Synthesis and Electrophilic Reactivity of Carbonylnitrosyl(cycloheptadienyl)-manganese Cations: Double Nucleophilic Addition to Cycloheptatriene

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Treatment of [(cycloheptadienyl(Mn(CO)$_2$L] (L = CO, PR$_3$) complexes with NOPF$_6$ generates [(cycloheptadienyl)Mn(CO)(NO)L]$^+$ cations that are attacked by P-, N-, H-, and C-donor nucleophiles to give functionalized cycloheptadiene complexes (**5**).

We recently described a simple procedure for the conversion of co-ordinated arenes to difunctionalized cyclohexadienes.[1] The chemistry involves nucleophilic addition to [(arene)-Mn(CO)$_3$]$^+$ to give stable [(cyclohexadienyl)Mn(CO)$_3$] complexes that are converted into [(cyclohexadienyl)Mn-(CO)$_2$NO]$^+$ cations upon treatment with NOPF$_6$. Subsequent addition of another nucleophile generates [(cyclohexadiene)Mn(CO)$_2$NO] complexes. In this report we show that this 'double addition' procedure is readily extended to seven-membered ring analogues, thereby providing a general route to difunctionalized cycloheptadienes.

Following published methods[2,3] the addition of NaBH$_4$, PhMgBr, and NaCH(CO$_2$Me)$_2$ to (**1**) occurred cleanly to give high yields of the ring adduct (**2**) as shown in equation (1). Photolysis of (**2**; R = H) in the presence of PPh$_3$ is known[2] to produce [(C$_7$H$_9$)Mn(CO)$_2$PPh$_3$]; we found that the PBu$^n{}_3$ and P(OMe)$_3$ analogues (**3**; R = H) are similarly synthesized in yields of 81 and 47%, respectively.

The addition of NOPF$_6$ to (**3**) in CH$_2$Cl$_2$ at room temperature led to rapid CO substitution according to equation (2). I.r. spectroscopy suggested that the formation of (**4**) was quantitative and the products were precipitated with diethyl ether as air-stable yellow salts in isolated yields of 53—93%. Typical i.r. bands for (**4**; L = CO) are at 2100, 2070, and 1840 cm^{-1} and for (**4**; L = PR$_3$) are at 2030 and 1780 cm^{-1}. The ^{1}H n.m.r. spectrum of (**4**; R = H, L = CO) in CD$_3$NO$_2$ is in accord with the η^5-dienyl formulation: δ 7.03 (t, *J* 7 Hz, H^3), 6.17 (H^{2,4}), 5.03 (H^{1,5}), 2.67 (d, *J* 11 Hz, H$^{6,7\text{-}endo}$), and 2.15 (d, *J* 11 Hz, H$^{6,7\text{-}exo}$). The n.m.r. spectra of (**4**; R ≠ H or L ≠ CO) were more complicated owing to lower symmetry and detailed assignments were difficult to make because traces of paramagnetic impurities limited the ability to resolve small couplings. Obtaining high resolution spectra is similarly difficult with the [(cyclohexadienyl)Mn(CO)(NO)L]$^+$ analogues, even with samples known to be pure by i.r. and mass spectral, *X*-ray, and analytical critiera.[1] It is likely that the trace impurities derive from very slow decomposition; we observed that solutions of (**4**) suffer significant decomposition over a period of 1—2 days. Mass spectra were recorded *via* the fast-atom bombardment (f.a.b.) method for [(**4**); R = H, L = CO; R = H, L = P(OMe)$_3$] with major peaks at *m/z* 234 (M^+), 206 (M^+ − CO), 178 (M^+ − 2CO), and 148 (M^+ − 2CO − NO), and *m/z* 330 (M^+), 302 (M^+ − CO), 272 (M^+ − CO − NO), and 148 [M^+ − CO − NO − P(OMe)$_3$], respectively.

The addition of nucleophiles to (**4**) (equation 3) is the second step in the difunctionalization of co-ordinated

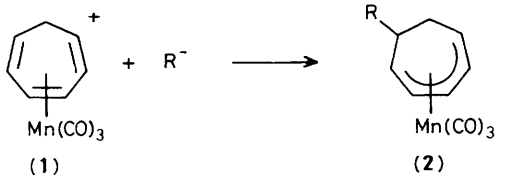
Table 1. Results of carbanion addition to $[(RC_7H_8)Mn(CO)(NO)L]^+$ cations (**4**).

R	L	Nucleophile	Solvent	*T*/°C	Ratio (**5**) : (**3**)[a]	Yield of (**5**)/%[b]
H	CO	PhMgBr	Et_2O	RT[g]	39 : 61	[c]
H	CO	MeLi	Et_2O	RT	40 : 60	21
H	CO	Me_2CuLi	Et_2O	0	50 : 50	30
H	CO	$Me_2Cu(CN)Li_2$	Et_2O	−78	72 : 28	22
H	CO	$NaCH(CO_2Me)_2$	$MeNO_2$	RT	77 : 23	[c]
Ph	CO	$NaCH(CO_2Et)_2$	THF	0	100 : 0	[c]
$CH(CO_2Me)_2$	CO	$NaCH(CO_2Me)_2$	THF	RT	71 : 29	59
H	PBu_3	Me_2CuLi	Et_2O	0	100 : 0	65
H	PBu_3	$NaCH(CO_2Me)_2$	THF	RT	100 : 0	70[d]
H	$P(OMe)_3$	Me_2CuLi	Et_2O	0	100 : 0	[e]
H	$P(OMe)_3$	$NaCH(CO_2Me)_2$	THF	RT	100 : 0	74[f]

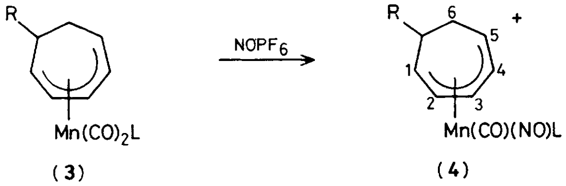
[a] Determined from i.r. spectrum of solution of product mixture. [b] Isolated yield. [c] Not isolated. [d] Satisfactory C,H analyses. [e] F.a.b. mass spectrum *m/z* 317 ($M^+ - CO$), and 163 [$M^+ - CO - NO - P(OMe)_3$]. [f] F.a.b. mass spectrum *m/z* 302 [$M^+ - CO - CH(CO_2Me)_2$], 279 [$M^+ - CO - NO - P(OMe)_3$], 272 [$M^+ - CO - NO - CH(CO_2Me)_2$], and 209 [$M^+ - CO - CH(CO_2Me)_2C_7H_9$]. [g] RT = room temperature.

cycloheptatriene. The chemistry of equation (3) was studied with P-, N-, H-, and C-donor nucleophiles. P- and N-donor nucleophiles react rapidly and cleanly with (**4**) in CH_2Cl_2 to give (**5**) in quantitative yield as judged by i.r. spectroscopy. (A detailed kinetic study of this reaction has been reported.[4]) Typically, a slight excess of nucleophile was added to (**4**) at room temperature. The solution was stirred for 30 min and cooled to −78 °C, and the product was precipitated with diethyl ether and filtered at −78 °C using a jacketed frit. The P-donor adducts decomposed in the solid state at room temperature over *ca.* 1 day; the N-donor adducts were less stable. This precluded elemental analysis, but i.r. and n.m.r. data leave no doubt about the correctness of the indicated structure for (**5**). Typical i.r. bands for (**5**; L = CO) are at 2040, 1980, and 1750 cm^{-1} and for (**5**; L = PR_3) are at 1950 and 1690 cm^{-1}. Decoupling and double deuteriation experiments with the P-donor adducts were used to assign the n.m.r. spectra and verify that the PR_3 nucleophile is situated *exo* to the metal in (**5**), *e.g.* the n.m.r. spectrum of (**5**; R = H, Nu = PPh_3, L = CO) in CD_2Cl_2 is: δ 7.73 (Ph, av.), 5.50, 5.08 (dd, *J* 5, 7 Hz; m, *J* 4, 7 Hz; $H^{2,3}$), 3.92 (t, *J* 12 Hz, H^5), 3.15 (t, *J* 7 Hz, H^1), 2.88 (dd, *J* 7, 16 Hz, H^4), 2.40, 1.37 (br.d, *J* ~16 Hz; m; $H^{6,7\text{-}exo}$), and 2.09, 1.84 (br.t, *J* ~15 Hz; m; $H^{6,7\text{-}endo}$).

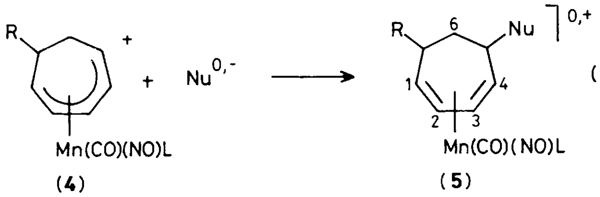
The addition of hydride to (**4**) produced the expected diene product (**5**) along with varying amounts of (**3**). The product ratio (**5**)/(**3**) was found to decrease as the hydride donor ability increased, *e.g.*, the reaction of (**4**; R = H, L = CO) in pentane gave the following ratios: $NaBH_3CN$ (4.0), $NaBH_4$ (2.0), $LiBEt_3H$ (0.25). Changing the L ligand in (**4**) to a better donor markedly increased the (**5**)/(**3**) ratio, *e.g.*, (**4**; R = H, L = CO) reacted with $LiBEt_3H$ in diethyl ether to give only (**3**) while (**4**; R = H, L = PBu_3) gave a ratio of 2.0. These results suggest that electron transfer from the nucleophile to (**4**) competes with nucleophilic addition, and this can be inhibited by making (**4**) more electron rich and/or decreasing the electron donating ability of the nucleophile (*vide infra*). The isolated yields of the hydride adduct (**5**) varied from 0 to 41%; the ^1H n.m.r. spectrum of (**5**; R = H, L = CO) in C_6D_6 is: δ 4.78 (dd, *J* 6, 3 Hz, $H^{2,3}$), 2.62 (m, $H^{1,4}$), 1.74, 1.64 (m, m, $H^{5,7\text{-}exo,endo}$), and 0.98 (m, $H^{6\text{-}exo,endo}$). The question of the stereochemical disposition of the added hydride is non-trivial since we showed previously[1] that hydride addition to [(cyclohexadienyl)Mn(CO)(NO)L]$^+$ cations occurs stereospecifically *endo*, in contrast to the normal pattern of *exo* addition of nucleophiles. For hydride addition to (**4**; R = H, L = CO) we were able to determine that the reaction is at least stereoselectively *endo*.



(1)



(2)



(3)

This was done by an n.m.r. analysis of the isomer ratios obtained after a sequence of reactions: D^- addition (with $NaBD_4$) to (**1**), abstraction of $H^-(D^-)$ by trityl cation, D^- addition, conversion into (**4**) with $NOPF_6$, and D^- addition. This sequence produced a 6 : 4 ratio of trideuteriated and dideuteriated (**5**). The stereochemistry of each step in the reaction sequence is known, except the final D^- addition to (**4**). If the addition to (**4**) is *endo* the relative intensities of $H^{5,7\text{-}exo}$ to $H^{5,7\text{-}endo}$ to $H^{6\text{-}exo,endo}$ are predicted to be 1.2 : 1.0 : 1.2. *exo*-Attack requires the ratios 1.0 : 10.0 : 6.0. The results were, within error, identical to that expected for *endo*-addition.

The addition of C-donor nucleophiles to (**4**) is the most important reaction from a synthetic standpoint. We report preliminary results for a number of such reactions. In a typical experiment, a slight excess of a solution of a carbanion was added to a solution (or suspension) of (**4**). After stirring (under nitrogen) and standard work-up procedures, an i.r. spectrum of the product(s) was taken before attempted separation *via* chromatography. In many cases the i.r. spectrum showed two products, namely the ring adduct (**5**) and the precursor complex (**3**) resulting from NO^+ substitution. As with the hydride reactions, the weaker carbanion and/or less electrophilic substrate (**4**) favoured the formation of (**5**). Table 1 summarizes the results. Preliminary electrochemical experiments[5] support the idea that (**3**) is formed in a bimolecular step after initial one-electron reduction of (**4**) by the nucleophile. This explains the dramatic improvement in product ratios and yields when CO is replaced by PBu_3 or $P(OMe)_3$ in (**4**) (see Table 1). The key to the successful utilization of (**4**) for the difunctionalization of cycloheptatriene lies in the prevention of electron transfer, and this is readily accomplished by phosphine substitution for CO in (**4**). Similar chemistry is obtained with the cyclohexadienyl analogues.[1]

Difunctionalization of cycloheptatriene is also possible using $Fe(CO)_2L^+$-mediated chemistry.[6] Thus, nucleophiles add to $[(cycloheptadienyl)Fe(CO)_2L]^+$ cations (**6**) to give $[(cycloheptadiene)Fe(CO)_2L]$ (**7**). Difunctionalization of the ring can be accomplished by reactivating (**7**) *via* hydride abstraction and treating with a second nucleophile. Thus the manganese and iron complexes offer alternative routes to difunctionalized cycloheptadienes. The relative synthetic advantages of each has yet to be delineated, although it is known[4] that the ability of the manganese and iron moieties in (**4**) and (**6**) to activate the ring is almost identical.

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