was extracted with 1:1 (v/v) $CHCl_3$–light petroleum. The extracts were evaporated to dryness under vacuum to give 5 mg (63%) of *fac*-$Cr(CO)_3(Ph_3P)(dppe)$ as a yellowish solid, mp 173–175 °C. $\tilde{\nu}_{max}/cm^{-1}$ 1950, 1901, 1855 (C≡O). δ_H ($CDCl_3$) 2.58 (d, $J_{PH} = 16$ Hz, 4 H, $2CH_2$), 7.35–7.58 (m, 35 H, $7C_6H_5$). δ(^{31}P) ($CDCl_3$) 55.73 (s, PPh_3), 74.76 (s, $2PPh_2$) (Found: C, 70.59; H, 4.82. $C_{47}H_{39}CrO_3P_3$ requires C, 70.85; H, 4.93%).

fac-$Cr(CO)_3(4\text{-}MeC_5H_4N)(dppe)$.—A 50 ml two-necked flask was charged with *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (13 mg, 0.01 mmol), 4-methylpyridine (0.01 ml, 0.10 mmol) and chlorobenzene (20 ml). The reaction mixture was refluxed for 6 h. Removal of the solvent under vacuum afforded a viscous residue, which was washed with light petroleum (2 × 20 ml) and then extracted with $CHCl_3$. The extracts were evaporated to dryness under vacuum to give 4.5 mg(72%) of *fac*-$Cr(CO)_3(4\text{-}MeC_5H_4N)(dppe)$ as a yellow solid, mp 150–152 °C. $\tilde{\nu}_{max}/cm^{-1}$ 1944, 1895, 1850 (C≡O). δ_H ($CDCl_3$) 0.84 (s, 3 H, CH_3), 2.59 (d, $J = 14$ Hz, 4H, $2CH_2$), 7.36–7.55 (m, 24 H, $4C_6H_5$, C_5H_4N). δ (^{31}P) ($CDCl_3$) 75.68 (s, $2PPh_2$) (Found: C, 66.94; H, 4.98; N, 2.23. $C_{35}H_{31}CrNO_3P_2$ requires C, 66.98; H, 4.71; N, 2.13%).

fac- *and* mer-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$.—A 100 ml two-necked flask was charged with $Cr(CO)_4(dppe)$ (57 mg, 0.10 mmol), C_{60} (72 mg, 0.10 mmol) and chlorobenzene (40 ml). The reaction mixture was refluxed for 24 h and then the same work-up was followed as that for the isomer *fac*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$. Unchanged C_{60} (10 mg) and 16 mg (15% based on consumed C_{60}) of an isomer mixture of *fac*- and *mer*-$Cr(CO)_3(dppe)(\eta^2\text{-}C_{60})$ were obtained as a greenish solid, mp 110–116 °C. $\tilde{\nu}_{max}/cm^{-1}$ 1930, 1877, 1860, 1799 (C≡O) 1433, 1183, 586, 519 (C_{60}). δ_H ($CDCl_3$) 2.58 (d, $J = 16$ Hz, 4 H, $2CH_2$), 2.52 (d, $J = 16$ Hz, 4 H, $2CH_2$), 7.24–7.58 (m, 20 H, $4C_6H_5$). δ(^{31}P) ($CDCl_3$) 77.39 (s, P of *fac* isomer), 76.38, 77.69 (s, s, P of *mer* isomer) UV-vis(toluene, 1.5×10^{-3} M): $\lambda_{max}(\log \varepsilon)$ 285.3 (2.97), 344.3 (2.43), 436.3 nm (1.79) (Found: C, 84.90; H, 2.03, $C_{89}H_{24}CrO_3P_2$ requires C, 85.17; H, 1.93%).

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References

1 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature* (*London*), 1990, **347**, 354.
2 P. J. Fagan, J. C. Calabrese and B. Malone, *J. Am. Chem. Soc.*, 1991, **113**, 9408.
3 A. L. Balch, V. J. Catalano and J. W. Lee, *Inorg. Chem.*, 1991, **30**, 3980.
4 I. J. Mavunkal, Y. Chi, S.-M. Peng and G.-H. Lee, *Organometallics*, 1995, **14**, 4454.
5 H.-F. Hsu and J. R. Shapley, *Proc. Electrochem. Soc.*, 1995, **95–10**, 1087; L.-C. Song, Y.-H. Zhu and Q.-M. Hu, *Polyhedron*, 1997, **16**, 2141.
6 W. H. Miles and P. M. Smiley, *J. Org. Chem.*, 1996, **61**, 2559.
7 J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1980, p. 86.
8 S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.
9 G. J. Kubas, G. D. Jarvinen and R. R. Ryan, *J. Am. Chem. Soc.*, 1983, **105**, 1883.