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

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Summary

A kinetic study is reported for the addition of phosphorus and nitrogen donor nucleophiles to the cycloheptadienyl ring in $(C_7H_8R)Mn(CO)(NO)L^+$ complexes (**3**, R = H, Ph; L = CO, PBu_3) to give cycloheptadiene complexes (**4**). A substituent at the C(6) carbon in **3** does not produce any detectable steric effect, and the relative nucleophilic reactivities closely parallel those observed with other electrophilic organometallic and organic systems. The reaction **3** → **4** is the second step in the manganese-mediated conversion of a cycloheptatriene to a difunctionalized cycloheptadiene.

Introduction

We recently described a synthetic procedure for the conversion of coordinated arenes to difunctionalized cyclohexadienes [1]. The chemistry involves complexation of the arene to form $(arene)Mn(CO)_3{}^+$, followed by addition of a nucleophile to give stable $(cyclohexadienyl)Mn(CO)_3$ complexes [2]. In the key step, treatment with $NOPF_6$ generates the electrophilic $(cyclohexadienyl)Mn(CO)_2NO^+$ cations that react with a second nucleophile to give $(cyclohexadiene)Mn(CO)_2NO$ complexes. We are currently exploring the applicability of this "double addition" procedure to other π-hydrocarbon complexes. In this report we describe some relevant chemistry of $(cycloheptatriene)Mn(CO)_3{}^+$, which is known [3] to react with P-, N-, and C-donor nucleophiles according to eq. 1. We find that complexes **2** (R = H, Ph; L = CO, PBu_3) react with $NOPF_6$ to give the corresponding cationic dienyl species **3**, which combine with nucleophiles as shown in eq. 2 [4].

The chemistry in eq. 2 is analogous to that reported for $(cycloheptadienyl)Fe(CO)_2L^+$ (**5**), which adds nucleophiles to give $(cycloheptadiene)Fe(CO)_2L$ complexes (**6**) [5]. Difunctionalization of the ring (as in **4**) is possible with the iron systems by reactivating **6** via hydride abstraction and treating with a second nucleophile. Thus the manganese and iron complexes offer alternative routes to

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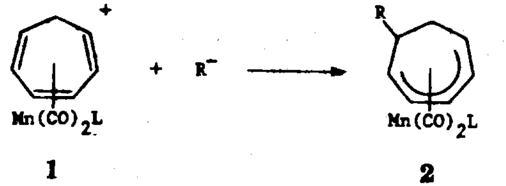
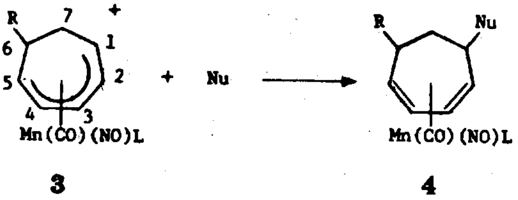


(1)



(2)

difunctionalized cycloheptadienes. In contrast, difunctionalized cyclohexadienes are only available via the manganese-mediated reactions for two reasons: (i) (cyclohexadienyl)Fe$(CO)_2L^+$ is very difficult to make with a substituent on the methylene carbon and (ii) hydride abstraction is not successful when there is a substituent on a carbon adjacent to the methylene group.

We previously reported a kinetic study of nucleophilic addition to (cyclohexadienyl)Mn(CO)(NO)L^+ complexes and found that ring substituents on the methylene carbon produce a large steric retardation and that the Mn(CO)(NO)L^+ and Fe$(CO)_2L^+$ fragments are electronically equivalent with respect to electrophile activation [6]. The present paper concerns the kinetics of reaction 2 and, where possible, a comparison to the analogous Fe$(CO)_2L^+$ complexes.

Experimental

The $[(C_7H_8R)Mn(CO)(NO)L]PF_6$ complexes (3; R = H, Ph; L = CO, PBu_3) were prepared as previously described [4]. The reaction with nucleophiles (eq. 2) was rapid and clean, although the diene products 4 decompose in solution or as solids over a period of hours to days [4]. In spite of this thermal instability, IR and NMR studies [4] leave no doubt about the correctness of the indicated structure for 4. Nitromethane was stored over 4Å molecular sieves for 30 min and then fractionally distilled and stored under nitrogen in the dark at 0°C. The purity was checked before each series of experiments by recording the IR spectrum of a solution of $[(\text{cycloheptatriene})Mn(CO)_3]PF_6$; this complex is extremely sensitive to impurities in the solvent. The kinetics of reaction 2 were studied in nitromethane with a Dionex 110 stopped-flow spectrophotometer at 25°C. Most reactions were followed at 387 nm with the metal complex at ca. 5×10^{-4} *M* and the nucleophile in at least a tenfold excess. Pseudo first order rate constants were obtained two or more times, usually at five nucleophile concentrations. Plots of k_{obs} versus nucleophile concentration gave excellent fits to the simple equation $k_{obs} = k[Nu]$. Several reactions were rapid enough to require second order conditions. In these cases plots of $x/(a-x)$ versus time gave the second order rate constant (k) from the slope.

Results and discussion

Under pseudo first order conditions, the addition of P- and N-donor nucleophiles to **3** gave clean kinetics that obeyed the rate law $k_{obs} = k[\mathrm{Nu}]$. The second order rate constants k are collected in Table 1. The estimated error in k is 10% or less, except for the reactions with PBu_3 and $P(2\text{-}MeOC_6H_4)_3$ which were so rapid that equimolar second order conditions were required.

The mechanism of reaction 2 is most likely a simple bimolecular one. This is suggested by the lack of any observable intermediates, the *exo* stereochemistry of the diene products [4,7], and the mounting evidence [7] that nucleophilic additions to coordinated π-hydrocarbons rarely occur with initial interaction at the metal or a nonreacting ligand, except in certain cases (especially Pd^{II} [8]) in which ligand substitution by the nucleophile precedes migratory insertion of the π-hydrocarbon. Hammett plots (log k vs. σ) for the addition of the four arylphosphines in Table 1 give excellent correlations with slopes (ρ) of -1.2 and -1.3 (per aryl group), respectively, for **3** (R = H; L = CO) and **3** (R = Ph; L = CO). Brønsted plots (log k vs. $pK_a(H_2O)$) for the same set of reactions also give good fits with slopes (α) of 0.51 and 0.54. These Hammett and Brønsted slopes are similar to that observed with other organometallic systems [7], and are almost identical to the values obtained for the reaction of arylphosphines with EtI and $PhCH_2Cl$, for which an early transition state has been established [9]. *N*-donors follow the same trend, e.g., pyridines react with EtI giving a Brønsted slope of 0.33 [10]. A value of 0.35 is obtained for **3**

TABLE 1

RATE CONSTANTS FOR NUCLEOPHILIC ADDITION TO $[(C_7H_8R)Mn(CO)_2NO]PF_6$ (3) AT 25°C [a]

R	Nucleophile	k (M^{-1} s^{-1})
H	$P(C_2H_4CN)_3$	2.7
H	$P(OBu)_3$	3.5
H	$P(4\text{-}ClC_6H_4)_3$	21
H	PPh_3	210
H	$P(4\text{-}MeC_6H_4)_3$	590
H	$P(4\text{-}MeOC_6H_4)_3$	1100
H	PBu_3	14000 [b]
H	$P(2\text{-}MeOC_6H_4)_3$	27000 [b]
H	imidazole	370
H	pyridine	350
H	2,6-Me_2-pyridine	5.4
H	2-Me-pyridine	150
H	3-Me-pyridine	550
H	4-Me-pyridine	680
C_6H_5	$P(C_2H_4CN)_3$	6.5
C_6H_5	$P(OBu)_3$	6.4
C_6H_5	$P(4\text{-}ClC_6H_4)_3$	47
C_6H_5	PPh_3	520
C_6H_5	$P(4\text{-}MeC_6H_4)_3$	1600
C_6H_5	$P(4\text{-}MeOC_6H_4)_3$	3200
C_6H_5	PBu_3	30000 [b]
C_6H_5	$P(2\text{-}MeOC_6H_4)_3$	50000 [b]

[a] Solvent is CH_3NO_2. [b] Obtained using second order conditions.

(R = H; L = CO) reacting with XC_5H_4N (X = H, 3-Me, 4-Me).

It was previously noted [6] that the $Fe(CO)_3{}^+$ and $Mn(CO)_2NO^+$ fragments are equivalent with respect to electrophilic activation of coordinated cyclohexadienyl rings. Comparison of the data in Table 1 with published results [7] shows that this is also true with cycloheptadienyl rings, e.g., the rate constant for PPh_3 addition is 210 M^{-1} s^{-1} for both $(C_7H_9)Mn(CO)_2NO^+$ and $(C_7H_9)Fe(CO)_3{}^+$. A survey of available data also shows that the cycloheptadienyl complexes are always less reactive than the analogous cyclohexadienyl ones by a factor between 20 and 70. While electronic factors may contribute to this difference, molecular models and published X-ray structural data suggest [11] that steric inhibition is clearly more substantial in the C_7H_9 complexes.

In (cyclohexadienyl)Mn(CO)(NO)L^+ complexes it was shown [6] that an *exo* substituent (Me, Ph) at the methylene carbon causes a rate retardation by a factor of 300 to 5000, depending on the size of the nucleophile. In contrast, one expects that an *exo* substituent at C(6) in the cycloheptadienyl analogues (see **3**) should have a much smaller effect because the nucleophile can attack at C(1) instead of C(5) and thereby minimize any steric effects due to the substituent. Indeed, the data in Table 1 shows that a C_6H_5 substituent in **3** causes no apparent steric retardation. In fact, all the rates constants increase by a factor of 1.9 to 2.9, which is ascribed to the inductive effect of the C_6H_5 group. After a statistical correction, the average rate increase is 4.8; the very weak dependence of this number on the nature of the nucleophile serves to confirm the absence of any significant steric influence due to a substituent at C(6).

The similarity of the mechanism of nucleophilic addition to $(C_7H_8R)Mn(CO_2$-NO^+ and to $(C_6H_7)Fe(CO)_3{}^+$ was tested by plotting log *k* for the latter versus log *k* for the former for the eight phosphine nucleophiles listed in Table 1. Figure 1 shows the graph for **3** (R = Ph). The plots are highly linear (correlation coefficients > 0.995) with a slope of 0.98 ± 0.02 for **3** (R = Ph) and 0.97 ± 0.03 for **3** (R = H). The unit slopes imply very similar transition states for the two sets of reactions and, incidentally, further demonstrates the lack of a steric effect in **3** (R = Ph).

Studies of a variety of (π-hydrocarbon)$M(CO)_2L^+$ (L = CO, NO) complexes showed that replacement of a CO ligand by PPh_3 reduces the rate of nucleophilic attack by a factor of 100 [7]. This effect seems to be independent of the nature of the nucleophile and the organometallic complex. Several preliminary experiments were done to determine the effect of replacing a CO ligand by PBu_3 in $(C_7H_9)Mn(CO)_2NO^+$. With the nucleophiles PBu_3 and $P(4\text{-}MeOC_6H_4)_3$, the rate constants (*k*) decreased by ca. 1000, showing the expected result that the stronger σ-donor PBu_3 reduces the electrophilicity of the coordinated π-hydrocarbon more than does PPh_3.

A survey of additions of P- and N-donors to coordinated π-hydrocarbons shows [7] that a Ritchie type relation [12] accurately describes the kinetic behavior if steric effects are absent. This is expressed by eq. 3 in which k_0 is the second order rate

$$\log k/k_0 = N_M \qquad (3)$$

constant for a reference nucleophile (usually $P(OBu)_3$) and N_M is a parameter dependent only on the nature of the nucleophile. In other words, relative nucleophilic reactivities are electrophile independent. Recent work [13] suggests that the same N_M parameters apply whether the electrophile is a free carbocation or a metal-co-

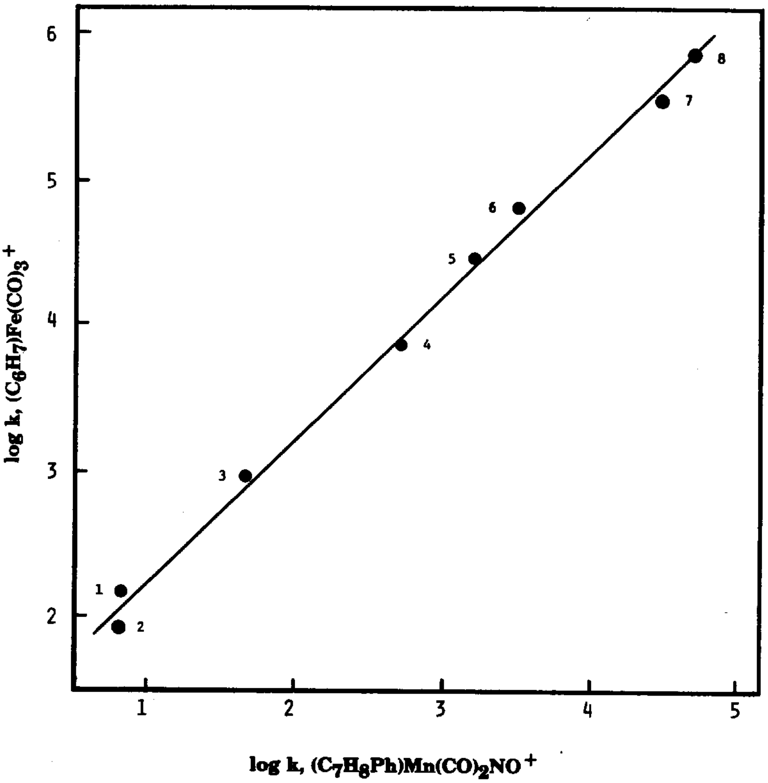


Fig. 1. Correlation of log k for the addition of eight P-donor nucleophiles to $(C_6H_7)Fe(CO)_3^+$ and $(C_7H_8Ph)Mn(CO)_2NO^+$. The key is: (1), $P(CH_2CH_2CN)_3$; (2), $P(OBu)_3$; (3), $P(4\text{-}ClC_6H_4)_3$; (4), PPh_3; (5), $P(4\text{-}MeC_6H_4)_3$; (6), $P(4\text{-}MeOC_6H_4)_3$; (7), PBu_3; (8), $P(2\text{-}MeOC_6H_4)_3$.

ordinated π-hydrocarbon. This implies that eq. 3 may represent a unified reactivity scale for electrophile-nucleophile combinations. Figure 2 shows a plot of log k vs. N_M for the addition of twelve nucleophiles to $(C_7H_9)Mn(CO)_2NO^+$. The N_M parameters are averages obtained from studies of other complexes containing various π-hydrocarbon and metal fragments. The maximum standard deviation in N_M is ± 0.2 units. If eq. 3 holds for a given electrophile, a plot of log k vs. N_M should have unit slope. This is the case for the plot in Fig. 2, which has a slope of 0.98 ± 0.04 (correlation coefficient = 0.992). It can be seen that the arylphosphines are slightly less reactive towards $(C_7H_9)Mn(CO)_2NO^+$ than would be predicted from their N_M values. This probably represents a steric retardation with these bulky nucleophiles. Overall, however, the adherence to eq. 3 is excellent. With **3** (R = Ph, L = CO) a plot (eight points) similar to that in Fig. 2 is obtained with a slope of 0.98 ± 0.03 (correlation coefficient = 0.998); this also shows the absence of any steric effects due to the C_6H_5 substituent.

A consideration of the data in Table 1 and that previously published [7] allows one to quantify the ability of various metal fragments (ML_n) to activate dienyl rings to electrophilic attack. This is conveniently expressed by electrophilic transferability numbers (T_E's) which are a measure of relative electrophilic reactivities of $(dienyl)ML_n^+$ complexes. In the absence of steric effects, the T_E's are the same for

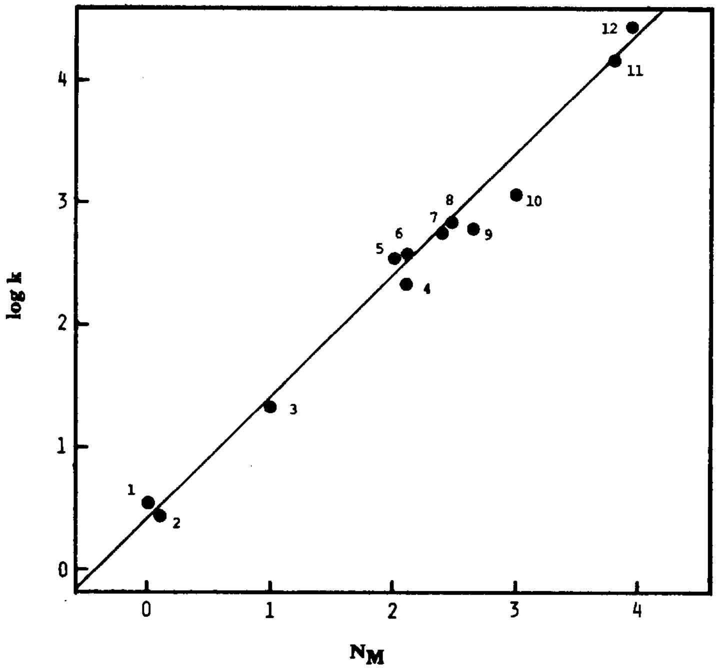


Fig. 2. Correlation of log k for addition to $(C_7H_9)Mn(CO)_2NO^+$ with nucleophilic reactivity parameter N_M (see text). The key is: (1), $P(OBu)_3$; (2), $P(CH_2CH_2CN)_3$; (3), $P(4\text{-}ClC_6H_4)_3$; (4), PPh_3; (5), pyridine; (6), imidazole; (7), 3-Me-pyridine; (8), 4-Me-pyridine; (9), $P(4\text{-}MeC_6H_4)_3$; (10), $P(4\text{-}MeOC_6H_4)_3$; (11), PBu_3; (12), $P(2\text{-}MeOC_6H_4)_3$.

TABLE 2

ELECTROPHILIC TRANSFERABILITY NUMBERS (T_E's) FOR NUCLEOPHILIC ADDITION TO COORDINATED DIENYL RINGS

Metal fragment	T_E
$Fe(CO)_3{}^+$	1700
$Mn(CO)_2NO^+$	1500
$Fe(CO)_2PPh_3{}^+$	20
$Mn(CO)(NO)PPh_3{}^+$	15
$Mn(CO)(NO)PBu_3{}^+$	2
$CoCp^+$	1

six- and seven-membered dienyl rings, and are given in Table 2. An analogous set of T_E's are available for triene complexes [7]. The T_E numbers are useful since they show at a glance how the π-hydrocarbon reactivity will change with the metal fragment and hence which ones would be of utility in a given synthetic procedure.

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