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Thermal Carbonyl Substitution Reactions of $Ru_3(CO)_{12}$

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Previously [1] we studied the kinetics of the mixed first and second order reactions of $Ru_3(CO)_{12}$ with a variety of phosphorus ligands to give substituted derivatives such as $Ru_3(CO)_9(PPh_3)_3$. Values of $\log k_2$ for substitution of the first carbonyl [*i.e.* formation of $Ru_3(CO)_{11}L$] were found to obey a moderately good linear free-energy relation when plotted against corresponding values of the relative half neutralisation potentials (Δ HNP) for titration of the ligands with perchloric acid in nitromethane. These relations, and deviations from them, enabled the relative contributions of bond making in the transition states to be assessed. Subsequently [2] it was discovered that $Ru_3(CO)_{12}$ undergoes facile photo-induced reactions with phosphines to give monomeric species: $Ru(CO)_4L$ and *trans*-$Ru(CO)_3L_2$. In the earlier kinetic studies [1] the reaction of triphenylphosphine with $Ru_3(CO)_{12}$ was monitored by continuously following the absorbance at 510 nm in the visible region. Reactions with other ligands were monitored by infrared spectroscopy with the exclusion of visible light. Although the infrared spectra of the final reaction mixtures containing triphenylphosphine taken from the visible spectrophotometer showed no bands due to monomeric species, it appeared possible that the carbonyl substitution reaction could have been accelerated by the spectrophotometer's light beam, with the result that observed rate constants overestimate the thermal reaction. This reaction has therefore been reexamined using the infrared monitoring method to test the validity of the previously reported results.

The second order rate constant for reaction of $PMePh_2$ with $Ru_3(CO)_{12}$ has been derived from pseudo first order rate constants obtained at 60 °C in decalin. Logarithms of second order rate constants for the range of phosphorus ligands for which results are available have been found to correlate with a measure of the enthalpy of bond formation in a platinum complex.

Results and Discussion

Excellent pseudo first order rate plots that were linear to 85% completion of reaction, based on decreasing absorbance time data for the highest νCO band of $Ru_3(CO)_{12}$, were obtained for reactions with PPh_3 and $PMePh_2$. These results obey the rate law:

$$-\frac{d[Ru_3(CO)_{12}]}{dt} = k_1[Ru_3(CO)_{12}] + k_2[Ru_2(CO)_{12}][L]$$

Values of k_1 and k_2 were obtained as previously described, using a weighted least mean squares procedure. The value of k_1 ($1.95 \pm 0.07 \times 10^{-4}\ s^{-1}$) [3] for L = PPh_3 at 60.0 °C is in agreement with that obtained by the visible spectrophotometric method ($2.49 \pm 0.05 \times 10^{-4}\ s^{-1}$ at 60.4 °C) when the temperature difference is taken into account. Similarly, the second order rate constants agree: $2.54 \pm 0.13 \times 10^{-3}\ l\ mol^{-1}\ s^{-1}$ (at 60.0 °C, this work) and $2.49 \pm 0.05 \times 10^{-3}\ l\ mol^{-1}\ s^{-1}$ (at 60.4 °C, visible spectrophotometer). The effect of the spectrophotometer's light beam on this reaction was therefore not significant, and the reported [1] rate parameters do refer to the pure thermal reaction. The k_1 values, and the derived activation parameters, are characteristic of a co-dissociative reaction path. Its value, at a given temperature, ought not to depend on the nature of the incoming ligand. However, the value for reaction with $PMePh_2$ ($1.04 \pm 0.21 \times 10^{-4}\ s^{-1}$) [4] is significantly less than that for reaction with triphenylphosphine at 60.0 °C. Small k_1 values were also obtained [5] for reaction with PBu^n_3, and it was concluded that the sensitivity of this ligand towards oxidation by traces of oxygen is, at least in part, responsible for this behaviour, and this may be the case with other reactive ligands. However, mechanistically significant factors may also be operating.

Second order rate constants (at 60.0 °C), for the reactions of the range of phosphorus ligands with $Ru_3(CO)_{12}$ we have now examined are plotted against Δ HNP (ref. 6), and appropriate cone angles [7] in the Figure. The reactivity of the bulkiest ligands employed, PPh_3 and $P(C_6H_{11})_3$ (cone angles 145° and 179° respectively) [8], is markedly less than that suggested by the correlation with Δ HNP for the other ligands (plot A). This effect is larger than for molybdenum and tungsten six-coordinate carbonyls, and has been interpreted [1b] in terms of a high degree of bond making in the transition state involving ruthenium. In keeping with this there is only a general trend of decreasing rate constant with increasing cone angle of the entering ligand (plot B). The fact steric factors do not dominate the overall observed reactivity pattern is illustrated by reactions with PBu^n_3 and $P(OPh)_3$, which have similar cone angles, but k_2 for the former is some thirty times larger than that for the latter.

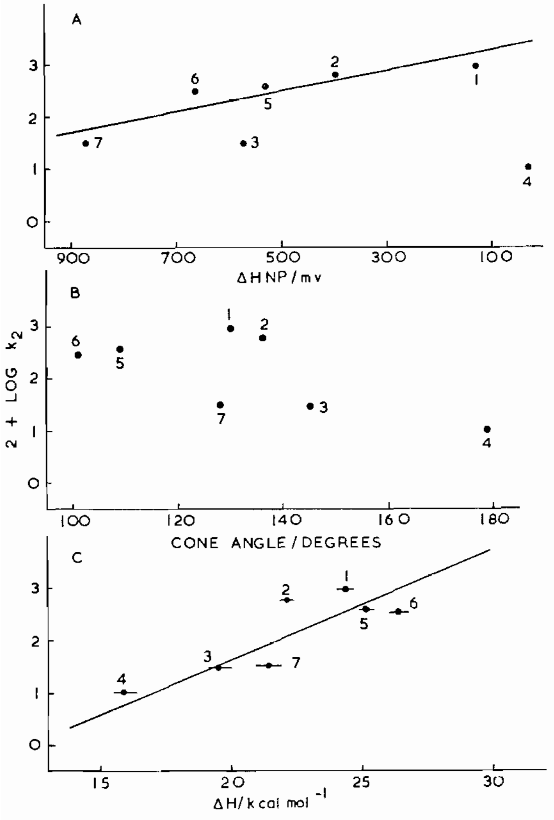

Figure. Plots of 2 + logk$_2$ for Ru$_3$(CO)$_{12}$ + L in decalin at 60.0 °C against the corresponding ligand properties: A) Half neutralisation potentials. B) Cone angle. C) Relative enthalpies of metal–ligand bond formation in *trans*-[MePt(PMe$_2$Ph)$_2$L]$^+$ in THF solution (error bars correspond to ±0.5 kcal mol^{-1}). Ligands: 1, PBu$^n_3$; 2, PMePh$_2$; 3, PPh$_3$; 4, P(C$_6$H$_{11}$)$_3$; 5, P(OEt)$_3$; 6, P(OCH$_2$)$_3$CEt; 7, P(OPh)$_3$.

Ideally, one would like to have enthalpies of ruthenium–ligand bond formation in Ru$_3$(CO)$_{11}$L to test further the proposed nature of the transition state. Unfortunately, very few calorimetric or stability constant studies on group 5 donor reactions have been reported. Very recently [9] enthalpies of Pt–L bond formation in *trans*-[CH$_3$Pt(PMe$_2$Ph)$_2$L]$^+$ in THF solution have been determined calorimetrically. Logk$_2$ values for formation of Ru$_3$(CO)$_{11}$L correlate fairly well with the enthalpy data for formation of the appropriate platinum complexes (plot C). Although the latter covers a range of some 10 kcal mol^{-1}, k$_2$ changes by less than two orders of magnitude. The different steric environments (four, and seven coordination – assuming a simple bimolecular ruthenium transition state), the different metal centres, and effects resulting from the charge on the platinum complex may contribute to this relative insensitivity of k$_2$. However, logk$_2$ values for reaction of the tetrahedral complex CoNO(CO)$_3$ with phosphorus ligands [10] do not correlate well with these enthalpy data. The significance of these observations is not fully understood, and further comments must await the determination of more thermodynamic parameters for relevant reactions.

Notes and References

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3 All quoted errors are standard deviations that have been corrected for the number of degrees of freedom such that doubling them produces 95% uncertainty limits.

4 At 60.0 °C k$_2$ = 5.62 ± 0.14 × 10^{-2} mol^{-1}s^{-1}.

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