

COMPLEXES OF POLYPYRAZOLYLBORATE LIGANDS

VI*. SOME COMPLEXES CONTAINING CYCLOHEPTATRIENYL GROUPS AND THEIR TRICARBONYLIRON ADDUCTS

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SUMMARY

Compounds of the type $\text{LMo}(\text{CO})_2\text{C}_7\text{H}_7$, with $\text{L} = \text{B}(\text{C}_3\text{N}_2\text{H}_3)_4$, $\text{HB}(\text{C}_3\text{N}_2\text{H}_3)_3$, $\text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H}_2)_3$ and $\text{H}_2\text{B}(3,5\text{-C}_3\text{N}_2\text{H}_2)_2$, have been shown to react with $\text{Fe}(\text{CO})_5$ to yield $\text{Fe}(\text{CO})_3$ adducts. Both the starting compounds and the adducts are fluxional, exhibiting single proton NMR lines for the C_7H_7 rings. All available evidence is consistent with the belief that each of the starting compounds contains a *trihapto*-cycloheptatrienyl ring and that the adducts are formed by binding of the $\text{Fe}(\text{CO})_3$ group to the butadiene portions of the C_7H_7 rings. The retention of fluxional character after attachment of the $\text{Fe}(\text{CO})_3$ groups means that these pairs of molecules are similar to the pair $(h^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(h^3\text{-C}_7\text{H}_7)$ and $(h^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{C}_7\text{H}_7)\text{-Fe}(\text{CO})_3$. The latter was, heretofore, the only example of a fluxional molecule in which two independent metal-containing moieties are simultaneously attached to the same polyene or polyenyl ring.

INTRODUCTION

Several complexes of the type $\text{LMo}(\text{CO})_2\text{C}_7\text{H}_7$, where L is a polypyrazolylborate ligand have been reported¹⁻⁴. Those with which this paper is concerned are the following: $\text{L} = \text{B}(\text{C}_3\text{N}_2\text{H}_3)_4$, (I); $\text{L} = \text{HB}(\text{C}_3\text{N}_2\text{H}_3)_3$, (II); $\text{L} = \text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H}_2)_3$, (III); $\text{L} = \text{H}_2\text{B}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H}_2)_2$, (IV); $\text{L} = \text{Et}_2\text{B}(\text{C}_3\text{N}_2\text{H}_3)_2$, (V).

Major interest in these compounds has previously centered around their structures, with particular reference to the mode of attachment and dynamical behavior of the cycloheptatrienyl group. In the case of (IV), there is conclusive evidence that both in solution³ and in the crystal⁴ the ring is bound in *trihapto* fashion. An 18-electron configuration at the molybdenum atom is achieved by the formation of

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a B-H-Mo two-electron, three-center bond. The h^3 -C₇H₇ ring in (IV) is fluxional, giving rise to a single, sharp PMR peak at room temperature which collapses at lower temperatures and at -120° gives a spectrum believed to be characteristic of an h^3 -C₇H₇ group⁵⁻⁷ but different from that of an h^5 -C₇H₇ group⁸.

The preparation and study of Fe(CO)₃ adducts of compounds containing h^3 -C₇H₇ groups is of interest for at least two reasons. First, the preparation of such an adduct affords chemical evidence in favor of the h^3 -C₇H₇ formulation of the initial compound. This line of evidence can be buttressed by spectroscopic data showing that the only spectral changes that occur upon adduct formation are those which would be anticipated as a consequence of attaching the Fe(CO)₃ moiety to a previously free 1,3-diene group.

Second, the dynamical behavior of the Fe(CO)₃ adduct is intrinsically interesting, as illustrated by earlier studies of (h^5 -C₅H₅)Mo(CO)₂(h^3 -C₇H₇) and its Fe(CO)₃ adduct^{9,10}. A detailed analysis of this fluxional adduct, especially in contrast to the nonfluxional *trans*-C₈H₈[Fe(CO)₃]₂, was made. It was concluded that fluxionality may be controlled by the magnitude of overlap between the π systems in the two bound polyene or polyenyl portions of the ring.

The formation of an Fe(CO)₃ adduct of compound (IV) has already been reported³ along with a description of the proton NMR spectrum at room temperature, which contains only a single line for the seven cycloheptatrienyl protons, thus showing that the molecule is fluxional. In this paper we report the synthesis and properties of the Fe(CO)₃ adducts of compounds (I) to (III), and discuss the fluxional character of all of the four similar compounds.

EXPERIMENTAL

General

Solvents were dried over molecular sieves and purged with nitrogen for at least 1 min immediately prior to use. Reactions were carried out in an atmosphere of purified nitrogen. Infrared spectra were taken using a Perkin-Elmer 337 grating infrared spectrometer and 0.1 or 1.0 mm pathlength sodium chloride cavity cells. The spectra were calibrated with polystyrene film. The proton magnetic resonance spectra were recorded with a Varian HA-100 spectrometer equipped with a variable-temperature probe. All chemical shifts were measured by internal referencing with tetramethylsilane (TMS) except in the case of high temperature experiments where cyclohexane was used. The temperature in the probe was measured with an uncalibrated Digitic Digital Thermocouple Thermometer (C-C Type T). Analyses were performed by Meade Microanalytical Laboratories, Amherst, Mass. and by Mrs. N. Alvord of M.I.T. Molecular weight measurements were made at Meade Laboratories by the vapor osmometry method using benzene at 50°. Melting points were measured with a Buchi hot stage and are uncorrected.

Preparation of compounds

Compounds (I)-(IV) were prepared according to published methods^{1,2}. They were identified on the basis of their infrared and NMR spectra. The Fe(CO)₃ adducts, (I')-(IV'), were prepared by a method similar to that used to prepare (h^5 -C₅H₅)(h^3 -C₇H₇)(CO)₂Mo·Fe(CO)₃⁹.

$[B(Pz)_4](C_7H_7)(CO)_2Mo \cdot Fe(CO)_3^*$, (I'). $[B(Pz)_4](C_7H_7)(CO)_2Mo$ (1.0 g) was added to a 300 ml round-bottom, three-neck pyrex flask fitted with a stopper, condenser and nitrogen inlet valve. The condenser was stoppered with a nitrogen inlet valve. Benzene (200 ml) was added to dissolve the solid. $Fe(CO)_5$ (20 ml) that had been filtered and dried over molecular sieves was added to the red solution. The solution was then irradiated for 24 to 27 h with a Hanovia Utility Model Quartz lamp (Cat. No. 30600). The lamp was placed about 15 cm from the flask which was set up in a fume hood in such a way that the draft of the hood kept the temperature of the solution below 30°. There was little change in the appearance of the solution during the irradiation except for the formation of a little $Fe_2(CO)_9$. After irradiation the solvent and excess $Fe(CO)_5$ were stripped and the brown residue was dried by pumping at 0.05 mmHg overnight. The residue was extracted with 50 ml of benzene, and this solution was filtered and freeze-dried to yield a fine brown powder. Portions of this powder were dissolved in benzene and chromatographed in benzene on a column of Woelm Alumina (neutral, activity 2) which was 32 cm long and 2.2 cm in diameter. Careful elution with benzene yielded first a red band identified as the product and second a yellowish-brown band identified by its infrared spectrum as starting complex. Freeze-drying of the red solution yielded the analytical sample. The substance decomposes under N_2 at 220°. Found: C, 44.1; H, 2.89; N, 16.9. Mol. wt., 656. $BC_{24}H_{19}FeMoN_8O_5$ calcd.: C, 43.50; H, 2.87; N, 16.92%. Mol. wt., 662).

Infrared spectrum (cm^{-1}): ν_{CO} , 2050 s, 1987 s, 1978 s, 1949 s, 1870 s in cyclohexane. Other bands, 3150 w(br), 3030 w, 2990 w, 1437 m, 1408 m, 1385 m, 1310 m, 1296 m, 1215 m(br), 1189 w, 1114 s, 1095 m, 1075 m, 1068 m, 1050 w, 927 w, 850 m, 815 m, 803 m, 760 s, 610 s(br) in CS_2 and CCl_4 .

NMR spectrum (in 0.7 ml CD_2Cl_2 plus 0.1 ml TMS at 25°): Pyrazolyl protons, 1.31(d, 1), 1.77(d, 1), 2.14(m, 4), 2.75(d, 2), 3.45(t, 1), 3.65(t, 1), 3.83(t, 2); the C_7H_7 ring appears as a broad peak, 0.44 ppm wide at half height, at τ 5.13; at -56° the C_7H_7 resonances are 4.20 (dd, 2), 4.82(t, 2), 5.29(dt, 1) and 5.95(c, 2) where dd = double doublet, t = triplet, dt = distorted triplet and c = complex. In 0.6 ml toluene- d^8 plus 0.1 ml C_6H_{12} at 83° the C_7H_7 resonance is a sharp peak (0.02 ppm wide) at τ 5.45.

$[HB(Pz)_3](C_7H_7)(CO)_2Mo \cdot Fe(CO)_3$, (II'). The preparative method was virtually identical to that described above for the tetrapyrazolylborate complex. The compound melts at 212° under nitrogen. (Found: C, 42.4; H, 2.82; N, 14.3. Mol. wt., 590. $BC_{21}H_{17}FeMoN_6O_5$ calcd.: C, 42.28; H, 2.85; N, 14.09%. Mol. wt., 596.)

Infrared spectrum (cm^{-1}): ν_{CO} , 2050 s, 1990 s, 1980 s, 1950 s, 1874 s in cyclohexane. ν_{B-H} , 2470 w in CS_2 . Other bands, 3040 w(br), 2989 w, 1475 w, 1407 s, 1356 w, 1309 m, 1225 m(br), 1210 m, 1130 m(br), 1075 w, 1055 s, 990 w, 815 w, 790 w, 761 s, 723 m, 609 s(br) in CS_2 and CCl_4 .

NMR spectrum (in 0.6 ml CD_2Cl_2 plus 0.075 ml TMS at 25°): pyrazolyl protons, 1.40(d, 1), 2.21(d, 2), 2.47(d, 2), 2.55(d, 1), 3.71 (t, 1), 3.83(t, 2). The C_7H_7 ring appears as a broad peak, 0.58 ppm wide at half height, at τ 5.20. At -42° the C_7H_7 resonances are 4.48(dd, 2), 4.87(t, 2), 5.41(dt, 1), 6.02(c, 2). In 0.6 ml toluene- d^8 at 83° the C_7H_7 resonance is a sharp peak (0.02 ppm wide) at τ 5.50.

$[HB(3,5-Me_2Pz)_3](C_7H_7)(CO)_2Mo \cdot Fe(CO)_3$, (III'). The preparation was the same as in the two preceding cases. The product was recrystallized from CH_2Cl_2 /

* Pz = pyrazolyl.

hexane solution. It decomposed at 195° under nitrogen. (Found: C, 48.0; H, 4.31; N, 12.5. Mol. wt., 700. $\text{BC}_{27}\text{H}_{29}\text{H}_{29}\text{FeMoN}_6\text{O}_5$ calcd.: C, 47.65; H, 4.26; N, 12.35%. Mol. wt., 680).

Infrared spectrum (cm^{-1}): ν_{CO} , 2040 s, 1979 s, 1970 s, 1925 s, 1842 s, in cyclohexane. $\nu_{\text{B-H}}$, 2520 w. Other bands, 2985 w, 2960 w, 2927 w, 1440 m, 1420 m, 1380 m, 1210 s(br), 1080 m, 1070 m, 1043 m, 987 w, 825 w, 783 s, 694 w, 630 m, 609 s(br).

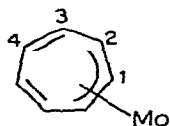
NMR spectrum (in 0.6 ml CD_2Cl_2 plus 0.075 ml TMS at 25°): Pyrazolyl protons, 3.70(s, 2), 3.79(s, 1). Methyl protons, 6.59(s, 3), 6.97(s, 6), 7.21(s, 6), 7.48(s, 3). The C_7H_7 ring appears as a sharp singlet (0.02 ppm wide) at τ 4.76. At -114° the C_7H_7 resonances are 3.91(dd, 2), 4.53(1), 5.16(t, 2), 5.59(c, 2). The chemical shifts of the methyl groups are very sensitive to the solvent used.

RESULTS AND DISCUSSION

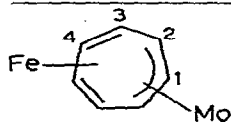
The infrared and NMR data have been given for individual compounds in the preparative section. NMR data for the C_7H_7 rings are summarized, assigned and compared with data for other compounds in Table 1. The infrared spectra in the

TABLE I

PROTON RESONANCES IN C_7H_7 METAL COMPLEXES



Compound	$\tau(H_1)$	$\tau(H_2)$	$\tau(H_3)$	$\tau(H_4)$	Ref.
$(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)(\text{CO})_2\text{Mo}$	7.68	5.41	3.50	4.60	11
$(\text{C}_7\text{H}_7)(\text{CO})_3\text{Co}$	6.50	5.15	≈ 3.5	4.20	7
$(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)(\text{CO})\text{Fe}$	6.92	5.25	3.90	4.85	6
(I)	8.66	5.26	3.16	4.24	^a
(II)	8.85	4.74	3.04	4.25	^a
(III)	^b	5.18	3.35	4.32	^a
(IV)	^b	5.00	4.20	4.75	^a



Compound	$\tau(H_1)$	$\tau(H_2)$	$\tau(H_3)$	$\tau(H_4)$	Ref.
$(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)(\text{CO})_2\text{Mo} \cdot \text{Fe}(\text{CO})_3$	5.02	5.50	6.17	4.60	9
(I')	5.29 ^c	4.82 ^c	5.95	4.20	^a
(II')	5.41 ^c	4.87 ^c	6.02	4.48	^a
(III')	4.53	5.16	5.59	3.91	^a

^a This work; solvent was $\text{CD}_2\text{Cl}_2/\text{TMS}$, assignment was made by comparison to Refs. 4, 6, 7 and 11. ^b This peak occurs in the CH_3 region and was not located. ^c Note that the relative shifts of the 2 and 3 protons have been reversed.

carbonyl region of the four $\text{Fe}(\text{CO})_3$ adducts have similar patterns of five bands, consistent with the presence of uncoupled $\text{M}(\text{CO})_3$ and $\text{M}'(\text{CO})_2$ systems. These patterns are very similar to that observed for $(h^5\text{-C}_5\text{H}_5)(h^3\text{-C}_7\text{H}_7)(\text{CO})_2\text{Mo}\cdot\text{Fe}(\text{CO})_3$ ⁹. Coordination of an $\text{Fe}(\text{CO})_3$ group to the C_7H_7 ring does not necessarily preclude the occurrence of conformers of the $\text{C}_7\text{H}_7\cdot\text{Fe}(\text{CO})_3$ unit with respect to the rest of the molecule. However, the spectra of the $\text{Fe}(\text{CO})_3$ adducts in the carbonyl region, examined in cyclohexane, CS_2 and CCl_4 , showed no splitting, and it appears that only a single conformer is present in each case.

The NMR spectra of the four compounds (I)–(IV) are fundamentally similar to each other. The pyrazole rings are found to exist in the ratio 2/1 for (II) and (III), 1/1 for (IV) and in the ratio 2/1/1 for (I), as reported previously¹. The C_7H_7 ring in these compounds is dynamic showing only a single proton resonance at room temperature. When the samples are cooled, this resonance broadens, collapses and eventually the resonances due to the C_7H_7 ring appear in a more complicated pattern. The resonances due to the C_7H_7 ring appear in a more complicated pattern. The resonances due to pyrazolyl protons and methyl groups do not change as the temperature is lowered. The low temperature spectra of the C_7H_7 rings are very similar to those for the $h^3\text{-C}_7\text{H}_7$ rings known to exist in $(h^5\text{-C}_5\text{H}_5)(h^3\text{-C}_7\text{H}_7)(\text{CO})_2\text{Mo}$ ¹¹, $(h^3\text{-C}_7\text{H}_7)(\text{CO})_3\text{Co}$ ⁷, and $(h^5\text{-C}_5\text{H}_5)(h^3\text{-C}_7\text{H}_7)(\text{CO})\text{Fe}$ ⁶, but different from the spectrum of the $h^5\text{-C}_7\text{H}_7$ ring in $(h^5\text{-C}_7\text{H}_7)(\text{CO})_3\text{Mn}$ ⁸ (Table 1).

Coordination of an $\text{Fe}(\text{CO})_3$ group to the C_7H_7 ring results in substantial changes in the rate of the C_7H_7 "ring whizzing". The basic pattern of pyrazolyl proton and methyl resonances does not change. However, while for (I)–(IV) the C_7H_7 appears as a single sharp peak at room temperature, for (I'), (II') and (IV') the ring resonance is very broad at room temperature. The compounds must be heated to 85° before the C_7H_7 ring becomes a sharp peak. The ring in (III') is similarly affected with respect to (III) as shown by its collapse at a much higher temperature. Cooling the $\text{Fe}(\text{CO})_3$ adducts results in collapse and reappearance of the resonances due to the C_7H_7 ring at much higher temperatures than for the parent compounds. The low temperature limiting pattern of the $\text{Fe}(\text{CO})_3$ adducts is much different from that of the parent compounds. The peak of intensity 1 which in the parent compounds appears in the region τ 8–9 now appears in the region τ 4–6, along with the other ring resonances. This shift and the general pattern of splittings is very similar to that observed for $(h^5\text{-C}_5\text{H}_5)(h^3\text{-C}_7\text{H}_7)(\text{CO})_2\text{Mo}\cdot\text{Fe}(\text{CO})_3$ ⁹ (Table 1).

Evidence for *trihapto*- C_7H_7 rings in compounds (I)–(IV) is provided by the synthesis of the $\text{Fe}(\text{CO})_3$ derivatives and the PMR data. These compounds and the similarity of their fluxional behavior to that of $(h^5\text{-C}_5\text{H}_5)(h^3\text{-C}_7\text{H}_7)(\text{CO})_2\text{Mo}\cdot\text{Fe}(\text{CO})_3$ constitute strong evidence for *trihapto* bonding. It would appear that the reaction resulting in the addition of $\text{Fe}(\text{CO})_3$ to a *trihapto* ring may be quite general and useful in structure determination provided that the complex can endure the reaction conditions.

The similarity in the fluxional behavior of (I)–(IV) to other *trihapto* C_7H_7 rings supports a *trihapto* formulation. A detailed line-shape analysis was not carried out, but other studies^{6,9,11} have led to the conclusion that proton averaging takes place by a sequence of 1,2 shifts. Visual comparison of line shapes of the variable temperature NMR data of (I)–(IV) and their $\text{Fe}(\text{CO})_3$ adducts to published data show no qualitative difference and suggest that 1,2 shifts are operative here as they are in

many fluxional olefin-metal complexes¹².

The compounds (I')-(IV') are additional examples of the class in which separate metal moieties are bound to different parts of the π electron system of one cyclic polyene. A correlation has been suggested¹⁰ that relates the degree of overlap between the π orbital systems bonded to each metal to the stereochemical nonrigidity of the polyene. The overlap is significant in $(h^5-C_5H_5)(h^3-C_7H_7)(CO)_2Mo \cdot Fe(CO)_3$ and the molecule is fluxional, whereas the overlap is small in *trans*- $C_8H_8[Fe(CO)_3]_2$ and it is not fluxional¹⁰. The NMR studies on the $Fe(CO)_3$ adducts of (I)-(IV) show their similarity with $(h^5-C_5H_5)(h^3-C_7H_7)(CO)_2Mo \cdot Fe(CO)_3$. The faster rate of rearrangement of the C_7H_7 rings in (I)-(IV) compared to the $Fe(CO)_3$ compounds is probably due to a decrease in overlap between the π orbital systems of the allyl and butadiene portions of the ring in the latter compounds.

One point of interest is the faster rate of fluxional behavior of (III) and (III') compared to (I), (II), (IV), (I'), (II') and (IV'). A spectrum for (III) in the slow exchange limit was never obtained while for (I), (II) and (IV) this was done relatively easily. The same trend held for the $Fe(CO)_3$ derivatives (I') and (II'). It is not clear why the C_7H_7 rings in (III) and (III') should encounter less of a barrier to "whizzing" as compared to the others. It is possible that the bulky methyl groups in (III) might cause the ring to be less securely bound and provide a sort of steric acceleration. This is especially true if, as has been suggested¹¹, the intermediate in the 1,2 shift process has a *monohapto* bonding mode.

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