Applied Organometallic Chemistry (1990) 4 475–480

0268-2605/90/050475-06$05.00

# Kinetics and mechanism of nucleophilic addition at the bridging vinyl ligand of the cluster $[HOs_3(\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$

Leon A P Kane-Maguire* and Tahany Ghazy
Department of Chemistry, University of Wollongong, PO Box 1144, Wollongong, NSW 2500, Australia

*Received 14 January 1990* *Accepted 16 March 1990*

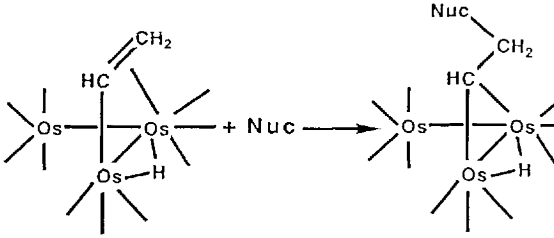
**Kinetic and spectroscopic studies are reported for the addition of a range of neutral phosphorus and nitrogen nucleophiles to the bridging $\eta^2$-vinyl ligand of the cluster $[HOs_3(\eta^2\text{-}CHCH_2)(CO)_{10}]$. With $PPh_3$, the reaction is reversible, and the rate law, $k_{obs} = k_1[\text{Nuc}] + k_{-1}$, is observed. This rate law is consistent with direct bimolecular addition ($k_1$) of $PPh_3$ to the $\eta^2$-vinyl ligand. With more basic triarylphosphine nucleophiles, the simple expression, $k_{obs} = k_1[PR_3]$, is obeyed. The second-order rate constant, $k_1$, varies markedly with the phosphine basicity. For the series $P(4\text{-}XC_6H_4)_3$, a linear Brönsted plot of $\log k_1$ vs $pK_a$ is obtained with a slope $\alpha$ of 0.46. The reversible addition of cyclohexylamine to this cluster also obeys a two-term rate law. Overall, nucleophilicity towards $[HOs_3(\eta^2\text{-}CHCH_2)(CO)_{10}]$ decreases in the order $C_6H_{11}NH_2 > P(4\text{-}MeOC_6H_4)_3 > P(4\text{-}MeC_6H_4)_3 > PPh_3$, which quantitatively parallels that previously found for the related mononuclear cation $[CpFe(CO)_2(\eta^2\text{-}CH_2CH_2)]^+$.**

**Keywords: Osmium, cluster, vinyl ligand, kinetics, mechanism, nucleophilic addition, nucleophilicity order**

## INTRODUCTION

Nucleophilic attack at coordinated hydrocarbon ligands in mononuclear $[ML_n\ (\text{hydrocarbon})]$ complexes has been the subject of extensive kinetic/mechanistic study.[1-3] Much is now known concerning the factors controlling hydrocarbon ligand reactivity in such mononuclear systems, and a comprehensive nucleophilicity scale ($N_{Fe}$) has been established[3] for some 40 different nucleophiles attacking the standard substrate $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ (I).

Similar quantitative data are surprisingly lacking for the reactivity of hydrocarbons when coordinated to multimetal centres in cluster complexes, despite intense recent interest in such systems. As part of a systematic study of such cluster reactions, we report here kinetic studies of nucleophilic addition to the $\eta^2$-vinyl ligand of the triosmium cluster $[HOs_3(\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ (II) by tertiary phosphines and the primary amine, cyclohexylamine. Cluster **II** has been reported by Deeming and Manning[4] to add a wide range of nucleophiles to the bridging vinyl ligand as shown in Eqn [1] (Nuc = $PMe_2Ph$, $CN^-$, $Et_2N^-$, $MeO^-$, $ArS^-$).



[1]

The rate and activation parameters obtained here for nucleophilic addition at the cluster-bound vinyl ligand in **II** are compared with previous data for analogous reactions at mononuclear substrates such as **I**. For this limited range of nucleophiles, the results suggest that similar factors control the reactivity of coordinated hydrocarbons in these two types of organometallic substrates.

## EXPERIMENTAL

### Materials

The cluster complex **II** was synthesized and purified using literature procedures.[5] The triarylphosphines were purchased in the purest forms

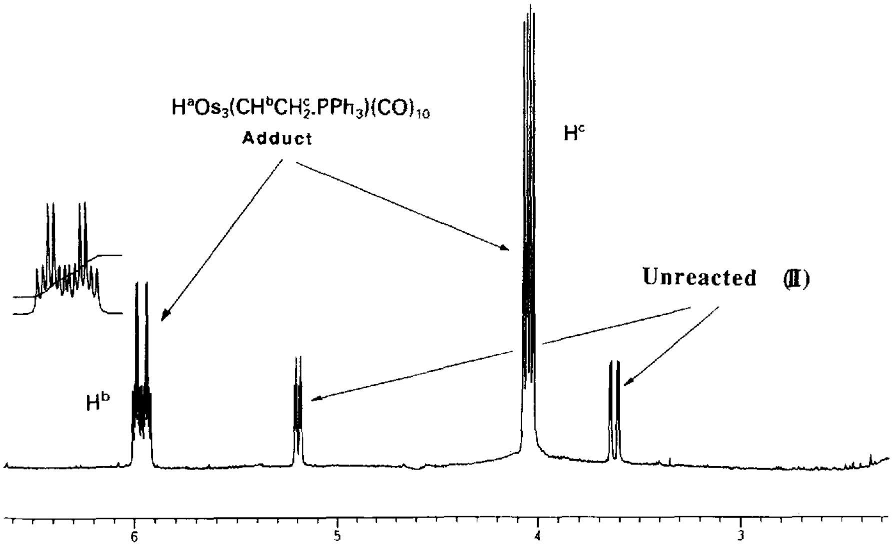


Figure 1 400 MHz $^1H$ NMR spectrum of an equimolar mixture (0.025 mol $dm^{-3}$) of cluster II and $PPh_3$ in $CD_3NO_2$.

available (Strem or Aldrich) and used as provided. Cyclohexylamine was purchased from Aldrich, and distilled at reduced pressure from KOH prior to use. Nitromethane solvent (Aldrich) was distilled in bulk and stored over molecular sieves (3 Å) under a dinitrogen atmosphere.

### Adducts from the reactions of II with $P(4\text{-}XC_6H_4)_3$

The phosphonium adducts [$HOs_3$-{$CHCH_2.P(XC_6H_4)_3$}$(CO)_{10}$] from the addition of $P(4\text{-}XC_6H_4)_3$ to the cluster **II** were characterized *in situ* from their IR and $^1H$ NMR spectra, which were closely analogous to those previously reported[4] for the $PMe_2Ph$ adduct.

### $HOs_3(CHCH_2.PPh_3)$ $(CO)_{10}$ (IIIa)

IR spectrum: $\nu$(CO) ($CH_3NO_2$) at 2080m, 2028vs, 2020s, 1995vs, 1965m, and 1944s. $^1H$ NMR ($CD_3NO_2$) ($[Os_3] = [PPh_3] = 0.025$ mol $dm^{-3}$): −16.5 (1H, dd, $H^a$), 4.04 (2H, dd, $H^c$; $J_{bc}$ 6.7 Hz, $J_{cP}$ 12.4 Hz), 5.96 (1H, ddt, $H^b$; $J_{ab}$ 3.4 Hz, $J_{bc}$ 6.8 Hz, $J_{bP}$ 18.5 Hz), 7.7–7.9 ppm (15H, m, P–Ar) (see Fig. 1).

### $HOs_3\{CHCH_2.P(4\text{-}MeOC_6H_4)_3\}$ $(CO)_{10}$ (IIIb)

IR spectrum: $\nu$(CO) (hexane) at 2080m, 2025vs, 1989vs, 1965w, 1945m. $^1H$ NMR ($CD_3NO_2$) ($[Os_3] = [PAr_3] = 0.02$ mol $dm^{-3}$): −16.3 (1H, dd, $H^a$), 3.9 (2H, m, $H^c$), 3.94 (3H, s, MeO), 5.98 (1H, ddt, $H^b$; $J_{ab}$ 3.3 Hz, $J_{bP}$ 18.8 Hz), 7.8 ppm (12H, m, P–Ar).

### $[HOs_3(CHCH_2.NHC_6H_{11})(CO)_{10}]^-$ (IIIc)

The amine adduct **IIIc** from the addition of cyclohexylamine to the cluster **II** was also characterized from *in situ* IR and $^1H$ NMR measurements. IR spectrum: $\nu$(CO)($CH_3CN$) at 2075 mw, 2030 s sh, 2020 vs, 1985 vs br, 1940 s. $^1H$ NMR ($CD_3NO_2$) ($[Os_3] = [C_6H_{11}NH_2] = 0.02$ mol $dm^{-3}$): 5.70 (1H, m, $H^b$) and 3.30 ppm (2H, m, $H^c$).

## Spectroscopic studies

IR spectra were recorded on a Perkin–Elmer 783 infrared spectrophotometer using matched 0.5 mm sodium chloride solution cells. Proton NMR (400 MHz) spectra were recorded in $CD_3NO_2$ using a JEOL GX400 spectrophotometer.

## Kinetic studies

All reactions were studied under pseudo-first-order conditions using a large excess of nucleophile {$[Os_3] = 3.0 \times 10^{-4}$ mol $dm^{-3}$, [Nuc] = $(1.0–11.0) \times 10^{-2}$ mol $dm^{-3}$}. Separate solutions of the cluster **II** and the appropriate nucleophile were freshly prepared in deoxygenated $CH_3NO_2$ and thermostated (± 0.1°C) at the desired temperature. Each of the rapid additions could be conveniently followed using a thermostated stopped-flow spectrometer, by monitoring the decrease in absorption at 390 nm during reaction.

Output from the photomultiplier detector was passed via an A/D converter to an Apple II Plus microcomputer (fitted with a Titan Accelerator II card) for acquisition and processing.

Pseudo-first-order rate constants, $k_{obs}$, were calculated, from the slopes of plots of $\log(A_t - A_\infty)$ versus time using a 'data process' program to be described elsewhere.[6] Linear first-order kinetics were generally obtained for at least two half-lives. Each $k_{obs}$ is the average of at least three separate runs, with an average reproducibility of ±4%. Least-squares analyses of $k_{obs}$ versus [Nuc] plots were used to obtain the forward second-order rate constants, $k_1$, and the reverse first-order rate constants, $k_{-1}$, together with their associated standard errors of estimate.

Activation parameters for the $PPh_3$ addition were calculated from a least-squares fit to the Arrhenius equation. The error quoted for $\Delta H_1$ is the standard error of estimate from this analysis. The entropy of activation, $\Delta S_1$, was estimated using the calculated second-order rate constant, $k_1$, at 20°C. The errors in the individual $k_{-1}$ values precluded the calculation of activation parameters for the reverse dissociation process.

## RESULTS AND DISCUSSION

### Spectroscopic studies

The nature of the reactions of cluster **II** with the triarylphosphines $P(4\text{-}XC_6H_4)_3$ (X = MeO, Me, H) and cyclohexylamine were clearly established from *in situ* IR and $^1H$ NMR spectroscopic studies (see the Experimental section).

The IR and $^1H$ NMR spectra of 1:1 mixtures of **II** and $PPh_3$ gave product peaks virtually identical to those previously reported[4] for the related $PMe_2Ph$ adduct $[HOs_3(CHCH_2.PMe_2Ph)(CO)_{10}]$. However, it is clear from the $^1H$ NMR spectrum in Fig. 1 that the addition of $PPh_3$ to **II** in $CD_3NO_2$ does not proceed to completion under the equimolar conditions employed ($[Os_3] = [PPh_3] = 0.025\ \text{mol dm}^{-3}$). As well as the strong adduct resonances at −16.0, 5.96 and 4.04 ppm, medium-intensity signals are also observed at *ca* 5.2 and 3.6 ppm associated with unreacted **II**. The equilibrium nature of reaction (**1**; Nuc = $PPh_3$) is also confirmed from the kinetic studies (*vide infra*).

Very similar spectral changes were observed for the addition of $P(4\text{-}MeOC_6H_4)_3$ to cluster **II** (see the Experimental section). However, with this more basic aryl phosphine, reaction [1] was found to proceed to completion (no unreacted **II** signals observed in the $^1H$ NMR spectrum of a 1:1 mixture of **II** and $P(4\text{-}MeOC_6H_4)_3$ ($[Os_3] = [PAr_3] = 0.02\ \text{mol dm}^{-3}$). This was also confirmed from the kinetic studies of reaction [1] [Nuc = $P(4\text{-}MeOC_6H_4)_3$], where no $k_{-1}$ term was observed in the rate law (*vide infra*).

Confirmation of the nature of the anionic amine adduct $[HOs_3(CHCH_2.NHC_6H_{11})(CO)_{10}]^-$ (**IIIc**) from the addition of cyclohexylamine to **II** comes from the close similarity of its IR spectrum to that previously reported[4] for the related $[HOs_3(CHCH_2.NEt_2)(CO)_{10}]$ adduct [$\nu$(CO)($PhNMe_2$): 2029 vs, 2022 s, 1994 s, 1982 s, and 1943 m], and from *in situ* $^1H$ NMR experiments (see the Experimental section). A 1:1 mixture in $CD_3NO_2$ ($[Os_3] = [C_6H_{11}NH_2] = 0.02\ \text{mol dm}^{-3}$) showed strong product resonances at 5.7 and 3.3 ppm, as expected for the anionic adduct **IIIc**. However, strong signals were also noted (at 5.2 and 3.6 ppm) for unreacted starting cluster **II**, confirming the equilibrium nature of adduct formation. A four-fold excess of $C_6H_{11}NH_2$ was required in order to drive reaction [1] (Nuc = $C_6H_{11}NH_2$) to completion, as evidenced by the disappearance of starting cluster signals in the $^1H$ NMR spectrum. No upfield shift of the proton resonances of **IIIc** were observed upon the addition of this four-fold excess of amine, confirming that deprotonation of the initially expected neutral adduct $[HOs_3(CHCH_2.NH_2C_6H_{11})(CO)_{10}]$ had already occurred under equimolar conditions ($[Os_3] = [C_6H_{11}NH_2] = 0.02\ \text{mol dm}^{-3}$).

### Kinetics and mechanism

#### Phosphine additions

Kinetic results for the addition of triaryl phosphines to the cluster $[HOs_3(\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ (**II**) in $CH_3NO_2$ are summarized in Tables 1 and 2. Analogous data for $PPh_3$ in dichloromethane solvent are collected in Table 3. In general, plots of $k_{obs}$ versus [Nuc] were linear with a non-zero intercept (e.g. Fig. 2), indicating adherence to the two-term expression [2]. This is consistent with reaction [1] (Nuc = $PAr_3$) being an equilibrium process in which $a$ is $k_1$, the second-order rate constant for nucleophilic addition at the $\eta^2$-vinyl ligand, and $b$ is $k_{-1}$, the first-order rate constant for the reverse dissociation.

$$k_{obs} = a[\text{Nuc}] + b \qquad [2]$$

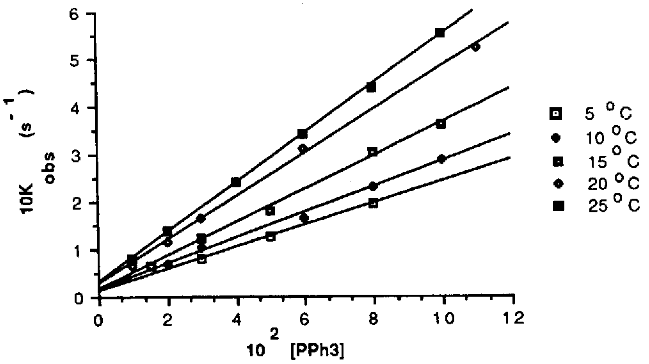


**Figure 2** Plots of $k_{obs}$ versus [PPh$_3$] for the addition of PPh$_3$ to cluster **II** in CH$_3$NO$_2$ at various temperatures.

Using $k_1$ and $k_{-1}$ values in Table 1, an equilibrium constant $K_1$ ($=k_1/k_{-1}$) of *ca* 200 is estimated for the addition of PPh$_3$ to **II** in CH$_3$NO$_2$ at 20°C. Considering the errors in the individual rate constants, this equilibrium constant is in reasonable agreement with the $K_1$ value of *ca* 350 estimated for this process from the $^1$H NMR experiment shown in Fig. 1.

However, in the case of the more basic nucleophile P(MeOC$_6$H$_4$)$_3$, the plot of $k_{obs}$ versus [Nuc] passes through the origin, within experimental error, indicating the simple rate law [3]. Similar behaviour is assumed for P(4-MeC$_6$H$_4$)$_3$.

$$\text{Rate} = k_{obs}\,[\text{Os}]$$

$$k_{obs} = k_1[\text{P(4-MeOC}_6\text{H}_4)_3]. \qquad [3]$$

For these triarylphosphine nucleophiles direct bimolecular addition, $k_1$, of the nucleophile to the $\eta^2$-vinyl ligand of **II** is believed to occur. Supporting this is low enthalpy of activation $\{\Delta H^\ddagger = 27.2(2.1)\ \text{kJ mol}^{-1}\}$ and large negative entropy of activation $\{\Delta S^\ddagger = -138(7)\ \text{J K}^{-1}\,\text{mol}^{-1}\}$ calculated for the PPh$_3$ reaction from an Arrhenius plot of the temperature dependence data in Table 1. These activation parameters are in the range previously observed[1] for the addition of PPh$_3$ to the $\pi$-hydrocarbon ligands of mononuclear organometallic substrates. No kinetic or spectroscopic evidence was obtained for any intermediates during reactions [1].

The basicity of the P(4-XC$_6$H$_4$)$_3$ nucleophiles has a marked influence on the rate of nucleophilic addition, with $k_1$ decreasing in the order P(4-MeOC$_6$H$_4$)$_3$ > P(4-MeC$_6$H$_4$)$_3$ > PPh$_3$. The Brönsted relationship [4] is obeyed (Fig. 3), with a moderate slope $\alpha$ of *ca.* 0.46. This Brönsted slope is the same as that recently found[7] for the addition of triarylphosphines to the ethene ligand of [CpFe(CO)$_2$ ($\eta^2$-C$_2$H$_4$)]$^+$, and is similar to the Brönsted slopes previously reported[1,7–9]

**Table 1** Kinetic data for the addition of PPh$_3$ to [HOs$_3$ ($\eta^2$-CH=CH$_2$)(CO)$_{10}$] in CH$_3$NO$_2$ [Os$_3$] = $3.0\times10^{-4}$ mol dm$^{-3}$

| Temperature (°C) | $10^2$[PPh$_3$] (mol dm$^{-3}$) | $10k_{obs}$ (s$^{-1}$) | $k_1$ (mol$^{-1}$ dm$^3$ s$^{-1}$)$^a$ |
|---|---|---|---|
| 5.0 | 3.0 | 0.820 | |
| | 5.0 | 1.26 | 2.29(0.05) |
| | 8.0 | 1.97 | |
| 10.0 | 2.0 | 0.686 | |
| | 3.0 | 1.03 | |
| | 6.0 | 1.67 | 2.70(0.12) |
| | 8.0 | 2.29 | |
| | 10.0 | 2.90 | |
| 15.0 | 1.5 | 0.646 | |
| | 3.0 | 1.24 | |
| | 5.0 | 1.81 | 3.51(0.11) |
| | 8.0 | 3.03 | |
| | 10.0 | 3.60 | |
| 20.0 | 1.0 | 0.657 | |
| | 2.0 | 1.16 | |
| | 3.0 | 1.67 | 4.58(0.09) |
| | 6.0 | 3.10 | |
| | 11.0 | 5.25 | |
| 25.0 | 1.0 | 0.804 | |
| | 2.0 | 1.38 | |
| | 4.0 | 2.43 | 5.18(0.07) |
| | 6.0 | 3.41 | |
| | 8.0 | 4.38 | |
| | 10.0 | 5.54 | |

$^a$Values in brackets are the standard errors of estimate from the least-squares fit to Eqn [2]: $k_{-1}$ (20°C) = 0.026 (0.005) s$^{-1}$.

**Table 2** Kinetic data for the addition of triarylphosphines P(4-XC$_6$H$_4$)$_3$ to [HOs$_3$($\eta$-CH=CH$_2$)(CO)$_{10}$] in CH$_3$NO$_2$ at 20.0°C
[Os$_3$] = 3.0 × 10$^{-4}$ mol dm$^{-3}$

| X | $10^2$[P(4-XC$_6$H$_4$)$_3$] (mol dm$^{-3}$) | $10k_{obs}$ (s$^{-1}$) | $k_1$ (mol$^{-1}$ dm$^3$ s$^{-1}$) |
|---|---|---|---|
| MeO | 1.0 | 2.78 | |
| | 2.0 | 6.35 | |
| | 3.0 | 9.27 | 34.8(0.2)$^a$ |
| Me | 1.0 | 1.26 | 12.6 |
| H | 1.0–11.0 | | 4.58 |

$^a$Value in brackets is the standard error of estimate from the least-squares fit to Eqn [3].

for analogous additions to a range of mononuclear $\pi$-hydrocarbon metal complexes (Table 4). The close agreement of the Brönsted slopes for each of these substrates suggests a similar position of the transition state along the reaction coordinate in each case. This indicates that the mononuclear and cluster $\pi$-hydrocarbon metal complexes, like the well-studied organic substrates EtI[10] and PhCH$_2$Cl,[11] have only moderate phosphorus–carbon formation in the transition state.

$$\log_{10} k_1 = \alpha pK_a + \text{constant} \qquad [4]$$

Comparison of rate constants in Tables 1 and 3 shows that the polarity of the solvent has little effect on the rate of phosphine addition to cluster **II**. The second-order rate constant, $k_1$, at 20.0°C is seen to decrease by only a factor of two upon changing from CH$_3$NO$_2$ to the relatively non-polar dichloromethane as solvent. This is not surprising for a reaction between two neutral reagents.

**Table 3** Kinetic data for addition of PPh$_3$ to [HOs$_3$($\eta^2$-CH=CH$_2$)(CO)$_{10}$] in CH$_2$Cl$_2$ at 20.0°C
[Os$_3$] = 3.0 × 10$^{-4}$ mol dm$^{-3}$

| $10^2$[PPh$_3$] (mol dm$^{-3}$) | $10k_{obs}$ (s$^{-1}$) | $k_1$ (mol$^{-1}$ dm$^3$ s$^{-1}$) |
|---|---|---|
| 1.0 | 0.645 | |
| 1.5 | 0.805 | |
| 2.0 | 0.990 | 2.01(0.13)$^a$ |
| 3.0 | 1.16 | |
| 4.5 | 1.38 | |
| 6.0 | 1.71 | |

$^a$Value in brackets is the standard error of estimate from the least-squares fit to Eqn [2]: $k_{-1}$ = 0.051(0.005) s$^{-1}$.

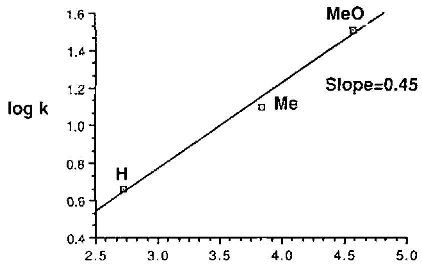
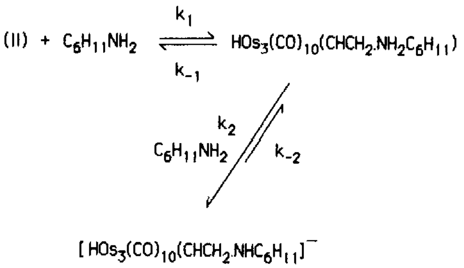


**Figure 3** Brönsted plot of $\log_{10} k_1$ versus p$K_a$ for the addition of P(4-XC$_6$H$_4$)$_3$ to cluster **II** in CH$_3$NO$_2$ at 20°C.

## Addition of cyclohexylamine

Kinetic results for the reaction of cluster **II** with cyclohexylamine are collected in Table 5. This reversible process, which leads to the anionic adduct [HOs$_3$(CHCH$_2$.NHC$_6$H$_{11}$)(CO)$_{10}$]$^-$(**IIIc**), is also seen to obey Eqn [2]. This behaviour is analogous to that previously found for the addition of anilines to the cyclohexadienyl cation [Fe(CO)$_3$($\eta^5$-C$_6$H$_7$)]$^+$,[12] and can be rationalized in terms of the mechanism outlined in Scheme 1.



Since this reaction involves two successive equilibria, derivation of a general rate expression would be complex. However, by making the reasonable assumption that equilibrium $K_2$ is established much more rapidly than $K_1$, one obtains the relationships [5] and [6] (where $K_a$ is the acid dissociation constant for protonated cyclohexylamine in the same solvent). This assumption is supported by failure to observe any intermediates during reactions [1]. It should be noted, however, that the final adduct (**IIIc**) has only been identified tentatively here by comparison of its IR and $^1$H NMR spectra with a previously reported[4] adduct from diethylamine. Full confirmation of its structure must await its isolation.

$$a = k_1 \qquad [5]$$

$$b = k_{-1}[\mathrm{H}^+]/([\mathrm{H}^+] + K_2K_a \qquad [6]$$

**Table 4** Brönsted slopes for the addition of triarylphosphine to various substrates

| Substrate | Solvent | Slope, $\alpha$ | Reference |
|---|---|---|---|
| $HOs_3(\eta^2\text{-}CH{=}CH_2)(CO_{10})$ | $CH_3NO_2$ | 0.46 | This work |
| $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ | Acetone | 0.50 | 8 |
| $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+$ | Acetone | 0.45 | 2 |
| $[Fe(CO)(NO)(PPh_3)(\eta^4\text{-}C_4H_4)]^+$ | $CH_3NO_2$ | 0.47 | 9 |
| $[FeCp(CO)_2(\eta^2\text{-}C_2H_4)]^+$ | Acetone | 0.46 | 7 |
| $[Mn(CO)_2(NO)(\eta^5\text{-}MeC_6H_6)]^+$ | $CH_3CN$ | 0.47 | 1 |
| Et I | Acetone | 0.49 | 10 |

**Table 5** Kinetic data for the addition of cyclohexylamine to $[HOs_3\ (\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ in $CH_3NO_2$ at 20°C
$[Os_3] = 3.0 \times 10^{-4}$ mol $dm^{-3}$

| $10^2\ [C_6H_{11}NH_2]$ (mol $dm^{-3}$) | $k_{obs}$ ($s^{-1}$) | $k_1$ ($mol^{-1}\ dm^3\ s^{-1}$) |
|---|---|---|
| 2.0 | 2.49 | 85.2 (0.9) |
| 4.0 | 4.12 | |
| 6.0 | 5.89 | |
| 8.0 | 7.58 | |

$k_{-1}$ (20°C) = 0.76(0.05) $s^{-1}$.

Combination of data in Tables 2 and 5 shows that the reactivity of nucleophiles towards the cluster **II** decreases along the series $C_6H_{11}NH_2 >$ $P(4\text{-}MeOC_6H_4)_3$ > $P(4\text{-}MeC_6H_4)_3$ > $PPh_3$ (relative rates 18:7.5:3:1). Interestingly, this order is quantitatively very similar to nucleophilicities previously observed[7] for addition to the mononuclear cation $[CpFe(CO)_2(\eta^2\text{-}C_2H_4)]^+$ ($C_6H_{11}NH_2$ > $P(4\text{-}MeOC_6H_4)_3$ > $P(4\text{-}MeC_6H_4)_3$ > $PPh_3$; relative rates 17:5:3:1). This suggests that for neutral phosphorus and nitrogen nucleophiles, the factors controlling the reactivity of mononuclear and cluster-bound hydrocarbons may be similar. However, much more extensive studies will be required to test this hypothesis.

*Acknowledgments* The Australian Research Council is thanked for financial support.

## REFERENCES

*1.* Kane-Maguire, L A P, Honig E D and Sweigart, D A *Chem Rev.*, 1984, 84: 525, and Refs therein

*2.* Evans, S G, Gilmore, K and Kane-Maguire, L A P *J. Chem. Soc. Dalton Trans.*, 1988, 2009

*3.* Ghazy, T and Kane-Maguire, L A P *J. Organomet Chem.*, 1988, 338: 47, and Refs therein

*4.* Deeming, A J and Manning, P J *J. Organomet. Chem.*, 1984, 265: 87

*5.* Deeming, A J, Hasso, S and Underhill, M *J. Chem. Soc., Dalton Trans.*, 1975, 1614

*6.* Bolton, P D, Chapman, S, Cheesman D and Kane-Maguire, L A P (unpublished results)

*7.* Chapman, S and Kane-Maguire, L A P *Organometallics* (submitted)

*8.* Atton, J G and Kane-Maguire, L A P *J. Chem. Soc., Dalton Trans.*, 1982, 1491

*9.* Choi, H S and Sweigart, D A *Organometallics*, 1982, 1: 60

*10* Henderson, W A and Buckler S A *J. Am. Chem. Soc.*, 1960, 82: 5794

*11.* McEwen, W E, Fountaine, J E, Schultz, D N and Shiau, W I *J. Org. Chem.*, 1976, 41: 1684

*12.* Kane-Maguire, L A P, Odiaka, T I, Turgoose, S and Williams, P A *J. Chem. Soc., Dalton Trans.*, 1981, 2489