Synthesis and Characterization of Novel 17 Electron Species of Manganese with Stable Metal–Alkyl Bonds

Anna Becalska and Ross H. Hill*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, V5A 1S6 Canada

The new 17 electron complexes, (η^5-C_5H_4Me)Mn(NO)R_2, R = Me, Et, Pr, prepared by alkylation of (η^5-C_5H_4Me)Mn(NO)(PPh_3)I, are stable in the absence of oxygen and have been characterized by their ^{1}H n.m.r. and e.s.r. spectra.

Herein, we report the synthesis and characterization of a novel type of stable 17 electron radicals. Although a wide variety of both 17 and 19 electron complexes are known[1,2] there are very few with two metal–carbon σ-bonds. The study of these compounds is made difficult since they are often not sufficiently stable to be isolated, and hence, only spectroscopic characterization is possible. Our results indicate that a complete characterization is possible by spectroscopic techniques relying primarily on ^{1}H n.m.r. spectroscopy.

Many examples of odd-electron complexes have been synthesized in which 19 e complexes are stabilized by the NO ligand.[3] The unpaired electron in 19 e complexes is believed to occupy the NO orbital such that the metal is 18 e and the NO ligand is reduced. Here we report the synthesis of a group of 17 e complexes in which the unpaired electron is localized primarily on the metal. It should be noted that both the 16 and 18 electron analogues, (η^5-C_5H_5)M(NO)Me_2, M = Mo,[4] Fe,[5] of these compounds are known.

These complexes were synthesised by the addition of alkylating agent to the known (η^5-C_5H_4Me)Mn(NO)(PPh_3)I[6] at reduced temperature, equation (1). Upon addition of the alkylating agent the colour of the reaction mixture changes from brown to green. The product complex can be separated by either sublimation at room temperature or distillation from the reaction mixture. In the case of (η^5-C_5H_4Me)Mn(NO)Me_2 an attempt was made to optimize the yield for the reaction. We found that at 0 °C and a molar ratio of alkylating agent to metal complex of 2:1, the yield of sublimed product, (η-C_5H_4Me)Mn(NO)Me_2, was 41% based on the limiting Mn reagent. The product thus obtained is a volatile oil. Sublimation at room temperature to a cold finger at 195 K leads to the recovery of green crystals in the case of (η-C_5H_4Me)Mn(NO)Me_2,† whereas the other derivatives are oils.

$$(\eta^5\text{-}C_5H_4Me)Mn(NO)(PPh_3)I + RM \rightarrow (\eta^5\text{-}C_5H_4Me)Mn(NO)R_2 \quad (1)$$

R = Me, Pr; M = Li
R = Et, Pr; M = MgI

Commonly, reduction of 18 e complexes containing NO results in what is best described as formal reduction of the NO ligand. In these cases ν(NO) shifts dramatically[2,3b] owing to occupation of the NO antibonding orbital. Each of the compounds reported here exhibit i.r. absorptions, ν(NO), in the region 1734—1753 cm^{-1}, Table 1, consistent with their formulation as terminal NO ligands. Although we cannot compare these NO absorption bands with that of the non-radical (either 16 or 18 e) we can compare them with bands for related molecules. The precursor, a Mn^I complex, exhibits an absorption, ν(NO), at 1721 cm^{-1}. Other Mn^I molecules of the type (η-C_5H_4Me)Mn(NO)LI, L = $P(OR)_3$, CO, or (η-C_5H_4Me)Mn(NO)(CO)L_2^+, L = PR_3, $P(OR)_3$, exhibit ν(NO) in the region 1707—1821 cm^{-1}.[7] These results do not appear to be indicative of a large change in electron occupation of the NO orbital.[8] Further evidence, supporting the notion that the odd electron is primarily on the metal, is obtained from the e.s.r. spectra.

Toluene solutions of (η^5-C_5H_4Me)Mn(NO)R_2 exhibit a readily observed e.s.r. signal, Table 1. In each case the hyperfine coupling to Mn (I = 5/2) results in the observation of a six-line pattern. The magnitude of a_{Mn} is 75 G (G = 10^{-4} T) and is independent of substitution either at the cyclopentadienyl ring or on the alkyl group. We note that, in accord with the i.r. results, this magnitude of hyperfine interaction is close to that of true metal-based radicals [*e.g.* in (η^5-

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† Although we have been able to obtain crystals easily we have, as yet, been unable to obtain diffraction-quality crystals.

Table 1. I.r.,[a] e.s.r.,[b] and ^1H n.m.r.[b] spectral data for the complexes $(\eta^5\text{-}C_5H_4R)Mn(NO)R'_2$.

	I.r.	E.s.r.		^1H N.m.r.[c]		MnR'		
Compound	$\nu(NO)$ /cm^{-1}	g	a_{Mn}/G	C_5H_5	$C_5H_4CH_3$	α-H	β-H	γ-H
$(\eta^5\text{-}C_5H_5)Mn(NO)Me_2$	1753	2.020	75	97.6	—	—[d]	—	—
$(\eta^5\text{-}C_5H_4Me)Mn(NO)Me_2$	1745	2.020[e]	75	102, 112	14.8	—[f]	—	—
$(\eta^5\text{-}C_5H_4Me)Mn(NO)Et_2$	1736	2.021	75	99, 91	21.8	−114	−37	—
$(\eta^5\text{-}C_5H_4Me)Mn(NO)Pr_2$	1733	2.021	75	90, 100	20	−145	−36	−3

[a] In pentane solution. [b] All data at room temperature in $[^2H_8]$toluene. [c] All data in p.p.m. relative to $SiMe_4$. [d] Not observed. [e] For the deuteriated complex, $(\eta\text{-}C_5H_4Me)Mn(NO)(CD_3)_2$, g = 2.019. [f] Chemical shift obtained from the ^2H n.m.r. spectrum of $(\eta\text{-}C_5H_4Me)Mn(NO)(CD_3)_2$ in toluene is −65 p.p.m. relative to external $CDCl_3$ (at 7.24 p.p.m.); the signal from the undeuteriated compound was too broad to observe in the ^1H n.m.r. spectrum.

$C_5H_4Me)MnCO(PPh_3)_2^+$ a_{Mn} is 93.2 G][9] and not ligand-based radicals [*e.g.* in the 17 e $Mn(CO)_3(Bu^tNCHCHNBu^t)$ a_{Mn} is 8.5 G].[10] We do not observe hyperfine interaction with either the nitrosyl nitrogen or protons on the ring and alkyl groups. The g value is also relatively insensitive to the nature of the alkyl group and varies from 2.019, R' = CD_3 to 2.021, R' = Et, Pr.

In order to establish that the e.s.r. signal was due to the complex rather than an impurity the relative spin density was compared with that of standard stock solutions of $Ti(acac)_3$ (H_{acac} = pentadione).‡ The result indicated, assuming a single unpaired electron per molecule, that the molecular weight of $(\eta^5\text{-}C_5H_4Me)Mn(NO)Me_2$ is 195 with an estimated error of 20%.

The complexes are stable as solids or in hydrocarbon solution as long as air is rigorously excluded. All the new complexes have been characterized by their ^1H n.m.r. spectra which are presented in Table 1. In spite of the unpaired electron, and the resultant broadening of the n.m.r. resonances, the series of complexes have been fully characterized by their n.m.r. signals. The signals for each of the complexes are broad and shift considerably from the normal region consistent with their formulation as paramagnetic compounds.

Owing to the large chemical shift in these complexes it is necessary to compare the n.m.r. spectra of the derivatives in order to assign the spectra. Fortunately the effect of derivatization on the chemical shifts in paramagnetic complexes is generally minor, and hence comparisons of derivatives is a valid approach.[13]

The simplest complex, $(\eta^5\text{-}C_5H_5)Mn(NO)Me_2$, has a single broad ^1H absorption at δ 97.6. If we compare this with the spectrum associated with $(\eta^5\text{-}C_5H_4Me)Mn(NO)Me_2$, δ 102, 112, 14.8, we see that the 102 and 112 resonances are associated with the $(\eta^5\text{-}C_5H_4Me)$ ring protons. In this derivative they are inequivalent and two signals are observed. The signal at δ 14.8 is associated with the methyl protons on the $(\eta^5\text{-}C_5H_4Me)$.

These three signals, two near δ 100 and a third near δ 15, are present in all the $(\eta^5\text{-}C_5H_4Me)$ derivatives as seen in Table 1. In order to confirm that none of the aforementioned peaks is due to protons on the Mn bound methyl groups we have prepared a deuteriated derivative, $(\eta^5\text{-}C_5H_4Me)Mn(NO)(CD_3)_2$. The ^1H n.m.r. shows peaks at δ 105, 111, and 15.6. This confirms the assignment of the observed peaks as above. The signal for the methyl group protons, which is too broad to observe in the ^1H n.m.r., is observed at δ −65 in the ^2H n.m.r. spectra of $(\eta^5\text{-}C_5H_4Me)Mn(NO)(CD_3)_2$.

The protons on the alkyl groups have also been observed for the ethyl and propyl derivatives. For the ethyl derivative the methyl group is observed at δ −37 and the CH_2 at δ −100. For the propyl derivative the methyl signal is seen at δ −3, whereas the CH_2 β to the metal resonates at δ −36 and the CH_2 α to the metal is observed at δ −145.

Mass spectral data are also consistent with the above formulations. For the complexes $(\eta^5\text{-}C_5H_4Me)Mn(NO)R_2$, R = Me, Pr, and $(\eta^5\text{-}C_5H_5)Mn(NO)(Me)_2$ peaks corresponding to the parent ions are the highest *m/z* peaks observed. For the ethyl derivative we do not observe the parent ion; the highest *m/z* peak observed in this case corresponds to loss of a single ethyl radical. No peak corresponding to loss of ethylene is observed. These results confirm the above formulations.

Currently we are investigating the chemistry and temperature dependent n.m.r. of these complexes.

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‡ This technique has been used previously. The e.s.r. spectra of both $(\eta\text{-}C_5H_4Me)Mn(NO)Me_2$ and $Ti(acac)_3$ were measured in benzene solution and the resultant integral of the absorption spectra calculated from a double integral of the derivative spectra. See refs. 11 and 12.