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THE LITHIUM ALUMINIUM HYDRIDE REDUCTION OF CYCLOHEXADIENYLMANGANESE COMPLEXES

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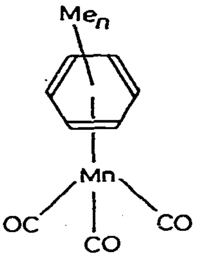
Summary

Reduction of cyclohexadienyltricarbonylmanganese or its ring-substituted derivatives with lithium aluminium hydride leads to dihydro-derivatives. Preparative and NMR spectral information is presented and interpreted on the basis of the C—H-bridged cyclohexenyl structure recently established for these products by Lamanna and Brookhart [3].

Introduction

In 1977 we reported [1] that the long known reduction of arenetricarbonylmanganese cations (I) by lithium aluminium hydride results not only in the formation of the cyclohexadienyl complexes (II; R = H) by ring attack, but also competitive attack at a carbonyl group leading to arene(methyl)dicarbonylmanganese complexes. We mentioned that a third type of product results from



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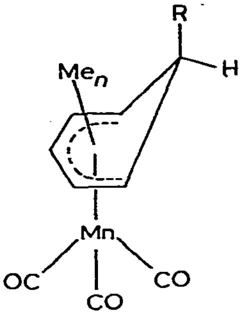

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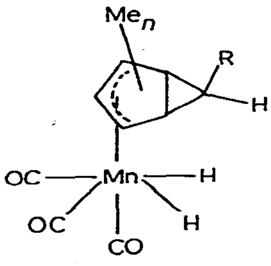

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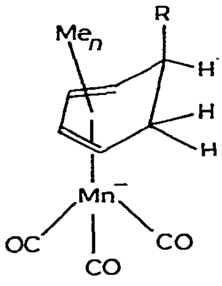

(IV)

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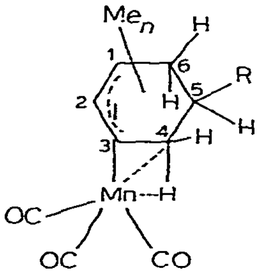
further hydride addition to the cyclohexadienyl compound. Since these additional, oily products give high field ^{1}H NMR signals (near δ —6 ppm) at room temperature and below, corresponding to two H atoms, we regarded them as dihydridomanganese complexes and in a subsequent review [2] our tentative formulation (III) was mentioned, together with the structure (IV) for the initial hydride adduct.

Results and discussion

Whereas the latter structure is apparently correct, Brookhart et al. [3], who have isolated salts of this anion (IV; R = H), have now shown that its protonation leads to the metal—carbon H-bridged structure V, i.e. that this rather than III is the correct structure for our supposed dihydride. Several difficulties in our formulation immediately disappear—notably the lack of obvious hydridic behaviour and the improbability of ring closure on protonation of the anion IV. As pointed out by Lamanna and Brookhart [3] there are few previous examples of such strong C—H bonding to a metal *. Moreover the static structure V should have only a 1 H signal at high field and indeed does so [3] near δ —13 ppm. They have, however, shown that exchange between positions 4 and 6 (in V) is so facile ($\Delta G^{\ddagger}$ = 8.5 kcal mol^{-1}) that in the temperature range studied by us (above —50°C) the *endo* hydrogens at these positions give a single, averaged signal. The higher energy process, probably involving the discrete hydride (VI; *R = H; n = 0 in the case of the parent compound*) as intermediate, which equilibrates all three *endo*-H atoms and simultaneously equilibrates the remaining H pool was observed by us and occurs with all the compounds studied, i.e. not only where R = H, *n* = 0 and deuterium-labelled analogues, but also R = Ph, *n* = 0 and R = H, *n* = 3.



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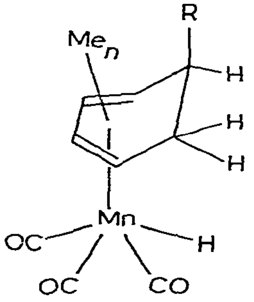

(VI)

The Experimental section includes preparative details for the above-mentioned as well as the *exo*-methyl H-bridged cyclohexenyl complexes (V; R = Me; *n* = 0 and *n* = 3) and such details of the NMR spectra as are additional to the spectra recorded by Lamanna and Brookhart [3], whose results are in excellent agreement with ours.

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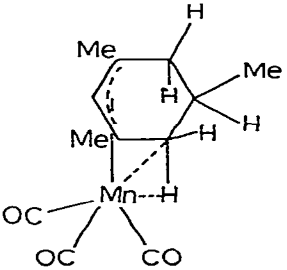
* The remarkably similar NMR characteristics of (1,3-cyclooctadiene)tris(trifluorophosphine)-chromium described by Blackborow et al. [5] suggest that it is another new example.

The equilibration between structures V and VI allows isomerisation, e.g. of the two possible mesitylene-derived reduction products VII and VIII. The ^1H NMR spectra in this case suggest that the former isomer is preferred although variable amounts (up to 25%) of isomer VIII may be present, depending on the conditions used.

The hydride reduction product of (6-*exo*-phenylcyclohexadienyl)tricarbonylmanganese (II; R = Ph; $n = 0$) gives rise to very complex spectra with approximately equally intense $H(4,6)_{endo}$ signals near δ —1.6, —5.8 and —9.8 ppm, suggesting that at least three of the four possible isomers are present [*endo*-H addition ensures that the phenyl group in this and methyl groups in the preceding case cannot occupy *endo* positions]. The wide separation of these $H(4,6)_{endo}$ signals is remarkable *.

The same equilibration results, on heating, in the reversible collapse of all the proton signals of the parent compound (V; R = H; $n = 0$) into two broad singlets (at 110°C, ratio 2 : 1) the smaller signal at approximately δ —3.88 ppm (in $C_6D_5CD_3$) corresponding to the three *endo* protons and the other (δ ~2.47 ppm) to the remaining six protons. When the hexadeuteriobenzene complex $[(C_6D_6)Mn(CO)_3]^+$ is reduced with first hydride, yielding (6-*exo*-protiohexadeuteriocyclohexadienyl)tricarbonylmanganese (II; $n = 0$; R = H; all other H replaced by D) then with $LiAlD_4$ and quenched with D_2O, the spectrum of the product as expected lacks signals corresponding to the *endo*-protons, but the single '*exo*-proton' is distributed over the remaining positions: 1(3), 2,4(6)-*exo* and 5-*exo* which therefore each give singlets in the ^1H NMR spectrum.



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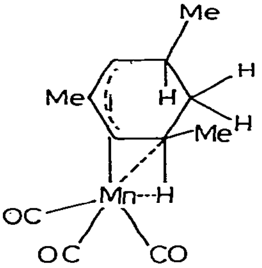

(VIII)

Introduction of a single deuterium atom into the *endo*-pool was accomplished by reduction of the cyclohexadienyl complex (II; R = H, $n = 0$) with $LiAlH_4$ and quenching with D_2O. This resulted in two signals for $H(4,6)_{endo}$. Since the D atom must remain in the *endo*-position, three isomers (IX; a—c) should be in equilibrium. Isomer (a) should differ little from the protio analogue and must account for the signal (δ —6.17 ppm in $C_6D_5CD_3$) at the 'normal' position. However, if the isotope effect makes (c) less favourable than (b) the 'hydride' charac-

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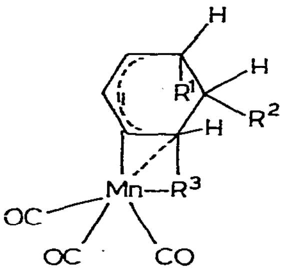
* Dr. M. Brookhart has kindly suggested that these three signals correspond to only two of the isomers. The "normal" signal at δ — 5.8 ppm would be due to the 2-phenyl-substituted complex in which $H(4)_{endo}$ and $H(6)_{endo}$ protons are equivalent; the other two signals arise from the 1-phenyl derivative where they are not equivalent (cf. isomers IX below). The peak ratios would indicate an approx. 1:2 ratio of these two isomers and in agreement with Brookhart's more detailed (unpublished) results on the methyl-substituted analogues, the remaining isomers would be present in such small proportions that our failure to resolve their signals is not surprising. (Added: Aug. 1981)



(IX)

a. $R^1 = R^3 = H$; $R^2 = D$
b. $R^2 = R^3 = H$; $R^1 = D$
c. $R^1 = R^2 = H$; $R^3 = D$

ter of the Mn-bonded H(4) will be increased and structure (b) provides a plausible explanation for the additional signal at δ —7.35 ppm.

Hydride addition to the cyclohexadienylmanganese complexes II is the only addition of this nucleophile to such a neutral complex known to us. In our hands it failed with the hexamethyl derivative (II; R = Me; $n = 5$) and with cycloheptadienyltricarbonylmanganese as well as with various other neutral complexes, including cyclohexadienylcyclopentadienyliron and benzenetricarbonylchromium. The last readily adds many carbon nucleophiles, but our attempts to add some of these to the manganese compounds II were equally unsuccessful.

The trimethyl substituted complex (VII and/or VIII) gave the isomer II (R = Me; $n = 2$) of the initial trimethylcyclohexadienyl complex (II; R = H; $n = 3$) on treatment with triphenylmethyl hexafluorophosphate, but the parent cyclohexenyl complex (V; R = H; $n = 0$) gave an unstable product which was not characterised.

Experimental

η^{1-3}-Cyclohexenyltricarbonylmanganese (V; R = H; $n = 0$)

Lithium aluminium hydride (0.4 g) was added under nitrogen to a stirred solution of cyclohexadienyltricarbonylmanganese (0.4 g) in tetrahydrofuran (40 cm^3). After 3 h, water (4 cm^3) was added dropwise and the solvent removed under reduced pressure. The residue was extracted with light petroleum (b.p. 40—60°C; 3 × 50 cm^3), the extracts dried ($MgSO_4$) and concentrated. Distillation at approx. 80°C/0.3 Torr yielded η^{1-3}-cyclohexenyltricarbonylmanganese (V; R = H; n = 0) as a very pale yellow oil (0.25 g; 62%). Its ^1H NMR spectrum (in $C_6D_5CD_3$ at −10°C) showed peaks at δ 4.47 (1 H, t, H(2)), 4.02 (2 H, m, H(1,3)) 0.88 (2 H, br. d. (centres at 0.96,0.80), $H(4,6)_{exo}$), 0.17 (1 H, m, $H(5)_{endo}$), —0.09 (1 H, m, $H(5)_{exo}$) and —6.18 ppm (2 H, m, $H(4,6)_{endo}$). Its ^{13}C NMR spectrum (proton decoupled) showed peaks due to the ring carbons (in $C_6D_5CD_3$ at −30°C) at δ 93.7 (C(2)), 69.4 (C(1,3)), 20.3 (C(4,6)) and 16.6 ppm (C(5)). (Found: C, 49.2; H, 4.3%; *M*, 219.9929. $C_9H_9MnO_3$ calcd.: C, 49.1; H, 4.1%; *M*, 219.9933).

Reduction of benzenetricarbonylmanganese hexafluorophosphate (I; $n = 0$)

(3 g) with lithium aluminium hydride (1 g) under the same conditions gave the same product (0.5 g, 27%).

Three deuteriated derivatives were made by the same procedure using: (a) Hexadeuteriobenzenetricarbonylmanganese [4] (0.9 g) which was reduced with lithium aluminium deuteride (80 mg) in tetrahydrofuran (3.0 cm^3) to yield heptadeuteriocyclohexadienyltricarbonylmanganese (0.3 g, 55%), ν(CO) (CCl_4) 2019, 1942 and 1933 cm^{-1}. Further reduction with lithium aluminium hydride and workup using H_2O then gave the heptadeuteriocyclohexenyl complex (V; $n = 0$) with both hydrogen atoms in the '*endo*'-pool. (b) Similarly, 1,2,3,4,5,6-*endo*-hexadeuteriocyclohexadienyltricarbonylmanganese [4] reduced with $LiAlD_4$ followed by workup using D_2O yielded the complex V($n = 0$) with the single ^1H atom confined to the '*exo*'-pool. (c) Lithium aluminium hydride (0.4 g) reduction of cyclohexadienyltricarbonylmanganese (II; R = H; $n = 0$) (0.4 g) in tetrahydrofuran (40 cm^3) followed after 3 h by workup using D_2O (4 cm^3) yielded the complex IX (0.2 g, 40%) with 1—1.5 deuterium atoms in the '*endo*'-pool.

(2,4,6-(and 1,3,5-)Trimethylcyclohexenyl)tricarbonylmanganese (VII and VIII).

Reduction of 1,3,5-trimethylcyclohexadienyltricarbonylmanganese (II; R = H; $n = 3$) (0.5 g) with lithium aluminium hydride, carried out as described for the unsubstituted complex, yielded the cyclohexenyl complex (0.32 g; 64%) as an oil, b.p. 140°C (bath)/0.01 Torr (Found: C, 55.3; H, 5.9; *M*, 262.0407. $C_{12}H_{15}MnO_3$ calcd.: C, 55.0; H, 5.8% ; *M*, 262.0402). The major component is regarded as VII on the basis of singlets in the ^1H NMR spectrum near δ 4.60 (in $(CD_3)_2CO$ at 0°C) or 4.42 ppm (in $C_6D_5CD_3$ at −20°C) attributed to H(2); its $H(4,6)_{endo}$ protons give a broad signal centred near $\delta -6.02$ ppm. Presence of isomer VIII is suggested by a second but much weaker high-field signal ($\delta -7.20$ ppm in $C_6D_5CD_3$ at −20°C) and the complexity of the low-temperature spectra.

(2,4,6-exo-Trimethylcyclohexadienyl)tricarbonylmanganese (II; R = Me; n = 2)

The preceding complex (VII and/or VIII) (200 mg) was added to a stirred solution of triphenylmethyl hexafluorophosphate (0.5 g) in dichloromethane. After 15 min the solvent was removed, the residue extracted with light petroleum (3 × 30 cm^3) and the extract chromatographed on alumina. The same solvent eluted (2,4,6-*exo*-trimethylcyclohexadienyl)tricarbonylmanganese (II; R = Me, $n = 2$) (70 mg, 35%) which crystallised on concentrating the solution and cooling to −78°C; m.p. approximately 20°C; ν(CO) (C_6H_{12}) 2016, 1943 and 1931 cm^{-1}; $\delta(CS_2)$ 5.5 (1 H, s, H(3)), 3.0 (2 H, d, H(1,5)), 2.55 (1 H, m, $H(6)_{endo}$), 1.8 (6 H, s, CH_3 at 2,4) and 9.6 ppm (3 H, d, CH_3 at 6-*exo*); (Found: C, 55.6; H, 5.1; *M*, 260.0244. $C_{12}H_{13}MnO_3$ calcd.: C, 55.4; H, 5.0%; *M*, 260.0245).

(5-exo-Methylcyclohexenyl)tricarbonylmanganese (V; R = Me; n = 0)

Lithium aluminium hydride reduction of (6-*exo*-methylcyclohexadienyl)tricarbonylmanganese (II; R = Me; $n = 0$) (0.5 g), as described for the parent complex (II; R = H; $n = 0$) yielded (5-*exo*-methylcyclohexenyl)tricarbonylmanganese (0.25 g, 50%) as a distillable oil (Found: C, 51.5; H, 4.7; M, 234.0082. $C_{10}H_{11}MnO_3$ calcd.: C, 51.3; H, 4.7%; *M*, 234.0089). Its ^1H NMR spectrum was complex and poorly resolved with the principal $H(4,6)_{endo}$ peak at $\delta -5.75$ ppm (in $C_6D_5CD_3$).

(5-exo-Phenylcyclohexenyl)tricarbonylmanganese (V; R = Ph; n = 0)

Lithium aluminium hydride (0.5 g) in tetrahydrofuran (40 cm^3) was employed in the same manner to reduce (6-*exo*-phenylcyclohexadienyl)tricarbonylmanganese (II; R = Ph; n = 0) (0.5 g), yielding a mixture probably containing at least three of the tautomeric 1-, 2-, 4-*exo*- and 5-*exo*-phenylcyclohexenyl complexes (e.g. V; R = Ph; n = 0). Distillation at 140°C/0.01 Torr gave a very pale yellow oil (0.2 g, 40%) whose complex ^{1}H NMR spectrum ($C_6D_5CD_3$ at room temperature) included $H(4,6)_{endo}$ peaks near δ —1.6, —5.8 and —9.8 ppm.

Reduction of (1,3,5,6-exo-tetramethylcyclohexadienyl)tricarbonylmanganese (II; R = Me; n = 3).

This was carried out similarly using the complex (II; R = Me; n = 3) (0.5 g) and yielded, after distillation 0.27 g (54%) of the corresponding cyclohexenyl complex. As in the preceding cases, the ^{1}H NMR spectra indicated that this is a mixture of tautomers (Found: C, 56.4; H, 6.2; *M*, 276.0561. $C_{13}H_{17}MnO_3$ calcd.: C, 56.5; H, 6.2%; *M*, 276.0559).

Acknowledgements

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