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KINETICS OF NUCLEOPHILIC ADDITION OF TERTIARY PHOSPHINES TO DICARBONYLNITROSYL(CYCLOBUTADIENE)IRON CATION AND TRICARBONYL(CYCLOHEPTATRIENE)MANGANESE CATION

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Summary

Tertiary phosphines rapidly add to the ring in dicarbonylnitrosyl(cyclobutadiene)iron cation and tricarbonyl(cycloheptatriene)manganese cation to form phosphonium adducts. Kinetic studies of this reaction support a mechanism consisting of direct bimolecular attack on the ring. Reactivity towards nucleophilic attack by phosphines follows the order: $[(C_7H_8)Mn(CO)_3]^+ > [(C_4H_4)Fe(CO)_2NO]^+ > [(C_6H_7)Fe(CO)_3]^+ > [(C_6H_6OMe)Fe(CO)_3]^+ \gtrsim [(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, W) $> [(C_6H_6)Mn(CO)_3]^+$. Coordinated cycloheptatriene is about 10^4 times more electrophilic towards phosphine nucleophiles than is coordinated benzene.

Introduction

The addition of tertiary phosphines to coordinated cyclic π-hydrocarbons to yield phosphonium adducts has attracted recent attention [1—7]. Quantitative kinetic studies of this reaction have been reported [8—10] for the cationic systems $[(C_6H_7)Fe(CO)_3]^+$, $[(C_4H_4)Fe(CO)_2NO]^+$, $[(\text{arene})Mn(CO)_3]^+$, and $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, W). Such work provides information concerning the mechanism of nucleophilic addition to coordinated rings and allows the formulation of a reactivity order towards nucleophilic attack.

Herein we report the kinetics of tertiary phosphine addition to $[(C_4H_4)Fe(CO)_2NO]^+$ and $[(C_7H_8)Mn(CO)_3]^+$ (reactions 1 and 2).

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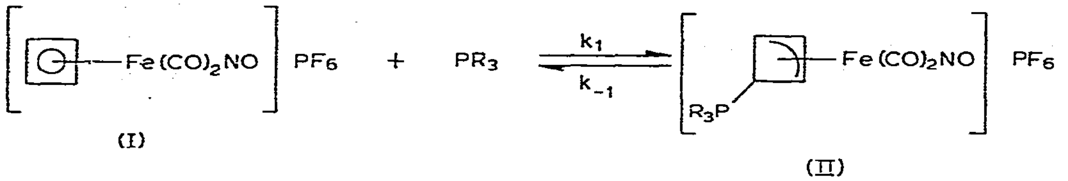

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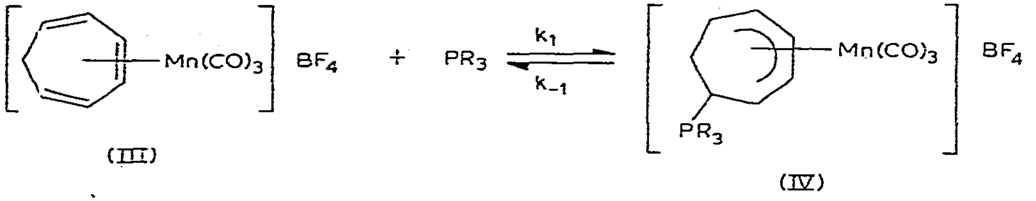

(2)

Experimental

All solvents were distilled and dried prior to use. The tertiary phosphines were crystallized from ethanol. Spectral measurements were made using Perkin—Elmer 337 (IR), Perkin—Elmer 323 (VIS/UV), and Hitachi Perkin—Elmer R-20B (NMR) instruments.

Complex I was prepared as described by Efraty et al. [11], and its identity confirmed by IR, NMR, and analytical data. (Found: C, 21.5; H, 1.2; N, 3.9. $C_6H_4F_6FeNO_3P$ calcd.: C, 21.3; H, 1.2, N, 4.1%.) The phosphonium adducts II were precipitated from methylene chloride upon the addition of ether to a solution containing complex I and excess tertiary phosphine. This method is essentially the same as that reported by Efraty et al. [12,13] who have fully characterized these compounds. With $P(p\text{-}ClC_6H_4)_3$ reaction I is readily reversible at room temperature and attempted precipitation of II from methylene chloride yields only the less soluble reactant I. This adduct was prepared, however, by precipitation at —50°C, at which temperature reaction 1 is essentially complete (K_{eq} large). The adducts II have IR bands in CH_3NO_2 at ν(CO) 2055, 2008 cm^{-1} and ν(NO) 1765 cm^{-1}.

Complex III was synthesized as described by Pauson et al. [14]. (Found: C, 37.7; H, 2.5. $C_{10}H_8BF_4MnO_3$ calcd.: C, 37.4; H, 2.7%.) The IR spectrum in CH_3NO_2 has CO bands at 2075 and 2015 cm^{-1}, and the ^{1}H NMR spectrum in CD_3NO_2 contains multiplets at τ 3.09 ($H^{3,4}$), 4.20 ($H^{2,5}$), 5.43 ($H^{1,6}$), 6.67 (H^7 *endo*), and 8.34 ppm (H^7 *exo*). $[(C_7H_8)Mn(CO)_3]BF_4$ is very reactive towards nucleophiles, and it is essential that the CH_3NO_2 solvent be carefully purified. In our work the CH_3NO_2 was freshly distilled from P_2O_5 and stored over molecular sieve in the dark.

Two phosphonium adducts of $[(C_7H_8)Mn(CO)_3]BF_4$ were prepared as white crystalline solids by the method described above for the adducts II. With P(*o*-tolyl)$_3$ a low temperature (≈ —50°C) was necessary because of the reversibility of reaction 2. However, even at low temperature the product contained some starting material (complex III). The tris(*p*-chlorophenyl)phosphine adduct, $[(C_7H_8)P(p\text{-}ClC_6H_4)_3Mn(CO)_3]BF_4$ was analyzed. (Found: C, 49.5; H, 3.2. $C_{28}H_{20}BCl_3F_4MnO_3P$ calcd.: C, 49.2; H, 2.95%.) The adducts IV have IR bands in CH_3NO_3 at ν(CO) 2020, 1945 cm^{-1}.

The kinetics of reactions I and 2 were studied in CH_3NO_2 and/or acetone using a Durrum stopped-flow apparatus. The metal complex concentration was (1.0—2.0) × 10^{-4} M and the nucleophile concentration was kept in pseudo-first-order excess (1.0—12.0) × 10^{-3} M. The kinetics were monitored at 455 and 390 nm for reactions 1 and 2, respectively.

Results and discussion

Mechanism of phosphine addition

1. $[(C_4H_4)Fe(CO)_2NO]PF_6$. Efraty et al. [13] have shown that tertiary phosphines rapidly add to the cyclobutadiene ring in $[(C_4H_4)Fe(CO)_2NO]^+$ to yield the *exo*-phosphonium adducts. We found that adduct formation in CH_3NO_2 is accompanied by changes in IR frequencies from $\nu(CO)$ 2125, 2100 cm^{-1}, $\nu(NO)$ 1880 cm^{-1} to $\nu(CO)$ 2055, 2008 cm^{-1}, $\nu(NO)$ 1765 cm^{-1}. Reaction 1 was shown to be reversible by IR dilution experiments and the equilibrium constant (K) for addition of $P(p\text{-}ClC_6H_4)_3$ in acetone calculated to be 1600 M^{-1} at 25°C. With excess nucleophile the rate constants for reaction 1, which are given in Table 1, were found to obey equation 3, from which one can calculate K as k_1/k_{-1}. The

$$k_{obs} = k_1[PR_3] + k_{-1} \tag{3}$$

value of K calculated from kinetic data (Table 1) at 24°C agrees well with the value found by the static IR method.

In view of the known *exo* configuration of the phosphonium adducts [13] it would seem that the most likely mechanism of addition is simply bimolecular or direct attack on the ring. It has recently been suggested [15] that in some cases nucleophilic addition may be preceded by attack at the metal. This does not seem to be the case with coordinated cyclobutadiene since the full absorbance change calculated for reaction 1 was observed experimentally with no

TABLE 1

RATE CONSTANTS FOR THE ADDITION OF PR_3 TO $[(C_4H_4)Fe(CO)_2NO]PF_6$

PR_3	Solvent	T (°C)	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})
$P(C_6H_5)_3$	$(CH_3)_2CO$	0	18600(500) [a]	—
$P(C_6H_5)_3$	$(CH_3)_2CO$	10	27800(500)	—
$P(C_6H_5)_3$	$(CH_3)_2CO$	16.5	41900(1700)	—
$P(C_6H_5)_3$	$(CH_3)_2CO$	25	47300(1800)	—
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	0.5	1840(100)	—
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	7.5	2580(40)	0.58(0.07)
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	13.5	3180(70)	1.33(0.17)
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	19.5	4020(70)	2.00(0.21)
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	24	5110(70)	3.07(0.17)
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	27	5380(130)	5.19(0.37)
$P(p\text{-}ClC_6H_4)_3$	CH_3NO_2	0.5	3200(70)	—
$P(p\text{-}ClC_6H_4)_3$	CH_3NO_2	20	6350(80)	2.03(0.23)
$P(p\text{-}ClC_6H_4)_3$	CH_3NO_2	25	7410(90)	3.84(0.25)
$P(p\text{-}ClC_6H_4)_3$	CH_3NO_2	30	9100(120)	5.44(0.35)
$P(p\text{-}ClC_6H_4)_3$	CH_3NO_2	34	10000(90)	7.39(0.24)

[a] Numbers in parentheses are standard deviations.

TABLE 2

RATE CONSTANTS FOR THE ADDITION OF PR_3 TO $[(C_7H_8)Mn(CO)_3]BF_4$ IN NITROMETHANE

PR_3	T (°C)	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})
$P(p\text{-}ClC_6H_4)_3$	1	30000	—
$P(p\text{-}ClC_6H_4)_3$	20	53000	—
$P(p\text{-}ClC_6H_4)_3$	35	98000	—
$P(o\text{-tolyl})_3$	0	170	—
$P(o\text{-tolyl})_3$	18	295(5) [a]	0.13(0.02)
$P(o\text{-tolyl})_3$	23.5	350(10)	0.20(0.10)
$P(o\text{-tolyl})_3$	30	505(5)	0.31(0.03)
$P(o\text{-tolyl})_3$	35	665(15)	0.77(0.13)

[a] Numbers in parentheses are standard deviations.

evidence for an intermediate. Also, initial attack at the metal would be expected to yield the *endo* product.

The activation parameters for reaction 1 (Table 3) are very reasonable for a bond formation step (k_1) and a bond breaking step (k_{-1}) and are similar to activation parameters obtained for coordinated arene complexes [10].

2. *$[(C_7H_8)Mn(CO)_3]BF_4$*. The coordinated ring in $[(C_7H_8)Mn(CO)_3]^+$ is very reactive towards nucleophiles. Pauson et al. [14] reported the addition of nucelophiles such as OR^-, H^-, and CN^-, but to our knowledge the phosphonium adducts have not been previously reported. Tertiary phosphines rapidly add to the ring producing a shift in IR bands (in CH_3NO_2) from ν(CO) 2075, 2015 to 2020, 1945 cm^{-1}. The spectral shifts are almost identical to those found with phosphine addition to $[(arene)Mn(CO)_3]^+$ [4,10]. As was the case for coordinated cyclobutadiene, phosphine addition to complex III was shown to be reversible by IR dilution experiments and for $P(o\text{-tolyl})_3$ the equilibrium constant was found to be 2000 M^{-1} in CH_3NO_2 at 25°C. This value agrees with that derived from the kinetic data (eq. 3, Table 2).

All of the absorbance change calculated for reaction 2 was observed. This coupled with the known [14,16] *exo* stereochemistry of the ring adducts of compound III with R^-, CN^- or OR^-, suggests, as discussed above, that the mechanism of phosphine addition is direct bimolecular attack on the ring. The activation parameters are given in Table 4 and are seen to be consistent with bond making and bond breaking steps. The reaction with $P(p\text{-}ClC_6H_4)_3$

TABLE 3

ACTIVATION PARAMETERS FOR THE ADDITION OF PR_3 TO $[(C_4H_4)Fe(CO)_2NO]PF_6$

PR_3	Solvent	Step	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal deg^{-1} mol^{-1})
$P(C_6H_5)_3$	$(CH_3)_2CO$	k_1	5.8(0.7) [a]	−17.5(0.6)
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	k_1	5.9(0.3)	−21.8(0.9)
$P(p\text{-}ClC_6H_4)_3$	$(CH_3)_2CO$	k_{-1}	16.7(1.3)	0(4)
$P(p\text{-}ClC_6H_4)_3$	CH_3NO_2	k_1	5.1(0.1)	−23.6(0.4)
$P(p\text{-}ClC_6H_4)_3$	CH_3NO_2	k_{-1}	16.1(1.4)	−2(5)

[a] Numbers in parentheses are standard deviations.

TABLE 4

ACTIVATION PARAMETERS FOR THE ADDITION OF PR_3 TO $[(C_7H_8)Mn(CO)_3]BF_4$ IN NITROMETHANE

PR_3	Step	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal deg^{-1} mol^{-1})
$P(p\text{-}ClC_6H_4)_3$	k_1	4.9(2.0) [a]	−20(10)
$P(o\text{-tolyl})_3$	k_1	5.7(0.6)	−27(2)
$P(o\text{-tolyl})_3$	k_{-1}	19.3(3.0)	3(7)

[a] Numbers in parentheses are standard deviations.

is very rapid and the corresponding rate constants and activation parameters are much less reliable than with $P(o\text{-tolyl})_3$.

It is interesting to note that $P(p\text{-tolyl})_3$ reacts with compound III at a rate we estimate to be at least 2000 times faster than $P(o\text{-tolyl})_3$ due, presumably, to steric effects. It is only because of the great electrophilicity of the coordinated cycloheptatriene ring that this reaction can be studied. $P(o\text{-tolyl})_3$, unlike $P(p\text{-tolyl})_3$, does not react with other coordinated cyclic π-hydrocarbons reported to date, including $[(C_4H_4)Fe(CO)_2NO]^+$, which is one of the most electrophilic systems yet found.

Electrophilicity of coordinated cyclic π-hydrocarbons

Kinetic studies of nucleophilic addition to coordinated π-hydrocarbons have been reported for only a few systems [8—10, 17—20]. This work significantly extends this area and allows a reactivity order towards addition of tertiary phosphines to be formulated: $[(C_7H_8)Mn(CO)_3]^+ > [(C_4H_4)Fe(CO)_2NO]^+ > [(C_6H_7)Fe(CO)_3]^+ > [(C_6H_6OMe)Fe(CO)_3]^+ \gtrsim [(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, W) $> [(C_6H_6)Mn(CO)_3]^+$. The relative reactivities are approximately 10000/1000/150/30/30/1. It is of interest to note that the arene ring in $[(C_6H_6)Mn(CO)_3]^+$ is less electrophilic than coordinated cycloheptatriene in $[(C_7H_8)Mn(CO)_3]^+$ by a factor of about 10^4. This is primarily due, no doubt, to the resonance energy of the arene ring.

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