

## Reaction Mechanisms of Metal–Metal-bonded Carbonyls. Part 15.<sup>1</sup> Reactions of Nonacarbonyl(triphenylphosphine)dimanganese and Octacarbonylbis(triphenylphosphine)dimanganese

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

Kinetics of reactions of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)\}_2]$  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  $[\text{Mn}(\text{CO})_3(\text{PPh}_3)_2]$  in cyclohexane after reaction with  $\text{PPh}_3$ . Reaction with oxygen proceeds by an additional path, not yet fully characterised but of almost equal importance. Data for reaction of  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$  with  $\text{CO}$ ,  $\text{PPh}_3$ , and oxygen are also reported. Kinetic, and some thermodynamic, parameters for reactions of the decacarbonyls  $[\text{M}_2(\text{CO})_{10}]$  ( $\text{M}_2 = \text{Mn}_2$ ,  $\text{Tc}_2$ ,  $\text{Re}_2$ , or  $\text{MnRe}$ ) 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

<sup>1</sup> Part 14, D. P. Keeton, S. K. Malik, and A. J. Poë, *J.C.S. Dalton*, 1977, 233.

in some cases.<sup>2-4</sup> We report here some kinetic studies, related to this question, of reactions of the axially substituted complexes  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]$  and  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$ .

#### 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  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]$  and  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$  has been described<sup>5</sup> and the procedures for kinetic runs were identical with those described previously in this series.

**Reaction of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]$  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  $\text{PPh}_3$  the phosphine was added initially. Thermal treatment in the absence of free  $\text{PPh}_3$  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  $\text{cm}^{-1}$  (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  $\text{cm}^{-1}$  ( $\epsilon$   $22 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) due to the bis(phosphine) complex, and the increasing intensity of the band at 1 997  $\text{cm}^{-1}$  ( $\epsilon$   $19 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 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  $\text{PPh}_3$ , except at the lower temperatures when they became more intense and additional bands at 2 098, 2 039, and 2 078  $\text{cm}^{-1}$  (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  $A_\infty$ . Above the mol fraction  $y_{\text{CO}} = \text{ca. } 0.2$  the observed rate constants were independent of  $y_{\text{CO}}$ , but at lower values they were lower and the yield of mono(phosphine) product decreased. Added  $\text{PPh}_3$  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  $y_{\text{CO}}$  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  $\text{PPh}_3$  during the reaction. The activation parameters were calculated from a least-squares analysis in which each value of  $k_{\text{obs}}$  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  $k_{\text{obs}}$  shows that the data are

TABLE 1

Rate data for reaction of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]^a$  with carbon monoxide in cyclohexane

$\frac{\theta_c}{^\circ\text{C}}$	$y_{\text{CO}}^b$	$10^3[\text{PPh}_3]$ mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}/\text{s}^{-1}$		Yield <sup>c</sup> (%)
			<i>c</i>	<i>d</i>	
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
	1.0	0	42.7	42.7	94
	1.0	0	43.1	43.5	92
39.9	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 <sup>f</sup>	0	43.7		80 <sup>f</sup>
	1.0	0	9.27	9.29	87
30.0	1.0	0	9.64	9.54	95
	1.0	0	2.12	1.71	70
	1.0	0	2.32	1.87	64

$\Delta H^\ddagger = 117.2 \pm 0.8 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 64.4 \pm 2.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma(k_{\text{obs}}) = \pm 3.5\%$ <sup>g</sup>

<sup>a</sup>  $3.2 \times 10^{-4} \text{ mol dm}^{-3}$ . <sup>b</sup> Mol fraction in  $\text{CO-N}_2$  mixture. <sup>c</sup> From loss of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]$ . <sup>d</sup> From appearance of  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$ . <sup>e</sup> Of  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$ . <sup>f</sup>  $y_{\text{O}_2} = 0.51$ ; yield is maximum before decomposition sets in. <sup>g</sup> All the uncertainties quoted are standard deviations.

highly self-consistent even though they were obtained from initial gradients of slightly curved rate plots.

Reaction with oxygen led simply to complete loss of reactant complex (even in the presence of added  $\text{PPh}_3$ ) 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.*  $3 \times 10^{-4} \text{ mol dm}^{-3}$  but not when the solutions were more dilute. Reactions were followed by monitoring the decreasing intensity of the i.r. band at 1 963  $\text{cm}^{-1}$  and, under air, by following the u.v.-visible band at 375 nm ( $\epsilon$   $3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). No bands were observed, in the range 1 600–1 800  $\text{cm}^{-1}$ , corresponding to those seen during reactions of oxygen

<sup>2</sup> J. P. Fawcett and A. J. Poë, *J.C.S. Dalton*, 1976, 2039.

<sup>3</sup> J. P. Fawcett, A. J. Poë, and K. R. Sharma, *J. Amer. Chem. Soc.*, 1976, **98**, 1401.

<sup>4</sup> J. P. Fawcett, R. A. Jackson, and A. J. Poë, *J.C.S. Chem. Comm.*, 1975, 733.

<sup>5</sup> J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **61**, 315.

with  $[\text{Mn}_2(\text{CO})_{10}]$ ,<sup>3</sup>  $[\text{TC}_2(\text{CO})_{10}]$ ,<sup>2</sup> and  $[\text{MnRe}(\text{CO})_{10}]$ <sup>3</sup> 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  $y_{\text{O}_2}$  down to 0.06, of  $[\text{PPh}_3]$  from 0.01 to 0.2 mol dm<sup>-3</sup>, and of initial concentration of complex from

TABLE 2  
Kinetic data for reaction of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]^a$  with oxygen in cyclohexane

$\frac{\theta_c}{^\circ\text{C}}$	$y_{\text{O}_2}$	$\frac{10^3[\text{PPh}_3]}{\text{mol dm}^{-3}}$	$\frac{10^4 k_{\text{obs.}}}{\text{s}^{-1}}$
49.9	1.0	0	31.7, 32.0
	0.21	0	31.0, 30.4, 32.8 <sup>b</sup>
	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 <sup>b</sup>
	0.21	29.6	33.4
	0.21	47.8	31.4 <sup>b</sup>
	0.21	153	33.7 <sup>b</sup>
	0.21	201	32.8
	1.0 <sup>c</sup>	0	7.40 <sup>c</sup>
	1.0	0	7.32, 7.48, 7.31
39.9	0.21	0	7.25 <sup>b</sup>
	0.21	30.0	7.20 <sup>b</sup>
	0.21	63.1	6.80 <sup>b</sup>
	1.00	0	1.60, 1.53
30.0	0.21	0	1.48, 1.52 <sup>b</sup>
	1.00	0	0.359, 0.353

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

<sup>a</sup> Followed at 1963 cm<sup>-1</sup>. Complex concentration =  $3.0 \times 10^{-4} \text{ mol dm}^{-3}$ , except where indicated. <sup>b</sup> Followed at 375 nm; complex concentration =  $5 \times 10^{-5} \text{ mol dm}^{-3}$ . <sup>c</sup> Reaction with NO.

$5 \times 10^{-5}$  to  $3 \times 10^{-4} \text{ mol dm}^{-3}$ . 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.

Reaction under an atmosphere of nitrogen monoxide at 40 °C gave an excellent first-order rate plot for loss of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]$ . Several weak i.r. bands grew between 1920 and 2040 cm<sup>-1</sup> but the main product showed bands at 1783w and 1692s cm<sup>-1</sup> and was therefore the complex  $[\text{Mn}(\text{NO})_3(\text{PPh}_3)]$ .<sup>6</sup>

Reaction with  $\text{PPh}_3$  in cyclohexane led to a product with i.r. bands at 1988w, 1938m, and 1861s cm<sup>-1</sup>, 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  $[\{\text{Mn}(\text{CO})_4(\text{P}(\text{O}(\text{Ph})_3)_2\}]$  with triphenyl phosphite<sup>7</sup> and of  $[\{\text{Re}(\text{CO})_4(\text{PPh}_3)_2\}]$ <sup>8</sup> with  $\text{PPh}_3$  are both half-order in [complex] and the same seems likely to be true here. The rate constants were virtually independent of  $[\text{PPh}_3]$  down to 0.01 mol dm<sup>-3</sup>. Even in the

absence of any  $\text{PPh}_3$  the rate remained the same but the nature of the products changed markedly; the nona-carbonylmono(phosphine) complex being formed in ca. 50% yield together with (1). Reaction with 0.2 mol dm<sup>-3</sup>  $\text{PPh}_3$  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 1951s and 1922m cm<sup>-1</sup>. These same bands were observed after the reaction of  $[\text{Mn}(\text{CO})_5\text{Br}]$  ( $4 \times 10^{-4} \text{ mol dm}^{-3}$ ) with  $\text{PPh}_3$  (0.02 mol dm<sup>-3</sup>) in cyclohexane at 70 °C, together with a weak band at 2037 cm<sup>-1</sup>. They are clearly due to *mer*- $[\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{Br}]$  (i.r. in chloroform:<sup>9</sup> 2046w, 1955s, and 1916m cm<sup>-1</sup>). The absorption coefficient of the band at 1951 cm<sup>-1</sup> in cyclohexane was estimated to be  $4.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . It was possible to deduce from this that the yield of the product of the reaction of  $\text{PPh}_3$  with  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]$  was  $\geq 20\%$  at 70 °C and  $\geq 50\%$  at 50 °C.

*Reaction of  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$  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 1942 cm<sup>-1</sup> due to  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$ , and the growth of the band at 2047 cm<sup>-1</sup> due to  $[\text{Mn}_2(\text{CO})_{10}]$ . The reaction went to completion except in

TABLE 3

Kinetic data for reaction of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}]$  ( $3.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) with triphenylphosphine in cyclohexane

$\frac{\theta_c}{^\circ\text{C}}$	$\frac{10^3[\text{PPh}_3]}{\text{mol dm}^{-3}}$	$\frac{10^7 k_{\text{obs.}}}{\text{mol}^{\frac{1}{2}} \text{ dm}^{-\frac{3}{2}} \text{ s}^{-1}}$
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

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

the presence of free  $\text{PPh}_3$  ( $9.5 \times 10^{-3} \text{ mol dm}^{-3}$ ) at 120 °C when an equilibrium mixture was formed. When  $[\text{CO}]$  is taken as  $5 \times 10^{-3} \text{ mol dm}^{-3}$ ,<sup>10</sup>  $K_1 = [\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]/[\text{CO}][\text{Mn}_2(\text{CO})_{10}][\text{PPh}_3]$  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  $[\text{Mn}_2(\text{CO})_{10}]$  with  $8.9 \times 10^{-3} \text{ mol dm}^{-3}$   $\text{PPh}_3$  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<sup>-3</sup>  $\text{PPh}_3$  under an atmosphere of CO provides an estimate of  $K_2 = [\{\text{Mn}(\text{CO})_4(\text{PPh}_3)_2\}][\text{CO}]/[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)][\text{PPh}_3] \lesssim 10^{-3}$ .

Reaction with  $\text{PPh}_3$  went to completion only when a continuous flow of argon was passed through the reacting

<sup>8</sup> D. G. DeWit, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1976, 528.

<sup>9</sup> E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

<sup>10</sup> M. Basato, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1974, 1350.

<sup>6</sup> H. Wawersik and F. Basolo, *J. Amer. Chem. Soc.*, 1967, **89**, 4626.

<sup>7</sup> D. M. Chowdhury and A. J. Poë, unpublished work.

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  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)\}_2]$  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

TABLE 4

Kinetic data for reaction of  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$  ( $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>) with carbon monoxide and triphenylphosphine in decalin

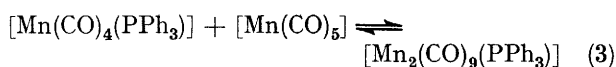
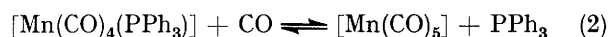
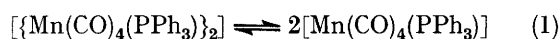
$\theta_c$ °C	$y_{\text{CO}}$	$10^3[\text{PPh}_3]$ mol dm <sup>-3</sup>	$10^5 k_{\text{obs.}}/\text{s}^{-1}$	
			<i>a</i>	<i>b</i>
120	1.0	0	135	144
	1.0	0	145	142
	0.27	0	136	
	1.00	9.5	36 <sup>c</sup>	
110	1.00	0	53.3	50.6
	1.00	0	52.0	52.8
	0	93.9	229	
	0	240	238	
100	0 <sup>d</sup>	0 <sup>d</sup>	80.5 <sup>d</sup>	
99.7	0	93.7	74.8	
	1.0	0	16.6	17.1
90.0	0	94.8	22.8	
	1.0	0	5.86	5.56
89.9	1.0	0	5.58	5.63
	1.0	0	5.58	5.63
80.1	0	95.2	6.16	
		$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\sigma(k_{\text{obs.}})$
		kJ mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>	(%)
With CO		123.9 ± 0.9	13.8 ± 2.5	3.5
With PPh <sub>3</sub>		133.1 ± 2.1	50.2 ± 5.4	5.0
With PPh <sub>3</sub> <sup>e</sup>		134.7 ± 2.1	55.7 ± 5.4	

<sup>a</sup> From loss of  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$ . <sup>b</sup> From growth of product. <sup>c</sup> Reaction approaches equilibrium; rate constant from initial gradient of rate plot with  $\Delta_\infty$  = theoretical value. <sup>d</sup> Reaction under pure oxygen. <sup>e</sup> In xylene, calculated from data in ref. 14.

under an atmosphere of oxygen. No C–O stretching bands grew during this reaction but an excellent first-order rate plot was obtained.

## DISCUSSION

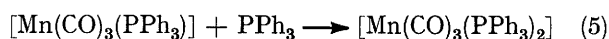
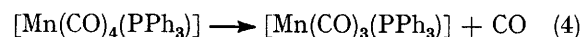
**Reactions of  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)\}_2]$ .**—Reaction with carbon monoxide rises to a limiting rate at higher values of  $y_{\text{CO}}$ , and is retarded by the presence of free triphenylphosphine. The rate at 49.9 °C is indistinguishable from the limiting rate for displacement of one PPh<sub>3</sub> ligand by P(OPh)<sub>3</sub>.<sup>4,11</sup> An extended study<sup>4,11</sup> 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  $y_{\text{CO}}$  and  $[\text{PPh}_3]$  are also qualitatively in accord with the mechanism out-



lined in equations (1)–(3), although the diversity of reaction products shows that additional reactions are

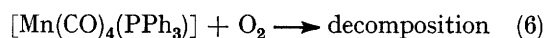
also important and prevents a quantitative analysis of the effects in terms of (1)–(3) alone.

Reaction with free PPh<sub>3</sub> produces a carbonyl-containing product in quite high yields. Since the temperatures are quite low the product is probably the monomeric radical  $[\text{Mn}(\text{CO})_3(\text{PPh}_3)_2]$ . It seems unlikely that any  $[\text{Mn}(\text{CO})_3(\text{PPh}_3)_2]$  radicals formed at these temperatures would be sufficiently reactive to abstract hydrogen from the solvent to form  $[\text{Mn}(\text{CO})_3\text{H}(\text{PPh}_3)_2]$ , or that orthometallation would occur under these conditions. The product cannot be simply the *trans*-bis(phosphine) isomer which should, by analogy with *trans*- $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2]$ ,<sup>12</sup> 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  $[\text{PPh}_3]$  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).

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,  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$  is formed in high yield so that reaction (6) and the corresponding reaction with  $[\text{Mn}(\text{CO})_5]$  must both be much slower than (2) and (3). The additional path cannot simply involve initial dissociation of PPh<sub>3</sub> because there seems to be no reason why the intermediate  $[\text{Mn}_2(\text{CO})_8(\text{PPh}_3)]$  produced should not simply react with CO or P(OPh)<sub>3</sub>, and the reaction with oxygen is not retarded by free PPh<sub>3</sub>. 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  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)\}_2]$ .

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  $[\text{Mn}(\text{CO})_4(\text{PPh}_3)]$  radicals formed by homolytic fission. This additional path may have led to the  $[\text{Mn}(\text{CO})_4(\text{NO})]$  formed when  $[\{\text{Mn}(\text{CO})_4(\text{PPh}_3)\}_2]$  was treated with NO at 95 °C.<sup>13</sup> Although, in our case,

<sup>11</sup> J. P. Fawcett, Ph.D. Thesis, London University, 1973.

<sup>12</sup> F. Nyman, *Chem. and Ind.*, 1965, 604.

weak bands assignable to  $[\text{Mn}(\text{CO})_4(\text{NO})]$  and  $[\text{Mn}(\text{CO})_3(\text{NO})(\text{PPh}_3)]$  were observed during the reaction, the main product was  $[\text{Mn}(\text{NO})_3(\text{PPh}_3)]$ . The complex  $[\text{Mn}(\text{CO})_4(\text{NO})]$  is known<sup>13</sup> to react quite rapidly with NO to form  $[\text{Mn}(\text{CO})(\text{NO})_3]$  and presumably  $[\text{Mn}(\text{CO})_3(\text{NO})(\text{PPh}_3)]$  can react similarly to form  $[\text{Mn}(\text{NO})_3(\text{PPh}_3)]$ .

*Reactions of  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$ .*—Our data for reaction with triphenylphosphine in decalin are in good agreement with those of Wawersik and Basolo<sup>14</sup> 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  $[\text{Mn}_2(\text{CO})_9(\text{PPh}_3)]$  with CO proceeds at a limiting rate about four times slower than that with  $\text{PPh}_3$ . 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  $[\text{Mn}_2(\text{CO})_{10}]$ ,  $K_1 = 0.3$  and  $K_2 \leq 0.001$  at 125 °C, and for  $[\text{MnRe}(\text{CO})_{10}]$  at 140 °C,  $K_1 = 0.8$  (for formation of the Re– $\text{PPh}_3$  isomer) and

$K_2 = 0.01$ .<sup>2</sup> The lower thermodynamic stability of the bis- relative to the mono-complex is, therefore, more pronounced in the dimanganese system. For the ditechneum<sup>2</sup> and dirhenium<sup>8</sup> 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  $\text{Mn}_2$  through the MnRe to the  $\text{Re}_2$  systems. The bis(phosphine) complex in the Tc<sub>2</sub> system is relatively more stable than in either the  $\text{Mn}_2$  or  $\text{Re}_2$  systems.

The trends in kinetic behaviour are much more thoroughly established. The values of  $\Delta H^\ddagger$  for homolytic fission of the decacarbonyls have been shown to correlate well with spectroscopic parameters related to the strength of the metal–metal bonds.<sup>15</sup> The effect of substitution of two triphenylphosphine ligands successively into decacarbonyldimanganese lowers the kinetic strength of the Mn–Mn<sup>16</sup> bond by  $30 \pm 2$  and  $6.7 \pm 1.3$  kJ mol<sup>−1</sup>, respectively. The effect of two triphenylphosphine substituents lowers the kinetic strength of the Mn–Mn,<sup>16</sup> Mn–Re,<sup>2,3</sup> Tc–Tc,<sup>2</sup> and Re–Re<sup>8,17</sup> bonds by  $37 \pm 2$ ,  $7 \pm 2$ ,  $22 \pm 3$ , and  $3 \pm 3$  kJ mol<sup>−1</sup>, 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.<sup>15,18</sup> Apart from the value of  $\Delta S^\ddagger$  for reaction of  $[\{\text{Tc}(\text{CO})_4(\text{PPh}_3)\}_2]$  with carbon monoxide, which is unusually low (42 J K<sup>−1</sup> mol<sup>−1</sup>),<sup>1</sup> the values for the decacarbonyls and the other bis(phosphine) complexes all lie in the range  $77 \pm 13$  J K<sup>−1</sup> mol<sup>−1</sup>.

We thank Erindale College and the National Research Council of Canada for support.

[6/2097 Received, 15th November, 1976]

<sup>13</sup> H. Wawersik and F. Basolo, *Inorg. Chem.*, 1967, **6**, 1066.

<sup>14</sup> H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 113.

<sup>15</sup> J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1973, 267.

<sup>16</sup> L. I. B. Haines, D. J. Hopgood, and A. J. Poë, *J. Chem. Soc. (A)*, 1968, 421.

<sup>17</sup> L. I. B. Haines and A. J. Poë, *J. Chem. Soc. (A)*, 1969, 2826.

<sup>18</sup> R. A. Jackson and A. J. Poë, *Proc. 16th Internat. Conf. Co-ordination Chem.*, Dublin, 1974, paper 3.20.