Reaction Mechanisms of Metal–Metal Bonded Carbonyls. Part XI.[1] Reactions of Nonacarbonyl(triphenylphosphine)dirhenium and Octacarbonylbis(triphenylphosphine)dirhenium

By **David G. DeWit, J. Paul Fawcett,** and **Anthony Poë,*** Erindale College and the Department of Chemistry, University of Toronto, Mississauga, Ontario L5L 1C6, Canada

The kinetics of the reversible reaction $[Re_2(CO)_9(PPh_3)] + PPh_3 \rightleftharpoons [Re_2(CO)_8(PPh_3)_2] + CO$ in decalin have been studied in each direction and activation parameters obtained. The kinetic behaviour is quite simple and is consistent with a ligand-dissociative mechanism. However, it is also consistent with metal-migration and homolytic-fission mechanisms. The reaction of $[Re_2(CO)_9(PPh_3)]$ with carbon monoxide has quite different activation parameters from the reaction with triphenylphosphine and these reactions cannot, therefore, both go *via* simple rate-determining homolytic fission. Reaction of $[Re_2(CO)_8(PPh_3)_2]$ with PPh_3 leads to mononuclear carbonylphosphine products and is half order in $[Re_2(CO)_8(PPh_3)_2]$. This reaction most probably does go *via* reversible homolytic fission. Reactions with oxygen, nitrogen monoxide, and iodine are also described.

REACTIONS of the decacarbonyls $[Mn_2(CO)_{10}]$, $[Tc_2(CO)_{10}]$, $[Re_2(CO)_{10}]$, and $[MnRe(CO)_{10}]$, and of their substituted derivatives, have been shown to proceed according to complicated kinetic paths and several mechanisms have been proposed, ideas changing as more extensive data were obtained.[1-3] Thermal decomposition of $[Mn_2(CO)_{10}]$, in decalin and under an inert atmosphere, is half order in [complex], while decomposition of $[Mn_2(CO)_{10}]$ and $[MnRe(CO)_{10}]$ under air changes from being half order in [complex] at high concentrations to first order at low concentrations.[1,2f] The effect of carbon monoxide on some of these reactions showed that a simple CO-dissociative mechanism could not be operating, but the results were consistent with an initial reversible homolytic-fission process.[1] The reaction of $[\{Mn(CO)_4(PPh_3)\}_2]$ with triphenyl phosphite increases in rate to a limiting value with increasing values of $[P(OPh)_3]$.[2b] Although this was initially thought[2b] to indicate reversible dissociation of triphenylphosphine as the initial step, the influence of added PPh_3 on reactions proceeding at less than the limiting rate is not in accord with this,[3] and these slower reactions are, in fact, half order in [complex].[4]

As part of an investigation of the various mechanistic paths followed by these relatively quite simple metal–metal bonded carbonyls and their derivatives, we have studied some reactions of the complexes $[Re_2(CO)_9(PPh_3)]$ and $[\{Re(CO)_4(PPh_3)\}_2]$.

EXPERIMENTAL AND RESULTS

Decacarbonyldirhenium (Strem Chemicals, Inc.) was used as received. Triphenylphosphine and triphenyl phosphite (B.D.H. Chemicals, Ltd.), respectively, were recrystallized from hexane and distilled under reduced pressure (3 mmHg) before use.* 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane (etpb) (Strem Chemicals, Inc.) was recrystallized from hexane. Decalin (J. T. Baker, analysed reagent), xylene (B.D.H. AnalaR), and cyclohexane (Fisher Scientific Co., A.C.S. certified) were dried over molecular sieves. Argon (99.998%) and carbon monoxide were 'Linde' Specialty Gases from Union Carbide of Canada, Ltd.

Octacarbonylbis(triphenylphosphine)dirhenium was prepared in low yield by the published method,[5] but improved yields were obtained when the reaction time was extended and a greater excess of ligand was used. Decacarbonyldirhenium (1.80 g, 2.76 mmol) and triphenylphosphine (2.16 g, 8.25 mmol) in xylene (80 cm³) were heated under reflux for 20 h. The pale yellow solution was cooled, and colourless crystals separated overnight. These were filtered off, washed with hexane (7 × 15 cm³), and dried *in vacuo*, yield 2.30 g (75%) (Found: C, 47.6; H, 2.55. $[\{Re(CO)_4(PPh_3)\}_2]$ requires C, 47.1; H, 2.70%). I.r. spectrum in decalin: 1 980w(sh) and 1 960 cm⁻¹ (ε 32 500 dm³ mol⁻¹ cm⁻¹) *cf.* spectrum in cyclohexane,[6] 1 988w and 1 965vs cm⁻¹. U.v.–visible spectrum in hexane: 340 (4) and 300 (10) nm. (Numbers in parentheses are relative absorption coefficients.)

Nonacarbonyl(triphenylphosphine)dirhenium was prepared by reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ with carbon monoxide. A stream of carbon monoxide was passed through a solution of $[\{Re(CO)_4(PPh_3)\}_2]$ (0.60 g, 0.54 mmol) in xylene (150 cm³) at 130 °C for *ca.* 30 h, after which the product mixture was shown by i.r. spectroscopy to have reached equilibrium. Solvent was removed under reduced pressure and the complex $[Re_2(CO)_9(PPh_3)]$ was separated from unchanged bis(phosphine) complex and traces of decacarbonyl by chromatography on a foil-wrapped column of silica gel (100—200 mesh) made up in hexane. The decacarbonyl was eluted with hexane, the monophosphine complex with hexane–toluene (2 : 1 v/v), and unchanged bis(phosphine) complex with toluene. Colourless crystals were isolated from the hexane–toluene eluate, washed with a little hexane, and dried *in vacuo*, yield 0.18 g (38%) (Found: C, 36.7; H, 1.85. $[Re_2(CO)_9(PPh_3)]$ requires C, 36.6; H, 1.70%). I.r. spectrum in decalin: 2 106 (2 800), 2 034 (1 800), 1 998 (27 500), 1 973w(sh), 1 967 (5 400), and 1 941 cm⁻¹ (ε 5 900 dm³ mol⁻¹ cm⁻¹). U.v.–visible spectrum in cyclohexane: 320 (8) and 288 (10) nm.

Kinetic runs were carried out in foil-wrapped reaction tubes, as previously described,[7,8] and monitored by i.r. spectroscopy with a Perkin-Elmer 257 spectrophotometer.

Reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ *with Carbon Monoxide.*—Because of the relative insolubility of the complex in decalin at room temperature, suspensions in deoxygenated decalin were heated at 100 °C *in vacuo* for *ca.* 5 min, when clear solutions were obtained. The space above the solutions in the reaction tubes was then filled with carbon monoxide, or carbon monoxide–nitrogen mixtures, before commencing the kinetic runs. Judging from i.r. spectra of the solutions, this procedure had no discernible effect on the complex which is quite stable in solution at 100 °C. The disappearance of the complex was monitored by observing the decrease in absorbance of its C–O stretching band at 1 960 cm⁻¹. Bands due to $[Re_2(CO)_9(PPh_3)]$ grew cleanly throughout the reaction. In the absence of added triphenylphosphine, the reaction went to completion, the band at 1 960 cm⁻¹ disappearing into the side of the 1 967 cm⁻¹ band of the product. First-order rate plots were linear for at least three half-lives. Rate data are shown in Table 1. The rate constants were independent of the mole fraction of carbon monoxide down to *ca.* 0.1. Activation parameters were obtained by an unweighted least-squares treatment of the dependence of log $(k_{obs.}/T)$ on $1/T$, only data for $y_{CO} > 0.1$ being used (y_{CO} is the mole fraction of CO in $CO–N_2$ mixtures). The quoted uncertainties are standard deviations corrected for the number of degrees of freedom.[9]

Reaction in the presence of added PPh_3 was slower and produced equilibrium mixtures of the mono- and bis-(phosphine) complexes. Equilibrium constants for replacement of PPh_3 by carbon monoxide were calculated from the intensities of the bands at equilibrium, the known intensities of the bands of the pure complexes, and the known solubility[8] of carbon monoxide from 20 to 75 °C. Corrections for the difference in temperature were made by taking into account only the changing vapour pressure of decalin, the

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* 1 mmHg ≈ 13.6 × 9.8 Pa, 1 G = 10^{-4} T, 1 atm = 101 325 Pa.

[1] Part X, J. P. Fawcett, A. J. Poë, and K. R. Sharma, *J. Amer. Chem. Soc.*, in the press.

[2] (*a*) D. Hopgood and A. J. Poë, *Chem. Comm.*, 1966, 831; (*b*) H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 113; (*c*) L. I. B. Haines, D. Hopgood, and A. J. Poë, *J. Chem. Soc.* (*A*), 1968, 421; (*d*) L. I. B. Haines and A. J. Poë, *ibid.*, 1969, 2826; (*e*) D. DeWit, J. P. Fawcett, A. J. Poë, and M. V. Twigg, *Coordination Chem. Rev.*, 1972, **8**, 81; (*f*) J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **51**, C17; (*g*) J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1973, 267.

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[6] P. W. Jolly and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5259.

[7] M. Basato and A. J. Poë, *J.C.S. Dalton*, 1974, 456.

[8] M. Basato, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton* 1974, 1350.

[9] A. J. Poë and M. V. Twigg, *J.C.S. Dalton*, 1974, 1860.

TABLE 1

Kinetic data for the reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ with carbon monoxide in decalin. $[Re_2(CO)_8(PPh_3)_2]_0 = 3.4 \times 10^{-4}$ mol dm^{-3}

θ_c/°C	y_{CO} *	$10^3[PPh_3]$/ mol dm^{-3}	$10^5\ k_{obs.}$/s^{-1}
150	1.0	0	446
	1.0	0	393
	1.0	0	430
140	1.0	0	125
	1.0	0	116
	1.0	0	127
130	1.0	0	39.4
	1.0	0	38.4
	1.0	0	42.5
120	1.0	0	11.5
	1.0	0	11.2
	1.0	0	11.6
	1.0	0	11.5
140	0.74	0	126
	0.50	0	122
	0.25	0	120
	0.13	0	122
	0.053	0	104
	0.024	0	76.5
	1.0	2.06	113
	1.0	5.22	91.6
	1.0	11.6	72.3
	1.0	21.9	55.5
	1.0	34.8	42.6
	1.0	45.8	50.0
	1.0	47.7	45.1
	1.0	62.5	37.0
	1.0	0.99	9.85
	1.0	2.18	9.75
	1.0	6.26	9.63
	1.0	10.1	9.74
	1.0	10.1	8.07
	1.0	20.3	6.31
	1.0	41.4	5.64

$\Delta H^{\ddagger} = 38.8 \pm 0.5$ kcal mol^{-1} (162.2 ± 2.1 kJ mol^{-1}), $\Delta S^{\ddagger} = 21.5 \pm 1.2$ cal K^{-1} mol^{-1} (89.9 ± 6.3 J K^{-1} mol^{-1}), and $\sigma(k_{obs.}) = \pm 6.5\%$.

* Mole fraction of carbon monoxide in $CO-N_2$ mixtures.

heat of solution having been shown to be very small.[3,8] Thus the concentrations of carbon monoxide were estimated to be 4×10^{-3} mol dm^{-3} at 140 °C and 4.6×10^{-3} mol dm^{-3} at 120 °C. The data for $10^3[PPh_3] = 21.9$, 34.8, 45.8, and 47.7 mol dm^{-3} at 140 °C led to an average value $K = 23$, with a mean deviation of ± 3. Those for $10^3[PPh_3] = 20.3$ and 41.4 mol dm^{-3} at 120 °C gave $K = 20 \pm 3$.*

Reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ *with Triphenyl Phosphite.*—This reaction proceeds smoothly with eventual loss of all the $[\{Re(CO)_4(PPh_3)\}_2]$, and the growth of i.r. bands at 2 072vw, 1 996w(sh), 1 976vs, and 1 925w cm^{-1}. The rates were measured by observing the decreasing absorbance of the reactant complex at 1 960 cm^{-1}, and first-order rate plots were linear for 2—3 half-lives. Rate data are given in Table 2. Two runs were also made using etpb when bands appeared at 2 080w, 2 022w, 1 981vs, and 1 936m cm^{-1}. The initial product of the reaction with 1.1×10^{-2} mol dm^{-3} triphenyl phosphite was allowed to react further at 140 °C when a strong band appeared at 1 982 cm^{-1}, the first-order rate constant for the appearance of this product being *ca.* 6×10^{-5} s^{-1}. It appears, therefore, that replacement of the triphenylphosphine ligands occurs in two stages by way of the mixed phosphinephosphite complex.

A few runs were made with added PPh_3 when an equilibrium mixture of complexes was formed. The spectra of the two complexes were not as well separated as those for the reaction with carbon monoxide, and equilibrium constants could not be calculated from the spectra of the product mixtures.

TABLE 2

Kinetic data for the reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ with triphenyl phosphite in decalin at 140 °C. $[Re_2(CO)_8(PPh_3)_2]_0 = 3.4 \times 10^{-4}$ mol dm^{-3}

$10^3[P(OPh)_3]$/mol dm^{-3}	$10^3[PPh_3]$/mol dm^{-3}	$10^5\ k_{obs.}$/s^{-1}
3.38	0	115
10.4	0	119
19.3	0	123
31.4	0	126
43.2	0	126
93.5	0	123
10.4	1.10	103
10.4	11.9	47.9
10.4	26.9	29.8
10.4	44.7	20.6
46.5 *	0	125
135 *	0	127

* Reaction with etpb.

Reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ *with Triphenylphosphine.*—This reaction occurred at conveniently measurable rates in decalin at 160—180 °C. I.r. bands grew and decayed during the reaction and a careful analysis of the changes of intensity with time enabled the bands to be grouped according to common behaviour within each group. The clearest behaviour was shown by three products, the major one, (I), having a single band at 1 931 cm^{-1}. This can be attributed to the bis(axial) form of the trigonal-bipyramidal complex $[Re(CO)_3(PPh_3)_2]$ which has been isolated and partly characterized [ν(CO) at 1 930 cm^{-1} in benzene].[10] Two other products, (II) and (III), showed initial growth until *ca.* 65% of the reactant complex was lost, after which their bands decreased in intensity. The band wavenumbers are 2 009s, 1 924s, and 1 908s cm^{-1}, and 2 074w, 1 984m, and 1 970s cm^{-1}, respectively, the main difference between the behaviour of the two products being the relatively greater intensity of the bands due to (II) as $[PPh_3]$ is increased. Product (II) has bands very close to those of the axial–equatorial trigonal-bipyramidal complexes $[Re(CO)_3(PMePh_2)_2]$ and $[Re(CO)_3(PMe_2Ph)_2]$ (2 005m, 1 928s, and 1 912s cm^{-1}, and 2 000m, 1 925s, and 1 910s cm^{-1}, respectively).[11] Product (III) has a similar pattern of bands to *ax*-$[Fe(CO)_4(PPh_3)]$ (2 052w, 1 980w, and 1 947s cm^{-1})[12] and this, coupled with the greater amount formed at lower phosphine concentrations, enables (III) to be formulated tentatively as *ax*-$[Re(CO)_4(PPh_3)]$. Depending on the conditions, two other products were sometimes formed in smaller and less reproducible amounts [(IV), 1 960m and 1 860s cm^{-1}; (V), 2 038w and 1 990s cm^{-1}] and these may be additional isomers of mononuclear phosphine complexes.

The e.s.r. spectrum of a decalin solution containing almost pure product (I) was measured for us by Dr. A. Bassindale with a Varian EPR 4 spectrometer. Scans were carried out over 1 000—4 000 G ranges, centred on 3 313 G, with a modulation amplitude of 16 G. A rather broad signal was obtained and fine structure due to hyperfine splitting was not very clearly defined due to an unfavourable signal : noise ratio. However, five of the six bands expected for an odd

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* K is the equilibrium constant of the reaction $[\{Re(CO)_4(PPh_3)\}_2] + CO \rightleftharpoons [Re_2(CO)_9(PPh_3)] + PPh_3$

[10] F. Nyman, *Chem. and Ind.*, 1965, 604.

[11] E. Singleton, J. T. Moelwyn-Hughes, and A. W. B. Garner, *J. Organometallic Chem.*, 1970, **21**, 449; J. T. Moelwyn-Hughes, A. W. B. Garner, and N. Gordon, *ibid.*, 1971, **26**, 373.

[12] D. J. Darensbourg, *Inorg. Chim. Acta*, 1970, **4**, 597.

electron coupled to a nucleus of spin $\frac{5}{2}$ were discernible and this supports the conclusion that mononuclear rhenium(0) species are present.

The rate of loss of [{Re(CO)$_4$(PPh$_3$)}$_2$] (followed by monitoring the band at 1 960 cm^{-1}) seemed to be relatively rapid over the first 10% of reaction. The reaction subsequently showed first-order rate plots, linear for 1—2 half-lives, after which the gradients increased. Half-order rate plots of $(A_t - A_\infty)^{\frac{1}{2}}$ against time were linear for more than 2 half-lives, apart from the initial, somewhat faster, 10% of reaction. The dependence of the subsequent rates on the concentration of complex was determined, the rates being measured by multiplying the concentrations by apparent first-order rate constants obtained from plots of $\log(A_t - A_\infty)$ against time. The results are shown in Figure 1 where a straight line of gradient 0.5 passes very close to the experimental points. Concentrations were corrected for expansion of the decalin.[13] Values of the half-order rate constants are in Table 3, together with the activation parameters calculated from data at [Re$_2$(CO)$_8$(PPh$_3$)$_2$]$_0$ = 3 × 10^{-4} mol dm^{-3}.

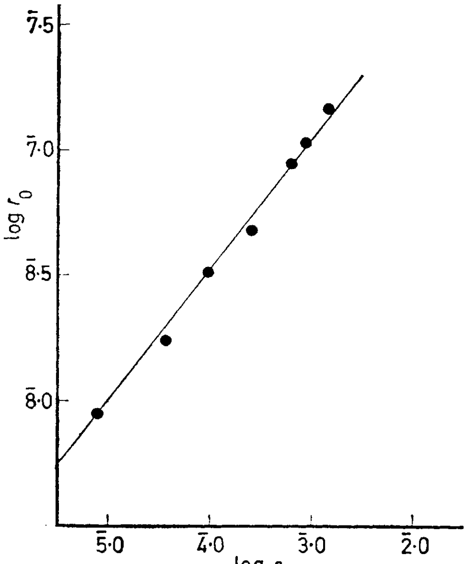

FIGURE 1 Concentration dependence of the initial rates of reaction of [{Re(CO)$_4$(PPh$_3$)}$_2$] with triphenylphosphine. Gradient of line = 0.5

Other Reactions of [{Re(CO)$_4$(PPh$_3$)}$_2$].—Reaction with oxygen was complete within 5 min at 140 °C. Measurable rates were obtained at 70—90 °C, but the results were very erratic although the growth of bands at 2 025m, 2 010s, 1 958m, and 1 900w(br) cm^{-1} was always observed. Reaction at 140 °C was completely inhibited by 0.2 mol dm^{-3} PPh$_3$. Reaction at 140 °C with *ca.* 1 : 1 mixtures of oxygen and carbon monoxide followed essentially the same path as the reaction under pure carbon monoxide, [Re$_2$(CO)$_9$(PPh$_3$)] being formed in 75% yield before decomposing.

Simple thermal decomposition in the absence of added reagents was rapid, at 180 °C, until *ca.* 80% completion of reaction. The complex [Re$_2$(CO)$_9$(PPh$_3$)] was formed as the major product together with some (I), (II), and (III), but this mixture then underwent slow decomposition, the intensities of all the i.r. bands decreasing and no new ones appearing. The presence of 2.7 × 10^{-3} mol dm^{-3} PPh$_3$ caused the fast reaction to proceed to only 20% completion, after which slow reaction occurred to form (I) and some (IV). At 140 °C, in the absence of added triphenylphosphine, [Re$_2$(CO)$_9$(PPh$_3$)] was formed in 50% yield and this reaction has a first-order rate constant of *ca.* 3 × 10^{-4} s^{-1}, which is *ca.* 25% of the rate with carbon monoxide. At 140 °C the complex reacted smoothly under 1 atm of nitrogen monoxide, [Re$_2$(CO)$_9$(PPh$_3$)] being formed in *ca.* 25% yield by 65% of reaction, together with some (II), after which general decomposition occurred slowly. A good first-order rate plot was obtained for loss of [{Re(CO)$_4$(PPh$_3$)}$_2$], the value (1 × 10^{-3} s^{-1}) being close to that for reaction with carbon monoxide.

TABLE 3

Kinetic data for reaction of [{Re(CO)$_4$(PPh$_3$)}$_2$] with triphenylphosphine in decalin at 180 °C

10^5[Re$_2$(CO)$_8$(PPh$_3$)$_2$]$_0$/mol dm^{-3}	10^3[PPh$_3$]/mol dm^{-3}	10^6 $k_{obs.}$/mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$ s^{-1}
0.796 [a]	22.4	2.96
3.58 [a]	22.4	2.88
9.31 [b]	22.4	3.34
25.7 [b]	22.4	2.99
65.1 [c]	22.4	3.45
88.0 [c]	22.4	3.53
148.0 [d]	22.4	3.74
30.0 [b]	21.6	2.99
30.0 [b]	78.5	2.84
30.0 [b]	134	2.63
30.0 [b]	279	2.89
30.0 [b,e]	20.8	1.32
30.0 [b,f]	21.2	0.56

$\Delta H^\ddagger$ = 30.6 ± 1.4 kcal mol^{-1} (128.0 ± 5.9 kJ mol^{-1}), $\Delta S^\ddagger$ = −17.3 ± 3.2 cal K^{-1} mol^{-1} (−72.4 ± 13.4 J K^{-1} mol^{-1}), and $\sigma(k_{obs.})$ = ±7%.

[a] 2.0 mm cell pathlength. [b] 1.0 mm pathlength. [c] 0.20 mm pathlength. [d] 0.11 mm pathlength. [e] At 170 °C. [f] At 160 °C.

Finally, reaction with iodine was too rapid to follow conventionally at room temperature, the products appearing to be *cis*- and *trans*-[Re(CO)$_4$I(PPh$_3$)] with i.r. bands at 2 103m, 2 023m, 2 006s, and 1 958m cm^{-1}, and 1 998s(sh) and 1 990s cm^{-1}, respectively, the assignments being made by comparison with the spectra of the bromo-analogues.[6] At 90 °C the *trans* isomer reacted smoothly to form the *cis* isomer, together with some other unidentified products, with a half-life of *ca.* 30 min.

Reaction of [Re$_2$(CO)$_9$(PPh$_3$)] *with Triphenylphosphine.*—This reaction was followed by observing the decreasing absorbance of the i.r. band at 1 995 cm^{-1} due to the nonacarbonyl. Reactions went to completion to form the complex [{Re(CO)$_4$(PPh$_3$)}$_2$]. First-order rate plots were linear for *ca.* 3 half-lives. The data are shown in Table 4, together with the activation parameters, the high precision of the data being concordant with the excellent linearity of the rate plots.

One reaction of this complex was followed in decalin under an atmosphere of oxygen at 160 °C. A good linear first-order rate plot was obtained by observing the loss of reactant complex, the rate constant being only *ca.* 20% slower than that for reaction with PPh$_3$. Product i.r. bands were observed to grow at 2 068w, 2 012s, and 1 972m cm^{-1} until the reaction was *ca.* 80% complete when they began to decrease in intensity.

Reaction of [Re$_2$(CO)$_9$(PPh$_3$)] *with Carbon Monoxide.*—This reaction was followed by measuring the decreasing

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[13] W. F. Seyer and C. H. Davenport, *J. Amer. Chem. Soc.*, 1941, **63**, 2425.

absorbance of the band at 1 941 cm^{-1}, due to the nonacarbonyl, and first-order rate plots were linear for 1—2 half-lives. The yield of product decacarbonyl decreased from 70 to 55% as the temperature increased, but quite good rate plots were also obtained over *ca.* 1 half-life when the theoretical value for A_∞ was used (ε 7 070 dm^3 mol^{-1} cm^{-1} at 2 070 cm^{-1}),[1d] and the rate constants were in good agreement with those from loss of reactant complex. The data are shown in Table 5.

TABLE 4

Kinetic data for the reaction of $[Re_2(CO)_9(PPh_3)]$ with PPh_3 in decalin. $[Re_2(CO)_9(PPh_3)]_0 \approx 4 \times 10^{-4}$ mol dm^{-3} $[PPh_3] = 1.99 \times 10^{-2}$ mol dm^{-3} (except where indicated)

θ_c/°C	$10^5\,k_{obs.}$/s^{-1}
130	5.29, 5.28, 5.44, 5.44, 5.33,[a] 5.53[b]
140	15.7, 15.6, 16.6
150	44.0, 44.3, 46.0
160	118, 114, 116

$\Delta H^\ddagger = 34.8 \pm 0.2$ kcal mol^{-1} (145.5 ± 1.3 kJ mol^{-1}), $\Delta S^\ddagger = 7.7 \pm 0.3$ cal K^{-1} mol^{-1} (32.2 ± 2.9 J K^{-1} mol^{-1}), and $\sigma(k_{obs.}) = \pm 3.0\%$.

[a] $[PPh_3] = 4.96 \times 10^{-3}$ mol dm^{-3}. [b] $[PPh_3] = 1.02 \times 10^{-2}$ mol dm^{-3}.

TABLE 5

Kinetic data for the reaction of $[Re_2(CO)_9(PPh_3)]$ with carbon monoxide in decalin. $[Re_2(CO)_9(PPh_3)]_0 \approx 4 \times 10^{-4}$ mol dm^{-3}, $y_{CO} = 1$

	$10^5\,k_{obs.}$/s^{-1}	
θ_c/°C	*a*	*b*
150	2.00	1.88
160	5.94	5.47
170	14.5	15.9
170	15.4	14.9
170	13.9[c]	
180	38.1	41.5
180	42.0	40.4

$\Delta H^\ddagger = 37.6 \pm 0.6$ kcal mol^{-1} (157.3 ± 2.5 kJ mol^{-1}), $\Delta S^\ddagger = 8.0 \pm 1.3$ cal K^{-1} mol^{-1} (33.5 ± 5.4 J K^{-1} mol^{-1}), and $\sigma(k_{obs.}) = \pm 5.6\%$.

[a] From loss of $[Re_2(CO)_9(PPh_3)]$. From growth of $[Re_2(CO)_{10}]$. [c] $y_{CO} = 0.27$.

DISCUSSION

The general behaviour of the reversible interchange reactions of the complex $[\{Re(CO)_4(PPh_3)\}_2]$ is entirely consistent with the dissociative mechanism shown in equations (1) and (2) [L = CO or $P(OPh)_3$] which leads to rate equation (3). At $[PPh_3] = 0$ the reaction goes to completion, k_{-2} can be neglected, and $k_{obs.} = k_1$. At a constant value of [L], $k_{obs.}$ should decrease with increasing values of $[PPh_3]$. Rearrangement of equation (3) leads to (4) so that plots of $k_{obs.}$ against $(k_1 - k_{obs.})/[PPh_3]$ should be linear with gradient $k_2[L]/k_{-1}$ and an intercept of k_{-2}. The data for $[L] = [CO] = 4.0 \times 10^{-3}$ mol dm^{-3} ($y_{CO} = 1$), and for $[L] = [P(OPh)_3] = 1.04 \times 10^{-2}$ mol dm^{-3}, at 140 °C are plotted in this way in Figure 2, reasonably good straight lines being obtained. The value of k_1 was taken to be $(12.3 \pm 0.1) \times 10^{-4}$ s^{-1} which was the mean of 12 determinations of the limiting rate constants with L = CO or $P(OPh)_3$, the standard deviation of an individual measurement being ±3%. The intercept of 2.0×10^{-4} s^{-1} for L = CO is in quite good agreement with the independently measured value of 1.6×10^{-4} s^{-1} for k_{-2} from Table 4. No directly measured value of k_{-2} is available for L = $P(OPh)_3$.

$$[\{Re(CO)_4(PPh_3)\}_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Re_2(CO)_8(PPh_3)] + PPh_3 \quad (1)$$

$$[Re_2(CO)_8(PPh_3)] + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Re_2(CO)_8(PPh_3)L] \quad (2)$$

$$k_{obs.} = \{(k_1k_2[L]/k_{-1}[PPh_3]) + k_{-2}\}/\{1 + (k_2[L]/k_{-1}[PPh_3])\} \quad (3)$$

$$k_{obs.} = k_{-2} + (k_2[L]/k_{-1})\,\{(k_1 - k_{obs.})/[PPh_3]\} \quad (4)$$

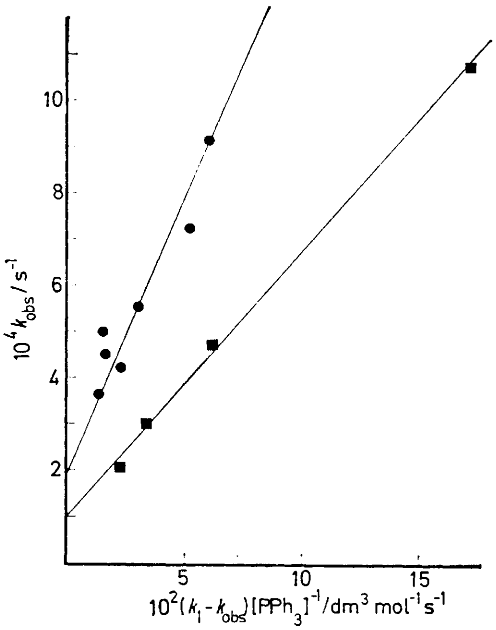

FIGURE 2 The influence of free triphenylphosphine on the kinetics of the reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ with carbon monoxide (●) and with triphenyl phosphite (■), in decalin at 140 °C

The kinetic data for L = CO at 140 °C lead to a value of k_2/k_{-1} (*i.e.* k_{CO}/k_{PPh_3}) of 3.0 and $K = 20$, in excellent agreement with the value of 23 ± 3 obtained from the equilibrium mixtures. The values of $k_{obs.}$ calculated by using $k_1 = 12.3 \times 10^{-4}$ s^{-1}, $k_{-2} = 2.0 \times 10^{-4}$ s^{-1}, and $k_2/k_{-1} = 3.0$ have a mean deviation of ±6% from the experimental values. The data for $[L] = [CO] = 4.6 \times 10^{-3}$ mol dm^{-3} at 120 °C are not as extensive or as well distributed as those at 140 °C. However, by taking $k_1 = 11.5 \times 10^{-5}$ s^{-1} (from the data when $[PPh_3] = 0$) and $k_{-2} = 1.7 \times 10^{-5}$ s^{-1} (obtained by extrapolation to 120 °C of the data in Table 4), we obtain $k_2/k_{-1} = 4$ and 6, and $K = 26$ and 40, from the values of $k_{obs.}$ at $10^3[PPh_3] = 20.3$ and 41.4 mol dm^{-3}, respectively. These values are in moderate agreement with the value $K = 20 \pm 3$ obtained from the equilibrium mixtures. The values of $k_{obs.}$ calculated for the various values of $[PPh_3]$ have a mean deviation of ±8% from the experimental values when k_2/k_{-1} was taken as 5. The data in Table 2 and Figure 2 for reaction with triphenyl phosphite lead to values of $k_{P(OPh)_3}/k_{PPh_3} = 0.6$ and $K = 7$ at 140 °C.

$$k_{obs.} = \{(k_1a[L]/[PPh_3]) + k_{-2}\}/\{1 + (a[L]/[PPh_3])\} \quad (5)$$

The data for these reactions are, therefore, all quite well represented by rate equation (5), this equation being characteristic of a reversible dissociative mechanism. The values $k_{CO}/k_{PPh_3} = 3$, and $k_{CO}/k_{P(OPh)_3} = 5$, are quite compatible with similar competition parameters for other co-ordinatively unsaturated intermediates.[9,14]

It can be shown,* however, that at least two other mechanisms for ligand interchange also lead to rate equation (5). One of these involves reversible homolytic fission as the first step, followed by a very rapidly attained equilibrium in which the PPh_3 in $[Re(CO)_4(PPh_3)]$ is replaced by L, the final stage being the combination of $[Re(CO)_4L]$ and $[Re(CO)_4(PPh_3)]$. The other mechanism involves a reversible metal-migration process followed by associative stepwise displacement of PPh_3 by L, as was proposed for reactions of the decacarbonyls of manganese and rhenium.[2c,d] This type of intermediate has also been proposed for some other reactions,[15] although direct kinetic evidence for such a mechanism is lacking. A kinetic distinction between these various mechanisms would only be possible if $k_{obs.}$ were to decrease below the limiting value $k_{obs.}(lim)$ as [L] is decreased, even in the absence of free PPh_3. Although there is some evidence that $k_{obs.}$ does decrease in this way (Tables 1 and 2), the deviation is not large enough to make promising a detailed attempt to distinguish these alternative mechanisms in this particular system.

However, the reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ with free PPh_3 clearly leads to a variety of mononuclear radical species such as $[Re(CO)_3(PPh_3)_2]$ in various isomeric forms, the most stable of which appears to be the bis-(axial) complex. The half-order kinetics {with respect to $[Re_2(CO)_8(PPh_3)_2]$} strongly suggest a reversible fission process of the type shown in equations (6) and (7). The

$$[\{Re(CO)_4(PPh_3)\}_2] \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} 2[Re(CO)_4(PPh_3)] \quad (6)$$

$$[Re(CO)_4(PPh_3)] + PPh_3 \xrightarrow{k_7} [Re(CO)_3(PPh_3)_2] \quad (7)$$

faster rate over the first 10% of reaction would then be due to the setting up of the steady-state concentration of $[Re(CO)_4(PPh_3)]$. Since the rates are independent of $[PPh_3]$, reaction (7) cannot be a straightforward S_N2 process, and the observed half-order rate constants are given by $0.5(k_6/k_{-6})^{\frac{1}{2}}k_7$.[1f] This reaction is very much slower than that with carbon monoxide {*ca.* 500 times slower at 160 °C and $[Re_2(CO)_8(PPh_3)_2] = 3 \times 10^{-4}$ mol dm^{-3}}, but these experiments do not, unfortunately, lead to independent values for k_6 for comparison with those for k_1.

Reaction of oxygen with $[Mn_2(CO)_{10}]$ and $[MnRe(CO)_{10}]$ has provided convincing kinetic evidence that these complexes undergo reversible thermal homolytic fission, and there are several reactions for which the very close similarity of the kinetic parameters for substitution and reaction with oxygen provides indirect evidence in support of the homolytic fission mechanism for substitution.[16] Direct evidence is also available for one substitution reaction.[4] This is not, unfortunately, the case here since the reaction with oxygen is very much faster than the substitutions, although it is not kinetically clean. The virtually complete suppression of this reaction by CO or PPh_3 does imply that the oxidation and substitution reactions do not proceed by completely independent paths. The detailed significance of this is uncertain as is that of the thermal reactions under argon and with nitrogen monoxide. Although reaction of NO with $[\{Mn(CO)_4(PPh_3)\}_2]$ leads[17] to formation of equimolar amounts of $[Mn(CO)_3(NO)(PPh_3)]$ and $[Mn(CO)_4(NO)]$, the absence of analogous products of reaction of the rhenium complex probably reflects the fact that no simple carbonylnitrosyl complexes of rhenium have yet been characterized. It is interesting that the reactions of both the bis- and mono-(phosphine) complexes with oxygen lead to spectroscopically definable products although the nature of these is quite unknown.

Finally, the reactions of $[Re_2(CO)_9(PPh_3)]$ with PPh_3 or CO cannot both be going by simple rate-determining homolytic fission since the rate parameters should then be identical and they are clearly not (Tables 4 and 5). The fact that reactions with oxygen and with PPh_3 proceed at about the same rate may signify that it is these reactions that proceed by rate-determining homolytic fission, in which case, by microreversibility, so must the reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ with CO. This is supported by the strong evidence for homolytic fission in the reaction of $[\{Re(CO)_4(PPh_3)\}_2]$ with PPh_3.

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* The derivation of rate equations for a variety of mechanisms for substitution and oxidation reactions of metal–metal bonded carbonyls will be described elsewhere.

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