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Complexes of Long Alkyl Chain Tertiary Phosphines. 4. Oxidative Addition of Methyl Iodide to *trans*-[RhCl(CO)(PR₃)₂]

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The kinetics of the oxidative addition of methyl iodide to *trans*-[RhCl(CO)L₂] have been determined. When L is a trialkylphosphine, the product of oxidative addition is *trans*-[RhClI(CH₃)(CO)L₂]; the influence of L on the rate of this reaction is P(*n*-C₈H₁₇)₃ > P(*n*-C₄H₉)₃ > P(*n*-C₁₈H₃₇)₃. When L is a triarylphosphine, two products are formed: *trans*-[RhClI(CH₃)(CO)L₂] and a rhodium(III)-acyl complex. The formation of two products precludes a simple linear treatment of the kinetic data. A nonlinear treatment was effected with use of the program FACSIMILE. This clearly shows, contrary to earlier reports, that *trans*-[RhClI(CH₃)(CO)L₂] is not a significant intermediate in the formation of the final acyl product. A mechanism is proposed which involves anionic rhodium species formed by reaction of dissociated phosphine ligands with methyl iodide to yield the corresponding methylphosphonium salts and iodide ions which subsequently coordinate to rhodium(I). Analysis of the data obtained shows that introduction of alkyl substituents in the para position of coordinated triphenylphosphine enhances oxidative addition at rhodium(I). Trialkylphosphines are more effective than triarylphosphines at promoting oxidative addition at rhodium(I); alkyl chains longer than butyl are marginally less effective than butyl itself.

Introduction

We have recently described the syntheses of two series of phosphines P(*n*-C_mH_{2m+1})₃ where *m* = 10-19 and P-(C₆H₄C_nH_{2n+1-p})₃ where *n* = 3-9.² These phosphines have rather different solubility properties to those previously available; in particular they are extremely soluble in aliphatic hydrocarbon and chlorinated aliphatic hydrocarbon solvents. We have prepared a number of palladium(II), platinum(II), platinum(O), and rhodium(I) complexes of these phosphines.³ Our reasons for doing this were twofold.

First, phosphine complexes have been widely used as homogeneous catalysts, and in many of their reactions the solvent plays a very important role. Complexes with rather different solvation properties might behave in a different and perhaps more useful way to those already known.

Second, if alkanes are ever going to be activated with use of homogeneous catalysts that activation will have to be effected in solvents that are chemically more inert than the alkanes themselves. No such solvents are, of course, available, and if homogeneous catalysts are to be used, then those catalysts must dissolve freely in the alkanes themselves.

A very important step in many homogeneous catalytic cycles, including alkane activation,⁴ is oxidative addition.⁵⁻⁷ Accordingly it was of interest to determine how effective the new phosphines were at promoting oxidative addition to transition metals. Since the oxidative addition of methyl iodide to *trans*-[RhCl(CO)(PR₃)₂] appeared to be well understood,⁸ it was decided to study this system first. The present paper reports this study and shows that the system is more complex than previously suggested. A preliminary account of this work has been given.⁹

Experimental Section

trans-[RhCl(CO)(PR₃)₂] was prepared as described previously.³ Solutions of *trans*-[RhCl(CO)(PR₃)₂] (2 × 10⁻² mol L⁻¹) in methyl iodide (redistilled) were prepared and their infrared spectra between

2100 and 1650 cm⁻¹ monitored as a function of time with use of a Perkin-Elmer Model 577 spectrometer. *Caution!* Methyl iodide is a depressant and should only be handled in well-ventilated areas. Solution infrared cells provided with sodium chloride windows were mounted in a methanol-jacketed cell housing which was maintained at constant temperature by a Techne C100 circulating bath coupled to a Techne 1000 refrigeration unit.

Data Analysis. (1) **PR₃ = Triarylphosphine.** The kinetic data obtained when PR₃ was a triarylphosphine was initially analyzed as described previously.⁸ In this analysis a series of assumptions are made in order to enable a linear analytical method to be used. It soon became apparent that the assumptions that must be made were invalid, and accordingly a nonlinear analysis was undertaken with use of the computer program FACSIMILE.¹⁰ The program uses the initial concentrations, molar absorptivities, rate equations, and guessed values of the rate coefficients to calculate the expected variation with time of the absorbances, *A_i*, of each component. It can vary any chosen parameters (such as molar absorptivities or rate coefficients) and calculates the values of these parameters which make the sum of the squares of the residuals, Σ*w*(*A_{obsd}* - *A_{calcd}*)², for all times and components a minimum. An *F* test¹¹ was used to determine whether the fit given by model a is better or worse than that given by model b. If *S_a* and *S_b* are the minimum sum of squares of residuals by the two models, then, if [(*S_a* - *S_b*)/*n_p*]/[*S_b*/(*n_o* - *n_p*)] is greater than *F_{n_o,n_p}* - *n_o,α*, model b is a better fit than model a at the α level, where *n_o* is the number of observations and *n_p* is the number of parameters determined from these.

The molar absorptivity, ε_i, of the initial rhodium(I) complex (species I) was known, but those, ε_{II} and ε_{III}, of the second and third rhodium complexes (species II and III, respectively) were not immediately available because the reaction proceeds further, albeit slowly, making it difficult to get reliable ε_{III} values. They were calculated as follows. For each species the absorbance due to that species *A_i* is given by eq 1, where *c_i* is the concentration of species *i* and *l* is the cell length.

$$A_i = \epsilon_i c_i l \quad (1)$$

If *c_o* is the total concentration of rhodium present, then

$$c_o = c_I + c_{II} + c_{III} \quad (2)$$

and substituting from eq 1 into eq 2 gives

$$\frac{A_I}{\epsilon_I l} + \frac{A_{II}}{\epsilon_{II} l} + \frac{A_{III}}{\epsilon_{III} l} = c_o \quad (3)$$

or

$$\frac{A_I}{\epsilon_I} + \frac{A_{II}}{\epsilon_{II}} + \frac{A_{III}}{\epsilon_{III}} - c_o l = 0 \quad (4)$$

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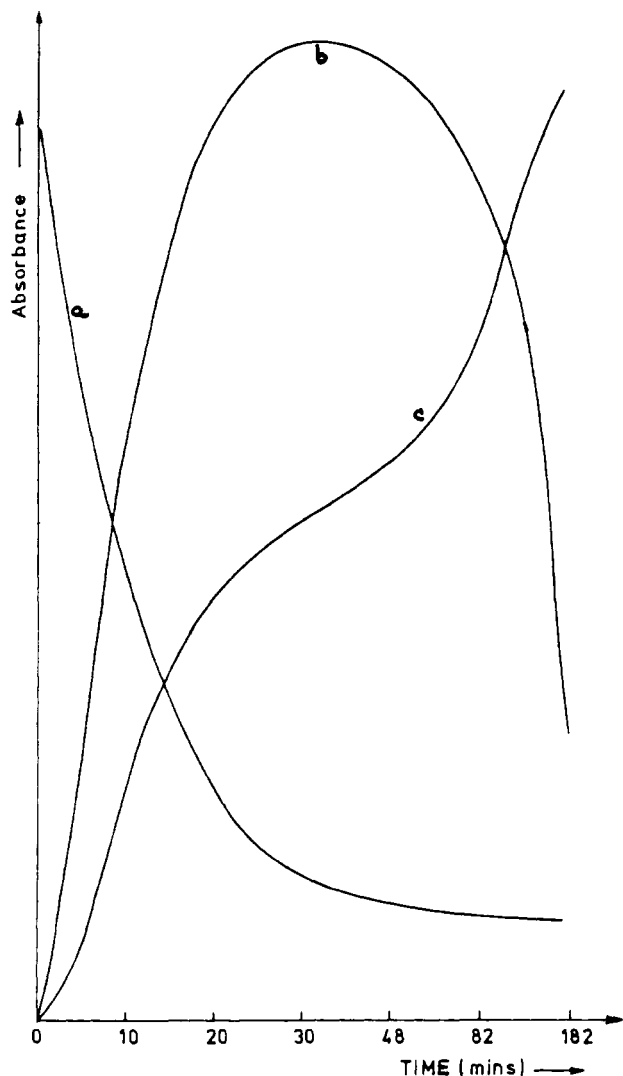


Figure 1. Observed absorbances for the reaction of $[\text{RhCl}(\text{CO})\{\text{P}-(\text{C}_6\text{H}_4\text{Bu}-p)_3\}]$ with methyl iodide at 36.3°C : (a) 1980 cm^{-1} ; (b) 2060 cm^{-1} ; (c) 1705 cm^{-1} . Note the nonlinearity of the time scale.

In order to obtain ϵ_{II} and ϵ_{III} from the known value of ϵ_{I} together with the sets of values of $A_{\text{I},t}$, $A_{\text{II},t}$, and $A_{\text{III},t}$ at different times, it is necessary to find the "best fit" values of ϵ_{II} and ϵ_{III} such that

$$\sum_{t=0}^{\infty} \left(\frac{A_{\text{I},t}}{\epsilon_{\text{I}}} + \frac{A_{\text{II},t}}{\epsilon_{\text{II}}} + \frac{A_{\text{III},t}}{\epsilon_{\text{III}}} - c_0 I \right)^2 = \text{minimum} \quad (5)$$

Condition 5 will be met when eq 6 and 7 are fulfilled. These are two

$$\frac{\partial}{\partial(1/\epsilon_{\text{II}})} \left\{ \sum_{t=0}^{\infty} \left(\frac{A_{\text{I},t}}{\epsilon_{\text{I}}} + \frac{A_{\text{II},t}}{\epsilon_{\text{II}}} + \frac{A_{\text{III},t}}{\epsilon_{\text{III}}} - c_0 I \right)^2 \right\} = 0 \quad (6)$$

$$\frac{\partial}{\partial(1/\epsilon_{\text{III}})} \left\{ \sum_{t=0}^{\infty} \left(\frac{A_{\text{I},t}}{\epsilon_{\text{I}}} + \frac{A_{\text{II},t}}{\epsilon_{\text{II}}} + \frac{A_{\text{III},t}}{\epsilon_{\text{III}}} - c_0 I \right)^2 \right\} = 0 \quad (7)$$

simultaneous equations which can be solved to give eq 8 and 9. A simple computer program was used to evaluate eq 8 and 9 from sets of absorbance data obtained as a function of time.

$$\epsilon_{\text{II}} = \frac{[\sum A_{\text{II}}^2 \sum A_{\text{III}}^2 - (\sum A_{\text{II}} A_{\text{III}})^2]}{[c_0 I (\sum A_{\text{III}}^2 \sum A_{\text{II}} - \sum A_{\text{II}} A_{\text{III}} \sum A_{\text{III}}) - (1/\epsilon_{\text{I}}) (\sum A_{\text{III}} A_{\text{I}} \sum A_{\text{II}}^2 - \sum A_{\text{II}} A_{\text{III}} \sum A_{\text{I}} A_{\text{II}})]} \quad (8)$$

$$\epsilon_{\text{III}} = \frac{[\sum A_{\text{II}}^2 \sum A_{\text{III}}^2 - (\sum A_{\text{II}} A_{\text{III}})^2]}{[c_0 I (\sum A_{\text{II}}^2 \sum A_{\text{III}} - \sum A_{\text{II}} A_{\text{III}} \sum A_{\text{II}}) - (1/\epsilon_{\text{I}}) (\sum A_{\text{III}} A_{\text{I}} \sum A_{\text{II}}^2 - \sum A_{\text{II}} A_{\text{III}} \sum A_{\text{I}} A_{\text{II}})]} \quad (9)$$

(2) **PR₃ = Trialkylphosphine.** First-order rate coefficients for compounds where PR₃ was a trialkylphosphine were calculated from the measured absorbance data with use of the usual equation,¹² {ln

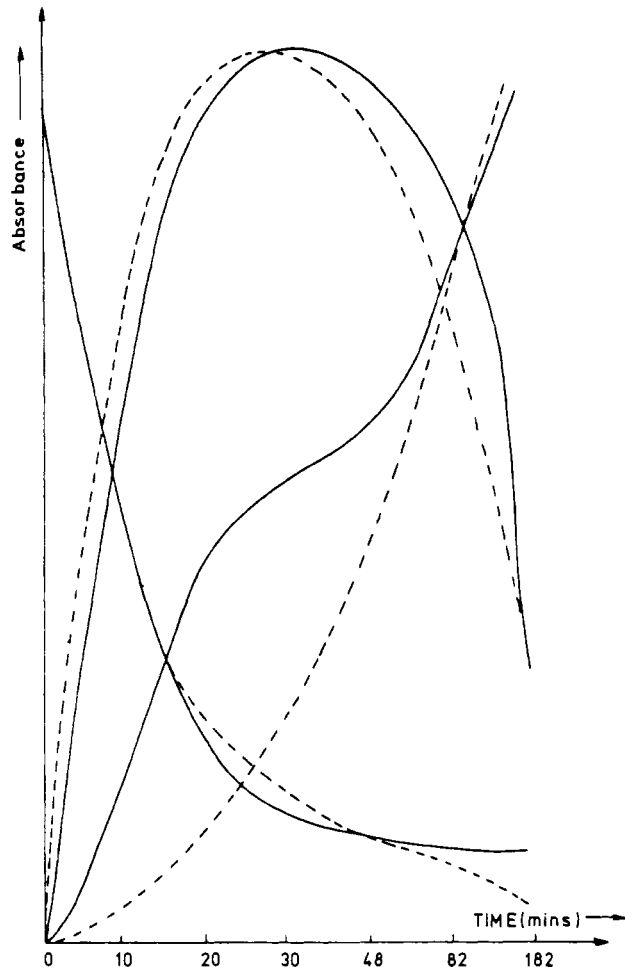
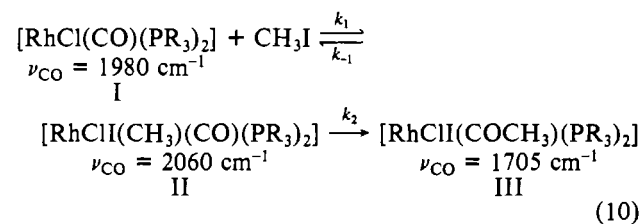


Figure 2. Observed (—) and calculated (---) absorbances for the reaction of $[\text{RhCl}(\text{CO})\text{L}_2]$, where $\text{L} = \text{P}(\text{C}_6\text{H}_4\text{Bu}-p)_3$, with methyl iodide at 36.3°C analyzed in terms of the model in eq 11.

$\{ (A_{\infty} - A_0)/(A_t - A_0) \} = k_1 t$, and a least-squares computer program.

Results

(i) **Triarylphosphines.** When *trans*- $[\text{RhCl}(\text{CO})(\text{PR}_3)_2]$, in which PR₃ is a triarylphosphine, is dissolved in methyl iodide, the initial infrared spectrum shows an absorption band at 1980 cm^{-1} . This band slowly decays in intensity, and a new band at 2060 cm^{-1} due to $[\text{RhCl}(\text{CH}_3)(\text{CO})(\text{PR}_3)_2]$ develops; in time this band also decays with the formation of a third band at 1705 cm^{-1} due to $[\text{RhCl}(\text{COCH}_3)(\text{PR}_3)_2]$. A typical record of absorbance against time for these three bands is shown in Figure 1. The reactions occurring have been suggested to be initial formation of the rhodium(III)-carbonylmethyl complex followed by combination of the carbonyl and methyl ligands to form the final rhodium(III)-acyl complex (reaction 10).⁸ In the presence of methyl iodide this can be examined



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Table I. Analysis of the Data for Oxidative Addition of Methyl Iodide to $[\text{RhCl}(\text{CO})(\text{PAr}_3)_2]$ according to the Models in Eq 11 and 12

| | Ar | | | | | | $\text{C}_6\text{H}_4\text{Et-p}$, 28.3 °C | | $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{p}$, 28.3 °C |
|---|--|--------------|--------------|-------------|---|--------------|---|-------------|---|
| | $\text{C}_6\text{H}_4\text{Bu-p}$ | | Ph | | added $n\text{-Pr}_4\text{N}^+\Gamma^-$ (0.006 M) | | no added $n\text{-Pr}_4\text{N}^+\Gamma^-$ | | |
| | 16.5 °C | 28.3 °C | 20.5 °C | 26.5 °C | 33.3 °C | 33.3 °C | | | |
| calcd rate const, s^{-1} | | | | | | | | | |
| $10^4 k_1$ | 4.57 ± 0.09 | 9.10 ± 0.23 | 21.5 ± 1.20 | 1.68 ± 0.12 | 5.21 ± 0.45 | 6.51 ± 0.22 | 9.70 ± 0.50 | 5.90 ± 0.11 | |
| $10^4 k_{-1}$ | 0.64 ± 0.06 | 3.22 ± 0.16 | 10.30 ± 0.80 | 1.93 ± 0.29 | 8.83 ± 1.10 | 3.36 ± 0.27 | 4.83 ± 0.49 | 2.06 ± 0.10 | |
| $10^4 k_2$ | 0.93 ± 0.05 | 4.11 ± 0.08 | 6.82 ± 0.23 | 1.31 ± 0.06 | 2.84 ± 0.09 | 6.07 ± 0.11 | 6.30 ± 0.22 | 3.10 ± 0.05 | |
| min sum of squares of differences (S_{12}) | 282 | 111 | 341 | 745 | 617 | 93 | 270 | 41.6 | |
| | Analysis according to Eq 12 | | | | | | | | |
| calcd rate const, s^{-1} | | | | | | | | | |
| $10^4 k_1$ | 5.24 ± 0.10 | 13.40 ± 0.62 | 33.20 ± 2.60 | 1.51 ± 0.12 | 9.07 ± 0.94 | 12.20 ± 1.00 | 18.40 ± 2.00 | 9.64 ± 0.58 | |
| $10^4 k_{-1}$ | 0.40 ± 0.07 | 3.21 ± 0.38 | 13.00 ± 1.50 | 0.27 ± 0.30 | 10.60 ± 2.00 | 3.56 ± 1.04 | 8.60 ± 1.80 | 2.79 ± 0.50 | |
| $10^4 k_3$ | 0.53 ± 0.04 | 2.32 ± 0.14 | 3.80 ± 0.25 | 1.43 ± 0.32 | 5.80 ± 0.54 | 7.34 ± 0.56 | 5.64 ± 0.56 | 2.58 ± 0.20 | |
| min sum of squares of differences (S_{11}) | 386 | 635 | 802 | 1512 | 1485 | 832 | 1400 | 552 | |
| | Analysis according to Eq 11 | | | | | | | | |
| ϵ_{II} | 466 | 466 | 466 | 717 | 717 | 683 | 683 | 413 | |
| ϵ_{III} | 371 | 371 | 371 | 334 | 334 | 286 | 286 | 335 | |
| no. of observns $[(S_{11} - S_{12})/3]/$ $[S_{12}/(n_0 - 3)]$ | 119 | 92 | 94 | 76 | 92 | 78 | 82 | 87 | |
| $F_{3,n_0-3,0.005}$ | 14.3 | 140 | 41.1 | 22.7 | 33.9 | 199 | 110 | 343 | |
| | 4.46 | 4.45 | 4.55 | 4.64 | 4.56 | 4.63 | 4.61 | 4.59 | |
| | Molar Absorptivities, $\text{L mol}^{-1} \text{cm}^{-1}$ | | | | | | | | |
| | | | | 717 | 717 | 683 | 683 | 413 | |
| | | | | 334 | 334 | 286 | 286 | 335 | |
| | | | | F Test Data | | | | | |
| | | | | 76 | 92 | 78 | 82 | 87 | |
| | | | | 22.7 | 33.9 | 199 | 110 | 343 | |

Table II. Activation Parameters for the Oxidative Addition of Methyl Iodide to $trans\text{-}[\text{RhCl}(\text{CO})(\text{PR}_3)_2]$ ($2 \times 10^{-2} \text{ mol L}^{-1}$) Yielding $trans\text{-}[\text{RhCl}(\text{CH}_3)(\text{CO})(\text{PR}_3)_2]$ in Methyl Iodide Solution

| PAr_3 | rate const | ΔH^\ddagger , kJ mol^{-1} | ΔS^\ddagger , $\text{J K}^{-1} \text{mol}^{-1}$ |
|--|---------------|--|---|
| PPh ₃ | k_1 | 113.4 ± 6.8 | 61.7 ± 22.8 |
| | k_{-1} | 166.7 ± 1.0 | 240.0 ± 3.4 |
| | k_3 | 59.5 ± 15.2 | -119.6 ± 50.7 |
| $\text{P}(\text{C}_6\text{H}_4\text{-Bu-p})_3$ | k_1 | 54.3 ± 10.9 | -122.0 ± 36.5 |
| | k_{-1} | 101.4 ± 3.3 | 24.6 ± 11.1 |
| | k_3 | 74.0 ± 11.4 | -65.9 ± 38.1 |

Table III. First-Order Rate Constants for the Oxidative Addition of Methyl Iodide to $trans\text{-}[\text{RhCl}(\text{CO})(\text{PR}_3)_2]$ ($2 \times 10^{-2} \text{ mol L}^{-1}$) Yielding $trans\text{-}[\text{RhCl}(\text{CH}_3)(\text{CO})(\text{PR}_3)_2]$ in Methyl Iodide Solution

| PR_3 | temp, °C | $10^3 k_1$, s^{-1} |
|--|----------|------------------------------|
| $\text{P}(n\text{-C}_8\text{H}_{17})_3$ | 18.3 | 12.5 ± 0.2 |
| $\text{P}(n\text{-C}_6\text{H}_{13})_3$ | 18.0 | 13.8 ± 0.1 |
| $\text{P}(n\text{-C}_{10}\text{H}_{21})_3$ | 10.5 | 5.2 ± 0.5 |
| | 19.0 | 7.8 ± 0.1 |

but a mixture of mainly $[\text{RhCl}(\text{COCH}_3)(\text{PR}_3)_2]$ together with a small amount of $[\text{RhCl}_2(\text{COCH}_3)(\text{PR}_3)]^-$ equivalent to the small amount of $(\text{PR}_3\text{Me})^+$ formed, since the observed carbonyl absorption in the final product is rather broad.

The mechanism in Scheme I envisages the observed slight increase in conductivity arising from the reaction of the dissociated tertiary phosphine ligand with methyl iodide to form the phosphonium iodide. Each iodide ion is thus formed in 1:1 ratio to the tertiary phosphine dissociated. Thus in the present system excess iodide ions are never present. However if excess iodide ions are intentionally added then they will compete with and displace chloride ions from rhodium which should promote oxidative addition at rhodium(I).¹⁶ That this is so was confirmed by studying the reaction of $[\text{RhCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{Et-}p)_3\}]$ in the presence and absence of added tetra-*n*-propylammonium iodide. It is apparent (see Table I) that addition of excess iodide has more effect on the k_1 rate constant than on k_3 . Again we believe that this is consistent with the scheme put forward because in the absence of intentionally added iodide there are no iodide ions free to take part in the k_1 step. When iodide ions are added intentionally, they will compete with chloride and so enhance the k_1 rate constant. Since iodide ions are present in the k_3 (effectively k_5) step whether or not tetra-*n*-propylammonium iodide is added, the effect of adding extra iodide ions on the k_3 step is relatively small.

Activation parameters were calculated for the rate constants in Table I evaluated according to the model in reaction 12. These are given in Table II.

(ii) **Trialkylphosphines.** When *trans*- $[\text{RhCl}(\text{CO})(\text{PR}_3)_2]$ complexes in which R was *n*-C₄H₉, *n*-C₈H₁₇, and *n*-C₁₈H₃₇ were dissolved in methyl iodide, rapid oxidative addition of methyl iodide to yield *trans*- $[\text{RhCl}(\text{CH}_3)(\text{CO})(\text{PR}_3)_2]$ occurred, but subsequent combination of methyl and carbonyl ligands to form an acyl complex did not take place. These reactions accordingly followed simple first-order rate laws. The first-order rate constants are given in Table III.

Discussion

First-order rate constants for the oxidative addition of methyl iodide to *trans*- $[\text{RhCl}(\text{CO})\text{L}_2]$, k_1 , can be seen from Tables I and III to decrease as a function of L in the order $\text{L} = \text{P}(\text{n-C}_8\text{H}_{17})_3 \gtrsim \text{P}(\text{n-C}_4\text{H}_9)_3 > \text{P}(\text{n-C}_{18}\text{H}_{37})_3 > \text{P}(\text{C}_6\text{H}_4\text{C}_4\text{H}_9\text{-}p)_3 \gtrsim \text{P}(\text{C}_6\text{H}_4\text{C}_2\text{H}_5\text{-}p)_3 > \text{P}(\text{C}_6\text{H}_4\text{C}_6\text{H}_{13}\text{-}p)_3 > \text{P}(\text{C}_6\text{H}_5)_3$. The greater ease of oxidative addition at rhodium(I) complexes containing trialkylphosphine ligands compared to those containing triarylphosphine ligands is expected on the basis of previous results and is ascribed to the greater electron density present at the rhodium atom when trialkylphosphine ligands are present. We anticipate that the electron-donating abilities of $\text{P}(\text{n-C}_n\text{H}_{2n+1})$ as *n* is varied from 4 to 8 to 18 will not vary significantly. Accordingly we ascribe

the decrease in first-order rate constants for the oxidative addition of methyl iodide to bis(trialkylphosphine)chloro-carbonylrhodium(I) complexes as the alkyl chain increases in length beyond eight carbon atoms to steric effects, whereby the phosphine with very long alkyl chains is slightly more sterically demanding, so decreasing the ease of oxidative addition.

The ease of oxidative addition to rhodium(I) complexes containing tris(para-substituted aryl)phosphines varied with the para substituent in the order *n*-C₄H₉ > C₂H₅ > *n*-C₆H₁₃ > H. The order *n*-alkyl > H is expected on electronic grounds. The order C₂H₅ > *n*-C₆H₁₃ could be due to the marginally greater steric demands of $\text{P}(\text{C}_6\text{H}_4\text{C}_6\text{H}_{13}\text{-}p)_3$ than $\text{P}(\text{C}_6\text{H}_4\text{C}_2\text{H}_5\text{-}p)_3$. However the position of the *n*-butyl substituted phosphine is anomalous, and we ascribe its position to subtle and not yet understood solvation factors. In doing this, it should be emphasized that the simplistic steric and electronic arguments we have advanced to explain the order of the remaining ligands may themselves, in reality, be not more than convenient conventional arguments. All the results may be dominated by solvation effects.

The rate of reductive elimination of methyl iodide from *trans*- $[\text{RhCl}(\text{CH}_3)(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{R-}p)_3\}]$, k_{-1} , decreases in the order C₂H₅ > *n*-C₄H₉ > *n*-C₆H₁₃ > H (Table I). The differences between the three alkyl groups are very small. The greater ease of reductive elimination from the complexes containing alkyl substituted phosphines compared to triphenylphosphine is probably a consequence of the greater steric demands of the alkyl substituted phosphines.

Since k_5 of Scheme I is the least of k_4 , k_5 , k_6 , and k_7 , the rate constants k_3 in Table I correspond to k_5 tempered by the equilibrium constant K_4 or the equilibrium constants K_{4a} and K_{4b} ; that is, they reflect the ease of oxidative addition at anionic rhodium(I) complexes containing tris(*p*-alkylaryl)phosphines. k_3 increases as a function of the alkyl substituent in the order C₂H₅ > *n*-C₄H₉ > *n*-C₆H₁₃ > H. The order *n*-alkyl > H is the same as found for oxidative addition to neutral rhodium(I) species, k_1 . The order within the alkyl groups could reflect the marginally increasing steric demands of the ligands as the alkyl group increases in size.

In conclusion the present work has demonstrated that the mechanism for the oxidative addition of methyl iodide to *trans*- $[\text{RhCl}(\text{CO})(\text{PR}_3)_2]$ is more complex than previously reported.⁸ The introduction of alkyl substituents in the para position of coordinated triphenylphosphine promotes oxidative addition at rhodium(I). Trialkylphosphines are more effective than triarylphosphines at promoting oxidative addition at rhodium(I); alkyl chains longer than *n*-butyl are marginally less effective than *n*-butyl itself.

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