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NUCLEOPHILIC ADDITION OF TERTIARY PHOSPHINES TO THE BIS(BENZENE)METAL(II) CATIONS OF THE IRON TRIAD

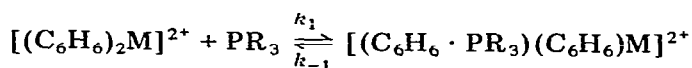
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Summary

The complexes $[(\text{benzene})_2\text{M}]^{2+}$ (M = Fe, Ru, Os) react rapidly and reversibly with tertiary phosphines to form cyclohexadienyl phosphonium ring adducts:



Addition to both benzene rings does not occur even in the presence of excess phosphine. The room temperature ^1H NMR spectra with $\text{P}(\text{n-Bu})_3$ are static, but with PPh_3 exchange averaged spectra result. The rate and equilibrium constants with PPh_3 were obtained via variable temperature ^{31}P and ^1H NMR. In contrast to previously reported phosphine addition reactions, the electrophilic reactivity (k_1) is very metal dependent: $\text{Fe} \gg \text{Ru} > \text{Os}$ (390 : 7 : 1). The reverse rate constant (k_{-1}) is only weakly metal dependent, and the resulting linear free energy relationship (LFER) between $K_{\text{eq}} = k_1/k_{-1}$ and k_1 implies considerable C– PPh_3 bond formation in the transition state. It is suggested that metal \rightarrow benzene π backbonding in $[(\text{C}_6\text{H}_6)_2\text{M}]^{2+}$ follows the order $\text{Ru}, \text{Os} \gg \text{Fe}$, and that this accounts for the greater thermodynamic and kinetic electrophilic properties of the iron complex. A mechanism for the phosphine addition reactions involving direct bimolecular attack on the arene is proposed. This and previous work allow the formulation of a rather extensive reactivity series for tertiary phosphine addition to coordinated cyclic π -hydrocarbons.

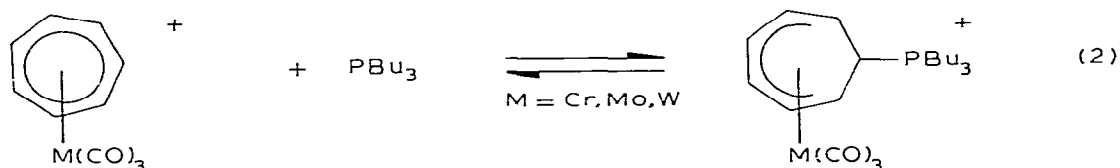
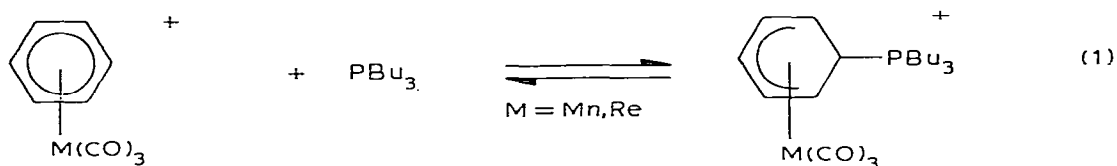
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** Contribution No. 2765.

Introduction

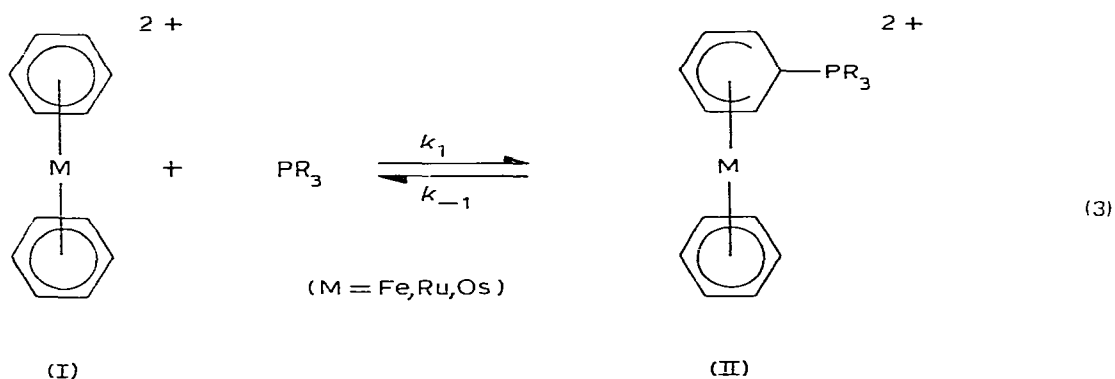
The addition of tertiary phosphines and phosphites to coordinated cyclic π -hydrocarbons is now a well characterized reaction. A number of kinetic studies have appeared [1–5] and have provided information about the reaction mechanism and the relative electrophilic character of coordinated rings. Knowledge of these factors allows predictions to be made about possible new nucleophilic addition reactions of synthetic utility.

Kinetic studies [1,2] of reactions 1 and 2 showed that the rate did not



depend very much on the metal within a given triad, and this was taken as support for a mechanism consisting of direct bimolecular addition to the ring without prior attack on the metal. The almost invariably *exo* conformation of the ring adducts with various types of nucleophiles also supports the direct addition mechanism.

We recently found [6] that the coordinated benzene in $[(\text{C}_6\text{H}_6)_2\text{Fe}]^{2+}$ is extremely electrophilic towards tertiary phosphines, reaction 3 ($\text{M} = \text{Fe}$). How-



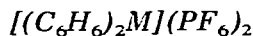
ever, in spite of the ease of addition of triphenylphosphine (PPh_3) and tri-*n*-butylphosphine (PBu_3) to one benzene ring, addition to the second ring did not occur even in the presence of a large excess of phosphine. The phosphonium salts II were readily isolated and represented the first example of phosphine addition to a non-substituted benzene ring that led to an isolable product.

Herein we report the thermodynamics and dynamics of reaction 3 with iron,

ruthenium, and osmium. In contrast to previous work, the equilibrium constant and forward rate constant (k_1) are shown to be strongly metal-dependent. Possible explanations for this behavior are discussed.

Experimental

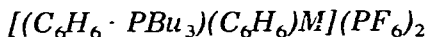
All solvents were distilled and dried prior to use. The phosphines PPh_3 and PBu_3 were purified by standard methods and checked for the presence of oxide by ^{31}P NMR. Electronic spectra were recorded on a Cary 17, NMR spectra (^1H , ^{13}C , ^{31}P) on a Bruker HFX-90 instrument operating in the FT mode, and X-ray photoelectron spectra on a Varial IEE-15. IR spectra were recorded in acetonitrile solvent on a Perkin-Elmer 221.



The iron complex was synthesized according to the method of Helling, et al. [7], and the ruthenium complex according to the method of Wilkinson, et al. [8].

Osmium-arene complexes are mentioned in a review by Fischer [9], but preparative details are not given. We prepared $[(\text{C}_6\text{H}_6)_2\text{Os}](\text{PF}_6)_2$ by heating Na_2OsCl_6 (4.7 g), Al powder (1.5 g), AlCl_3 (6.0 g), and benzene (25 ml) in a bomb at 150°C for 17 hours. The excess benzene was filtered off, and the residue treated with cold H_2O -MeOH (2 : 1). The reaction mixture must be kept cold to avoid decomposition. After filtration and washing with diethyl ether, the aqueous phase was treated with NH_4PF_6 . The off-white precipitate was washed with water, alcohol, and finally ether. The crude product was purified by dissolution in acetonitrile, filtration, and precipitation with diethyl ether.

Carbon and hydrogen analyses were satisfactory for the complexes.



The tri-*n*-butylphosphine adducts were easily synthesized by adding excess PBu_3 to a slurry of the bis-benzene complexes in acetonitrile. The starting material dissolved within a few seconds as the phosphonium adduct formed. Filtration and precipitation with diethyl ether yielded orange ($\text{M} = \text{Fe}$) or white crystals ($\text{M} = \text{Ru}, \text{Os}$). The yields were quantitative. The iron complex was shown by analytical, IR, and NMR data to crystallize with one mole of uncoordinated CH_3CN . The other adducts did not crystallize with CH_3CN . Carbon and hydrogen analyses agreed with the proposed structures.



The triphenylphosphine adduct was synthesized as described above for the PBu_3 complexes. With $\text{M} = \text{Ru}$ and Os , the equilibrium constants of reaction 3 are too small to allow the synthesis of the PPh_3 adducts.

Kinetic studies

The dynamics of reaction 3 with PPh_3 were studied via ^{31}P $\{^1\text{H}\}$ NMR. A CD_3CN solution of $[(\text{C}_6\text{H}_6)_2\text{Fe}](\text{PF}_6)_2$ and PPh_3 , typical concentrations 0.03 *M* and 0.06 *M* respectively, was cooled to -40°C . A static spectrum corresponding to free and "coordinated" PPh_3 was obtained. Warming to room tempera-

ture is accompanied by coalescence of the two resonances. For the particular concentrations used, the fractional populations of the two sites were calculated from area measurements and from the known equilibrium constant (see below). With reaction 3, abbreviated as in equation 4, the line broadening in the slow exchange region, $\Delta\nu = \nu - \nu_0$, is given in equations 5 and 6. ν_0 is the limiting



$$\frac{1}{\tau_{MP}} = \pi \Delta\nu_{MP} = k_{-1} \quad (5)$$

$$\frac{1}{\tau_P} = \pi \Delta\nu_P = k_1[M] = k_{-1} \frac{[MP]}{[P]} \quad (6)$$

slow exchange line width. The measured line widths showed the concentration dependence required by equations 5 and 6. The rate constants were also calculated by full like shape simulation using the program PZDMX [10]. The rate constants and activation parameters determined by using equations 5 and 6 in the slow exchange region were almost identical to the results obtained by using the simulation program over a wider temperature range extending above coalescence.

With the M = Ru and Os complexes the small equilibrium constants (see below) made it inconvenient to use the simulation program, and the rate constants were calculated using equations 5 and 6 in the slow exchange region. Rate constants were also calculated for these complexes by measuring the line broadening of the ^1H resonance of $[(\text{C}_6\text{H}_6)_2\text{M}]^{2+}$ in solutions containing varying concentrations of PPh_3 . Activation parameters, ΔH^\ddagger and ΔS^\ddagger , were calculated by least-squares fitting to the Eyring equation.

Equilibrium constants

For all three complexes the equilibrium constants for reaction 3 in CD_3CN were determined by area measurements in the slow exchange region of the ^1H and ^{31}P NMR spectra. In the fast exchange region the ^1H chemical shift, weighted according to the relative populations of M and MP, was used to calculate K_{eq} . For this latter method the static chemical shifts were obtained from spectra at -40°C . The ^1H NMR chemical shifts for M and MP in the absence of exchange are not temperature dependent over the range -40°C to 25°C . This was verified by direct measurement in the slow exchange region and by limiting average resonance in the fast exchange region for the M = Fe complex, for which K_{eq} was independently measured by visible spectroscopy by following the shift in absorbance at 465 nm as a function of the PPh_3 concentration and temperature.

The thermodynamic functions, ΔH^0 and ΔS^0 , for reaction 3 were obtained from the equilibrium constants by least-squares fitting to the standard Van 't Hoff equation.

Results

The phosphonium adducts II are easily prepared as crystalline salts. Conduc-

TABLE 1

¹H NMR CHEMICAL SHIFTS FOR [(C₆H₆ · PR₃)(C₆H₆)M](PF₆)₂^a

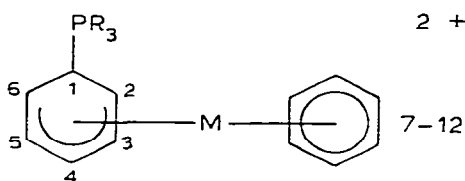
PR ₃	M	H(7-12)	H(4)	H(3, 5)	H(1)	H(2, 6)
PBu ₃ ^b	Fe	3.64	2.86	4.89	5.84	6.46
PBu ₃ ^b	Ru	3.68	3.41	4.67	5.95	6.25
PBu ₃ ^b	Os	3.63	3.12	4.45	5.9	5.9
PPh ₃ ^c	Fe	3.66	3.11	5.30	4.50	6.35
PPh ₃ ^c	Ru	3.70	4.23	5.06	4.60	6.08
PPh ₃ ^c	Os	3.66	3.94	4.84	4.59	5.76

^a Solvent CD₃CN; see text for numbering scheme; resonance positions given in τ scale relative to TMS.^b At 25°C. ^c At -40°C.

tivity measurements in nitromethane showed that they are 2 : 1 electrolytes.

Helling and coworkers [11] have shown that various carbon, nitrogen, and oxygen nucleophiles add to [(arene)₂Fe]²⁺ salts to yield the *exo* conformer. That the phosphonium adducts II in reaction 3 also have the expected *exo*-stereochemistry was shown by the absence of an *exo* C—H stretch near 2800 cm⁻¹ in the IR spectrum of [C₆H₆ · PBu₃](C₆H₆)Fe](PF₆)₂.

¹H NMR spectra of [(C₆H₆)₂M](PF₆)₂ in CD₃CN at 24°C consist of the single resonance 3.00 τ (Fe); 3.17 τ (Ru); 2.99 τ (Os). Data for the phosphine adducts II are given in Table 1, and correlate with the following number scheme:



The PBu₃ adducts give static spectra at room temperature. With PPh₃ fast exchange at room temperature leads to an averaged resonance; at -40°C static spectra are obtained (Table 1).

Except for the H(7-12) resonance, which is a singlet, the cyclohexadienyl ring resonances are all triplets or doublets of doublets. The assignments in Table 1 were made with the help of decoupling experiments and are in conformity with numerous reports [8,12] of ¹H NMR spectra of cyclohexadienyl complexes.

TABLE 2

³¹P {¹H} CHEMICAL SHIFTS FOR [(C₆H₆ · PR₃)(C₆H₆)M](PF₆)₂^a

PR ₃	M	Shift
PBu ₃ ^b	Fe	25.7
PBu ₃ ^b	Ru	28.6
PBu ₃ ^b	Os	35.9
PPh ₃ ^c	Fe	6.3
PPh ₃ ^c	Ru	10.4
PPh ₃ ^c	Os	18.6

^a In CD₃CN; shifts in ppm downfield from 85% H₃PO₄; PF₆⁻ resonances not listed. ^b At 25°C.^c At 40°C.

TABLE 3
THERMODYNAMIC AND KINETIC DATA FOR REACTION 3 WITH PPh₃^a

M	ΔH°	ΔS°	ΔH_1^\ddagger	ΔS_1^\ddagger	ΔH_{-1}^\ddagger	ΔS_{-1}^\ddagger
Fe	-8.2 ± 0.3	-17.5 ± 1	4.2 ± 0.9^b	-19 ± 3^b	12.3 ± 0.6	-1 ± 2
Ru	-5.1 ± 1.0	-16 ± 4	7.2 ± 2.0^b	-16 ± 8^b	12.3 ± 1.0	0 ± 4
Os	-5.0 ± 1.0	-17 ± 4	8.8 ± 1.5^c	-14 ± 5^c	13.8 ± 2.5	3 ± 9

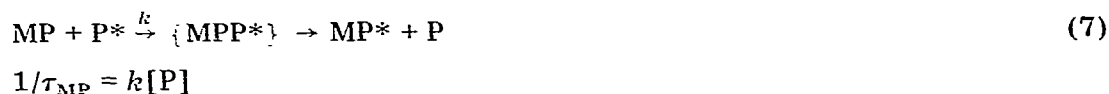
^a Solvent CD₃CN; errors are 95% confidence limits; units are kcal/mol and cal/deg mol. ^b Calculated from K_{eq} and k_{-1} . ^c Calculated from ¹H NMR data.

The ¹³C {¹H} NMR spectra of [(C₆H₆)₂M](PF₆)₂ in CD₃CN at 24°C consist of resonances at 95.3 (Fe); 95.9 (Ru); 89.5 (Os). (The chemical shifts are ppm downfield from TMS.) ¹³C {¹H} spectra of the PBu₃ adducts consist of numerous resonances, with the following partial results: C(7–12) = 93.4 (Fe); 93.2 (Ru).

Table 2 gives the ³¹P {¹H} NMR chemical shifts for the phosphine adducts.

Kinetic and thermodynamic data for reaction 3 with PPh₃ are given in Table 3. The temperature range used in this study was –40°C to +25°C, and data was collected at intervals of approximately 7°. The ³¹P NMR experiments gave values of k_{-1} and these combined with K_{eq} gave k_1 . With M = Os, k_1 was also calculated from ¹H NMR data.

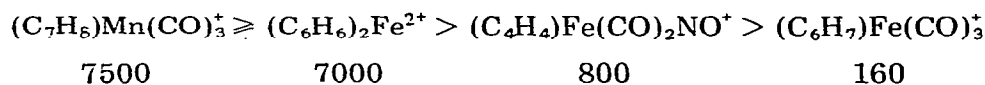
It is clear from the results for reaction 3 that a simple dissociative mechanism holds. The rate constants $k_{-1} = 1/\tau_{MP}$ were independent of phosphine concentration, as required by equations 4 and 5. If the exchange process were associative, as in equation 7, the line broadening would be linear in the PPh₃ concentration.

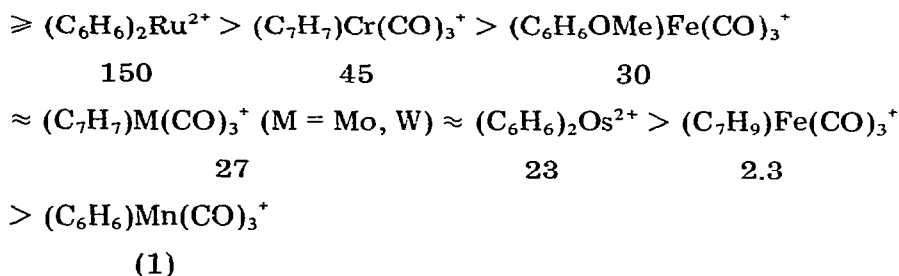


Discussion

The coordinated benzene rings in [(C₆H₆)₂M]²⁺ are remarkably electrophilic, and this work is the first report of an unsubstituted benzene ring being sufficiently activated to react with PPh₃. We are currently investigating the possibility that aromatic nucleophiles such as dimethylaniline or pyrrole may couple to the coordinated benzene in compounds I. This could provide a way to couple aromatic molecules via an electrophilic aromatic substitution reaction with coordinated benzene serving as the electrophile.

Since 1975 a sufficient number of kinetic investigations have been reported [1–5] to allow the formulation of the following reactivity order with respect to tertiary phosphine addition to coordinated cyclic π -hydrocarbons:





The reactivities are relative to $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$. This series shows that $[(\text{C}_6\text{H}_6)_2\text{Fe}]^{2+}$ is close to being the most reactive system yet found.

As discussed above, the rate of phosphine addition (k_1) did not depend strongly on the metal for the complexes $[(\text{C}_7\text{H}_7)\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[(\text{C}_6\text{H}_6)\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Mn}, \text{Re}$). Table 4 gives some rate and equilibrium constants for reaction 3 at 0°C , and shows that phosphine addition to $[(\text{C}_6\text{H}_6)_2\text{M}]^{2+}$ is strongly metal-dependent. John and Kane-Maguire [13] recently found that *N,N*-dimethylaniline couples through the *para*-carbon to the cyclohexadienyl ring in $[(\text{C}_6\text{H}_7)\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$), and that at 45°C the relative rates are $\text{Fe} > \text{Os} > \text{Ru}$ (41 : 3.6 : 1). This reaction involves proton loss from the aniline as well as nucleophilic addition to the ring, and so is not as easy to interpret as the simple phosphine addition reactions. Nevertheless, the fact that we also find the reactivity order $\text{Fe} \gg \text{Ru}, \text{Os}$ suggests that it is probably a general phenomenon.

It is possible that there is a change in the mechanism of phosphine addition in reaction 3 as the metal is changed. Initial interaction of the nucleophile directly with the metal prior to migration to the ring would be expected to be more likely with ruthenium and osmium. For example, Lewis, et al., [14] found that methoxide rapidly attacks a coordinated CO in $[(\text{C}_6\text{H}_7)\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) to give the ester which for ruthenium and osmium, but not iron, is relatively stable and only slowly converts to the *exo* ring adduct. With iron the conversion is rapid. Although the results of Lewis, et al., do not involve direct attack at the metal, they do indicate an increased tendency of nucleophilic attack in the immediate vicinity of the metal as the triad is descended. The rate of phosphine addition in reaction 3 may vary with the metal due to initial formation of an intermediate with a $\text{M}-\text{PPh}_3$ bond. However, since nucleophiles are known to add *exo* to coordinated rings, it is difficult to see how such an intermediate could lead to product in a concerted step. Most likely the formation of a $[(\text{C}_6\text{H}_6)_2\text{M}-\text{PPh}_3]^{2+}$ species would represent a "dead end" equilibrium and would not be detected by a measurement on a sys-

TABLE 4

EQUILIBRIUM AND RATE CONSTANTS FOR PPh_3 ADDITION TO $[(\text{C}_6\text{H}_6)_2\text{M}]^{2+}$ AT 0°C IN CD_3CN

M	K (M^{-1})	k_1 ($\text{M}^{-1} \text{s}^{-1}$)	k_{-1} (s^{-1})
Fe	500	175000	450
Ru	3.8	3100	820
Os	1.9	450	230

tem at equilibrium (NMR) unless it were present in significant concentration. With the ruthenium and osmium complexes I the equilibrium constants are small enough that reaction 3, even at -40°C , did not go more than ca. 50% to completion under our experimental conditions, and there was no evidence for any species other than the reactant and product in reaction 3.

The probability of a metal-phosphine intermediate being important in the mechanism of reaction 3 is remote. A more satisfying explanation for the metal dependence of the rates is that metal \rightarrow arene π -backbonding increases in the order Os, Ru $>$ Fe, and this renders the benzene ring less electrophilic for ruthenium and osmium. Ru^{II} and Os^{II} are known to have considerable π backbonding ability [15], more so than Fe^{II}. This proposal is consistent with the similar rates of reaction 2 for all three metals of the chromium triad; there appears [16] to be very little difference in π -backbonding ability in this triad. We feel that all of the phosphine addition reactions reported [1-5] to date fit a mechanism of direct bimolecular attack on the coordinated ring. The similar activation parameters for k_1 (low ΔH^{\ddagger} , very negative ΔS_1^{\ddagger}) for all these reactions support this view.

If increased π -backbonding is responsible for the decreased electrophilic character of the ruthenium and osmium complexes, one might expect this to be reflected in some physical properties of the $[(\text{C}_6\text{H}_6)_2\text{M}]^{2+}$ complexes. The ^1H chemical shifts would seem a likely candidate. The resonance of the ruthenium complex is indeed at higher field than the iron analogue (3.17 τ vs 3.00 τ), but the osmium complex has its resonance at 2.99 τ . However, it is not obvious that one would expect a clear correlation to the ^1H data since the complex $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$ has its resonance at 3.10 τ , and this complex is a very weak electrophile and does not react with PPh_3 .

The coordinated benzene carbon $1s$ core electron binding energies for compounds I were measured by the ESCA technique. Relative to the same internal standard, namely the F $1s$ and P $2p$ IP's in PF_6^- , all three complexes have the same C $1s$ binding energy, 285 eV. This result is of dubious value however, because the weak electrophile $[(\text{C}_6\text{H}_6)\text{M}(\text{CO})_3]^+$ was found to have the same benzene C $1s$ IP. Proton chemical shifts and C $1s$ IP's are primarily measurements of properties of filled MO's. Since the PPh_3 in reaction 3 presumably interacts with an empty orbital, it can be argued that it is not ground state but excited state energies that are important.

Of course, the equilibrium constants in Table 3 are independent of whatever the reaction mechanism is. The differences in the K_{eq} values must relate to differences in the C- PPh_3 bond energy, the loss of resonance energy upon adduct formation, and the energetics involved in the deformation of the ring from planarity in the products. There is no simple way to differentiate between these related quantities.

Tables 3 and 4 show that the reverse rate constant (k_{-1}) is only weakly metal-dependent while the differences in k_1 are responsible for the K_{eq} variation. If it is argued that the K_{eq} differences reflect the C- PPh_3 bond strengths, one concludes that the linear free energy relationship (LFER) between K_{eq} and k_1 implies considerable C- PPh_3 bond formation in the transition state, and conversely little bond breakage for the reverse reaction. This may account for the approximately zero values for ΔS_{-1}^{\ddagger} . The observed LFER is also of interest

when compared to the work of Ritchie [17] with electrophile–nucleophile combination reactions involving only bond formation. Ritchie finds little correlation between rate and equilibrium constants for the addition of neutral or charged nucleophiles to electrophiles such as tropylium cation or dinitrohalobenzene. The phosphine addition reactions discussed in this paper are in a general sense the same type as Ritchie's, and it will be of interest to see if the LFER found for reaction 3 can be extended to other coordinated π -hydrocarbon-nucleophile addition reactions, especially with nucleophiles other than phosphines. Such experiments are planned. There is sufficient data at this time to suggest that the correlation between k_1 and K_{eq} cannot be extrapolated to other phosphine addition reactions if both the phosphine and electrophile changed. For example [1], the K_{eq} for PBU_3 addition to benzene in $[(\text{C}_6\text{H}_6)\text{-Mn}(\text{CO})_3]^+$ at 0°C is about 1700 M^{-1} , which is three times that for PPh_3 addition to benzene in $[(\text{C}_6\text{H}_6)_2\text{Fe}]^{2+}$, yet the rate constants are in the ratio 295 : 175000. However, this result may be simply due to the "anomalously" high reactivity previously observed [5] with PPh_3 .

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