Synthesis, Structure, and Bonding of Fulvene Complexes of Titanium, Molybdenum, and Tungsten *

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The compounds $[M(\eta\text{-}C_6H_5R)(\sigma,\eta^5\text{-}C_5H_4CR'_2)]$ (M = Mo or W, R = H, R' = Me or Ph; M = W, R = Me, R' = Me or Ph), $[W(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(\sigma,\eta^5\text{-}C_5H_4CPh_2)]$, $[Ti(\sigma,\eta^5\text{-}C_5H_4CPh_2)_2]$, and $[Ti(\sigma,\eta^5\text{-}C_5H_4CPh_2)_2(CO)]$ are described. The crystal structures of the compounds where M = Mo, R = H, R' = Me or Ph; M = W, R = Me, R' = Me or Ph; and $[Ti(\sigma,\eta^5\text{-}C_5H_4CPh_2)_2]$ have been determined and reveal that the exocyclic carbon of the fulvene ligands is strongly bent out of the plane of the C_5-ring carbons and bonds directly to the metal. The metal–fulvene bonding is discussed in the light of the structures, the photoelectron spectra, and molecular orbital calculations.

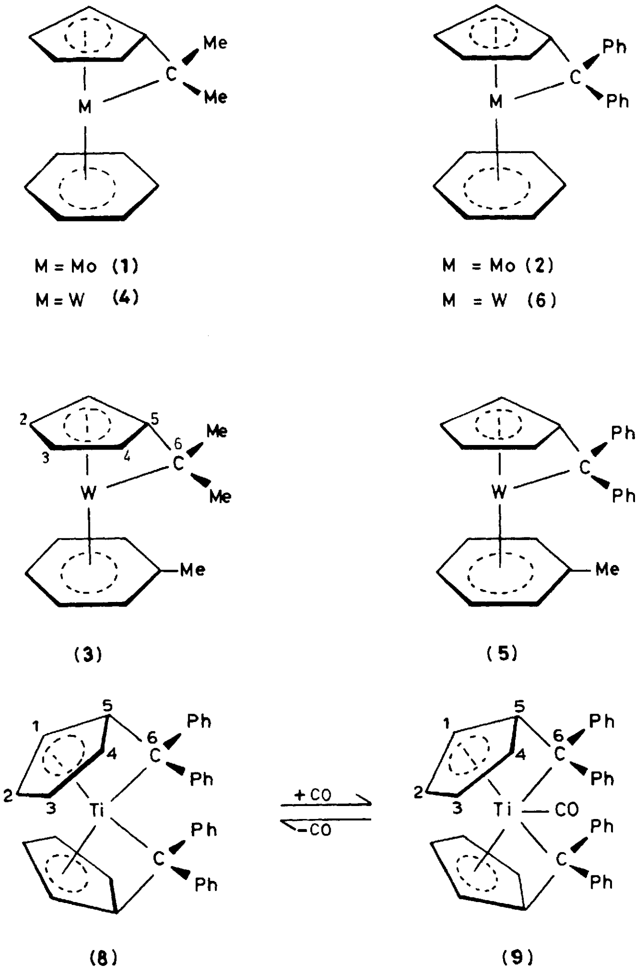
The fulvene ligand can bond to transition metals in several different modes. In unusual examples, fulvenes bond through one of the ring double bonds, as in $[Pt(\eta^2\text{-}C_5H_4CPh_2)(PPh_3)_2]$,[1] or through the exocyclic double bond, as in $[Pt(\eta^2\text{-}C_5Ph_4CH_2)(1,5\text{-}C_8H_{12})]$[1] and $[Rh(\eta^2\text{-}C_5H_4CPh_2)(CO)_2Cl]$.[2] The two cyclic double bonds can co-ordinate in an η^4 fashion, as in $[Fe(CO)_3(\eta^4\text{-}C_5H_4CPh_2)]$,[3] or the two cyclic bonds can each act as η^2 ligands to separate metals and thus bridge the two metal centres, as in $[(CO)_4Fe(\mu\text{-}C_4H_4CCMe_2)Fe(CO)_4]$.[3]

More commonly, fulvene ligands act as six-electron donors and structural and spectroscopic data indicate that the metal–fulvene bonding can vary in an interesting and subtle manner[4,5] as discussed below.

In this paper we describe the ready displacement of arenes in bis(η-arene) complexes of molybdenum and tungsten by fulvenes giving new metal–fulvene compounds whose structure and bonding are described. Part of this work has been communicated briefly.[6]

Results and Discussion

Synthesis and Characterization.—Bis(η-benzene)molybdenum in toluene was treated with 6,6-dimethylfulvene for 2 d at 50 °C giving purple needles in high yield. Slow sublimation gave crystals suitable for *X*-ray diffraction studies. The data given in Table 1 and the crystal structure determination show the compound to be $[Mo(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CMe_2)]$ (**1**). Compound (**1**) is air-sensitive, soluble in light petroleum and in methanol in which it slowly decomposes. The ^1H n.m.r. spectrum showed two triplets at δ 5.05 and 4.57 assignable to a C_5H_4 unit, a singlet at δ 3.82, assignable to η-benzene, and a singlet at δ 1.66 assignable to two methyl groups. The parent ion in the mass spectrum appeared at *m/e* = 282 (100%), corresponding to $[Mo(C_6H_6)(C_5H_4CMe_2)]^+$.



M = Mo (**1**)
M = W (**4**)

M = Mo (**2**)
M = W (**6**)

(**3**)

(**5**)

(**8**)

(**9**)

Scheme.

In a similar manner, treatment of $[Mo(\eta\text{-}C_6H_6)_2]$ with 6,6-diphenylfulvene gave red crystals of $[Mo(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CPh_2)]$ (**2**). The ^1H n.m.r. spectrum showed complex absorptions at δ 7.40, 7.08, and 6.98 of relative intensity 4, 4, and 2 respectively, assignable to two phenyl units, two triplets of intensity 2 at δ 4.78 and 4.55 assignable to C_5H_4, and a singlet at δ 3.93 assignable to $\eta\text{-}C_6H_6$. The mass spectrum exhibited the parent ion at *m/e* = 406 (100%) attributed to $[Mo(C_6H_6)(C_5H_4CPh_2)]^+$. Crystals of (**2**) suitable for *X*-ray crystal structure determination were obtained by sublimation at 150 °C.

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* *Supplementary data available* (No. SUP 56266, 6 pp.): isotropic and anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: eV ≈ 1.60×10^{-19} J, atm = 101 325 Pa.

Table 1. Analytical and spectroscopic data

		Analysis[a] (%)		
Compound	Colour	C	H	N.m.r. data[b]
(1)[c]	Purple	59.7 (60.0)	5.3 (5.7)	5.05 (2 H, t, 2 H of C_5H_4), 4.57 (2 H, t, 2 H of C_5H_4), 3.82 (6 H, s, η-C_6H_6), 1.66 (6 H, s, CMe_2)
(2)	Red	71.0 (71.3)	4.8 (5.0)	7.40 (4 H, c, *o*-H of Ph), 7.08 (4 H, c, *m*-H of Ph), 6.98 (2 H, c, *p*-H of Ph), 4.78 (2 H, t, 2 H of C_5H_4), 4.55 (2 H, t, 2 H of C_5H_4), 3.93 (6 H, s, η-C_6H_6)
(3)[d]	Red			4.86 (4 H, m, C_5H_4), 3.78 [1 H, t, *J* 4.1, *p*-H of η-C_6H_5], 3.54 (4 H, m, *o*- and *m*-H of η-C_6H_5), 1.94 (3 H, s, Me of η-C_6H_5Me), 1.76 [6 H, t, *J*(W–H) 2.56, CMe_2] ^{13}C-{^1H} N.m.r.:[e] 95 [C(6)], 87.4 [C(2,3)], 82.7 [C(5)], 81.0 [C(1,4)]; other bands at 71.6, 71.2, 70.9, 66.5, 26.0, 21
(4)[f]	Red			4.99 (2 H, t, *J* 1.77, 2 H of C_5H_4), 4.79 (2 H, t, *J* 1.77, 2 H of C_5H_4), 3.527 (6 H, s, η-C_6H_6), 1.70 (6 H, t, *J* 2.21, CMe_2)
(5)[g]	Red	59.3 (59.3)	4.4 (4.35)	7.2 (10 H, m, CPh_2), 4.84 (2 H, t, *J* 2.21, 2 H of C_5H_4), 4.58 (2 H, t, *J* 2.21, 2 H of C_5H_4), 4.24 (1 H, t, *J* 5.3, *p*-H of η-C_6H_5), 3.84 (2 H, t, *J* 5.7, *m*-H of η-C_6H_5), 3.36 (2 H, d, *J* 5.3, *o*-H of η-C_6H_5), 1.69 (3 H, s, Me)
(6)	Red			7.3 (10 H, m, CPh_2), 4.84 (2 H, t, *J* 2.21, 2 H of C_5H_4), 4.65 (2 H, t, *J* 2.2, 2 H of C_5H_4), 3.65 (6 H, s, η-C_6H_6)
(7)[h]	Dark red	61.2 (60.6)	5.8 (4.8)	7.2 (10 H, m, CPh_2), 4.82 (2 H, t, *J* 2.21, 2 H of C_5H_4), 4.32 (2 H, t, *J* 2.21, 2 H of C_5H_4), 3.68 (3 H, s, η-C_6H_3), 1.99 (9 H, s, Me_3)
(8)	Dark green	84.6 (85.0)	6.3 (5.5)	7.31 (4 H, d, *J* 7, CPh_2), 6.99 (4 H, t, *J* 6, CPh_2), 6.88—6.79 (8 H, m, CPh_2), 6.54—6.49 (4 H, m, CPh_2) (total intensity *ca.* 20, 4 Ph); 6.40 (2 H, ddd, *J* 3.3, 2.5, 1.8, 2 H of C_5H_4), 5.57 (2 H, ddd, *J* 3.3, 1.8, 3.4, 2 H of C_5H_4), 4.87 (2 H, ddd, *J* 2.5, 1.8, 3.3, 2 H of C_5H_4), 4.07 (2 H, ddd, *J* 1.8, 3.4, 3.3, 2 H of C_5H_4) ^{13}C N.m.r.: 144.9 [C(7,13)], 142.8 [C(13,7)], 132.1 [C(6)], 128.8 [C(9,11) or C(15,17)], 128.6 [C(15,17) or C(9,11)], 127.3 [C(14,18) or C(12,8)], 126.8 [C(12,8) or C(14,18)], 125.5 [C(10) or C(16)], 124.4 [C(16) or C(10)], 121.7 [one of C(1,2,3,4)], 116.2 [one of C(1,2,3,4)], 111.8 [C(5)], 109.5 [one of C(1,2,3,4)], 108.1 [one of C(1,2,3,4)][i]
(9)[j]	Dark red			7.45 (4 H, d, *J* 7.2, *o*-H of Ph), 7.25 (4 H, d, *J* 8.4, *o*-H of Ph), 7.07 (4 H, t, *J* 7.5, *m*-H of Ph), 6.99 (4 H, t, *J* 7.5, *m*-H of Ph), 6.93 (2 H, t, *J* 7.3, *p*-H of Ph), 6.89 (2 H, t, *J* 7.2, *p*-H of Ph), 5.46 (2 H, 6 lines, c, 2 H of C_5H_4), 5.29 (2 H, 6 lines, c, 2 H of C_5H_4), 4.52 (2 H, 4 lines, c, 2 H of C_5H_4), 4.41 (2 H, 4 lines, c, 2 H of C_5H_4) ^{13}C N.m.r.: 219.4(CO), 141.4, 132.3, 131.8, 125.4, 124.2, 117.9, 111.9, 110.6, 103.2, 94.6, 91.6

[a] Calculated values are given in parentheses. [b] In C_6D_6 at 300 MHz. Given as: chemical shift (δ/p.p.m.) (relative intensity, multiplicity, *J* in Hz [for *J*(H–H) unless otherwise stated], assignment); c = complex, m = multiplet. [c] $M/e = 282$ [P^+]. [d] $M/e = 382$ [P^+]. [e] All bands were broad, for labelling see the Scheme. [f] $M/e = 368$ [P^+]. [g] $M/e = 506$ [P^+]. [h] $M/e = 532$ [P^+]. [i] For numbering, see Figure 3(*a*). [j] ν(CO) = 2 043s cm^{-1}; unstable, see text.

When bis(η-benzene)tungsten and 6,6-dimethylfulvene in toluene were heated at 85 °C for one week, red crystals were obtained. The ^1H and ^{13}C n.m.r. spectra and crystal structure determination characterise the product as the η-toluene derivative $[W(\eta\text{-}C_6H_5Me)(\sigma,\eta^5\text{-}C_5H_4CMe_2)]$ (**3**).

The analytical and spectroscopic data for (**1**)—(**3**) and all other new compounds are given in Table 1. It is interesting that the synthesis of (**3**) involves the exchange of both the η-C_6H_6 rings of $[W(\eta\text{-}C_6H_6)_2]$. Compound (**3**) was also formed when $[W(\eta^6\text{-}PhCH_2Ph)_2]$ [7] was heated with 6,6-dimethylfulvene in toluene as solvent.

Treatment of bis(η-benzene)tungsten in benzene solution with 6,6-dimethylfulvene gave the expected complex $[W(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CMe_2)]$ (**4**). The compound was characterised by analysis and especially by comparison of the ^1H n.m.r. spectrum with that of (**1**). The mass spectrum of (**4**) gave a highest mass ion at $M/e = 368$.

Treatment of bis(η-toluene)tungsten in toluene with 6,6-diphenylfulvene at 100 °C for one week gave a red solution from which red crystals were obtained. These were characterised by the data in Table 1 and by *X*-ray diffraction studies as the compound $[W(\eta\text{-}C_6H_5Me)(\sigma,\eta^5\text{-}C_5H_4CPh_2)]$ (**5**). Similarly bis(η-benzene)tungsten in benzene with 6,6-diphenylfulvene gave red crystals $[W(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CPh_2)]$ (**6**).

In a preliminary study of η-arene ring-exchange phenomena, the ^1H n.m.r. spectrum of $[W(\eta\text{-}C_6H_6)_2]$ in [$^2H_8$]toluene at 100 °C was monitored and showed there was a slow substitution of one η-benzene ligand. The mass spectrum confirmed that the only product was the mixed sandwich compound $[W(\eta\text{-}C_6H_6)(\eta\text{-}C_6D_5CD_3)]$, and no bands assignable to $[W(\eta\text{-}C_6D_5CD_3)_2]$ were observed. Further, no ligand exchange was observed between $[W(\eta\text{-}C_6H_6)(\sigma,\eta^5\text{-}C_5H_4CMe_2)]$ (**4**) in [$^2H_8$]toluene at 100 °C. In confirmation of this observation, the ^1H n.m.r. spectra showed that when a mixture of $[W(\eta\text{-}C_6H_6)_2]$ and (**4**) was heated in [$^2H_8$]toluene at 100 °C one η-C_6H_6 ligand of bis(η-benzene)tungsten could be exchanged. No exchange was observed when $[W(\eta\text{-}C_6H_5Me)_2]$ was heated at 100 °C in [$^2H_8$]toluene.

After $[W(\eta\text{-}C_6H_5Me)_2]$ and 6,6-diphenylfulvene had been heated at 100 °C in mesitylene for four days, fractional crystallization of the reaction mixture yielded the compounds $[W(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$,[8] (**5**), and $[W(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(\sigma,\eta^5\text{-}C_5H_4CPh_2)]$ (**7**).

Treatment of $[Ti(\eta\text{-}C_6H_5Me)_2]$ with 6,6-diphenylfulvene in toluene resulted in the immediate formation of a green solution from which large green cubic crystals could be isolated. The data in Table 1 and a crystal structure determination showed the compound to be $[Ti(\sigma,\eta^5\text{-}C_5H_4CPh_2)_2]$ (**8**). The ^1H n.m.r. spectrum of (**8**) shows multiplets at 6.40, 5.57, 4.87, and 4.07 which are assignable to four different cyclopentadienyl hydrogens. Selective decoupling of the spectrum in this region allowed a consistent set of coupling constants to be determined. The two fulvene ligands appear to be identical and related by a C_2 axis. The complex signals from 7.31 to 6.49 are assignable to two different phenyl groups.

Treatment of (**8**) in toluene–light petroleum (b.p. 60–80 °C)

Table 2. Bond lengths (Å) and angles (°)

Compound (**1**)

Mo(1)–C(3)	2.37(1)	C(3)–C(3′)	1.47(2)	C(3′)–C(3)–C(4)	108.0(7)	C(22′)–C(21)–C(22)	119.0(9)
Mo(1)–C(4)	2.28(1)	C(3)–C(4)	1.45(2)	C(3)–C(4)–C(5)	107(1)	C(21)–C(22)–C(23)	120.6(7)
Mo(1)–C(5)	2.13(2)	C(4)–C(5)	1.45(2)	C(4)–C(5)–C(4′)	110(1)	C(22)–C(23)–C(24)	119.8(7)
Mo(1)–C(6)	2.31(2)	C(5)–C(6)	1.42(2)	C(5)–C(6)–C(7)	120.4(9)	C(23)–C(24)–C(23′)	119.4(9)
Mo(1)–C(21)	2.35(2)	C(6)–C(7)	1.54(2)	C(7)–C(6)–C(7′)	109(2)		
Mo(1)–C(22)	2.27(1)	C(21)–C(22)	1.43(2)				
Mo(1)–C(23)	2.25(1)	C(22)–C(23)	1.46(2)				
Mo(1)–C(24)	2.31(2)	C(23)–C(24)	1.44(2)				

Compound (**2**)

Mo(1)–C(1)	2.240(3)	C(12)–C(7)	1.382(5)	C(1)–C(2)–C(3)	108.9(4)	C(13)–C(14)–C(15)	121.1(4)
Mo(1)–C(2)	2.324(4)	C(13)–C(14)	1.381(5)	C(2)–C(3)–C(4)	108.8(4)	C(14)–C(15)–C(16)	120.2(4)
Mo(1)–C(3)	2.329(4)	C(14)–C(15)	1.394(5)	C(3)–C(4)–C(5)	107.8(4)	C(15)–C(16)–C(17)	119.3(3)
Mo(1)–C(4)	2.251(3)	C(15)–C(16)	1.375(6)	C(4)–C(5)–C(1)	106.4(3)	C(16)–C(17)–C(18)	120.7(4)
Mo(1)–C(5)	2.125(3)	C(16)–C(17)	1.373(6)	C(5)–C(1)–C(2)	107.9(4)	C(17)–C(18)–C(13)	120.9(4)
Mo(1)–C(6)	2.374(3)	C(17)–C(18)	1.382(5)	C(5)–C(6)–C(7)	119.1(3)	C(18)–C(13)–C(14)	117.7(3)
C(1)–C(2)	1.406(5)	C(18)–C(13)	1.395(5)	C(5)–C(6)–C(13)	116.5(3)	C(19)–C(20)–C(21)	119.2(4)
C(2)–C(3)	1.429(7)	Mo(1)–C(19)	2.252(3)	C(7)–C(6)–C(13)	112.7(3)	C(20)–C(21)–C(22)	121.2(4)
C(3)–C(4)	1.403(6)	Mo(1)–C(20)	2.232(3)	C(7)–C(8)–C(9)	121.1(4)	C(21)–C(22)–C(23)	119.2(4)
C(4)–C(5)	1.462(5)	Mo(1)–C(21)	2.286(4)	C(8)–C(9)–C(10)	120.5(4)	C(22)–C(23)–C(24)	118.8(4)
C(5)–C(1)	1.454(5)	Mo(1)–C(22)	2.223(4)	C(9)–C(10)–C(11)	119.3(4)	C(23)–C(24)–C(19)	121.8(3)
C(5)–C(6)	1.437(4)	Mo(1)–C(23)	2.255(4)	C(10)–C(11)–C(12)	120.1(5)	C(24)–C(19)–C(20)	118.6(4)
C(6)–C(7)	1.507(5)	Mo(1)–C(24)	2.305(3)	C(11)–C(12)–C(7)	121.6(4)		
C(6)–C(13)	1.514(4)	C(19)–C(20)	1.408(6)	C(12)–C(7)–C(8)	117.4(3)		
C(7)–C(8)	1.394(5)	C(20)–C(21)	1.404(6)				
C(8)–C(9)	1.383(6)	C(21)–C(22)	1.408(6)				
C(9)–C(10)	1.376(7)	C(22)–C(23)	1.413(6)				
C(10)–C(11)	1.377(7)	C(23)–C(24)	1.396(5)				
C(11)–C(12)	1.385(6)	C(24)–C(19)	1.422(5)				

Compound (**3**)

W(1)–C(3)	2.34(1)	W(1)–C(21)	2.32(2)	C(3′)–C(3)–C(4)	109.5(8)	C(22′)–C(21)–C(22)	120(2)
W(1)–C(4)	2.28(1)	W(1)–C(22)	2.22(1)	C(3)–C(4)–C(5)	104(1)	C(21)–C(22)–C(23)	122(2)
W(1)–C(5)	2.13(2)	W(1)–C(23)	2.23(2)	C(4)–C(5)–C(4′)	113(2)	C(22)–C(23)–C(24)	119(2)
W(1)–C(6)	2.39(3)	W(1)–C(24)	2.31(2)	C(5)–C(6)–C(7)	122(1)	C(23)–C(24)–C(23′)	117(2)
C(3)–C(3′)	1.45(3)	C(21)–C(22)	1.37(2)	C(7)–C(6)–C(7′)	112(3)	C(25)–C(21)–C(22)	119(1)
C(3)–C(4)	1.47(2)	C(22)–C(23)	1.41(3)				
C(4)–C(5)	1.45(2)	C(23)–C(24)	1.45(2)				
C(5)–C(6)	1.45(3)	C(25)–C(21)	1.50(3)				
C(6)–C(7)	1.49(3)						

Compound (**5**)

W(1)–C(1)	2.26(1)	C(13)–C(14)	1.43(2)	C(1)–C(2)–C(3)	110(1)	C(13)–C(14)–C(15)	120(2)
W(1)–C(2)	2.34(2)	C(14)–C(15)	1.41(3)	C(2)–C(3)–C(4)	108(1)	C(14)–C(15)–C(16)	121(2)
W(1)–C(3)	2.31(2)	C(15)–C(16)	1.37(3)	C(3)–C(4)–C(5)	105(1)	C(15)–C(16)–C(17)	120(2)
W(1)–C(4)	2.24(1)	C(16)–C(17)	1.43(3)	C(4)–C(5)–C(1)	109(1)	C(16)–C(17)–C(18)	119(2)
W(1)–C(5)	2.11(1)	C(17)–C(18)	1.40(2)	C(5)–C(1)–C(2)	108(1)	C(17)–C(18)–C(13)	122(2)
W(1)–C(6)	2.33(1)	C(18)–C(13)	1.37(2)	C(5)–C(6)–C(7)	118(1)	C(18)–C(13)–C(14)	119(2)
C(1)–C(2)	1.36(2)	W(1)–C(19)	2.23(2)	C(5)–C(6)–C(13)	117(1)	C(19)–C(20)–C(21)	120(2)
C(2)–C(3)	1.45(3)	W(1)–C(20)	2.20(2)	C(7)–C(6)–C(13)	112(1)	C(20)–C(21)–C(22)	120(1)
C(3)–C(4)	1.44(2)	W(1)–C(21)	2.30(2)	C(7)–C(8)–C(9)	122(1)	C(21)–C(22)–C(23)	119(1)
C(4)–C(5)	1.46(2)	W(1)–C(22)	2.23(2)	C(8)–C(9)–C(10)	122(2)	C(22)–C(23)–C(24)	119(1)
C(5)–C(1)	1.45(2)	W(1)–C(23)	2.25(1)	C(9)–C(10)–C(11)	119(1)	C(23)–C(24)–C(19)	121(1)
C(5)–C(6)	1.44(2)	W(1)–C(24)	2.30(2)	C(10)–C(11)–C(12)	120(2)	C(24)–C(19)–C(20)	120(1)
C(6)–C(7)	1.51(2)	C(19)–C(20)	1.40(3)	C(11)–C(12)–C(7)	120(2)	C(25)–C(20)–C(21)	118(2)
C(6)–C(13)	1.50(2)	C(20)–C(21)	1.42(2)	C(12)–C(7)–C(8)	117(1)	C(25)–C(20)–C(19)	122(2)
C(7)–C(8)	1.38(2)	C(21)–C(22)	1.46(2)				
C(8)–C(9)	1.36(2)	C(22)–C(23)	1.43(2)				
C(9)–C(10)	1.37(3)	C(23)–C(24)	1.42(2)				
C(10)–C(11)	1.39(3)	C(24)–C(19)	1.43(3)				
C(11)–C(12)	1.42(2)	C(20)–C(25)	1.52(3)				
C(12)–C(7)	1.41(2)						

Compound (**8**)

Ti(1)–C(1)	2.256(8)	C(18)–C(13)	1.385(7)	Ti(1)–C(19)	2.264(9)	C(17)–C(18)–C(13)	120.3(4)
Ti(1)–C(2)	2.392(9)	C(19)–C(20)	1.396(12)	Ti(1)–C(20)	2.400(9)	C(23)–C(19)–C(20)	108.6(8)
Ti(1)–C(3)	2.399(9)	C(20)–C(21)	1.379(12)	Ti(1)–C(21)	2.371(8)	C(19)–C(20)–C(21)	109.0(8)
Ti(1)–C(4)	2.249(9)	C(21)–C(22)	1.408(12)	Ti(1)–C(22)	2.235(9)	C(20)–C(21)–C(22)	108.4(9)
Ti(1)–C(5)	2.121(8)	C(22)–C(23)	1.433(12)	Ti(1)–C(23)	2.124(8)	C(21)–C(22)–C(23)	108.1(8)
Ti(1)–C(6)	2.347(8)	C(23)–C(19)	1.424(11)	Ti(1)–C(24)	2.348(8)	C(22)–C(23)–C(19)	105.8(8)

Table 2 (*continued*)

Compound (**8**)

C(1)–C(2)	1.400(11)	C(23)–C(24)	1.458(11)	C(5)–C(1)–C(2)	108.6(8)	C(19)–C(23)–C(24)	119.9(8)
C(2)–C(3)	1.382(12)	C(24)–C(25)	1.506(10)	C(1)–C(2)–C(3)	108.4(9)	C(22)–C(23)–C(24)	119.8(8)
C(3)–C(4)	1.377(12)	C(24)–C(31)	1.519(10)	C(2)–C(3)–C(4)	109.8(8)	C(23)–C(24)–C(25)	118.7(8)
C(4)–C(5)	1.455(11)	C(25)–C(26)	1.381(7)	C(3)–C(4)–C(5)	108.5(8)	C(23)–C(24)–C(31)	118.1(7)
C(5)–C(1)	1.441(11)	C(26)–C(27)	1.394(7)	C(4)–C(5)–C(1)	104.6(8)	C(25)–C(24)–C(31)	113.8(7)
C(5)–C(6)	1.446(11)	C(27)–C(28)	1.373(7)	C(1)–C(5)–C(6)	121.4(8)	C(23)–C(24)–Ti(1)	62.8(5)
C(6)–C(7)	1.525(10)	C(28)–C(29)	1.375(7)	C(4)–C(5)–C(6)	119.5(8)	C(24)–C(25)–C(26)	121.3(6)
C(6)–C(13)	1.501(10)	C(29)–C(30)	1.393(7)	C(5)–C(6)–C(7)	116.6(7)	C(24)–C(25)–C(30)	119.3(6)
C(7)–C(8)	1.386(7)	C(30)–C(25)	1.388(7)	C(5)–C(6)–C(13)	118.6(7)	C(26)–C(25)–C(30)	119.4(4)
C(8)–C(9)	1.393(7)	C(31)–C(32)	1.383(7)	C(7)–C(6)–C(13)	116.7(7)	C(25)–C(26)–C(27)	120.2(4)
C(9)–C(10)	1.372(7)	C(32)–C(33)	1.392(7)	C(5)–C(6)–Ti(1)	62.8(4)	C(26)–C(27)–C(28)	120.0(4)
C(10)–C(11)	1.371(7)	C(33)–C(34)	1.374(7)	C(6)–C(7)–C(8)	120.3(6)	C(27)–C(28)–C(29)	120.2(4)
C(11)–C(12)	1.392(7)	C(34)–C(35)	1.370(7)	C(6)–C(7)–C(12)	120.6(6)	C(28)–C(29)–C(30)	120.1(4)
C(12)–C(7)	1.387(7)	C(35)–C(36)	1.393(7)	C(8)–C(7)–C(12)	119.2(4)	C(29)–C(30)–C(25)	120.0(4)
C(13)–C(14)	1.392(7)	C(36)–C(31)	1.387(7)	C(7)–C(8)–C(9)	120.2(4)	C(24)–C(31)–C(32)	119.7(6)
C(14)–C(15)	1.397(7)	C(101)–C(102)	1.54(4)	C(8)–C(9)–C(10)	120.2(4)	C(24)–C(31)–C(36)	120.9(6)
C(15)–C(16)	1.369(8)	C(102)–C(103)	1.33(10)	C(9)–C(10)–C(11)	119.9(4)	C(32)–C(31)–C(36)	119.4(4)
C(16)–C(17)	1.375(7)	C(103)–C(104)	1.47(5)	C(10)–C(11)–C(12)	120.5(4)	C(31)–C(32)–C(33)	120.1(4)
C(17)–C(18)	1.400(7)	C(104)–C(105)	1.24(8)	C(11)–C(12)–C(7)	120.0(4)	C(32)–C(33)–C(34)	120.0(4)
				C(6)–C(13)–C(14)	120.0(6)	C(33)–C(34)–C(35)	120.3(4)
				C(6)–C(13)–C(18)	120.8(6)	C(34)–C(35)–C(36)	120.1(4)
				C(14)–C(13)–C(18)	119.2(4)	C(35)–C(36)–C(31)	120.0(4)
				C(13)–C(14)–C(15)	119.9(4)	C(101)–C(102)–C(103)	123(4)
				C(14)–C(15)–C(16)	120.4(4)	C(102)–C(103)–C(104)	116(3)
				C(15)–C(16)–C(17)	120.3(4)	C(103)–C(104)–C(105)	107(4)
				C(16)–C(17)–C(18)	119.9(4)		

with carbon monoxide caused an immediate colour change from green to red. On removal of the carbon monoxide the original green colour was restored. The i.r. spectrum confirmed that the green colour was due to (**8**). The ^{1}H and ^{13}C n.m.r. spectra of the red solution were broadly similar to (**8**) indicating the presence of a compound with a similar C_2 symmetry, (**9**). The arene signals separated into two sets of 2:2:1 signals (doublets and two triplets respectively).

The ^{13}C n.m.r. spectrum shows that the C(5) and C(6) resonances show shifts from the free ligand value of -33.4 and -34.1 p.p.m. respectively. The chemical shift of C(5) is similar to that of (**8**), but the shielding of C(6) in (**9**) is greater than for (**8**). A resonance assignable to a CO ligand molecule was found at 219.4 p.p.m. Attempts to isolate the pure red compound (**9**) were unsuccessful. The material proved to be unstable as a solid except under an atmosphere of carbon monoxide and it was not possible to obtain a mull i.r. spectrum or to carry out microanalysis.

A solution i.r. spectrum of a dilute sample in light petroleum (b.p. 40—60 °C), saturated with carbon monoxide showed a single band at 2 043 cm^{-1} assignable to a co-ordinated stretch. The value is similar to that in [M(η-C_5H_5)$_2$$H_2$(CO)] (M = Hf or Zr).[9] The presence of only one band in the carbonyl region of the i.r. spectrum of the titanium compound suggests that there is only one molecule of carbon monoxide bound to the metal centre. The ^{13}C n.m.r. spectrum of (**9**) also supports the presence of a single carbonyl group since the intensity of the band at 219.4 p.p.m. assignable to the CO is approximately half the intensity of the other quaternary signals.

Structural Studies.—Molecular structures of the compounds (**3**), (**5**), and (**8**) with appropriate numbering schemes are given in Figures 1—3.[10] Table 2 contains selected distances and angles with estimated standard deviations (e.s.d.s) for (**1**)—(**3**), (**5**), and (**8**) [for compounds (**1**) and (**3**) atoms generated by a mirror plane are indicated by adding a prime]. The molecules in all five complexes are separated by van der Waals distances and no unusually close intermolecular contacts are observed.

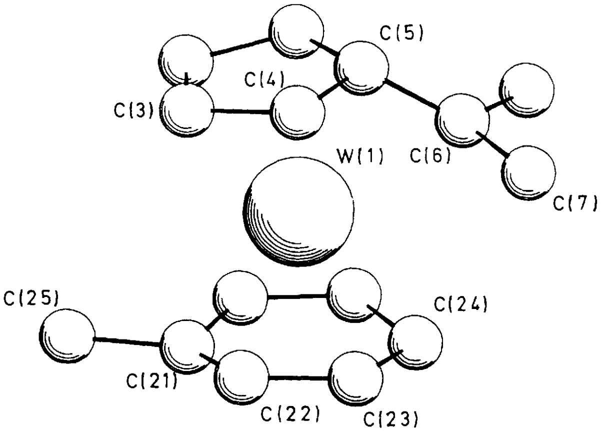


Figure 1. Molecular structure of (**3**). Compound (**1**) is isostructural, with benzene replacing toluene as the arene ligand

For (**2**), (**5**), and (**8**) the asymmetric unit contains one molecule at a general position; for (**1**) and (**3**) the molecules lie on crystallographic mirror planes with the mirror bisecting the fulvene and arene ligands and passing through the heavy atoms. The molecule (**8**) has a non-crystallographic two-fold axis. The central Ti atom is sandwiched between the two η-cyclopentadienyl rings with an interplanar dihedral angle of 27.1°. The view down the pseudo-two-fold axis [Figure 3(*b*)] shows that two phenyl groups from different ligands [C(7)—C(12) and C(25)—C(30)] are close together to give a rather rigid, rotationally hindered molecule. In the mixed-ligand complexes (**1**), (**2**), (**3**), and (**5**) the metal atom is sandwiched between the five-membered ring of the fulvene ligand and the arene. The bonded rings are approximately parallel with interplanar dihedral angles of 5.34 for (**1**), 13.90 for (**2**), 5.86 for (**3**), and 15.95° for (**5**). The metal atom is found directly above the arene ring centroid at 1.772, (**1**), 1.767, (**2**), 1.762, (**3**), and 1.744 Å, (**5**) from the ring. As in other transition metal–arene complexes[11] the arene ligands are found to be significantly non-coplanar being folded about the C(21)–C(24) vector by 7.3, (**1**), 8.6, (**2**), 9.6, (**3**), and 10.1°, (**5**). In the toluene complex (**5**) the folding axis does not include the substituted carbon atom. The phenyl rings of the diphenylfulvene ligands in (**2**), (**5**), and (**8**) are found to be planar within experimental error.

Uncomplexed fulvenes have a coplanar six-atom skeleton with clear alternation of double and single bonds.[12–14] The cyclopentadienyl rings in (**1**), (**2**), (**3**), (**5**), and (**8**) show some distortion from this diene-like structure. For the most reliable structure, (**2**), we observe an equivalencing of the bond lengths C(1)–C(2), C(2)–C(3), and C(3)–C(4) with C(1)–C(5) and C(4)–C(5) being markedly longer. This trend is mirrored in (**8**) but not so clear in (**1**), (**3**), and (**5**). The metal–carbon distances to the five-membered ring in all five structures form an obvious pattern, *i.e.* M–C(2), M–C(3) > M–C(1), M–C(4) > M–C(5). This is reflected in a displacement of the metal–ring perpendicular from the ring centroid towards C(5).

There is substantial metal–C(6) bonding in all five structures resulting in lengthening of the C(5)–C(6) bond in comparison with the values found for fulvene[12] and 6,6-dimethylfulvene[13] (1.348 and 1.343 Å respectively). Relevant distances are given in Table 3. The exocyclic bond C(5)–C(6) is bent from the plane of the η-cyclopentadienyl ring towards the metal centre by

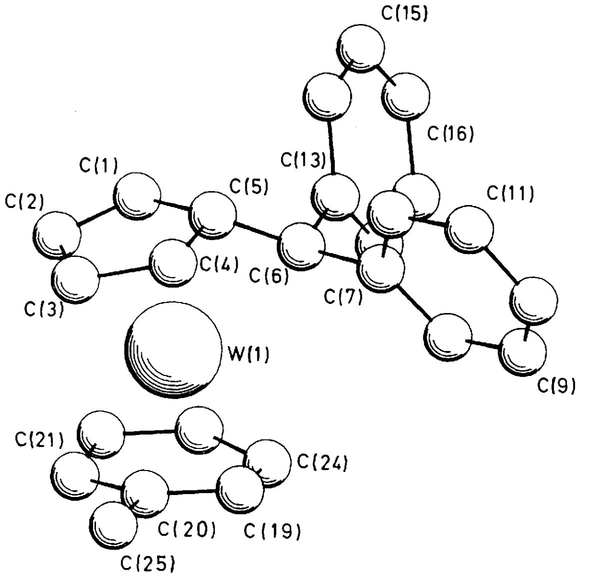


Figure 2. Molecular structure of (**5**). Compound (**2**) is isostructural, with benzene replacing toluene as the arene ligand

Table 3. Comparison between fulvene ligands of (**1**)—(**3**), (**5**), and (**8**)

Compound	(**1**)	(**2**)	(**3**)	(**5**)	(**8**)
θ/°	39	38	37	39	36, 37
M–C(*exo*)/Å	2.31(2)	2.374(3)	2.39(3)	2.33(1)	2.347(8), 2.348(8)
C–C (mean)/Å	1.45	1.431	1.46	1.43	1.411, 1.408
C(5)–C(6)/Å	1.42(2)	1.437(4)	1.45(3)	1.44(2)	1.446(11), 1.458(11)
M–C_5H_5/Å	1.914	1.888	1.898	1.884	1.923, 1.921
M–C_5H_5* (centroid)/Å	0.22	0.20	0.19	0.21	0.29, 0.28

* Distance of M-plane vector from ring centroid ($\triangle x$ in Figure 4).

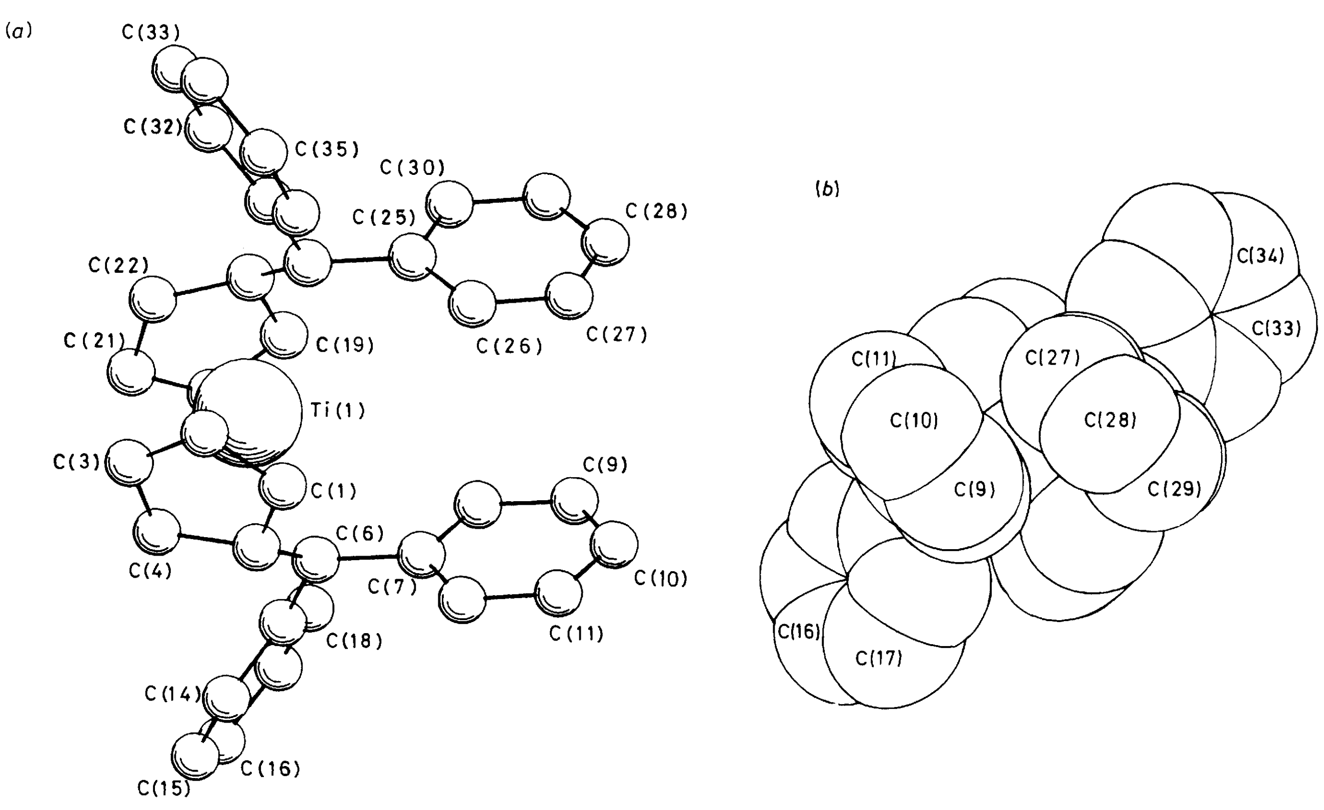
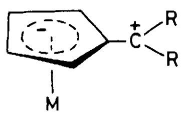


Figure 3. (*a*) Molecular structure of (**8**). (*b*) Space-filling model of (**8**) showing restricted rotation of the phenyl groups

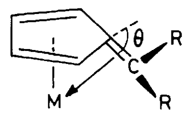
Table 4. Examination of bending angle (θ) and the molecular orbital coefficient for a number of fulvene compounds

Compound	θ/°	*s*-Orbital coefficient on C(6)[a] of ψ_4	C(5)–C(6)/ Å	Ref.
(**10**) $C_5H_4\overline{CSCH_2CH_2S}$	0	0.000 91	1.369(16)	5, *b*
$[Cr(C_5H_4CRR')(CO)_3]$				
(**11**) RR′ = SCH=CHS	6	0.050 98	1.398(7)	5
(**12**) R = H, R′ = NMe_2	10	0.049 56	1.404(10)	5, *c*
(**13**) RR′ = SCH_2CH_2S	19	0.108 63	1.398(6)	5
(**14**) R = R′ = $\overline{CHCH_2CH_2}$	27	0.110 42	1.404(5)	5
(**15**) R = R′ = SMe	28	0.187 10	1.390(6)	5
(**16**) R = R′ = Ph	31	0.198 62	1.446(12)	4, *d*, *e*
(**17**) R = R′ = H	35	0.063 18	1.37(1)	*f*

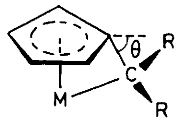
[a] See ref. 18. [b] H. Burzlaff, K. Hartke, and R. Salamon, *Chem. Ber.*, 1970, **103**, 156. [c] B. Lubke and U. Behrens, *J. Organomet. Chem.*, 1978, **149**, 327. [d] V. G. Andrianov, Y. T. Struchkov, V. N. Setkina, V. I. Zdanovich, A. Zhakaeva, and D. N. Kursanov, *J. Chem. Soc., Chem. Commun.*, 1975, 117. [e] V. G. Andrianov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1977, **18**, 318. [f] O. Koch, F. Edelmann, and U. Behrens, *Chem. Ber.*, 1982, **115**, 1313.



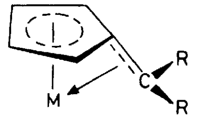
(**A**)



(**B**)



(**C**)



(**D**)

36—39°, with the five-membered rings remaining essentially coplanar.

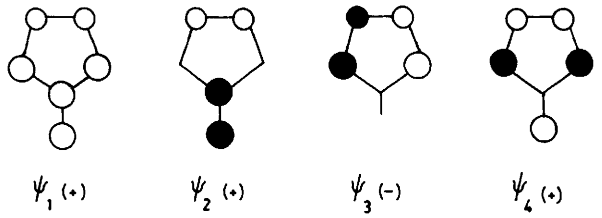
The fulvene ligand as a six-electron donor is characterized by displacement of the metal–ring perpendicular from the centroid of the ring towards C(5) resulting in the spread of metal–ring carbon distances observed for (**1**)—(**3**), (**5**), and (**8**). Three extreme representations, namely (**A**), (**B**), and (**C**), serve as a basis for the discussion of the bonding in fulvene–metal compounds.[4,5] Whether a ligand is of type (**A**), (**B**), or (**C**) is indicated by M–C(6) distance, the angle describing the displacement of C(6) from the C_5-ring plane (defined here as θ), the C(5)–C(6) distance, and, to a lesser extent, the distribution of distances in the C_5 ring.

The bonding tends towards case (**A**) when there are substituents on C(6) of the fulvene which delocalize positive charge. This enhances the polarization of the C(5)–C(6) double bond which, in consequence, is longer. Also the C–C alternation observed in the un-co-ordinated fulvenes[12,13] is less well defined. Examples of case (**A**) are $[Cr(C_5H_4CRR')(CO)_3]$ (R′ R = SCH=CHS;[5] R = H, R′ = NMe_2[5]) in which the Cr–C(6) distance is non-bonding and θ is small. Previous structural studies on a series of fulvene–chromium complexes shows there to be a transition between the extremes represented by (**A**) and (**C**) (Table 4). Data for unco-ordinated $C_5H_4\overline{CSCH_2CH_2S}$ are also given.

Cases (**B**) and (**C**) both require bending of the *exo*-CR_2 group towards the metal but may be distinguished by the pattern of C–C bond lengths, (**B**) requiring alternating long and short bonds as found for the free ligand, whereas (**C**) implies equalizing of bond lengths in the η-cyclopentadienyl ring and a lengthening of the C(5)–C(6) distance. Fulvene ligands whose C(6) substituents are alkyl or related substituents which do not enhance charge delocalization favour structures (**B**) or (**C**). The compound $[Cr(C_5H_4CH_2)(CO)_3]$ (**17**) has θ = 35° and has been ascribed a case (**B**) structure. This bonding description is supported by extended Hückel calculations[15,16] which show that folding of the *exo* bond stabilizes the molecule. Watts[4] has represented the bonding in these chromium compounds slightly differently from (**B**) or (**C**), namely as in (**D**).

The data in Table 3 show that the dip angles (θ) for the dimethylfulvene complexes (**1**) and (**3**) and the diphenylfulvene complexes (**2**) and (**5**) are approximately equal. In principle, the phenyl groups of 6,6-diphenylfulvene could delocalize charge and thus favour a structure of type (**A**). However, steric requirements force the phenyl groups to adopt a 'propeller-like' conformation which is unfavourable for conjugation with C(5)–C(6). Therefore, the diphenylfulvene ligands, like the dimethylfulvene ligands, of the compounds in Table 3 occur as type (**C**) ligands.

The balance between (**B**) and (**C**) will be determined also by the nature of the metal centre to which the fulvene is bound. This can be clarified by consideration of the π orbitals of the fulvene skeleton (below). The orbitals ψ_1, ψ_2, and ψ_3 bear a resemblance to the a_1 and e_1 π levels of the cyclopentadienyl ring, but the bond orders are such that alternation of bond lengths occurs in the free ligand, C(1)–C(2), C(3)–C(4), and C(5)–C(6) having the highest bond orders. It is evident that extensive donation into ψ_4 by the metal will lengthen these three bonds. The orbital ψ_4 has a very high weighting on C(6), and maximum overlap will be achieved between the metal and ψ_4 if C(6) is bent towards the metal. This distortion will of course decrease the overlap between the π orbitals on C(5) and C(6), uncouple C(6) from the π system of the ring, and decrease the weighting of C(6) in ψ_1 and ψ_2, thus increasing the resemblance of these lower orbitals to those of the cyclopentadienyl ligand.



Molecular orbital (m.o.) calculations have been carried out on $[Cr(C_5H_4CH_2)(CO)_3]$[15] and $[Fe(\eta\text{-}C_5H_5)(C_5H_4\text{-}CH_2)]^+$,[17] which point to the prime role of ψ_4 in the distortion of the fulvene group. The calculations of Hoffmann and co-workers[15] predict an energy minimum at a dip angle of 21° for $[Cr(C_5H_4CH_2)(CO)_3]$.

We have carried out a similar extended Hückel molecular orbital calculation on $[Mo(\eta\text{-}C_6H_6)(C_5H_4CH_2)]$ to test

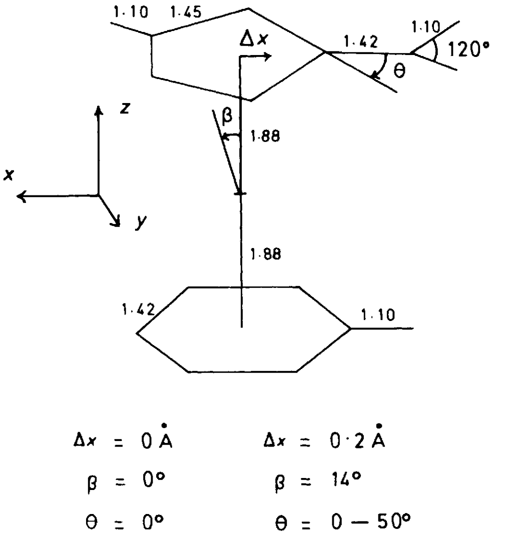


Figure 4. The geometry of [Mo(η-C_6H_6)($C_5H_4CH_2$)] used for the calculations

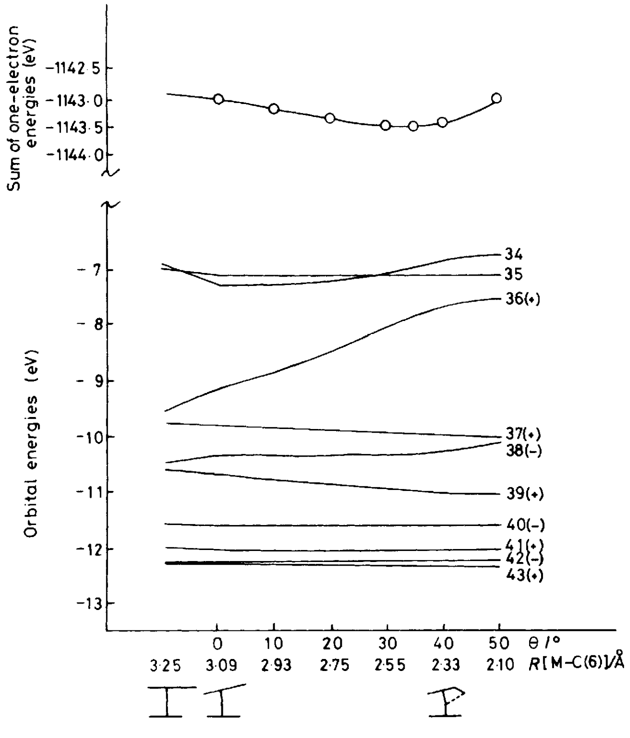


Figure 5. Sum of one electron energies and individual energies as a function of θ

whether the model would predict a greater dip angle (θ) when the fulvene was bonded to the more electron-rich metal centre and to serve as a basis for the interpretation of the photoelectron (p.e.) spectra that we have obtained on (**1**), (**4**), and (**6**).

The extended Hückel m.o. calculation was performed on the geometries indicated in Figure 4. Initially the two rings were parallel, the fulvene ligand and the metal disposed between the two ring centroids. The fulvene ring was then tipped by an angle (β) of 14° and also slipped so that the metal–ring perpendicular approached 0.2 Å closer to C(5). Subsequent calculations were performed with C(6) being displaced towards the metal, with dip angles (θ) between 0 and 50°. A mirror plane is retained throughout the calculation.

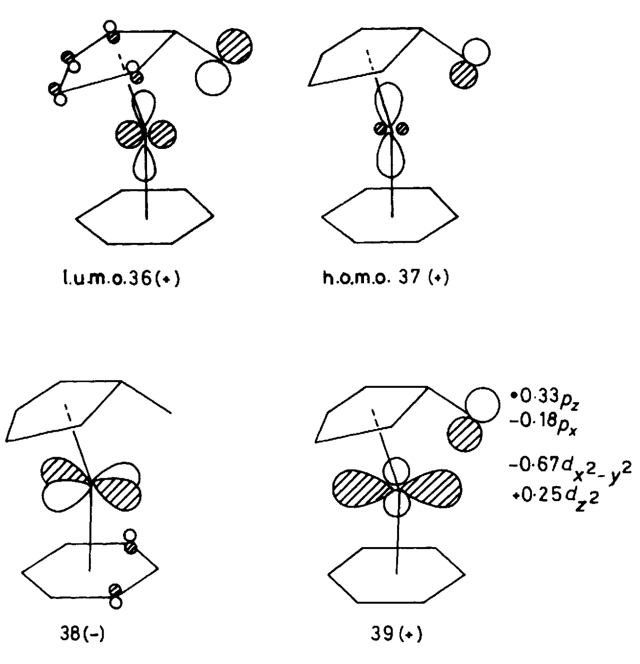


Figure 6. Representations of the orbitals 36—39; h.o.m.o. = highest occupied molecular orbital

The sum of the one-electron energies and the energies of the more interesting orbitals are represented in Figure 5. The minimum of the sum of one-electron energies occurs at a dip angle (θ) of 35°. This is largely due to stabilization of orbitals 37(+) and 39(+).

Figure 6 gives a representation of orbitals 36—39 and Figure 7 a m.o. correlation scheme. They are discussed below in combination with the results from photoelectron spectroscopy.

Further GAUSSIAN80 m.o. calculations[18] on the fulvenes which occur in Table 4 shed light on the bonding by the metal to the fulvenes. The determined structural parameters of the complexed fulvenes were used in the calculations on the fulvene fragments. The results, given in Table 4, indicate a correlation between the *s*-orbital contribution on the exocyclic carbon atom C(6) to the lowest unoccupied molecular orbital (l.u.m.o.) ψ_4 with the magnitude of the bending angle θ. Thus, as we move from (**11**) to (**16**) (Table 4) we observe an increase in σ-bonding between the chromium metal atom and C(6).

Photoelectron Spectra.—The p.e. spectra of [Mo(η-C_6H_6)(σ,η^5-$C_5H_4CMe_2$)] (**1**) and [W(η-C_6H_6)(σ,η^5-$C_5H_4CMe_2$)] (**4**) are given in Figure 8. That of [W(η-C_6H_6)(σ,η^5-C_5H_4-CPh_2)] (**6**) had a similar appearance in the low-energy region (5—8 eV) but with additional structure in the region 8—11 eV, presumably due to ionizations from the upper π orbitals of the phenyl ring. As no He-II spectrum was obtained for this compound the ensuing assignment is discussed in terms of the two dimethylfulvene complexes and the assignment of (**6**) given in Table 5 is by analogy.

Assignment. Assignment of the spectra is straightforward and may be carried out by comparison with the results of the m.o. calculation and the p.e. spectra of Mo and W sandwich compounds such as [Mo(η-C_6H_6)$_2$],[19] [W(η-C_6H_6)$_2$],[20] and [Mo(η-C_5H_5)(η-C_6H_6)].[20]

In the region above 11 eV, ionizations occur from the σ orbitals and the lowest π orbital of each ring. Thus for these 18-electron compounds we expect seven ionizations below 11

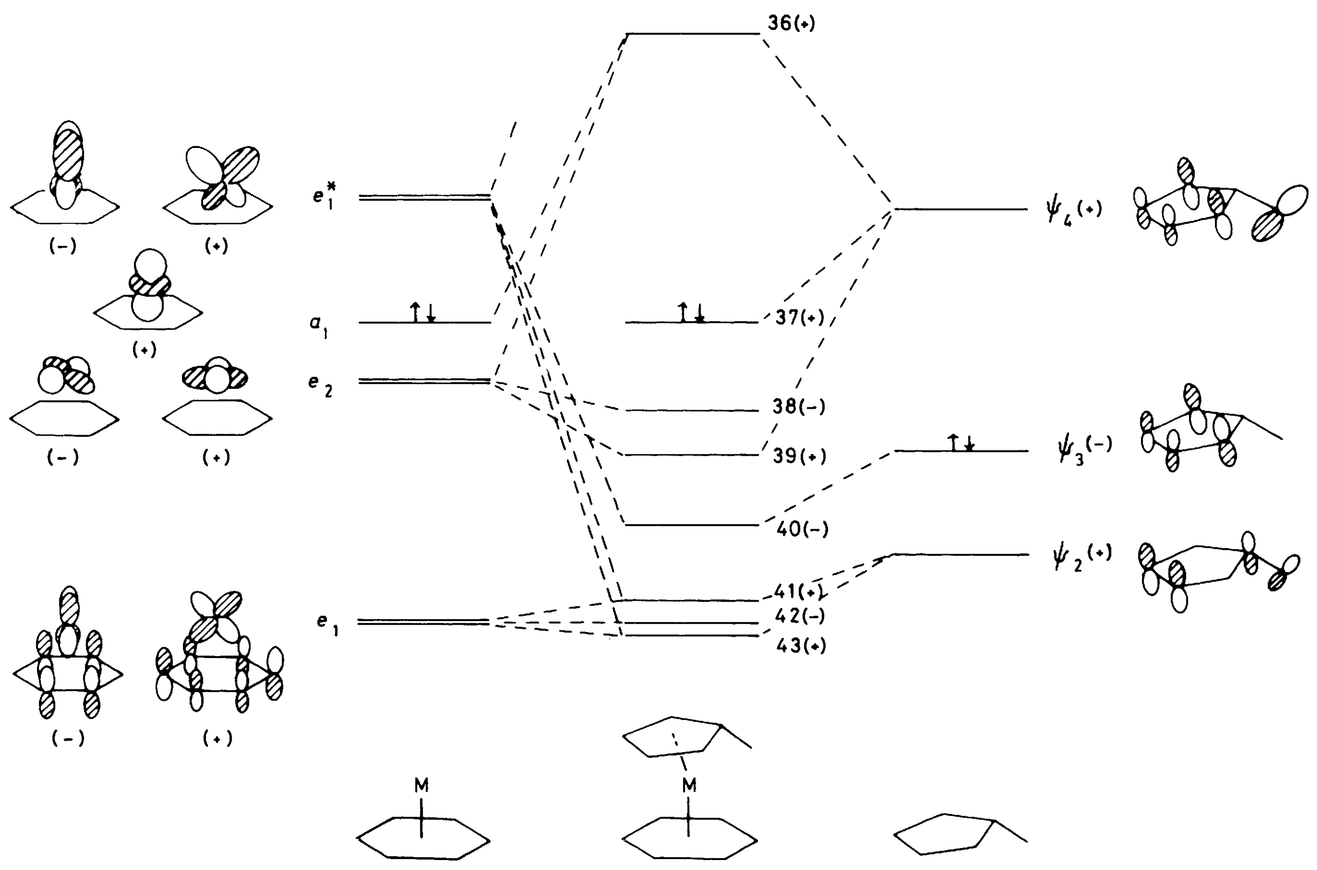


Figure 7. M.o. correlation scheme for [Mo(η-C_6H_6)($C_5H_4CH_2$)]

Table 5. Ionization energies (eV) and band intensities for (**1**), (**4**), and (**6**)[a]

(*i*) Ionization energies

	Orbital					
Compound	37(+)	38(−)	39(+)	40(−)	41(+)	42(−), 43(+)
(**1**)	6.00 (a)	6.56 (b)	7.45 (c)	8.79 (d)	9.31 (e)	9.92 (f)
(**4**)	6.05 (a)	6.65 (b)	7.64 (c)	8.86 (d)	9.40 (e)	10.01 (f)
(**6**)	6.16	6.65	7.61	9.07		10.01

(*ii*) Band intensities

		Band					
Compound	Spectrum	(a)	(b)	(c)	(d)	(e)	(f)
(**1**)	He-I	1.9	1.6	1.9	2.3	2.8	3.4
(**1**)	He-II	2.0	2.1	2.0	1.9	2.4	3.5
(**1**)	He-II/He-I	1.1	1.3	1.1	0.8	0.9	1.0
(**4**)	He-I[b]	1.8	1.9	2.1	2.1	2.8	3.4

[a] The assignments given are related to the results of the calculations, the nature of the associated orbitals being given in Figure 6 and discussed in the section on bonding. [b] The intensity pattern of the He-II spectrum appeared to be closely similar to that of compound (**1**). However, the signal to noise ratio of the He-II spectrum of (**4**) was such that quantitative estimation of the areas was unreliable.

eV. Six are clearly observed, (a)—(f), and from intensity data it is reasonable to suggest that band (f) comprises two ionizations. Indeed the smoothed spectra suggest a shoulder on the high-energy side of this band. The ionization energies (i.e.s) of bands (f) (Mo, 9.92; W, 10.01 eV) are similar to those of the e_{1g} ionizations of the bis(benzene) analogues (Mo, 10.15; W, 10.3 eV) and a similar assignment to orbitals 42(−) and 43(+) is suggested by the m.o. calculation. The calculation gives 42(−) and 43(+) as having contributions from d_{yz} and d_{xz} respectively. Orbital 43(+) has contributions from $\psi_2(+)$ of the fulvene ring and the $e_1(+)$ orbital of benzene; orbital 42(−) on the other hand has very little fulvene contribution but a major weighting of the $e_1(-)$ benzene orbital. The He-II/He-I intensity ratio also suggests significant Mo *d* content.

Band (e) has an ionization energy (Mo, 9.31; W, 9.40 eV) close to that of the e_{1u} ionization of [M(η-C_6H_6)$_2$] (M = Mo, 9.47; M = W, 9.58 eV) and also to that of ψ_2 of fulvene (9.54 eV). Orbital 41(+) has negligible *d* content but a small metal p_x contribution and is largely an in-phase combination of fulvene $\psi_2(+)$ and benzene $e_1(+)$. Band (d) (Mo, 8.79; W, 8.86 eV) occurs in the same region as the fulvene $\psi_3(-)$ ionization (8.55 eV), and may be assigned to orbital 40(−) which is largely $\psi_3(-)$ in character. Of the bands (a)—(f), (d) and (e) have the smallest He-II/He-I intensity ratios consistent with the low *d* character of 41(+) and 40(−) predicted by the calculation.

Bands (a), (b), and (c) are reasonably assigned to orbitals 37(+), 38(−), and 39(+) respectively. Orbital 37(+) has as its sandwich parent the a_{1g} orbital which is largely d_{z^2} in character and gives rise to a very sharp low ionization energy p.e. band (Mo, 5.52; W, 5.40 eV). Band (a), although the narrowest of the *d* bands of the fulvene complexes, is less sharp than the a_{1g} band of [M(η-C_6H_6)$_2$] and has a higher ionization energy (Mo, 6.00; W, 6.05 eV). The calculation indicates that the major contributor to 37(+) is the d_{z^2} orbital (mixed with some $d_{x^2-y^2}$) and there is a small bonding interaction with the *p* orbital on the exocyclic carbon, C^6.

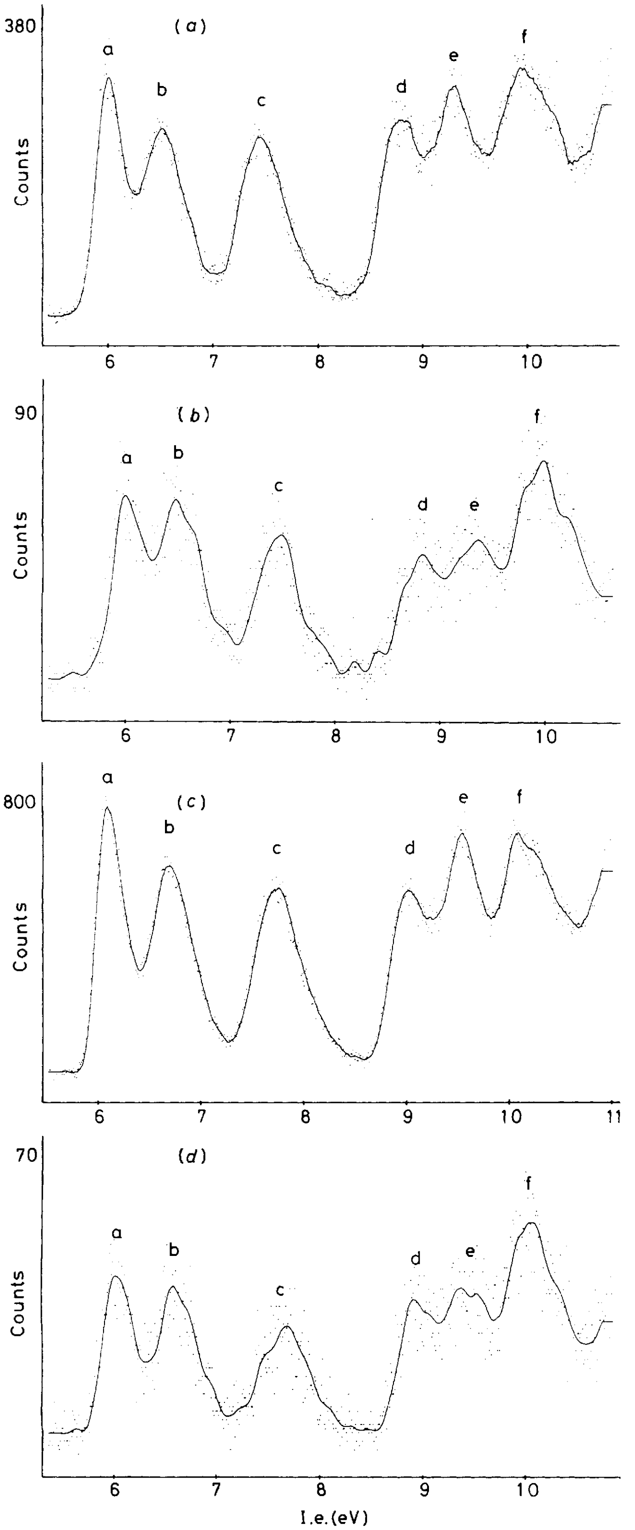


Figure 8. Photoelectron spectra of (**1**) and (**4**): (*a*) He-I of (**1**), (*b*) He-II of (**1**), (*c*) He-I of (**4**), (*d*) He-II of (**4**)

Band (b) (Mo, 6.56; W, 6.65 eV) lies close in energy to the $^2E_2$ band of [M(η-C_6H_6)$_2$] (Mo, 6.59; W, 6.56, 6.99) ($^2E_{5/2}$ and $^2E_{3/2}$ spin orbit states). Orbital 38($-$) is very similar to that of the parent sandwich, being mainly d_{xy} in character.

Band (c) however is considerably displaced from the e_2 ionizations of [M(η-C_6H_6)$_2$] occurring at 7.45 eV (Mo) and 7.64 eV (W). This indicates that the $d_{x^2-y^2}$ orbital has become involved in substantial bonding in the fulvene complex. This is borne out by the calculation. Orbital 39(+) to which band (c) is assigned consists of a metal hybrid largely $d_{x^2-y^2}$ in character, mixed with a small amount of d_{z^2} which improves its directional properties, for bonding to the exocyclic carbon of the ring. The ligand contribution is primarily from $\psi^4(+)$ the fulvene l.u.m.o.

Table 6. Carbon-13 n.m.r. shift data (δ/p.p.m.)

Compound	θ/°	^{13}C shift* C(5)	^{13}C shift* C(6)
[Fe(η-C_5H_5)($C_5H_4CPh_2$)]$^+$	21	-50	$+18$
[Cr($C_5H_4CPh_2$)(CO)$_3$]	31	-37	-26
[Mo(η-C_6H_6)(σ,η^5-$C_5H_4CPh_2$)]	38	-49	-49
[Ti(σ,η^5-$C_5H_4CPh_2$)$_2$]	36, 37	-32.2	-19.9

* Shift from C(5) and C(6) of free $C_5H_4CPh_2$, at 144.0 and 152.0 p.p.m.

Carbon-13 *N.M.R. data.*—Comparison of the ^{13}C n.m.r. spectra of (**2**) and (**8**) with that of 6,6-diphenylfulvene[21] shows that there is a large high-field shift of the quaternary carbon atoms C(5) and C(6) of *e.g.* in (**8**) of -32.2 and -19.9 p.p.m. relative to the free ligand, respectively, see Table 6.

It has been proposed for other diphenylfulvene metal complexes that the ^{13}C chemical shift is closely related to the electron density at the carbon atom concerned.[4,17]

In the case of the iron compound [Fe(η-C_5H_5)(C_5H_4-CH_2)]$^+$, it seems that there is a large degree of localization of the positive charge at the exocyclic carbon atom. The shifts to high field in the chromium, titanium, and molybdenum complexes are indicative of enhanced electron densities at both the carbon atoms C(5) and C(6).

Conclusions

The p.e. spectral studies, the ^{13}C n.m.r. data, and the m.o. calculations all give a consistent picture of the bonding in these fulvene complexes. The degree of bending of the fulvene ligand is seen to be primarily a function of the electron richness of the metal centre. The metal arene system is an excellent electron donor and the fulvene enhances its electron-acceptor abilities by bending so that C(6) becomes as close to the metal as the other five carbons. Donation occurs from the metal d_{z^2} and $d_{x^2-y^2}$ orbitals (as defined by the co-ordinate system in Figure 4). A measure of the degree of stabilization of these orbitals can be obtained by a comparison of the associated p.e. bands in [M(η-C_6H_6)($C_5H_4CH_2$)] and [M(η-C_6H_6)$_2$]. This i.e. of the 'd_{z^2}' type orbitals increases by *ca.* 0.5 eV while that of the '$d_{x^2-y^2}$' type orbital increases by *ca.* 1 eV (1 eV $\equiv$ 98 kJ mol^{-1}). The substantial metal-to-fulvene donation found in these systems means that the closest formal extreme description of the bonding is case (C), hence a σ,η^5 classification of the fulvene ligand. However, as the exocyclic carbon is not ideally placed for interaction with the available *d* orbitals, the M–C(6) σ bond may be expected to be rather weaker than a typical M–CR_3 bond.

Further bonding is prevented by an unfavourable interaction between the substituents on the exocyclic carbon and the filled d_{xy} orbital 38($-$). The folding of the arene ring is predicted by the calculations, the two arene carbon atoms lying in the mirror plane have smaller Mo–C overlap populations than the other four. This is because the (+) fulvene orbitals ψ_2 and ψ_4 compete more effectively with the arene orbitals for binding to molyb-

Table 7. Crystal data and experimental conditions for (**1**), (**2**), (**3**), (**5**), and (**8**)

Compound	(**1**)	(**2**)	(**3**)	(**5**)	(**8**)
Formula	$C_{14}H_{16}Mo$	$C_{24}H_{20}Mo$	$C_{15}H_{18}W$	$C_{25}H_{22}W$	$C_{36}H_{28}Ti\cdot0.33\,C_5H_4$
M	280.2	404.3	382.1	506.3	532.6
System	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Cubic
a/Å	10.342(5)	9.368(5)	10.556(3)	10.670(9)	25.919(2)
b/Å	10.725(5)	18.189(6)	10.757(3)	16.321(5)	
c/Å	10.997(5)	10.598(3)	10.888(5)	11.461(7)	
β/°		97.71(3)		111.79(7)	
U/Å^3	1 219.7	1 789.5	1 236.3	1 853.2	17 412.2
Space group	*Pnam*	$P2_1/n$	*Pnam*	$P2_1n$	*Pa*3
Z	4	4	4	4	24
D_c/Mg m^{-3}	1.53	1.50	2.05	1.81	1.22
F(000)	568	824	728	984	6 720
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Cu-K_α
λ/Å	0.710 69	0.710 69	0.710 69	0.710 69	1.5418
μ/cm^{-1}	10.21	7.25	98.49	65.98	27.60
Crystal size/mm	0.2 × 0.1 × 0.06	0.35 × 0.3 × 0.13	0.6 × 0.4 × 0.15	0.7 × 0.5 × 0.2	0.45 × 0.45 × 0.375
$\theta_{max.}$/°	27	27	30	25	50
Scan	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Scan angle/°	0.75 + 0.35tanθ	0.75 + 0.35tanθ	1.2 + 0.35tanθ	1.2 + 0.35tanθ	0.75 + 0.14tanθ
R_{merge}	8.09	2.54	6.10	6.59	5.37
$N_{obs.}$	1 079	2 751	1 213	2 505	1 602
No. of parameters	76	308	83	237	219
R,*R*′ *	0.0940, 0.1003	0.0297, 0.0373	0.0639, 0.0885	0.0593, 0.0721	0.0625, 0.0754
Weighting scheme parameters	Unit weights	160.19, 221.68 65.52	13 072.7, 17 422.4 4 357.6, 2.30, −0.17	96.97, 130.70, 47.05	98.45, 130.30 41.06

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

denum than the (−) fulvene orbitals ψ_3 and ψ_5. For example, as discussed above, 42(−) has very little fulvene contribution, but significant arene $e_1(-)$ and molybdenum *d* content, whereas 40(−) is largely ψ_3 in character. The fulvene $\psi_2(+)$, on the other hand, makes a major contribution to 43(+) so that the arene, $e_1(+)$, contribution to this orbital is less than is found for 42(−).

The carbonyl ligand in the d^0 compound (**9**) has a lowered stretching frequency. In the absence of *d* electrons there can be no formal back-donation to the antibonding orbitals of the carbonyl group, and apparently no synergic stabilization. Bercaw[9] has proposed that the observed weakening of the C≡O bond in the compounds $[M(\eta\text{-}C_5Me_5)_2H_2(CO)]$ (M = Zr or Hf) as witnessed by the change in stretching frequency, must reflect a donation of electron density from the metal–hydride bonds. A similar scheme for carbonylbis(6,6-diphenylfulvene)-titanium would take the electron density from the metal–carbon σ bonds, and donate it to the antibonding orbital of the carbon monoxide.

Finally, we note that the compound (**1**) is readily prepared in high yield from bis(η-benzene)molybdenum and that it is a useful precursor to an extensive chemistry of $Mo(\eta\text{-}C_5H_4Pr^i)$ derivatives.[6]

Experimental

All manipulations of solvents and air-sensitive materials were carried out with rigorous exclusion of water and oxygen. Argon was purified by passage through 4 Å molecular sieves and Fluka BTS catalyst. Glass reaction vessels were heated to *ca.* 300 °C under vacuum prior to use. Hydrocarbon solvents and tetrahydrofuran (thf) were collected after prolonged refluxing over molten Na, K, or an alloy of the two, and dichloromethane was dried over activated 4 Å molecular sieves. Solvents for n.m.r. studies were stored over Na/K alloy or molecular sieves, where appropriate. Proton n.m.r. spectra were determined on MX-60, 300-MHz Bruker 300, or 400-MHz Bruker 400 instruments. Carbon-13 n.m.r. spectra were determined using Bruker 300 (75.4 MHz) or AM 250 (62.8 MHz) instruments. Mass spectra were measured on a MSS 90 instrument. Infrared spectra were determined on a Pye-Unicam SP 2000 spectrometer. The ligands $C_5H_4CMe_2$ and $C_5H_4CPh_2$ were prepared by the literature methods.[22,23]

η-Benzene(σ,1′—5′-η-cyclopentadienyldimethylmethanido)-molybdenum, (**1**).—A solution and partial suspension of $[Mo(\eta\text{-}C_6H_6)_2]$ (12.7 g, 50.4 mmol) in toluene (100 cm^3) was treated with $C_5H_4CMe_2$ (19 g, 179 mmol). The reaction mixture was stirred at 50 °C for 2 d and the initially green solution became an intense deep purple. The solvent and excess ligand were removed under reduced pressure giving an oily purple solid and transparent crystals. The mixture was extracted with methanol (2 × 150 cm^3). The solution was concentrated under reduced pressure and the concentrate was cooled to −20 °C for 12 h. Purple needles separated which were collected and washed with cold methanol (2 × 20 cm^3); yield 13.9 g (98%).

η-Benzene(σ,1′—5′-η-cyclopentadienyldiphenylmethanido)-molybdenum, (**2**).—A solution of $[Mo(\eta\text{-}C_6H_6)_2]$ (1.0 g, 4.0 mmol) was treated with excess $C_5H_4CPh_2$ (2.0 g, 8.7 mmol). The reaction mixture was stirred at 100 °C overnight giving a purple solution. The solvent was removed under reduced pressure and the excess ligand extracted with cold (0 °C) light petroleum (40—60 °C). The residue was recrystallized from toluene–light petroleum (b.p. 100—120 °C; 1:3) giving a red crystalline solid; yield 1.5 g (94%).

(σ,1′—5′-η-Cyclopentadienyldimethylmethanido)(η-toluene)-tungsten, (**3**).—The compound $[W(\eta\text{-}C_6H_6)_2]$ (1 g, 2.9 mmol) in toluene (50 cm^3) was treated with $C_5H_4CMe_2$ (2 cm^3). The mixture was heated to 85 °C for 4—5 d. The solvent was removed from the resulting deep red solution under reduced

pressure giving a red oil. The residue was extracted with light petroleum (b.p. 30—40 °C) and cooling the extract to −20 °C separated red crystals; yield 0.9 g (*ca.* 80%).

η-Benzene(σ,1′—5′-η-*cyclopentadienyldimethylmethanido*)-*tungsten*, (**4**).—The compound [W(η-C_6H_6)$_2$] (1 g, 2.9 mmol) in benzene (60 cm^3) was treated with $C_5H_4CMe_2$ (2 cm^3). The mixture was heated to 80 °C for 4 d. The solvent was removed from the resulting deep red solution under reduced pressure giving a red oil. This was purified from the dimethylfulvene dimer by short-path distillation onto a liquid-dinitrogen cooled probe. The residue was extracted with light petroleum (b.p. 30—40 °C) and cooling to −20 °C separated red crystals; yield *ca.* 40%. Final purification of a small quantity was achieved by fractional sublimation.

(σ,1′—5′-η-*Cyclopentadienyldiphenylmethanido*)(η-*toluene*)-*tungsten*, (**5**).—The compound [W(η-C_6H_5Me)$_2$] (2 g, 5.4 mmol) in toluene (100 cm^3) was treated with excess $C_5H_4CPh_2$ (2 g) and the solution was heated to 100 °C for 5 d, giving a red-orange solution. The solvent was removed under reduced pressure and the residual solid was washed with cold (0 °C) light petroleum (b.p. 40—60 °C) giving an orange solution of the excess fulvene. This was repeated until the washings were pale pink. The remainder of the solid was extracted with hot (100 °C) light petroleum (b.p. 100—120 °C), giving a red solution, until the washings became colourless. The red light petroleum solution was reduced to half its initial volume and cooled to −20 °C giving red crystals; yield 2.2 g (*ca.* 80%). The above reaction was carried out under the same conditions except that mesitylene replaced toluene as the solvent. Fractional crystallization of the light petroleum (b.p. 40—60 °C) extract gave (**7**), (**5**), and [W(η-$C_6H_3Me_3$-1,3,5)$_2$] in small yields (*ca.* 5—15%).

Compound (**6**) was prepared in the same manner as (**5**) starting with [W(η-C_6H_6)$_2$] in benzene.

Bis(σ,1′—5′-η-*cyclopentadienyldiphenylmethanido*)*titanium*, (**8**).—A mixture of 6,6-diphenylfulvene (2.0 g) and bis(η-toluene)titanium (1.0 g, 4.3 mmol) was made from the solids. Toluene was added and a dark green colour was rapidly formed. The solvent was removed to give a green oil which was extracted with light petroleum (b.p. 40—60 °C; 50 cm^3) and the solution filtered and cooled to −80 °C. A mass of fine very dark green crystals was formed. These were recrystallized from a mixture of light petroleum (b.p. 40—60 °C) and toluene as large cubic crystals; yield >70%.

Reaction of Bis(σ,1′—5′-η-*cyclopentadienyldiphenylmethanido*)*titanium with Carbon Monoxide: Preparation of Compound* (**9**).—A solution of [Ti(σ,η^5-$C_5H_4CPh_2$)$_2$] (**8**) in a mixture of toluene and light petroleum (b.p. 40—60 °C) was treated with pure carbon monoxide (1 atm). The initially dark green solution became an intense dark red. This solution showed no further change when kept under carbon monoxide for at least 24 h. Removal of the carbon monoxide and some solvent under reduced pressure restored the original green colour. The i.r. spectrum of the recovered green compound showed it to be unchanged (**8**). Proton and ^{13}C n.m.r. samples were prepared in all-glass devices with the starting material, first dissolved in deuteriobenzene, and the solution then saturated with carbon monoxide. The solution was frozen and the vessel was evacuated before sealing. The i.r. spectrum was obtained using matched cells and a solution of the starting material, in light petroleum (b.p. 60—80 °C), saturated by an atmosphere of carbon monoxide.

Crystal Structure Determinations.—Crystals of compounds (**1**)—(**3**), (**5**), and (**8**) were mounted in Lindemann glass capillaries under an inert atmosphere and examined by Weissenberg methods. They were mounted on a CAD4-F diffractometer for data collection. Crystal data and experimental conditions are given in Table 7. Cell dimensions were obtained from the positions of up to 25 carefully centred reflections. During data collection three intensity control reflections were measured every hour and three orientation controls were checked after each 200 measurements. There was no significant variation in the magnitude of the intensity controls throughout each data collection.

Lorentz and polarization corrections were applied [and also for (**1**), (**3**), (**5**), and (**8**) an empirical absorption correction[24]], equivalent reflections were merged and only those for which $I > 3\sigma(I)$ were included in refinement [where $\sigma(I)$ is the standard deviation based on counting statistics]. The heavy-atom method was used to solve the structures of (**1**)—(**3**) and (**5**), while direct methods[25] were required for (**8**).

Refinement of (**1**) and (**3**) was by full-matrix least-squares methods and for (**2**), (**5**), and (**8**) by a large-block approximation to the normal matrix. For (**3**) systematic absences were consistent with the centrosymmetric space group *Pnam* or its non-centrosymmetric equivalent *Pna*2$_1$, though refinement showed *Pnam* to be more probable. Compound (**1**) is isomorphous with (**3**); therefore when there was difficulty in locating the carbon atoms of the benzene ring for (**1**) in a difference Fourier synthesis and a torus of electron density was observed, the co-ordinations of the same moiety in (**3**) were used. The structure of (**1**) is disordered and because no satisfactory model was found for this disorder it was necessary to use extensive dimensional restraints[26] during refinement and the final difference map for (**1**) contains a number of peaks around molybdenum and the benzene ring. Compound (**8**) crystallizes with solvent which was revealed in difference Fourier syntheses as a cylinder of electron density along the three-fold axes of this cubic space group. It was possible to visualize a five-carbon-atom fragment from generalized difference electron-density sections of this region and refinement of this solvent model gave an improved fit to the electron-density distribution. The presence of solvent was also suggested by the presence of solvent bands in the ^1H n.m.r. spectrum of samples derived from large crystals. For this compound it was necessary to impose weak restraints on the phenyl rings and to refine these carbon atoms isotropically.

It was not possible to locate hydrogen atoms for (**1**), (**3**), or (**5**). For (**2**) all hydrogen atoms were located and refined isotropically. For (**8**) hydrogen atoms were located for the 6,6-diphenylfulvene ligands but included in calculated positions which were adjusted between cycles of refinement. Corrections for anomalous dispersion and isotropic extinction[27] were made in the final cycles of refinement for (**2**), (**3**), (**5**), and (**8**) and Chebyshev weighting schemes[28] were used with parameters as in Table 7. Anisotropic refinement involved all non-hydrogen atoms for (**1**), (**2**), (**3**), and (**5**) but only the cyclopentadienyl and exocyclic carbon atoms for (**8**). The final positional parameters for all compounds are recorded in Table 8. All calculations were performed on the VAX11/750 in the Chemical Crystallography Laboratory and on the University ICI 2980 computer using the Oxford CRYSTALS system,[29] except where stated. Atomic scattering factors and anomalous dispersion coefficients were taken from International Tables.[30]

Photoelectron Spectra.—The p.e. spectra were recorded on a PES Laboratories photoelectron spectrometer, model 0078. Data were collected both on an *X*–*Y* recorder, and using a Research Machines 380Z microprocessor with multiple scanning. Spectra were calibrated with ionization bands from Xe and N_2 (ionized by He-I) and He (ionized by He-II). Band intensities were estimated using a curve-fitting programme and

Table 8. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound (**1**)							
Mo(1)	0.110 1(2)	0.021 3(1)	0.2500	C(7)	0.402 1(17)	0.036 9(14)	0.363 9(16)
C(3)	0.089 9(14)	0.230 7(10)	0.317 0(9)	C(21)	−0.105 7(20)	−0.048 2(21)	0.2500
C(4)	0.210 2(12)	0.175 4(10)	0.357 8(12)	C(22)	−0.042 6(18)	−0.077 5(15)	0.361 8(11)
C(5)	0.278 5(15)	0.134 8(15)	0.2500	C(23)	0.076 4(20)	−0.151 2(14)	0.362 7(11)
C(6)	0.332 9(21)	0.013 4(15)	0.2500	C(24)	0.131 4(24)	−0.193 0(16)	0.2500
Compound (**2**)							
Mo(1)	0.180 8(1)	0.134 8(1)	−0.018 2(1)	C(23)	0.380 4(4)	0.196 7(2)	0.064 0(4)
C(1)	0.031 0(4)	0.202 5(2)	−0.154 1(3)	C(24)	0.340 4(3)	0.154 8(2)	0.163 8(3)
C(2)	0.077 3(5)	0.145 9(3)	−0.229 2(4)	H(1)	0.041(4)	0.251(2)	−0.162(4)
C(3)	0.033 2(5)	0.076 9(2)	−0.183 0(4)	H(2)	0.131(5)	0.148(3)	−0.293(5)
C(4)	−0.041 6(4)	0.089 7(2)	−0.078 9(4)	H(3)	0.046(5)	0.032(3)	−0.219(4)
C(5)	−0.037 9(3)	0.168 8(2)	−0.053 5(3)	H(4)	−0.082(3)	0.060(2)	−0.029(3)
C(6)	−0.004 2(3)	0.195 1(2)	0.074 9(3)	H(8)	−0.269(4)	0.144(2)	0.073(4)
C(7)	−0.069 0(3)	0.156 8(2)	0.179 9(3)	H(9)	−0.372(6)	0.093(3)	0.244(5)
C(8)	−0.212 5(4)	0.134 4(2)	0.158 8(4)	H(10)	−0.238(5)	0.073(2)	0.444(4)
C(9)	−0.277 8(5)	0.102 7(3)	0.255 0(5)	H(11)	0.000(5)	0.108(3)	0.473(4)
C(10)	−0.201 7(5)	0.092 1(3)	0.373 9(5)	H(12)	0.098(5)	0.161(3)	0.316(4)
C(11)	−0.059 8(6)	0.113 7(3)	0.396 4(4)	H(14)	−0.184(4)	0.298(2)	−0.010(4)
C(12)	0.005 0(4)	0.146 1(2)	0.300 3(4)	H(15)	−0.186(4)	0.424(2)	0.005(4)
C(13)	0.003 9(3)	0.277 6(2)	0.092 3(3)	H(16)	0.008(5)	0.485(3)	0.129(5)
C(14)	−0.106 8(4)	0.320 6(2)	0.033 1(4)	H(17)	0.194(4)	0.416(2)	0.233(4)
C(15)	−0.106 0(5)	0.396 7(2)	0.048 5(4)	H(18)	0.184(4)	0.285(2)	0.214(3)
C(16)	0.005 9(5)	0.430 5(2)	0.123 8(4)	H(19)	0.267(4)	0.054(2)	0.209(4)
C(17)	0.115 7(5)	0.388 4(2)	0.185 0(4)	H(20)	0.321(5)	−0.006(3)	0.026(4)
C(18)	0.115 1(4)	0.312 8(2)	0.170 4(4)	H(21)	0.405(4)	0.062(2)	−0.138(4)
C(19)	0.308 7(4)	0.078 6(2)	0.149 6(4)	H(22)	0.437(4)	0.191(3)	−0.114(4)
C(20)	0.335 0(4)	0.043 2(2)	0.036 8(4)	H(23)	0.394(4)	0.248(2)	0.072(4)
C(21)	0.393 6(4)	0.083 7(2)	−0.056 6(4)	H(24)	0.324(4)	0.176(2)	0.241(3)
C(22)	0.405 4(4)	0.160 8(2)	−0.049 1(4)				
Compound (**3**)							
W(1)	0.116 6(1)	0.014 8(1)	0.2500	C(21)	−0.086 0(18)	−0.069 3(19)	0.2500
C(3)	0.086 0(15)	0.219 6(13)	0.316 4(15)	C(22)	−0.025 3(15)	−0.090 5(15)	0.358 8(14)
C(4)	0.206 9(15)	0.170 5(12)	0.361 3(14)	C(23)	0.090 7(18)	−0.156 0(18)	0.364 1(17)
C(5)	0.274 9(17)	0.137 2(16)	0.2500	C(24)	0.148 6(29)	−0.197 4(19)	0.2500
C(6)	0.342 9(25)	0.020 1(19)	0.2500	C(25)	−0.200 8(24)	0.012 5(20)	0.2500
C(7)	0.402 0(16)	−0.030 5(24)	0.363 5(26)				
Compound (**5**)							
W(1)	−0.089 0(1)	−0.129 4(1)	0.132 8(1)	C(13)	−0.150 3(15)	0.061 1(8)	0.201 9(13)
C(1)	−0.166 2(16)	−0.034 4(8)	−0.020 4(14)	C(14)	−0.212 4(15)	0.1258 (11)	0.116 2(15)
C(2)	−0.159 0(15)	−0.104 2(9)	−0.083 1(15)	C(15)	−0.158 4(20)	0.205 5(11)	0.141 1(17)
C(3)	−0.242 9(19)	−0.167 6(11)	−0.061 8(15)	C(16)	−0.052 0(22)	0.222 3(11)	0.250 0(21)
C(4)	−0.310 3(14)	−0.133 4(10)	0.015 3(14)	C(17)	0.009 4(21)	0.157 9(10)	0.337 7(20)
C(5)	−0.254 9(13)	−0.050 9(9)	0.047 2(13)	C(18)	−0.042 2(17)	0.078 2(11)	0.309 7(15)
C(6)	−0.211 4(14)	−0.023 0(9)	0.175 0(14)	C(19)	−0.039 9(19)	−0.209 1(13)	0.301 4(17)
C(7)	−0.301 0(15)	−0.040 6(9)	0.247 7(14)	C(20)	−0.039 5(18)	−0.256 3(10)	0.199 9(16)
C(8)	−0.251 0(16)	−0.053 8(11)	0.375 9(16)	C(21)	0.052 3(17)	−0.237 2(10)	0.140 2(16)
C(9)	−0.334 1(18)	−0.065 1(11)	0.440 6(16)	C(22)	0.125 8(17)	−0.159 4(11)	0.167 4(17)
C(10)	−0.471 7(20)	−0.064 9(12)	0.381 8(18)	C(23)	0.123 5(14)	−0.111 6(9)	0.271 1(15)
C(11)	−0.527 7(17)	−0.050 2(10)	0.253 6(16)	C(24)	0.047 7(15)	−0.139 8(9)	0.341 8(14)
C(12)	−0.442 2(15)	−0.039 5(10)	0.185 2(16)	C(25)	−0.126 6(25)	−0.332 3(13)	0.157 7(21)
Compound (**8**)							
Ti(1)	0.721 5(1)	0.096 5(1)	0.154 0(1)	C(21)	0.767 9(4)	0.094 9(4)	0.232 9(3)
C(1)	0.685 4(4)	0.051 7(3)	0.088 8(3)	C(22)	0.799 2(3)	0.106 6(4)	0.190 0(3)
C(2)	0.734 6(4)	0.029 7(4)	0.091 7(4)	C(23)	0.779 8(3)	0.152 7(3)	0.166 6(3)
C(3)	0.740 1(4)	0.007 0(4)	0.139 6(4)	C(24)	0.774 7(3)	0.155 7(3)	0.110 7(3)
C(4)	0.696 1(4)	0.014 8(3)	0.168 4(4)	C(25)	0.745 8(3)	0.200 5(3)	0.087 7(3)
C(5)	0.660 0(3)	0.045 1(3)	0.137 8(3)	C(26)	0.710 2(3)	0.193 4(3)	0.048 7(3)
C(6)	0.631 8(3)	0.086 7(3)	0.161 8(3)	C(27)	0.684 6(3)	0.235 6(3)	0.027 4(3)
C(7)	0.604 0(3)	0.123 9(3)	0.125 8(3)	C(28)	0.694 5(4)	0.284 5(3)	0.045 4(4)
C(8)	0.607 0(3)	0.176 7(3)	0.133 9(3)	C(29)	0.729 2(4)	0.291 9(3)	0.084 7(4)
C(9)	0.581 4(3)	0.210 6(2)	0.101 0(3)	C(30)	0.754 8(3)	0.249 9(3)	0.106 4(3)
C(10)	0.554 0(4)	0.192 1(3)	0.059 7(3)	C(31)	0.819 5(3)	0.137 0(3)	0.077 9(3)
C(11)	0.551 3(4)	0.140 0(3)	0.051 0(3)	C(32)	0.869 3(3)	0.140 8(3)	0.096 6(3)
C(12)	0.575 7(4)	0.105 5(2)	0.084 2(3)	C(33)	0.910 8(3)	0.125 8(4)	0.066 0(3)

Table 8 (*continued*)

Atom	x	y	z	Atom	x	y	z
Compound (**8**)							
C(13)	0.607 4(3)	0.077 4(3)	0.213 5(3)	C(34)	0.902 4(3)	0.108 1(4)	0.016 7(3)
C(14)	0.590 0(4)	0.028 3(3)	0.226 6(3)	C(35)	0.853 2(3)	0.103 8(4)	−0.002 0(3)
C(15)	0.567 8(4)	0.019 7(3)	0.275 0(4)	C(36)	0.811 3(3)	0.118 3(4)	0.028 4(3)
C(16)	0.561 9(4)	0.059 5(4)	0.309 2(3)	C(101)	0.538 4(9)	−0.038 4(9)	0.038 4(9)
C(17)	0.578 2(4)	0.108 4(3)	0.296 5(3)	C(102)	0.561(2)	−0.055(2)	0.090(2)
C(18)	0.600 7(4)	0.117 5(2)	0.248 2(3)	C(103)	0.594(2)	−0.094(2)	0.094(2)
C(19)	0.738 5(3)	0.169 6(3)	0.198 8(3)	C(104)	0.612(3)	−0.106(2)	0.147(2)
C(20)	0.731 8(4)	0.133 6(4)	0.238 3(3)	C(105)	0.643(1)	−0.143(1)	0.143(1)

Table 9. Parameters used for extended Hückel m.o. calculations

	Orbital H_{ii} (orbital exponent) {coefficient}		
Element	s	p	d
Mo	−8.34 (1.96)	−5.24 (1.90)	−10.50 (4.54) {0.589 88} (1.90) {0.589 88}
C	−21.4 (1.625)	−11.4 (1.625)	
H	−13.6 (1.300)		

dividing the band area by the kinetic energy of the associated electrons, to compensate for the decreasing sensitivity of the analyser with decrease in kinetic energy of the electrons.

Whereas both He-I and He-II spectra were obtained for (**1**) and (**4**) at temperatures of *ca.* 78 [(**1**)] and 112 °C [(**4**)], only an He-I spectrum of (**6**) was obtained (at 178 °C) as, under the measurement conditions, resolution and intensity of the spectra deteriorated over a period of 30 min.

Spectra are shown in Figure 8. The dots represent experimental data and the continuous line a least-squares fit to this.

The calculations were carried out by the extended Hückel method, using Hoffmann's program ICON8.[16] The idealized structural data used are indicated in Figure 4. Parameters used in the calculation were as in Table 9.

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