Reaction of Bis-μ-diethylphosphido-bis(tetracarbonylmetal) (*M*–*M*) (M = Cr or W) with Tri-n-butylphosphine: Kinetics and Mechanism of a Reaction involving Seven-co-ordinate Complexes *

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The complexes $[(OC)_4\overline{M(\mu\text{-}PEt_2)_2M}(CO)_4]$ (M = Cr or W) undergo a two-step CO–PBu_3 exchange, in decalin, giving $[(Bu_3P)(OC)_3\overline{M(\mu\text{-}PEt_2)_2M}(CO)_4]$ and $[(Bu_3P)(OC)_3\overline{M(\mu\text{-}PEt_2)_2M}(CO)_3(PBu_3)]$. All the substitutions for the forward and reverse reactions occur by a dissociative mechanism involving the reactive intermediate $[L(OC)_3\overline{M(\mu\text{-}PEt_2)_2M}(CO)_3]$ (L = CO or PBu_3). Values of the competition ratio $k(CO)/k(PBu_3)$ (up to 10^5) indicate that bimolecular attack of CO on this intermediate is largely favoured compared with that of PBu_3. This unexpected sensitivity of the co-ordinatively unsaturated metal centre towards the nature of the incoming ligand is higher for chromium than for tungsten derivatives and increases from the first to the second substitution. Activation parameters corresponding to the rate constants and competition ratios, together with equilibrium data, for these reactions are reported.

Polynuclear complexes of transition metals, having two or more adjacent metal sites, might be useful model compounds for heterogeneous metallic catalysts.[1] Despite some controversy regarding the validity of this approach,[2] it seems useful to investigate the general properties of this class of compounds, which may combine the high reactivity and stability of the heterogeneous catalysts with the better selectivity of the homogeneous ones. Particularly interesting in this regard are clusters which retain their metal skeleton in solution, so enabling, in principle, novel modes of substrate–complex interaction and new reaction paths through adjacent metals.[3–8] From this point of view, mechanistic studies of 'simple' reactions of bridged binuclear metal carbonyls with phosphines could offer basic information on the general properties of polynuclear metal complexes and their reactive intermediates.

I report here, as an extension of a previous investigation on the molybdenum derivative,[9] a study of the thermal reaction of bis-μ-diethylphosphido-bis(tetracarbonylmetal) (*M*–*M*) compounds (M = Cr or W) with tri-n-butylphosphine. Both complexes have a solid-state structure which is characterized by a planar M–P–M–P ring. Each metal atom is at the centre of a seven-co-ordinate structure, which can be seen as resulting from distortion of a *cis*-$M(CO)_4P_2$ unit to allow metal–metal bond formation. A value of 3.05 Å has been reported for the W–W bond distance,[10] and a value of 2.91 Å for the Cr–Cr bond distance can be safely inferred from literature data for the corresponding dimethyl- (2.905 Å) [11] and diphenyl-phosphido- (2.93 Å) [12] chromium complexes.

The reaction of these complexes with PBu_3 gives, as with Mo,[9] mono- and bis-substituted products and this paper reports a detailed kinetic and mechanistic study of reactions (i) and (ii) (M = Cr or W) in decalin (decahydronaphthalene) as solvent.

$$[(OC)_4\overline{M(\mu\text{-}PEt_2)_2M}(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3\overline{M(\mu\text{-}PEt_2)_2M}(CO)_4] + CO \quad \text{(i)}$$

$$[(Bu_3P)(OC)_3\overline{M(\mu\text{-}PEt_2)_2M}(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3\overline{M(\mu\text{-}PEt_2)_2M}(CO)_3(PBu_3)] + CO \quad \text{(ii)}$$

Experimental

The complex $[(OC)_4\overline{Cr(\mu\text{-}PEt_2)_2Cr}(CO)_4]$, (1), was prepared following Hayter's method for the dimethylphosphido-analogue.[13] The i.r. spectrum in decalin showed peaks at 2 010s and 1 951vs, br cm^{-1} (*cf.* in chloroform: 2 003s and 1 942vs, br cm^{-1}).[14] $[(Bu_3P)(OC)_3\overline{Cr(\mu\text{-}PEt_2)_2Cr}(CO)_4]$, (2), was prepared by reaction of (1) (0.24 g, 0.47 mmol) with PBu_3 (0.81 g, 4.0 mmol) in carefully deoxygenated methylcyclohexane (9 cm^3) under argon. The solution was refluxed for 3 d, after which it was chromatographed on an alumina column with n-hexane as eluant. The main red eluate gave, by solvent removal under reduced pressure, deep red crystals which were recrystallized from ethanol, yield ⩾ 40% (Found: C, 47.1; H, 7.0. Calc. for $C_{27}H_{47}Cr_2O_7P_3$: C, 47.6; H, 7.0%). I.r. spectrum in decalin: 2 024m, 1 970m, 1 928vs, 1 899m, and 1 871w cm^{-1}. $[(Bu_3P)(OC)_3\overline{Cr(\mu\text{-}PEt_2)_2Cr}(CO)_3(PBu_3)]$, (3), was prepared in solution. Typically, 4.1 mg of complex (2) were dissolved in decalin (25 cm^3) containing various quantities of PBu_3 (0.15—0.50 mol dm^{-3}) and argon bubbled for 8 h at 80 °C. I.r. spectrum in decalin: 1 947m, 1 891s, and 1 878(sh) cm^{-1}; *cf.* spectra in decalin for the corresponding molybdenum (1 965w and 1 901s cm^{-1}) [9] and tungsten (see below) derivatives.

The complex $[(OC)_4\overline{W(\mu\text{-}PEt_2)_2W}(CO)_4]$, (1′), was prepared following Hayter's method for the dimethylphosphido-analogue.[13] The red oil obtained as a crude product was purified by chromatography on an alumina column with n-hexane as eluant. I.r. spectrum in decalin: 2 025s, 1 967m, and 1 951vs cm^{-1} (*cf.* in chloroform: 2 024s and 1 946vs, br cm^{-1}).[14] The complex $[(Bu_3P)(OC)_3\overline{W(\mu\text{-}PEt_2)_2W}(CO)_4]$, (2′), was prepared by reaction of (1′) (0.30 g, 0.39 mmol) with PBu_3 (0.16 g, 0.79 mmol) in methylcyclohexane (15 cm^3) at 90 °C, under a 25% CO–Ar mixture. After 10 h, solvent was removed under reduced pressure and the resulting orange solid chromatographed on an alumina column with n-hexane as eluant. The second orange eluate, upon solvent removal, gave a red oil, from which red crystals were obtained by treatment with ethanol and subsequent recrystallization of the crude solid from chloroform–ethanol, yield ⩾ 30% (Found: C, 35.0; H, 5.0. Calc. for $C_{27}H_{47}O_7$-

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* *Non-S.I. unit employed:* atm = 101 325 Pa.

Table 1. Rate and equilibrium data for the reaction $[(OC)_4Cr(\mu\text{-}PEt_2)_2Cr(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_4] + CO$ in decalin.[a] [Complex] = (1.5—8.0) × 10^{-4} mol dm^{-3}

θ_c / °C	$10^3[PBu_3]$ / mol dm^{-3}	y_{CO}[b]	$10^3[CO]$ / mol dm^{-3}	$10^5(k_f + k_r)$ / s^{-1}	$[(2)]_e/[(1)]_e$	10^5k_f / s^{-1}	10^5k_r / s^{-1}
70.0	1 040	0.00 [c]	0.00 [c]			38.5	
	540	0.00 [c]	0.00 [c]			37.2	
80.0	1 030	0.00 [c]	0.00 [c]			136	
	536	0.00 [c]	0.00 [c]			126	
90.0	99.6	0.251	1.47	3.00	2.42	2.12	0.88
	272	0.251	1.47	7.85	5.51	6.64	1.21
	462	0.251	1.47	10.2	13.0	9.47	0.73
	532	0.00 [c]	0.00 [c]	433		433	
	631	0.251	1.47	17.9	15.6	16.8	1.08
	1 022	0.00 [c]	0.00 [c]			455	
100.0	98.7	0.251	1.42	11.2	2.16	7.66	3.54
	272	0.251	1.42	28.2	4.45	23.0	5.17
	458	0.251	1.42	42.0	10.1	38.2	3.78
	458	1.00	5.7	11.7	2.37	8.23	3.47
	626	0.251	1.42	45.2	15.6	42.5	2.72
110.0	<0.38	0.251	1.37				5.94 [d]
	<0.40	1.00	5.5				5.11 [d]
	<0.38	1.00 [e]	7.7				5.25 [d]
	101	0.251	1.37	30.0	2.32	21.0	9.04
	270	0.251	1.37	56.8	6.18	48.9	7.91
	454	0.251	1.37	68.0	13.9	63.4	4.56
	620	0.251	1.37	103	19.9	98.1	4.92
120.0	<0.38	1.00	5.2				11.8 [d]
	<0.38	1.00 [e]	7.4				12.5 [d]
130.0	<0.15	1.00	4.9				28.9 [d]
	<0.38	1.00 [e]	7.0				30.4 [d]

[a] Starting from $[(OC)_4Cr(\mu\text{-}PEt_2)_2Cr(CO)_4]$, (1), or from $[(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_4]$, (2); values of 10^2 K are 3.59 (90.0), 3.01 (100.0) and 3.72 (110.0 °C) ($\Delta H^\ominus = 2$ kJ mol^{-1}, $\Delta S^\ominus = -24$ J K^{-1} mol^{-1}). [b] Mole fraction of carbon monoxide in the CO–Ar mixture. Total pressure including solvent vapour pressure, 1.1 atm. [c] Bubbling argon. [d] Starting from complex (2); all other runs started from (1). [e] Total pressure 1.5 atm.

P_3W_2: C, 34.3; H, 5.0%). I.r. spectrum in decalin: 2 035m, 1 984m, 1 937m (sh), 1 927vs, 1 913m (sh), and 1 869w cm^{-1}.

The complex $[(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_3(PBu_3)]$, (3′), was prepared by reaction of (1′) (90 mg, 0.12 mmol) with PBu_3 (0.10 g, 0.49 mmol) in methylcyclohexane (5 cm^3) at 90 °C under an argon stream. After 10 h, the solvent was removed under reduced pressure and the resulting oil treated with ethanol. The orange crystals so obtained were filtered off, washed with methanol, and recrystallized from hexane–methanol, yield ⩾30% (Found: C, 41.0; H, 6.7. Calc. for $C_{38}H_{74}O_6P_4W_2$: C, 40.8, H, 6.7%). I.r. in decalin: 1 961m and 1 891s cm^{-1}.

Tri-n-butylphosphine (EGA-Chemie) was distilled under reduced pressure and kept under argon. Decalin (Baker Analysed Reagent) was stored over molecular sieves. Argon and carbon monoxide were high-purity SIO products. Certified CO–Ar mixtures were provided by SIAD, relative errors in their analysed contents always being less than 0.5%.

Procedure.—Solutions were prepared and deoxygenated and concentrations of carbon monoxide determined as previously described.[15] Kinetic runs were carried out in aluminium foil-wrapped reaction tubes, from which at suitable times aliquot portions of the solutions were taken out through a capillary system and analysed by i.r. spectroscopy with a Perkin-Elmer 452 spectrophotometer.

Results

Reaction of $[(OC)_4Cr(\mu\text{-}PEt_2)_2Cr(CO)_4]$, (1), *with* PBu_3.—The reaction proceeds in two clearly distinct stages, the first being characterized by growth of the i.r. bands of $[(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_4]$, (2), and the second by decay of these bands and growth of those characteristic of $[(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_3(PBu_3)]$, (3).

The forward reaction of the first stage gave under bubbling argon quantitative formation of complex (2), whereas under CO an equilibrium mixture of (1) and (2) was obtained. The reaction was monitored by following the decreasing intensity of the band of (1) at 2 010 cm^{-1}. Under pseudo-first-order conditions plots of log ($A_t - A_\infty$) against time were linear over three half-lives. The observed rate constants, $k_{obs.}$, then represent under Ar the observed rate of the forward reaction $k_{f(Ar)}$, and under CO, where $A_\infty = A_e$, the sum of the observed rate constants of the forward and reverse reactions, $k_{f(CO)} + k_r$.[16] In the latter case the two terms were separated by introducing the spectrophotometrically determined concentration ratio, at equilibrium, of complexes (1) and (2). The forward reaction of the first stage follows the rate equations $k_{f(Ar)} = a$, under Ar, and $k_{f(CO)} = b[PBu_3]/[CO]$, under CO.

The observed rate of the reverse reaction was almost constant for all investigated CO and PBu_3 concentrations, according to the rate equation $k_r = c$. This constancy was also confirmed by studying the quantitative conversion of

Table 2. Rate and equilibrium data for the reaction [$(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_4$] + PBu_3 $\rightleftharpoons$ [$(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_3(PBu_3)$] + CO in decalin.[a] [Complex] = (1.0—3.0) × 10^{-4} mol dm^{-3}

θ_c/°C	10^3[PBu$_3$]/mol dm^{-3}	y_{CO}[b]	10^3[CO]/mol dm^{-3}	10^5k_f/s^{-1}	10^5k_r/s^{-1}
60.0	477	0.00 [c]	0.00 [c]	7 [d]	
	910	0.00 [c]	0.00 [c]	6 [d]	
70.0	474	0.00 [c]	0.00 [c]	17 [d]	
	904	0.00 [c]	0.00 [c]	18 [d]	
80.0	474	0.00 [c]	0.00 [c]	55 [d]	
100.0	147	1.00	5.7		7.70 [e]
	466	1.00	5.7		6.25 [e]
	752	0.048	0.27	9.80	13.8 [f]
	1 540	0.048	0.27	16.5	11.1 [g]
110.0	146	1.00	5.5		22.2 [e]
	461	1.00	5.5		18.0 [e]
120.0	144	1.00	5.2		58.0 [e]
	381	1.00	5.2		77.0 [e]

[a] Starting from [$(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_4$], (2), or from [$(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_3(PBu_3)$], (3). [b] Mole fraction of carbon monoxide in the CO–Ar mixture. Total pressure, including solvent vapour pressure, 1.1 atm. [c] Bubbling argon. [d] Approximate value (see text). [e] Starting from complex (3); all other runs started from (2). [f] $10^5(k_f + k_r) = 23.6$ s^{-1}, $[(3)]_e/[(2)]_e = 0.71$, and $10^4\ K = 2.55$. [g] $10^5(k_f + k_r) = 27.6$ s^{-1}, $[(3)]_e/[(2)]_e = 1.48$, and $10^4\ K = 2.59$.

complex (2) into (1) in the absence of added PBu$_3$, at various CO pressures. Consistent values were in fact obtained for the pseudo-first-order rate constants determined by following the disappearance of the peak at 1 928 cm^{-1} due to (2).

The small equilibrium constant for the second CO substitution by PBu$_3$ prevented a very detailed kinetic study of this stage. The forward reaction gave under bubbling Ar quantitative formation of the bis-substituted complex (3). Plots of log $(A_t - A_\infty)$ [A = absorbance of the peak at 1 928 cm^{-1} due to (2)] *versus* time are curved, the reaction becoming faster with time. This effect is much more pronounced at 80 °C as a consequence of the more difficult CO removal due to a higher rate of CO release from (2). In all cases the slopes towards the end of the reaction (lower complex concentration and lower rate of CO release) were considered to determine an approximate value of $k_{obs.}$ at [CO] *ca.* 0. The values so obtained are independent of phosphine concentration giving the rate law $k_{f(Ar)} = d$. At 100 °C only the reaction was studied also under a 4.8% CO–Ar mixture and high PBu$_3$ concentrations (0.752 and 1.54 mol dm^{-3}). An equilibrium mixture of complexes (2) and (3) was obtained in these cases. The reaction was followed by monitoring the i.r. peak of (2) at 1 928 cm^{-1} and kinetic data were obtained as described above for the forward reaction of the first stage. The observed rate of the forward reaction of this second stage is consistent with the rate equation $k_f = e[PBu_3]/[CO]$, whereas for the reverse reaction it is of the type $k_r = f$. The last rate equation has been confirmed by studying the reaction of complex (3) with 1 atm CO in the presence of added phosphine (0.144—0.466 mol dm^{-3}). Complex (3) completely disappeared forming (2), which in turn reacted further to give an equilibrium mixture of (2) and (1). The $k_{obs.}$ values obtained from the decrease in absorbance with time of the peak of (3) at 1 891 cm^{-1} are higher (*ca.* 80%) than those obtained under equilibrium conditions, indicating that some side-reactions are occurring under these 'drastic conditions'. These data are nevertheless accurate enough for the present purposes.

All rate data, together with the equilibrium constants, for the first and second stages are collated in Tables 1 and 2, respectively.

Reaction of [$(OC)_4W(\mu\text{-}PEt_2)_2W(CO)_4$], (1′), *with* PBu$_3$.— The reaction proceeds, as for the chromium analogue, in two clearly distinct stages with successive formation of the mono- and bis-phosphine-substituted complexes (2′) and (3′).

The forward reaction of the first stage gave both under Ar and under 1 atm carbon monoxide (for [PBu$_3$] ≥ *ca.* 5 × 10^{-2} mol dm^{-3}) quantitative formation of complex (2′), whereas smaller [PBu$_3$]/[CO] ratios produced an equilibrium mixture of (1′) and (2′). Kinetic data were obtained with the procedure described above, by following the decreasing intensity of the peak at 2 025 cm^{-1} due to (1′). A good linearity of the logarithmic plots against time was obtained in all cases. The pseudo-first-order rate constants of the first stage obey the rate equations $k_f = f/\{1 + (g[CO]^n/[PBu_3])\}$ for the forward reaction, and $k_r = h$ for the reverse. Consistent results were obtained both starting from complex (1′) or (2′). In the last case the decreasing intensity of the peak at 1 927 cm^{-1} was monitored. In a few cases not very rigorous pseudo-first-order conditions were used, the phosphine concentration varying during the run by less than *ca.* 7%. The initial slopes of the logarithmic plots were used in these cases for the determination of $k_{obs.}$ values.

A very similar behaviour was observed for the second stage, the main difference being associated with a smaller equilibrium constant for the carbon monoxide substitution. Bubbling argon and 4.8% CO–Ar mixtures were used to study the forward reaction. The reaction was followed by monitoring the absorbance of the peak at 1 984 and/or 1 927 cm^{-1} of complex (2′) and kinetic data obtained as above for the cases where the reaction reaches an equilibrium or goes to completion. The reverse reaction was better studied under 1.1— 1.5 atm CO in the absence of added phosphine, by following the peak at 1 891 cm^{-1} due to complex (3′). Complex (3′) completely disappeared forming (2′), which in turn reacted further to give (1′). The kinetic data so obtained are consistent with those resulting from the study of the forward reaction. The rate equations are $k_f = i/\{1 + (l[CO]^n/[PBu_3])\}$ and $k_r = m$ for the forward and reverse reactions, respectively.

All kinetic and equilibrium data for the first and second stages are collated in Tables 3 and 4, respectively.

Discussion

The observed kinetic behaviour is strictly similar to that found in the case of the molybdenum analogue;[9] all substitutions occur through a dissociative mechanism according to reactions (iii) and (iv) (M = Cr or W; L = CO for the first stage and PBu$_3$ for the second). By applying the steady-state treatment to the reactive intermediate [$L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_3$], rate equation (v) is obtained, where the two terms

$$[L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_4] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_3] + CO \quad \text{(iii)}$$

$$[L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_3] + PBu_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_3(PBu_3)] \quad \text{(iv)}$$

$$k_{obs.} = k_f + k_r = (k_1/\{1 + (k_{-1}[CO]/k_2[PBu_3])\}) + (k_{-2}/\{1 + (k_2[PBu_3]/k_{-1}[CO])\}) \quad \text{(v)}$$

Table 3. Rate and equilibrium data for the reaction $[(OC)_4W(\mu\text{-}PEt_2)_2W(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_4] + CO$ in decalin.[a] [Complex] = (1.0—8.0) × 10^{-4} mol dm^{-3}

θ_c °C	10^3[PBu$_3$] mol dm^{-3}	y_{CO}[b]	10^3[CO] mol dm^{-3}	$10^5(k_f + k_r)$ s^{-1}	$[(2')]_e$ / $[(1')]_e$	10^5k_f s^{-1}	10^5k_r s^{-1}	K
90.0	34.6	1.00	5.9	3.77	*ca.* 15	3.53	*ca.* 0.24	*ca.* 2
	64.2	0.00[c]	0.00[c]			10.3		
	64.2	1.00	5.9			5.92		
	133	1.00	5.9			7.05		
	273	1.00	5.9			8.37		
	282	0.00	0.00			9.96		
	686	0.00	0.00			10.4		
	686	1.00	5.9			9.96		
100.0	10.6	1.00	5.7	5.14	7.73	4.55	0.59	4.16[d]
	12.1	0.00[c]	0.00[c]			37.2		
	12.1	0.00	0.00			*ca.* 29		
	34.3	1.00	5.7	15.5	*ca.* 20	14.8	0.76	*ca.* 3
	65.2	1.00	5.7			18.6		
	123	1.00	5.7			24.0		
	279	0.00	0.00			39.2		
	284	0.00[c]	0.00[c]			36.2		
	284	1.00	5.7			30.4		
	465	0.00[c]	0.00[c]			38.5		
	465	1.00	5.7			35.0		
	549	0.00[c]	0.00[c]			37.0		
	680	0.00	0.00			38.5		
	922	0.00[c]	0.00[c]			36.6		
	922	1.00	5.7			38.9		
110.0	<0.13	1.00	5.5				1.48[e]	
	<0.15	1.00[f]	7.7				1.42[e]	
	2.29[g]	1.00	5.5	3.26	1.96	2.26	1.10	4.68[d]
	2.29[h]	1.00	5.5	2.90[e]	2.22[e]	2.00[b]	0.90[e]	
	10.5	1.00	5.5	16.2	7.82	14.4	1.84	
	36.7	1.00	5.5			49.6		
	130	1.00	5.5			82.5		
	277	0.00	0.00			134		
	282	0.00[c]	0.00[c]			131		
	282	1.00	5.5			111		
	461	0.00[c]	0.00[c]			134		
	461	1.00	5.5			120		
	674	0.00	0.00			139		
	914	0.00[c]	0.00[c]			128		
	914	1.00	5.5			123		
120.0	<0.13	1.00	5.2				6.35[e,i]	
	<0.15	1.00[f]	7.4				4.40[e]	
	1.66[g]	1.00	5.2	11.0	1.88	7.18	3.82	5.90[d]
	1.66[h]	1.00	5.2	10.7[e]	1.82[e]	6.91[e]	3.79[e]	
130.0	<0.13	1.00	4.9				25.1[e,i]	
	<0.15	1.00[f]	7.0				12.9[e]	
	1.81[g]	1.00	4.9	33.9	1.76	21.6	12.3	4.56[d]
	1.81[h]	1.00	4.9	33.5[e]	2.14[e]	22.8[e]	10.7[e]	
	2.21[g]	1.00	4.9	41.2	1.52	24.8	16.4	
	2.21[h]	1.00	4.9	36.2[e]	1.88[e]	23.6[e]	12.6[e]	

[a] Starting from $[(OC)_4W(\mu\text{-}PEt_2)_2W(CO)_4]$, (1′), or from $[(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_4]$, (2′). [b] Mole fraction of carbon monoxide in the CO–Ar mixture. Total pressure, including solvent vapour pressure, 1.1 atm. [c] Bubbling argon. [d] $\Delta H^{\ominus} = 1$ kJ mol^{-1}, $\Delta S^{\ominus} = 16$ J K^{-1} mol^{-1}. [e] Starting from complex (2′); all other runs started from (1′). [f] Total pressure 1.5 atm. [g] Initial phosphine concentration, final −*ca.* 7% (see text); $k_{obs.}$ value not used in the computation of kinetic parameters. [h] Initial phosphine concentration, final *ca.* +4%; $k_{obs.}$ value not used in the computation of kinetic parameters. [i] High value due to decomposition pathways, not used in the computation of kinetic parameters.

represent respectively the observed rate constants of the forward and reverse reactions.

Equation (v) reduces to those derived experimentally as follows. The observed rate of the forward reaction for both stages takes the form $k_{obs.} = k_{f(Ar)} = k_1$ under Ar, and $k_{obs.} = k_{f(CO)} = k_1/\{1 + (k_{-1}[CO]/k_2[PBu_3])\}$ under CO. This last rate equation can be further reduced to the form found for the chromium derivative $k_{f(CO)} = k_1k_2[PBu_3]/k_{-1}[CO]$, if under the experimental conditions $k_{-1}[CO]/k_2[PBu_3] \gg 1$, or can be rearranged as $1/k_{f(CO)} = (1/k_1) + (k_{-1}[CO]/k_1k_2[PBu_3])$ to fit the kinetic data of the tungsten derivative. Good linear plots were indeed obtained in the last case by plotting $1/k_{f(CO)}$ against $1/[PBu_3]$. Also the observed rate of the reverse reaction is easily seen to be consistent with the experimental ones; in most cases the reverse reaction was studied starting from the mono- or bis-phosphine derivative in the absence of added PBu$_3$ so that $k_2[PBu_3]/k_{-1}[CO] \ll 1$ and $k_r = k_{-2}$. For those equilibration reactions where the term $k_2[PBu_3]/k_{-1}[CO]$ was not negligible compared with 1 the expected decrease in k_r was observed. Convincing support of the proposed mechanism

Table 4. Rate and equilibrium data for the reaction $[(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_3(PBu_3)] + CO$ in decalin.[a] [Complex] = (1.0—4.0) × 10^{-4} mol dm^{-3}

θ_c/°C	$10^3[PBu_3]$/mol dm^{-3}	y_{CO}[b]	$10^3[CO]$/mol dm^{-3}	$10^5(k_f + k_r)$/s^{-1}	$[(3')]_e/[(2')]_e$	10^5k_f/s^{-1}	10^5k_r/s^{-1}
80.0	484	0.00[c]	0.00[c]			6.92	
	688	0.00[c]	0.00[c]			7.00	
90.0	64.5	0.048	0.28	3.85	1.85	2.50	1.35
	94.9	0.048	0.28	5.47	2.76	4.02	1.45
	127	0.048	0.28	5.78	4.23	4.67	1.11
	220	0.048	0.28	10.5	7.00	9.19	1.31
	475	0.00[c]	0.00[c]			22.6	
	479	0.00[c]	0.00[c]			25.1	
	479	0.048	0.28	13.1	15.7	12.3	0.78
	681	0.00[c]	0.00[c]			21.5	
	985	0.048	0.28			19.5	
100.0	<0.22	1.00	5.7				2.57[d]
	0.16	1.00[e]	7.9				2.66[d]
	94	0.048	0.27	15.6	3.51	12.1	3.46
	218	0.048	0.27	28.2	11.0	25.9	2.35
	470	0.048	0.27	37.0	19.0	35.2	1.85
	475	0.00[c]	0.00[c]			85.0	
	652	0.00[c]	0.00[c]			85.5	
	652	0.048	0.27			43.3	
	976	0.048	0.27			52.5	
110.0	<0.22	1.00	5.5				6.72[d]
	<0.19	1.00[e]	7.7				6.84[d]
	63.2	0.048	0.26	23.1	2.67	16.8	6.29
	93.2	0.048	0.26	28.3	4.68	23.3	4.98
	470	0.048	0.26	90.6	17.8	85.8	4.82
	646	0.048	0.26			119	
	967	0.048	0.26			165	
120.0	<0.22	1.00	5.2				15.7[d]
	<0.50	1.00[e]	7.4				15.2[d]

[a] Starting from $[(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_4]$, (2′), or from $[(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_3(PBu_3)]$, (3′). Values of 10^3K are 8.72 (90.0), 11.5 (100.0), and 11.5 (110.0 °C) ($\Delta H^{\ominus}$ = 16 kJ mol^{-1}, $\Delta S^{\ominus}$ = 5 J K^{-1} mol^{-1}). [b] Mole fraction of carbon monoxide in the CO–Ar mixture. Total pressure, including solvent vapour pressure, 1.1 atm. [c] Bubbling argon. [d] Starting from complex (3′); all other runs started from (2′). [e] Total pressure 1.5 atm.

Table 5. Kinetic parameters[a] obtained from the rate equations $k_{f(Ar)} = k_1$, $k_{f(CO)} = (k_1k_2/k_{-1}[CO])[PBu_3]$,[b] and $k_r = k_{-2}$[c] for the reaction $[(OC)_4Cr(\mu\text{-}PEt_2)_2Cr(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_4] + CO$

θ_c/°C	10^5k_1/s^{-1}	$10^7(k_1k_2/k_{-1})$/s^{-1}	$10^{-3}(k_{-1}/k_2)$[d]	10^5k_{-2}/s^{-1}
70.0	37.8			
80.0	131		8.46	
90.0	444	3.34	9.76	
100.0		11.0	11.4	
110.0		22.5		5.43
120.0				12.1
130.0				29.6

$\Delta H_1^{\ddagger}$ = 125(3) kJ mol^{-1}, $\Delta S_1^{\ddagger}$ = 51(8) J K^{-1} mol^{-1}, $\sigma[k_{f(Ar)}]$ = 5.3%; $\Delta H_1^{\ddagger} + \Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger}$ = 108(8) kJ mol^{-1}; $\Delta S_1^{\ddagger} + \Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger}$ = −71(20) J K^{-1} mol^{-1}, $\sigma[k_{f(CO)}]$ = 20.3%; $\Delta H_{-1}^{\ddagger} - \Delta H_2^{\ddagger}$ = 17(9) kJ mol^{-1}, $\Delta S_{-1}^{\ddagger} - \Delta S_2^{\ddagger}$ = 122(22) J K^{-1} mol^{-1}; $\Delta H_{-2}^{\ddagger}$ = 105(5) kJ mol^{-1}, $\Delta S_{-2}^{\ddagger}$ = −54(13) J K^{-1} mol^{-1}, $\sigma(k_r)$ = 9.0%

[a] Uncertainties in parentheses are standard deviations (see text). [b] Using 25.1% CO–Ar mixtures. [c] Using the more accurate values obtained in the runs which started from complex (2). [d] From the derived activation parameters.

Table 6. Kinetic parameters[a] obtained from the rate equations $k_{f(Ar)} = k_1$, $k_{f(CO)} = (k_1k_2/k_{-1}[CO])[PBu_3]$,[b] and $k_r = k_{-2}$[c] for the reaction $[(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3Cr(\mu\text{-}PEt_2)_2Cr(CO)_3(PBu_3)] + CO$

θ_c/°C	10^5k_1/s^{-1}	$10^8(k_1k_2/k_{-1})$/s^{-1}	$10^{-5}(k_{-1}/k_2)$	10^5k_{-2}/s^{-1}
60.0	6[d]			
70.0	17[d]			
80.0	55[d]			
100.0		3.14	1[e]	6.97
110.0				20.1
120.0				67.5

$\Delta H_1^{\ddagger}$ = *ca.* 100 kJ mol^{-1}, $\Delta S_1^{\ddagger}$ = *ca.* −26 J K^{-1} mol^{-1}; $\Delta H_{-2}^{\ddagger}$ = 135(14) kJ mol^{-1}, $\Delta S_{-2}^{\ddagger}$ = 35(35) J K^{-1} mol^{-1}, $\sigma(k_r)$ = 24.9%

[a] Uncertainties in parentheses are standard deviations (see text). [b] Using 4.8% CO–Ar mixtures. [c] Using the more accurate values obtained in the runs which started from complex (3). [d] Approximate value (see text). [e] By combination of the kinetic constants k_1 (using an extrapolated value) and k_1k_2/k_{-1}.

and its mathematical treatment is also given by the consistency of the kinetic data obtained starting both from complex (1′) or (2′).

All the reported kinetic parameters (Tables 5—8) were obtained by a least-squares analysis of the data. For a particular set of data, the same percentage standard deviation in $k_{obs.}$ was generally assumed at all temperatures. For the dependence of $k_{f(CO)}$ on $[PBu_3]$ for M = W only, each $k_{f(CO)}$ value was weighted assuming the same percentage standard deviation at a given temperature. All the tabulated uncertainties are standard deviations (95% confidence limits).

Analysis of the kinetic parameters indicates for Cr and W a general behaviour similar to that found for the molybdenum derivative.[9] The main points can be briefly outlined: (*i*) the rate of CO dissociation, k_1, is scarcely affected by substitution of one CO group with PBu_3 at the adjacent metal; (*ii*) the competition ratio k_{-1}/k_2 for bimolecular attack on the six-coordinate intermediate $[L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_3]$ (M = Cr, Mo, or W; L = CO or PBu_3) is markedly in favour of CO and is enhanced about hundred times in the second CO substitution; (*iii*) the rate of PBu_3 dissociation, k_{-2}, is always much lower than k_1 and is scarcely affected by substitution at the adjacent metal.

The effect of the nature of the metal centre can be better seen by analysis of the data in Table 9. This Table collects the kinetic and equilibrium constants, at 100 °C, together with the corresponding activation and thermodynamic parameters for the derivatives of Cr, Mo, and W. The rate of CO dissociation can be usefully compared with that observed for the corresponding hexacarbonyl complexes. The higher reactivity observed in the present case indicates that the 'ligand' $Et_2P\text{-}M(CO)_3L\text{-}PEt_2$ (M = Cr, Mo, or W; L = CO or PBu_3) has a marked labilizing effect, similar to that exhibited by 'hard' Lewis bases.[17] The origin of this phenomenon can be attributed to a stabilization of the unsaturated 16-electron transition state in the presence of the strong σ-donor phosphido-ligands.[18] The reactivity towards CO dissociation depends also on the nature of the metal centre and decreases in the order Mo $\gtrsim$ Cr > W, as generally found for Group 6A metal carbonyl compounds.[17] The activation parameters are typical for these types of processes, with high activation enthalpies and largely positive activation entropies.

The rate of PBu_3 dissociation is 30—2 × 10^3 times slower than the corresponding rate of CO dissociation. Similar

Table 7. Kinetic parameters [a] obtained from the rate equations $k_{f(Ar)} = k_1$, $1/k_{f(CO)} = (1/k_1) + (k_{-1}[CO]/k_1k_2[PBu_3])$,[b] and $k_r = k_{-2}$[c] for the reaction $[(OC)_4W(\mu\text{-}PEt_2)_2W(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_4] + CO$

	$10^5k_1/s^{-1}$			
θ_c/°C	*d*	*e*	k_{-1}/k_2[e]	$10^5k_{-2}/s^{-1}$
90.0	10.2	10.8 (1.2)	10.8 (3.1)	
100.0	37.6	40.5 (3.3)	12.9 (2.7)	
110.0	133	139 (13)	14.5 (3.2)	1.45
120.0				4.40
130.0				12.9

$\Delta H_1^\ddagger$ = 146(1) kJ mol^{-1},[d] $\Delta S_1^\ddagger$ = 78(4) J K^{-1} mol^{-1},[d] $\sigma[k_{f(Ar)}]$ = 3.3%; $\Delta H_1^\ddagger$ = 145(8) kJ mol^{-1},[e] $\Delta S_1^\ddagger$ = 76(21) J K^{-1} mol^{-1};[e] $\Delta H_{-1}^\ddagger - \Delta H_2^\ddagger$ = 17(18) kJ mol^{-1},[e] $\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger$ = 66(49) J K^{-1} mol^{-1};[e] $\Delta H_{-2}^\ddagger$ = 137(4) kJ mol^{-1}, $\Delta S_{-2}^\ddagger$ = 18(9) J K^{-1} mol^{-1}, $\sigma(k_r)$ = 4.7%

[a] Uncertainties in parentheses are standard deviations (see text). [b] Under pure carbon monoxide. [c] Using the more accurate values obtained in the runs which started from complex (2′). [d] From the rate equation $k_{f(Ar)} = k_1$. [e] From the rate equation $1/k_{f(CO)} = (1/k_1) + (k_{-1}[CO]/k_1k_2[PBu_3])$. The standard deviations take into account the covariance of the parameters $1/k_1$ and k_{-1}/k_1k_2; $\sigma[k_{f(CO)}]$ = 12.0 (90.0), 12.1 (100.0), and 13.1% (110.0 °C).

Table 8. Kinetic parameters [a] obtained from the rate equations $k_{f(Ar)} = k_1$, $1/k_{f(CO)} = (1/k_1) + (k_{-1}[CO]/k_1k_2[PBu_3])$,[b] and $k_r = k_{-2}$[c] for the reaction $[(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3W(\mu\text{-}PEt_2)_2W(CO)_3(PBu_3)] + CO$

	$10^5k_1/s^{-1}$				
θ_c/°C	*d*	*e*	$10^{-6}(k_{-1}/k_1k_2)$[e]/s	$10^{-3}(k_{-1}/k_2)$[f]	$10^5k_{-2}/s^{-1}$
80.0	6.96				
90.0	23.1	*ca.* 30	7.72 (0.90)	1.65	
100.0	85.2	*ca.* 80	2.31 (0.31)	2.42	2.61
110.0		*ca.* 400	1.45 (0.13)	3.47	6.78
120.0					15.4

$\Delta H_1^\ddagger$ = 134(5) kJ mol^{-1},[d] $\Delta S_1^\ddagger$ = 54(14) J K^{-1} mol^{-1},[d] $\sigma[k_{f(Ar)}]$ = 10.1%; $\Delta H_1^\ddagger + \Delta H_2^\ddagger - \Delta H_{-1}^\ddagger$ = 91(8) kJ mol^{-1}, $\Delta S_1^\ddagger + \Delta S_2^\ddagger - \Delta S_{-1}^\ddagger$ = −126(21) J K^{-1} mol^{-1}; $\Delta H_{-1}^\ddagger - \Delta H_2^\ddagger$ = 43(9) kJ mol^{-1}; $\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger$ = 180(25) J K^{-1} mol^{-1}; $\Delta H_{-2}^\ddagger$ = 105(3) kJ mol^{-1}, $\Delta S_{-2}^\ddagger$ = −52(7) J K^{-1} mol^{-1}, $\sigma(k_r)$ = 4.4%

[a] Uncertainties in parentheses are standard deviations (see text). [b] Using 4.8% CO–Ar mixtures. [c] Using the more accurate values obtained in the runs which started from complex (3′). [d] From the rate equation $k_{f(Ar)} = k_1$. [e] From the rate equation $1/k_{f(CO)} = (1/k_1) + (k_{-1}[CO]/k_1k_2[PBu_3])$. The standard deviations take into account the covariance of the parameters $1/k_1$ and k_{-1}/k_1k_2; $\sigma[k_{f(CO)}]$ = 15.8 (90.0), 11.2 (100.0), and 11.4% (110.0 °C). [f] From the derived activation parameters.

Table 9. Kinetic and equilibrium parameters, at 100 °C, of the reaction $[L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_4] + PBu_3 \rightleftharpoons [L(OC)_3M(\mu\text{-}PEt_2)_2M(CO)_3(PBu_3)] + CO$ (L = CO or PBu_3; M = Cr, Mo, or W)

	L = CO			L = PBu_3		
Parameter	Cr	Mo [a]	W	Cr	Mo [a]	W
k_1/s^{-1}	1.14×10^{-2}	1.55×10^{-2}	3.76×10^{-4}	*ca.* 3×10^{-3}	2.42×10^{-2}	8.52×10^{-4}
$\Delta H_1^\ddagger$/kJ mol^{-1}	125	136	146	—	132	134
$\Delta S_1^\ddagger$/J K^{-1} mol^{-1}	51	83	78	—	76	54
k_{-1}/k_2	1.14×10^4	1.52×10^2	12.9	*ca.* 1×10^5	5.81×10^4	2.42×10^3
$(\Delta H_{-1}^\ddagger - \Delta H_2^\ddagger)$/kJ mol^{-1}	17	43	17	—	35	43
$(\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger)$/J K^{-1} mol^{-1}	122	157	66	—	185	180
k_{-2}/s^{-1}	2.36×10^{-5}	7.97×10^{-6}	4.52×10^{-6}	6.97×10^{-5}	1.91×10^{-5}	2.61×10^{-5}
$\Delta H_{-2}^\ddagger$/kJ mol^{-1}	105	133	137	*ca.* 135	112	105
$\Delta S_{-2}^\ddagger$/J K^{-1} mol^{-1}	−54	12	18	*ca.* 35	−37	−52
K	3.01×10^{-2}	23.0 [b]	4.16	2.6×10^{-4}	2.16×10^{-2}	1.15×10^{-2}
$\Delta H^\ominus$ [b]/kJ mol^{-1}	3	−40	−8	—	−15	−14
$\Delta S^\ominus$ [b]/J K^{-1} mol^{-1}	−17	−86	−6	—	−72	−74

[a] From ref. 9. [b] From kinetic parameters.

behaviour was observed for a series of $[Cr(CO)_5L]$ complexes and was attributed to different ground-state Cr–L bond energies.[19] However, analysis of the activation parameters obtained in this study indicates that steric factors are important. The negative activation-entropy values found for the bis(phosphine) derivatives of Mo and W and mono(phosphine) derivative of Cr indicate severe steric restrictions in the transition state. This interpretation is supported by the slightly positive $\Delta S^\ddagger$ for the less crowded mono(phosphine) complexes of Mo and W. The slight dependence of the rate of PBu_3 dissociation on the nature of the metal centre and on the extent of CO substitution thus appears to be the result of a balance between electronic and steric factors. More crowded complexes (Cr > Mo ≈ W and bis- > mono-phosphine complexes) exhibit lower $\Delta H^\ddagger$ (lower M–PBu_3 bond energies) but greater steric rearrangements. It is worth noting how the activation values of the bis(phosphine) derivative of tungsten (3′) ($\Delta H^\ddagger$ = 105 kJ mol^{-1}, $\Delta S^\ddagger$ = −52 J K^{-1} mol^{-1}) almost perfectly match those of the mono(phosphine) chromium derivative (2).

The competition ratio k_{-1}/k_2 for bimolecular attack by CO and PBu_3 on the reactive intermediate $[L(OC)_3\overline{M(\mu\text{-}PEt_2)_2M}(CO)_3]$ (M = Cr, Mo, or W; L = CO in the first stage and PBu_3 in the second one) reaches values up to 10^5. This discriminating ability of the co-ordinatively unsaturated intermediate towards the nature of the entering ligand greatly contrasts with literature values close to unity.[17] The values obtained suggest that the intermediate behaves as a co-ordinatively saturated complex towards bimolecular attack. The activation parameters support this interpretation; attack of the poor nucleophile CO is enthalpically unfavourable ($\Delta H_{-1}^\ddagger - \Delta H_2^\ddagger$ = 17—43 kJ mol^{-1}), but significantly entropically favourable ($\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger$ = 66—185 J K^{-1} mol^{-1}) compared with attack of the more nucleophilic, but very hindering, PBu_3. The importance of steric factors is revealed by the effect of the metal centre on the order of k_{-1}/k_2 values, Cr ≫ Mo > W, which parallels fairly well the steric hindrance at the metal expected on the basis of the M–M bond distance (M–M = Cr < Mo ∼ W). Furthermore the higher value observed in the second stage indicates that replacement of a small CO group with a large PBu_3 ligand should make approach to the adjacent metal relatively more difficult for PBu_3 than for CO and higher $\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger$ values are indeed observed.

A final comment is required by the equilibrium constants for both substitutions. As expected from the previous discussion on k_1, k_{-2}, and k_{-1}/k_2, the variations in K mainly reflect the dependence of the k_{-1}/k_2 term on the nature of the metal centre and on the degree of substitution at the adjacent metal. So the equilibrium constants are in the order Cr < Mo ≈ W, and their value for a given metal decreases by a factor of up to *ca.* 1 000 with substitution.

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References

1 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91.
2 M. Moskovits, *Acc. Chem. Res.*, 1979, **12**, 229.
3 H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 379.
4 B. F. G. Johnson (ed.), 'Transition Metal Clusters,' Wiley, New York, 1980.
5 M. H. Crisholm and I. P. Rothwell, *Prog. Inorg. Chem.*, 1982, **29**, 1.
6 D. A. Roberts and G. L. Geoffroy, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. Abel, Pergamon Press, London, 1982, ch. 40.
7 R. Poilblanc, *Inorg. Chim. Acta*, 1982, **62**, 75.
8 E. L. Muetterties and M. J. Krause, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 135.
9 M. Basato, *J. Chem. Soc., Dalton Trans.*, 1976, 1678.
10 M. H. Linck and L. R. Nassimbeni, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 1105.
11 H. Vahrenkamp, *Chem. Ber.*, 1978, **111**, 3472.
12 B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organomet. Chem.*, 1974, **70**, 413.
13 R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711.
14 J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1964, 1005.
15 M. Basato, *J. Chem. Soc., Dalton Trans.*, 1975, 911 and refs. therein.
16 A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, Tokyo, 1961, p. 186.
17 D. J. Darensbourgh, *Adv. Organomet. Chem.*, 1982, **21**, 113 and refs. therein.
18 J. D. Atwood, M. J. Wovkulich, and D. C. Sonnenberger, *Acc. Chem. Res.*, 1983, **16**, 350 and refs. therein.
19 M. J. Wovkulic and J. D. Atwood, *J. Organomet. Chem.*, 1980, **184**, 77.

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