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Preliminary communication

METALATION REACTIONS

VI*. METALATION OF SUBSTITUTED FERROCENES WITH METHYLPENTACARBONYL-MANGANESE AND -RHENIUM; FORMATION OF HOMOANNULAR METALATED FERROCENES AND OF THE NOVEL FERROCENYLMETHYL(METHYL)AMINOMETHYLENETETRACARBONYLMANGANESE

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Summary

The isolation and characterization of tetracarbonyl-2-(acetyl)ferrocenylrhenium and tetracarbonyl-2-(acetyl)ferrocenylmanganese from the reaction of acetylferrocene with methylpentacarbonylrhenium (Ia) and -manganese (Ib) respectively, are reported. In addition tetracarbonyl-2-(dimethylaminomethyl)ferrocenylrhenium has been prepared from dimethylaminomethylferrocene (IV) and Ia, but treatment of IV with Ib results in formation of the novel ferrocenylmethyl(methyl)aminomethylenetetracarbonylmanganese.

Recent report of the palladation of thioacetylferrocene [2] prompts us to communicate results of our studies of the reaction of substituted ferrocenes with $CH_3M(CO)_5$, (Ia, M = Re; Ib, M = Mn) following earlier observations of the metalation of functionalized aromatic rings [3] with these reagents. We find that acetylferrocene (II) is metalated in refluxing hydrocarbons resulting in the formation of the homoannular metalation products IIIa and IIIb*** each in 40 % yield. The reaction with dimethylaminomethylferrocene (IV) however, gave contrasting results. With Ia the homoannular metalation product V is produced in 50 % yield but with Ib, we obtain a product in which an alternative metalation path is observed, as discussed below.

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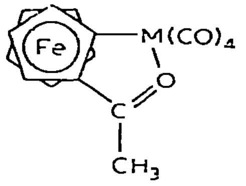
[*] For part V see ref. 1.

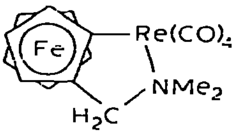
[**] Contribution no. 3421.

[***] Mass spectra of IIIa, IIIb, V and VI exhibit *m/e* appropriate to the parent ion peak. Carbon and hydrogen microanalyses of IIIb, V and VI are acceptable for the assigned molecular formulas.



(IIIa) M = Re

(IIIb) M = Mn



(V)

The properties of the crystalline compounds synthesized in this work are summarized in Table 1.

Upon exposure to air, solutions of these compounds decompose overnight; solids are more resistant to decomposition, yielding some insoluble material after a few days exposure to air. Decomposition also occurs during chromatography on silica gel, Florisil or active alumina. Reaction mixtures can be purified, however, by chromatography on activity V neutral alumina* (15 % H_2O) and compounds are recrystallized from hexane (IIIa, IIIb and VI) or ether/hexane (V).

The spectroscopic data confirm the structures assigned to IIIa, IIIb and V. Each of these compounds have four terminal metal—carbonyl stretching frequencies as expected (see Table 1). The IR spectra of IIIa and IIIb also show a fairly intense absorption attributable to the stretching mode of the coordinated acyl group [4] at 1530 cm^{-1}. NMR spectra** of IIIa, IIIb and V

TABLE 1

DATA FOR METALATION PRODUCTS[a]

Compound	Color	ν(CO) (cm^{-1})[b]	ν(C=O—M)[c] (cm^{-1})	Melting range[d] (°C)
IIIa	Purple	2092 m, 1986 s, 1976 s, 1939 s	1530	127.5—129.5
IIIb	Red	2060 m, 1994 s, 1986 s, 1947 s	1530	126 —127.5
V	Red-orange	2084 m, 1978 s, 1968 s, 1933 s	—	117 —118.5
VI	Orange	2055 m, 1975 m, 1944 vs, 1936 s	—	107.5—110

[a] The molar ratio of reactants, solvent, reaction temperature, and time for preparation of each of these compounds are given as follows: for IIIa, Ia + II (1/1) decane, 180°, 2 h; for IIIb, Ib + II (3/1) heptane, 98—99°, 1.8 h; for V, Ia + IV (1/1) octane, 126°, 2.3 h; and for VI, Ib + IV (1/1) heptane, 98-99°, 5.3 h. [b] Cyclohexane solution, Beckman IR-4. [c] KBr mull, Perkin—Elmer 421. [d] Uncorrected in capillary sealed under vacuum.

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*Since acetylferrocene darkens on an activity V neutral alumina column when exposed to daylight, the reaction mixtures containing IIIa and IIIb are chromatographed in dim light.

** NMR spectra were recorded on a Varian A60D spectrometer in benzene-d_6 with tetramethylsilane as internal reference as follows (s, singlet; q, quartet; m, multiplet): for IIIa, τ 5.25m, 5.45 m, 5.68m (combined area 3.1), τ 6.11s (5.0), 8.15s (2.9); for IIIb, τ 5.07m, 5.35m, 5.52m (combined area 2.9), τ 6.00s (5.1), 8.18s (3.1): for V, τ 5.88 (apparent singlet), 5.92 (much more intense singlet) (combined areas 9.0), τ 6.90q (*J*(*gem*-H—H) 13.5 Hz), τ 7.50s (combined areas 5.1), τ 8.50s (2.9).

all show resonances between τ 5 and 6.1 for the cyclopentadienyl rings in total relative area of eight confirming the loss of a cyclopentadienyl proton through the metalation of the respective ferrocene starting materials. The appearance of a sharp singlet at τ 6.05 to 6.00 in each spectrum indicates an unsubstituted cyclopentadienyl ring from which we deduce that metalation has occurred on the functionalized ring.

As mentioned above, an alternative path is observed in the reaction of Ib with IV. An orange crystalline solid VI is isolated in 35 % yield. Carbon and hydrogen analysis and mass spectral data indicate the molecular formula $C_{17}H_{16}NO_4FeMn$. The proton NMR spectrum of VI is shown in Fig.1. From the relative intensity of nine of the resonances in the region τ 5.7 to 6.3, we observe that the nine hydrogen atoms of the original metallocene are still present. The sharp singlet at τ 6.18 is due to the unsubstituted ring (C_5H_5) while the three multiplets centered at τ 5.78, 6.06 and 6.28 represent the protons on the functionalized ring (C_5H_4) whose chemical shifts differ as a result of the asymmetric nitrogen center. This latter is also responsible for the *AB* quartet centered at τ 7.00 (rel. intensity 2.1, *J*(*gem*-H—H) 13.5 Hz) assigned to the methylene group connecting the C_5H_4 ring to the nitrogen atom. The spectrum also displays two doublets (τ 7.67, 7.86 *J*(*gem*-H—H) 2 Hz) each of area one and a singlet (τ 8.14, rel. intensity 3.0) attributable to one remaining methyl group of the two formerly on nitrogen. On the basis of these assignments we are led to the inescapable conclusion that a methyl group on nitrogen has been metalated while both metallocene rings remain as in the starting material.

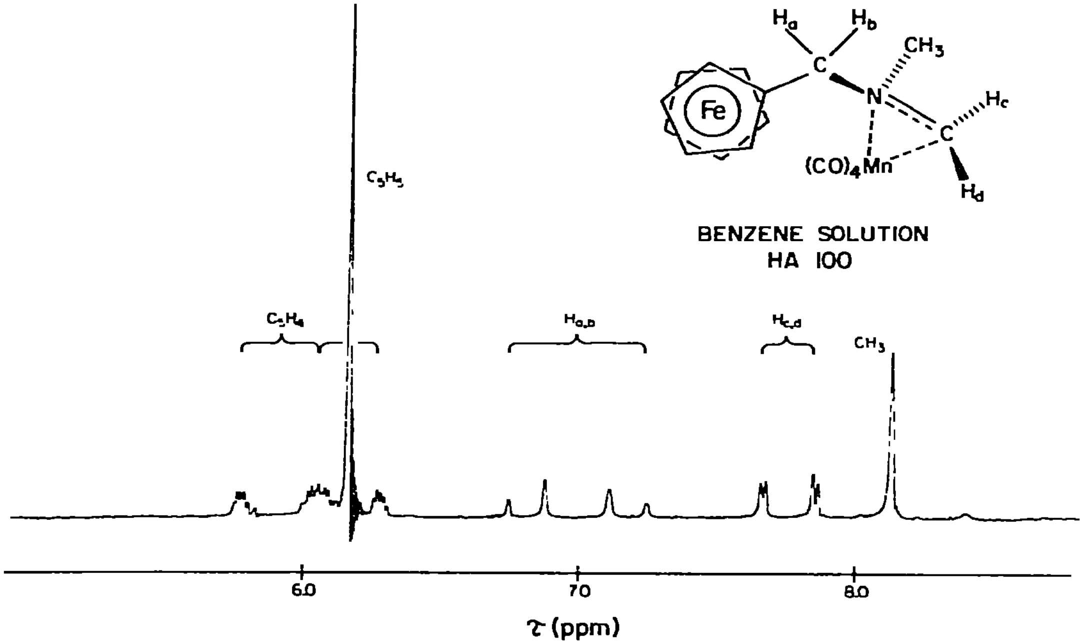

Fig. 1. Proton NMR spectrum of ferrocenylmethyl(methyl)aminomethylenetetracarbonylmanganese (VI) in benzene solution; 100 Mc, TMS internal reference. See text for discussion of the assignments.

Precedent for the type of structure shown in Fig.1 has been established in the complex $\overline{\mathrm{CH_2CH_2NCH_2M}}\mathrm{n(CO)_4}$ obtained from the reaction of $\overline{\mathrm{CH_2CH_2N}}\mathrm{CH_2SnR_3}$ with $\mathrm{MnBr(CO)_5}$ [5]. The dimethylamino analogue $\mathrm{Me_2}\overline{\mathrm{NCH_2M}}\mathrm{n(CO)_4}$ (VIII) may be obtained in like manner as an orange liquid from $\mathrm{Me_2NCH_2Sn(n\text{-}Bu)_3}$ and $\mathrm{BrMn(CO)_5}$ [5]. The IR spectrum of VI (see Table 1) shows a pattern for the carbonyl stretching absorptions remarkably similar to that of VIII (ν(CO), cyclohexane solution, Beckman IR-4, 2058 m 1967 m 1951 vs 1937 s $\mathrm{cm^{-1}}$). The carbonyl absorption patterns for VI and VIII, however, differ significantly from those of the other derivatives shown in Table 1. Proton NMR of VIII consists of two singlets τ 7.97 and 8.04, of relative areas 2/6. Thus in both VI and VIII the resonances of the hydrogens of the metal-bonded $\mathrm{CH_2}$ group occur at lower field than that of the $\mathrm{CH_3}$ group on nitrogen. A second example of a dialkylaminomethylene group coordinated to a metal has recently been reported by Matsumoto et al. [6] and metalation of a methyl group on coordinated phosphorus has been reported earlier [7a] and recently confirmed by structure determination [7b]. Thus our observation of a metalated methyl group on nitrogen is not unique but remarkable in view of its formation in competition with potential metalation of metallocene rings also available to the metal center. Indeed the reaction of dimethylbenzylamine with Ib in refluxing octane leads to the more common metalation of the aromatic ring in the product $\mathrm{(CO)_4}\overline{\mathrm{MnC_6H_4CH_2N}}\mathrm{Me_2}$ whose structure has also been determined [8]. Further investigation of these reactions is in progress.

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