(s), 726 (s), 686 (ms). The ^{19}F NMR spectrum contained a singlet at −72.0 ppm.

Anal. Calcd: C, 17.32; F, 61.65; I, 15.25. Found: C, 17.39; F, 61.3; I, 15.20.

Pb with (CF₃)₃COCl. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.499 mmol of Pb and 4.50 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (90 h) and at room temperature (50 h); an additional 1.63 mmol of $(CF_3)_3COCl$ was added and again maintained at room temperature (24 h). The materials volatile at −78 °C were periodically removed during this time. The materials volatile at room temperature were removed under vacuum, leaving 0.508 mmol of a light tan solid, $Pb[(CF_3)_3CO]_2$, in ~100% yield. Separation and analysis of the volatile materials found $(CF_3)_2CO$, CF_3Cl, and Cl_2 (0.49 mmol, theoretical yield 0.50 mmol).

The infrared spectrum of $Pb[(CF_3)_3CO]_2$ shows bands (cm^{-1}) at 1304 (ms), 1248 (s, b), 1214 (sh), 1184 (m), 1140 (s), 970 (s), 766 (m), 724 (ms), 674 (w). The ^{19}F NMR spectrum contained a singlet at −74.0 ppm.

Anal. Calcd: C, 14.19. Found: C, 12.81.

Si with (CF₃)₃COCl. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 0.602 mmol of silicon and 0.933 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (18 h) and then at room temperature (24 h). The volatile material contained only $(CF_3)_2C=O$ and CF_3Cl. The weight of the solid left behind increased only 0.0060 g. The reaction was not studied further.

S with (CF₃)₃COCl. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 2.59 mmol of sulfur and 3.59 mmol $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (2 h). Separation and analyses of the volatile material found Cl_2 and S_2Cl_2/SCl_2. The white solid left behind was found to be 0.701 mmol of $S[(CF_3)_3CO]_4$ which was formed in 78% yield. Melting point and spectral data agree with literature values.[5]

Te with (CF₃)₃COCl. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.429 mmol of Te and 3.67 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (100 h), at room temperature (90 h), and between 25 and 30 °C (2 h); an additional 1.08 mmol of $(CF_3)_3COCl$ was added and the reaction again maintained at room temperature (24 h). The materials volatile at −78 °C were periodically removed during

this time. The materials volatile at room temperature were removed under vacuum, leaving 0.385 mmol of the white solid, $Te[(CF_3)_3CO]_4$, in 90% yield. Separation and analysis of the volatile materials found $(CF_3)_2CO$, CF_3Cl, and Cl_2 (0.85 mmol, theoretical yield 0.86 mmol). The new compound sublimes in vacuo at 70 °C and melts in a sealed tube at 94 ± 1 °C.

The infrared spectrum of $Te[(CF_3)_3CO]_4$ shows bands (cm^{-1}) at 1308 (sh), 1260 (s), 1172 (m), 968 (ms), 760 (sh), 724 (s), 626 (vs, b). The ^{19}F NMR spectrum contained a singlet at −72.1 ppm.

Anal. Calcd: C, 17.99. Found: C, 17.17.

Bi with (CF₃)₃COCl. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.427 mmol of Bi and 1.941 mmol $(CF_3)_3COCl$. Additional amounts of $(CF_3)_3COCl$ were added later (2.86, 3.28, and 0.71 mmol). Cumulatively, the reaction mixture was maintained at 0 °C (40 h), room temperature (94 h), and 25–30 °C (6 h). The materials volatile at −78 °C were removed periodically during this time. The materials volatile at 25 °C were removed under vacuum, leaving 0.40 mmol of the white solid, $Bi[OC(CF_3)_3]_3$, in 93% yield. Separation and analyses of volatile materials found CF_3Cl, $(CF_3)_2C(O)$, $(CF_3)_3COH$, and Cl_2.

The infrared spectrum of $Bi[OC(CF_3)_3]_3$ shows bands (cm^{-1}) at 1303 (ms), 1245 (s), 1207 (sh), 1153 (s), 965 (s), 765 (w), 723 (s). The ^{19}F NMR spectrum contained a singlet at −74.2 ppm.

Anal. Calcd: C, 15.77; F, 56.12. Found: C, 15.45; F, 54.4.

Registry No. $VO[(CF_3)_3CO]_3$, 88391-96-2; $Ti[(CF_3)_3CO]_4$, 88391-97-3; $CrO_2[(CF_3)_3CO]_2$, 88391-99-5; $Pb[(CF_3)_3CO]_2$, 88392-01-2; $I[(CF_3)_3CO]_3$, 88392-00-1; $S[(CF_3)_3CO]_4$, 71906-37-1; $Te[(CF_3)_3CO]_4$, 88392-02-3; $Bi[(CF_3)_3CO]_3$, 88392-03-4; $(CF_3)_3C-OH·(CH_3CH_2)_2NH$, 88391-98-4; NOCl, 2696-92-6; $(CF_3)_3COCl$, 27579-40-4; $(CF_3)_3CONO$, 677-88-3; *trans*-[IrCl(CO)(PPh₃)₂], 15318-31-7; I_2, 7553-56-2; Pb, 7439-92-1; S, 7704-34-9; Te, 13494-80-9; Bi, 7440-69-9.

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Cis Effect of the Phosphorus Ligand, L, in Six-Coordinate Ru(CO)₃(L)(SiCl₃)₂ Compounds. Importance of the Steric Factor[1]

KAREN L. CHALK and ROLAND K. POMEROY*

The rate of substitution of the equatorial carbonyl by P(OMe)₃ has been investigated for 24 different molecules of the type *mer*-Ru(CO)₃(L)(SiCl₃)₂ (SiCl₃ groups mutually cis; L a phosphorus donor ligand). Detailed studies on the substitution in Ru(CO)₃(PPh₃)(SiCl₃)₂ were entirely consistent with a dissociative mechanism for the process. Rates, at 40 °C, vary by ~10³ depending on the nature of L. With four exceptions, the activation parameter $\Delta H^\ddagger$ was found to be approximately constant for each case. This is interpreted as signifying that ground-state electronic effects are unimportant in determining the differences in rates. In contrast, for these nonexceptional examples, the $\Delta S^\ddagger$ values vary from 4 to 19 cal mol^{-1} deg^{-1}. Furthermore, there is a reasonably linear correlation between $\Delta S^\ddagger$ and the size of the phosphorus ligand as measured by the cone angle, θ, of L. It is concluded that the origin of the cis effect of L in these complexes is almost entirely steric.

Introduction

The most common mechanism by which metal carbonyl complexes undergo substitution reactions is by the initial dissociation of CO as the rate-determining step.[2] In substituted metal carbonyl compounds it appears for most cases

that the CO groups cis to the non-carbonyl substituent are labilized with respect to dissociation.[3] This, of course, is in contrast to ligand-displacement reactions in square complexes where the trans effect is of dominant importance.[4] Brown and co-workers have developed the site-preference model in

(1) Taken in part from: Chalk, K. L. M.S. Thesis, Simon Fraser University, 1982.
(2) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.
(3) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3161.
(4) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980, p 1199.

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Table I. Effects of the Concentration of the Entering Ligand (P(OMe)$_3$) and of Light on the Rate of Substitution of *mer*-Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ (at 40.2 °C)

entering ligand: complex ratio	$10^4 k$, s^{-1}	entering ligand: complex ratio	$10^4 k$, s^{-1}
1:1	7.6	9.5:1	8.7
3.3:1^a	8.8	21:1	8.6
3.3:1^b	8.6		

^{a} Carried out in normal laboratory lighting. ^{b} Carried out in the dark (simultaneously with the experiment in normal lighting).

Table II. Effect of the Identity of the Entering Ligand (L') on the Rate of Substitution of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ (in Toluene at 40.2 °C)

L'	θ,^{a} deg	$10^4 k$, s^{-1}	L'	θ,^{a} deg	$10^4 k$, s^{-1}
P(OCH$_2$)$_3$CEt	101	9.2	PMe$_2$Ph	122	8.7
P(OMe)$_3$	107	9.1	P(n-Bu)$_3$	132	9.6
P(OEt)$_3$	109	9.0	P(OPh)$_3$	128	5.0
P(OMe)$_2$Ph	115	9.2	PPh$_3$	145	no reacn

^{a} From ref 9.

order to account for the cis labilization of ligand dissociation in six-coordinate metal carbonyl complexes.[3,5] In this model the cis-labilizing ligand is thought to stabilize the transition state as a result of preferentially occupying a basal site in a square-pyramidal transition state or an axial site in one of trigonal-bipyramidal geometry. This preference is primarily electronic and arises because, in most cases, the non-carbonyl ligand is a poorer π-acceptor than CO.

The compound *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ is unusual in that the CO groups trans to the SiCl$_3$ ligands are labile and undergo stereospecific exchange with ^{13}CO under very mild conditions (eq 1 and 2; L = L' = ^{13}CO).[6] Not surprisingly, *cis*-Ru-
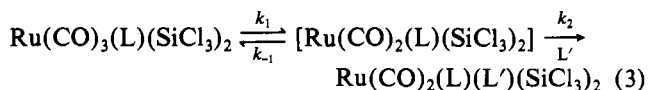

(1)

1

(2)

2
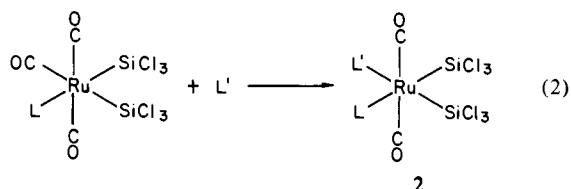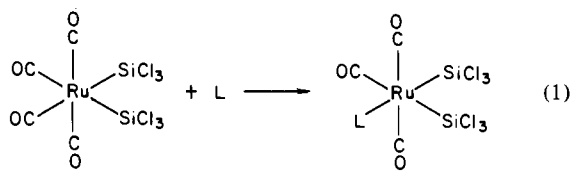
(CO)$_4$(SiCl$_3$)$_2$ undergoes facile substitution by two-electron-donor ligands to give compounds of types **1** and **2** (L, L' = two-electron-donor ligand).[7] In this paper we describe a kinetic study of the cis effect of the ligand L on the rate of substitution of the remaining equatorial carbonyl ligand in compounds of type **1**, i.e., the rate of reaction 2. The study restricts itself to the case where L is a phosphorus donor ligand.

Results and Discussion

Nature of the Reaction. The reactions investigated were of type 2 with L a phosphorus donor ligand. For most cases they proceed at rates, in the temperature range 25–80 °C, that could be conveniently monitored by infrared spectroscopy. The measured rates, which varied by a factor of $\sim 10^3$, depend on the nature of L. In this section some preliminary experiments are described that establish the nature of the reaction in order that the differences in rates may be truly attributed to a cis effect of the ligand L.

For a dissociative mechanism (eq 3) the reaction should

$$\text{Ru(CO)}_3(\text{L})(\text{SiCl}_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{Ru(CO)}_2(\text{L})(\text{SiCl}_3)_2] \xrightarrow{k_2}{\text{L'}}$$
$$\text{Ru(CO)}_2(\text{L})(\text{L'})(\text{SiCl}_3)_2 \quad (3)$$

follow the rate law rate = $k_1 k_2 [\text{Ru(CO)}_3(\text{L})(\text{SiCl}_3)_2][\text{L'}]/(k_2[\text{L'}] + k_{-1}[\text{CO}])$. For the case where L is in a large excess,

Figure 1. ^{31}P{^{1}H} NMR spectra of a toluene solution of Ru(CO)$_2$-(^{13}CO)(PPh$_3$)(SiCl$_3$)$_2$ (A) and Ru(CO)$_3$[P(p-MeC$_6$H$_4$)$_3$](SiCl$_3$)$_2$ (B) taken at different times after mixing the two components. From the ^{13}C–^{31}P coupling exhibited by the signals, it is clear the ^{13}CO group becomes distributed between A and B in the later stages. This indicates that the ^{13}CO is completely free of the coordination sphere of A in the initial dissociation step, as required by a dissociative mechanism.

$k_2[\text{L'}] \gg k_{-1}[\text{CO}]$ and the rate law reduces to rate = k_1-[Ru(CO)$_3$(L)(SiCl$_3$)$_2$].

The rate of reaction of Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ with P(OMe)$_3$, in toluene at 40.2 °C, was found to be independent of the concentration of the phosphite, provided it was present in at least a 3 molar excess (Table I). For the same reaction, only with a different entering ligand, the rate was found to be independent (within experimental error) of the identity of the ligand, provided it was small (Table II).

From Table II it can be seen that the rate was dependent on the nature of the entering ligand when it was large, e.g., P(OPh)$_3$ and PPh$_3$.[8] Indeed, for the case of L' = PPh$_3$ the bis-substituted product Ru(CO)$_2$(PPh$_3$)$_2$(SiCl$_3$)$_2$ did not form. In these two cases it is probable that steric interaction between the entering ligand L' and the coordinated ligand L in the intermediate hindered or prevented the forward reaction.

The complex Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$ showed no detectable decomposition when a solution of it was stirred (under a static nitrogen atmosphere) by itself for several hours. This raised the question of whether the CO that is replaced is actually completely free of the coordination sphere of the ruthenium complex in the initial dissociation step. This is a requirement for a dissociative mechanism (D) as defined by Langford and Gray.[10] That this was almost certainly the case was indicated

(5) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.
(6) Pomeroy, R. K.; Gay, R. S.; Evans, G. O.; Graham, W. A. G. *J. Am. Chem. Soc.* **1972**, *94*, 272.
(7) Pomeroy, R. K.; Wijesekera, K. S. *Inorg. Chem.* **1980**, *19*, 3729.

(8) It is interesting that the rate of reaction for L' = P(n-Bu)$_3$ was normal even though the cone angle of this ligand is greater than that of P(OPh)$_3$ (132° vs. 128°).[9] It may be that, besides the steric factor, the nucleophilic strength of the ligand L' is important in the determination of k_2. This would then allow k_2[L] > k_{-1}[CO] for P(n-Bu)$_3$ and pseudo-first-order kinetics to be maintained.
(9) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(10) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965; Chapter 1.

in a double-label experiment that involved the molecules A and B.

A   B
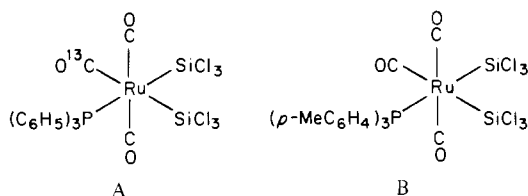
From the results that are reported later in the discussion it was known that A and B underwent substitution of the equatorial CO by P(OMe)$_3$ at approximately the same rate. The resonances in the ^{31}P{^{1}H} NMR spectrum of each compound were found to be well separated, and, due to ^{13}C–^{31}P coupling, the ^{13}C-labeled compound could be readily distinguished from the unlabeled species (Figure 1). Approximately equimolar concentrations of A and B (in toluene solution) were stirred together at ca. 30 °C for 170 min. This time period corresponded to about 3 half-lives, where the half-life refers to that found for the rate of substitution of Ru(CO)$_3$-(PPh$_3$)(SiCl$_3$)$_2$ by P(OMe)$_3$, in the same solvent and at the same temperature. A ^{31}P{^{1}H} NMR spectrum of the solution at this stage revealed that the labeled CO group was more than 80% distributed between both A and B. Although it was only possible to carry out this experiment in a semiquantitative fashion, the result clearly indicates that the CO ligand completely leaves the coordination sphere of the ruthenium complex in the initial dissociative step and, therefore, that a dissociative (D) mechanism is operative.

Cis Effect of the Ligand L. For most cases the entering ligand (L', eq 2) was trimethyl phosphite. A 10-fold excess was employed to ensure that pseudo-first-order kinetics were observed. In some cases, when the coordinated ligand was small, there was infrared evidence for the slow loss of L from Ru(CO)$_3$(L)(SiCl$_3$)$_2$ at the temperature required to bring about a convenient rate of substitution of the carbonyl group. For these compounds an entering ligand of L was used for the rate determinations (e.g., P(OCH$_2$)$_3$CEt was used as the substituting ligand, L', in the kinetic study of Ru(CO)$_3$[P-(OCH$_2$)$_3$CEt](SiCl$_3$)$_2$). In this way, the same complex was regenerated if L became dissociated from the original complex and, therefore, this dissociation did not hinder the measurement of the rate of substitution of the carbonyl ligand. For Ru(C-O)$_3$(PF$_3$)(SiCl$_3$)$_2$, dissociation of PF$_3$ was faster than for the equatorial CO, and Ru(CO)$_3$[P(OMe)$_3$](SiCl$_3$)$_2$ was the major product of the reaction between Ru(CO)$_3$(PF$_3$)(SiCl$_3$)$_2$ and P(OMe)$_3$. Although several attempts were made, reproducible results for the rate of substitution of CO by PF$_3$ in Ru(C-O)$_3$(PF$_3$)(SiCl$_3$)$_2$ could not be obtained. The corresponding PCl$_3$ analogue appeared even less stable, and the kinetics were not studied. There were also examples where the Ru(CO)$_2$-(L)[P(OMe)$_3$](SiCl$_3$)$_2$ compounds reacted further to give Ru(CO)$_2$[P(OMe)$_3$]$_2$(SiCl$_3$)$_2$, a product which may be considered as a result of the cis effect of P(OMe)$_3$ on L. This reaction did not proceed via Ru(CO)$_3$[P(OMe)$_3$](SiCl$_3$)$_2$ since this complex was known to have one of the slowest rates of substitution (to give Ru(CO)$_2$[P(OMe)$_3$]$_2$(SiCl$_3$)$_2$) and it would have been detected in the infrared spectrum of the reaction solution. The subsequent formation of Ru(CO)$_2$[P-(OMe)$_3$]$_2$(SiCl$_3$)$_2$, therefore, did not affect the measurement of the rate of the initial substitution in Ru(CO)$_3$(L)(SiCl$_3$)$_2$.

The rate of substitution was obtained by monitoring the disappearance of the highest energy CO stretching frequency in the infrared spectrum of the Ru(CO)$_3$(L)(SiCl$_3$)$_2$ compound in question,[11] which was well separated from the other ab-

Table III. Activation Parameters and Calculated Rate Constants at 40 °C for the Substitution of Ru(CO)$_3$(L)(SiCl$_3$)$_2$ Compounds

L	θ,[a] deg	ν,[b] cm^{-1}	$\Delta S^{\ddagger} \pm$ 3, cal mol^{-1} deg^{-1}	$\Delta H^{\ddagger} \pm$ 1, kcal mol^{-1}	$10^6 k$,[c] s^{-1}
P(OCH$_2$)$_3$CEt	101	2087.3	5	28.4	1.1
P(OMe)$_3$	107	2079.0	5	27.4	7.3
P(O-n-Bu)$_3$	109	2076.0	4	27.0	6.7
P(OMe)$_2$Ph	115	2075.8	5	26.9	11.3
PCl$_2$Ph	122	2092.1	4	25.5	110
PMe$_2$Ph	122	2065.3	7.5	27.5	19.0
P(O-p-ClPh)$_3$	128	2089.3	10	28.5	13.0
P(CH$_2$CH=CH$_2$)$_3$	132	2065.0	7	27.2	21.0
P(n-Bu)$_3$	132	2060.0	11	28.7	140
P(OMe)Ph$_2$	132	2072.0	8	27.5	23.0
PMePh$_2$	136	2067.0	10	27.4	71
PClPh$_2$	137	2080.7	9	26.5	166
PPh$_3$	145	2068.9	14	27.1	900
P(p-FC$_6$H$_4$)$_3$	145	2071.3	13	27.0	750
P(p-ClC$_6$H$_4$)$_3$	145	2072.8	13	27.0	670
P(p-MeOC$_6$H$_4$)$_3$	145	2066.1	13	26.8	755
P(p-MeC$_6$H$_4$)$_3$	145	2066.7	13	26.9	840
PPh$_2$(i-Pr)	150	2065.7	14	28.7	640
P(m-CH$_3$C$_6$H$_4$)$_3$	165	2067.2	16	27.5	1300
P(m-ClC$_6$H$_4$)$_3$	165	2075.6	19	28.7	963

[a] Cone angle of L (taken from ref 9 or calculated from information given therein). [b] Electronic parameter of L (from ref 12). [c] Calculated rate constant at 40 °C.

sorptions of the starting compound and the product. Activation parameters (Table III) were obtained from rates of substitution measured at at least four different temperatures, for each Ru(CO)$_3$(L)(SiCl$_3$)$_2$ molecule. Relative rates of substitution at 40 °C for each compound, as obtained from the Eyring equation, are also reported in Table III along with the steric[9] and electronic[12] parameters of L.

For a dissociative reaction, $\Delta H^{\ddagger}$ is often related to the bond strength of the bond that is broken in the rate-determining step. For the molecules with L = PCl$_2$Ph and P(n-Bu)$_3$ the $\Delta H^{\ddagger}$ parameter changes in a manner expected from conventional bonding arguments. For Ru(CO)$_3$(PCl$_2$Ph)(SiCl$_3$)$_2$ (ν(CO) 2126 w, 2087 m, 2081 m, 2065 s cm^{-1}; hexane solution), $\Delta H^{\ddagger}$ was found to be 25.5 kcal mol^{-1} whereas for Ru-(CO)$_3$[P(n-Bu)$_3$](SiCl$_3$)$_2$ (ν(CO) 2112 w, 2062 m, 2044 s cm^{-1}; hexane solution) $\Delta H^{\ddagger}$ was 28.7 kcal mol^{-1}. This may reflect increased back-donation from the metal to the carbonyl groups in the P(n-Bu)$_3$ derivative. However, the difference is barely significant, and for most of the other compounds studied here $\Delta H^{\ddagger}$ is constant (27.4 kcal mol^{-1}) within experimental error. For example, all five complexes of the type Ru(CO)$_3$[P(p-XC$_6$H$_4$)$_3$](SiCl$_3$)$_2$ (X = H, F, Cl, Me, MeO) have $\Delta H^{\ddagger}$ = 27.0 ± 0.2 kcal mol^{-1}. There is no correlation of the activation parameters with the Tolman electronic parameter of the phosphorus ligand[13] or the CO stretching frequencies of the complexes (which parallel the electronic parameters). It is concluded that, for the most part, electronic effects are relatively unimportant in determining the differences in the cis effects of the ligands. (The ligands PCl$_2$Ph and PMe$_2$Ph, which have the same θ value but very different electronic parameters, do show a difference in their cis effects that may be due to a small electronic effect.)

The difference in rates of substitution in the Ru(CO)$_3$-(L)(SiCl$_3$)$_2$ molecules can be traced to the difference in the entropies of activation, $\Delta S^{\ddagger}$, for the particular reactions. The $\Delta S^{\ddagger}$ values (besides four exceptions) are positive as expected for a dissociative mechanism. Moreover, the values increase with the size of the ligand L.[14] A measure of the size of a

(11) A typical infrared spectrum (carbonyl region) of a Ru(CO)$_3$(L)(SiCl$_3$)$_2$ complex is shown in ref 7.

(12) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956; see also ref 9.
(13) A figure that illustrates this point is given in the M.S. thesis of K.L.C. (see ref 1).
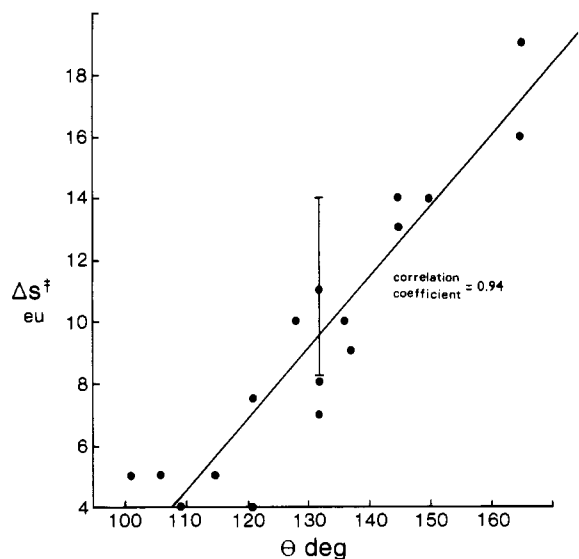
Figure 2. Plot of $\Delta S^{\ddagger}$ vs. θ, where $\Delta S^{\ddagger}$ is the entropy of activation found for the substitution of $Ru(CO)_3(L)(SiCl_3)_2$ and θ is the cone angle of the phosphorus ligand L.

phosphorus ligand is the cone angle, θ (as defined by Tolman[9]), and as can be seen in Figure 2, there is a reasonably linear correlation between $\Delta S^{\ddagger}$ and θ, especially in view of the fact that the $\Delta S^{\ddagger}$ parameters are subject to large errors as are, to a lesser extent, the θ values.[15] It thus appears that the origin of the cis effect in this system is relief of steric strain in the ground state. The increase in entropy in the transition state is assumed to be due to increased rotation about the various bonds in the five-coordinate intermediate, e.g., rotation about the Ru–P, P–substituent, and Ru–Si bonds.[16]

Steric acceleration by phosphorus donor ligands has been observed before in the substitution reactions of both mononuclear[17] and cluster[18] carbonyl compounds. For the molecules *cis*-Mo(CO)$_4$L$_2$ crystallographic evidence has been found for steric interaction between the phosphine ligands especially when they were bulky; e.g., the P–Mo–P angle in *cis*-Mo-(CO)$_4$(PPh$_3$)$_2$ was found to be 104.62°.[19] It was concluded that the steric requirements of the ligands L make a major contribution to the kinetics of phosphine substitution in these molecules.[19] There is, therefore, precedence for cis labilization attributable to steric effects. This is in contrast to the model of Brown and co-workers, who attribute the origin of cis labilization in substituted metal carbonyls to electronic effects.[3] It may be that because all the $Ru(CO)_3(L)(SiCl_3)_2$ molecules investigated in this study had a phosphorus donor ligand in

(14) Substitution in complexes where the cis ligand had a cone angle greater than ca. 175° proceeded at rates that were too fast to be measured by the technique employed in this study; e.g., for L = P(o-MeC$_6$H$_4$)$_3$ (θ = 194°) the rate of substitution was fast even at 0 °C (cf. L = P(p-MeC$_6$H$_4$)$_3$).

(15) Because of the errors associated with $\Delta S^{\ddagger}$ (and θ), a more detailed analysis was not justified. It is probable that $\Delta S^{\ddagger}$ can be separated into two terms: one associated with the liberation of the CO and the second due to the gain in entropy in the formation of the five-coordinate intermediate. Only the latter term would be expected to show a relationship to the cone angle of L.

(16) The solution infrared spectra of some compounds of the type Ru-(CO)$_3$(PX$_2$Y)(SiCl$_3$)$_2$ (e.g., Ru(CO)$_3$(PMe$_2$Ph)(SiCl$_3$)$_2$) reveal that the CO stretching frequency due to the equatorial carbonyl is split into two bands of different intensities. Since both bands shift to lower frequency in Ru(CO)$_2$(^{13}CO)(PX$_2$Y)(SiCl$_3$)$_2$, the splitting is confidently assigned to the presence of different conformers in solution arising from the restricted rotation of the PX$_2$Y group about the Ru–P bond. (The stretching modes due to the axial carbonyls are not split.) (Chalk, K. L.; Hu, X.; Pomeroy, R. K., unpublished work.)

(17) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.

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Table IV. Results of the Kinetic Study of *mer*-Ru(CO)$_3$(L)(SiCl$_3$)$_2$ (L = P(CH$_2$Ph)$_3$, P(OPh)$_3$, P(O-o-MeC$_6$H$_4$)$_3$, PPh$_2$(o-MeOC$_6$H$_4$) at 40 °C

L	$10^6 k$, s^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	θ,[a] deg	ν,[b] cm^{-1}
P(CH$_2$Ph)$_3$	637	1	23.0	165	2066.0
P(OPh)$_3$	19.8	0	25.2	128	2085.1
P(O-o-MeC$_6$H$_4$)$_3$	15.8	−6.5	23.5	141	2084.1
PPh$_2$(o-MeOC$_6$H$_4$)	1470	4	23.6	171	2066.1

[a] Cone angle of L (from ref 9). [b] Electronic parameter of L (from ref 12).

the cis position, the differences in electronic effects were negligible. This might not be the case when ligands with different donor atoms are compared.

It is apparent that further work on this subject is needed. It is also pertinent at this stage to reiterate that it is the trans effect of the SiCl$_3$ ligands that is primarily responsible for the lability of the equatorial carbonyl and that this effect is presumably electronic. Also, the lability of the equatorial carbonyl groups in the parent compound *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$[6,7] and the CO group trans to SiCl$_3$ in *cis*-Ru(CO)$_4$(SiCl$_3$)(H)[20] is comparable to that of the analogous ligand in Ru(CO)$_3$-(PPh$_3$)(SiCl$_3$)$_2$. It is doubtful that the lability of the carbonyl in the first two compounds can be attributed to steric effects of the cis ligand.

Four Exceptions. Four exceptions were found to the generalities regarding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameters. These were for Ru(CO)$_3$(L)(SiCl$_3$)$_2$ molecules where L = P(OPh)$_3$, P(O-p-MeC$_6$H$_4$)$_3$, P(CH$_2$Ph)$_3$, and PPh$_2$(o-MeOC$_6$H$_4$). For the substitution in these compounds the $\Delta H^{\ddagger}$ value was lower than expected while the $\Delta S^{\ddagger}$ parameter was found to be close to zero or negative (Table IV). Since the cis ligands L in the exceptional cases have secondary donor sites, it is possible that the five-coordinate intermediate is stabilized in a manner like that shown in C for L = P(OPh)$_3$. Complexes with ligands

C
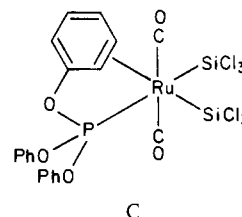
such as PPh$_3$ and P(OC$_6$H$_4$Cl)$_3$ did not show anomalous activation parameters. It may be that the secondary interaction does not occur because of less favorable steric requirements (PPh$_3$) or for electronic reasons (P(OC$_6$H$_4$Cl)$_3$). Attempts to isolate the proposed intermediate by stirring a solution of Ru(CO)$_3$[P(OPh)$_3$](SiCl$_3$)$_2$ (for example) under vacuum were unsuccessful. This result and the observation that the rates for the exceptional cases are hardly different from what one would expect in the absence of the interaction suggest the secondary interaction is very weak.

Experimental Section

Unless otherwise stated, all reactions (and the purification of solvents) were carried out under nitrogen with the use of standard Schlenk techniques. Solvents were dried, distilled, and stored under nitrogen prior to use. Carbon-13 monoxide ($\sim$93% isotopic enrichment) was obtained from Monsanto Research Corp. Trimethyl phosphite as obtained commercially was opened in the drybox and stored under nitrogen; it was pure by ^{31}P{^{1}H} NMR spectroscopy. The preparation of many of the compounds of the type Ru(CO)$_3$(L)(SiCl$_3$)$_2$ has been previously described.[7] New complexes were prepared in a

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similar manner. For several of the new compounds satisfactory carbon and hydrogen analyses (by the microanalytical laboratory of Simon Fraser University) were obtained; for the remaining compounds characterization by infrared spectroscopy was considered sufficient. In some cases (but not all) where the ligand L, in $Ru(CO)_3(L)(SiCl_3)_2$, was asymmetric (e.g., PMe_2Ph), the infrared spectrum exhibited an extra terminal CO stretch. Further study has shown that this can be confidently assigned to the presence of different conformers in solution; details of this study will form the subject of a subsequent publication. Analytical and spectroscopic data for new $Ru(CO)_3$-$(L)(SiCl_3)_2$ compounds have been deposited as supplementary material.

Infrared spectra were recorded with the use of a Perkin-Elmer 237 spectrometer fitted with an external recorder. The spectra, in the carbonyl region, were calibrated with carbon monoxide. The solution spectra were obtained with use of NaCl cells of 1.0-mm path length. The $^{31}P\{^1H\}$ spectra were obtained at 40.5 MHz on a modified Varian XL-100 instrument, operating in the Fourier transform mode.

Preparation of $Ru(CO)_2(^{13}CO)(PPh_3)(SiCl_3)_2$. (The reaction was carried out in a round-bottom flask, of approximately 50-mL capacity fitted with a Teflon valve.) A flask with $Ru(CO)_3(PPh_3)(SiCl_3)_2$ (0.20 g, 0.28 mmol) in CH_2Cl_2 (15 mL) was cooled to -196 °C and evacuated; the solution was degassed with a freeze–thaw cycle. The flask was allowed to warm to room temperature and then pressurized with ^{13}CO (2 atm). The solution was stirred at room temperature for 72 h. An infrared spectrum of the solution at this stage indicated that exchange was complete. The CH_2Cl_2 was removed on the vacuum line to leave $Ru(CO)_2(^{13}CO)(PPh_3)(SiCl_3)_2$ as a white solid (ν(CO) 2109 vw, 2050 s, 2030 m cm^{-1}; CH_2Cl_2 solution).

Exchange of ^{13}CO between $Ru(CO)_2(^{13}CO)(PPh_3)(SiCl_3)_2$ and $Ru(CO)_3[P(p\text{-}MeC_6H_4)_3](SiCl_3)_2$. Two solutions were prepared: one contained $Ru(CO)_2(^{13}CO)(PPh_3)(SiCl_3)_2$ (0.168 g, 0.23 mmol) in toluene (2.5 mL); the other, $Ru(CO)_3[P(p\text{-}MeC_6H_4)_3](SiCl_3)_2$ (0.134 g, 0.176 mmol) also in toluene (2.5 mL). The solutions were thoroughly mixed, and a sample (0.5 mL) was sealed (under nitrogen) in a 5-mm NMR tube. A $^{31}P\{^1H\}$ NMR spectrum of the sample was taken as soon as possible after this procedure. The original mixture was left standing at room temperature, and samples were removed at approximately 100 min, 170 min, and 8 days and $^{31}P\{^1H\}$ NMR spectra obtained. The results are shown in Figure 2.

Kinetic Studies

General Procedures. The reactions were carried out in standard Schlenk flasks that were placed in a constant-temperature bath maintained at ± 0.1 °C. Solutions were rapidly stirred during the course of the reaction. Each substitution was followed by monitoring the disappearance of the highest energy CO stretching band in the infrared spectrum of the starting complex. This band was far removed from the other CO stretches in the spectrum and also from the single CO absorption of the product. (A typical solution infrared spectrum of a $Ru(CO)_3(L)(SiCl_3)_2$ compound is shown in ref 7.) Approximately ten transmittance readings were made during the course of a single substitution reaction. (Each reading was the average of three individual measurements.) The transmittance values of the peaks in question were converted into the corresponding absorbances, and a plot of $\ln (A_t/A_0)$ vs. time was constructed, where A_0 was the initial absorbance and A_t the absorbance at time t. In each case a linear plot was obtained, which demonstrated the reactions were first order with respect to the metal complex. The slope of the plot (calculated by means of a least-squares linear regression) yielded the rate constant. Rate constants were reproducible to within 4% over different ratios of complex:ligand provided there was at least a 10-fold excess of ligand.

Kinetic Studies on $Ru(CO)_3(PPh_3)(SiCl_3)_2$. Effect of the Concentration of the Entering Ligand. All reactions were carried out at a temperature of 40.2 ± 0.5 °C. A known weight of $Ru(CO)_3(PPh_3)(SiCl_3)_2$ was placed in the reaction vessel, toluene (6.0 mL) added, and the system allowed to come to thermal equilibrium in the constant-temperature bath. The appropriate quantity of $P(OMe)_3$, to give the desired complex:ligand ratio, was added to the solution by means of a calibrated syringe. Aliquots (0.2 mL) were periodically re-

moved from the stirred solution for the infrared measurements. Results are given in Table I. It was also noted that stirring a solution of $Ru(CO)_3(PPh_3)(SiCl_3)_2$ in the absence of an entering ligand did not cause a significant drop in the intensity of the CO stretching bands during the time needed for a normal kinetic experiment (indeed, solutions of $Ru(CO)_3$-$(PPh_3)(SiCl_3)_2$ may be left for days without apparent decomposition).

Effect of Light on the Reaction Rate. Two reaction vessels were placed in the constant-temperature bath: one was a regular reaction vessel; the other was painted black to exclude light. Each vessel contained a solution with similar concentrations in complex and $P(OMe)_3$. The reactions were carried out simultaneously and monitored in the manner previously described. The results, which indicated that light had a negligible effect on the rate, are also recorded in Table I.

Effect of the Identity of the Entering Ligand (L'). The rate measurements followed the general method given above except that the entering ligand (L') was varied. The concentration of $Ru(CO)_3(PPh_3)(SiCl_3)_2$ in toluene was in the range 2.5 × 10^{-2} – 4.2 × 10^{-2} M (0.11 – 0.18 g in 6 mL of toluene). Most of the ligands were liquids and were introduced into the flask by means of a syringe; solid ligands ($P(OCH_2)_3CEt$, PPh_3) were introduced directly into the vessel.

Effect of the Identity of the Cis Ligand (L). Again, the procedure described in detail for the measurement of the rate of substitution of CO in $Ru(CO)_3(PPh_3)(SiCl_3)_2$ by $P(OMe)_3$ was employed. The concentration of the $Ru(CO)_3(L)(SiCl_3)_2$ complex was usually adjusted so that the high-energy CO stretching absorption in the infrared spectrum had a transmittance of 65–85%. The solvent employed was toluene, except in the case of $Ru(CO)_3[P(OCH_2)_3CEt](SiCl_3)_2$ where for reasons of solubility 1,2-dichlorobenzene was used. The entering ligand was $P(OMe)_3$ (in at least a 10-fold excess) except with the complexes where L was $P(O\text{-}n\text{-}Bu)_3$, $P(OMe)_2Ph$, and $P(OCH_2)_3CEt$. In these cases there was evidence in the reaction with $P(OMe)_3$ for the competitive loss of the coordinated phosphorus ligand to give $Ru(CO)_3[P(OMe)_3](SiCl_3)_2$. For the kinetic studies on these complexes, therefore, the entering ligand (L') had the same identity as the coordinated ligand (L). In most cases the rate was only measured once at a given temperature. However, for a particular complex, the rate of substitution was measured at at least four different temperatures. From these the activation parameters, ΔH^* and ΔS^*, for the process were obtained by a least-squares fit to the Eyring equation. The errors associated with the ΔH^* and ΔS^* values (supplementary material) were those obtained from the linear-regression analyses. The activation parameters are reported in Table III, as are the rates at 40 °C (calculated from the activation parameters) for each $Ru(CO)_3(L)(SiCl_3)_2$ complex. The actual experimentally determined rates are deposited as supplementary material.

1 (L = P(OPh)₃), 75030-86-3; **1** (L = P(O-*o*-MeC₆H₄)₃), 88229-58-7; **1** (L = PPh₂(*o*-MeOC₆H₄)), 88229-59-8; P(OCH₂)₃CEt, 824-11-3; P(OEt)₃, 122-52-1; P(OMe)₂Ph, 2946-61-4; PMe₂Ph, 672-66-2; P(*n*-Bu)₃, 998-40-3; P(OPh)₃, 101-02-0; PPh₃, 603-35-0; P(OMe)₃, 121-45-9; CO, 630-08-0.

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A Multinuclear NMR Investigation of Stannous Chloride Promoted Ligand Exchange of Platinum Phosphole Complexes

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A thorough investigation by ³¹P{¹H}, ¹¹⁹Sn, and ¹⁹⁵Pt{¹H} NMR spectroscopy of solutions containing dichlorobis(1-R-3,4-dimethylphosphole)platinum(II) (L₂PtCl₂) and SnCl₂ under a variety of conditions [various solvents, substituents (R = CH₃, *n*-C₄H₉, *t*-C₄H₉, C₆H₅, and C₆H₅CH₂), stoichiometries, times, and temperatures] demonstrated that the addition of solid anhydrous SnCl₂ to solutions of the phosphole complexes labilizes these phosphole complexes toward complete ligand exchange producing several species in solution. These include *cis*- and *trans*-L₂Pt(SnCl₃)Cl, *trans*-L₂Pt(SnCl₃)₂, *cis*-L₂PtCl₂, and, surprisingly, the pentacoordinate species L₃PtCl₂. The L₃PtCl₂ species are significant as their presence demonstrates that addition of a chloride acceptor (SnCl₂) to a solution of a noble-metal complex not only labilizes the metal–chloride bond as anticipated but also labilizes the other metal–ligand bonds as well.

Introduction

The interaction of platinum chlorides with stannous chloride has a long and interesting history.[2] As early as 1907, Wohler[3] noted the intense colors of these solutions and this later served as a basis for the analytical determination of platinum.[4] The exact nature of all the species responsible for the colors of these solutions remains in some doubt, but we have recently shown by ¹¹⁹Sn and ¹⁹⁵Pt NMR spectroscopy and X-ray crystallography that one yellow species is[5,6] *cis*-[PtCl₂(SnCl₃)₂]²⁻ and a deep red species is[5,7] [Pt(SnCl₃)₅]³⁻. Our efforts in this area were aided greatly by the seminal NMR investigations of Pidcock[8] and Pregosin.[9]

The original NMR investigations were prompted by several observations. Stannous chloride catalyzes the formation of analogues to Zeise's salt, [PtCl₃(RCH═CH₂)]⁻, from PtCl₄²⁻ and alkenes.[10,11] Stannous chloride combined with either PtCl₆²⁻ or (R₃P)₂PtCl₂ becomes an efficient homogeneous

Scheme I
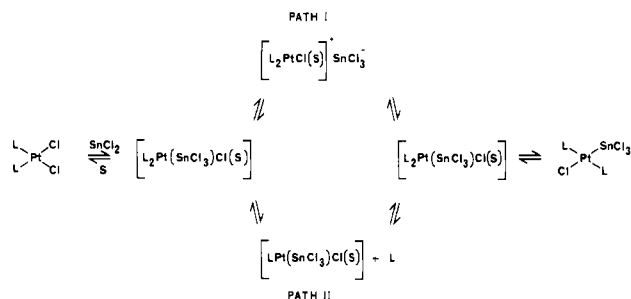
catalyst for hydrogenation and isomerization of alkenes and alkynes,[12] including asymmetric hydrogenation.[13] These same mixtures have also been found to be good catalysts for hydroformylation,[14] carboalkoxylation,[15] and the water gas shift reaction.[16]

While the catalytic mechanisms are still being actively investigated,[17] the work to date clearly establishes that the in-

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