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ELECTROPHILIC REACTIVITY OF THE DIENYL RING IN CARBONYLNITROSYL(CYCLOHEXADIENYL)MANGANESE CATIONS

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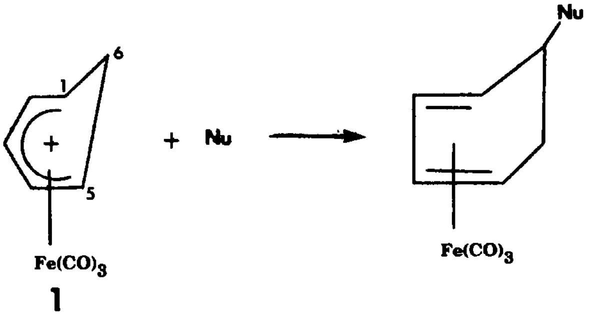
Summary

A kinetic study is reported for the addition of phosphorus and nitrogen donor nucleophiles to the ring in (cyclohexadienyl)Mn(CO)(NO)L$^+$ complexes (**2**, L = CO, PPh_3) to give cyclohexadiene complexes. It is shown that (i) the Mn(CO)(NO)L$^+$ moiety is electronically equivalent to $Fe(CO)_2L^+$ for activating a cyclohexadienyl ring and (ii) that a substituent (Me, Ph, CN) at the C(6)-saturated carbon in **2** produces a large steric retardation of the rate of nucleophile addition.

Introduction

The addition of nucleophiles to coordinated π-hydrocarbons has been utilized in a variety of synthetic and catalytic procedures. The best known work [1] with cyclic π-hydrocarbons involves (cyclohexadienyl)$Fe(CO)_3{}^+$ complexes (**1**) which react with an impressive array of donors to give coordinated cyclohexadienes according to reaction 1. Complexes **1** are prepared from arenes by Birch reduction to the diene,



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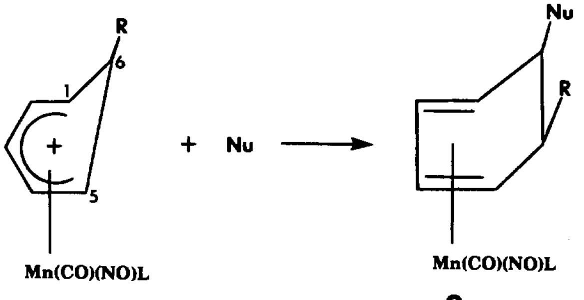
complexation to $Fe(CO)_3^+$, and hydride abstraction. This procedure imposes limitations on possible arene ring substituents. Reaction 1 is also limited in that it is quite difficult to synthesize **1** with a substituent at the C(6) carbon [2].

We are developing the chemistry of (cyclohexadienyl)Mn(CO)(NO)L^+ complexes (**2**), which react according to eq. 2 [3]. Reactions 1 and 2 have their respective advantages, and together complement each other nicely as a synthetic route to



2 **3**

(2)

functionalized cyclohexadienes. The manganese complexes (**2**) are prepared from arenes by complexation to $Mn(CO)_3^+$, nucleophilic addition of a carbon donor R (a mild, high yield reaction [4]), and substitution of a CO ligand by NO^+. The range of nucleophiles in reaction 2 includes H-, N-, and P-donors [3]. With L = CO, redox chemistry limits the usefulness of carbon donors. However, changing to $L = PR_3$ inhibits electron transfer processes and carbon donors then react to give good yields of **3** [5]. Overall, this manganese mediated chemistry corresponds to double nucleophilic addition to an arene to give a difunctionalized cyclohexadiene. Note that only monofunctionalization is convenient with complexes **1**.

Kinetic studies of nucleophilic addition to a wide variety of coordinated π-hydrocarbons has shown that relative nucleophilic reactivities of N- and P-donors are independent of the electrophile [6] and the same as that seen with free carbocations electrophiles [7]. These observations permit confident predictions of the rates of a great number of electrophile-nucleophile combinations and are likely to prove useful for devising new synthetic procedures. In this paper we report the results of kinetic studies of reaction 2 with a variety of N- and P-donor nucleophiles. The purpose of this work is (i) to quantitatively compare the ability of $Fe(CO)_2L^+$ and Mn(CO)(NO)L^+ to activate π-hydrocarbons and (ii) to investigate possible steric effects of substituents at the C(6) position in **2**. The results with **2** (R = H, CH_3, C_6H_5, CN; L = CO, PPh_3) show that the $Fe(CO)_3^+$ and $Mn(CO)_2NO^+$ moieties are virtually identical in activating power and that substitution at the C(6) position exerts a very large influence on the reaction rates.

Experimental

The manganese complexes **2** were prepared as the PF_6^- salts as previously described [3]. Acetonitrile was distilled from calcium hydride under nitrogen and nitromethane was fractionally distilled under nitrogen. Solid phosphines were recrystallized from ethanol or methanol. Liquid phosphines were dried with sodium and distilled under reduced pressure. Pyridines and aniline were distilled from KOH under nitrogen. Kinetic measurements were made at 390 nm on a Dionex 110 stopped flow spectrophotometer operating at 25°C. Several of the slowest reactions were also followed via the appearance or disappearance of CO and NO bands in the IR. Pseudo first order conditions were used with the nucleophile in at least a tenfold excess over the metal complex concentration, which was typically 10^{-4} M. Second order rate constants were calculated from the equation $k_{obs} = k[\text{Nu}]$. At least three, and usually five separate nucleophile concentrations were utilized, with k_{obs} being measured three times at each concentration. With some of the nitrogen donors, the diene products **3** were unstable and slowly decomposed to unidentified products. For this reason the infinity absorbance values in the kinetic runs were occasionally unstable. This, however, amounted to only a slow drifting of the infinity absorbance and did not substantially impair the precision with which k_{obs} could be calculated. The decomposition reactions were slow enough so that high quality IR spectra could be obtained from products made in situ as well as from products isolated as solids by adding diethyl ether to acetonitrile or nitromethane solutions of **3**. The set of ν(CO) and ν(NO) bands of **3** (L = CO, Nu = a nitrogen donor) are all within 10 cm^{-1} of 2040, 1990, and 1750 cm^{-1}. This is identical to that found for the diene products with phosphorus donors, which are more thermally stable and have been isolated and fully characterized as described [3].

Results and discussion

All of the nucleophiles reacted with **2** according to the simple rate law $k_{obs} = k[\text{Nu}]$ (correlation coefficient at least 0.99). Table 1 collects the results. Complex **2** (R = CN; L = CO) was found to decompose in solution in the presence of room light ($t_{1/2}$ about 20 min) to give unidentified products which did not contain coordinated CO or NO. Solutions kept in the dark, however, were stable and kinetic measurements were possible by minimizing exposure to light.

It is probable [6] that the mechanism of reaction 2 is simple bimolecular attack. This follows from the lack of any observed intermediates and from the known [8] *exo* stereochemistry of the diene products **3**. Additional mechanistic insight is available from an examination of linear free energy relationships. For $P(p\text{-}C_6H_4X)_3$ addition to **2** ($R = CH_3$; L = CO) a Hammett plot (log k vs. σ) has a slope $\rho = -1.0$ and a Brønsted plot (log k vs. $pK_a(H_2O)$) has a slope $\alpha = 0.47$. These values are analogous to ones obtained previously for tertiary phosphine additions to other coordinated cyclic π-hydrocarbon systems [6]. They are also very similar to values obtained for tertiary phosphine attack on EtI and $PhCH_2Cl$ [9], for which an early transition state has been established. The Brønsted slope of 0.47 shows that nucleophile basicity is quite important in reaction 2, in contrast to nucleophilic attack at soft metal centers like Pt^{II}, for which α is close to zero [10].

One of the primary reasons for the work reported herein was to assess the relative ability of the $Fe(CO)_3{}^+$ and $Mn(CO)_2NO^+$ fragments to activate a cyclohexadienyl ring to nucleophilic attack. This information is desirable in view of the synthetic potential of these systems. The data in Table 1 leads to the conclusion that $Fe(CO)_3{}^+$ and $Mn(CO)_2NO^+$ are virtually identical in activating power. This conclusion is drawn from the last three entries in Table 1, for which the R substituent at C(6) in **2** is hydrogen. Ironically, $(C_6H_6R)Mn(CO)_2NO^+$ can not be made with hydrogen as the R substituent at C(6), while the $(C_6H_6R)Fe(CO)_3{}^+$

TABLE 1

RATE CONSTANTS FOR NUCLEOPHILIC ADDITION TO $[(C_6H_6R)Mn(CO)(NO)L]PF_6$ (**2**) AT 25°C [a]

R	L	Nucleophile	k (M^{-1} s^{-1})
CH_3	CO	$P(OBu)_3$	0.20 [b]
CH_3	CO	PPh_3	2.0
CH_3	CO	PPh_3	3.4 [b]
CH_3	CO	$P(4\text{-}MeC_6H_4)_3$	6.9
CH_3	CO	$P(4\text{-}MeOC_6H_4)_3$	13
CH_3	CO	$P(4\text{-}MeOC_6H_4)_3$	21 [b]
CH_3	CO	$P(2\text{-}MeOC_6H_4)_3$	200
CH_3	CO	$P(2\text{-}MeOC_6H_4)_3$	360 [b]
CH_3	CO	PBu_3	400
CH_3	CO	PBu_3	750 [b]
CH_3	CO	pyridine	13
CH_3	CO	3-Me-pyridine	31
CH_3	CO	4-Me-pyridine	33
CH_3	CO	aniline	1.2
CH_3	CO	4-Me-aniline	4.6
CH_3	CO	4-MeO-aniline	10
C_6H_5	CO	$P(OBu)_3$	0.30 [b]
C_6H_5	CO	PPh_3	0.56
C_6H_5	CO	PBu_3	1000 [b]
C_6H_5	CO	pyridine	6.8
C_6H_5	CO	3-Me-pyridine	21
C_6H_5	CO	4-Me-pyridine	25
C_6H_5	CO	aniline	1.6
CN	CO	PPh_3	330
CN	CO	PPh_3	450 [b]
CN	CO	4-Me-pyridine	350
CH_3	PPh_3	PBu_3	2.1
H	PPh_3	$P(OBu)_3$	0.85
H	PPh_3	PPh_3	88
H	PPh_3	PBu_3	4500

[a] Refer to structure **2**; solvent is CH_3CN unless otherwise noted. [b] Solvent is CH_3NO_2.

analogues are only available with hydrogen as the R substituent. This means that a direct comparison of $(C_6H_6R)Fe(CO)_3^+$ with most of the manganese complexes in Table 1 is not possible. One might anticipate that $(C_6H_7)Fe(CO)_3^+$ and $(C_6H_6Me)Mn(CO)_2NO^+$ would differ in reactivity to an extent primarily reflecting the electronic influence of $Fe(CO)_3^+$ and $Mn(CO)_2NO^+$. Indeed, the former is ca. 1000 times more reactive than the latter, but we show below that this difference is almost entirely steric in origin. However, a direct comparison of (C_6H_7)-$Fe(CO)_2PPh_3^+$ [6] and $(C_6H_7)Mn(CO)(NO)PPh_3^+$ reacting with PPh_3 in CH_3CN is possible and shows that they have similar reactivities (1.3/1). It is known [6] from studies of a variety of (π-hydrocarbon)$M(CO)_2L^+$ ($L = CO$, NO) complexes that replacing a CO ligand by PPh_3 decreases the reactivity by a factor of 100. With this assumption we estimate the reactivity of $(C_6H_7)Mn(CO)_2NO^+$ as 100 times that of $(C_6H_7)Mn(CO)(NO)PPh_3^+$ (Table 1). Using published [6] data for $(C_6H_7)Fe(CO)_3^+$, the relative reactivity $(C_6H_7)Fe(CO)_3^+/(C_6H_7)Mn(CO)_2NO^+$ as a function of nucleophile is calculated to be: $P(OBu)_3$ 1.0; PPh_3 0.9; PBu_3 0.8. Hence our

TABLE 2

RELATIVE REACTIVITIES OF $(C_6H_7)Fe(CO)_3^+$ AND $(C_6H_6Me)Mn(CO)_2NO^+$ (2) FOR NUCLEOPHILIC ADDITION TO THE RING [a]

Nucleophile	k_{Fe}/k_{Mn}
$P(OBu)_3$	670
PBu_3	850
PPh_3	3700
$P(4\text{-}MeC_6H_4)_3$	4100
$P(4\text{-}MeOC_6H_4)_3$	4900
pyridine	350
aniline	3500

[a] Data from ref. 6 and Table 1.

conclusion that $Fe(CO)_3^+$ and $Mn(CO)_2NO^+$ are essentially equivalent with respect to electrophilic activation, although mechanistic and stereochemical aspects of nucleophilic addition may differ for the two systems, e.g., hydride adds *exo* to the ring in $(C_6H_7)Fe(CO)_3^+$, but adds *endo* to (cyclohexadienyl)$Mn(CO)_2NO^+$ complexes.

The second primary reason for the present study was to determine the steric influence that a substituent at C(6) has on the reactivity of **2**. Table 2 gives the relative reactivities of $(C_6H_7)Fe(CO)_3^+$ and $(C_6H_6Me)Mn(CO)_2NO^+$ as a function of nucleophile. It is seen that the iron complex is in each case much more reactive. Since substitution of a methyl for hydrogen at C(6) would be expected to have a minimal electronic influence, and in view of the conclusion stated above that $Fe(CO)_3^+$ and $Mn(CO)_2NO^+$ have equal activation power, we conclude that the large k_{Fe}/k_{Mn} ratios derive predominantly from the steric effect of the C(6) substituent. The steric influence of a Ph group at C(6) is even larger (e.g., $k_{Fe}/k_{Mn} = 13000$ with PPh_3 as the nucleophile), and for most nucleophiles outweighs any rate increase due to the electron-withdrawing nature of the Ph group. Placing the electron withdrawing and smaller CN group at C(6) in **2** leads to a rate increase, but a marked steric effect is still evident ($k_{Fe}/k_{Mn} = 23$ for PPh_3 addition).

Considering the tertiary phosphines in Table 2, it can be seen that the k_{Fe}/k_{Mn} ratio depends on the steric bulk (cone angle) of the nucleophile. This, of course, is expected and is probably also responsible for the different k_{Fe}/k_{Mn} ratio for pyridine and aniline. Pyridine is less sterically demanding because the attacking orbital is in the molecular plane and directed away from the atomic framework. The corresponding orbital in aniline is normal to the molecular plane and is in a more sterically congested environment. A related way to quantify these steric effects is via the N_M parameters given by eq. 3, in which k_0 is the second order rate constant for addition of a reference nucleophile (usually $P(OBu)_3$). It is known [6] that in the

$$\log k/k_0 = N_M \tag{3}$$

absence of steric effects the value of N_M is independent of the electrophile. This means that the k_{Fe}/k_{Mn} ratios in Table 2 would be nucleophile-independent if the rate differences were electronic in origin. The normal value of N_M for PPh_3 relative to $P(OBu)_3$ is 2.1 ± 0.1. In other words, PPh_3 is about 100 times more reactive than $P(OBu)_3$. For the manganese complexes **2** the reactivity of PPh_3 relative to $P(OBu)_3$ can be calculated to be: 100 (R = H; L = PPh_3); 17 (R = Me; L = CO); 2 (R = Ph;

L = CO). This clearly shows that steric effects are important when R ≠ H. Actually, these numbers only reflect the change in steric effect upon increasing the cone angle from that for $P(OBu)_3$ (110°) to PPh_3 (145°). The absolute steric effect is more accurately judged from the k_{Fe}/k_{Mn} ratios (Table 2).

In view of the large steric effects noted above, it seems surprising that $P(2\text{-}MeOC_6H_4)_3$ is ca. 15 times more reactive than $P(4\text{-}MeOC_6H_4)_3$. However, such behavior has been observed before with both organometallic and organic electrophiles and is believed to be due to anchimeric assistance in which a pair of $2p$ electrons on the methoxy oxygen overlap with a vacant $3d$ orbital on the phosphorus [6,9]. This interaction helps to delocalize the positive charge buildup on the phosphorus atom in the transition state.

In summary, we have shown that (i) the $Mn(CO)_2NO^+$ moiety is electronically equivalent to $Fe(CO)_3{}^+$ for activating cyclohexadienyl rings towards nucleophilic attack and (ii) large steric effects obtain when the cyclohexadienyl ring is substituted at the C(6) carbon. This information should find utility in designing synthetic procedures for the functionalization of cyclohexadienes.

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