

## Preliminary communication

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### Bimolecular substitution reactions of dodecacarbonyltriruthenium

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#### SUMMARY

Bimolecular substitution reactions of dodecacarbonyltriruthenium with phosphorus- and arsenic-donor ligands in decalin have been studied kinetically. Activation parameters, and the dependence of the rate constants on the nature of the ligands, suggest that the degree of bond-making in the transition states is exceptionally high.

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Bimolecular substitution reactions of dodecacarbonyltriruthenium with group five donor ligands occur quite generally even with weak nucleophiles like triphenylarsine and triphenylphosphite, in contrast to an earlier report<sup>1</sup>. Although some of the reactions appear to proceed by stepwise substitution of up to three carbon monoxide ligands, rates of loss of the dodecacarbonyl can easily be followed by measuring the decreasing intensity of its characteristic C–O stretching frequency in the IR. Good pseudo-first-order rate plots are observed and the rate law  $k_{\text{obs}} = k_1 + k_2 [\text{L}]$  is followed over the temperature range 40–70°. When  $\text{L} = \text{PPh}_3$  or  $\text{AsPh}_3$ ,  $k_2$  is relatively small and rate parameters for the first order process are  $\Delta H_1^\ddagger = 31.9 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1}$  ( $133 \pm 1 \text{ kJ}\cdot\text{mol}^{-1}$ ) and  $\Delta S_1^\ddagger = 20.4 \pm 0.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  ( $85.3 \pm 2.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) in good agreement with the values  $31.8 \pm 1.2 \text{ kcal}\cdot\text{mol}^{-1}$  and  $21.3 \pm 3.9 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  calculated from published data for the <sup>14</sup>CO-exchange reaction in benzene<sup>2</sup> (Uncertainties are standard deviations). The reaction with triphenylphosphite under 1 atm of carbon monoxide shows that the first order path is retarded by carbon monoxide in a way quantitatively consistent with reversible dissociation of carbon monoxide as the first stage of substitution. Carbon monoxide competes slightly more successfully than triphenylphosphite for the coordinatively unsaturated intermediate  $\text{Ru}_3(\text{CO})_{11}$ . Dissociation of carbon monoxide occurs much more readily from ruthenium than from molybdenum carbonyl<sup>3</sup> but this is entirely due to a more favourable value of  $\Delta S_1^\ddagger$ .

Kinetic parameters for the bimolecular reaction are given in Table 1, and the reaction probably involves nucleophilic attack at the metal atom. Attack at the carbon of a coordinated carbonyl ligand seems to be restricted to "hard" nucleophiles such as azide, methoxide, etc.<sup>4</sup>. Reversible heterolytic ring opening is an unlikely step in view of the small effect of replacing decalin by the polar 1,4-dioxane as solvent, and in any case would be unlikely to lead to substitution of carbon monoxide. The value of  $\Delta H_2^\ddagger$  for reaction with tri-*n*-butylphosphine (the most highly nucleophilic ligand used) is significantly lower than values for the other ligands but no very clear distinction between these others is detectable.

TABLE 1

RATE DATA FOR BIMOLECULAR SUBSTITUTION REACTIONS OF DODECACARBONYL-TRIRUTHENIUM IN DECALIN

Ligand	$\Delta H_2^\ddagger$ (kJ·mol <sup>-1</sup> )	$\Delta S_2^\ddagger$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$10^4 k_2$ (50 °C) (l·mol <sup>-1</sup> ·s <sup>-1</sup> )	$\Delta HNP^a$ (mV)
AsPh <sub>3</sub>	ca. 55 <sup>b</sup>	ca. -160 <sup>b</sup>	ca. 4	—
PPh <sub>3</sub>	64.6 ± 0.6	-101 ± 2	12	573
PPh <sub>3</sub> <sup>c</sup>	64.5 ± 1.2	-101 ± 4	14	573
P(OPh) <sub>3</sub>	60.1 ± 1.0	-113 ± 3	16	875
P(OCH <sub>2</sub> ) <sub>3</sub> CEt	57.7 ± 1.9	-101 ± 6	160	650
P(OEt) <sub>3</sub>	59.6 ± 0.4	-94 ± 1	190	520
P( <i>n</i> -Bu) <sub>3</sub>	50.2 ± 3.1	-115 ± 10	520	131
P( <i>n</i> -Bu) <sub>3</sub> <sup>d</sup>	90.5 ± 5.4	-62 ± 14	0.1	131

<sup>a</sup> See text. <sup>b</sup> Estimated graphically, low precision. <sup>c</sup> In 1,4-dioxane. <sup>d</sup> Reaction with molybdenum hexacarbonyl,  $k_2$  obtained by extrapolation of data in ref. 3.

The values of  $\Delta H_2^\ddagger$  and  $\Delta S_2^\ddagger$ , even for the less nucleophilic ligands, are considerably lower than corresponding values for reaction of tri-*n*-butylphosphine with octahedral molybdenum hexacarbonyl<sup>3</sup>, and the values of  $\Delta H_2^\ddagger$  are even lower than those for corresponding reactions of the less sterically crowded ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Rh(CO)<sub>2</sub> and Co(NO)(CO)<sub>3</sub><sup>5</sup>. Unless this is due to some special property of the metal-metal bonds it suggests a particularly high degree of bond-making in the transition states. This is also indicated by a consideration of the linear free energy relationship (LFER) shown in Fig. 1. The nucleophilic character of ligands in such bimolecular reactions can be related to the relative half-neutralization potentials ( $\Delta HNP$ ) for titration with perchloric acid in nitromethane<sup>5</sup>, and excellent linear plots of  $\log k_2$  against  $\Delta HNP$  have been found for reactions of Co(NO)(CO)<sub>3</sub><sup>5</sup>. Reasonably good linear plots are also found for the reactions of ruthenium, molybdenum and tungsten carbonyls. Such scatter as there is can be ascribed to the greater steric effects expected in six-coordinate complexes. In particular, in all three cases the point for triphenylphosphine lies below the line determined by the other points whereas this point lies on the line for Co(NO)(CO)<sub>3</sub><sup>5</sup>. This suggests that the bulky triphenylphosphine suffers greater steric inhibition in the reactions of the six-coordinate complexes than do the other smaller ligands. The effect is much greater for ruthenium

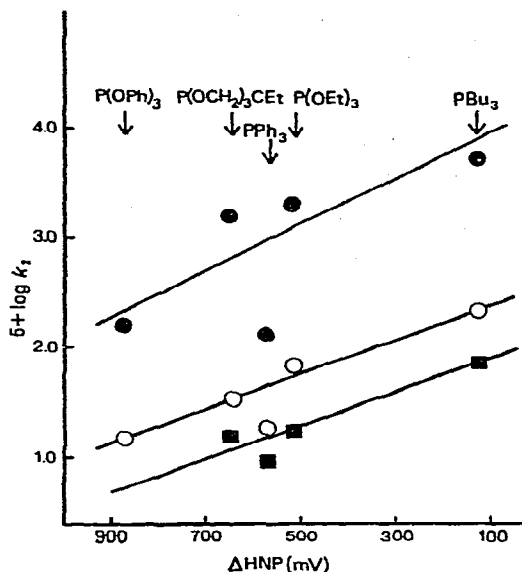


Fig. 1. LFER for bimolecular substitution reactions of some metal carbonyls. ●,  $Ru_3(CO)_{12}$  at  $50^\circ C$ ; ○,  $Mo(CO)_6$  at  $112.0^\circ$ ; ■,  $W(CO)_6$  at  $165.7^\circ$ .

carbonyl than for molybdenum carbonyl whereas one would have expected smaller steric effects with the former since the small Ru—Ru—Ru angle results in a OC—Ru—CO angle of  $103^\circ$  for those carbon monoxide ligands in the plane of the ruthenium cluster<sup>6</sup>. This apparent anomaly again implies a relatively greater degree of bond-making in reactions of the ruthenium carbonyl so that steric effects become correspondingly more important in spite of the greater geometrical accessibility of the ruthenium atoms. The gradients of the  $\log k_2$  vs.  $\Delta HNP$  plots for the six-coordinate carbonyls are about equal, and 2–3 times smaller than that for  $Co(NO)(CO)_3$ . This does not necessarily conflict with a high degree of bond-making in the ruthenium reactions since it can be ascribed to significant steric repulsion in the reaction with the relatively quite bulky tri-*n*-butylphosphine compared with the more compact phosphites and this would lower the gradient. The greater contribution of steric effects in the reactions of the ruthenium carbonyl also accounts for the greater scatter in its linear free energy plot.

The reason for the high susceptibility to nucleophilic attack of ruthenium carbonyl compared with that of molybdenum carbonyl might be in part the fact that, although both are six-coordinate  $d^6$  complexes, the ruthenium atom has two more protons in its nucleus and is correspondingly more electrophilic. Some specific property of the metal–metal bonds may also contribute. Whatever may be the cause it is great enough to make the ruthenium atoms more susceptible to nucleophilic attack even than the formally  $d^8$  rhodium(I) atoms in  $(\pi-C_5H_5)Rh(CO)_2$  and the formally  $d^{10}$  cobalt(-I) atoms in  $Co(NO)(CO)_3$  in spite of their less unfavourable steric properties.

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