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A kinetic study of nucleophilic addition to the alkene in dicarbonyl(alkene)(arene)manganese cations

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Abstract

Nucleophilic addition of tertiary phosphines to (arene)$Mn(CO)_2(alkene)^+$ cations occurs at the alkene ligand to give σ-alkyl type products. A kinetic and thermodynamic study of this reaction shows that the transition state is an early one. The relative nucleophilic reactivities are the same as those found for addition to coordinated cyclic π-hydrocarbons and free carbocations.

Introduction

Nucleophilic addition to π-hydrocarbons coordinated to transition metals is one of the fundamental reactions of organometallic chemistry. Extensive kinetic studies [1] of the addition of phosphorus and nitrogen-donor nucleophiles established that the behavior is governed by the simple expression in eq. 1, in which k is the second order rate constant for

$$\log k/k_0 = N_M \tag{1}$$

addition of a given nucleophile and k_0 is that for a reference nucleophile. Both k and k_0 depend on the electrophile, but the ratio does not, meaning that the relative nucleophilic reactivity (N_M) is electrophile-independent. This surprising result is also seen with nucleophile addition to free carbocations [2]. The practical value of eq. 1 is that it permits reactivity to be predicted from knowledge of a single nucleophile-dependent (but electrophile-independent) parameter (N_M). This contrasts with multiple parameter equations that describe metal or carbon-centered substitution reactions, for which relative nucleophilic reactivities change, often greatly, with the electrophile.

Most kinetic studies of nucleophilic addition to coordinated π-hydrocarbons have involved cyclic systems. In this paper we report an investigation of reaction 2,

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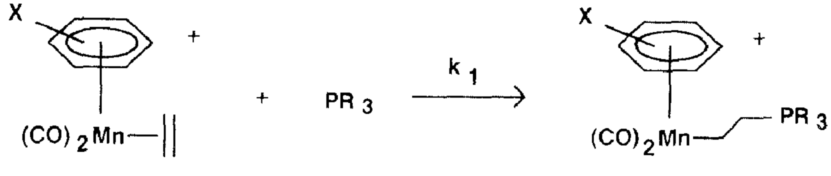

1 2 (2)

in which phosphine nucleophiles attack coordinated ethylene to give σ-alkyl type products. Complexes like **1** can be synthesized with a variety of X substituents and with a variety of coordinated alkenes and alkynes [3]; they represent a new class of electrophilic complexes that undergo attack at the acyclic π-hydrocarbon with P- and C-donor nucleophiles (phosphines, Grignard reagents, cuprates). Particular synthetic interest in **1** stems from the possibility of stereospecifically functionalizing the arene ring by induced alkyl ligand migration in **2** and its analogues.

Recent kinetic studies have been reported [4] for phosphine and amine addition to the coordinated alkene in the well known [5] complexes CpFe(CO)$_2$(alkene)$^+$. The results presented herein for reaction 2 show that (C$_6$Me$_6$)Mn(CO)$_2$(C$_2$H$_4$)$^+$ is much less electrophilic than CpFe(CO)$_2$(C$_2$H$_4$)$^+$, yet both complexes adhere to eq. 1 with the same N_M values that obtain with cyclic systems. Also discussed herein is the dependence of the rate of reaction 2 on arene methyl substituents and on changing the alkene from ethylene to propene.

Experimental

The solvent used in the studies, CH$_2$Cl$_2$, was distilled under nitrogen from calcium hydride. The complexes [(arene)Mn(CO)$_2$(alkene)]PF$_6$ (arene = C$_6$Me$_6$, C$_6$HMe$_5$; alkene = C$_2$H$_4$, C$_3$H$_8$) were synthesized as previously described [3]. IR, mass spectral, and NMR data clearly showed that phosphine nucleophiles attack the alkene (and not the arene), according to reaction 2. Most kinetic studies of reaction 2 were done at 25 °C and 390 nm with a Dionex stopped-flow instrument. The phosphine was in pseudo first order excess over the complex concentration, which was ca. 2.5×10^{-4} *M*. Typically rate constants were measured at five or more nucleophile concentrations spanning a range of ten or more in relative magnitude. Some of the slower reactions were followed with a Mattson FT-IR (complex at ca. 2×10^{-3} *M*); the ν(CO) bands at ca. 2010 and 1970 cm^{-1} were cleanly replaced by product bands at ca. 1950 and 1880 cm^{-1}. Standard treatment of the absorbance-time data gave pseudo first order rate constants, k_{obs}. Plots of k_{obs} versus nucleophile concentration were linear with the slopes providing the second order constants, k. Thermodynamic studies of reaction 2 were conveniently done via FT-IR.

Results and discussion

We previously demonstrated [3] that a variety of nucleophiles cleanly attack the coordinated alkene in (arene)Mn(CO)$_2$(alkene)$^+$ according to reaction 2. That the open (alkene) hydrocarbon is attacked in preference to the closed (arene) hydrocarbon was anticipated [6]. In Table 1 the kinetic and thermodynamic data are given. The relative reactivity parameters N_M are shown, based on P(OBu)$_3$ as the

Table 1

Data [a] for phosphine addition to the alkene in (arene)$Mn(CO)_2$(alkene)$^+$ according to reaction 2.

Arene	Alkene	PR_3	k ($M^{-1}s^{-1}$)	N_M	K (M^{-1}) [b]
C_6Me_6	C_2H_4	$P(OBu)_3$	0.0050	(1)	
C_6Me_6	C_2H_4	PPh_3	0.41	1.9	27
C_6Me_6	C_2H_4	P(*p*-MeOPh)$_3$	3.1	2.8	6600
C_6Me_6	C_2H_4	PBu_3	14	3.4	
C_6Me_6	C_2H_4	P(*o*-MeOPh)$_3$	70	4.1	
C_6Me_6	C_3H_6	PBu_3	1.0		
C_6HMe_5	C_2H_4	P(*p*-MeOPh)$_3$	11		

[a] In dichloromethane at 25°C. [b] K is the equilibrium constant for reaction 2.

reference nucleophile; these are quite close to the values found [1,4] for addition to coordinated cyclic π-hydrocarbons and to the ethylene in $CpFe(CO)_2(C_2H_4)^+$, indicating further that N_M is truly electrophile-independent. A comparison of the data in Table 1 with that for $CpFe(CO)_2(C_2H_4)^+$ shows that the ethylene in $(C_6Me_6)Mn(CO)_2(C_2H_4)^+$ is ca. 150 times less electrophilic.

While the rate constants in Table 1 increase with nucleophile basicity, the two equilibrium constants measured show a much stronger basicity dependence. The presumed LFER between log k and log K has a slope of 0.37. Although this is based on only two points, it suggests that P–C bond formation and sp^2 to sp^3 rehybridization is only about one-third complete in the transition state. Thus the transition state is an early one, as might be expected for reactions obeying a relationship like eq. 1. Interestingly, the slope of 0.37 is virtually identical to that found [1] with the cyclic systems $(C_6H_7)Fe(CO)_3{}^+$ and $(C_4H_4)Fe(CO)(NO)(PPh_3)^+$, for which a more extensive range of data are available.

Several other points can be made concerning the data in Table 1. As expected, changing the alkene from ethylene to propene reduces the electrophilicity. The reduction is a factor of 14 with PBu_3; this factor is very similar to that found [4] with $CpFe(CO)_2$(alkene)$^+$. It may also be seen that reducing the arene ring methylation from C_6Me_6 to C_6HMe_5 increases the alkene electrophilicity. It is likely that this reflects the anticipated decrease in electron density donation to the metal with C_6HMe_5. Also noteworthy is the approximately twentyfold greater reactivity of P(*o*-MeOPh)$_3$ compared to P(*p*-MeOPh)$_3$. This occurs in spite of the greater steric interaction expected with the former nucleophile and can be attributed to anchimeric assistance involving the 2*p* lone pair electrons on the methoxy oxygen, as previously documented with organometallic [1] and organic [7] reactions.

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