Synthesis and characterisation of Ti, Cr, Mo and W bis(fluorene) complexes

F.G.N. Cloke [b], Alberto Romão Dias [a], Adelino M. Galvão [a], João L. Ferreira da Silva [a,*]

[a] *Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, Lisboa Codex 1096, Portugal*
[b] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9RQ, UK*

Abstract

The new η^6-bisfluorene complexes of Ti, Cr, Mo, and W were prepared using the Metal Vapour Synthesis (MVS) technique and characterised by spectroscopic methods. The reactivity displayed by fluorene using MVS is different than for other ligands with acidic hydrogens: cyclopentadiene produces the same η^5 complexes that can be obtained by more conventional synthesis, while indene (where acidic hydrogens coexist with an aromatic ring) originates both η^5 or/and η^6 complexes, sometimes as an isomeric mixture (Mo and W). In the present case of fluorene, only η^6 complexes were isolated by MVS. In order to explain this reactivity the stability of Mo and W η^5 and η^6 metal complexes with fluorene, indene and cyclopentadiene is interpreted using Molecular Orbital Calculations by determining the corresponding Overlap Populations. These calculations are also used to explain the chemical shifts observed in the ^{1}H NMR spectra of the bisfluorene complexes of group 6 metals in terms of p_z electronic density. © 1997 Elsevier Science S.A.

Keywords: Organometallics; Metal vapour synthesis; Sandwich complexes; Titanium; Chromium; Molybdenum; Tungsten; Bis(fluorenes)

1. Introduction

The reactivity of transition metal atoms and ring ligands has been intensively studied. Main feature of these studies is the synthesis of bis-arene complexes of several transition metals and lanthanides in reasonably high yields [1–5] by reacting metal and arene vapours. Reactions between cyclopentadiene (CpH) and metal vapours originated various kinds of complexes according to the metal used: Cr and Fe produced the η^5-η^5 chromocene [6] and ferrocene [7], while reactions with Co [6] and Ni [7] resulted in a η^5(Cp)-η^4(CpH) and a η^5(Cp)-η^3(CpH$_2$) complexes, respectively; when Mo and W were used the bis(η^5-Cp)di-hydride complexes were obtained [8,9].

Metal vapour reactions with ring ligands containing acidic hydrogens were extended to a system with two rings (one benzene and one CpH), indene. While Fe produced again the analogous complex to ferrocene by

coordinating η^5 to the Cp ring [1], this time Cr coordinated η^6 to two benzene rings [10]; re coordinates to one indene η^6 by the benzene ring and to another η^5 by the Cp ring [11]. But the most remarkable result was obtained when indene was cocondensed with Mo and W: three 18-electron complex isomers (Eq. (1) were obtained [9].

$$M = Mo, W$$

(1)
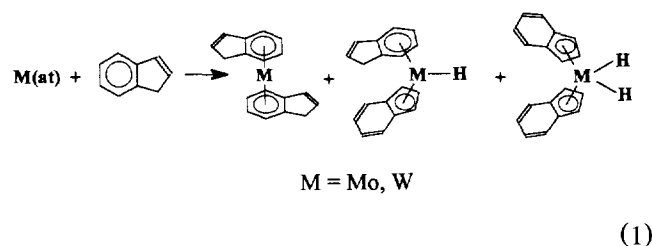
The purpose of our work was to study the evolution in the reactivity of ring systems containing acidic hydrogens by MVS, moving to a ligand, fluorene, where the acidity is considerably lower than for CpH or indene, using metals that could produce different types of co-ordination. We were particularly interested on reac-

* Corresponding author.

tions with molybdenum and tungsten, due to the possibility of obtaining an isomer mixture similar to the indene reactions.

There is already some evidence in the literature [12] that the reaction of chromium and fluorene vapours, followed by oxidation with air, produced $Cr(fluorene)_2BF_4$.

Our major interest was to prepare, isolate and characterise the bis(η^6-fluorene) complexes themselves, a synthesis that has never been reported either by MVS or any other synthetic method, extending this reaction to various metals.

2. Results

Bis(η^6-fluorene) complexes of Ti, Cr, Mo, and W were prepared by cocondensing metal and fluorene vapours at 77 K, allowing the mixture to regain room temperature (Eq. (2)).

Products were extracted with 40/60 petrol, pumped dry and purified by sublimation and/or recrystallisation from a toluene/petrol solution.

$$M(at) + \text{[fluorene]} \longrightarrow M\text{[complex]} + M\text{[complex]} \quad (2)$$

M = Ti, Cr, Mo, W
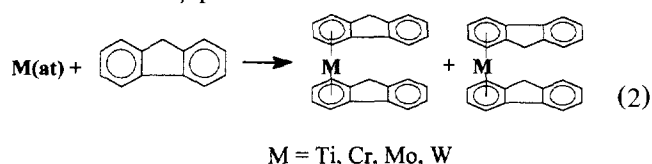
Separation of the two isomers (obtained in a ca. 1:1 ratio) using solvents of various polarities or chromatography proved unsuccessful for the four complexes.

Physical characteristics of this complexes are displayed in Table 1.

The reaction of fluorene and iron vapours produced, after removing the extraction solvent, an orange solid. The ^{1}H NMR spectra of this solid indicated the presence of excess fluorene and a product with a peak at 4.62 ppm (in the shift region of Cp protons). However, every attempt to isolate this product resulted in its decomposition.

Reactions of fluorene with Co, Ni and Re produced no identifiable products.

Table 1
Physical characteristics of fluorene complexes

Metal	Ti	Cr	Mo	W
Colour	Dark-green	Orange	Orange	Orange–red
Form	Powder	Crystals	Microcrystals	Crystals
Yield (%)	24.3	38.1	34.7	32.8
Decomposition temp. (°C)	80	–	160	130
Sublimation temp. (°C)	–	125	140	–

3. Experimental

All manipulations were carried out under argon (dried and deoxigenised by passage through 4 Å molecular sieves and BTS catalyst) or in vacuum using conventional Schlenk techniques and in a Miller–Howe glovebox filled with nitrogen (< 5 ppm H_2O, < 1 ppm O_2).

Fluorene (Aldrich) was used as received and the metals (Goodfellow) were degassed (except Cr) by melting with the electron gun before use. The solvents were dried and distilled under a dinitrogen atmosphere over sodium–benzophenone, potassium or sodium–potassium alloy, as appropriate, and kept under dinitrogen.

The Metal Vapour Reactor [5] was equipped with a ligand inlet system ending in a ring that sprayed the ligand over the inside surface of the reaction flask. The whole ligand system could be warmed using heating tapes (the outside tubing) or by resistive heating (the inside tubing and the ring); temperatures up to 300°C can be obtained.

IR spectra were recorded on Perkin-Elmer 1720 FT or 683, using KBr and CsI cells and Nujol.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 500 and were calibrated using the solvents as internal standards.

Mass spectra were obtained with an Finnigan Model 200-DT FTICR mass spectrometer, interfaced to a Spectra-Physics pulsed Nd:YAG laser, operating at the fundamental wavelength (1064 nm). The air sensitive complexes were transferred to the automatic solids probe of the instrument under argon.

3.1. Reactions: bis(fluorene) molybdenum

A pre-melted lump of molybdenum was placed on the hearth of the electron-gun furnace, the apparatus was assembled and evacuated to better than 10^{-6} mbar, and the reaction vessel was cooled to -195°C. The power input for the electron-gun was slowly increased up to ca. 1800 W. Fluorene was introduced by sublimation in a flask at 220°C. The ligand inlet system was also warmed to 240–250°C.

The experiment continued for 2 h. During that time molybdenum (1.42 g) and fluorene (20 g) were cocondensed. The electron-gun was switched off and the reaction mixture regained room temperature under dinitrogen. The products of the reaction were washed down into a receiving Schlenk vessel using 40/60 petrol as the washing solvent. The orange–brown solution was immediately filtered through Celite to remove metallic precipitates. The solvent was removed under reduced pressure at room temperature and the excess ligand was sublimed at 60°C at 10^{-4} mbar, leaving an orange brown solid. Bis(fluorene) molybdenum was isolated as an orange powder by sublimation in a tube at 145°C and

10^{-6} mbar. It can also be isolated, again as a powder, by recrystallisation in toluene/petrol at $-20°C$. The yield was 1.8 g, ca. 35%, based on the amount of molybdenum cocondensed with fluorene. Mass calculated (positive ion): 430.061356 amu; Mass determined: 430.05972 amu.

3.2. Other bis(fluorene) complexes

The experiments were carried out in essentially the same manner as described above for the molybdenum compound.

3.2.1. Tungsten

A power of 3000 W was used to evaporate 3.15 g of tungsten during 1 h 45 min. After filtering through Celite and removing the solvent and excess ligand a red–brown solid was obtained. Recrystallisation from toluene–petrol at $-20°C$ allowed the isolation of small red crystals; attempts to sublime the solid only produced a very small red band in the sublimation tube, due to the thermal decomposition of the bis(fluorene) tungsten at the sublimation temperature ($130°C$). The yield was 2.41 g, ca. 33%, based on the amount of tungsten cocondensed with fluorene (2.41 g).

Mass calculated: 516.106903 amu; Mass determined: 516.11590 amu.

3.2.2. Chromium

During 2 h 30 min, 5.70 g of chromium were evaporated using a power of 800 W. The orange–brown solid left after filtration and removal of solvent and excess ligand was sublimed and bis(fluorene) chromium was isolated at $125°C$. It was also isolated by recrystallisation in toluene–petrol at $-20°C$. Yield was 8.68 g, ca. 38%, based on the amount of metal cocondensed with fluorene (3.08 g).

Mass Calculated: 384.096461 amu; Mass determined: 384.09573 amu.

3.2.3. Titanium

1.58 g were evaporated during 1 h 25 min using a power of 1100 W and were cocondensed with 12 g of fluorene. After filtering a dark-green solid was obtained. Sublimation of this solid at $80°C$ and 10^{-6} mbar resulted in thermal decomposition. Bis(fluorene) titanium was isolated by recrystallisation in toluene–petrol at $-20°C$, as a dark-green powder. Yield was 3.05 g, ca. 24%, based on the cocondensed metal (0.65 g).

Mass calculated: 380.103897 amu; mass determined: 380.10459 amu.

3.2.4. Fluorene–iron reaction

2.18 g of iron were cocondensed during 2 h with 10.5 g of fluorene, using 450 W. The ^1H NMR of the mixture obtained after filtration shows, apart from the

peaks of uncoordinated fluorene, a peak at 4.62 ppm that could belong to the proton of a coordinated Cp ring.

Attempts to purify this mixture removing the excess ligand by sublimation ($70°C$ 10^{-6} mbar), recrystallisation and chromatography always resulted in the destruction of this Fe–fluorenyl complex.

3.2.5. Reactions with Re, Co, Ni

Reaction mixtures obtained after filtration of all these three runs presented ^1H NMR spectra showing no peaks that could be related with any compound similar to the ones previously isolated in benzene–cyclopentadiene systems.

Reaction conditions were the following:
Re - 7.71 g cocondensed in 3 h (2816 W) with 20 g of fluorene
Co - 4.10 g cocondensed in 2 h (800 W) with 15 g of fluorene
Ni - 1.40 g cocondensed in 2 h (648 W) with 15 g of fluorene

4. FTIR spectra

The spectra of all the listed compounds was performed using Nujol over NaCl and CsI cells, prepared inside a glove-box, due to high air-sensitivity displayed by the compounds. From 4000 to 400 cm^{-1} the spectra only show peaks identical to the fluorene spectrum with very slight deviations. For wavelengths lower than 400 cm^{-1} no conclusions could be taken on the attribution of peaks to metal–ligand vibrations.

5. NMR spectra

5.1. ^1H NMR spectra

The ^1H NMR of bis(fluorene) molybdenum is composed of three groups of peaks. One group is located between 4.7 and 5.45 ppm, corresponding to the protons of the coordinated ring (1–4), another around 7 ppm, corresponding to the protons of the uncoordinated benzene ring (5–8) and finally, a third group of four doublets further up field, corresponding to the two protons of the CpH ring (9,10). This assignment is confirmed by the integration obtained for this three groups (4:4:2) and matches the peak distribution obtained for monofluorene complexes [13].

This pattern immediately rules out the possibility of bis-η^5 coordinated fluorenyls or mixed η^5-η^6 products (Eq. (1)).

The four doublets obtained for the protons of the five membered ring are a clear indication that the result of the reaction was a mixture of two isomers (Eq. (2)).

Table 2
¹H NMR chemical shifts (δ ppm) and coupling constants (Hz) of bis(fluorene) complexes

H	Fluorene[a]	Ti(FlH)₂	Cr(FlH)₂	Mo(FlH)₂	W(FlH)₂
1–4	7.27–7.76	4.91–5.46	4.10–4.98	4.70–5.45	4.90–5.65
5–8	7.27–7.76	6.83–7.64	6.81–7.22	6.77–7.23	6.68–7.64
9	3.87	3.24(d)	3.07(d)	3.08(d)	2.89(d)
9′	–	3.46(d)	3.25(d)	3.31(d)	3.13(d)
10	3.87	1.86(d)	2.31(d)	1.74(d)	1.42(d)
10′	–	2.77(d)	3.03(d)	2.54(d)	2.22(d)
J_{9-10}		21.2	20.3	20.3	20.3
$J_{9'-10'}$		21.0	20.3	20.4	20.2

d: dublets.
[a][15,16].
Solvent: d_8-THF.

Each proton produces a doublet, that is split by the coupling with the other proton. The coupling constant for this two protons is 20.3 Hz, similar to coupling constant values for monofluorene complexes (21.7 Hz for η^6-$C_{13}H_{10}Cr(CO)_3$ [14]). The two isomers are not interconvertible. Small differences in the integration allowed us to separate the doublets of each isomer, although an assignment to a particular isomer was not possible. The assignment of the exo (9 and 9′) and endo (10 and 10′) protons is based on the increase of shielding in the endo protons caused by metal pulling of the C–H bond electrons towards itself.

Table 2 shows the assignments of the peaks of this compound, as well as of the other bis(fluorene) complexes and respective H^9–H^{10} coupling constants in d_6-benzene.

All these compounds show a similar peak pattern, so the final products of these reactions are also mixtures of two isomers like the ones shown in Eq. (2).

5.2. ¹³C NMR spectra

¹³C NMR Spectra of bis(fluorene) tungsten presents four groups of peaks. By comparison of the ¹³C and DEPT spectra of this complex it is possible to conclude that the 4 peaks between 140 and 150 ppm correspond to the quaternary carbon of the five membered ring (5, 6, 8 and 9). The CH_2 carbons of the two isomers (7) fall into the 30–40 ppm region; finally, the two remain-

ing sets of 8 peaks result from the CH carbons of the uncoordinated (115–130 ppm, carbons 10–13) and of the coordinated (65–80 ppm, carbons 1–4) benzene rings. All these assignments are in good agreement with the spectra obtained for monofluorene complexes and for fluorene itself [17].

The assignment of peaks for this and the other three bis(fluorene) complexes is indicated in Table 3.

5.3. Mass spectra

The complexes were also characterised by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR/MS), using both electron impact (EI) and laser desorption–ionisation (LDI). Positive EI mass spectra could only be obtained for the volatile Cr and Mo complexes, at probe temperatures of ca. 100°C, and showed prominent molecular ion peaks at low electron beam energies. Positive LDI mass spectra were obtained for all the bis(fluorene) compounds.

LDI Mass spectra of the reaction mixture obtained by reacting iron and fluorene never showed the peak corresponding to the bis(fluorenyl) complex, probably due to its decomposition under experimental conditions; however, a peak corresponding to monofluorenyl iron could be detected. The EI spectra of this mixture only showed fluorene.

6. MO calculations

In order to understand the reactivity of 'sandwich type' ML_2 organometallic complexes (M=Fe, Cr and Mo; L=C_5H_5 (Cp), C_6H_6 (Bz), C_9H_7 (In), $C_{13}H_9$ (Fl) and $C_{13}H_{10}$ (FlH), extended Hückel MO calculations were carried out (see Appendix A). The FMO formalism was used to discuss the interaction between the organic ligands and the metal centre.

Two types of coordination were analysed depending on the electron counting of the metal centre: η^5-coordination (e.g., Fig. 1 left) for d^6 sandwich type iron complexes and d^2 bent metallocene molybdenum complexes (e.g., Fig. 1 middle); η^6-coordination for d^6 sandwich molybdenum complexes (Fig. 1 right).

Table 3
¹³C NMR chemical shifts (δ ppm) of bis-fluorene complexes

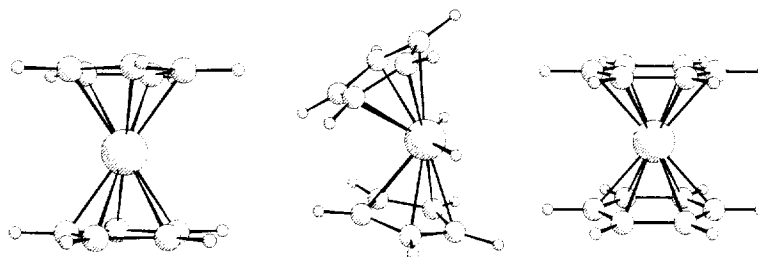| Carbon	Ti(FlH)₂	Cr(FlH)₂	Mo(FlH)₂	W(FlH)₂
1–4	75.05–84.32 (8)	70.29–76.34 (8)	70.81–77.06 (8)	65.37–72.88 (8)
5, 6	101.69–106.35 (4)	62.45–96.43 (4)	93.94–97.54 (4)	89.91–94.12 (4)
7	35.87–37.06 (2)	34.54–35.76 (2)	34.35–36.35 (2)	35.91–37.46 (2)
8, 9	140.71–143.07 (4)	142.67–145.54 (4)	141.79–144.54 (4)	141.75–145.26 (4)
10–13	116.61–126.81 (8)	119.36–126.57 (8)	118.64–126.53 (4)	118.47–127.02 (4)

#: number of peaks.

Fig. 1. Model complexes for sandwich type η^5-coordination (left), type η^6-coordination (right) and η^5-d^2 bent metallocenes (middle).

The FMO analysis shows that in η^5 iron complexes the overlap population between the metal centre and the L_2 fragment decreases in the order Cp (1.35 e$\overset{\circ}{A}^{-3}$)–In (1.16 e$\overset{\circ}{A}^{-3}$)–Fl (0.98 e$\overset{\circ}{A}^{-3}$). The same trend is observed in bent bis η^5 d^2 molybdenum complexes of the type Mo(η^5-L)$_2$H$_2$ (Cp 0.86 e$\overset{\circ}{A}^{-3}$, In 0.68 e$\overset{\circ}{A}^{-3}$ and Fl 0.49 e$\overset{\circ}{A}^{-3}$).

On the contrary, similar calculations for sandwich type Mo complexes (η^6-InH and FlH complexes) show that the overlap population between the metal centre and the organic ligand is approximately equal (InH and FlH = 0.74 e$\overset{\circ}{A}^{-3}$), in both cases smaller than for the benzene ligand (Bz = 0.87 e$\overset{\circ}{A}^{-3}$).

Table 4 summarises the overlap populations found for the series of compounds studied.

7. Discussion of results

The reactivity of a metal–ligand system by MVS is strongly dependent of the relative thermodynamic stability of the possible products [18]: the ratio between the amounts of two products from the same MVS run is a function of the ratio between their stability constants [19].

When unsaturated hydrocarbons and metal atoms interact the principal reactions that occur are: (a) π-bonding orbital mixing processes, and (b) insertion of the metal fragment into a C–H bond adjacent to a double bond (an active hydrogen) by an oxidative addition process.

Table 4
Overlap populations between aromatic ligands and metal centre

Metal centre	Ligand					
	Bz$_2$	(InH)$_2$	(FlH)$_2$	Cp$_2$	In$_2$	Fl$_2$
Ti	1.15	0.73	0.63	–	–	–
Cr	1.00	0.90	0.90	–	–	–
Mo	0.87	0.74	0.74	–	–	–
W	0.99	0.87	0.88	–	–	–
Fe	–	–	–	1.35	1.16	0.98
MoH$_2$	–	–	–	0.86	0.68	0.49
WH$_2$	–	–	–	1.01	0.83	0.65

Carbon p_z orbital populations for the η^6 coordinated rings of M(FlH)$_2$ complexes.

The first reaction is responsible for the formation of the bis(η^6-fluorene) complexes of Ti, Cr, Mo and W.

However, in the cases of Mo, W, Fe, and all the other metals where η^5 coordination was expected, no η^5 products where isolated or, if formed, decompose on isolation (Fe).

Insertion reaction begins with coordination to the ligand π-system that brings the metal and the active hydrogen together, leaving them in close juxtaposition, promoting the interaction [18].
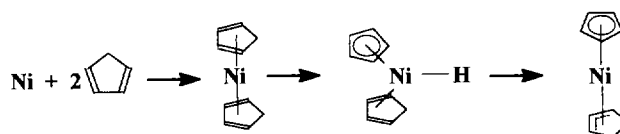
The driving force of this reaction for the ligands whose reactivity is compared (CpH, InH and FlH) is the formation of an aromatic cyclopentadienyl ring.

However, this driving force can be smaller if this ring is fused to benzene rings. The effect of the benzene rings is quite evident in the values of pKa for this three molecules (18, 20.1, 22.6) [20–22], implying reduced stabilisation of the anion relative to the hydrocarbon for these fused systems.

Calculations using the Extended Hückel Method show that the overlap population decreases in η^5 Fe com-
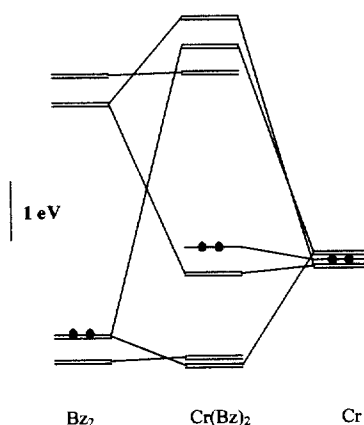

Fig. 2. FMO diagram depicting the interaction between Bz$_2$ and metal (Cr) fragments.

plexes in the order Cp (1.35 e$\mathring{A}^{-3}$), indenyl (1.16 e$\mathring{A}^{-3}$), fluorenyl (0.98 e$\mathring{A}^{-3}$).

Therefore, the iron bis(fluorenyl) complex, if formed, will have a weaker bond between ligand and metal than bis(Cp) or bis(indenyl), which could result in its decomposition during purification procedures.

The same trend is observed for the η^5 Mo and W complexes: Cp (0.86, 1.01 e$\mathring{A}^{-3}$), indenyl (0.68, 0.83 e$\mathring{A}^{-3}$), fluorenyl (0.49, 0.65 e$\mathring{A}^{-3}$). This explains why the η^5 fluorenyl isomers are not formed while the corresponding indenyl complexes can be obtained from the reaction of indene and metal vapours.

For Mo and W η^6 complexes, however, the overlap population for the fluorene (0.74, 0.88 e$\mathring{A}^{-3}$) complexes is similar to the one of the indene complexes (0.74, 0.87 e$\mathring{A}^{-3}$), suggesting that their stabilities should also be similar.

These calculations also explain why the protons of the coordinated benzene rings appear at lower values of δ for the bis(fluorene) Cr than for the analogues of Mo and W (in this order), and why these values are all much smaller than for the uncoordinated rings.

The FMO diagram shown in Fig. 2 illustrates the bonding in η^6—sandwich type complexes.

The average electron density in the $2p_z$ orbitals of the carbon atoms of the coordinated ring is smaller for the Cr complex (0.98 e) than for Mo (1.03 e) or W (1.04 e) complexes, due to a stronger bonding and a smaller antibonding interaction (d metal orbitals are lower in energy than Mo or W ones). This effect can produce a weakening of the ring current, so the protons of the Cr complex will behave in the NMR field more like olefinic protons than the ones of the Mo and W complexes (Table 2). If we assume, based on p_z orbital populations, that the more deshielded protons are the ones *ortho* (1) to the 5-membered ring of the fluorene molecule and that the *meta* (3) ones are the less deshielded, from the data in Tables 2 and 5, we can draw the trendlines shown in Fig. 3.
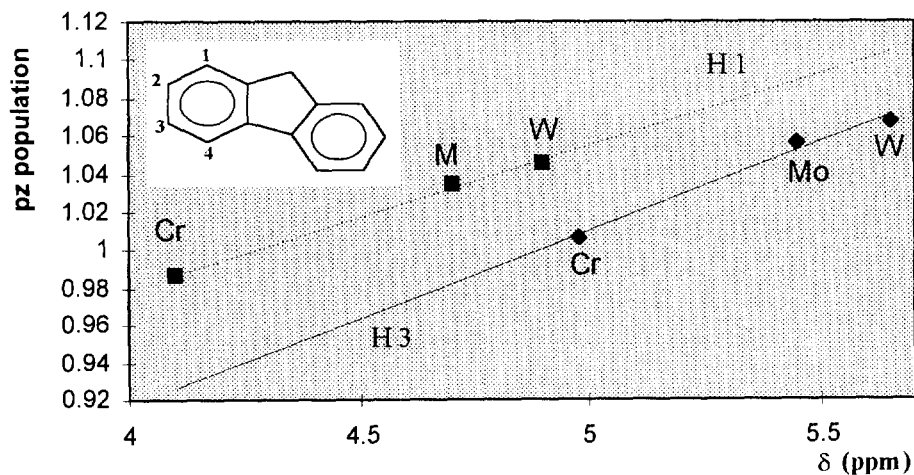
Table 5

	C 1 Pz orb. pop.	C 2 Pz orb. pop.	C 3 Pz orb. pop.	C 4 Pz orb. pop.	C 5 Pz orb. pop.	C 6 Pz orb. pop.	Average Pz orb. pop.
Cr(FlH)₂	1.007	0.990	0.987	1.001	0.967	0.931	0.98
Mo(FlH)₂	1.057	1.045	1.035	1.054	1.011	0.980	1.03
W(FlH)₂	1.068	1.060	1.046	1.066	1.023	0.991	1.04

Appendix A

All the Extended Hückel [15,16] calculations were made with CACAO [23] with modified H$_{ij}$'s [24]. The basis set for the metal atoms consisted of ns, np, $(n - 1)$d orbitals. The s and p orbitals were described by single Slater type wave functions, and d orbitals were taken as contracted linear combinations of two Slater type wave functions. The five and six-membered rings were taken as regular 140 pm side pentagons and hexagons, respectively. 108 pm was used for all the C–H distances. The indenyl and fluorenyl ligands were kept planar. The metal–ligand distances were 161 pm for sandwich η^6-coordinated ligands and 166 pm for sandwich η^5-coordinated ligands. For bent bis(hydride)

Fig. 3. Correlation between p_z population and ^{1}H NMR chemical shifts.

metallocenes the 170 pm was used for metal–hydrogen distances while 200 pm were used for metal–ligand bond lengths. The ligand–metal–ligand and H–metal–H angles of the bent metallocenes were kept frozen at 135°C and 140°C respectively.

Standard atomic parameters were used for all atoms.

References

[1] P.L. Timms, T.W. Turney, Adv. Organomet. Chem. 15 (1977) 53.

[2] M.L.H. Green, J. Organomet. Chem. 200 (1980) 119.

[3] W.E. Silverthorn, Adv. Organomet. Chem. 13 (1975) 48.

[4] J.G. Brennan, et al., J. Chem. Soc. Chem. Comm., (1987) 1668.

[5] F.G.N. Cloke, et al., J. Chem. Soc. Chem. Comm., (1987) 1667.

[6] P.L. Timms, Adv. Chem. Radiochem. 14 (1972) 121.

[7] P.L. Timms, J. Chem. Soc. Chem. Comm., (1969) 1033.

[8] M.J. D'Aniello, E.K. Barefield, J. Organomet. Chem. 76 (1974) C50.

[9] E.M. Van Dam et al., J. Am. Chem. Soc. 97 (1975) 467.

[10] V. Graves, J. Lagowski, Inorg. Chem. 15 (1976) 577.

[11] M.L.H. Green et al., J. Organomet. Chem. 355 (1988) 315.

[12] R. Middleton (P. Timms), Ph.D. Thesis, Univ. Bristol (1974).

[13] Y. Luzikov et al., J. Organomet. Chem. 202 (1980) 291.

[14] A. Nesmayanov et al., J. Organomet. Chem. 154 (1978) 45.

[15] R. Hoffmann, J. Chem. Phys. 39 (1963) 1397.

[16] R. Hoffmann, W.N. Lipscomb, J. Chem. Phys. 36 (1962) 2179.

[17] Y. Oprunenko et al., J. Organomet. Chem. 231 (1982) 137.

[18] J.R. Blackborrow, D. Young, Metal Vapour Synthesis in Organometallic Chemistry, Springer-Verlag, Berlin, 1979.

[19] B.E. Wilburn, P.S. Skell, J. Am. Chem. Soc. 104 (1982) 6989.

[20] F. Bordwell, G. Drucker, H. Fried, J. Org. Chem. 46 (1981) 632.

[21] F. Bordwell, G. Drucker, J. Org. Chem. 45 (1980) 3325.

[22] F. Bordwell et al., J. Am. Chem. Soc. 97 (1975) 7006.

[23] C. Mealli, D.M. Proserpio, J. Chem. Ed. 67 (1990) 399.

[24] J.H. Ammeter, H.-B. Bürgi, J.C. Thibeault, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 3686.