Reaction Mechanisms of Metal–Metal-bonded Carbonyls. Part 15.[1] Reactions of Nonacarbonyl(triphenylphosphine)dimanganese and Octacarbonylbis(triphenylphosphine)dimanganese

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Kinetics of reactions of $[\{Mn(CO)_4(PPh_3)\}_2]$ with carbon monoxide, oxygen, and triphenylphosphine are reported and the major reaction path in each case is concluded to involve initial reversible homolytic fission. Infrared evidence is adduced for the formation of substantial amounts of $[Mn(CO)_3(PPh_3)_2]$ in cyclohexane after reaction with PPh_3. Reaction with oxygen proceeds by an additional path, not yet fully characterised but of almost equal importance. Data for reaction of $[Mn_2(CO)_9(PPh_3)]$ with CO, PPh_3, and oxygen are also reported. Kinetic, and some thermodynamic, parameters for reactions of the decacarbonyls $[M_2(CO)_{10}]$ (M_2 = Mn_2, Tc_2, Re_2, or MnRe) and their triphenylphosphine derivatives are compared, and the importance of steric effects in determining the kinetic strengths of the metal–metal bonds is pointed out.

KINETIC studies of reactions of simple metal–metal-bonded carbonyls are of interest in their potential for providing activation parameters related to the strengths of the M–M bonds. For this potential to be fully realised the mechanism followed must involve initial fission of the M–M bonds and this has been established

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[1] Part 14, D. P. Keeton, S. K. Malik, and A. J. Poë, *J.C.S. Dalton*, 1977, 233.

in some cases.[2-4] We report here some kinetic studies, related to this question, of reactions of the axially substituted complexes $[\{Mn(CO)_4(PPh_3)\}_2]$ and $[Mn_2(CO)_9(PPh_3)]$.

EXPERIMENTAL AND RESULTS

Chemicals.—Decacarbonyldimanganese (Strem Chemicals Inc.) was recrystallised from hexane. Cyclohexane (Certified A.C.S., Fisher Scientific Co.) and decalin ('Baker Analysed' reagent) were dried over molecular sieves. All the other reagents used were as described in previous papers in this series. The preparation of samples of the axially substituted complexes $[\{Mn(CO)_4(PPh_3)\}_2]$ and $[Mn_2(CO)_9(PPh_3)]$ has been described [5] and the procedures for kinetic runs were identical with those described previously in this series.

Reaction of $[\{Mn(CO)_4(PPh_3)\}_2]$ *with Carbon Monoxide, Oxygen, and Triphenylphosphine in Cyclohexane.*—The bis(triphenylphosphine) complex is difficult to dissolve in cyclohexane. Solutions were prepared by degassing a suspension in cyclohexane, contained in a Schlenk tube, on a vacuum line. Still *in vacuo*, the suspension was heated, with intermittent vigorous shaking, in an oil-bath at *ca.* 80 °C for some minutes. The clear solution so obtained was then rapidly cooled to below room temperature and the tube was filled with the appropriate gas. For reactions in the presence of free PPh_3 the phosphine was added initially. Thermal treatment in the absence of free PPh_3 led to the formation of a little mono(triphenylphosphine) complex and an additional product (1) with i.r. bands at 2 023, 1 948, and 1 915 cm^{-1} (relative absorbance 1 : 1 : 0.6).

Reaction with carbon monoxide was monitored by following the decreasing intensity of the i.r. band at 1 963 cm^{-1} (ε 22 × 10^3 dm^3 mol^{-1} cm^{-1}) due to the bis(phosphine) complex, and the increasing intensity of the band at 1 997 cm^{-1} (ε 19 × 10^3 dm^3 mol^{-1} cm^{-1}) due to the mono(phosphine) product. The mono(phosphine) complex is thermally stable at the temperatures used. Reaction led to complete loss of the bis(phosphine) complex, under all the conditions used, and the formation mainly of the mono(phosphine) complex. The intensity of the bands due to (1) remained constant throughout the runs with no added PPh_3, except at the lower temperatures when they became more intense and additional bands at 2 098, 2 039, and 2 078 cm^{-1} (relative absorbance 1 : 2 : 5) also grew. The formation of these products in variable amounts accounts for the variable and less-than-quantitative yields of the mono(phosphine) complex, shown in Table 1 together with the kinetic data. First-order rate plots for loss of reactant complex were linear only for between one and two half-lives after which the gradients decreased. The rate constants were, however, in satisfactory agreement with those from measurements of growth of bands due to the mono(phosphine) complex, although these were no more linear owing to uncertainties in estimating the relatively large values of A_∞. Above the mol fraction y_{CO} = *ca.* 0.2 the observed rate constants were independent of y_{CO}, but at lower values they were lower and the yield of mono(phosphine) product decreased. Added PPh_3 markedly reduced the rate of reaction and, less markedly, the yield of mono(phosphine) product. Rate plots for loss of reactant complex under these conditions were quite poor, although those for growth of product were linear for *ca.* 2 half-lives. The reaction in the presence of free phosphine and/or at low values of y_{CO} is therefore complicated by the formation of side-products, but data for reaction with pure carbon monoxide are quite good, the curvature of the rate plots being accountable for by the release of PPh_3 during the reaction. The activation parameters were calculated from a least-squares analysis in which each value of $k_{obs.}$ was assumed to have the same percentage standard deviation. Only data for loss of reactant complex under pure CO were used. The low standard deviation of an individual measurement of $k_{obs.}$ shows that the data are highly self-consistent even though they were obtained from initial gradients of slightly curved rate plots.

TABLE 1

Rate data for reaction of $[\{Mn(CO)_4(PPh_3)\}_2]$ [a] with carbon monoxide in cyclohexane

θ_c/°C	y_{CO} [b]	$10^3[PPh_3]$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}		Yield [e] (%)
			c	*d*	
49.0	1.0	0	181	169	97
	1.0	0	174	161	95
	1.0	0	182	163	90
	1.0	1.55	39.7	40.0	95
	1.0	2.48	28.7	30.6	92
	1.0	3.38	22.0	22.5	93
	1.0	6.42	13.0	13.5	90
	1.0	12.7	7.10	7.48	80
	0.79	0	179	158	88
	0.51	0	176	170	60
	0.20	0	151	160	50
	0.11	0	7.4		30
39.9	1.0	0	42.7	42.7	94
	1.0	0	43.1	43.5	92
	1.0	1.88	8.5	9.00	90
	1.0	3.98	4.8	5.20	84
	1.0	8.45	3.3	3.91	68
	0.49 [f]	0	43.7		80 [f]
30.0	1.0	0	9.27	9.29	87
	1.0	0	9.64	9.54	95
20.9	1.0	0	2.12	1.71	70
	1.0	0	2.32	1.87	64

$\Delta H^\ddagger = 117.2 \pm 0.8$ kJ mol^{-1}, $\Delta S^\ddagger = 64.4 \pm 2.5$ J K^{-1} mol^{-1}, $\sigma(k_{obs.}) = \pm 3.5\%$ [g]

[a] 3.2 × 10^{-4} mol dm^{-3}. [b] Mol fraction in $CO-N_2$ mixture. [c] From loss of $[\{Mn(CO)_4(PPh_3)\}_2]$. [d] From appearance of $[Mn_2(CO)_9(PPh_3)]$. [e] Of $[Mn_2(CO)_9(PPh_3)]$. [f] $y_{O_2} = 0.51$; yield is maximum before decomposition sets in. [g] All the uncertainties quoted are standard deviations.

Reaction with oxygen led simply to complete loss of reactant complex (even in the presence of added PPh_3) without formation of any carbonyl-containing products. A flocculent brown suspension, presumably of manganese oxides, was observed towards the end of the reactions when the initial concentration of complex was *ca.* 3 × 10^{-4} mol dm^{-3} but not when the solutions were more dilute. Reactions were followed by monitoring the decreasing intensity of the i.r. band at 1 963 cm^{-1} and, under air, by following the u.v.–visible band at 375 nm (ε 3 × 10^4 dm^3 mol^{-1} cm^{-1}). No bands were observed, in the range 1 600—1 800 cm^{-1}, corresponding to those seen during reactions of oxygen

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[2] J. P. Fawcett and A. J. Poë, *J.C.S. Dalton*, 1976, 2039.

[3] J. P. Fawcett, A. J. Poë, and K. R. Sharma, *J. Amer. Chem. Soc.*, 1976, **98**, 1401.

[4] J. P. Fawcett, R. A. Jackson, and A. J. Poë, *J.C.S. Chem. Comm.*, 1975, 733.

[5] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **61**, 315.

with $[Mn_2(CO)_{10}]$,[3] $[Tc_2(CO)_{10}]$,[2] and $[MnRe(CO)_{10}]$[3] in decalin at higher temperatures. These were ascribed to products of solvent oxidation.

Excellent first-order rate plots were obtained and the rate constants for loss of complex (Table 2) were independent of y_{O_2} down to 0.06, of $[PPh_3]$ from 0.01 to 0.2 mol dm^{-3}, and of initial concentration of complex from 5×10^{-5} to 3×10^{-4} mol dm^{-3}. Reaction with a 1 : 1 mixture of carbon monoxide and oxygen at 40 °C proceeded at a rate equal to that with CO alone (Table 1), and the mono(phosphine) complex was formed in 80% yield, some 20% greater than in the absence of oxygen at 50 °C. An excellent rate plot was obtained.

TABLE 2

Kinetic data for reaction of $[\{Mn(CO)_4(PPh_3)\}_2]$ [a] with oxygen in cyclohexane

θ_c/°C	y_{O_2}	$10^3[PPh_3]$/mol dm^{-3}	$10^4 k_{obs.}$/s^{-1}
49.9	1.0	0	31.7, 32.0
	0.21	0	31.0, 30.4, 32.8 [b]
	0.06	0	30.6
	1.0	10.4	28.0
	1.0	35.0	33.3
	1.0	51.4	30.9
	1.0	99.7	31.6
	1.0	220	34.3
	0.21	24.5	34.7 [b]
	0.21	29.6	33.4
	0.21	47.8	31.4 [b]
	0.21	153	33.7 [b]
	0.21	201	32.8
40.0	1.0 [c]	0	7.40 [c]
39.9	1.0	0	7.32, 7.48, 7.31
	0.21	0	7.25 [b]
	0.21	30.0	7.20 [b]
	0.21	63.1	6.80 [b]
30.0	1.00	0	1.60, 1.53
	0.21	0	1.48, 1.52 [b]
20.9	1.00	0	0.359, 0.353

$\Delta H^\ddagger = 120.0 \pm 0.6$ kJ mol^{-1}, $\Delta S^\ddagger = 77.8 \pm 1.7$ J K^{-1} mol^{-1}, $\sigma(k_{obs.}) = \pm 2.8\%$.

[a] Followed at 1 963 cm^{-1}. Complex concentration = 3.0×10^{-4} mol dm^{-3}, except where indicated. [b] Followed at 375 nm; complex concentration = 5×10^{-5} mol dm^{-3}. [c] Reaction with NO.

Reaction under an atmosphere of nitrogen monoxide at 40 °C gave an excellent first-order rate plot for loss of $[\{Mn(CO)_4(PPh_3)\}_2]$. Several weak i.r. bands grew between 1 920 and 2 040 cm^{-1} but the main product showed bands at 1 783w and 1 692s cm^{-1} and was therefore the complex $[Mn(NO)_3(PPh_3)]$.[6]

Reaction with PPh_3 in cyclohexane led to a product with i.r. bands at 1 988w, 1 938m, and 1 861s cm^{-1}, and an electronic absorption band at 425 nm. First-order rate plots from loss of reactant complex were very curved, the gradients increasing smoothly with time. Half-order plots were linear up to *ca.* 70% completion of reaction, and the data are expressed as half-order rate constants in Table 3. Although a study of the dependence of initial rate on concentration of complex was not possible, owing to the limited solubility, the reactions of $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ with triphenyl phosphite[7] and of $[\{Re(CO)_4(PPh_3)\}_2]$[8] with PPh_3 are both half-order in [complex] and the same seems likely to be true here. The rate constants were virtually independent of $[PPh_3]$ down to 0.01 mol dm^{-3}. Even in the absence of any PPh_3 the rate remained the same but the nature of the products changed markedly, the nonacarbonylmono(phosphine) complex being formed in *ca.* 50% yield together with (1). Reaction with 0.2 mol dm^{-3} PPh_3 at 70 °C in decalin led to no product observable in the i.r., and the rate was five times slower than in cyclohexane.

Attempts to isolate the product of reaction in cyclohexane were unsuccessful so an attempt to identify it was made by reaction with bromine. Immediate precipitation occurred, presumably of bromotriphenylphosphonium bromide, and the supernatant solution showed stable i.r. bands at 1 951s and 1 922m cm^{-1}. These same bands were observed after the reaction of $[Mn(CO)_5Br]$ (4×10^{-4} mol dm^{-3}) with PPh_3 (0.02 mol dm^{-3}) in cyclohexane at 70 °C, together with a weak band at 2 037 cm^{-1}. They are clearly due to *mer*-$[Mn(CO)_3(PPh_3)_2Br]$ (i.r. in chloroform:[9] 2 046w, 1 955s, and 1 916m cm^{-1}). The absorption coefficient of the band at 1 951 cm^{-1} in cyclohexane was estimated to be 4.2×10^3 dm^3 mol^{-1} cm^{-1}. It was possible to deduce from this that the yield of the product of the reaction of PPh_3 with $[\{Mn(CO)_4(PPh_3)\}_2]$ was $\gtrsim 20\%$ at 70 °C and $\gtrsim 50\%$ at 50 °C.

Reaction of $[Mn_2(CO)_9(PPh_3)]$ *with Carbon Monoxide and Triphenylphosphine in Decalin.*—Reaction with carbon monoxide was followed by observing both the decreasing intensity of the i.r. band at 1 942 cm^{-1} due to $[Mn_2(CO)_9(PPh_3)]$, and the growth of the band at 2 047 cm^{-1} due to $[Mn_2(CO)_{10}]$. The reaction went to completion except in the presence of free PPh_3 (9.5×10^{-3} mol dm^{-3}) at 120 °C when an equilibrium mixture was formed. When [CO] is taken as 5×10^{-3} mol dm^{-3},[10] $K_1 = [Mn_2(CO)_9(PPh_3)][CO]/[Mn_2(CO)_{10}][PPh_3]$ was estimated to be *ca.* 0.2. A value of $K_1 = 0.3$ at 125 °C was estimated from the spectrum at the end of a reaction of $[Mn_2(CO)_{10}]$ with 8.9×10^{-3} mol dm^{-3} PPh_3 under pure carbon monoxide. The detection of trace amounts of the bis(phosphine) complex at the end of reaction with *ca.* 0.4 mol dm^{-3} PPh_3 under an atmosphere of CO provides an estimate of $K_2 = [\{Mn(CO)_4(PPh_3)\}_2][CO]/[Mn_2(CO)_9(PPh_3)][PPh_3] \lesssim 10^{-3}$.

TABLE 3

Kinetic data for reaction of $[\{Mn(CO)_4(PPh_3)\}_2]$ (3.0×10^{-4} mol dm^{-3}) with triphenylphosphine in cyclohexane

θ_c/°C	$10^3[PPh_3]$/mol dm^{-3}	$10^7 k_{obs.}$/mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$ s^{-1}
70.0	0	17.2
	13.8	14.5
	97.3	18.2
	146	17.3
	203	17.7
60.1	87.2	9.8
49.9	48.2	5.6
	103	5.2

$\Delta H^\ddagger = 51.5 \pm 1.7$ kJ mol^{-1}, $\Delta S^\ddagger = -206 \pm 5$ J K^{-1} mol^{-1}, $\sigma(k_{obs.}) = \pm 4.5\%$.

Reaction with PPh_3 went to completion only when a continuous flow of argon was passed through the reacting

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[6] H. Wawersik and F. Basolo, *J. Amer. Chem. Soc.*, 1967, **89**, 4626.

[7] D. M. Chowdhury and A. J. Poë, unpublished work.

[8] D. G. DeWit, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1976, 528.

[9] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

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

solution to remove CO as it was released. First-order rate plots were then linear up to *ca.* 60% completion of reaction but the points tended to be rather scattered, perhaps owing to irregular removal of the CO. Under the conditions used, the product $[\{Mn(CO)_4(PPh_3)\}_2]$ is unstable and never accumulated in more than 60% yield. Data for these reactions are in Table 4 as well as the result for a reaction under an atmosphere of oxygen. No C–O stretching bands grew during this reaction but an excellent first-order rate plot was obtained.

TABLE 4

Kinetic data for reaction of $[Mn_2(CO)_9(PPh_3)]$ (5.0×10^{-4} mol dm^{-3}) with carbon monoxide and triphenylphosphine in decalin

$\dfrac{\theta_c}{°C}$	y_{CO}	$\dfrac{10^3[PPh_3]}{mol\ dm^{-3}}$	$10^5k_{obs.}/s^{-1}$ *a*	$10^5k_{obs.}/s^{-1}$ *b*
120	1.0	0	135	144
	1.0	0	145	142
	0.27	0	136	
	1.00	9.5	36 [c]	
110	1.00	0	53.3	50.6
	1.00	0	52.0	52.8
	0	93.9	229	
	0	240	238	
100	0 [d]	0 [d]	80.5 [d]	
99.7	0	93.7	74.8	
	1.0	0	16.6	17.1
90.0	0	94.8	22.8	
89.9	1.0	0	5.86	5.56
	1.0	0	5.58	5.63
80.1	0	95.2	6.16	

	$\dfrac{\Delta H^‡}{kJ\ mol^{-1}}$	$\dfrac{\Delta S^‡}{J\ K^{-1}\ mol^{-1}}$	$\sigma(k_{obs.})$ (%)
With CO	123.9 ± 0.9	13.8 ± 2.5	3.5
With PPh_3	133.1 ± 2.1	50.2 ± 5.4	5.0
With PPh_3 [e]	134.7 ± 2.1	55.7 ± 5.4	

[a] From loss of $[Mn_2(CO)_9(PPh_3)]$. [b] From growth of product. [c] Reaction approaches equilibrium; rate constant from initial gradient of rate plot with Δ_∞ = theoretical value. [d] Reaction under pure oxygen. [e] In xylene, calculated from data in ref. 14.

DISCUSSION

Reactions of $[\{Mn(CO)_4(PPh_3)\}_2]$.—Reaction with carbon monoxide rises to a limiting rate at higher values of y_{CO}, and is retarded by the presence of free triphenylphosphine. The rate at 49.9 °C is indistinguishable from the limiting rate for displacement of one PPh_3 ligand by $P(OPh)_3$.[4,11] An extended study [4,11] of the latter reaction has shown that all the data are consistent with reversible homolytic fission as the initial step and the coincidence of limiting rates suggests, therefore, that the reaction with CO also proceeds by this process. The effects of varying y_{CO} and $[PPh_3]$ are also qualitatively in accord with the mechanism outlined in equations (1)—(3), although the diversity of reaction products shows that additional reactions are also important and prevents a quantitative analysis of the effects in terms of (1)—(3) alone.

$$[\{Mn(CO)_4(PPh_3)\}_2] \rightleftharpoons 2[Mn(CO)_4(PPh_3)] \quad (1)$$

$$[Mn(CO)_4(PPh_3)] + CO \rightleftharpoons [Mn(CO)_5] + PPh_3 \quad (2)$$

$$[Mn(CO)_4(PPh_3)] + [Mn(CO)_5] \rightleftharpoons [Mn_2(CO)_9(PPh_3)] \quad (3)$$

Reaction with free PPh_3 produces a carbonyl-containing product in quite high yields. Since the temperatures are quite low the product is probably the monomeric radical $[Mn(CO)_3(PPh_3)_2]$. It seems unlikely that any $[Mn(CO)_3(PPh_3)_2]$ radicals formed at these temperatures would be sufficiently reactive to abstract hydrogen from the solvent to form $[Mn(CO)_3H(PPh_3)_2]$, or that orthometallation would occur under these conditions. The product cannot be simply the *trans*-bis(phosphine) isomer which should, by analogy with *trans*-$[Re(CO)_3(PPh_3)_2]$,[12] have only one band in the i.r., but which other isomer might be present instead, or as well, is not yet clear. The rate is independent of $[PPh_3]$ and much slower than the limiting rate with carbon monoxide. This reaction can, therefore, be envisaged to go *via* equations (1), (4), and (5), the reverse of (1), and reaction (5), both being much faster than reaction (4).

$$[Mn(CO)_4(PPh_3)] \longrightarrow [Mn(CO)_3(PPh_3)] + CO \quad (4)$$

$$[Mn(CO)_3(PPh_3)] + PPh_3 \longrightarrow [Mn(CO)_3(PPh_3)_2] \quad (5)$$

Reaction with oxygen proceeds at a rate *ca.* 70% faster than that with carbon monoxide although the activation parameters are almost indistinguishable. It seems more probable that this faster rate is due to the occurrence of a reaction additional to (1), rather than alternative to it, since it seems unlikely that reaction (6) would not occur under these conditions. This additional path must be completely inhibited by CO because reaction with a 1 : 1 mixture of carbon monoxide and oxygen proceeds at a rate equal to that with CO alone. Moreover, $[Mn_2(CO)_9(PPh_3)]$ is formed in high yield so that reaction (6) and the corresponding reaction with $[Mn(CO)_5]$ must both be much slower than (2) and (3). The additional path cannot simply involve initial dissociation of PPh_3 because there seems to be no reason why the intermediate $[Mn_2(CO)_8(PPh_3)]$ produced should not simply react with CO or $P(OPh)_3$, and the reaction with oxygen is not retarded by free PPh_3. Retardation by carbon monoxide, however, suggests that the additional path involves CO dissociation but further work is necessary to elucidate this. In any case, the activation enthalpy for reaction with CO is the one to be preferred as a measure of the kinetic strength of the Mn–Mn bond in $[\{Mn(CO)_4(PPh_3)\}_2]$.

$$[Mn(CO)_4(PPh_3)] + O_2 \longrightarrow \text{decomposition} \quad (6)$$

Reaction with nitrogen monoxide proceeded at the same rate as that with oxygen so NO is capable of reacting with the unknown intermediate as well as with the $[Mn(CO)_4(PPh_3)]$ radicals formed by homolytic fission. This additional path may have led to the $[Mn(CO)_4(NO)]$ formed when $[\{Mn(CO)_4(PPh_3)\}_2]$ was treated with NO at 95 °C.[13] Although, in our case,

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[11] J. P. Fawcett, Ph.D. Thesis, London University, 1973.

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

weak bands assignable to [$Mn(CO)_4(NO)$] and [$Mn(CO)_3(NO)(PPh_3)$] were observed during the reaction, the main product was [$Mn(NO)_3(PPh_3)$]. The complex [$Mn(CO)_4(NO)$] is known [13] to react quite rapidly with NO to form [$Mn(CO)(NO)_3$] and presumably [$Mn(CO)_3(NO)(PPh_3)$] can react similarly to form [$Mn(NO)_3(PPh_3)$].

Reactions of [$Mn_2(CO)_9(PPh_3)$].—Our data for reaction with triphenylphosphine in decalin are in good agreement with those of Wawersik and Basolo [14] for reaction in xylene. Since the reverse reaction has been concluded to occur *via* homolytic fission this reaction must proceed, at least in part, by that mechanism. The equality of the rates of reaction with oxygen and triphenylphosphine, and the considerable sensitivity of the rates of substitution to the presence of even small amounts of CO, suggest that CO dissociation could also be involved. Reaction of [$Mn_2(CO)_9(PPh_3)$] with CO proceeds at a limiting rate about four times slower than that with PPh_3. Carbon monoxide dissociation cannot provide a reaction path in this case so this reaction could proceed entirely by homolytic fission. In this case it is the enthalpy of activation for reaction with carbon monoxide rather than with oxygen or triphenylphosphine that should be used as a kinetic measure of the strength of the Mn–Mn bond.

Energetics of the Reactions.—A few approximate values of equilibrium constants (K_1 and K_2, respectively) for the successive formation of mono- and bis-(triphenylphosphine) complexes from the decacarbonyls have now been obtained. For [$Mn_2(CO)_{10}$], $K_1 = 0.3$ and $K_2 \lesssim 0.001$ at 125 °C, and for [$MnRe(CO)_{10}$] at 140 °C, $K_1 = 0.8$ (for formation of the Re–PPh_3 isomer) and $K_2 = 0.01$.[2] The lower thermodynamic stability of the bis- relative to the mono-complex is, therefore, more pronounced in the dimanganese system. For the ditechnetium [2] and dirhenium [8] systems at 140 °C, K_2 is 0.2 and 0.05, respectively. The stability of the bis- relative to the mono-complexes therefore increases monotonically from the Mn_2 through the MnRe to the Re_2 systems. The bis(phosphine) complex in the Tc_2 system is relatively more stable than in either the Mn_2 or Re_2 systems.

The trends in kinetic behaviour are much more thoroughly established. The values of $\Delta H^‡$ for homolytic fission of the decacarbonyls have been shown to correlate well with spectroscopic parameters related to the strength of the metal–metal bonds.[15] The effect of substitution of two triphenylphosphine ligands successively into decacarbonyldimanganese lowers the kinetic strength of the Mn–Mn [16] bond by 30 ± 2 and 6.7 ± 1.3 kJ mol^{-1}, respectively. The effect of two triphenylphosphine substituents lowers the kinetic strength of the Mn–Mn,[16] Mn–Re,[2,3] Tc–Tc,[2] and Re–Re [8,17] bonds by 37 ± 2, 7 ± 2, 22 ± 3, and 3 ± 3 kJ mol^{-1}, respectively. This, coupled with a considerable amount of other data, has led to the suggestion that steric effects are much more important than electronic effects in kinetically weakening the metal–metal bonds.[15,18] Apart from the value of $\Delta S^‡$ for reaction of [$\{Tc(CO)_4(PPh_3)\}_2$] with carbon monoxide, which is unusually low (42 J K^{-1} mol^{-1}),[1] the values for the decacarbonyls and the other bis(phosphine) complexes all lie in the range 77 ± 13 J K^{-1} mol^{-1}.

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[13] H. Wawersik and F. Basolo, *Inorg. Chem.*, 1967, **6**, 1066.

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[15] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1973, 267.

[16] L. I. B. Haines, D. J. Hopgood, and A. J. Poë, *J. Chem. Soc.* (*A*), 1968, 421.

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