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SUBSTITUTION REACTIONS OF $Ru_3(CO)_{12}$

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SUMMARY

The kinetics of substitution reactions of $Ru_3(CO)_{12}$ using Group V donor ligands to yield complexes of the type $Ru_3(CO)_9L_3$ have been studied. By comparison with published $Ru_3(CO)_{12}/CO$ exchange experiments, the rate determining step for substitution is thought to be the reversible dissociation of CO, yielding the intermediate $Ru_3(CO)_{11}$. The formation of radical intermediates $[{}^{\cdot}Ru(CO)_4]$ or $[(CO)_4\dot{R}u\text{–}Ru(CO)_4\text{–}\dot{R}u(CO)_4]$ appears unlikely. No indication of formation of stable complexes $Ru_3(CO)_{11}PPh_3$ or $Ru_3(CO)_{10}(PPh_3)_2$ during the course of the reaction with PPh_3 could be found.

INTRODUCTION

Kinetic studies on exchange and substitution reactions of metal carbonyls with nucleophilic reagents have hitherto been carried out almost exclusively using mononuclear metal carbonyls[1]. Notable exceptions are the reactions of triphenylphosphine with $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (refs. 2–4). The kinetic pattern obtained for the substitution reactions with mononuclear carbonyls usually contains a rate law which is either first order in complex and zero order in nucleophile, or first order in both complex and nucleophile. In some substitution reactions a combination of these rate laws applies.

With increasing interest in polynuclear metal carbonyls, and also the recent discoveries of heteroatomic polynuclear carbonyls, *e.g.* $Ru_xOs_{3-x}(CO)_{12}$ and $Ru_xFe_{3-x}(CO)_{12}$ (refs. 5 and 6), it has become important to determine the effects of metal–metal bonding and of bridging carbonyl groups on the kinetics and mechanism of substitution reactions involving these clusters.

$Ru_3(CO)_{12}$ is an air-stable orange solid, soluble in most organic solvents to yield solutions which, although stable in air, do undergo photochemical decomposition. Substitution reactions of $Ru_3(CO)_{12}$ with various nucleophiles have recently been studied and, as is common with reactions of complexes of Period 2 and especially Period 3 metals, the metal–metal bond is retained[7]. The product of such a reaction with a ligand L is usually of the formula $Ru_3(CO)_9L_3$.

A kinetic study of these reactions may show whether the intermediate mononuclear species $Ru(CO)_4L$ is produced which then trimerises with the loss of CO, or if the co-ordinatively unsaturated $[{}^{\cdot}Ru(CO)_3L]$ is formed as a transient intermediate.

EXPERIMENTAL

Reagents

$Ru_3(CO)_{12}$ was prepared from commercial ruthenium trichloride and recrystallised from cyclohexane. PPh_3, $AsPh_3$, $SbPh_3$ were recrystallised from ethanol. IR analysis gave no indication of the corresponding oxides. $P(n\text{-}Bu_3)_3$ was obtained from K & K Laboratories Inc., and other alkyl phosphines were prepared by standard procedures. $P(OPh)_3$ was obtained from BDH Ltd. and used without purification.

$Ru(CO)_4PPh_3$ and $Ru(CO)_3(PPh_3)_2$ were synthesised[7d,8] from the reaction of $Ru_3(CO)_{12}$ and PPh_3 under a pressure of CO.

Solvents were dried and redistilled under nitrogen before use.

Kinetic procedure

Reactions were carried out under nitrogen unless otherwise stated.

The kinetics of the reaction between the Group V donor atom ligands and $Ru_3(CO)_{12}$ were followed by sampling the reaction mixtures and observing changes in the visible spectra. The spectrophotometric measurements were normally taken at a wavelength at which a maximum absorbance occurs in the product. These are shown in Table 1.

TABLE 1

MOLAR EXTINCTION COEFFICIENTS OF COMPLEXES

L	λ (mμ)	$Ru_3(CO)_9L_3$	$Ru_3(CO)_{12}$
PPh_3	508	12,390[a]	300
PPh_2Et	490	11,500[b]	600
$PPhEt_2$	475	10,790[b]	900
PEt_3	460	9,840[a]	1600
$P(n\text{-}Bu)_3$	460	9,840[c]	1600
$P(OPh)_3$	450	8,790[b]	2100
$AsPh_3$	470	8,620[a]	1050
$SbPh_3$	375	22,700[a]	6300

[a] Measured from prepared sample and value after several half-lives. [b] Value after several half-lives. [c] Assumed value same as $Ru_3(CO)_9(PEt_3)_3$.

It was found that sunlight causes decomposition and decolourisation of the product, so the kinetic studies were carried out using darkened flasks. Reactions involving alkyl phosphines were carried out in a darkened 20 ml glass syringe immersed in the thermostat. Samples were ejected directly into the spectrophotomeric cell via a long curved stainless steel needle projecting above the water surface, thus avoiding exposure of the reaction solution to air. Identical results were obtained by the syringe technique and by the ordinary sampling procedure.

The concentrations of $Ru_3(CO)_{12}$ and L were in the ranges $1.64 \cdot 10^{-5}$ M–$1.64 \cdot 10^{-3}$ M and $1.6 \cdot 10^{-4}$ M–1.18 M respectively. First and second order rate constants were calculated by plotting $\log_e(A_\infty - A_t)$ against time (where A = absorbance) using an IBM 360 computer. Observed first order reaction plots were linear up to 60–70% reaction. Reactions of $Ru_3(CO)_{12}$ with PPh_3 and PPh_2Et were carried out at several different temperatures from 39.8°–64.9°, and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the equation

$$k = \frac{k \cdot T}{h} \cdot e^{\Delta S^{\ddagger}/R} \cdot e^{-\Delta H^{\ddagger}/R \cdot T}$$

using an IBM 1130 computer. Errors have been calculated by the method of least squares.

The absorbance of the reaction solution obtained from $Ru_3(CO)_{12}$ ($1.2 \cdot 10^{-4}$ M) and PPh_3 (1.10^{-3} M) in methylcyclohexane at 50° was at least 95% of that predicted from the spectrum of pure $Ru_3(CO)_9(PPh_3)_3$.

RESULTS

The observed first order rate constants are given in Table 2; they were calculated from optical density measurements at single wavelengths. Observations at

TABLE 2

FIRST ORDER RATE CONSTANTS, k, FOR THE SUBSTITUTION OF $Ru_3(CO)_{12}$[a] BY L

Conc. ($10^4 M$)	Temp. (°C)	Solvent	10^5 k(sec^{-1})[b]
L = PPh_3			
1.72	39.8	MCH[c]	2.11 (0.12)
1.57	44.9	MCH	3.78 (0.13)
5.68	44.9	$CHCl_3$	4.04 (0.26)
3.06	44.9	C_6H_6	5.22 (0.31)
3.98	49.9	MCH	9.9 (0.2)
5.92	49.9	MCH	9.5[d]
6.53	49.9	MCH	10.0[e]
6.28	49.9	MCH	10.4 (0.5)
9.30	49.9	MCH	9.6 (0.3)
50.9	49.9	MCH	10.0 (0.7)
91.1	49.9	MCH	11.1 (0.5)
201	49.9	MCH	12.4 (1.6)
255	49.9	MCH	10.8 (1.1)
1.6	55.0	MCH	20.9 (0.9)
11.0	59.8	MCH	48.0 (3.7)
L = PPh_2Et			
1.57	44.9	MCH	3.64 (0.12)
5.4	44.9	$CHCl_3$	6.01 (3.3)
16.2	49.1	MCH	10.1 (0.3)
81.2	49.1	MCH	14.1 (1.4)
1.6	55.0	MCH	18.1 (0.9)
16.2	59.8	MCH	42.1 (3.5)
16.2	64.9	MCH	66.3 (9.9)
L = $PPhEt_2$			
6.44	44.9	MCH	2.7 (0.13)
15.0	44.9	MCH	4.4 (0.7)
62.7	44.9	MCH	9.7 (0.3)
111	44.9	MCH	14.9 (0.2)

(*Continued*)

TABLE 2 (*continued*)

Conc. ($10^4 M$)	Temp. (°C)	Solvent	$10^5 k$ (sec^{-1})
L = PEt$_3$			
5.41	44.9	MCH	6.3 (0.4)
9.79	44.9	MCH	3.4 (0.5)
17.6	44.9	MCH	5.4 (0.8)
19.5	44.9	MCH	5.4 (0.3)
57.6	44.9	MCH	10.7 (0.9)
79.6	44.9	MCH	11.7 (1.1)
145	44.9	MCH	11.4 (2.5)
190	44.9	MCH	20.3 (2.4)
L = PBu$_3$			
32.5	44.9	MCH	5.6 (1.1)
90.4	44.9	MCH	10.5 (1.1)
126	44.9	MCH	9.3 (0.8)
196	44.9	MCH	10.1 (0.7)
L = AsPh$_3$			
2.72	44.9	C_6H_6	4.0 (0.4)
3.06	44.9	C_6H_6	3.8 (0.3)
L = SbPh$_3$			
3.06	44.9	C_6H_6	3.3 (0.5)
30.6	44.9	C_6H_6	4.0 (0.5)
L = P(OPh)$_3$			
14.3	45.3	MCH	1.5 (0.6)

[a] $Ru_3(CO)_{12}$ concentration: $2.69 \cdot 10^{-5}$–$1.63 \cdot 10^{-4}$ *M*. [b] Least squares error ($\times 10^5$) in parentheses. [c] MCH = methylcyclohexane. [d] $Ru_3(CO)_{12} = 3.64 \cdot 10^{-5}$ *M*. [e] $Ru_3(CO)_{12} = 1.63 \cdot 10^{-4}$ *M*.

TABLE 3

FIRST ORDER RATE CONSTANTS (*k*) AT 44.9° AND ACTIVATION PARAMETERS FOR THE SUBSTITUTION OF $Ru_3(CO)_{12}$ BY L[a]

L	*k* (sec^{-1})	$\Delta H^{\ddagger}$ (kcal/mole)[b]	$\Delta S^{\ddagger}$ (e.u.)[b]
PPh_3	$3.8 \cdot 10^{-5}$	32.2 (1.7)	22.7 (3.7)
PPh_2Et	$3.6 \cdot 10^{-5}$	29.7 (2.2)	14.8 (6.9)
$PPhEt_2$	$2.3 \cdot 10^{-5} + 11.6 \cdot 10^{-3} \cdot [PPhEt_2]$		
PEt_3	$4.1 \cdot 10^{-5} + 6.9 \cdot 10^{-3} \cdot [PEt_3]$		
PBu_3	$6.2 \cdot 10^{-5} + 2.5 \cdot 10^{-3} \cdot [PBu_3]$		
$AsPh_3$ (benzene)	$5.9 \cdot 10^{-5}$		
$SbPh_3$ (benzene)	$3.7 \cdot 10^{-5}$		
$P(OPh)_3$	$1.5 \cdot 10^{-5}$		

[a] Solvent methylcyclohexane unless otherwise indicated. [b] Least-square errors in parentheses.

other wavelengths gave identical results. The activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in Table 3.

Since the initial product isolated is $Ru_3(CO)_9L_3$, the following attempts have been made to observe the possible intermediates $Ru_3(CO)_{11}L$ and $Ru_3(CO)_{10}L_2$ and also the mononuclear complexes $Ru(CO)_4L$ and $Ru(CO)_3L_2$.

Visible spectra

The visible spectrum of the reaction solution was run periodically during the course of the reaction and showed a smooth change from $Ru_3(CO)_{12}$ to the product $Ru_3(CO)_9L_3$. Fig. 1 shows the spectral change during the reaction between $Ru_3(CO)_{12}$ and PPh_3 in methylcyclohexane at 50°. In experiments where isosbestic points between reactants and products are possible, *e.g.* when $L = PEt_3$, $P(n\text{-}Bu)_3$, these isosbestic points remain essentially constant during the course of the reaction (Fig. 2).

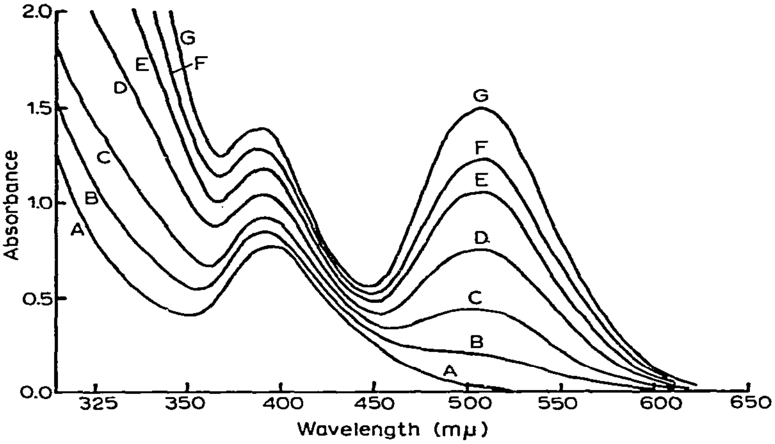


Fig. 1. Reaction of $Ru_3(CO)_{12}$ ($1 \cdot 10^{-4} M$) and PPh_3 ($3 \cdot 10^{-3} M$) in methylcyclohexane at 50°. Visible spectra of the reaction solution after time: (A) 0, (B) 30 min, (C) 1 h 10 min, (D) 2 h 30 min, (E) 3 h 55 min, (F) 5 h, (G) 21 h.

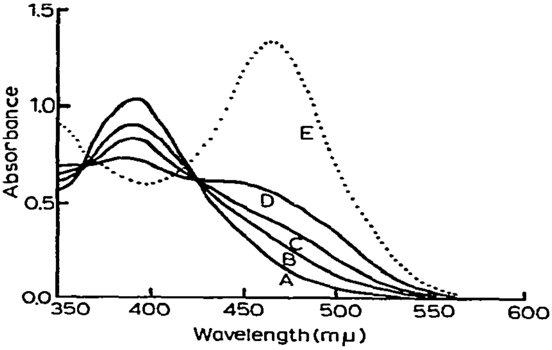


Fig. 2. Reaction of $Ru_3(CO)_{12}$ ($1.4 \cdot 10^{-4} M$) and PEt_3 ($1 \cdot 10^{-3} M$) in methylcyclohexane at 50°. Visible spectra of the reaction solution after time (A) 0, (B) 12 min, (C) 25 min and (D) 65 min. (E) is the spectrum of a solution of $Ru_3(CO)_9(PEt_3)_3$ at the same concentration.

IR Spectra

$Ru_3(CO)_{12}$ ($1.56 \cdot 10^{-3} M$) and PPh_3 ($4.8 \cdot 10^{-3} M$) in methylcyclohexane/benzene (9/1) were reacted at 45°. The carbonyl region of the IR spectrum of the reaction solution was run periodically in a 100 μ cell. After 5 h (approximately one half-life) no carbonyl bands were observed other than those of $Ru_3(CO)_{12}$ (2060, 2030 and 2010 cm^{-1}) and $Ru_3(CO)_9(PPh_3)_3$ (1983 and 1971 cm^{-1}).

Thin-layer chromatography

$Ru_3(CO)_{12}$ ($1 \cdot 10^{-3}$ *M*) was reacted with PPh_3 ($1 \cdot 10^{-3}$ *M*) or PEt_3 ($1 \cdot 10^{-3}$ *M*) in benzene at 60° in darkened flasks. Samples of the reaction mixtures were taken at various time intervals during the reaction, and the products were separated on a silica gel plate using cyclohexane/benzene (3/2) as eluent. In each case, only two coloured compounds were seen, $Ru_3(CO)_{12}$ (yellow) and $Ru_3(CO)_9(PPh_3)_3$ (purple-red) or $Ru_3(CO)_9(PEt_3)_3$ (orange-red). The latter compounds had the same R_F value as authentic samples.

Reactions of Ru(CO)₄PPh₃

$Ru(CO)_4PPh_3$ ($1 \cdot 10^{-2}$ *M*) in methylcyclohexane was heated to 60°. After 16 h the visible spectrum showed a maximum in absorbance at 378 mμ, although no change in the IR spectrum could be detected.

$Ru(CO)_4PPh_3$ ($1 \cdot 10^{-2}$ *M*) was treated with a 20-fold excess of PPh_3 in methylcyclohexane at 60°. After 16 h, pale yellow crystals were isolated, and identified by IR as $Ru(CO)_3(PPh_3)_2$ [ν(C=O) 1900 cm⁻¹].

Ligand exchange reactions

The following reactions were carried out at 60–70° in benzene (reactants ~ 10^{-3} *M*) in darkened flasks. The products were separated by thin layer chromatography on silica gel using cyclohexane/benzene (3/2) as eluent.

$Ru_3(CO)_9(PPh_3)_3/Ru_3(CO)_9(PEt_3)_3$. In an equimolar mixture of these two complexes no exchange of phosphine ligands occurred in 30 min.

$Ru_3(CO)_9(PEt_3)_3/PPh_3$. With excess PPh_3, no exchange occurred in 30 min.

$Ru_3(CO)_9(PPh_3)_3/PEt_3$. With a small excess of PEt_3, conversion to $Ru_3(CO)_9(PEt_3)_3$ and PPh_3 was complete after 30 min. PPh_3 was identified on the TLC plate by exposing the plate to iodine vapour. $Ru_3(CO)_9(PPh_3)_3/PEt_3$ (mole ratio 1/2) gave four coloured spots on the TLC plate. Those with lowest and highest R_F values were $Ru_3(CO)_9(PPh_3)_3$ and $Ru_3(CO)_9(PEt_3)_3$ respectively; the other two spots could correspond to $Ru_3(CO)_9(PPh_3)_2(PEt_3)$ and $Ru_3(CO)_9(PPh_3)(PEt_3)_2$. Thus successive replacement of PPh_3 ligands by PEt_3 is indicated, giving stable intermediates which contain different phosphine ligands.

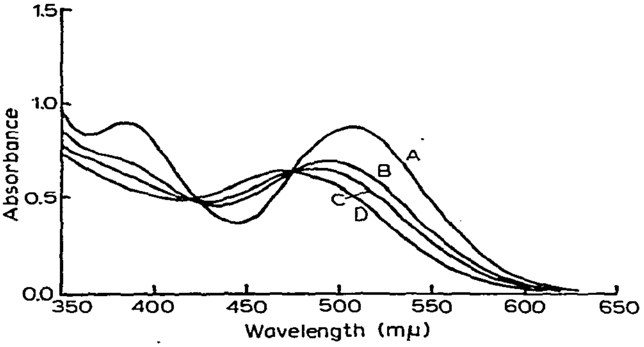


Fig. 3. Reaction of $Ru_3(CO)_9(PPh_3)_3$ ($7.1 \cdot 10^{-5}$ *M*) and $P(OPh)_3$ ($1.4 \cdot 10^{-3}$ *M*) in methylcyclohexane at 50°. Visible spectra of the reaction solution after time (A) 0, (B) 8 min, (C) 18 min, (D) 28 min.

The same products were obtained by heating an excess of $Ru_3(CO)_{12}$ with PPh_3/PEt_3 (mole ratio 1/1).

$Ru_3(CO)_9(PPh_3)_3$/other nucleophiles. At 60° reaction with pyridine and diethyl sulphide caused decomposition of the phosphine complex and no substitution products were obtained. With triphenylphosphite, replacement of PPh_3 occurred giving $Ru_3(CO)_9[P(OPh)_3]_3$ and PPh_3. Fig. 3 shows the spectral course of the reaction. PCl_3 also replaced PPh_3 at 60° to give a new complex, but the reaction products were unstable and quickly decomposed.

Reactions under CO

$Ru_3(CO)_{12}$ ($1.2 \cdot 10^{-4}$ *M*) and PPh_3 ($8.15 \cdot 10^{-4}$ *M*) were reacted at 50° under CO (1 atm.) in methylcyclohexane. No change in absorbance at 508 mμ was observed in 90 min. The solution was then purged with N_2, whereupon the reaction proceeded normally, showing an increase in absorbance at 508 mμ, yielding a first order rate constant, $k = \sim 7 \cdot 10^{-5}$ sec^{-1}. Conversely, when the reaction of $Ru_3(CO)_{12}$ ($1.2 \cdot 10^{-4}$ *M*) and PPh_3 ($8.14 \cdot 10^{-4}$ *M*) was performed under N_2, the formation of product, $Ru_3(CO)_9(PPh_3)_3$, was stopped by changing N_2 for CO after approximately one half-life. With a high PPh_3 concentration ($3.6 \cdot 10^{-2}$ *M*, 300-fold excess over $Ru_3(CO)_{12}$) the formation of $Ru_3(CO)_9(PPh_3)_3$ at 50° was retarded but not completely inhibited by 1 atmosphere of CO.

$Ru_3(CO)_9(PPh_3)_3$ ($1 \cdot 10^{-4}$ *M*) in methylcyclohexane/benzene (10/1) was heated at 50° under 1 atmosphere of CO. After 25 min the peak at 508 mμ had diminished and a maximum was observed at 410 mμ. ($Ru(CO)_4PPh_3$ has no maximum in this region.) When the solution was purged with nitrogen and heated at 50° for 120 min, the spectrum indicated that ~ 70% $Ru_3(CO)_9(PPh_3)_3$ was reformed.

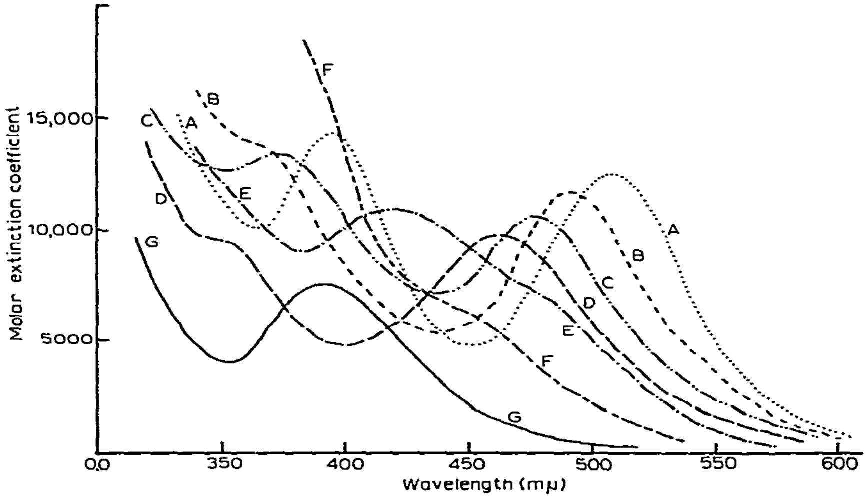


Fig. 4. Electronic spectra of complexes $Ru_3(CO)_9L_3$ where L = PPh_3 (A), PPh_2Et (B), $PPhEt_2$ (C), PEt_3 (D), $AsPh_3$ (E), $SbPh_3$ (F) and $Ru_3(CO)_{12}$ (G). Solutions (E) and (F) in benzene, the remainder in methylcyclohexane.

DISCUSSION

Electronic spectra

The visible spectra of the complexes $Ru_3(CO)_9L_3$, where L = PPh_3, PPh_2Et, $PPhEt_2$, PEt_3 (Fig. 4) have a band in the region 460–510 mμ with extinction coefficients of ~ 10,000 in addition to a band in the region 360–400 mμ. This latter band is also present in $Ru_3(CO)_{12}$. The low energy band could be the result of charge transfer from the σ-donor to the metal. This is consistent with the increase in energy of this band with increasing σ-donor capacity in the order predicted from the spectrochemical series and also the high extinction coefficients[9]. $Ru_3(CO)_9[P(OPh)_3]_3$ has a band at ~450 mμ which is also the position expected from the spectrochemical series. The spectra of the $AsPh_3$ and $SbPh_3$ substituted complexes appear to be anomalous. This may be due to the formation of complexes of the type $Ru_3(CO)_{10}L_2$ in solution[10].

Kinetic studies from spectral measurements

L = PPh_3. Most kinetic studies were performed in methylcyclohexane. Other solvents, benzene and chloroform, show that the rate constant is altered little by solvent, in agreement with previous studies of reactions of uncharged metal carbonyls with uncharged ligands[1a]. In chloroform the product slowly decomposed and in this case A_∞ was calculated from the absorbance of a prepared sample of $Ru_3(CO)_9(PPh_3)_3$. Attempts to study the kinetics of the reaction in methanol, methylene chloride and carbon tetrachloride were unsuccessful because of decomposition of reactant and/or products in these solvents. In methylcyclohexane no trend in the first order rate constants could be seen over a 50-fold increase in PPh_3 concentration. The second order path, dependent on PPh_3 concentration, appeared to be negligible at this temperature (49.9°).

L = PPh_2Et. This ligand showed similarities to PPh_3 in both rate and the effect of solvents.

L = $PPhEt_2$. The observed first order rate constant increases with increasing concentration of $PPhEt_2$, the rate expression having the form $k_{obs} = k_1 + k_2 \cdot [PPhEt_2]$

L = PEt_3. As with $PPhEt_2$, the kinetics follow the equation, rate $= k_1 \cdot [Ru_3(CO)_{12}] + k_2 \cdot [Ru_3(CO)_{12}] \cdot [PEt_3]$. The rate constant k_1 has approximately the same value as that obtained with other nucleophiles. The lower value of the second order rate constant k_2 for PEt_3 as the nucleophile compared with $PPhEt_2$ may be due to experimental error, since for most nucleophiles reacting with metal carbonyls the associative reaction path rate constant k_2 decreases in the order $PEt_3 \sim P(n\text{-}Bu)_3 > PPhEt_2$ (ref. 1a).

L = $P(n\text{-}Bu)_3$. A pure complex could not be isolated from the reaction between $Ru_3(CO)_{12}$ and $P(n\text{-}Bu)_3$ in hexane. The rate constants were therefore obtained from the assumption that the electronic spectrum of $Ru_3(CO)_9[P(n\text{-}Bu)_3]_3$ is identical to $Ru_3(CO)_9(PEt_3)_3$. The observed first order rate constant increases with increasing $P(n\text{-}Bu)_3$ concentration.

L = $P(OPh)_3$. Slow decomposition of the product (probably $Ru_3(CO)_9[P(OPh)_3]_3$ occurred during the reaction. The rate constant was therefore calculated from initial rates using Guggenheim's method[11]. The visible spectrum of the product is very similar to that obtained from the ligand exchange between $Ru_3(CO)_9(PPh_3)_3$ and $P(OPh)_3$.

$L = AsPh_3$ and $SbPh_3$. The kinetics of reactions using these nucleophiles could not be studied in methylcyclohexane as the products decompose during the course of the reaction. The arsine and stibine complexes were, however, sufficiently stable in benzene for kinetic measurements.

$L = PCl_3$. Reaction with this nucleophile in methylcyclohexane occurred, the solution turning orange (the appearance of a λ_{max} at 420 mμ was indicated). However the reaction mixture soon became cloudy making a kinetic study impossible.

$L = Ph_2PCH_2CH_2PPh_2$. Reaction occurred at 50° with the appearance of a peak at 460 mμ. The product was very insoluble and precipitated during the course of the reaction.

Reaction studies under CO atmosphere

It has been found for the reaction between $Mn_2(CO)_{10}$ and PPh_3 that 1 atm. of CO reduces the observed rate constant by $\sim 40\%$[3], although CO has no effect on the rate of substitution of $Re_2(CO)_{10}$ by PPh_3[4]. The reaction of $Ru_3(CO)_{12}$ and PPh_3 under 1 atm. of CO was completely inhibited for low PPh_3 concentrations. The slight non-linearity from first order kinetics at the latter stages of the reactions under N_2 could therefore be due to the formation of CO during the reaction. Although the reaction under N_2 went essentially to completion, forming $Ru_3(CO)_9(PPh_3)_3$, this was not the reaction product when the reaction was carried out under CO. Possible products are $Ru_3(CO)_{12-n}(PPh_3)_n$ where n is 1 or 2, although this was not investigated further.

Mechanism of the reaction $Ru_3(CO)_{12} + L$

Apart from the reactions of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $Co_2(CO)_8$ with PPh_3, no kinetic studies on Group V ligand substitution reactions of polynuclear metal carbonyls have been reported. With $Co_2(CO)_8$ the rate of PPh_3 substitution is proportional to PPh_3 concentration when the ratio $PPh_3/Co_2(CO)_8$ is less than 2/1, but independent of PPh_3 when this ratio is greater than 2/1 (ref. 2). Similarly, the rate of the reaction between $Mn_2(CO)_{10}$ and PPh_3 increases with increasing PPh_3 concentration up to a $PPh_3/Mn_2(CO)_{10}$ ratio of $\sim 100/1$, becoming independent of PPh_3 concentration at higher concentrations[3]. With $Re_2(CO)_{10}$ the reaction rate is independent of PPh_3 concentration[4].

The reaction of phosphines with $Ru_3(CO)_{12}$ does not follow the kinetic patterns shown by these binuclear complexes. It does, however, show similarities to the reactions of mononuclear octahedral carbonyls $Mo(CO)_6$ and $W(CO)_6$ with phosphine ligands[1a]. With the more basic ligands *e.g.* PEt_3, $P(n\text{-}Bu)_3$, these complexes undergo substitution by both a first and second order path which have been interpreted as a dissociative (S_N1) and an associative (S_N2) mechanism. Support for this comes from the rate of exchange of radioactive CO with $Mo(CO)_6$ and $W(CO)_6$ which give rate constants very similar to those obtained for the first order dissociative path of these carbonyls with PPh_3[1a]. Similarities between the kinetic patterns of substitution of these octahedral carbonyls and of $Ru_3(CO)_{12}$ may be expected from stereochemical considerations since the ligands around each Ru atom can be considered octahedral, comprising four CO groups and two Ru–Ru "bent bonds"[10].

The observed rate constants and the activation parameters for the ^{14}CO exchange with $Ru_3(CO)_{12}$ are almost identical with those obtained from the present results[12]. This, together with the inhibiting effect of CO on the rate of reaction, strongly indicates that a dissociative mechanism operates, the initial step being of the form

$$Ru_3(CO)_{12} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ru_3(CO)_{11}+CO$$

An alternative path could be the reversible cleavage of a single Ru–Ru bond to form a diradical which can react with ligand L

$$Ru_3(CO)_{12} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [(CO)_4\dot{R}u\text{–}Ru(CO)_4\text{–}\dot{R}u(CO)_4] \xrightarrow{L} \text{products}$$

This mechanism is similar to that proposed[3] for the reactions of $Mn_2(CO)_{10}$ with PPh_3 and I_2 (although this type of homolytic fission mechanism is not favoured for the corresponding reactions with $Re_2(CO)_{10}$, ref. 4).

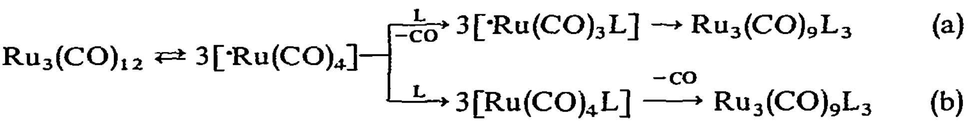
$$Mn_2(CO)_{10} \rightleftharpoons 2[{}^{\cdot}Mn(CO)_5] \xrightarrow{L} \text{products}$$

The rate determining step in this reaction is the homolytic fission of $Mn_2(CO)_{10}$ into monomeric radicals.

It is impossible at this stage to decide conclusively between the above two initial steps, although we favour the step involving the initial dissociation of CO.

The first order rate constant, k_1 (Table 3) which is $\sim 3\text{–}5 \cdot 10^{-5}$ sec^{-1} for all nucleophiles, can be identified with k_3 (or k_4). The $\Delta H^{\ddagger}$ for this path (32.2 kcal/mole) can also be compared with the high $\Delta H^{\ddagger}$ for the reaction of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with PPh_3 (36.3 and 38.6 kcal/mole respectively).

Another mechanism could be the initial cleavage of $Ru_3(CO)_{12}$ into monomeric derivatives:

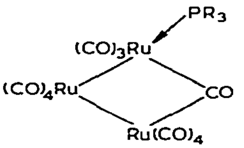


$$Ru_3(CO)_{12} \rightleftharpoons 3[{}^{\cdot}Ru(CO)_4] \xrightarrow[-CO]{L} 3[{}^{\cdot}Ru(CO)_3L] \rightarrow Ru_3(CO)_9L_3 \quad (a)$$

$$Ru_3(CO)_{12} \rightleftharpoons 3[{}^{\cdot}Ru(CO)_4] \xrightarrow{L} 3[Ru(CO)_4L] \xrightarrow{-CO} Ru_3(CO)_9L_3 \quad (b)$$

This type of mechanism has been suggested[7c] for the reaction of $Ru_3(CO)_{12}$ with X_2 where $X = Cl$, Br or I. It is also very similar to the mechanism suggested[3] for the substitution of $Mn_2(CO)_{10}$ by PPh_3. This mechanism would predict that decomposition of $[{}^{\cdot}Ru(CO)_4]$ (into Ru metal and CO) should occur in the absence of a nucleophile. However, analysis of $Ru_3(CO)_{12}$ in deoxygenated methylcyclohexane at 60° suggests that the rate constant for its decomposition is less than 1×10^{-7} sec^{-1}. Path (a) cannot be excluded since it is not possible to isolate the intermediate $^{\cdot}Ru(CO)_3L$. Path (b) is shown to be impossible, since $Ru(CO)_4PPh_3$ does not trimerise to $Ru_3(CO)_9(PPh_3)_3$ under the conditions used for the kinetic runs. Also, no evidence of $Ru(CO)_4L$ as an intermediate could be observed by either IR or visible spectral analysis during the course of the reaction.

The second order reaction path which is observed with alkyl phosphines may result from nucleophilic attack on $Ru_3(CO)_{12}$ forming an activated complex containing a 7-coordinate Ru atom, or it may involve CO-bridged intermediates such as



a species too transient to be detected by IR.

Although $Fe_3(CO)_{11}PPh_3$ can be prepared[13] from PPh_3 and a large excess of $Fe_3(CO)_{12}$, and $Ru_3(CO)_{10}(AsPh_3)_2$ has been reported[10], investigation of the reaction products during the reaction has not yielded any phosphine complexes of the type $Ru_3(CO)_{11}L$ or $Ru_3(CO)_{10}L_2$. This suggests that the overall reaction has the following general features.

$$Ru_3(CO)_{12} \xrightarrow[\text{slow}]{L} Ru_3(CO)_{11}L \xrightarrow[\text{fast}]{L} Ru_3(CO)_{10}L_2 \xrightarrow[\text{fast}]{L} Ru_3(CO)_9L_3$$

The fast subsequent steps could be the result of CO labilising by the L ligand in $Ru_3(CO)_{11}L$ either by the trans effect or by the steric crowding brought about by the group thus accelerating expulsion of further CO ligands.

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