mmol) in acetone (20 mL) at 0 °C. The solution was stirred for 70 min at 0 °C, followed by rotary evaporation to ca. 10 mL at 0 °C and addition of cold hexane. When the solution was cooled to ca. −20 °C for 1 h, the product formed as a cream crystalline solid (49%). ^{1}H NMR ($CDCl_3$, δ): 12.07 (s, 1, CH), 8.90 (d, 2, J_{45} = 2.4 Hz, H5, pz trans to PdMe), 8.82 (d, 1, J_{45} = 2.3 Hz, H5, pz trans to $PdCH_2Ph$), 7.63 (d, 1, J_{34} = 2.1 Hz, H3, pz trans to $PdCH_2Ph$), 7.15 (m, 1, H4, Ph), 7.04 (t, 2, ^3J = 7.5 Hz, H3,5, Ph), 6.96 (m, 4, H3, pz trans to PdMe, and H2,6, Ph), 6.40 ("t", 1, H4, pz trans to $PdCH_2Ph$), 6.28 ("t", 2, H4, pz trans to PdMe), 3.62 (s, CH_2), 1.71 (s, PdMe).

[*fac*-$Pd(CH_2Ph)Me_2\{(pz)_3CH\}]BF_4$. Addition of silver tetrafluoroborate (0.4 mmol) in acetone to a stirred solution of $[Pd(CH_2Ph)Me_2\{(pz)_3CH\}]Br$ (0.2 g, 0.38 mmol) in acetone at 0 °C resulted in the immediate precipitation of AgBr. Filtration, followed by addition of hexane at 0 °C, gave the product as a white crystalline solid, which was isolated by filtration and washed with hexane (89%). ^{1}H NMR ($CDCl_3$, δ): 9.48 (s, 1, CH), 8.43 (m, 3, H5, pz), 7.66 (d, 1, J_{34} = 2.1 Hz, H3, pz trans to $PdCH_2Ph$), 7.17 (m, 1, H4, Ph), 7.05 (m, 2, H3,5, Ph), 6.96 (m, 3, H3, pz trans to PdMe, and H2,6, Ph), 6.43 ("t", 1, H4, pz trans to $PdCH_2Ph$), 6.31 (m, 2, H4, pz trans to PdMe), 3.62 (s, CH_2), 1.72 (s, PdMe).

$[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}][Pd(\eta^3\text{-}C_3H_5)Br_2]$. 2-Propenyl bromide (0.06 mL, 0.69 mmol) was added to a solution of $PdMe_2\{(pz)_3CH\}$ (0.20 g, 0.57 mmol) in acetone, and the solution was stirred for 60 min. Addition of hexane and slow evaporation of acetone under reduced pressure at 0 °C gave the product as a dark yellow crystalline solid, which was isolated by filtration and washed with hexane (39%). ^{1}H NMR ($(CD_3)_2CO$, δ): at 25 °C, 9.26 (s(b), 1, CH), 8.07 (d(b), 3, H5), 7.75 (d(b), 3, H3, pz), 6.47 ("t"(b), 4, H4), 5.56 (m(b), 2, H3), 4.11 (d(b), 4, H2), 3.17 (d(b), 4, H1); at −60 °C, cation, 10.04 (s(b), 1, CH), 8.79 (d(b), 3, H5, pz), 8.13 (d(b), 3, H3, pz), 6.66 (s(b), 3, H4, pz), 6.04 (m, 1, H3), 4.46 (d, J_{23} = 6.5 Hz, 2, H2), 3.37 (d, J_{13} = 12.0 Hz, 2, H1), anion, 5.33 (m, 1, H3′), 3.85 (d, J_{23} = 6.8 Hz, 2, H2′), 2.81 (d, J_{13} = 12.1 Hz, 2, H1′). Anal. Calcd for $C_{16}H_{20}N_6Br_2Pd$: C, 28.7; H, 3.0; N, 12.6. Found: C, 29.1; H, 3.0; N, 12.5.

An identical procedure employing 2-propenyl iodide gave $[Pd(\eta^3\text{-}C_3H_5)I]_2$ in 90% yield. The ^{1}H NMR spectrum ($CDCl_3$) is identical with that reported.[22]

$[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}][Pd(\eta^3\text{-}C_3H_5)Br_2]$. A similar procedure gave this complex in 63% yield. ^{1}H NMR ($(CD_3)_2CO$; see Figure 2; δ): at 25 °C all resonances are broad and definite assignments have not been attempted, 7.89, 7.70, 6.38, 5.58, 4.14, 3.10, 2.40; at −60 °C, 3.69–3.63 (m, H1, cation, and H2′, anion), cation, conformers C and D, 8.59 (d, J_{45} = 2.8 Hz, H5, pz), 6.16 (m, H3), 2.80 (s) and 2.76 (s) and 2.42 (s, Me), conformer A, 8.26 (d, J_{34} = 1.9 Hz, H3, pz), 6.73 ("t", H4, pz), 4.49 (d, J_{23} = 6.7 Hz, H2), conformer B, 8.20 (s, H3, pz), 6.70 ("t", H4, pz), 4.68 (d, J_{23} = 6.7 Hz, H2), anion, 5.06 (m, H3′), ~3.81 (m, H2′), 2.62 (d, J_{13} = 12.0 Hz, H1′). Anal. Calcd for $C_{15}H_{22}N_4Br_2Pd$: C, 28.6; H, 3.5; N, 8.9. Found: C, 28.8; H, 3.5; N, 8.9.

$[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]BF_4$. A procedure similar to that for the synthesis of $[Pd(CH_2Ph)Me_2\{(pz)_3CH\}]BF_4$ gave the complex as a white crystalline solid (22%). ^{1}H NMR ($(CD_3)_2CO$, δ): at 25 °C, 8.43 (d, J_{45} = 2.8 Hz, 2, H5, pz), 8.10 (d, J_{45} = 1.8 Hz, 2, H3, pz), 6.63 (dd, J_{34} = 1.7, J_{45} = 2.8 Hz, 2, H4, pz), 6.12 (m, 1, H3), 4.56 (d, J_{23} = 7.0 Hz, 2, H2), 3.63 (d, J_{13} = 12.4 Hz, 2, H1), 2.74, 2.56 (s, 6, Me); At −70 °C, conformers C and D, 8.56 (d, J_{45} = 2.4 Hz, H5, pz), 6.14 (m, H3), conformer C, 8.26 (d, J_{34} = 2.0 Hz, H3, pz), 6.75 ("t", H4, pz), 4.50 (d, J_{23} = 6.8 Hz, H2), 3.60 (d, J_{13} = 12.5 Hz, H1), 2.73 (s) and 2.42 (s, Me), conformer D, 8.17 (d, J_{34} = 2.0 Hz, H3, pz), 6.71 ("t", H4, pz), 4.67 (d, J_{23} = 6.9 Hz, H2), 3.66 (d, J_{13} = 12.5 Hz, H1), 2.77 (s) and 2.75 (s, Me). Anal. Calcd for $C_{12}H_{17}N_4BF_4Pd$: C, 35.1; H, 4.2; N, 13.6. Found: C, 35.0; H, 4.1; N, 13.4.

Acknowledgment. We thank the Australian Research Council and the University of Tasmania for financial support, the Commonwealth Government for a Postgraduate Research Award (to P.K.B.), and Johnson Matthey Ltd. for a generous loan of palladium chloride.

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Pressure and Solvent Dependence of the Substitution Behavior of Octahedral Metal Carbonyl Complexes: Influence of Electronic Effects on Reaction Mechanism

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The kinetics of the substitution reaction $M(phen)(CO)_4 + P \rightleftarrows$ *fac*-$M(phen)(CO)_3P + CO$ (phen = 1,10-phenanthroline, P = $P(OMe)_3$) has been studied in six different solvents for M = Mo at 50 °C. The pressure dependence of the forward reaction was studied in 1,2-dichloroethane (M = Mo, Cr) and in toluene (M = Mo). In addition, the reverse reaction of $Cr(phen)(CO)_3P$ with CO in dichloroethane was studied as a function of pressure, and the partial molar volumes of all species were determined. For molybdenum, a two-term rate law, rate = $(k_i + k_L [P])$[complex], was observed in each case, while for chromium a complex rate law gave limiting rate constants at zero and high phosphite concentrations. The rate constants of the k_i pathway in the six solvents are correlated with the MLCT band energies and discussed in terms of transition-state stabilization. The volumes of activation (M = Mo: $\Delta V^{*}_{k_i}$ = +8.4 ± 0.7 and +2 ± 2 $cm^3 \cdot mol^{-1}$ and $\Delta V^{*}_{k_L}$ = −21 ± 2 and −13 ± 1 $cm^3 \cdot mol^{-1}$ for CO-saturated dichloroethane and toluene, respectively; M = Cr: ΔV^{*} = +13.8 ± 0.5 and +19.2 ± 0.5 $cm^3 \cdot mol^{-1}$ for the forward and reverse reactions, respectively) are in full agreement with the proposed scheme of parallel associative and dissociative reversible reactions. The reaction volume obtained from the volume profile for the substitution of $Cr(phen)(CO)_4$ by $P(OMe)_3$ (−4 ± 1 $cm^3 \cdot mol^{-1}$) is in good agreement with that calculated from the kinetic data (−5.4 ± 0.5 $cm^3 \cdot mol^{-1}$).

Introduction

Both square-planar and octahedral complexes undergo under certain circumstances substitution according to a two-term rate law:[1-3]

$$\text{rate} = (k_i + k_L[\text{nucleophile}])[\text{complex}] \quad (1)$$

The controversy over the dissociative or associative nature of the intimate mechanism (here represented by the k_i

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pathway) in the case of square-planar complexes was settled by a study of the effect of high pressure on the observed kinetics.[4] Both pathways were shown to be associative, the k_i route being solvent-assisted. Furthermore, $\Delta V^\ddagger$ was shown to be far more sensitive in revealing solvent contributions to the mechanism than $\Delta S^\ddagger$.

Initially it was proposed that the octahedral complexes exhibiting two-term rate laws react via competitive associative (k_L) and dissociative (k_i) paths.[5] Such a mechanism is treated with scepticism[6,7] for two major reasons: first, the steric constraints on an octahedral geometry are far more stringent than those on a coordinatively unsaturated square-planar geometry, so that an associative attack, especially on a small metal center in a low oxidation state (such as in chromium carbonyl complexes), is considered exceptional; second, the octahedral complexes of d^6 metal centers are 18-electron species, and a dissociative route via a 16-electron species is expected to be the preferred mechanism.[8] Howell and Burkinshaw[9] interpreted the k_L term as an I_d pathway, in spite of negative reaction entropies (in one case, for example, -71 $J{\cdot}K^{-1}{\cdot}mol^{-1}$). Sometimes the apparent 18-electron count can be rationalized by a formal oxidation of the metal center or a decrease in the number of electrons donated by a cyclic ligand (ring slippage).[10]

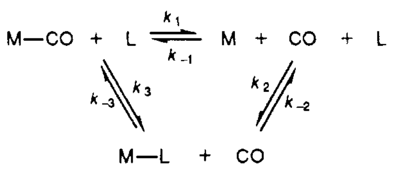
Recently a systematic changeover in mechanism from dissociative to associative activation was reported in going from smaller to larger metal centers during solvent exchange and complex formation reactions of first-row transition metals[11,12] and during chelate substitution of group VIb metal complexes.[13] To throw more light on this subject, we have investigated the substitution behavior of strongly solvatochromic complexes of molybdenum and chromium[14] and now report the solvent and pressure dependence of the substitution reactions in (2) (M = Cr or Mo).

$$M(phen)(CO)_4 + P(OMe)_3 \rightleftarrows M(phen)(CO)_3(P(OMe)_3) + CO \quad (2)$$

Experimental Section

General Procedures and Instrumentation. All solutions were prepared by using dried and distilled solvents, saturated with nitrogen or carbon monoxide by bubbling the required gas through the solvent for at least 15 min. Infrared spectra were recorded on a Nicolet 5SX FTIR spectrophotometer using a 0.1-mm path-length solution cell with KBr windows. UV–visible spectra and kinetics were measured on a Shimadzu UV-250 or an Hitachi U-3200 spectrophotometer, each fitted with an electronically thermostated cell changer (±0.1 °C). High-pressure kinetics were performed on a Zeiss PMQ II spectrophotometer operating in a double-beam mode and modified to hold a high-pressure cell.[15] The sample cell was of the quartz pillbox type.[16] The pillbox was filled under nitrogen or carbon monoxide atmosphere by using an apparatus designed to transfer the solution via a double-tipped-needle technique.[17]

Scheme I



M = Cr(phen)(CO)$_3$ or Mo(phen)(CO)$_3$

Trimethyl phosphite (Merck) was distilled under vacuum (40 mmHg) and stored for up to 10 days in the dark at −4 °C under the required gas. The chromium and molybdenum tetracarbonyl complexes and the monophosphite products, $M(phen)(CO)_3(P(OMe)_3)$, were prepared by photochemical and thermal means, respectively, as described in a previous paper.[14]

Partial Molar Volume Measurements. Partial molar volume measurements were performed on an Anton Paar (Vienna) DMA02 precision densitometer that was fitted with a tightly sealing stopper on the outlet port. The temperature was controlled at 25.000 ± 0.003 °C. The partial molar volumes were measured in solution according to eq 3, where Φ = partial molar volume

$$\Phi = \frac{M}{\rho_s} - \frac{1000(\rho - \rho_s)}{c\rho_s} \quad (3)$$

of solute, ρ_s = density of solvent, ρ = density of solution, M = molar mass of solute, and c = concentration. The concentrations were varied from 2×10^{-3} to 8×10^{-3} $mol{\cdot}dm^{-3}$, but within these limits no concentration effect on the partial molar volume was observed. To increase the thermal stability of $Cr(phen)(CO)_4$ and $Cr(phen)(CO)_3P(OMe)_3$, carbon monoxide saturated 1,2-dichloroethane (DCE) and 0.1 M $P(OMe)_3$ in DCE, respectively, were used as solvents. The density of these solvents was measured immediately prior to the complex molar volume determination.

No concentration dependence study was undertaken in the case of CO. DCE was degassed by means of five freeze–pump–thaw cycles, and a small volume of CO was introduced into the Schlenk tube to allow sample removal under reduced pressure, whereafter the remainder was allowed to equilibrate under an atmosphere of 0.1 MPa of CO at 25 °C (the saturation concentration is 6.0 $\times 10^{-3}$ $mol{\cdot}dm^{-3}$).[18] The quoted molar volume is the average of five determinations.

Kinetics. All solutions were prepared and transferred to a cuvette or a pillbox cell under nitrogen or carbon monoxide atmosphere. For high-pressure experiments at 50 °C and phosphite concentrations >0.2 M, a stock solution of the complex (concentration (1.4–1.6) $\times 10^{-4}$ M) and the required ligand concentration was prepared and stored in the dark at 4 °C for up to 5 days during use. All other solutions were freshly prepared.

The disappearance (or appearance in the case of phosphite complexes reacting with CO, henceforth referred to as "the reverse reaction") of the d–d band at 400 nm for molybdenum and 430 nm for chromium was monitored continuously. Reactions were followed for at least 2 half-lives, and the values of k_{obs} were obtained by using the method of Swinbourne.[19] In general the rate constants are an average of three or more repetitions which are reproducible to within 7%. Second-order rate constants were obtained from the slope of a plot of k_{obs} vs phosphite concentration at all pressures. The activation volume was obtained in the usual

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Table I. Solvent Data for the Reaction
$Mo(phen)(CO)_4 + P(OMe)_3 \rightleftarrows Mo(phen)(CO)_3(P(OMe)_3) + CO$

solvent[b]	$\bar{\nu}$ of CT band, cm^{-1}	$\bar{\nu}$ of CO stretch, cm^{-1}				$k_i \times 10^4$,[a] s^{-1}	$k_3 \times 10^4$,[a] $M^{-1}\ s^{-1}$
		ν_1	ν_2	ν_3	ν_4		
toluene	20 202	2011	1902	1887	1847	0.31 ± 0.01	1.72 ± 0.05
toluene (N_2)						0.33 ± 0.06	1.2 ± 0.2
benzene	20 366	2011	1901	1886	1844	0.32 ± 0.09	1.6 ± 0.1
chlorobenzene	20 790	2011	1902	1882	1839	0.70 ± 0.02	1.6 ± 0.1
chloroform[c]	20 660	2014	1909	1880	1832	0.96 ± 0.03	1.2 ± 0.6
dichcloromethane	21 368	2014	1904	1878	1832	1.96 ± 0.02	0.88 ± 0.03
dichloroethane	21 505	2013	1904	1877	1833	1.79 ± 0.02	1.48 ± 0.05
dichloroethane (N_2)						1.86 ± 0.02	1.41 ± 0.04

[a] At 50 °C. [b] Under CO atmosphere unless otherwise stated. [c] Ordered in the table according to ν(CO), k_i, and k_3.

way from a plot of ln k vs P, the slope of which represents $-\Delta V^{\ddagger}/RT$. In all cases the relationship was linear up to 100 MPa.

Mechanisms and Rate Constant Expressions. We have proposed that the mechanism for substitution of $M(phen)(CO)_4$ by phosphite can be described by Scheme I with the applicable rate constant expression (4).[14] Several observations simplify this

$$k_{obs} = \frac{k_1 k_2[L] + k_{-1}k_{-2}[CO]}{k_{-1}[CO] + k_2[L]} + k_{-3}[CO] + k_3[L] \qquad (4)$$

expression. First, $k_{-1}[CO] \ll k_2[L]$ for all concentrations of phosphite employed (except for the reverse reactions where [L] = 0!). Second, the k_3/k_{-3} pathway is not available for chromium, while the $k_{-1}k_{-2}[CO]/k_2[L]$ term is negligibly small for molybdenum. Thus the relevant rate constant expressions for chromium and molybdenum are given in (5) and (6), respectively. Although

$$k_{obs} = k_1 + \frac{k_{-1}k_{-2}[CO]}{k_2[L]} \qquad (5)$$

$$k_{obs} = (k_1 + k_{-3}[CO]) + k_3[L] \qquad (6)$$

the ligand-independent term in (6) is a composite one, we shall henceforth refer to it as k_i, the constant obtained from the intercept of a k_{obs} vs [L] plot.

At sufficiently high phosphite concentrations, k_{obs} in (5) will give the limiting rate constant k_1, while a study of the reverse reaction of (2) with no added ligand will yield the limiting rate constant k_{-2}, since $k_{-1}[CO] \gg k_2[L]$ in (4).[14]

Results and Discussion

Solvent Data. Table I lists the energy of the solvatochromic metal-to-ligand charge-transfer (MLCT) band together with the CO stretching frequency in the IR spectrum and values found for k_i and k_3 in various solvents for the substitution reaction of $Mo(phen)(CO)_4$. It can be seen that k_i increases significantly as the MLCT energy increases, while k_3 shows a slight decreasing trend. As observed by tom Dieck et al., the infrared carbonyl bands ν_3 and ν_4 also display solvatochromism[20] and show a corresponding decrease in energy.

The choice of solvent was limited to those in which the tetracarbonyl complexes were stable. Donor solvents were unsuitable. Those solvents used also have low acceptor numbers. On account of the marked solvatochromism, "solvent polarity"[21,22] seemed an appropriate parameter. Instead of the conventional spectral shifts of solvatochromic dyes[21,23] however, we have used the MCLT band energy of $Mo(CO)_4(phen)$ itself as an internal measure of polarity. In this way we were able to include halogen-containing solvents in a correlation with aromatic solvents, which is not normally possible.[23] In Figure 1 the rate of the largely dissociatively activated route, k_i, is plotted against the MLCT energy. Because the differences in CO concentrations are minimal (between 6×10^{-3} and 8.4×10^{-3} M) and the (unknown) contributions from k_{-3} are expected to be small, the observed linear correlation represents, as a good approximation, the relationship between the dissociatively activated route k_1 and ΔE_{MLCT}.

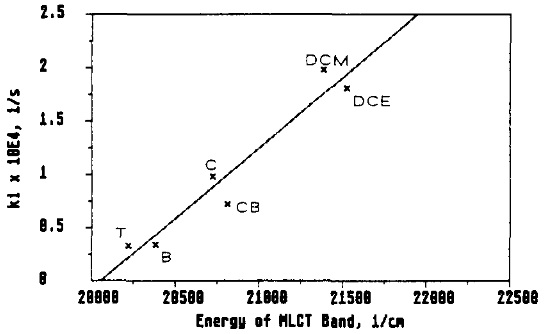

Figure 1. Graph of the ligand-independent rate constant in various solvents vs the energy of the MLCT band in that solvent at 50 °C for the reaction $Mo(phen)(CO)_4 + P(OMe)_3 \rightleftarrows Mo(phen)(CO)_3(P(OMe)_3) + CO$. T = toluene, B = benzene, C = chloroform, CB = chlorobenzene, DCM = dichloromethane, DCE = dichloroethane.

In an attempt to explain this effect, one must consider the influence of the solvent on bonding: the σ-bond contributions to the N → M bond were assumed to be relatively independent of solvent effects; the π-contributions are, however, strongly affected by the behavior of the trans-CO ligands competing for the electrons in the same d-orbital. The more polar solvents also tend to have the higher acceptor numbers (e.g., polar DCE, 16.7; nonpolar benzene, 8.2) and can interact with the lone pair on an oxygen atom, promoting stronger back-bonding to the trans-CO and hence withdrawing electron density from the chelate–metal π-bond. Spectral evidence corroborates this fact (Table I). There is a decrease in the CO stretching frequencies involving the CO ligands trans to phen,[22] indicating increased back-bonding between the metal and CO. Furthermore, the more polar solvents stabilize a polar ground state, viz., M ← L, with little back-bonding, so ΔE_{MLCT} increases with the decrease in IR stretching frequency. The buildup of charge on the metal is only partially compensated for by back-bonding, and the electron density on the metal is higher than in the case of a nonpolar solvent. The effect can be seen in the observed trends in ΔE_{MLCT} and IR stretching frequencies in Table I. Resonance Raman studies show that the electrons in

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Table II. Pressure Dependence of k_{obs} for the Reaction
$Mo(phen)(CO)_4 + P(OMe)_3 \rightleftarrows Mo(phen)(CO)_3(P(OMe)_3) + CO$
at 50 °C in DCE (A) and Toluene (B) and of k_i and k_3 (See Scheme I) in Both Solvents (C)

A1: $(DCE)_{N_2}$

	$k_{obs} \times 10^4$, s^{-1}, at ligand concn				
pressure, MPa	0.1 M	0.2 M	0.3 M	0.4 M	0.5 M
5	1.76 ± 0.04	1.99 ± 0.04	2.04 ± 0.08	2.17 ± 0.04	2.4 ± 0.2
25	1.69 ± 0.05	1.90 ± 0.04	2.0 ± 0.1	2.16 ± 0.03	2.28 ± 0.05
50	1.60 ± 0.02	1.83 ± 0.03	1.96 ± 0.09	2.14 ± 0.02	2.29 ± 0.04
75	1.53 ± 0.04	1.75 ± 0.02	1.89 ± 0.03	2.1 ± 0.1	2.28 ± 0.01
100	1.47 ± 0.02	1.73 ± 0.03	1.89 ± 0.07	2.11 ± 0.01	2.32 ± 0.04

A2: $(DCE)_{CO}$

	$k_{obs} \times 10^4$, s^{-1}, at ligand concn		
pressure, MPa	0.1 M	0.3 M	0.5 M
5	1.85 ± 0.09	2.14 ± 0.06	2.36 ± 0.02
25	1.81 ± 0.04	2.09 ± 0.06	2.39 ± 0.03
50	1.66 ± 0.04	2.05 ± 0.09	2.44 ± 0.06
75	1.61 ± 0.02	2.05 ± 0.05	2.48 ± 0.08
100	1.56 ± 0.05	2.09 ± 0.01	2.62 ± 0.04

B: $(Toluene)_{CO}$

	$k_{obs} \times 10^4$, s^{-1}, at ligand concn				
pressure, MPa	0.1 M	0.2 M	0.3 M	0.4 M	0.5 M
5	0.46 ± 0.01	0.66 ± 0.07	0.78 ± 0.01	0.95 ± 0.01	1.14 ± 0.06
25	0.46 ± 0.02	0.68 ± 0.03	0.82 ± 0.02	1.04 ± 0.02	1.22 ± 0.02
50	0.47 ± 0.02	0.72 ± 0.03	0.96 ± 0.05	1.13 ± 0.02	1.32 ± 0.04
75	0.50 ± 0.06	0.79 ± 0.03	0.97 ± 0.02	1.21 ± 0.03	1.42 ± 0.09
100	0.51 ± 0.02	0.85 ± 0.02	1.06 ± 0.04	1.31 ± 0.04	1.62 ± 0.02

C: Pressure Dependence of k_i and k_3 (from Plots of ln k_{obs} vs $[P(OMe)_3]$ at Each Pressure)

	$(DCE)_{N_2}$		$(DCE)_{CO}$		toluene	
pressure, MPa	$k_i \times 10^4$, s^{-1}	$k_3 \times 10^4$, M^{-1} s^{-1}	$k_i \times 10^4$, s^{-1}	$k_3 \times 10^4$, M^{-1} s^{-1}	$k_i \times 10^5$, s^{-1}	$k_3 \times 10^4$, M^{-1} s^{-1}
5	1.63	1.46	1.73	1.26	3.0	1.65
25	1.58	1.42	1.66	1.43	2.8	1.88
50	1.46	1.69	1.47	1.92	2.9	2.12
75	1.36	1.85	1.39	2.14	3.0	2.26
100	1.28	2.08	1.30	2.61	2.7	2.66

Table III. Pressure Dependence for the Reaction
$Cr(phen)(CO)_4 + P(OMe)_3 \rightleftarrows Cr(phen)(CO)_3(P(OMe)_3) + CO$
in DCE at 50 °C at Two Limiting Nucleophile Concentrations

	$k_{obs} \times 10^4$, s^{-1}, at ligand concn	
pressure, MPa	0.6 M	0 M (reverse reaction)
5	3.91 ± 0.09	2.7 ± 0.1
25	3.48 ± 0.03	2.3 ± 0.1
50	3.15 ± 0.05	1.9 ± 0.1
75	2.74 ± 0.09	1.6 ± 0.1
100	2.36 ± 0.06	1.3 ± 0.1

other diimine complexes are also shifted toward the metal in polar solvents.[25a] It is clear that a nucleophilic attack at the more negative center would be suppressed, which is indeed observed since k_3 decreases with increasing ΔE_{MLCT}. Simultaneously, a dissociative reaction (k_1) would also be promoted, as is discussed below.

A higher electron density on the metal could also strengthen the back-bonding to the cis-CO ligands in the MLCT excited state. No distinct tendency is observed. In fact, a trend in the opposite direction might be inferred. This is perhaps because the cis-CO ligands compete with each other in the same orbital, and the only possible shift of electron density must therefore be via a decrease in σ bonding. Angelici[25] suggested this possibility, but it was not generally accepted. Furthermore, resonance Raman studies have shown recently that there is a delocalization of electron density over the cis-CO ligands in the MLCT excited state,[26] and it was concluded that this delocalization facilitated the photochemical dissociation of a cis-CO ligand when the complex was irradiated in the MLCT band. The trend in k_1 in this work does not agree with this conclusion. We believe that, as the through-space delocalization would increase the $C \rightarrow M$ σ-bond at the same time that the back bond is weakened, little change will result in the cis-M–CO bond strength. The decrease in the rate of dissociation seen here is probably kinetic in nature and reflects the higher energy requirement of the transition state when a CO ligand departs, with its bonding electrons, from a more positive metal center in a nonpolar solvent. This argument is fully in accord with the electroneutrality principle of Pauling.[27]

We attribute the greater solvent effect on the dissociative reaction to the smaller size of the CO molecule relative to the phosphite molecule. Thus its passage through the first solvation sheath during the formation of a five-coordinate intermediate is not as sensitive to the type of solvent molecule as the approach of a bulky phosphite molecule. Furthermore, the electronic changes on the

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Table IV. Activation Parameters for the Reaction $M(phen)(CO)_4 + P(OMe)_3 \rightleftarrows M(phen)(CO)_3(P(OMe)_3) + CO$

solvent	rate constant	$\Delta V^{\ddagger}$,[a] $cm^{-3}\cdot mol^{-1}$	$\Delta H^{\ddagger}$,[b] $kJ\cdot mol^{-1}$	$\Delta S^{\ddagger}$,[b] $J\cdot K^{-1}\cdot mol^{-1}$
		(a) M = Mo		
DCE	k_i (N_2)	+7.1 ± 0.4	111 ± 2	+27 ± 6
	k_i (CO)	+8.4 ± 0.7		
DCE	k_3 (N_2)	−11 ± 2	82 ± 3	−67 ± 12
	k_3 (CO)	−21 ± 2		
toluene	k_i	+2 ± 2	135 ± 9	+85 ± 30
	k_3	−13 ± 1	69 ± 2	−106 ± 7
		(b) M = Cr		
DCE	k_1	+13.8 ± 0.5[a]	122.9 ± 0.9	+71 ± 3
	k_{-2}	+19.2 ± 0.5[c]	117 ± 2	+65 ± 6

[a] At 50 °C. [b] Data from ref 8. [c] At 35 °C.

metal center directly affect the bonding with CO but are partially shielded from an incoming nucleophile by the ligands.

Pressure Data. Table II presents the dependence of the observed rate constant on ligand concentration and pressure in dichloroethane (DCE) and toluene at 50 °C for molybdenum as central atom. The pressure dependence of the constants k_i and k_3 is also included. The analogous data for chromium in DCE at 50 °C at the limiting conditions of 0.6 M phosphite (k_1) and no added phosphite (reverse reaction, k_{-2}) is given in Table III. The activation parameters extracted from the pressure and temperature data are summarized in Table IV.

Molybdenum. In complete agreement with the suggested mechanism, both the activation entropies and volumes are negative in DCE and toluene for the k_3 path. The activation enthalpy is moderate, as expected for an associative reaction. The smaller enthalpy term and larger negative terms for both the activation entropy and activation volume in toluene speak for a transition state with more bond making in that solvent than in DCE, as is expected for a metal center with increased electron density.

The values of $\Delta V^{\ddagger}(k_3)$ are in close agreement with those reported recently for the substitution reactions of $Mo(CO)_4(S\text{-}S)$ with $P(OR)_3$, viz., −11.3 ± 0.5 (S–S = 2,5-dithiahexane (DTH), R = Me), −10.2 ± 0.8 (S–S = DTH, R = *i*-Pr), −9.3 ± 0.4 (S–S = DTH, R = Ph), and −9.4 ± 0.2 $cm^3\cdot mol^{-1}$ (S–S = 3,6-dithiaoctane, R = *i*-Pr).[13] It follows that a $\Delta V^{\ddagger}$ value of between −9 and −20 $cm^3\cdot mol^{-1}$ is characteristic for an associative substitution process on a $Mo(CO)_4(L\text{-}L)$ complex.

In discussing k_i, it must be kept in mind that this constant contains a dissociative contribution (k_1), as well as an associative contribution (k_{-3}[CO]), which are respectively suppressed and favored in toluene. Furthermore, the saturation concentration of CO is marginally higher in toluene (7.4×10^{-3} $mol\cdot dm^{-3}$) than in DCE (6.0×10^{-3} $mol\cdot dm^{-3}$).[18] Both these effects should cause a relative decrease in $\Delta V^{\ddagger}$ in toluene. The activation volume is dramatically decreased from +7 to +2 $cm^3\cdot mol^{-1}$, which might reflect a gain in importance of k_{-3} or point to a shift in mechanism from D to I_d. The energy parameters are not as easy to interpret. The large positive enthalpies and entropies are consistent with a dissociative mechanism, but the increase in entropy is difficult to explain. The large standard deviations are probably significant. The k_i, obtained from the intercepts of linear plots, involve large errors. Furthermore, the temperature dependence of a composite rate constant would be expected to be curved. Because of the slow reactions, only higher temperatures were employed. Over this range the expected curvature was not evident, and the energy parameters are expected to reflect predominantly the dissociative reaction. Again, the activation volume seems to be more discriminating. Unfortunately the pressure dependence of the reverse reaction could not be studied due to the formation of a precipitate at elevated pressure during the reaction.

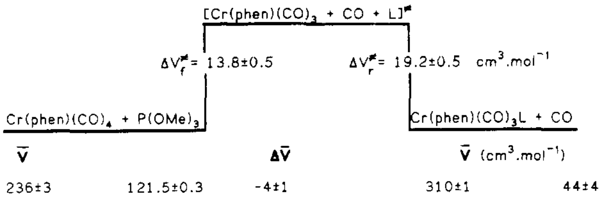

Figure 2. Volume profile for the reaction $Cr(phen)(CO)_4 + P(OMe)_3 \rightleftarrows Cr(phen)(CO)_3(P(OMe)_3) + CO$.

The data for CO-saturated solvents are expected to be more reliable than those under N_2-saturated conditions. In general under ambient conditions the intercepts (k_i) are larger and the slopes (k_L) are smaller. If the buildup of CO in the solution were negligible, one would expect a smaller intercept and the same slope. However, pseudo-first-order conditions are not maintained, and during the reaction [CO] = [product], which cannot be neglected if k_{-3} or k_{-1} play a significant role.

Chromium. The activation parameters are summarized in Table IV. Partial molar volumes and the volume profile are shown in Figure 2. All activation parameters, for both forward and reverse reactions, agree with the proposed mechanism. The entropies are very similar and positive; the enthalpies are large and positive, as are the activation volumes. The value of $\Delta V^{\ddagger}(k_1)$ is very typical for the dissociation of CO. Other values reported in the literature for such reactions vary between +16 and +21 $cm^3\cdot mol^{-1}$ and are considered to be characteristic for the operation of a D mechanism.[28,29] The smaller enthalpy and larger activation volume of the reverse reaction reflect the weaker Cr–P bond and the larger molar volume of $P(OMe)_3$. The overall reaction volume calculated from the volumes of activation for the forward and reverse reaction is −5.4 ± 0.5 $cm^3\cdot mol^{-1}$. The reaction volume obtained from partial molar volumes of all species is −4 ± 1 $cm^3\cdot mol^{-1}$. This good agreement further supports the proposed double-equilibrium mechanism.

Conclusions

High-pressure kinetic results are in full agreement with a two-term rate law arising from the parallel associative and dissociative reversible reactions outlined in Scheme I. Solvent studies indicate that the energy of the metal-to-ligand charge-transfer band is a measure of the relative contributions of the associative and dissociative pathways. When this energy barrier is high, the dissociative route is more important. The evidence obtained from the solvent study adds weight to the argument that the associative reaction with octahedral $Mo(diimine)(CO)_4$ complexes is in accordance with the 18-electron rule by virtue of a shift of electron density on to the diimine ligand in the transition state.

It appears quite general that the larger molybdenum as metal center has available to it an associative type pathway that the smaller chromium ion does not. This is in line with the observed changeover in mechanism from I_d to I_a in going to larger metal centers in the first transition series.[11,12] Furthermore, this study adds to the growing body

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of information[13,30] that shows that molybdenum is a borderline case in group VIb between chromium, which follows a D mechanism, and tungsten, which reacts associatively.

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Registry No. Cr(phen)$(CO)_4$, 14168-63-9; Mo(phen)$(CO)_4$, 15740-78-0; $P(OMe)_3$, 121-45-9.

Cluster Synthesis. 26. Condensation of $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ to $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)_2(\mu_4\text{-}S)_2$ and $Ru_6(CO)_{13}(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$

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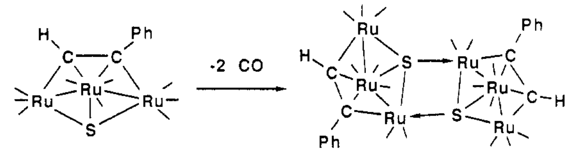
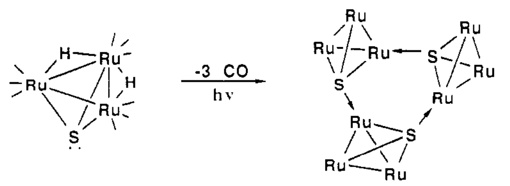
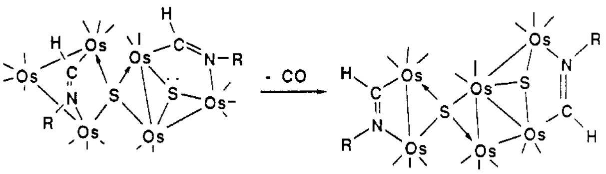
$Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **1**, undergoes a sequence of decarbonylations that leads to the coupling and fusing of two triruthenium groups. The hexaruthenium compounds $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$, **2**, and $Ru_6(CO)_{13}(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$, **3**, were obtained by decarbonylation at 97 °C. Compound **2** was converted to **3** independently by decarbonylation at 97 °C. **2** and **3** were both characterized crystallographically. Compound **2** consists of a doubly spiked electron-rich butterfly tetrahedral cluster of metal atoms held together by sulfido ligands with inverted tetrahedral geometries, two bridging ynamine ligands, and one normal and two weak ruthenium–ruthenium bonds. Compound **3** consists of a monocapped pentagonal bipyramidal cluster for six ruthenium atoms and two sulfido ligands. It contains one-edge bridging and one triply bridging ynamine ligand. Crystal data for **2**: space group $P2_1/c$, $a = 14.912$ (5) Å, $b = 11.207$ (3) Å, $c = 24.046$ (4) Å, $\beta = 103.75$ (2)°, $V = 3903$ (2) Å^3, $Z = 4$, $R = 0.040$, and $R_w = 0.046$ for 3060 reflections. For **3**: space group $P2_1/n$, $a = 9.564$ (2) Å, $b = 31.383$ (5) Å, $c = 11.527$ (2) Å, $\beta = 103.80$ (1)°, $V = 3360$ (2) Å^3, $Z = 4$, $R = 0.027$, and $R_w = 0.028$ for 2280 reflections.

Introduction

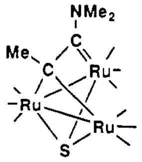
The ability of sulfido ligands to promote the synthesis of metal carbonyl cluster complexes by facilitating the agglomerization of metal-containing groups has been amply demonstrated.[1-6] In recent studies, we have shown that sulfido ligands can assist in the agglomerization of clusters through formation of donor/acceptor bonds, S → M, from the sulfido ligand on one cluster to a metal atom of another cluster, eqs 1[3] and 2[4]. Vacant sites on the metal are usually formed by thermal decarbonylation processes. In this first step, the agglomerization may occur without the formation of metal–metal bonds between the clusters. In certain cases, we have observed cluster growth by the transfer of a metal atom from one cluster to the other, e.g., eq 3.[5,6]

2  (1)

3  (2)

 (3)

In our recent studies of the chemistry of ynamine ligands in metal carbonyl cluster complexes, we have prepared the complex $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **1**.[7]



1

We have now observed that **1** undergoes a facile thermal elimination of CO accompanied by the condensation of two triruthenium cluster groupings. A sequence of two hexaruthenium cluster complexes, $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)_2(\mu_4\text{-}S)_2$, **2**, and $Ru_6(CO)_{13}(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$, **3**, are formed in which the fusing of the clusters by metal–metal bond formation is a central

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