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A New Synthetic Route to Neutral η^6-Arene Complexes of Manganese

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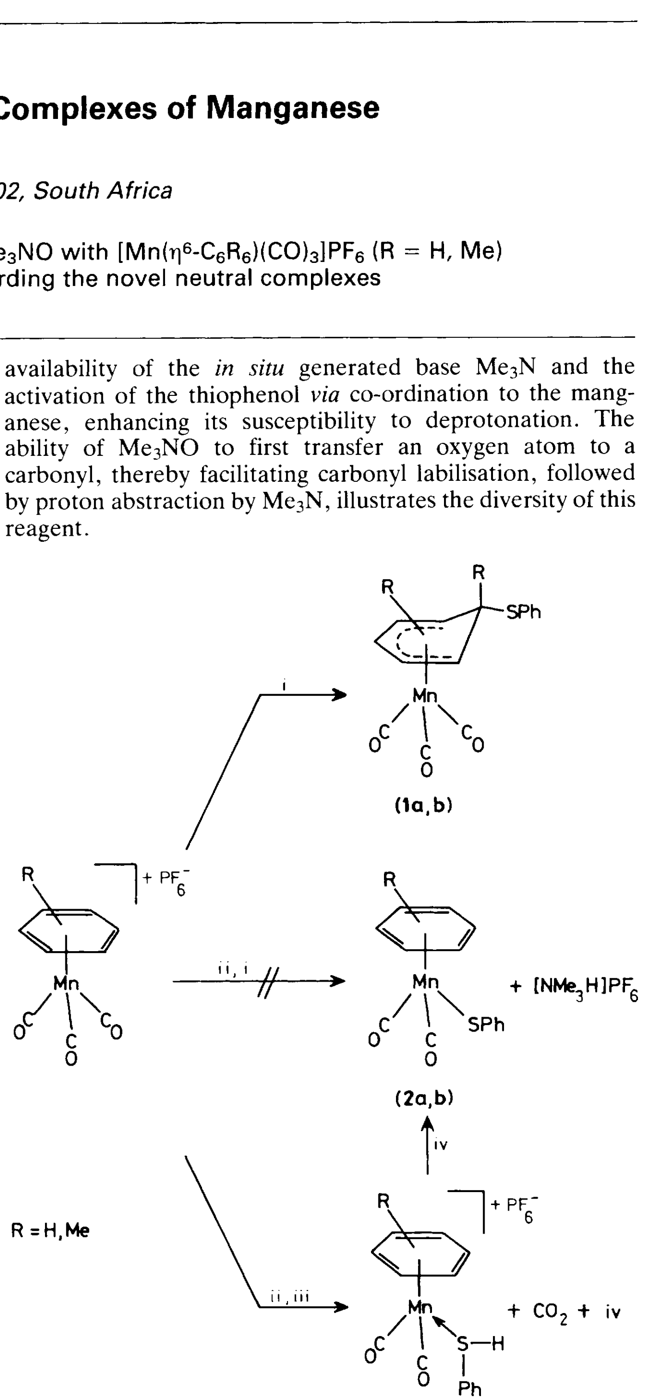
The Me_3N generated in the carbonyl labilising reaction of Me_3NO with $[Mn(\eta^6\text{-}C_6R_6)(CO)_3]PF_6$ (R = H, Me) deprotonates the subsequently co-ordinated thiophenol affording the novel neutral complexes $[Mn(\eta^6\text{-}C_6R_6)(CO)_2SPh]$.

Although extensive research has been done on the nucleophilic attack at the arene ring[1] of $[Mn(\eta^6\text{-arene})(CO)_3]^+$, the formation of neutral complexes $[Mn(\eta^6\text{-}C_6R_6)(CO)_2Y]$ (R = H or Me; Y an anionic heteroatom ligand) poses an interesting synthetic challenge. The use of trimethylamine *N*-oxide to labilise carbonyl ligands is now a well established procedure in metal carbonyl chemistry[2] and was also used to successfully synthesise the cationic manganese complexes $[Mn(\eta^6\text{-}C_6Me_6)(CO)_2PR_3]PF_6$ (R = Ph, OMe) as well as the neutral complexes $[Mn(\eta^6\text{-}C_6H_{6-n}Me_n)(CO)_2X]$ (X = I, Br, Cl; n = 1—6).[3]

The reaction of $[Mn(\eta^6\text{-}C_6R_6)(CO)_3]PF_6$ with LiSPh in a tetrahydrofuran (THF) solution at −20 °C afforded the cyclohexadienyl complexes (**1a**) or (**1b**) (Scheme 1), with (**2a**) or (**2b**) as minor products, which verifies the highly electrophilic character of the arene ring inhibiting attack of nucleophiles on a carbonyl carbon or the metal centre. To overcome this restriction, the cation $[Mn(\eta^6\text{-}C_6R_6)(CO)_3]PF_6$ was dissolved in dichloromethane, cooled to −30 °C and a small excess of Me_3NO added. After stirring for a few minutes, the colour of the reaction mixture changed to pink which indicated a vacated co-ordination site on the manganese. Subsequent treatment with LiSPh again produced the corresponding cyclohexadienyl complexes (**1a**) or (**1b**). Addition of thiophenol however, yielded the neutral complexes $[Mn(\eta^6\text{-}C_6R_6)(CO)_2SPh]$ (**2a**), (**2b**) as air- and light-sensitive wine-red solids in high (65—75%) yields. Elemental analysis and spectroscopic (^{1}H n.m.r., i.r. and mass) data† for the products are consistent with their formulation. Contrary to previous results,[1a,c] indicating that the degree of methylation on the arene ring affects the position of nucleophilic attack, the method presented here does not exhibit any distinction when exchanging benzene for hexamethylbenzene.

Unique features of the proposed mechanism (Scheme 1) for the formation of the neutral complexes (**2a**) or (**2b**) are the availability of the *in situ* generated base Me_3N and the activation of the thiophenol *via* co-ordination to the manganese, enhancing its susceptibility to deprotonation. The ability of Me_3NO to first transfer an oxygen atom to a carbonyl, thereby facilitating carbonyl labilisation, followed by proton abstraction by Me_3N, illustrates the diversity of this reagent.



a; R = H
b; R = Me

Scheme 1. *Reagents*: i, PhSLi; ii, Me_3NO; iii, PhSH; iv, Me_3N.

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† Satisfactory elemental analysis obtained for all new compounds. For (**2a**) m.p. 85 °C. ^{1}H N.m.r. ($CDCl_3$, 300 MHz, δ-values): 5.54 (s, 6H), 7.03 (m, 2H), 7.47 (m, 3H). I.r. (CH_2Cl_2, ν_{CO}, cm^{-1}): 1985, 1943. Mass spectroscopy: *m/z* 298 (M^+, 5%); for (**2b**) m.p. 111 °C (decomp.). ^{1}H N.m.r. ($CDCl_3$): 2.10 (s, 18H), 7.04 (m, 2H), 7.35 (m, 3H). I.r. (CH_2Cl_2, ν_{CO}, cm^{-1}): 1975, 1923. Mass spectroscopy: *m/z* 382 (M^+, 2%).

We are presently studying the reaction mechanism, exploring the range of nucleophiles accessible through this method and developing the chemistry of these compounds. An *X*-ray structural study of (**2a**) is being undertaken.

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