

## SYNTHESIS AND CHARACTERIZATION OF HETERODINUCLEAR COMPLEXES PENTACARBONYL[(DIMETHYLAMINOMETHYL)-FERROCENE]MOLYBDENUM AND PENTACARBONYL-[(DIMETHYLAMINOMETHYL)FERROCENE]TUNGSTEN

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*Dedicated to Professor K.-H. Thiele on the occasion of his 70th birthday in recognition of his outstanding contribution to the organometallic chemistry of transition elements.*

(Dimethylaminomethyl)ferrocene (HFcR, R = CH<sub>2</sub>NMe<sub>2</sub>) reacts with Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub> under substitution of one CO group and formation of the donor-acceptor complexes of the formula HFcR-M(CO)<sub>5</sub> (M = Mo, W). These yellow microcrystalline derivatives were characterized by mass, UV-VIS, IR, NMR and Mössbauer spectroscopy.

**Key words:** (Dimethylaminomethyl)ferrocene; Donor-acceptor complexes; Molybdenum; Tungsten; NMR spectroscopy; UV-VIS spectroscopy; IR spectroscopy; Mössbauer spectroscopy; Metallocenes; Ferrocenes; Carbonyl complexes.

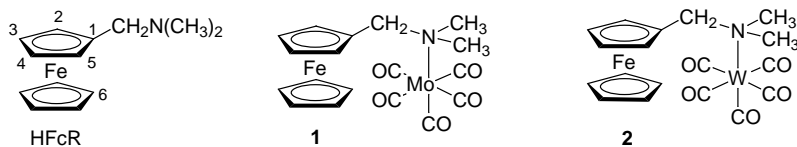
In many cases, reactions of the [(dimethylaminomethyl)ferrocenyl]lithium with anhydrous metal chlorides lead to homo- or heteroleptic 2-(dimethylaminomethyl)ferrocenyl derivatives of these main group or transition metals. In such derivatives, the ligand group is either  $\sigma$ -bonded or present as (C,N- $\eta^2$ ) chelate<sup>1</sup>. On the contrary, reactions of carbonyls of transition metals with non-lithiated (dimethylaminomethyl)ferrocene are restricted to the transition metals such as manganese or rhenium, leading to defined dinuclear complexes<sup>2</sup>, e.g. (FcR)Re(CO)<sub>4</sub>. On the other hand, HFcR is also able to act as a Lewis base towards metal chlorides MCl<sub>4</sub> (M = Sn, Ti, Zr) yielding

typical donor-acceptor complexes<sup>3</sup>. Taking into consideration the well-known finding that HFcR by treatment with BuLi converts<sup>4</sup> to the organometallic group carrier  $\text{Li}^+(\text{FcR})^-$ , it was of interest to investigate whether reactions of HFcR with  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) associated with CO substitution yield heterodinuclear complexes  $(\text{FcR})\text{M}(\text{CO})_5$  or donor-acceptor complexes of the formula  $\text{HFcR}\cdot\text{M}(\text{CO})_5$  including M-N interaction. The results of this study are reported here.

## EXPERIMENTAL

### General Procedures

All syntheses and manipulations were carried out under argon atmosphere using the standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl prior to use. All starting chemicals ((dimethylaminomethyl)ferrocene, hexacarbonylmolybdenum and -tungsten) were used as received from Sigma-Aldrich. Mass spectra were obtained using an AMD-type instrument AMD-Intectra (electron impact (EI) ionization, 70 V, 150 °C). Mössbauer spectra were measured with a Wissel instrument (transmission geometry, velocity calibration:  $\alpha$ -iron;  $\gamma$ -ray source:  $^{57}\text{Co}$  in Rh-matrix, 1.8 GBq). IR spectra were recorded using a Perkin-Elmer 684 spectrophotometer coupled to a Data Station 3060 ( $\nu$  in  $\text{cm}^{-1}$ ). UV-VIS spectra were measured using a Hewlett-Packard 8453 spectrophotometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectra were recorded using a Bruker AMX 360 instrument operating at 360.136 ( $^1\text{H}$ ), 90.556 ( $^{13}\text{C}$ ) and 36.501 MHz ( $^{15}\text{N}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were referred to TMS,  $^{15}\text{N}$  NMR chemical shifts were referred to external neat  $\text{CH}_3\text{NO}_2$ . Two-dimensional spectra (H,H and C,H COSY) were obtained by using a special software<sup>5</sup>. The adopted numbering scheme for HFcR is shown in Scheme 1.



SCHEME 1

### Pentacarbonyl[(dimethylaminomethyl)ferrocene]molybdenum (1)

To a solution of (dimethylaminomethyl)ferrocene (2.76 g, 11.36 mmol) in 100 ml of toluene  $\text{Mo}(\text{CO})_6$  (3 g, 11.36 mmol) was added with stirring. The reaction mixture was heated to reflux for 24 h. After cooling the precipitated yellow crystallites were filtered off and dried *in vacuo* (52%; m.p. 130 °C dec.). For  $\text{C}_{18}\text{H}_{17}\text{FeMoNO}_5$  (478.9) calculated: 45.09% C, 3.35% H, 11.16% Fe, 2.93% N; found: 45.14% C, 3.68% H, 11.10% Fe, 2.95% N. EI-MS,  $m/z$ : 479 (15%,  $\text{M}^+$ ); 423 (28.6%,  $\text{M} - 2 \times \text{CO}$ ); 243 (80%, HFcR); 199 (90%,  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ); 121 (30%,  $\text{C}_5\text{H}_5\text{Fe}$ ). IR (Nujol, KBr,  $\text{CHCl}_3$ ): 3 096 m, 2 987 m, 2 071 ms, 1 989 s, 1 941 vs, 1 923 vs, 1 888 vs, 1 475 vs, 1 462 m, 1 427 w, 1 414 w, 1 404 w, 1 328 w, 1 290 w, 1 236 s, 1 179 w, 1 137 vw, 1 107 s, 1 058 w, 1 041 s, 1 030 m, 1 005 s, 977 m, 929 w, 893 w, 884 w, 840 s, 830 m, 809 vs, 771 m, 614 m, 602 vs, 543 vs, 513 m, 502 m, 488 s, 436 w, 358 vs.  $^1\text{H}$  NMR

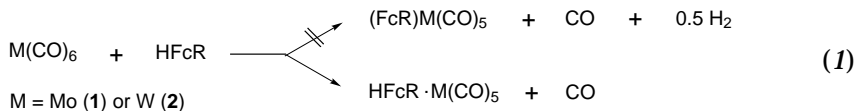
(360.14 MHz,  $\text{CDCl}_3$ ): 4.22 s, 2 H ( $\text{C}_5\text{H}_4$ ); 4.19 s, 2 H ( $\text{C}_5\text{H}_4$ ); 4.13 s, 5 H ( $\text{C}_5\text{H}_5$ ); 3.95 s, 2 H ( $\text{CH}_2$ ); 2.51 s, 6 H ( $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (90.57 MHz,  $\text{CDCl}_3$ ): 214.19 (*trans*-CO); 204.11 (*cis*-CO); 77.21, 71.72, 70.26 ( $3 \times \text{C}_5\text{H}_4$ ); 68.53 ( $\text{C}_5\text{H}_5$ ); 69.00 ( $\text{CH}_2$ ); 54.00 ( $\text{CH}_3$ ). UV-VIS ( $\text{CDCl}_3$ ;  $\nu$ ,  $\text{cm}^{-1}$  ( $\epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 21 350 sh, 24 700 (81).

### Pentacarbonyl[(dimethylaminomethyl)ferrocene]tungsten (2)

To a solution of (dimethylaminomethyl)ferrocene (2.07 g, 8.53 mmol) in 100 ml of toluene  $\text{W}(\text{CO})_6$  (3 g, 8.53 mmol) was added with stirring. The reaction mixture was refluxed for 24 h. After cooling, the precipitated yellow microcrystalline solid was filtered off and dried *in vacuo* (64.2%; m.p. 150 °C dec.). For  $\text{C}_{18}\text{H}_{17}\text{FeNO}_5\text{W}$  (566.8) calculated: 38.11% C, 2.99% H, 9.85% Fe, 2.47% N; found: 38.12% C, 2.76% H, 10.18% Fe, 2.32% N. EI-MS, *m/z*: 567 (45%,  $\text{M}^+$ ); 483 (5%,  $\text{M} - 3 \times \text{CO}$ ); 455 (20%,  $\text{M} - 4 \times \text{CO}$ ); 427 (60%,  $\text{M} - 5 \times \text{CO}$ ); 383 (35%,  $\text{HFcRW} - \text{NMe}_2$ ); 369 (25%,  $\text{HFcRW} - \text{NMe}_2, - \text{CH}_2$ ); 243 (100%,  $\text{HFcR}$ ); 199 (60%,  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ); 121 (15%,  $\text{C}_5\text{H}_5\text{Fe}$ ). IR (Nujol, KBr,  $\text{CHCl}_3$ ): 3 107 w, 3 094 w, 2 070 m, 1 983 s, 1 932 vs, 1 919 vs, 1 885 s, 1 475 m, 1 426 w, 1 413 w, 1 405 m, 1 330 w, 1 289 w, 1 234 w, 1182 vw, 1 143 vw, 1 108 ms, 1 059 w, 1 043 ms, 1 031 w, 1 005 ms, 970 w, 928 w, 893 w, 839 ms, 831 w, 810 m, 803 m, 772 w, 613 w, 603 m, 585 vs, 549 m, 513 w, 490 m, 473 vs, 373 vs.  $^1\text{H}$  NMR (360.14 MHz,  $\text{CDCl}_3$ ): 4.25 s, 2 H ( $\text{C}_5\text{H}_4$ ); 4.23 s, 2 H ( $\text{C}_5\text{H}_4$ ); 4.19 s, 5 H ( $\text{C}_5\text{H}_5$ ); 4.12 s, 2 H ( $\text{CH}_2$ ); 2.78 s, 6 H ( $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (90.57 MHz,  $\text{CDCl}_3$ ): 201.72 t,  $^1J(^{183}\text{W}, ^{13}\text{C}) = 152.60$  (*trans*-CO); 199.54 t,  $^1J(^{183}\text{W}, ^{13}\text{C}) = 132.94$  (*cis*-CO); 77.61 ( $\text{C}_5\text{H}_4$ ); 71.83 ( $\text{C}_5\text{H}_4$ ); 70.04 ( $\text{CH}_2$ ); 69.30 ( $\text{C}_5\text{H}_4$ ); 68.80 ( $\text{C}_5\text{H}_5$ ); 55.73 ( $\text{CH}_3$ ).  $^{15}\text{N}$  NMR (36.50 MHz,  $\text{CDCl}_3$ ): -369.0. UV-VIS ( $\text{CDCl}_3$ ;  $\nu$ ,  $\text{cm}^{-1}$  ( $\epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 22 000 (24), 24 860 (105), 26 800 sh.

## RESULTS AND DISCUSSION

The respective reactions of the colourless hexacarbonylmolybdenum or -tungsten with equivalent amounts of brownish-red viscous (dimethylaminomethyl)ferrocene (HFcR) in boiling toluene as solvent yield yellow crystallites (Eq. (1)).



While the displaced CO is detectable by gas chromatography, the formation of  $\text{H}_2$  was not observed. This finding suggests to the probable formation of the donor-acceptor complexes  $\text{HFcR} \cdot \text{M}(\text{CO})_5$ , but not to the generation of heterodinuclear derivatives of the formula  $(\text{FcR})\text{Mo}(\text{CO})_5$  containing such heavy d elements. Furthermore, this assumption is corroborated by the insensitivity of both complexes to air as well as by the occurrence of the respective molecular ion peaks (479 *m/z*  $\text{Mo}^+$ ; 567 *m/z*  $\text{W}^+$ ) and of the HFcR peak at 243 *m/z* in the mass spectra of the complexes.

*Mössbauer Spectroscopy*

The  $^{57}\text{Fe}$ -Mössbauer spectra of the  $\text{HFcR}\cdot\text{Mo}(\text{CO})_5$  (**1**) and  $\text{HFcR}\cdot\text{W}(\text{CO})_5$  (**2**) were recorded at 295 and 100 K, respectively (Fig. 1). Obviously, the 100 K spectra of both complexes exhibit the same shape each consisting of a doublet D1 assigned, on the basis of the spectral parameters listed in Table I, to the formally divalent iron atom of the HFcR ligand and of a doublet D2 with slight quadrupole splitting. In accordance with literature data<sup>6</sup>, the latter is attributed to a partial ferricenium cation and, consequently, to participation of the formally trivalent iron. The intensities (see Table I) of the partial spectra prove the conversion of the above oxidation to be higher in the compound  $\text{HFcR}\cdot\text{W}(\text{CO})_5$  than in its molybdenum analogue. The 295 K spectra show a substantially poorer statistical distribution that may be due to the reduced Debye–Waller factor at room temperature. The observed charge transfer can be attributed to the electron-attracting action of the CO

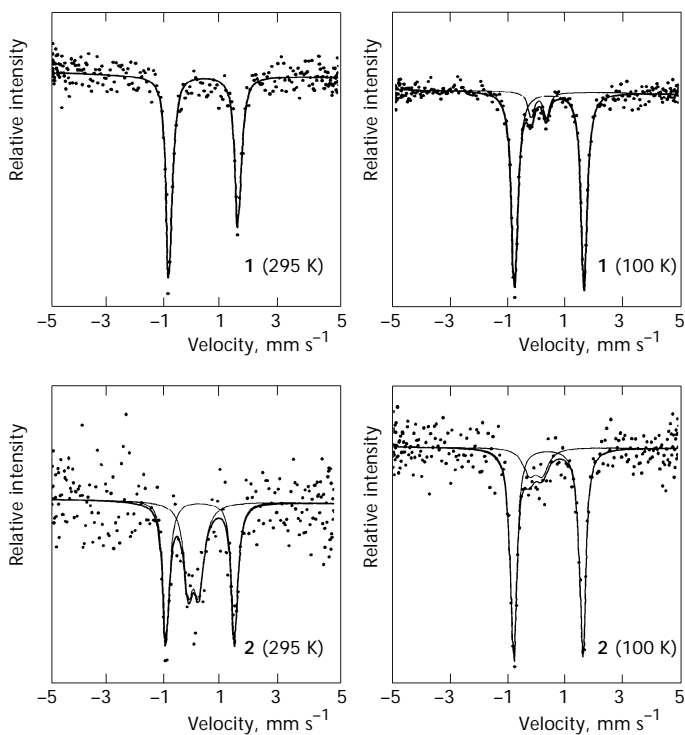


FIG. 1

$^{57}\text{Fe}$ -Mössbauer spectra of the  $\text{HFcR}\cdot\text{M}(\text{CO})_5$  (M = Mo (**1**), W (**2**)) at temperatures 295 and 100 K

ligands on the one hand and also to the decrease in the electronegative partial charge on the nitrogen atom of the HFcR molecule, due to its donor binding to the corresponding  $M(\text{CO})_5$  moiety, on the other. Evidently, this causes the reduction in electron density on the formally divalent iron atom and hence the partial oxidation (Fe(II)/Fe(III)) *via* the substituted  $\text{C}_5\text{H}_4$  ring of the HFcR.

TABLE I  
Mössbauer parameters of the complexes HFcR- $M(\text{CO})_5$  ( $M = \text{Mo}$  (1),  $\text{W}$  (2)) at 100 and 295 K

Com- plex	Temp. K	$D_1$					$D_2$				
		dt %	$\delta$ $\text{mm s}^{-1}$	$\epsilon$ $\text{mm s}^{-1}$	$\Gamma$ $\text{mm s}^{-1}$	$I$ %	$\delta$ $\text{mm s}^{-1}$	$\epsilon$ $\text{mm s}^{-1}$	$\Gamma$ $\text{mm s}^{-1}$	$I$ %	
1	295		0.42(3)	2.34(7)	0.23(1)	100	–	–	–	–	
	100	12	0.512(2)	2.36(4)	0.24(6)	12	0.28(2)	0.52(3)	0.25(4)	88	
2	295	19	0.498(5)	2.348(9)	0.25(2)	19	–14(7)	0.44(1)	0.52(2)	81	
	100	48	0.42(1)	2.34(3)	0.24(4)	48	0.19(3)	0.36(5)	0.40(0)	52	

dt, degree of transformation;  $\delta$ , isomer shift;  $\epsilon$ , quadrupole splitting;  $\Gamma$ , line width;  $I$ , intensity

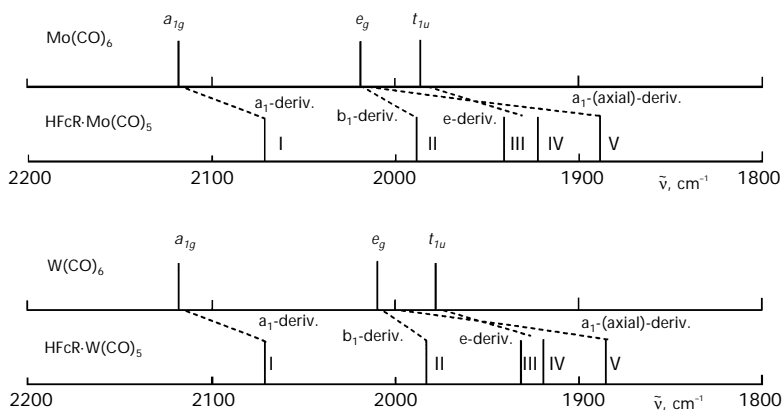


FIG. 2

IR spectra of the HFcR- $(\text{CO})_5$  complexes 1 and 2 (in  $\text{CHCl}_3$  and Nujol) and correlation of the CO stretching modes between  $M(\text{CO})_6$  and HFcR- $M(\text{CO})_5$ . Fundamental CO stretching frequencies for  $M(\text{CO})_6$  are taken from solution spectra<sup>13</sup>

## Infrared Spectroscopy

The IR spectra of the HFcR-M(CO)<sub>5</sub> complexes exhibit a number of characteristic bands originating from the fundamental vibrations of the ferrocene ligand moiety (3 100–2 800, 1 500–800, 513, 488, 358 cm<sup>-1</sup>). Typical IR spectral features of the complexes **1** and **2** are the CO stretching frequencies occurring in the 2 100–1 880 cm<sup>-1</sup> region (Fig. 2). Both the solution and solid IR spectra of each complex exhibit five bands. An excellent understanding of the isolated M(CO)<sub>5</sub> system makes band assignment of the IR spectra quite unambiguous<sup>7–12</sup>. The five CO groups in the LM(CO)<sub>5</sub> C<sub>4v</sub> molecules (L = monoatomic or axial biatomic ligand, for example) give rise to the five fundamental CO stretching vibrations classified according to the symmetry species of the C<sub>4v</sub> point group as a<sub>1</sub>(equatorial), a<sub>1</sub>(axial), b<sub>1</sub>(equatorial), e(equatorial). The two a<sub>1</sub> and e vibrations are both IR- and Raman-active, the b<sub>1</sub> mode being Raman-active only. Thus, the LM(CO)<sub>5</sub> C<sub>4v</sub> compounds should have three IR active CO stretching fundamentals 2a<sub>1</sub> + e. The IR spectra of various LM(CO)<sub>5</sub> C<sub>4v</sub> species invariably displayed (in solution) the predicted three CO stretching bands and these have been assigned on the basis of intensity considerations<sup>7,10,11</sup>. From these vibrational spectral studies, the following frequency order of CO stretching fundamentals has been inferred: ν(a<sub>1</sub>, equatorial) > ν(b<sub>1</sub>) > ν(e) > ν(a<sub>1</sub>, axial)<sup>7,8,11</sup>. Moreover, Orgel<sup>7</sup> has suggested that if in a complex L'M(CO)<sub>5</sub> (L' = polyatomic ligand) the L'-M group lacks axial symmetry, all four fundamental vibrations becomes IR-active and the degeneracy of the e mode is also removed. Indeed, we see that in the recorded IR spectra of the HFcR-M(CO)<sub>5</sub> complexes **1** and **2** (Fig. 2), five CO stretching fundamentals can be observed. These results confirm that with **1** and **2**, all of the fundamental CO stretching frequencies are IR-active, and the e mode is split. Evidently, with these HFcR-M(CO)<sub>5</sub> complexes, the overall symmetry of the molecule cannot actually be higher than C<sub>1</sub> because the local symmetry of the asymmetric HFcR ligand cannot be higher than C<sub>1</sub>. When this is combined with the C<sub>4v</sub> symmetry of the M(CO)<sub>5</sub> molecular fragment, all symmetry elements (except for the identity element) disappeared. Thus, in principle, all the CO stretching fundamentals become IR-active and the motions corresponding to the e mode are no longer degenerate. These considerations make it possible to assign the highest- and lowest-frequency bands denoted I and V in Fig. 2 to the a<sub>1</sub>(equatorial)- and a<sub>1</sub>(axial)-derived modes, respectively. Band II can be assigned to the b<sub>1</sub>-derived mode while the remaining strong bands III and IV must then be assigned to the e-derived mode whose degeneracy is removed. The splitting of this

e-derived band amounts to  $18\text{ cm}^{-1}$  for **1** and **2**. The pentacarbonylmolybdenum complex **1** shows the same separation of the two  $a_1$ -derived modes ( $183\text{ cm}^{-1}$ ) as does the tungsten compound **2** ( $186\text{ cm}^{-1}$ ). Since the splitting of the e-derived mode as well as the appearance of the  $b_1$ -derived mode was observed not only in the solid state but also in the solution spectra, it may be concluded that the effect is a fundamental property of individual  $\text{HFcr}\cdot\text{M}(\text{CO})_5$  molecules.

Poilblanc and Bigorgne<sup>9</sup> have pointed to the correlations between fundamental CO stretching modes of  $\text{M}(\text{CO})_5$   $C_{4v}$  unit and those of the parent  $\text{M}(\text{CO})_6$   $O_h$  hexacarbonyls. The regular octahedral hexacarbonyls of molybdenum and tungsten each have<sup>13</sup> three fundamental CO stretching vibrations of symmetries  $a_{1g}$  (Mo/W 2 117/2 116  $\text{cm}^{-1}$ ),  $e_g$  (Mo/W 2 019/2 010  $\text{cm}^{-1}$ ), and  $t_{1u}$  (Mo/W 1 986/1 977  $\text{cm}^{-1}$ ). The four CO stretching modes of the  $C_{4v}$   $\text{M}(\text{CO})_5$  correlate with those of the parent hexacarbonyls in the following way:  $a_1$ (equatorial) with  $a_{1g}$ ,  $a_1$ (axial) with  $e_g$ ,  $b_1$ (equatorial) with  $e_g$ , and e(equatorial) with  $t_{1u}$ . On this basis, the correlation between fundamental CO stretching modes of **1** and **2** and those of the parent hexacarbonyls has been established (Fig. 2). At first sight it is evident that the overall vibrational patterns of **1** a **2** relative to those of  $\text{Mo}(\text{CO})_6$  or  $\text{W}(\text{CO})_6$  are significantly shifted to lower wavenumbers. The reason for the shifts as well as for the individual CO modes is easily understandable and explainable. The donor-acceptor bonding  $\text{N}\rightarrow\text{M}$  increases negative charge on M which leads to expansion of the d-orbitals of M with attendant increase in the overlap  $\text{M}(\text{d}\pi)\text{-CO}(\pi^*)$ . In other words, the CO stretching frequencies of  $\text{M}(\text{CO})_5$  moieties in **1** a **2** decrease as the extent of  $\pi$ -electron back-donation from the metal to the CO groups increases. Moreover, it is seen from Fig. 2 that CO groups *cis* to the ligand HFcr in **1** and **2** have higher stretching frequencies than that *trans* to such ligand, in accord with Cotton-Kraihanzel's<sup>8</sup> "rule 4". The  $a_1$ (axial)-derived mode possesses the lowest frequency of all the five CO stretching modes in **1** a **2**. This is due to the *trans* effect of the HFcr ligand. Ligands in mutual *trans* positions compete for the electrons of a particular d-orbital of the M. By replacing one strong  $\pi$ -acceptor CO group with ligand HFcr which is  $\sigma$ -donor only and no  $\pi$ -acceptor, the M-CO bond in the *trans* position is strengthened and the C-O bond weakened which manifests in the value of  $\nu(\text{trans-CO})$ .

In the region  $700\text{--}300\text{ cm}^{-1}$ , bands due to the M-CO bond bending and the M-C bond stretching occur<sup>12</sup>. The force-constant calculations<sup>14-17</sup> on Group 6 hexacarbonyls have clearly demonstrated that all the M-C stretching vibrations lie below the M-CO bending vibrations. This order of fre-

quencies is retained in substituted  $\text{LM}(\text{CO})_5$  complexes<sup>18</sup>. The  $C_{4v}$   $\text{M}(\text{CO})_5$  moiety should have six  $\delta(\text{MCO})$  fundamentals ( $a_1 + a_2 + b_2 + 3e$  – four IR-active) and four  $\nu(\text{MC})$  fundamentals ( $2a_1 + b_1 + e$  – three IR-active). Therefore, for the  $C_1$   $\text{M}(\text{CO})_5$  unit in **1** and **2** as many as nine  $\delta(\text{MCO})$  and five  $\nu(\text{MC})$  vibrations are to be expected in the IR spectra. In fact, eight (in **1**) or seven (in **2**) bands are seen in the 700–350  $\text{cm}^{-1}$  region which can be assigned to these vibrations.

### UV-VIS Spectroscopy

The electronic spectra of the complexes **1** and **2** are very similar. Each of these complexes exhibits a band in the vicinity of  $\approx 400$  nm (**1**: 404 nm (24 700  $\text{cm}^{-1}$ ); **2**: 402 nm (24 860  $\text{cm}^{-1}$ )) and a shoulder on this band at  $\approx 460$  nm (**1**: 468 nm (21 350  $\text{cm}^{-1}$ ); **2**: 455 nm (22 000  $\text{cm}^{-1}$ )), the only difference being that for **2**, a clear shoulder at 373 nm (26 800  $\text{cm}^{-1}$ ) was found while no corresponding shoulder was seen for **1**. The assignment of these transitions seems to be straightforward. The octahedral molybdenum and tungsten hexacarbonyls exhibit the spin-allowed d-d transition  ${}^1A_{1g}(t_{2g}^6) \rightarrow {}^1T_{1g}(t_{2g}^5 e_g^1)$  near 30 000  $\text{cm}^{-1}$  (Mo: 30 200  $\text{cm}^{-1}$ ; W: 30 000  $\text{cm}^{-1}$ )<sup>19</sup>. Under the  $C_{4v}$  symmetry the  ${}^1T_{1g}$  ligand-field term splits into lower- ${}^1E(e^3 b_2^2 a_1^1)$  and higher-energy  ${}^1A_2(e^4 b_2^1 b_1^1)$  ligand-field terms (the  $O_h$  ground state  ${}^1A_{1g}(t_{2g}^6)$  transforms under  $C_{4v}$  symmetry as  ${}^1A_1(e^4 b_2^2)$ )<sup>20,21</sup>. Therefore, the 400-nm band of both complexes **1** and **2** can be assigned as a transition derived from the ligand-field  ${}^1A_1 \rightarrow {}^1E$  transition of the formally  $C_{4v}$   $\text{M}(\text{CO})_5$  moiety of the HFcR-complexes. The 455-nm shoulder on the higher-energy tail of the 400-nm band can be assigned either as the ligand-field transition to the higher lying sublevel arising from the further splitting of the  ${}^1E$  term due to low ( $C_1$ ) symmetry of the  $\text{W}(\text{CO})_5$  unit or as the symmetry forbidden  ${}^1A_1(e^4 b_2^2) \rightarrow {}^1A_2(e^4 b_2^1 b_1^1)$  transition which is no longer strictly symmetry-forbidden due to the low effective symmetry ( $C_1$ ) of the  $\text{W}(\text{CO})_5$  moiety in **2**. For comparison, the amine complexes  $\text{LM}(\text{CO})_5$  (M = Mo, W; L =  $\text{NH}_3$ ,  $\text{PrNH}_2$ , piperidine)<sup>21</sup> all exhibit corresponding  ${}^1A_1 \rightarrow {}^1E$  band at  $\approx 400$  nm.

The shoulder at  $\approx 460$  nm can be unequivocally assigned to the  ${}^1A_{1g} \rightarrow {}^1E_{1g}$  d-d transition of the ferrocenyl moiety<sup>22</sup> comprised in the HFcR ligand. It is well known that this d-d transition occurring at 440 nm (22 800  $\text{cm}^{-1}$ ) in ferrocene itself responds to the presence of a substituent on the cyclopentadienyl ring: an electron-donor substituent such as  $\text{CH}_2\text{N}(\text{CH}_3)_2$  group causes a characteristic shift to lower wavelengths (HFcR: 438 nm (22 840  $\text{cm}^{-1}$ )) while an electron-acceptor substituent acts in the opposite direction. As to



the HFcR-complexes **1** and **2**, the remarkable shifts of this “ferrocene” d-d band to higher wavelengths were observed. Their cause should be seen in the reduced partial negative charge on the N atom of HFcR due to the donor-acceptor N→M interaction bringing about the electron draw to the CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> group or its “Umpolung” from the electron-releasing to the electron-attracting substituent.

### <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR Spectroscopy

The <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectral data for the complexes **1** and **2** together with those for the *N*-protonated (**b**) and *N*-methylated (**c**) parent HFcR (**a**) amine are summarized in Table II including the protonation, *N*-methylation and coordination shift data.

The monosubstituted ferrocenyl group in **a**, **b**, **c**, **1** and **2** exhibits three distinct signals in its <sup>1</sup>H NMR spectra, namely those which arise from the unsubstituted ring protons (H6; five-proton signal), those which arise from the 2- and 5-positioned protons (H2, 5; two-proton signal) and those which arise from 3- and 4-positioned protons (H3, 4; two-proton signal) and four distinct signals in its <sup>13</sup>C NMR spectra, one arising from the unsubstituted ring carbon (C6), one arising from *ipso* carbon (C1), one arising from 2- and 5-positioned carbons (C2, 5) and one arising from 3- and 4-positioned carbons (C3, 4). In addition, the <sup>1</sup>H NMR spectra of the HFcR moiety in compounds **b**, **c**, **1** and **2** as well as of the HFcR (**a**) itself exhibited two-proton resonance for one CH<sub>2</sub> group and six-proton signal for two CH<sub>3</sub> groups. Similarly, the <sup>13</sup>C NMR spectra exhibited one resonance for one CH<sub>2</sub> group and one resonance for two CH<sub>3</sub> groups. While all <sup>1</sup>H signals of **1** and **2** (and also those of **b** and **c**) are shifted downfield with respect to the parent HFcR (**a**), this effect is pronounced for the CH<sub>2</sub> and CH<sub>3</sub> groups which are directly attached to nitrogen. The same holds for the <sup>13</sup>C resonances with the remarkable exception of the *ipso* carbon C1 of the monosubstituted ferrocenyl group which is shifted upfield.

Several trends can be seen in the <sup>13</sup>C NMR spectra of **1** and **2** concerning the carbonyl carbon shielding data: (i) The carbonyl resonances of both complexes are at lower field than the carbonyl shielding of the parent metal hexacarbonyls (Mo(CO)<sub>6</sub> at 201.00 ppm; W(CO)<sub>6</sub> at 191.10 ppm; our data in CDCl<sub>3</sub>). Since the interaction of metal d-orbitals with CO π\* orbitals strongly influences carbonyl shielding<sup>24,25</sup>, this trend can be interpreted as being due to the σ-donor only and virtually no π-acceptor ability of the HFcR ligand compared with CO. (ii) The carbonyl *trans* to the HFcR ligand is more deshielded than the *cis* carbonyls. Butler<sup>26</sup> has established that in-

TABLE II  
 $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectra of the complexes  $\text{HFcR-M}(\text{CO})_5$  ( $\text{M} = \text{Mo}$  (1),  $\text{W}$  (2)), of the HFcR ligand and of the protonated and methylated HFcR salts

$^1\text{H}$ NMR <sup>a,b</sup>								
Compound	H(2,5)	H(3,4)	H(6)	CH <sub>2</sub>	CH <sub>3</sub>			
HFcR (a) <sup>c,d</sup>	4.06	4.11	4.05	3.22	2.12			
H <sub>2</sub> FcR <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> (b) <sup>d,e</sup>	4.33 (0.27)	4.46 (0.35)	4.23 (0.18)	4.24 (1.02)	2.83 (0.71)			
HFcR' (c) <sup>d,f,g</sup>	4.37 (0.31)	4.59 (0.48)	4.28 (0.23)	4.70 (1.48)	314 (1.02)			
1 <sup>c</sup>	4.19 (0.13)	4.22 (0.11)	4.13 (0.08)	3.95 (0.73)	2.51 (0.39)			
2 <sup>c</sup>	4.23 (0.17)	4.25 (0.14)	4.19 (0.14)	4.12 (0.90)	2.78 (0.66)			
$^{13}\text{C}$ NMR <sup>a,b</sup>								
Compound	C(1)	C(2,5)	C(3,4)	C(6)	CH <sub>2</sub>	CH <sub>3</sub>	trans-CO	cis-CO
HFcR (a) <sup>c,d</sup>	82.91	69.83	67.76	68.24	58.71	44.37		
H <sub>2</sub> FcR <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> (b) <sup>d,e</sup>	75.08 (-7.81)	71.27 (1.44)	72.40 (68.14)	70.37 (2.13)	59.36 (0.65)	43.13 (-1.24)		
HFcR' (c) <sup>d,f,g</sup>	71.29 (-11.52)	71.06 (1.23)	(4.64)	69.23 (0.99)	65.67 (6.96)	50.98 (6.61)		
1 <sup>c</sup>	77.21 (-5.70)	71.72 (1.89)	70.26 (2.50)	68.53 (0.19)	69.00 (10.29)	54.00 (9.63)	214.19	204.11
2 <sup>c</sup>	77.61 (-5.30)	71.83 (2.00)	69.30 (1.54)	68.80 (0.56)	70.04 (11.33)	55.73 (11.36)	201.73	199.54
$^{15}\text{N}$ NMR <sup>a,b,h</sup>								
Compound	CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>							
HFcR(a) <sup>c</sup>	-350.1							
H <sub>2</sub> FcR <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> (b) <sup>d,e</sup>	-336.4 (13.7)							
HFcR' (c) <sup>d,f</sup>	-328.6 (21.5)							
2 <sup>c</sup>	-369.0 (-18.4)							

<sup>a</sup> Chemical shifts in ppm. <sup>b</sup> Numbers in brackets indicate protonation [ $\delta(\text{b})-\delta(\text{a})$ ], methylation [ $\delta(\text{c})-\delta(\text{a})$ ], and coordination [ $\delta(1/2)-\delta(\text{a})$ ] shifts. <sup>c</sup> In  $\text{CDCl}_3$ . <sup>d</sup> In  $\text{CD}_3\text{NO}_2$ . <sup>e</sup> In  $\text{CDCl}_3-\text{CD}_3\text{NO}_2$ . <sup>f</sup> See ref.<sup>22</sup>. <sup>g</sup>  $\text{CD}_3\text{NO}_2$  as reference.

creasing CO stretching force constants are paralleled by increased  $^{13}\text{C}$  shieldings. According to Cotton–Kraihanzel's<sup>8</sup> rule 4, CO groups *cis* to  $\text{HFcR}\cdot\text{M}(\text{CO})_5$  should have higher stretching force constants than the *trans*-CO. This trend parallels with the IR spectral results above suggesting again that the *trans* carbonyl gains metal d-orbital electron density *via*  $\pi$  backbonding more readily than *cis* carbonyls. (iii) Changing the metal from Mo to W in  $\text{HFcR}\cdot\text{M}(\text{CO})_5$  results in an upfield shift of the carbonyl resonances (12.47 ppm for *trans*-CO; 4.96 ppm for *cis*-CO), which is the same trend noted for the parent metal hexacarbonyls (9.90 ppm).

As far as the coupling constants  $^1J(^{138}\text{W}, ^{13}\text{C})$  are concerned, the larger values of both couplings found for **2** (*trans*  $^1J(^{138}\text{W}, ^{13}\text{C}) = 150.50$  Hz; *cis*  $^1J(^{138}\text{W}, ^{13}\text{C}) = 132.85$  Hz) compared with that for  $\text{W}(\text{CO})_6$  ( $^1J(^{138}\text{W}, ^{13}\text{C}) = 126.2$  Hz in  $\text{CDCl}_3$ ) as well as the larger value of the *trans* coupling relative to the *cis* suggest<sup>25</sup> the importance of  $[\psi_n(\text{O})]^2$ . It may be noted that the  $^{13}\text{C}$  NMR spectral CO characteristics observed for the HFcR amine complex **2** are very similar to those found for another amine- $\text{W}(\text{CO})_5$  complex (for cyclohexylamine:  $\delta(\text{CO})$  *trans*, 201.9 ppm;  $\delta(\text{CO})$  *cis*, 199.1 ppm; *trans*  $^1J(^{138}\text{W}, ^{13}\text{C}) = 127$  Hz)<sup>27</sup>.

For the complex **2**, the  $^{15}\text{N}$  resonance of the HFcR ligand has been found at -369.0 ppm yielding the coordination shift of -18.4 ppm relative to the parent HFcR (in contrast, both the protonation and *N*-methylation  $^{15}\text{N}$  shifts are positive). For the amine  $d^6$  metal complexes, the coordination  $^{15}\text{N}$  shifts are largely upfield, while the protonation  $^{15}\text{N}$  shifts are usually downfield<sup>28</sup>, which is also the HFcR case.

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