

Synthesis and Protonation of Cyclohexadienyl Manganese Acylmetallates; Alkyl and Aryl Group Transfer from an Acyl to a Dienyl Ligand

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Reaction of the cyclohexadienyl complex $[(\eta^5\text{-C}_6\text{H}_7)\text{Mn}(\text{CO})_3]$ (**1**) with RLi gives the acylmetallates $[\text{Li}(\text{OEt}_2)][(\eta^5\text{-C}_6\text{H}_7)\text{Mn}(\text{CO})_2\{\text{O}\}\text{R}]$ (**2a,b**) ($\text{R} = \text{Me, Ph}$) in 80–90% isolated yield, which, following protonation with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, undergo aryl or alkyl group transfer to the cyclohexadienyl ring; the products are new cyclohexenyl complexes $[(\eta^4\text{-C}_6\text{H}_8\text{R})\text{Mn}(\text{CO})_3]$ (**3a,b**) that contain an agostic *endo* C–H bond and an *endo* R group.

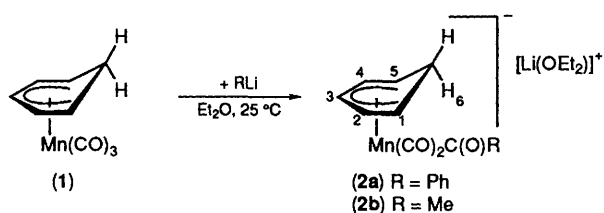
Transition metal cyclohexadienyl complexes have proved to be valuable reagents in the syntheses of a number of natural products¹ as well as in the conversion of arenes to *cis*-disubstituted cyclohexadienes.² Similarly, transition metal acyl derivatives have been utilized in many organic transformations from the formation of stable enolates³ to their use in carbonylation reactions.⁴ Surprisingly, both of these reactive ligands have not been used for carbon–carbon bond forming reactions within a single complex, owing in part to the paucity of syntheses of polyenyl–acyl complexes. We now report the syntheses of such complexes and their novel rearrangement following protonation that ultimately results in an alkyl or aryl migration to the *endo* face of the co-ordinated cyclohexadienyl ring.

The cyclohexadienyl complex $[(\eta^5\text{-C}_6\text{H}_7)\text{Mn}(\text{CO})_3]$ ⁵ (**1**), generated *via* hydride addition to $[\text{Mn}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)][\text{PF}_6]$,⁶ reacts cleanly with organolithium reagents in ether to give the acylmetallates (**2a,b**) as air-sensitive orange crystalline solids (Scheme 1). This addition proceeds in quantitative yield (IR spectroscopy), precipitating (**2**) as the $[\text{Li}(\text{OEt}_2)]^+$ salts which can be isolated in 80–90% yield for (**2a**). The new acylmetallates were characterized using ¹H and ¹³C NMR, and IR

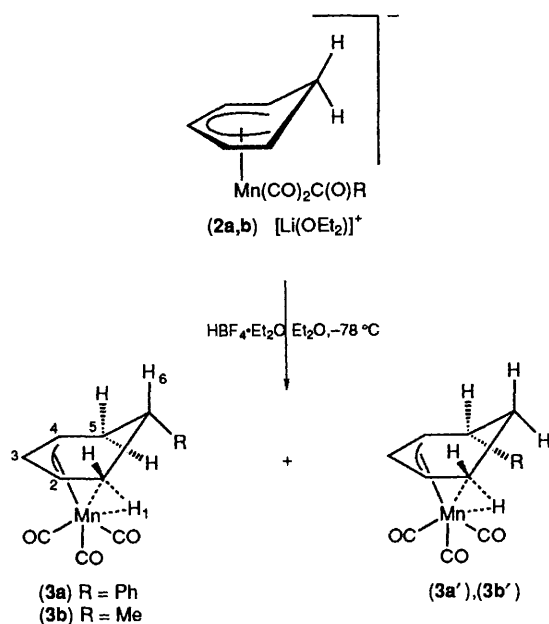
spectroscopy.[†] The alkyl- or aryl-lithium reaction with (**1**) is new despite its similarity to the well known Fischer acyl complex syntheses,⁷ and it demonstrates that carbanions can readily be added to complexes like (**1**). Previous studies have shown that only $\text{K}[\text{BHEt}_3]$ ⁸ or $\text{Li}[\text{AlH}_4]$ ⁹ effectively delivered hydride to (**1**) forming a cyclohexadiene complex $[(\eta^4\text{-C}_6\text{H}_8)\text{Mn}(\text{CO})_3]^-$.

Complexes (**2a,b**) undergo a novel reaction with proton sources. Thus, dropwise addition of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or excess of water to (**2**) results in protonation of the cyclohexadienyl ring and migration of the phenyl or methyl group from the acyl

[†] The $[\text{Li}(\text{OEt}_2)]^+$ salts of (**2**) are highly air-sensitive and repeated attempts at obtaining satisfactory elemental analyses proved unsuccessful. Representative data are as follows: (**2a**): IR (Et_2O) $\nu(\text{CO})$ 1907 and 1803 cm^{-1} ; (KBr) $\nu(\text{CO})$ 1904 and 1801 cm^{-1} , $\nu(\text{CO})$ acyl 1402 cm^{-1} ; ¹H NMR (C_6D_6) δ 0.47 [6H, br.s, $\text{O}(\text{CH}_2\text{Me})_2$], 1.69 (1H, br.s, 6-H *exo*), 2.21 (3H, br, 1-, 5-, 6-H *endo*), 2.58 [4H, br.s, $\text{O}(\text{CH}_2\text{Me})_2$], 3.86 (2H, br.s, 2-, 4-H), 5.11 (1H, br. s, 3-H), and 6.61 (5H, m, Ph); ¹³C {¹H} NMR ($[\text{C}_2\text{H}_5]_2\text{tetrahydrofuran}$; 15 °C) 16.2 (C-6), 46.3 (C-1, -5), 79.4 (C-3), 99.9 (C-2, -4), 124.4, 129.5, 156.9 (Ph), 236.6 (CO), and 318.6 (CO, acyl).



Scheme 1

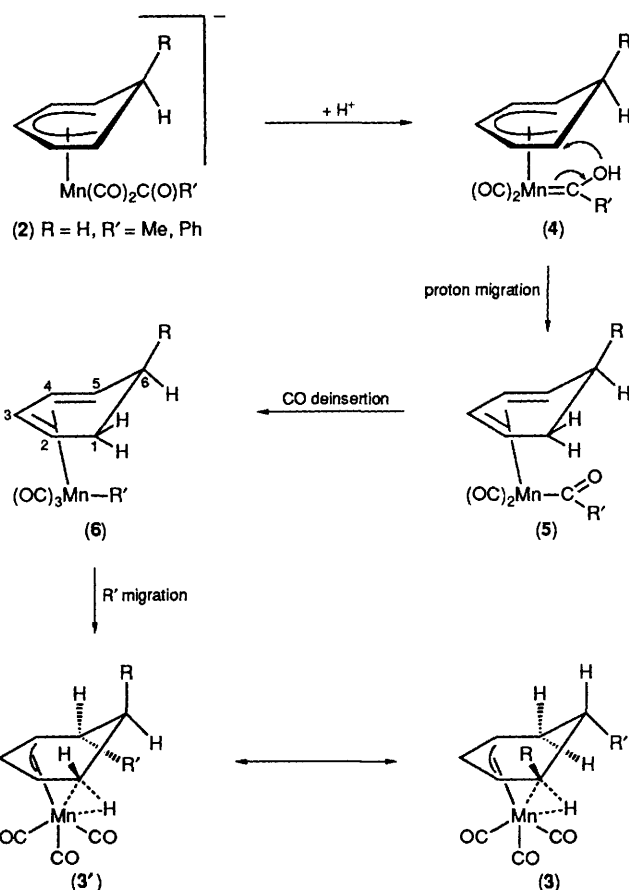


Scheme 2

ligand to the *endo* face of the ring. This remarkable transformation leads to new cyclohexenyl complexes (3) that have one agostic *endo* C–H bond (Scheme 2). When $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ is used at -78°C , and the mixture is allowed to warm slowly to room temperature, analytically pure samples of (3a) can be isolated in 85–95% yields.

Complex (3b) was characterized by comparison of its ^1H NMR spectrum with that reported by Brookhart and co-workers¹⁰ for (3b) prepared by a different route. The new agostic species (3a) was also spectroscopically characterized,[‡] and shows both ^1H and ^{13}C NMR data consistent with fluxional processes reported for (3b);¹⁰ *i.e.*, a signal at $\delta -5.72$ for 1- and 5-H as well as a small peak at $\delta -13.3$ assigned to a minor isomer (3a') (*ca.* 2%). These fluxional processes result in 1- and 5-H being equivalent and the interconversion of (3a,b) and (3a',b') via a hydride intermediate.¹⁰

The conversion of (2) to (3) is a novel transformation involving protonation of the cyclohexadienyl ring, deinsertion of the acyl CO ligand, and migration of an alkyl or aryl group to the *endo* face of the ring. We suggest this reaction proceeds as outlined in Scheme 3 with initial H^+ addition to the acyl



Scheme 3

oxygen forming a hydroxy carbene derivative (4). Similar protonation of an acyl ligand was found in the reaction of HBF_4 with $[(\text{C}_5\text{H}_5)(\text{Ph}_3\text{P})(\text{NO})\text{ReC}(\text{O})\text{Ph}]$,¹¹ and in our laboratory we have shown that alkylation of (2) with $[\text{Me}_3\text{O}][\text{BF}_4]$ at the acyl oxygen to give deep-red carbene complexes.¹² Indeed, addition of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ to (2a) at -78°C initially gives a deep-red intermediate which slowly transforms into the pale-orange (3a) upon warming to room temperature. We propose that this latter transformation proceeds *via* H transfer to the *endo* face of the ring in (4) forming a formally 16-electron diene/acyl derivative (5). This could then deinsert CO from the acyl ligand forming (6) with subsequent migration of the alkyl or aryl group to the ring giving (3') and (3).

As shown, the added proton becomes an *endo* hydrogen on C-1 or C-5, and the R' group is shown to migrate to C-5, adjacent to the methylene carbon (C-6) of intermediate (6). Alternatively R' may migrate to C-2 and, based upon this scheme, there appears no preference for migration to proceed to C-2 over C-5 or *vice versa*. To investigate both the stereochemistry of the protonation and the regiochemistry of R' migration, the following experiments were performed.

First, the perdeuterio cyclohexadienyl complex $[(\eta^5\text{-C}_6\text{D}_7)\text{Mn}(\text{CO})_3]$ (1D) was treated with PhLi then protonated to give (3a). This product contained only *endo* protons, indicating that addition of H^+ to (2) cannot occur from direct *exo* protonation to the ring, but either from initial addition to the *endo* face of the ring or to the metal and its ancillary ligands.

A second labelling experiment was performed to probe whether R' migration is 1,2 or 1,3 with respect to the *exo*

‡ Satisfactory elemental analyses were obtained for (3a); m/z 296 (M^+), 268 ($M^+ - \text{CO}$), 240 ($M^+ - 2\text{CO}$), and 212 ($M^+ - 3\text{CO}$); IR (hexane) $\nu(\text{CO})$ 2023, 1944, and 1937 cm^{-1} ; ^1H NMR (C_6D_6) $\delta -5.72$ (2H, br.s, 1-, 5-H *endo*), 1.20 (2H, d, 1-, 5-H *exo*), 1.35 (1H, m, 6-H *exo*), 4.06 (2H, s, 2-, 4-H), 4.50 (1H, dd, 3-H), and 6.80 (5H, m, Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 29.2 (C-1, -5), 34.9 (C-6), 69.2 (C-2, -4), 94.3 (C-3), 127.4 (m, Ph), 144.0 (*ipso* Ph), and 222.3 (CO).

substituent on C-6. Thus, (**3a**) was synthesized from $[(\eta^5\text{-C}_6\text{D}_6\text{H-}exo)\text{Mn}(\text{CO})_3]$ and showed a proton both 1,2 and 1,3 with respect to the phenyl group. Both the above experiments also revealed that intermolecular *endo* D-H exchange occurs, since the *endo* proton signals for labelled (**3a**) integrated to more than the 1 proton.

Earlier studies¹⁰ have demonstrated that complexes like (**3**) can be converted to cyclohexadienes following treatment with KH and O₂, and if used in conjunction with the reactions herein should lead to *trans*-disubstituted dienes that ultimately derive from the addition of two nucleophiles to an arene. These and other reactions of the new acylmetallates are currently under investigation.

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