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Systematic Substituent Effects on Dissociative Substitution Kinetics of $Ru(CO)_4L$ Complexes (L = P-, As-, and Sb-Donor Ligands)

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The kinetics of dissociation of CO from $Ru(CO)_4L$ (L = a wide variety of P-, As-, and Sb-donor ligands) have been studied, and the values of the rate constants can be resolved quantitatively into electronic and steric effects. The curved steric profile obtained shows that steric effects are quite small for small substituents such as $P(OCH_2)_3CEt$ and $P(OEt)_3$, but they increase steadily and substantially as the size of the substituent increases. A similar analysis of data in the literature for CO dissociative reactions of other substituted carbonyl complexes is also successful in resolving electronic and steric effects, and a clear dependence of steric effects on the coordination number of the complexes is shown. The analysis can be applied to some methyl migration reactions that involve CO loss, and the results can help to indicate the relative importance of CO loss and methyl migration in the transition states. Trends in the C–O stretching frequencies in the axial $Ru(CO)_4L$ and diaxial $Ru(CO)_3L_2$ complexes are described.

Introduction

The most prevalent mechanism for substitution reactions of mononuclear binary metal carbonyls is reversible CO dissociation[1] and ligand dissociation kinetics play a major role in determining the efficiency of important catalytic reactions.[2] Substituent effects can also determine catalytic efficiency,[2] and systematic quantitative studies of substituent effects on the kinetics of dissociative reactions are, therefore, obviously of considerable practical as well as academic importance. The quantitative separation of steric and electronic effects of different nucleophiles in determining the rates of associative reactions of a wide range of metal carbonyls has been known to be possible for many years,[3] but the corresponding analysis of the effects of different substituents on dissociative reaction rates has been less extensively explored.[1,4]

Early studies of reactions of $Ni(CO)_3L$[5] and *cis*-$Mn(CO)_4(L)Br$[6] complexes (L = a small number of P-donor ligands) showed the importance of steric effects. However, it was over 20 years before a study of the effect of a much wider range of substituents on rates of CO dissociation from *mer*-$Ru(CO)_3L(SiCl_3)_2$ was reported and the overriding importance of steric effects clearly shown.[7]

Rates of CO dissociation from $Ru(CO)_4L$ (L = P-*n*-Bu_3,[8] PPh_2Me,[9] and PPh_3[9]) suggest that steric effects are important here as well, and since data for substitution kinetics for dissociative reactions of 5-coordinate metal carbonyls are still relatively rare,[1,10] we have extended the study of reaction 1 to include a much wider variety of types of L.

$$Ru(CO)_4L + L' \xrightarrow{k_1} Ru(CO)_3LL' + CO \qquad (1)$$

Experimental Section

Dodecacarbonyltriruthenium (Strem Chemicals) was used as received. *n*-Heptane (BDH) was distilled from sodium under nitrogen and stored over molecular sieves. Liquid phosphorus ligands (triphenyl phosphite, triethyl phosphite, tri-*n*-butylphosphine, triethylphosphine, diethylphenylphosphine, diphenylethylphosphine, and tri-*tert*-butylphosphine) were obtained from commercial sources and were purified by distillation under low pressures of argon or nitrogen immediately before use. Etpb ($P(OCH_2)_3CEt$, Strem Chemicals) was sublimed (50 °C, 0.12 mmHg) immediately before use. Other ligands were obtained and used as described previously.[11] Ethylene (99.5%) was obtained from Matheson Gas Products Canada.

Complexes of the type $Ru(CO)_4L$ can easily be prepared and characterized in situ by reaction of L with $Ru(CO)_4(C_2H_4)$, which is generated in heptane solution by photolysis of $Ru_3(CO)_{12}$ under an atmosphere of ethylene.[12] Photochemical reactions were generally carried out in 10 cm^3 of solution in the Pyrex Schlenk tube used for the kinetic studies (see below). Saturated (ca. 5×10^{-4} M) solutions of $Ru_3(CO)_{12}$ in *n*-heptane were thoroughly degassed by one or more freeze–pump–thaw cycles and the tubes filled with ethylene. They were then exposed to light from a slide projector at room temperature. This led rapidly (ca. 5 min) and quantitatively to $Ru(CO)_4(C_2H_4)$ (eq 2), which had characteristic IR bands at 2104 (m), 2021 (vs), and 1995 (s) cm^{-1}, exactly as reported in the literature.[12] The phosphorus ligands were then added to the solution whereupon the $Ru(CO)_4(C_2H_4)$ was quantitatively converted to $Ru(CO)_4L$ within about 5–10 min (eq 3), as evidenced by the total disappearance of the IR spectrum due to $Ru(CO)_4(C_2H_4)$ and the simultaneous appearance of IR spectra due to $Ru(CO)_4L$.[13]

$$Ru_3(CO)_{12} + 3C_2H_4 \xrightarrow{h\nu} 3Ru(CO)_4(C_2H_4) \qquad (2)$$

$$Ru(CO)_4(C_2H_4) + L \rightarrow Ru(CO)_4L + C_2H_4 \qquad (3)$$

Infrared spectra were measured on a Nicolet 10 DX spectrophotometer in the absorbance mode using 1.0 mm path length solution cells with NaCl windows.

Kinetic studies were carried out with the reaction solutions in a Schlenk tube wrapped with aluminum foil and equipped with a rubber septum cap to allow convenient sample removal by using a syringe with a stainless-steel needle. The temperature was maintained constant to within ±0.1 °C by immersion of the Schlenk tube in a Lauda constant-temperature bath, Model RCS-6.

Results

The IR spectra of $Ru(CO)_4L$ usually gave three bands in the CO stretching region (Table I). The number of bands agrees with that predicted[13] from C_{3v} symmetry of axially substituted trigonal-bipyramidal $Ru(CO)_4L$ and the frequencies and relative intensities of the bands for the complexes that have previously been prepared are in excellent agreement with reported[8,12,13] spectra. In some of the axially substituted species the E vibrational mode (ν_3) splits into two bands of nearly equal intensities, and in other cases the axially substituted complexes were found to be in equilibrium with equatorially substituted isomers.[13] Thus, bands assigned to *eq*-$Ru(CO)_4L$ show when L = $AsPh_3$, $SbPh_3$, and etpb,[13] and similar bands that are presumed also to be due to the equatorial isomer occur for L = $P(OPh)_3$.

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Table I. Infrared Spectra of $Ru(CO)_4L$ and $Ni(CO)_3L$ Compounds[a,b]

	ν(CO), cm^{-1}						
	$Ru(CO)_4L$						
L	ν_1(eq)	ν_1(ax)	ν_2(eq)	ν_2(ax)	ν_3(eq)	ν_3(ax)	$Ni(CO)_3L$[c]
etpb	2093	2077	2015	2007		1976	2086.8
$P(OPh)_3$	2092	2074	2014	2005		1976, 1967	2085.3
$P(OMe)_3$[d]		2072		2002		1971, 1957	2079.5
$P(CH_2CH_2CN)_3$[e]		2071		1998		1956	2077.9
$P(OEt)_3$		2070		1998		1969, 1953	2076.3
$P(p\text{-}ClPh)_3$		2066		1993		1958	2072.8
PPh_3		2062		1988		1953	2068.9
PPh_2Me[f]		2060		1986		1948	2067.0
PPh_2Et		2062		1987		1954, 1947	2066.7
$P(p\text{-}tol)_3$		2060		1985		1952	2066.7
PBz_3[g]		2060		1987		1950	2066.4
$P(p\text{-}MeOPh)_3$		2058		1985		1950	2066.1
PMe_3[d]		2061		1985		1947	2064.1
$PPhEt_2$		2060		1985		1952, 1945	2063.7
$P(NMe_2)_3$		2059		1983		1944	2061.9
PEt_3		2060		1984		1945	2061.7
$P\text{-}n\text{-}Bu_3$		2059		1983		1944	2060.3
PCy_3[h]		2056		1978		1943, 1936	2056.4
$P\text{-}t\text{-}Bu_3$		2056		1974		1937	2056.1
$AsPh_3$	2079	2061	1998	1986		1958	
$SbPh_3$	2078	2061	1998	1987	1967		

[a] Spectra recorded in heptane unless otherwise indicated. [b] Assignments of bands to equatorial (eq) or axial (ax) isomers made as in ref 13. [c] Data from ref 15. [d] In hexane; see ref 13. [e] In 1,2-dichloroethane. [f] In hexane; see ref 12. [g] $P(CH_2Ph)_3$. [h] $P(C_6H_{11})_3$.

Table II. IR Spectra of $Ru(CO)_3L_2$ Compounds in Heptane

L	ν(CO), cm^{-1}	L	ν(CO), cm^{-1}
$P(OPh)_3$	1934	$P(p\text{-}MeOPh)_3$	1900
$P(OEt)_3$	1929, 1917	$PPhEt_2$	1901, 1890
$P(p\text{-}ClPh)_3$	1915	$P(NMe_2)_3$	1890
PPh_3	1910	PEt_3	1889
PPh_2Et	1905, 1895	$P\text{-}n\text{-}Bu_3$	1890
$P(p\text{-}tol)_3$	1892	PCy_3	1882, 1867

The IR spectra taken throughout the reactions of L with most of the $Ru(CO)_4L$ complexes show the growth of single bands (Table III) characteristic of the E modes of diaxial $Ru(CO)_3L_2$ products of D_{3h} symmetry.[13] In several cases the band is split due to lower symmetry of the two substituents.[13] Sharp isosbestic points were evident throughout the reaction, and the product spectra were stable for several days at room temperature.

Reaction of $Ru(CO)_4(AsPh_3)$ with $AsPh_3$ showed the growth of a sharp band at 1908 cm^{-1}, which is very close to that for diaxial $Ru(CO)_3(PPh_3)_2$. In addition there are bands at 2016, 1963, and 1947 cm^{-1} that indicate the presence of an additional, less symmetrical, isomer of the $Ru(CO)_3(AsPh_3)_2$ product. Reaction of $Ru(CO)_4(SbPh_3)$ with $SbPh_3$ shows the growth of a very weak shoulder at ca. 1915 cm^{-1} so that only a very little diaxial $Ru(CO)_3(SbPh_3)_2$ is formed. The main changes observed involve the growth of three clear bands at 2030, 2016, and 1957 cm^{-1} together with less well-defined bands, of variable intensity, at 2045 and 1948 cm^{-1}. The initial reaction of $Ru(CO)_4(AsPh_3)$ with $AsPh_3$ to form the isomeric mixture of $Ru(CO)_3(AsPh_3)_2$ is followed by a much slower reaction accompanied by the growth of two bands at 1963 and 1947 cm^{-1}. This might be due to formation of $Ru(CO)_2(AsPh_3)_3$, but no attempts to confirm this were made. Further reaction of the $Ru(CO)_3(SbPh_3)_2$ isomers with $SbPh_3$ were very slow and product spectra could not be clearly analyzed. Reaction of $Ru(CO)_4(SbPh_3)$ with $P(OEt)_3$ or PPh_3 shows clear evidence for displacement of the $SbPh_3$ ligand.

Reaction of $Ru(CO)_4$(etpb) with etpb showed the growth only of two bands of low intensity, and even these almost completely disappeared before loss of $Ru(CO)_4$(etpb) was complete. Reaction of $Ru(CO)_4(P\text{-}t\text{-}Bu_3)$ with $P\text{-}t\text{-}Bu_3$ did not show the growth of any bands although the intensities of those due to the complex decreased steadily to zero. When $P(OEt)_3$ was used as the entering ligand for reactions of $Ru(CO)_4$(etpb) and $Ru(CO)_4(P\text{-}t\text{-}Bu_3)$ strong bands grew at 1944 and 1933 cm^{-1} and 1902 and 1887 cm^{-1}, respectively. The latter bands were also seen to grow in the reaction of $Ru(CO)_4[P(OEt)_3]$ with $P\text{-}t\text{-}Bu_3$ as the entering ligand, so that it is clear that the complexes $Ru(CO)_3[P(OEt)_3]L$ (L = etpb or $P\text{-}t\text{-}Bu_3$) are both stable while $Ru(CO)_3L_2$ (L = etpb or $P\text{-}t\text{-}Bu_3$) are not.

Rate constants were obtained from plots of ln $(A_t - A_\infty)$ against time obtained from the decreasing intensities of the stronger bands due to $Ru(CO)_4L$. The values of the rate constants obtained from different bands are in excellent agreement with each other and with those obtained by monitoring the growth in intensity of the product bands and plotting log $(A_\infty - A_t)$ against time. The observed rate constants do not depend on the nature or concentration of the entering ligands and the average rate constants, k_1, are collected in Table III.

The values of ΔH_1^* and ΔS_1^* were obtained by a nonweighted linear least-squares analysis of the dependence of the individual values of ln (k_{obsd}/T) on $1/T$ and are listed in Table IV. The assumption was made that there was a constant percentage uncertainty in each individual value of k_{obsd}. The uncertainties quoted are standard deviations corrected for the number of degrees of freedom so that 95% confidence limits can be obtained by multiplying by the appropriate Student's *t* factor (1.96) for an infinite number of degrees of freedom.[14] The uncertainties in ΔH_1^* and ΔS_1^* and the probable errors, $\sigma(k_{obsd})$, of individual measurements of k_{obsd} over the temperature ranges used are almost all very small and show the excellent precision of the data.

Discussion

Vibrational Frequency Correlations. The complexes $Ru(CO)_4L$ exist generally as the axially substituted isomer and the frequencies of the three bands show excellent correlations with the A_1 frequencies of the $Ni(CO)_3L$ complexes taken by Tolman[15] as a measure of the electronic effect of L. Thus, eq 4–6 show the linear

$$\chi_1 = (-1.42 \pm 0.63) + (0.671 \pm 0.041)\ \chi(Ni(CO)_3L)\ \text{cm}^{-1} \tag{4}$$

$$R = 0.969 \qquad \sigma(\chi_1) = \pm 1.6\ \text{cm}^{-1}$$

$$\chi_2 = (2.19 \pm 0.59) + (0.993 \pm 0.039)\ \chi(Ni(CO)_3L)\ \text{cm}^{-1} \tag{5}$$

$$R = 0.987 \qquad \sigma(\chi_2) = \pm 1.5\ \text{cm}^{-1}$$

$$\chi_3 = (2.01 \pm 0.92) + (1.11 \pm 0.06)\ \chi(Ni(CO)_3L)\ \text{cm}^{-1} \tag{6}$$

$$R = 0.976 \qquad \sigma(\chi_3) = \pm 2.3\ \text{cm}^{-1}$$

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Table III. Kinetic Data[a] for the Reaction of $Ru(CO)_4L$ with L′ in Heptane

L	T, °C	no. of diff [L′](no. of diff ν(CO))	θ_L, deg	10^4k_1, s^{-1}
CO	60.0		95	111 ± 5[b]
etpb	60.0	3 (3)	101	1.05 ± 0.01
	70.0	3 (3)		4.23 ± 0.02
		2 (3)		4.20 ± 0.07[c]
	80.1	3 (3)		15.6 ± 0.06
$P(OEt)_3$	60.0	1 (4)	109	1.25 ± 0.04[d]
	60.0	1 (4)		1.16 ± 0.004
	60.1	2 (4)		1.19 ± 0.01
	70.0	3 (4)		4.79 ± 0.02
	80.0	4 (4)		17.9 ± 0.07
$P(OPh)_3$	60.0	3 (6)	128	2.75 ± 0.04
P-*n*-Bu_3	60.0	3 (2)	132	2.49 ± 0.04
		1 (3)		1.20 ± 0.01[e]
				1.3[e,f]
		3 (2)		2.57 ± 0.04[g]
PEt_3	60.0	3 (3)	132	1.93 ± 0.02
$P(C_2H_4CN)_3$	60.0	3 (4)	132	4.24 ± 0.07[g]
$PMePh_2$	60.0		136	2.92[e,h]
$PPhEt_2$	60.0	3 (4)	136	4.73 ± 0.03
PPh_2Et	60.0	3 (4)	140	6.94 ± 0.04
PPh_3	60.0		145	7.64[h]
P(*p*-MePh)$_3$	60.0	2 (3)	145	7.23 ± 0.14
		1 (3)		6.75 ± 0.09[c]
P(*p*-MeOPh)$_3$	60.0	2 (3)	145	5.66 ± 0.08
		1 (3)		5.84 ± 0.08[c]
P(*p*-ClPh)$_3$	60.0	3 (3)	145	7.22 ± 0.08
$P(NMe_2)_3$	60.0	3 (4)	157	4.89 ± 0.05
PBz_3	60.0	2 (3)	165	4.66 ± 0.07[c]
PCy_3	40.0	2 (2)	170	2.76 ± 0.14
	50.0	2 (2)		9.64 ± 0.45
	55.0	4 (2)		21.3 ± 0.4
	60.0	3 (2)		41.3 ± 0.6
P-*t*-Bu_3	10.0	3 (2)		2.02 ± 0.04[c]
	20.0	3 (2)		9.53 ± 0.11[c]
	30.0	3 (2)	182	39.8 ± 0.4[c]
$AsPh_3$	60.0	3 (5)	142	5.68 ± 0.06
$SbPh_3$	60.0	2 (5)	138	0.28 ± 0.02

[a] Rate constants are generally averages of those obtained by monitoring three to four different IR bands and with three different values of [L′] covering ranges of ca. $(1-10) \times 10^{-2}$ *M*. The uncertainties are uncertainties of the averages. [complex] = ca. 8×10^{-4} *M*; L′ = L unless otherwise indicated. [b] Calculated value from: Huq, R.; Poë, A. J.; Chawla, S. *Inorg. Chim. Acta* **1980**, *38*, 121–125. [c] L′ = $P(OEt)_3$. [d] L′ = P-*t*-Bu_3. [e] In decalin. Note that there is a significant effect on k_{obsd} due to this solvent compared with the value determined in heptane. [f] From ref 8. [g] In 1,2-dichloroethane. The rate constants in this solvent are not significantly different from those in heptane. [h] From ref 9.

Table IV. Activation Parameters for the CO Dissociative Reactions of $Ru(CO)_4L$

L	$\Delta H_1^\ddagger$, kcal mol^{-1}	$\Delta S_1^\ddagger$, cal K^{-1} mol^{-1}	$\sigma(k_{obsd})$, %
CO[a]	27.6 ± 0.2	15.2 ± 1.3	
etpb[b]	30.7 ± 0.1	15.1 ± 0.3	1.9
$P(OEt)_3$[b]	31.0 ± 0.1	16.3 ± 0.4	3.1
P-*n*-Bu_3[c]	31.6 ± 0.2	18.3 ± 0.5	3.2
$PMePh_2$[d]	29.7 ± 0.2	14.1 ± 0.6	
PPh_3[d]	30.1 ± 0.3	17.3 ± 0.8	
PCy_3[b]	27.7 ± 0.6	13.6 ± 1.7	9.2
P-*t*-Bu_3[b]	25.0 ± 0.2	12.6 ± 0.6	3.8

[a] From: Huq, R.; Poë, A. J.; Chawla, S. *Inorg. Chim. Acta* **1980**, *38*, 121–125. In cyclohexane. [b] This work, in heptane. [c] From ref 8, in heptane. [d] From ref 9, in decalin.

dependence of $\chi_i = \nu_i\,(Ru(CO)_4L) - \nu_i(Ru(CO)_4P\text{-}t\text{-}Bu_3)$ on $\chi(Ni(CO)_3L) = \nu(Ni(CO)_3L) - 2056.1\ cm^{-1}$ ($2056.1\ cm^{-1}$ is the frequency of the complex $Ni(CO)_3L$ for L = P-*t*-Bu_3). When the ν_3 band was correlated, averages of the frequencies of the two bands found when the band is split were used.

The response of the frequencies ν_2 and ν_3 for *ax*-$Ru(CO)_4L$ to the nature of L is very similar to that of the A_1 frequency of $Ni(CO)_3L$, but all the frequencies of the $Ru(CO)_4L$ complex are shifted down by ca. 80 and 116 cm^{-1} for ν_2 and ν_3, respectively, compared to those for $Ni(CO)_3L$. This presumably indicates a greater capacity for the Ru atom to donate π electrons to its CO ligands. The frequency ν_1 for *ax*-$Ru(CO)_4L$ is less sensitive to the nature of L than is the A_1 frequency for $Ni(CO)_3L$.

The frequencies of the E bands for $Ru(CO)_3L_2$ (or of the average of the two bands when the E band is split) also correlate well with the $Ni(CO)_3L$ frequencies as shown in eq 7 where, in

$$\chi = (4.34 \pm 2.53) + (1.88 \pm 0.16)\ \chi(Ni(CO)_3L)\ cm^{-1} \qquad (7)$$

$$R = 0.977 \qquad \sigma(\chi) = \pm 4.9\ cm^{-1}$$

this case, $\chi = \nu(Ru(CO)_3L_2) - 1874.5\ cm^{-1}$. The frequency 1874.5 cm^{-1} is that of the complex $Ru(CO)_3L_2$ for L = PCy_3. This is used as the reference frequency since no value is available for $Ru(CO)_3(P\text{-}t\text{-}Bu_3)_2$. The greater sensitivity to L of the E mode for the disubstituted complexes, compared with that for the monosubstituted compound, must simply be due to the greater number of substituents.

Relative Stabilities of Axial and Equatorial Isomers. Very approximate estimates of the equilibrium constants, *K*, for the labile equilibrium in (8) can be made as follows. The molar

$$ax\text{-}Ru(CO)_4L \overset{K}{\rightleftharpoons} eq\text{-}Ru(CO)_4L \qquad (8)$$

extinction coefficients of the axial isomers can be obtained for those complexes that exist only in this form. The values for the ν_1(ax) ($A_1(1)$ mode) frequencies do not vary greatly for the 15 complexes listed in Table I, and an average value of $(3.12 \pm 0.52) \times 10^3\ M^{-1}\ cm^{-1}$ can be obtained, where the uncertainty represents the standard deviation of an individual value. If we assume that this average is valid also for those cases where the equatorial isomer exists as well, the equilibrium constant can be obtained from eq 9, where [*ax*-$Ru(CO)_4L$] is given by the absorbance of the ν_1 band

$$K = \{[Ru(CO)_4L]_{tot} - [ax\text{-}Ru(CO)_4L]\}/[ax\text{-}Ru(CO)_4L] \qquad (9)$$

for *ax*-$Ru(CO)_4L$ divided by the average extinction coefficient. The value obtained for L = $SbPh_3$ is 5.0 ± 1.0, which implies that ca. 80% of the complex exists in the equatorial form. Knowing this, we can estimate an approximate molar extinction coefficient of $(2.02 \pm 0.34) \times 10^3\ M^{-1}\ cm^{-1}$ for the ν_1 ($A_1(1)$ mode) band of *eq*-$Ru(CO)_4(SbPh_3)$. If we make a second, rather drastic, assumption that the ν_1 bands of the other equatorial isomers have the same extinction coefficient, then we can also obtain approximate estimates of *K* for those complexes, and these are 0.43 ± 0.07, 0.07 ± 0.01, and 0.15 ± 0.03 for L = $P(OPh)_3$, etpb, and $AsPh_3$, respectively. The factors governing the existence of axial and equatorial isomers of $M(CO)_4L$ (M = Fe, Ru, Os) have been thoroughly discussed.[13] The trend is for axial isomers to become relatively less stable as L varies along the series PPh_3 > $AsPh_3$ > $SbPh_3$. The same seems to be true for the $Ru(CO)_3L_2$ complexes to judge by the decreasing relative importance of the bands due to the diaxial isomers relative to those assignable to one or more less symmetrical isomers.

Stoichiometric Mechanism of the Reaction. The effect of CO on the rates of reactions of $Ru(CO)_4L$ (L = P-*n*-Bu_3[8] and PPh_3[9]) have shown that these complexes react by a straightforward reversible CO dissociative path, and this is supported by the quite high values of $\Delta H_1^\ddagger$, the substantially positive values of $\Delta S_1^\ddagger$, and the fact that the rates are independent of the nature and concentration of the entering ligand.

Trends in the Kinetic Parameters. The electronic nature of L has only a very small effect on the rates of reaction. Thus the rate constants for L = $P(OPh)_3$ and P-*n*-Bu_3 are very similar. These ligands have very similar cone angles of 128 and 132°,[15] respectively, but very different values of pK_a[16] (which measures the σ-basicity of L) and ν(CO) in $Ni(CO)_3L$[15] or $Ru(CO)_4L$

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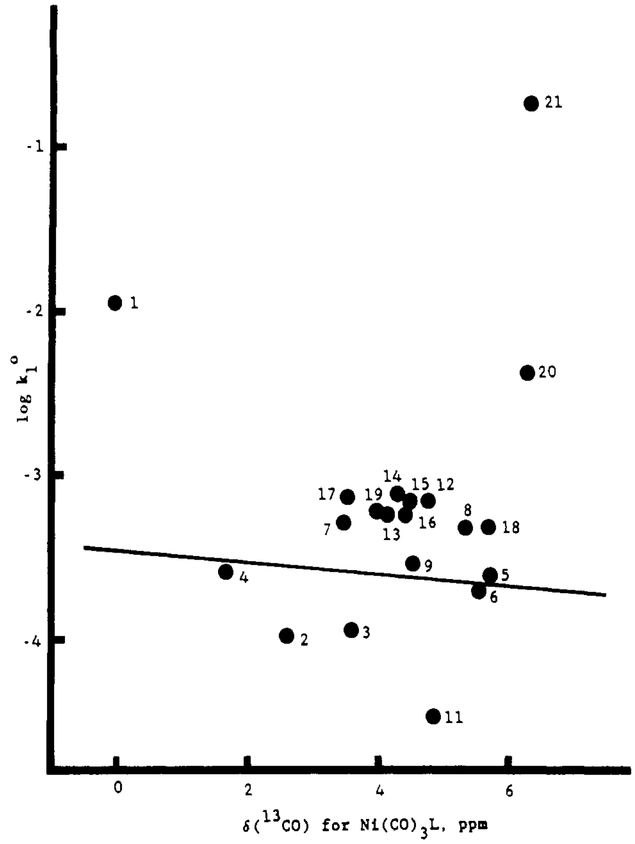

Figure 1. Dependence of log k_1 (60.0 °C) for dissociation of CO from Ru(CO)$_4$L (in heptane or 1,2-dichloroethane) on the value of δ. The numbering corresponds to the various substituents as follows, with the numbers in parentheses, here and in the caption to Figure 3, being the cone angles (deg) and δ values (ppm), respectively: 1, CO (95, 0); 2, etpb (101, 2.60); 3, P(OEt)$_3$ (109, 3.61); 4, P(OPh)$_3$ (128, 1.69); 5, P-*n*-Bu$_3$ (132, 5.69); 6, PEt$_3$ (132, 5.54); 7, P(CH$_2$CH$_2$CN)$_3$ (132, 3.47); 8, PPhEt$_2$ (136, 5.36); 9, PMePh$_2$ (136, 4.53); 11, SbPh$_3$ (138, 4.86); 12, PPh$_2$Et (140, 4.78); 13, AsPh$_3$ (142, 4.16); 14, PPh$_3$ (145, 4.30); 15, P(*p*-MeC$_6$H$_4$)$_3$ (145, 4.50); 16, P(*p*-MeOC$_6$H$_4$)$_3$ (145, 4.43); 17, P(*p*-ClC$_6$H$_4$)$_3$ (145, 3.54); 18, P(NMe$_2$)$_3$ (157, 5.68); 19, PBz$_3$ (165, 3.98); 20, PCy$_3$ (170, 6.32); 21, P-*t*-Bu$_3$ (182, 6.37). Cone angles for a large number of ligands, including SbPh$_3$ and AsPh$_3$, have been reported by Imyanitov (Imyanitov, N. S. *Sov. J. Coord. Chem.* (Engl. Transl.) **1985**, *11*, 663–670). All of the cone angles for P-donor ligands are almost exactly 5° larger than those of Tolman.[15] We have subtracted this from the values for SbPh$_3$ and AsPh$_3$ quoted by Imyanitov to give values compatible with those for P-donor ligands given by Tolman, who did not report values for As- and Sb-donor ligands.

(which measure the combined effects of σ-basicity and π-acidity of L). Since the effects of L on the stretching frequencies for Ru(CO)$_4$L and Ni(CO)$_3$L are so similar, the balance between the σ-donor and π-acid effects of L must be essentially the same in these two complexes. Further, it is known that the values of δ(^{13}CO), the shift in the ^{13}C NMR resonance on substitution of L into Ni(CO)$_4$, correlate well with the values of ν(CO) for Ni(CO)$_3$L.[17] It follows that the values of δ also correlate well with the values of ν_{CO} in Ru(CO)$_4$L, and we choose to use the δ parameter for Ni(CO)$_3$L as a measure of the combined σ-donor and π-acid effect of L in the Ru(CO)$_4$L complexes. This choice is made because the δ values are more precise than the values of ν(CO) in the sense that the ratio of the spread of the values of δ (over the range of ligands considered) compared with the precision of the values of δ is ca. 2 times greater than the corresponding ratio for ν(CO).[17] In addition, values of δ are also known for L = CO and for As and Sb donor ligands,[17] and this enables such ligands to be included in any examination of electronic effects of different ligands.[18]

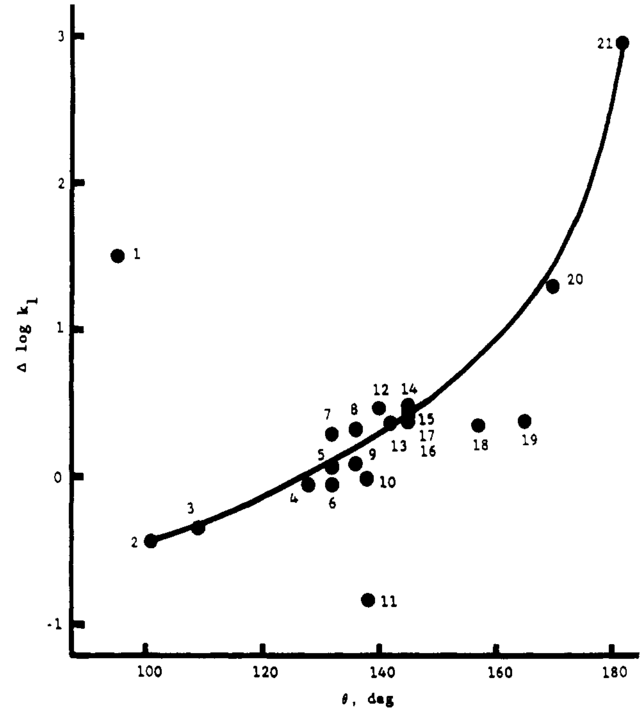

Figure 2. Steric profile for CO dissociative reactions of *ax*-Ru(CO)$_4$L. Point 10 is for L = SbPh$_3$, plotted by assuming that the equatorial isomer is completely unreactive (see text). Point 11 is based on the experimental value of log k_1 for the mixture of axial and equatorial isomers of Ru(CO)$_4$(SbPh$_3$).

A plot of log k_1 vs δ is shown in Figure 1. The straight line drawn joins data for L = P(OPh)$_3$ and P-*n*-Bu$_3$, which have been modified slightly to account for the small differences in cone angle according to the steric effects discussed below. These ligands differ profoundly in their electronic effects on a metal, P(OPh)$_3$ being a weak σ-base and quite a strong π-acid while P-*n*-Bu$_3$ is essentially just a strong σ-base.[19] The very small difference in their effects on the rates of CO dissociation shows that the net electronic effects on ground and transition states must be very similar. Thus if ground-state effects were more important, Ru(CO)$_4$[P(OPh)$_3$] would lose CO more rapidly than Ru(CO)$_4$(P-*n*-Bu$_3$) because of the much smaller amount of Ru → CO back-bonding in the former complex and the consequently weaker Ru–CO bond. Since this is not the case, we must conclude that transition-state effects almost exactly compensate for these ground-state effects. Although P(OPh)$_3$ is better at weakening the Ru–CO bonds it is less good at compensating the Ru for the decrease of electron density when the CO leaves.

Data for other substituents lie well off the line defined by L = P(OPh)$_3$ and P-*n*-Bu$_3$, smaller ligands having slower rates and larger ones having faster rates. We have therefore plotted (Figure 2) the deviations from the straight line in Figure 1 against the cone angle, θ, of the substituents and obtain, with some deviations, a very regular smooth trend showing what must be quite pure steric effects. These steric effects appear to diminish as θ decreases so that they might disappear if suitable ligands with cone angles of ≤ 90° were available. On the other hand, when θ increases above ca. 170°, the steric effect increases the rates almost catastrophically so that complexes having substituents with cone angles above 180° are unlikely to be at all stable.

The average of the activation enthalpies for ligands with cone angles from 101 to 145° is 30.6 ± 0.8 kcal mol^{-1} so that the steric effects for these ligands are almost entirely accounted for by changes in ΔS_1^*. The activation enthalpies for L = PCy$_3$ and

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(17) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951–1958.

(18) (a) Hanckel, J. M.; Lee, K. W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* **1986**, *25*, 1852–1856. (b) Rushman, P.; Brown, T. L. *Inorg. Chem.* **1987**, *109*, 3632–3639.

(19) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981–1991.

P-*t*-Bu$_3$ show a progressive decrease with increasing θ so that the steric effects for these ligands manifest themselves in terms of lower values of ΔH_1^* as well.

The mode of operation of the steric effect must originate in part from a decrease in ligand–ligand repulsions consequent upon the loss of the CO ligands, and this decrease is greater the larger the substituent. Examination of the structures of the analogous complexes Fe(CO)$_4$L (L = PPh$_3$ or P-*t*-Bu$_3$)[20] show that the average bond angle P–Fe–C(eq) increases from 88.8° (L = PPh$_3$; θ = 145°) to 93.3° (L = P-*t*-Bu$_3$; θ = 182°), thus showing a pronouced increase in the L–CO repulsions with increasing ligand size. However, the Fe–P bond lengths increase from 2.244 (1) (L = PPh$_3$) to 2.364 (1) Å (L = P-*t*-Bu$_3$), showing that the larger ligand, as well as causing greater L–CO repulsion, is also incapable of approaching as close to the metal as the smaller one. This is unlikely to be an intrinsic feature of the different Fe–P bond strengths because the larger bond length actually corresponds to the more basic ligand, which should, therefore, form the stronger and shorter bond. What it does suggest is that the steric effect due to the larger ligand may also originate in the shortening and strengthening of the Ru–P bond that can accompany the decrease in coordination number when the CO is lost.[21] This effect only occasionally manifests itself in a decrease in ΔH_1^* as the size of the substituent increases, and the strengthening of the Ru–P bonds on proceeding to the transition states must generally be offset by an increasing degree of Ru–CO bond breaking in the transition states. The latter evidently leads to higher values of ΔS_1^*.

The fact that the data for L = CO lie well above the smooth curve shown in Figure 2 must indicate that the CO ligand is quite different from the P-donor ligands in its effect on the kinetics. The rate of loss of CO from Ru(CO)$_5$ is almost the same as that for reaction of Ru(CO)$_4$(PCy$_3$) (Figure 1), and the effect is clearly electronic in nature. This may be due to the very different balance between σ and π effects in CO compared with that in the P-donor ligands.

The data for Ru(CO)$_4$(AsPh$_3$) fit well on the curve in Figure 2 and show that P- and As-donor ligands behave in similar ways. However, the data for Ru(CO)$_4$(SbPh$_3$) lie well below the curve, but this complex is known to exist mainly as the equatorially substituted isomer. If this isomer were completely unreactive, the data for *ax*-Ru(CO)$_4$(SbPh$_3$) would lie quite close to the curve (see point 10 in Figure 2). It is therefore possible that the Sb-donor axial ligand behaves in the same way as the P- and As-donor axial substituents, but this is true only if the equatorially substituted isomer is quite inert for some reason.

Intimate Mechanism of the Reactions. It seems highly probable that it is an equatorial CO ligand which dissociates from these axially substituted complexes and that the coordinatively unsaturated intermediate is planar d^8 Ru(CO)$_3$L. The case for this being so has been well argued.[10] If an axial CO were to leave, the steric acceleration would have to be attributed to formation of tetrahedral Ru(CO)$_3$L, and this seems unlikely.

Electronic and Steric Effects in Dissociation Reactions of Other Mononuclear Metal Carbonyls. The success of the above analysis of data for Ru(CO)$_4$L suggests that similar analysis of data for reactions of other mononuclear complexes might be profitable.

Chalk and Pomeroy have reported kinetic data for CO dissociative reactions of *mer*-Ru(CO)$_3$(L)(SiCl$_3$)$_2$ containing a wide variety of P-donor substituents.[7] The importance of steric effects was demonstrated by a reasonably linear correlation between ΔS_1^* and the cone angles of the substituents. The electronic effect can be shown to be very small by plots of log [k_1(40°)] vs δ for five substituents P(p-XC$_6$H$_4$)$_3$ with identical cone angles and quite a wide variation of δ. A good straight line, with a slope β_L = 0.08 ± 0.04 ppm^{-1}, was obtained. A plot against θ of the values of log $k_1°$ = log k_1 − $\beta_L\delta$ gave a reasonably straight line with values of log $k_1°$ covering a range of ca. 3 (Figure 3). The data for L = P(O-*o*-MeC$_6$H$_4$)$_3$ deviated most from the line and were omitted from the plot and from a least-squares analysis of the data in terms of eq 10. P(O-*o*-MeC$_6$H$_4$)$_3$ was one of four substituents that led

$$\log k_1 = \alpha + \beta_L\delta + \gamma_L\theta \qquad (10)$$

to significantly lower values of ΔH_1^*, and less positive values of ΔS_1^*, than the others, the remaining deviant ligands being P(OPh)$_3$, PBz$_3$, and PPh$_2$(*o*-MeC$_6$H$_4$). Although the values of log $k_1°$ for complexes with these three substituents do not lie much below the steric profile, their deviations would increase with increasing temperatures, and we have also omitted these data from the analysis. The parameters obtained are given in Table V.

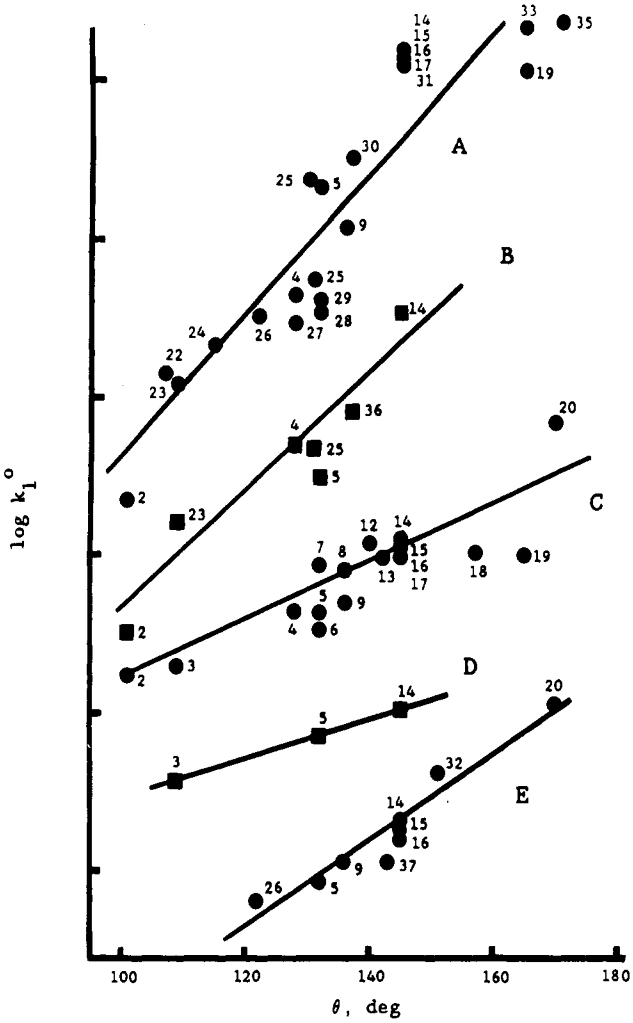

Figure 3. Steric profiles: (A) *mer*-Ru(CO)$_3$L(SiCl$_3$)$_2$; (B) *cis*-Mn(CO)$_4$LBr; (C) Ru(CO)$_4$L; (D) Ni(CO)$_3$L; (E) (η^5-C$_5$H$_5$)Mo(CO)$_2$L(COMe). The numbering is as in Figures 1 and 2 with additional ligands numbered as follows (cone angles (deg) and δ values (ppm) in parentheses): 22, P(OMe)$_3$ (107, 3.18); 23, P(O-*n*-Bu)$_3$ (109, 3.95); 24, P(OMe)$_2$Ph (120, 3.48); 25, PCl$_2$Ph (131, 0.69); 26, PMe$_2$Ph (122, 4.76); 27, P(O-*p*-ClPh)$_3$ (128, 1.32); 28, P(CH$_2$CH=CH$_2$)$_3$ (132, 4.92); 29, P(OMe)Ph$_2$ (132, 3.96); 30, PClPh$_2$ (137, 2.49); 31, P(p-FC$_6$H$_4$)$_3$ (145, 3.77); 32, PPh$_2$(*i*-Pr) (151, 4.78); 33, P(*m*-CH$_3$C$_6$H$_4$)$_3$ (165, 4.48); 34, P(*m*-ClC$_6$H$_4$)$_3$ (165, 3.08); 35, PPh$_2$(*o*-MeOC$_6$H$_4$) (171, 5.37); 36, PPh$_2$Cl (137, 2.49); 37, P-*i*-Bu$_3$ (143, 5.40). The position on the vertical axis is arbitrary. The scale is 1 log unit/division. The linear profile for Ru(CO)$_4$L is drawn as the least-squares line through all the data except those for L = P-*t*-Bu$_3$ and SbPh$_3$. The values of the gradients, γ_L, are given in Table V.

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(20) (a) Pickardt, J.; Rosch, L.; Schumann, H. *J. Organomet. Chem.* **1976**, *107*, 241–248. (b) Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159–165.

(21) It is interesting that the Ru–P bond lengths in the clusters Ru$_3$(CO)$_{11}$L (L = etpb,[22] P(OMe)$_3$,[23] P(OCH$_2$CF$_3$)$_3$,[22] PPh(OMe)$_2$,[22] PEt$_3$,[23] PPh$_3$,[22] PCy$_3$[22]) increase[22] linearly[23] with increasing cone angle of L as do the Mo–P bond lengths in *cis*-Mo(CO)$_4$L$_2$.[24]

(22) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 157–180 and references therein.

(23) Brodie, N. M. J.; Chen, J.; Poë, A. J.; Sawyer, J. F., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, in press.

(24) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661–2666.

Table V. Values of the Parameters α_L, β_L, and γ_L (eq 10) for CO Dissociative Reactions

complex	temp, °C	α_L	β_L, ppm^{-1}	γ_L, deg^{-1}	$\sigma(\log k_1)$
$Ru(CO)_3L(SiCl_3)_2$	40.0	-10.7 ± 0.7	0.04 ± 0.07	0.049 ± 0.005	0.37
$Mn(CO)_4LBr$	40.0	-9.4 ± 0.8	0.13 ± 0.06	0.038 ± 0.007	0.25
$Ru(CO)_4L$	60.0	-5.8 ± 0.4^a	-0.01 ± 0.05^a	0.018 ± 0.004^a	0.21^a
		-6.0 ± 0.3^b	-0.11 ± 0.06^b	0.023 ± 0.004^b	0.10^b
$Ni(CO)_3L$	25.0	-5.0^c	0.020^c	0.013^c	
$(\eta^5\text{-}C_5H_5)Mo(CO)_2L(COMe)$	60.0	-8.5 ± 0.5	-0.10 ± 0.08	0.028 ± 0.004	0.13

[a] Obtained from all the data except for L = P-*t*-Bu_3 or $SbPh_3$. These values were used to draw the line in Figure 3. [b] These parameters were obtained by using only data for which the values of $\Delta H_1^{\ddagger}$ are constant so that the parameters will be essentially independent of temperature. [c] No uncertainties are available since these parameters were obtained from data for only three different substituents. However, the three ligands cover a wide range of values of δ and θ so that the parameters will be quite precise.

Giering et al. have analyzed these data in a more detailed and subtle way.[16] They plotted the steric profile and see it as a sharp increase to one plateau followed by another sharp increase to another plateau. (Yet another sharp rise is also implied by the qualitatively very rapid reaction of $Ru(CO)_3(P(o\text{-}MeC_6H_4)_3)(SiCl_3)_2$.)[7] The first two plateaus were interpreted in a very ingenious way, but we worry about the precision with which the data are expected to fit with the rather complex model. Experience with analysis of other kinetic data in terms of electronic and steric factors[3e] and the intrinsic uncertainty surrounding both the values and the specific effects of different ligand cone angles[25] suggest that fairly pronounced and not easily explicable deviations are often found,[3e] and we are inclined to believe that a less detailed analysis is all that is justified at this stage.

We have also analyzed data for reactions of *cis*-$Mn(CO)_4(L)Br$[6] and $Ni(CO)_3L$[5] according to our procedure, and their steric profiles are shown in Figure 3. The values of α_L, β_L, and γ_L are given in Table V.

It is clear from Figure 3 that the gradients of the steric profiles for the two octahedral complexes are quite similar, and this is confirmed by the γ_L values shown in Table V. The value of γ_L for *mer*-$Ru(CO)_3(L)(SiCl_3)_2$ is, in fact, slightly greater than that for the less highly substituted *cis*-$Mn(CO)_4(L)Br$ as might be expected. However, the closeness of the values might indicate that an important steric factor in these two complexes is not so much the absolute values of any ligand–ligand repulsion energies but the fact that in all cases the space gained during the formation of the coordinatively unsaturated intermediate is the same, namely the space vacated by the departing CO ligand.

The steric profile for $Ni(CO)_3L$ is clearly also linear, but the gradient is much less than that for the octahedral complexes as might be expected from its lower coordination number. This will result in lower ligand–ligand repulsions, and also the space vacated by the departing CO ligand would effectively be larger.

Although the steric profile for $Ru(CO)_4L$ was drawn as a curve (Figure 2), in the absence of the data for L = P-*t*-Bu_3, it would have been reasonable to draw it as a straight line as is indicated in Figure 3. In this the data resemble those for *mer*-$Ru(CO)_3L(SiCl_3)_2$ where the data for L = $P(o\text{-}MeC_6H_4)_3$ (θ = 194°) lie qualitatively[7] well above the straight line. An analysis of the data according to eq 10 leads to the values for α_L, β_L, and γ_L shown in Table V from which it can be seen that the value for γ_L is intermediate between those for the octahedral and tetrahedral complexes. The parameters for $Ru(CO)_3L(SiCl_3)_2$ and $Ru(CO)_4L$ are essentially independent of temperature, and we believe this is likely to be true for the other complexes as well. These data suggest, therefore, that the values of γ_L increase monotonically with coordination number and that, for the octahedral complexes, the values of γ_L appear to increase slightly with the number of ligands other than CO in the complex. Whether these trends are general or not will only become apparent when more data for related systems become available.

The electronic effects in these complexes are generally small and in accord with the roughly equal effects on the ground and transition states discussed above for the $Ru(CO)_4L$ complexes, and the steric effects are also found not to be dependent on the particular parameter chosen to detect the electronic effect.

Electronic and Steric Effects in a Methyl Migration Reaction. Some quite extensive data have been reported for the methyl migration reaction shown in eq 11.[26] These have been analyzed

$$(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)(COMe) \rightarrow (\eta^5\text{-}C_5H_5)Mo(CO)_2(L)(Me) + CO \quad (11)$$

by Giering et al,[19] making use of the pK_a values for the substituents. A somewhat curved steric profile was obtained. We have repeated this analysis but have used the δ values for the substituents, for reasons given above, and find that the data are in good accord with eq 10 so that the steric profile is essentially linear. The profile is shown in Figure 3, and the values of α_L, β_L, and γ_L are given in Table V. The important feature of these results is not so much the linearity of the steric profile but the fact that the value of γ_L is positive and quite high. If the reactions were concerted, one might have obtained a negative value of γ_L (Mo···Me bond making more important than Mo···CO bond breaking) because of an effective increase of coordination number. If the extent of bond making and bond breaking were similar, so that the effective space occupied by the entering Me group balanced that made available by the leaving CO group, then a negligible value of γ_L would be obtained. As it is, the quite substantial positive value of γ_L suggests that bond breaking is more important than bond making in the transition states. Whether bond breaking is complete before bond making begins is difficult to decide. The effective coordination number of the initial complex must be greater than 5 because of the nature of $\eta^5\text{-}C_5H_5$-ligand, but it is almost certainly not as high as 7 (when $C_5H_5^-$ is assumed to be effectively tridentate). The fact that the value for γ_L is between those for 5- and 6-coordinate complexes could allow for complete bond breaking (and no bond making) if the effective coordination number were ca. 5.5. This was the intimate mechanism that was originally proposed.[26]

Conclusions

The new data reported for CO dissociative reactions of $Ru(CO)_4L$ confirm that the kinetic data for such reactions can be resolved into electronic and steric effects that can be expressed graphically by electronic and steric profiles. When data in the literature for other CO dissociative reactions are analyzed in the same way, linear steric profiles are obtained, and the data can be successfully expressed in terms of the parameters α_L, β_L, and γ_L. The gradients of the steric profiles show a dependence of steric effects on coordination number and, to a lesser extent, on the number of ligands other than CO. The same approach can be used for some methyl migration reactions that involve stoichiometric CO loss; the magnitude of the steric effect provides some evidence that the intimate mechanism cannot involve major amounts of bond making compared to bond breaking, and simple CO loss could well be rate determining. The method of data analysis is therefore successful in quantitatively resolving the relative contributions of electronic and steric effects in a number of CO dissociative reactions, and the quantitative estimates of the steric effects can be related meaningfully to the nature of the complexes involved. Extension of the method to related but different reactions involving CO loss can lead to useful conclusions

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(25) Footnote 26 in ref 16.

(26) Barnett, K. W.; Pollman, T. G. *J. Organomet. Chem.* **1974**, *69*, 413–421.

about the intimate mechanism involved, and we suggest that the method should be of wide and profitable application. Indeed, a very recent study[27] of isomerizations of some $Ru(CO)_2Cl_2L_2$ complexes has shown that they proceed via a CO dissociative mechanism and that rates increase with increasing size of L but decrease with increasing basicity. Only four different ligands were involved, and the data are unfortunately not suitable for quantitative analysis according to the method described here.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council, Canada, for support and Professor R. K. Pomeroy for helpful comments.

Registry No. etpb, 824-11-3; *ax*-$Ru(CO)_4$etpb, 121916-49-2; $Ru(CO)_4P(OEt)_3$, 75627-87-1; *ax*-$Ru(CO)_4P(OPh)_3$, 121808-89-7; $Ru(CO)_4P$-*n*-Bu_3, 57967-87-0; $Ru(CO)_4PEt_3$, 121808-90-0; $Ru(CO)_4P(CH_2CH_2CN)_3$, 121808-91-1; $Ru(CO)_4PPhEt_2$, 121808-92-2; $Ru(CO)_4PPh_2Et$, 121808-93-3; $Ru(CO)_4P(p\text{-}MeOPh)_3$, 121808-94-4; $Ru(CO)_4P(p\text{-}MePh)_3$, 121808-95-5; $Ru(CO)_4P(p\text{-}ClPh)_3$, 121808-96-6; $Ru(CO)_4P(NMe_2)_3$, 121808-97-7; $Ru(CO)_4PBz_3$, 121808-98-8; $Ru(CO)_4PCy_3$, 121808-99-9; $Ru(CO)_4P$-*t*-Bu_3, 69661-89-8; *ax*-$Ru(CO)_4AsPh_3$, 85848-64-2; *ax*-$Ru(CO)_4SbPh_3$, 85848-65-3; $P(OEt)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; P-*n*-Bu_3, 998-40-3; PEt_3, 554-70-1; $P(CH_2CH_2CN)_3$, 4023-53-4; $PPhEt_2$, 1605-53-4; PPh_2Et, 607-01-2; $P(p\text{-}MeOPh)_3$, 855-38-9; $P(p\text{-}MePh)_3$, 1038-95-5; $P(p\text{-}ClPh)_3$, 1159-54-2; $P(NMe_3)_3$, 1608-26-0; PBz_3, 7650-89-7; PCy_3, 2622-14-2; P-*t*-Bu_3, 13716-12-6; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1; *eq*-$Ru(CO)_4$etpb, 121916-47-0; *eq*-$Ru(CO)_4P(OPh)_3$, 121916-48-1; *eq*-$Ru(CO)_4AsPh_3$, 85781-13-1; *eq*-$Ru(CO)_4SbPh_3$, 71356-99-5.

Supplementary Material Available: A table of all the rate constants for different values of [L] or [L′] obtained from different values of ν(CO) (5 pages). Ordering information is given on any current masthead page.

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(27) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D.; Jacobson, R. A. *Inorg. Chem.* **1988**, *27*, 4294–4307.

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Comparative Kinetic Study of Oxygen Atom Transfer Reactions of Oxohydroxodiperoxomolybdenum(VI) and Oxo(oxalato)diperoxomolybdenum(VI) in Aqueous Solution

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The conditional equilibrium constants at 25 °C and pH 4.0 for the reactions $MoO_3(C_2O_4)^{2-} + 2H_2O_2 = MoO(O_2)_2(C_2O_4)^{2-} + 2H_2O$ and $Mo(VI) + 2H_2O_2 =$ oxohydroxodiperoxomolybdenum(VI) are $(2.6 \pm 0.8) \times 10^7$ M^{-2} and $(6 \pm 3) \times 10^8$ M^{-2}, respectively. The corresponding rate laws for the formation of these oxodiperoxo complexes are $k_7K_6[H_2O_2]^2/(1 + K_6[H_2O_2])$, where $k_7 = 160 \pm 15$ M^{-1} s^{-1} and $K_6 = 17 \pm 3$ M^{-1}, and $(1.9 \pm 0.1) \times 10^3$ M^{-1} s^{-1} [Mo(VI)][H_2O_2]. A reaction scheme is proposed to account for the unusual formation rate expression for $MoO(O_2)_2(C_2O_4)^{2-}$. The oxygen atom transfer reactions from peroxo ligands in $MoO(O_2)_2(C_2O_4)^{2-}$ and $MoO(OH)(O_2)_2^-$ to the sulfur atom in $(en)_2Co(SCH_2CH_2NH_2)^{2+}$, $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$, and $(CH_3)_2SO$ obey the rate expression rate = k[oxodiperoxo complex][substrate] under our experimental conditions. At 25 °C and pH 4.0 the values of the rate constants (M^{-1} s^{-1}) are $(3.9 \pm 0.1) \times 10^4$, 103 ± 5, and $(2.3 \pm 0.1) \times 10^{-2}$, respectively, for $MoO(O_2)_2(C_2O_4)^{2-}$ and $(4.4 \pm 0.5) \times 10^3$, 13 ± 1, and $(2.7 \pm 0.1) \times 10^{-3}$, respectively, for $MoO(OH)(O_2)_2^-$. These values are 3–4 orders of magnitude larger than those observed for hydrogen peroxide and demonstrate the remarkable activation of peroxide in these oxodiperoxo complexes. There are no coordination sites at the metal center available in $MoO(O_2)_2(C_2O_4)^{2-}$ for the sulfur acceptor in the substrates, and no rate retardation is observed for this complex compared to $MoO(OH)(O_2)_2^-$. We therefore conclude that direct attack of the sulfur atom in the substrates at an η^2-bound peroxo ligand in the oxodiperoxo complexes is the dominant pathway in these reactions.

Introduction

The oxo diperoxo complexes of molybdenum(VI) and tungsten(VI) are remarkable oxygen atom transfer reagents. There is substantial evidence that the structure of these complexes both in the solid state and in solution is pentagonal bipyramidal, with an apical oxo ligand and two η^2-equatorial peroxo ligands.[1,2] Most of the reported work has dealt with organic substrates in weakly coordinating solvent systems. Two principal mechanisms have been proposed—either direct attack by the substrate at the peroxo ligand or coordination of the substrate to the metal center prior to oxygen atom transfer from an adjacent peroxo ligand.[3-7] A distinction between the two pathways can usually be made by comparing the reaction rates of a heteroligand oxo diperoxo complex with no available coordination sites on the metal center with that of the "bare" oxo diperoxo complex or one containing labile ligands.

We have examined some oxygen atom transfer reactions of the oxo diperoxo complexes of Mo(VI) and W(VI) in aqueous solution.[8,9] We have found that these complexes are orders of magnitude more reactive toward a variety of substrates than is hydrogen peroxide. We have established that the source of the oxygen atom gained by both a (thiolato)- and a (sulfenato)cobalt(III) complex is peroxidic by means of oxygen-18 tracer experiments.[8] These studies did not, however, establish if a direct attack by the substrate at the peroxo ligand occurred without prior coordination to the molybdenum(VI) center. We have now examined this mechanistic feature by use of a heteroligand oxodiperoxomolybdenum(VI) complex in which no coordination site on the metal is available for the substrate. In aqueous solution, it is more difficult to establish that the heteroligand complex is intact throughout the reaction due to the coordinating ability of water molecules and hydroxide ions.

We have used the $MoO(O_2)_2(C_2O_4)^{2-}$ complex ion in solutions buffered at pH 4.0 by use of $HC_2O_4^-$ and $C_2O_4^{2-}$ for our studies. We will show that this species is robust under our experimental

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