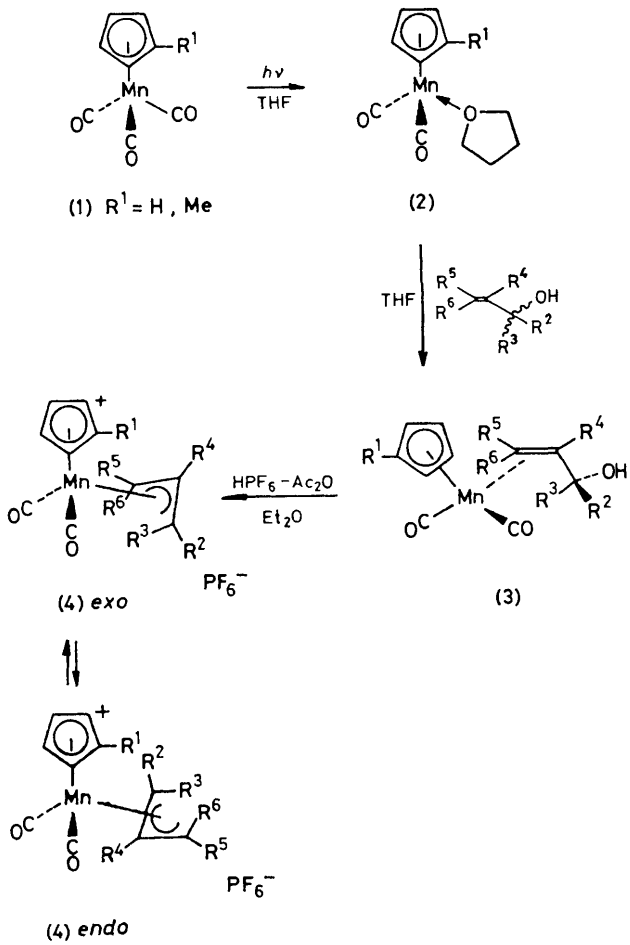
Synthesis of η^3-Allyl-(η^5-cyclopentadienyl)dicarbonylmanganese Cations

By ALAN M. ROSAN

(*Allied Chemical Corporation, Corporate Research & Development, Morristown, New Jersey* 07960)

Summary The reaction of photochemically generated (η^5-C_5H_4R)$Mn(CO)_2$THF (R = H, Me; THF = tetrahydrofuran) with allylic alcohols, followed by prototopic elimination of water, provides the title cationic complexes.

CONSIDERABLE interest has been shown in the dynamic properties[1] and synthetic potential[2] of the η^3-allyl species of general type $(\eta^5\text{-}C_5H_5)M(L)_x(\eta^3\text{-}C_3H_5)$. We now report the synthesis and characterization of a new member of this series, the cyclopentadienyl and substituted cyclopentadienyl dicarbonyl allyl manganese complexes (**4**) which were prepared as illustrated in the Scheme. We exploit the fact that the readily accessible 16-electron photofragment $(\eta^5\text{-}C_5H_4R)Mn(CO)_2$ (R = H, Me)[3] displays considerable co-ordination flexibility,[4] and complexes with olefins,[5] dienes,[6] carbenes,[7] and alkynes.[8] Co-ordination of this fragment to functionalized olefins allows further elaboration.



a; R^1—R^6 = H; for **b**—**f**, R^1—R^6 = H unless otherwise noted.
b; R^1 = Me
c; R^4 = Me
d; R^1 = R^4 = Me
e; R^2 = Me
f; R^2 = R^3 = Me
g; R^2 = R^5 = Me

SCHEME

Reaction of the photochemically generated† red complex (**2**) (10 °C, 0·05—0·10 M THF, 15—30 min) with allyl alcohol or substituted homologues provided the substituted η^2-olefin complexes (**3**). The olefin complexation appears to be kinetically controlled.

The olefin complexes (**3**) were readily converted into the salts (**4**)‡ by proton-induced elimination of water. These reactions constitute a general route to cationic allyl complexes. It is not necessary to isolate the intermediate complexes (**3**). From this three-step reaction sequence the salts (**4**) were isolated as yellow solids in low to moderate yield. Both internal and terminal as well as cyclic olefins could be used in these reactions.

The parent complex (**4a**) appears to exist as a rapidly equilibrating mixture of conformational isomers. The ^1H n.m.r. resonances associated with H_{syn} (R^2,R^5) and H_{anti} (R^3,R^6) are broadened at −90 °C but the slow exchange limit spectra have not yet been obtained. In (**4a**) and (**4b**) the predominant conformer is the *exo* species, while the *endo* conformer is preferred in (**4c**) and (**4d**). These assignments follow from the relatively high field resonance of H_A (≡ R^2) in (**4a**) and (**4b**) (δ 2·43 and 2·36 respectively) and from the lack of significant shift of the H_A resonance in (**4d**) *vs.* (**4c**) (δ 3·43 and 3·61 respectively). In (**4d**) the *exo* conformer is expected to be sterically destabilized. Comparison of the ^1H n.m.r. parameters of (**4c**) and (**4d**) shows them to display essentially the same conformational preference.

The butenyl complex (**4e**) may be prepared utilizing either but-2-en-1-ol (*cis*, *trans* mixture) or but-3-en-2-ol. Surprisingly, the ^1H n.m.r. spectrum of the resulting cation displays two methyl doublets (δ 2·22 and 1·26, 2·5:1 ratio) assigned to the *syn*- and *anti*-methyl species. The assignments are based on comparison with the spectra of the *exo*-1,1-dimethyl- and 1,3-dimethyl-allyl cations (**4f**) and (**4g**).

The pure *exo-syn*-methyl cation can be prepared by protonation of the η^2-butadiene complex.[6] This reaction occurs by unremarkable proton addition at C-4.[9]

The ^1H n.m.r. spectrum of the cation (**4g**) shows the presence of three isomers assigned as the *exo*- and *endo-syn,syn* and *exo-syn,anti* cations (relative proportions 4:1·5:1). The major isomer displays a high-field signal associated with H_A (δ 2·98). In CD_3NO_2 at 100 °C, conditions are realized wherein the *exo*- and *endo-syn,syn* complexes execute rapid interconversion (H_A δ 3·20; $W_{\frac{1}{2}}$ 30 Hz; one *syn*-methyl doublet δ 2·15) while the high field *anti*-methyl resonance (δ 1·32) remains sharp. For this cation, configurational isomerization *via* σ–π interchange is slower than conformational isomerization.

The unexpected formation of the thermodynamically less stable *anti*-isomers of both (**4e**) and (**4g**) arises as a consequence of irreversible co-ordination of the allylic alcohol on both enantiotopic faces. Subsequent antiperiplanar elimination of water provides configurationally isomeric *syn*- and *anti*-cations.

† Irradiations were conducted in a water-cooled Pyrex reactor. A Blak-Ray Lamp Model 8-100A (Ultraviolet Products, San Gabriel, California), λ = 365 nm, $I = 7 \times 10^3$ mW cm^{-2} at 12 inches was used.

‡ Satisfactory elemental analyses were obtained for all new compounds.

I thank Drs. W. B. Hammond, R. Brambilla, and R. Hogan for assistance in obtaining the n.m.r. spectra and microanalytical data.

(*Received, 26th November* 1980; *Com.* 1263.)

[1] J. W. Faller, *Adv. Organomet. Chem.*, 1977, **16**, 211.
[2] R. D. Adams, D. F. Chodosh, J. W. Faller, and A. M. Rosan, *J. Am. Chem. Soc.*, 1979, **101**, 2570.
[3] W. Strohmeier, *Fortschr. Chem. Forsch.*, 1968, **10**, 306.
[4] P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 536.
[5] J. B. Woell and P. Boudjouk, *J. Organomet. Chem.*, 1979, **172**, C43; I. B. Benson, S. A. R. Knox, R. F. D. Stansfield, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1977, 404.
[6] M. L. Ziegler and R. K. Sheline, *Inorg. Chem.*, 1965, **4**, 1230.
[7] M. Creswick, I. Bernal, and W. A. Herrmann, *J. Organomet. Chem.*, 1979, **172**, C39; W. A. Herrmann, *Chem. Ber.*, 1975, **108**, 486; P. Friedrich, G. Besl, E. O. Fischer, and G. Huttner, *J. Organomet. Chem.*, 1977, **139**, C68.
[8] M. Franck-Neumann and F. Brion, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 688.
[9] J. W. Faller and A. M. Rosan, *Ann. N.Y. Acad. Sci.*, 1977, **295**, 186.