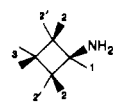
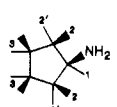


Table IV. Chemical Shifts (ppm) and $\Delta\delta$ (Complex-Ligand) of the $K[\text{Pt}(\text{am})\text{Cl}_3]$ Complexes in D_2O

am	H_1	H_2	$\text{H}_{2'} + \text{H}_3$
$^1\text{CH}_3\text{-NH}_2$ (pH 7)	2.37 (s + d)		
$\Delta\delta$	0.07		
$^1\text{CH}_3\text{-NH}_2$ (pH 4)	2.37 (t + dt)		
$\Delta\delta$	0.07		
$^2\text{CH}_3\text{-}^1\text{CH}_2\text{-NH}_2$	2.67 (q + dq)	1.23 (t)	
$\Delta\delta$	0.12	0.20	
$(^2\text{CH}_3)_2\text{-}^1\text{CH-NH}_2$	3.11 (m)	1.27 (d)	
$\Delta\delta$	0.11	0.25	
	3.47 (m)	2.24 (m)	1.65 (m)
$\Delta\delta$	0.16	0.14	0.05
	3.35 (m)	2.05 (m)	1.59 (m)
$\Delta\delta$	0.15	0.12	0.07

measured in a slightly acid medium, coupling of the methyl protons with the amine protons were observed with $^3J(\text{CH}_3\text{-NH}_2) = 7$ Hz. At neutral pH or slightly basic pH, the coupling was absent. Proton exchange is rapid in free amines but is considerably slower when the amines are complexed to a metal. The coupling constant $^3J(\text{H}_1\text{-H}_2)$ in the ethylamine and isopropylamine complexes is 8 Hz. For the cyclic amines, the four protons in position 2 are not equivalent. The two protons (H_2) that are closer to the amino group are more deshielded upon coordination than the other two ($\text{H}_{2'}$).

Acknowledgment. The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and to the Ministère de l'Éducation (FCAR) for financial support.

Registry No. $K[\text{Pt}(\text{CH}_3\text{NH}_2)\text{Cl}_3]$, 39729-73-2; $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_2]_2$, 105691-65-4; $[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)_2]_2$, 105691-66-5; $[\text{Pt}(c\text{-C}_4\text{H}_7\text{NH}_2)_2]_2$, 105691-70-1; $[\text{Pt}(c\text{-C}_5\text{H}_9\text{NH}_2)_2]_2$, 105709-78-2; $[\text{Pt}(\text{NH}_3)_2]_2$, 105691-63-2; $[\text{Pt}(\text{CH}_3\text{NH}_2)_2]_2$, 105691-64-3; $K[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)\text{Cl}_3]$, 109282-42-0; $K[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)\text{Cl}_3] \cdot 1/2\text{H}_2\text{O}$, 109282-43-1; $K[\text{Pt}(c\text{-C}_4\text{H}_7\text{NH}_2)\text{Cl}_3]$, 109282-44-2; $K[\text{Pt}(c\text{-C}_5\text{H}_9\text{NH}_2)\text{Cl}_3]$, 109282-45-3; $K(\text{Pt}(\text{NH}_3)\text{Cl}_3) \cdot \text{H}_2\text{O}$, 20574-25-8.

Supplementary Material Available: Tables SI–SIII, listing anisotropic temperature factors, fixed coordinates of the hydrogen atoms, and the weighted least-squares plane (2 pages); Table SIV, listing observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Pressure Enhancement of Substitution and Oxidative-Addition Reactions of Rhodium(I) Complexes

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Our interest in the intimate nature of substitution reactions of square-planar systems has led to a series of detailed studies on complexes of Pt(II) and Pd(II).^{2,3} The various reaction steps, viz. solvolysis, solvent substitution, and ligand substitution, were

studied as a function of steric hindrance and leaving- and entering-group effects. The reported activation parameters underline the associative nature of these reactions under all conditions. High-pressure kinetic measurements proved to be of significant help in the assignment of further mechanistic details.

Relatively few kinetic studies have been reported on the substitution reactions of Rh(I) complexes,^{4,5} and to our knowledge the effect of pressure on such reactions was not studied to date. These complexes are furthermore of particular interest because of their ability to produce octahedral Rh(III) complexes via oxidative-addition reactions, which play an important role in homogeneous catalysis.⁶ Earlier studies on oxidative-addition reactions of Ir(I) complexes resulted in volumes of activation as large as $-44 \text{ cm}^3 \text{ mol}^{-1}$, which means that the second-order rate constant will double on increasing the pressure by 400 bar (i.e. 40 MPa).⁷ The systems investigated in this study were studied at ambient pressure before,^{5,8,9} and the reported kinetic parameters suggested a promising pressure enhancement. This could be of significant importance in synthetic and homogeneous catalytic cycles involving these or related complexes of Rh(I).

Experimental Section

$\text{Rh}(\text{acac})(\text{P}(\text{O}Ph)_3)_2$, $\text{Rh}(\text{tfac})(\text{P}(\text{O}Ph)_3)_2$, $\text{Rh}(\text{acac})(\text{cod})$, and $\text{Rh}(\text{tfac})(\text{cod})$ were synthesized as described before^{5,10} (acac = acetylacetonate, tfac = trifluoroacetylacetonate, cod = cycloocta-1,5-diene). $\text{Rh}(\text{cup})(\text{CO})(\text{PPh}_3)$ was synthesized as described for $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ by using cupferron (ammonium salt of *N*-nitrosophenylhydroxylamine) instead of acetylacetonate.¹¹ Chemical analysis and UV-vis spectra were in good agreement with the theoretically expected values and those reported before, respectively. Rate constants for the substitution reactions were obtained by following the formation of $\text{Rh}(\text{phen})(\text{cod})^+$ at 482 nm on a thermostated (± 0.1 °C) high-pressure stopped-flow system.¹² The oxidative-addition reactions were followed at 340, 400, and 385 nm for the acac, tfac, and cup complexes, respectively, with a modified Zeiss PMQII spectrophotometer equipped with a thermostated high-pressure cell.¹³ All the reactions were studied under pseudo-first-order conditions. The observed first-order rate constants were calculated from plots of $\ln(A_t - A_\infty)$ vs. t , where A_t and A_∞ are the absorbances at time t and infinity, respectively. Such plots were linear for at least 2–3 half-lives of the reaction.

Results and Discussion

The investigated reactions are such that the observed first-order rate constant, k_{obsd} , depends linearly on the concentration of phen (1,10-phenanthroline) and methyl iodide for substitution and oxidative addition, respectively. This can be expressed as in (1),

$$k_{\text{obsd}} = k[\text{L}] \quad (1)$$

where L = phen or CH_3I . The experimental data confirm this expression, and no evidence could be found for a two-term rate law usually observed for substitution reactions of square-planar complexes.² Accordingly, the pressure dependence of k was estimated from the pressure dependence of k_{obsd} at constant [L],¹⁴

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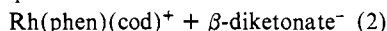
Table I. k as a Function of Pressure for the Substitution and Oxidative-Addition Reactions at 25 °C

reacn	P , bar	k^a $M^{-1} s^{-1}$	ΔV^\ddagger , $cm^3 mol^{-1}$
[Rh(acac)(cod)] + phen in MeOH ^b	50	28.1 ± 0.3	-6.9 ± 0.2
	250	29.8 ± 0.4	
	500	32.2 ± 0.4	
	750	34.7 ± 0.3	
	1000	36.7 ± 0.5	
[Rh(tfac)(cod)] + phen in MeOH ^c	50	(10.7 ± 0.1) × 10 ²	-6.0 ± 0.1
	250	(11.3 ± 0.1) × 10 ²	
	500	(12.0 ± 0.2) × 10 ²	
	750	(12.7 ± 0.1) × 10 ²	
	1000	(13.6 ± 0.2) × 10 ²	
[Rh(acac)(P(OPh) ₃) ₂] + CH ₃ I in acetone ^d	50	(8.17 ± 0.10) × 10 ⁻²	-17.3 ± 0.7
	500	(11.2 ± 0.2) × 10 ⁻²	
	1000	(15.2 ± 0.7) × 10 ⁻²	
	1500	(23.5 ± 2.0) × 10 ⁻²	
[Rh(tfac)(P(OPh) ₃) ₂] + CH ₃ I in acetone ^e	50	(9.3 ± 0.3) × 10 ⁻³	-14.5 ± 0.8
	500	(12.7 ± 0.4) × 10 ⁻³	
	1000	(17.3 ± 0.5) × 10 ⁻³	
	1500	(22.0 ± 0.6) × 10 ⁻³	
[Rh(cup)(CO)(PPh ₃) ₂] + CH ₃ I in acetone ^f	50	(1.48 ± 0.04) × 10 ⁻³	-17.1 ± 0.8
	500	(2.00 ± 0.08) × 10 ⁻³	
	1000	(2.82 ± 0.10) × 10 ⁻³	
	1500	(4.23 ± 0.14) × 10 ⁻³	
[Rh(cup)(CO)(PPh ₃) ₂] + CH ₃ I in MeOH ^g	50	(3.28 ± 0.1) × 10 ⁻³	-24.9 ± 0.5
	500	(5.40 ± 0.1) × 10 ⁻³	
	1000	(8.69 ± 0.2) × 10 ⁻³	
	1500	(14.6 ± 0.3) × 10 ⁻³	

^a $k_{obsd} = k[L]$; mean value of six kinetic runs for the substitution reactions and two to three kinetic runs for the oxidative-addition reactions. ^b [Rh(I)] = 5 × 10⁻⁴ mol dm⁻³; [phen] = 2.0 × 10⁻² mol dm⁻³. ^c [Rh(I)] = 5 × 10⁻⁴ mol dm⁻³; [phen] = 5.0 × 10⁻³ mol dm⁻³. ^d [Rh(I)] = 1.5 × 10⁻⁴ mol dm⁻³; [CH₃I] = 1.0 × 10⁻² mol dm⁻³. ^e [Rh(I)] = 5.0 × 10⁻⁴ mol dm⁻³; [CH₃I] = 5.0 × 10⁻² mol dm⁻³. ^f [Rh(I)] = 1.5 × 10⁻⁴ mol dm⁻³; [CH₃I] = 3.0 × 10⁻¹ mol dm⁻³. ^g [Rh(I)] = 1.5 × 10⁻⁴ mol dm⁻³; [CH₃I] = 1.28 × 10⁻¹ mol dm⁻³.

and the results are summarized in Table I. The volumes of activation, ΔV^\ddagger , were calculated in the usual way from the slope ($= -\Delta V^\ddagger/RT$) of $\ln k$ vs. pressure. Such plots proved to be linear within the experimental error limits for all the reactions investigated. Throughout, k increases with increasing pressure, which results in negative volumes of activation.

Substitution Reactions of Rh(I) Complexes. The investigated substitution reactions are of the general form given in (2), and all go to completion in the presence of an excess of phen. Our Rh(β -diketonate)(cod) + phen →

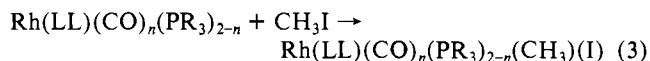


earlier ambient-pressure study⁵ demonstrated that electronegative substituents on the β -diketonate, viz. the CF₃ groups, have a significant influence on the lability of the complex. This, along with the observed linear free energy relationship and the strongly negative entropies of activation, was interpreted as evidence for an associative mechanism. Furthermore, this is the reaction mode usually observed for square-planar complexes² and is in agreement with the negative volumes of activation reported in Table I. The nature of the solvent as well as the bidentate nature of the leaving groups (β -diketonate) presumably prohibits a solvolysis reaction to contribute toward the overall substitution process.

Volumes of activation are generally discussed in terms of intrinsic (ΔV^\ddagger_{intr}) and solvational volume changes (ΔV^\ddagger_{solv}), i.e. volume changes due to changes in bond lengths and bond angles and changes in electrostriction, respectively. During the associative attack of phen in reaction 2, no major changes in electrostriction are expected and the reported ΔV^\ddagger values mainly represent ΔV^\ddagger_{intr} . The average value of -6 cm³ mol⁻¹ (Table I) is rather typical for associative-substitution reactions of square-planar complexes.² Due to the lack of any comparable data for other Rh(I) systems, the results are compared to substitution data for other square-planar

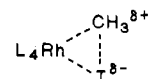
complexes. Our earlier studies^{15,16} revealed typical volumes of activation of between -3 and -14 cm³ mol⁻¹ for substitution reactions of Pd(II) complexes, depending on the nature (charge and size) of the entering and leaving groups. These data can all be interpreted in terms of a limiting A mechanism,² although the absolute values are probably smaller than expected. However, this expectation is based on related data reported for substitution reactions of octahedral complexes, which are characterized by more negative ΔV^\ddagger values for limiting A processes.⁷ It is important to keep in mind that the formation of a five-coordinate transition state during associative substitution of a square-planar complex may be accompanied by structural changes from tetragonal pyramidal to trigonal bipyramidal and an associated volume increase. The latter can counterbalance the volume decrease due to bond formation and account for the relatively low absolute ΔV^\ddagger values. Nevertheless, the results are, on the basis of our earlier experience,² very typical for an associative-substitution mechanism. The rate-determining binding of phen is followed by a fast ring-closure reaction and the loss of the β -diketonate ligand.

Oxidative-Addition Reactions of Rh(I) Complexes. The investigated oxidative-addition reactions are all of the type shown in (3), where LL = a singly charged bidentate anion, $n = 0$ or 1, and R = Ph or OPh. Our earlier studies on the kinetics of



these reactions^{8,9} suggested an ionic S_N2 (associative) addition mechanism. However, a concerted three-center cis-addition mechanism, as suggested for the addition of homonuclear molecules like H₂ and I₂,¹⁷ could not be ruled out on the basis of the available data.

The results in Table I demonstrate that the acac complex is ca. 10 times more reactive than the tfac complex. The introduction of the trifluoro group decreases the electron density on the metal center, making it a weaker nucleophile (Lewis base) and less reactive toward oxidative addition. The reactions in acetone exhibit an average ΔV^\ddagger of -16 cm³ mol⁻¹, which is, for instance, in close agreement with the value of -20 cm³ mol⁻¹ reported for the oxidative addition of CH₃I to Ir(PPh₃)₂(CO)Cl in acetone¹⁸ and values between -15 and -30 cm³ mol⁻¹ for this reaction in other solvents. During oxidative addition, a volume decrease is expected because of bond formation (ΔV^\ddagger_{intr}) and increasing electrostriction (ΔV^\ddagger_{solv}) due to a polar transition state involving heterolytic cleavage of the CH₃-I bond. Treatment of the ΔV^\ddagger data for the oxidative addition of CH₃I to Ir(PPh₃)₂(CO)Cl as a function of the solvent parameter q_p ¹⁹ resulted in a ΔV^\ddagger_{intr} value (the intercept of a plot of ΔV^\ddagger vs. q_p) of -17 cm³ mol⁻¹.^{2,18} This would mean that the ΔV^\ddagger value of -16 cm³ mol⁻¹ found in the present study for the reactions in acetone mainly represents the intrinsic volume decrease due to bond formation. It was argued before¹⁸ that such a ΔV^\ddagger value is not negative enough to suggest the simultaneous formation of two bonds between the rhodium center and the CH₃I moieties in a concerted three-center mechanism. However, in the light of the substitution ΔV^\ddagger reported in this paper, a value of -16 cm³ mol⁻¹ may be interpreted in terms of the formation of two bonds. On the other hand, the reaction must involve a polar transition state since ΔV^\ddagger is significantly more negative for this reaction in MeOH (Table I). A more polar solvent can stabilize a polar transition state and account for the increase in k reported in Table I. We thus propose a transition state for the three-center mechanism of the form



It should, however, be kept in mind that at some stage during the

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(19) $q_p = (D - 1)/(2D + 1)$, where D is the dielectric constant of the solvent.

process the formal oxidation state of rhodium changes from +1 to +3, which will be accompanied by a significant decrease in volume. This could also partly contribute toward the value of $-16 \text{ cm}^3 \text{ mol}^{-1}$ found in this study, which would then favor a linear transition state of the type $\text{L}_4\text{Rh} \cdots \text{CH}_3 \cdots \text{I}$ as suggested before.¹⁸ We are confident that a combined solvent/pressure dependence study, presently under way in our laboratories, will enable us to differentiate between these two possible transition states.

The pressure enhancement observed for the oxidative-addition reaction is quite significant, corresponding to a doubling of the rate constant for an increase in pressure of 100 MPa. The significantly higher pressure sensitivity of the oxidative-addition reactions as compared to the substitution reactions of Rh(I) complexes is partly due to the formation of more than one bond and partly due to the polar nature of the transition state.

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Registry No. Rh(acac)(cod), 12245-39-5; Rh(tfac)(cod), 32610-46-1; Rh(acac)(P(OPh)₃)₂, 25966-19-2; Rh(tfac)(P(OPh)₃)₂, 95041-07-9; Rh(cup)(CO)(PPh₃)₃, 105833-24-7; 1,10-phenanthroline, 66-71-7; methyl iodide, 74-88-4.

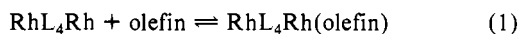
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Trinity University, San Antonio, Texas 78284

Olefin Coordination with Rhodium(II) Perfluoroalkanoates in Solution

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The coordination of olefins to rhodium(II) carboxylates is not generally observed in solution, and its absence has been interpreted to indicate that these transition-metal compounds are incapable of such association.^{1,2} We recently reported olefin coordination with dirhodium(II) tetrakis(trifluoroacetate) in dichloromethane solution.³ The complexes were characterized by a slight, but significant, decrease in λ_{max} for the $\pi^*_{\text{RhRh}} \rightarrow \sigma^*_{\text{RhRh}}$ absorption band⁴ and a substantial increase in molar absorptivity, as well as by increases in the NMR chemical shifts of olefinic protons resulting from the combination of the dirhodium tetracarboxylate with alkenes. Only 1:1 adducts were formed (eq 1, L = carboxylate), and their apparent equilibrium constants for association,



which ranged over 2 orders of magnitude, increased with increasing electron-donating ability of olefin substituents. Dirhodium(II) tetraacetate gave no evidence for adduct formation under these conditions.

Recently Schurig has reminded us⁵ of evidence that he obtained which established olefin coordination with a variety of di-

rhodium(II) tetracarboxylates that included the acetate and benzoate derivatives.^{6,7} Relative stability constants were determined from retention data by complexation gas chromatography⁸ rather than from spectroscopic measurement. Although the two methods operate on different phases, the lack of spectroscopic evidence for complexation of alkanes by dirhodium(II) tetraacetate in solution is disconcerting and requires explanation.

Drago and co-workers have reported that dirhodium(II) tetrakis(heptafluorobutyrate) has significantly greater covalent and electrostatic σ -acceptor properties than the corresponding butyrate.⁹ This report prompted our prior use of $\text{Rh}_2(\text{OOCF}_3)_4$ to examine olefin coordination.³ In the present study we describe the enhanced capability of $\text{Rh}_2(\text{pfb})_4$ (pfb = perfluorobutyrate) for coordination with alkenes and the linear correspondence between solution association constants and relative stability constants determined by complexation gas chromatography.

Experimental Section

Rhodium(II) Carboxylates. $\text{Rh}_2(\text{OOCCH}_3)_4$ was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$,¹⁰ and $\text{Rh}_2(\text{pfb})_4$ was obtained from rhodium(II) acetate in refluxing perfluorobutyric acid containing perfluorobutyric anhydride.⁹ The isolated product was purified by continuous extraction in anhydrous dichloromethane and, following concentration of the blue solution, $\text{Rh}_2(\text{pfb})_4$ was obtained as finely divided blue crystals. Green crystals were obtained upon drying in a vacuum oven. Proton NMR spectral analyses demonstrated the absence of acetate, and spectrophotometric determinations in dichloromethane provided a λ_{max} value of 626 nm ($\epsilon = 248 \text{ M}^{-1} \text{ cm}^{-1}$). Rhodium(II) tetrafluoroacetate was prepared according to the methods described by Telsler and Drago.¹¹

Association Constants. Rhodium(II) perfluorobutyrate is very hygroscopic, and extreme care was taken to exclude traces of water, which cause a spectral shift to λ_{max} 615–618 nm. Dichloromethane was distilled from calcium hydride and stored over molecular sieves. Solutions of $\text{Rh}_2(\text{pfb})_4$ in CH_2Cl_2 were prepared in an inert-atmosphere glovebox under nitrogen, and they were transferred to quartz cells sealed by double septa. A similar procedure was employed with the less hygroscopic $\text{Rh}_2(\text{OOCF}_3)_4$. Olefins were distilled under reduced pressure before use and stored under nitrogen.

Spectrophotometric determinations were performed following sequential injections of 2.5–5.0 μL of a concentrated solution of the olefin in dichloromethane (0.500–1.00 M) into the rhodium(II) carboxylate solution (3.00 mL). Spectral scans were obtained from a HP 8451A diode array spectrophotometer, and olefin additions were continued through at least eight sequential injections until the limiting λ_{max} of the rhodium(II) carboxylate-olefin complex could be determined, which in all cases was $585 \pm 5 \text{ nm}$ with no evident dependence on the structure of the olefin. The initial addition of olefin to $\text{Rh}_2(\text{pfb})_4$ generally produced a shift in λ_{max} from 626 nm to 605–610 nm, and much smaller changes in λ_{max} occurred with subsequent olefin additions. A similar effect was not evident in olefin additions to $\text{Rh}_2(\text{OOCF}_3)_4$, whose initial λ_{max} was 610 nm.

Equilibrium constants were calculated from the measured absorbances at several wavelengths in the range of 550–590 nm for $\text{Rh}_2(\text{pfb})_4$ complexes and in the range of 570–600 nm for $\text{Rh}_2(\text{OOCF}_3)_4$ complexes. A plot of $1/\Delta A$ vs. $1/[\text{olefin}]$ provided a linear relationship (correlation coefficient > 0.99) that described a 1:1 complex between the rhodium(II) carboxylate and olefin from which the apparent equilibrium constant was calculated. The first one or two absorbance measurements for experiments performed with $\text{Rh}_2(\text{pfb})_4$ were not included in these determinations because of their apparent deviation from this relationship. At least two independent measurements were made for each determination. Reproducible values for equilibrium constants were obtained from measurements at two or more wavelengths.

Spectral Analyses of Olefin Complexes. In addition to spectrophotometric methods, proton NMR analyses were performed on a Varian FT-80A spectrometer to evaluate the influence of the rhodium(II) carboxylate on proton chemical shifts. The rhodium(II) carboxylate was dissolved in CDCl_3 , and fixed amounts of the alkene were injected through a septum into the NMR tube. Spectra were taken immediately after addition and also at 30–60 min following addition of the olefin.

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