Activation Volumes of Substitution Reactions on Neutral and Cationic Organometallic Platinum(IV) Complexes: Definite Proof of Selective Associative Activation

Carlos Gallego,[†] Gabriel González,[†] Manuel Martínez,*[,†] and André E. Merbach[‡]

Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain, and Institut de Chimie Moléculaire et Biologique, École Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland

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The activation volumes for the substitution reactions of a series of Pt(IV) sulfide organometallic complexes have been determined as a function of the entering and leaving ligands, as well as the inert organometallic skeleton. The results agree with the existence of a tunable associatively/dissociatively activated mechanism operating on these complexes, depending on the electronegativity of the substitution-inert spectator ligands.

Introduction

Substitution on inert Pt(IV) octahedral t_{2g}^6 complexes has been a difficult subject to deal with, given the important amount of side reactions which appear in most of the processes not involving organometallic compounds.[1−5] Furthermore, the importance of the oxidative-addition−reductive-elimination reactions in most of the catalytic cycles in which platinum compounds are involved has hindered the effort dedicated to the subject.[6−10] Nevertheless, it is clear that any of these reactions is usually preceded by a substitution process involving complexes with Pt−C σ-bonds. These bonds are expected to produce important inductive effects on the platinum center, which results in a certain tendency for dissociatively activated reactions.[11]

We have been involved in the study of the mechanisms by which electrophilic C−H bond activation takes place on Pd(II) and Rh(II) complexes.[12−14] Furthermore, the study of the mechanism for the oxidative-addition reactions of these bonds on square-planar Pt(II) dimethyl complexes has also been carried out for some known cyclometalated complexes.[15,16] All of these reactions have been found to operate via a dissociation of one of the ligands around the platinum center as an initial step prior to the oxidative addition of the C−X bond.[17−20] The existence of these three-coordinate intermediates had already been proposed in some instances where the number of Pt−C bonds existing in the complex seemed to play a crucial role.[11,21−24]

We have also studied the substitution reactions on similar cyclometalated octahedral Pt(IV) complexes.[25−28] The effect of two Pt−CH_3 and a Pt−C^{aryl} bond seems clearly to produce complexes where Pt(IV) resembles Pt(II), and in most of the cases the reaction mechanism is dissociatively activated, as expected,[24] including the formation of a pentacoordinated unsaturated intermediate.[29−31] Nevertheless, when the Pt(IV) center is coordinated to highly electron withdrawing groups or atoms, such as F and $CC_5F_4CH{=}NCH_2Ph$, and with

[†] Universitat de Barcelona.
[‡] École Polytechnique Fédérale de Lausanne.

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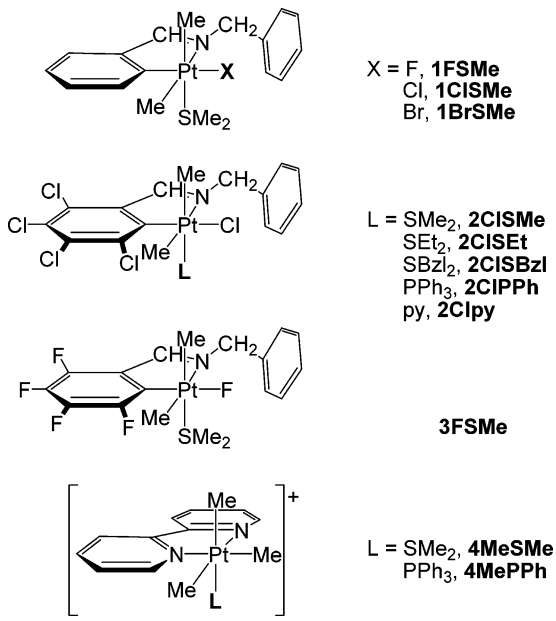
Chart 1



relatively small entering (PPh_3) and leaving (SMe_2) ligands the presence of an associatively activated path has been detected.[25]

We present in this paper the study of the activation volumes for the substitution reactions of a series of neutral and cationic Pt(IV) octahedral t_{2g}^6 complexes depicted in Chart 1. The values obtained agree with the operation of a dissociatively activated mechanism for all the systems studied, the volume of activation being directly related to the size of the leaving ligand, as well as its intramolecular interactions with the inert skeleton on decoordination. Furthermore, for the neutral systems, the solvent effects detected for systems with suitable proton centers, which allow solvent-assisted interactions of the leaving ligand with the rest of the molecule in the transition state, are made evident by the activation volume data determined. For the cationic complexes, the solvent effects agree very well with what should be expected from both the polarity of solvent used and the degree of increase of electrostriction in the transition state once the leaving ligand has began dissociation.

Results and Discussion

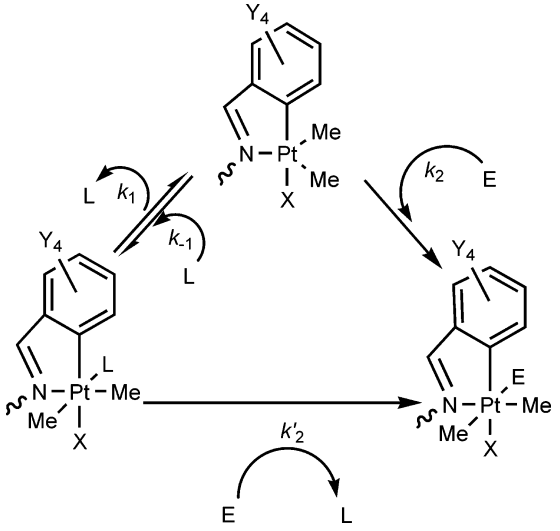
Substitution processes taking place on the neutral complexes indicated in Chart 1 (**1FSMe**, **1ClSMe**, **1BrSMe**, **2ClSMe**, **2ClSEt**, **2ClSBzl**, **2ClPPh**, **2Clpy**, **3FSMe**) have been found to occur through the combination of dissociatively and associatively activated reaction mechanisms shown in Scheme 1.[25] Nevertheless, only for the compound **3FSMe** has the path described by the rate constant k_2' been found to be operative when the entering phosphine ligands have cone angles $\theta \leq 165°$. The rate laws indicated in eqs 1 and 2 have been applied

$$k_{obs} = \frac{k_{-1}k_{-2}[L] + k_1k_2[E]}{k_{-1}[L] + k_2[E]} \xrightarrow{[E] \gg [L]} k_{obs} = k_1 \quad (1)$$

$$k_{obs} = k_{2'}[E] \quad (2)$$

in all cases; the value of the limiting first-order rate

Scheme 1



constant for the dissociatively activated mechanism, k_1, has been found to be the same as the value obtained for the exchange of coordinated SMe_2, k_{ex}, as measured from magnetization transfer data.[32] Furthermore, monitoring of the substitution reactions in the absence of leaving ligand produced well-behaved first-order absorbance versus time traces, from which the value of k_1 is obtained as k_{obs}.[27,28] This behavior allows an easy determination of k_1, as well as of the corresponding volume of activation, with a single set of experiments. For the associatively activated process, k_2', a full range of entering ligand concentrations had to be used at each pressure for the measurements.

For the dissociatively activated substitution processes occurring on complexes **2ClSMe**, **2ClSEt**, **2ClSBzl**, **2ClPPh**, and **2Clpy** the volumes of activation shown in Table 1 correlate with the bulk of the leaving ligand dissociating in the transition state. That is, for systems in which no solvent involvement in the transition state has been established from the values of $\Delta S^{\ddagger}$ (**2ClSMe**, **2ClPPh**, and **2Clpy** in acetone solution and **2ClSEt** and **2ClSBzl** in toluene solution),[25] the values increase monotonically on going from SMe_2 to SEt_2, $SBzl_2$, and PPh_3. Even for the substitution processes studied in acetone solution for complexes with solvent involvement in the transition state (**2ClSEt** and **2ClSBzl**), the trend is the same, although the difference between the expansion on dissociative activation in acetone and toluene for the SEt_2 is larger. If the solvent-assisted interaction of the CH_2 protons of the ligand[35] with the complex spectator ligands is responsible for the negative values obtained for $\Delta S^{\ddagger}$, the less bulky SEt_2 ligand could more

(32) Magnetization transfer experiments between free and coordinated SMe_2 have been carried out on **1ClSMe** at different temperatures. The proton signal of the dimethyl sulfide ligand was separated enough from that of free SMe_2 to run such experiments (Figure S1, Supporting Information). The values obtained for the chemical transfer constant, k_{ex}, using the CIFIT program[33,34] (1.8×10^{-2}, 8.3×10^{-2}, 2.9×10^{-1} and 86×10^{-1} s^{-1} at 10, 20, 30, and 40 °C), are in perfect agreement with the substitution-measured decoordination k_1 values (Figure S2, Supporting Information). The same sort of experiments could not be carried out with the other complexes studied, due to the proximity of the bound and free SMe_2 proton signals.

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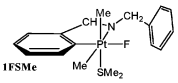
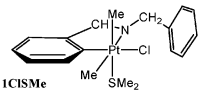
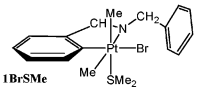
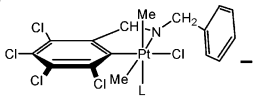
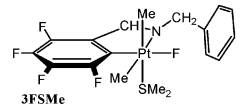
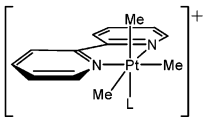
Table 1. Kinetic and Activation Parameters for the Substitution Reactions Studied According to Chart 1

Compound	Leaving ligand, L	Entering ligand	Solvent	$10^3 \times {}^{298}k_1$ /s^{-1}	$\Delta H_1^{\ddagger}$ /kJ mol^{-1}	$\Delta S_1^{\ddagger}$ /J $K^{-1}mol^{-1}$	$\Delta V_1^{\ddagger}$ (T /K)[a] /cm^3mol^{-1}
 1FSMe	SMe_2	PPh_3	Acetone/ Toluene	37[b]	70±4[b]	−39±12[b]	13.0±0.8 (312.1)
 1ClSMe	SMe_2	PPh_3	Acetone	150[b]	92±3[b]	48±10[b]	20.0±0.3 (303.2)
 1BrSMe	SMe_2	PPh_3	Acetone/ Toluene	210[b]	99±3[b]	72±9[b]	18.7±0.2 (303.2)
	SMe_2	PPh_3	Acetone/ Toluene	40[b]	91±3[b]	31±10[b]	16.3±0.4 (312.1)
	SEt_2	PPh_3	Acetone	210[b]	57±4[b]	−69±12[b]	9.4±0.3 (303.2)
 2ClSMe 2ClSEt 2ClSBzl 2ClPPh 2Clpy			Toluene	520[b]	88±6[b]	42±19[b]	18.4±0.6 (293.7)
	$SBzl_2$	PPh_3	Acetone	530[b]	57±2[b]	−62±8[b]	17.3±0.4 (293.4)
			Toluene	910[b]	78±2[b]	15±7[b]	21.4±0.6 (293.7)
	PPh_3	py	Acetone	0.10[b]	112±3[b]	52±11[b]	25.1±1.9 (313.0)
	py	PPh_3	Acetone	3.1[c]	91±4[c]	11±14[c]	13.5±1.1 (286.1)
 3FSMe	SMe_2	PCy_3	Acetone	12[b]	75±4[b]	−33±14[b]	10.3±0.3 (322.9)
		PPh_3	Acetone	k_2[d] 3.9 $M^{-1}s^{-1}$	33±3[d]	−125±10[d]	−18.3±0.6 (278.6)
 4MeSMe 4MePPh	SMe_2	PPh_3	Acetone	13[e]	88±5	13±15	6.1±1.9 (283.1)
			Toluene	5.3[e]	88±2	6±7	12.1±0.8 (283.1)
	PPh_3	py	Acetone	0.029[e]	111±3	38±9	15.5±0.7 (312.1)

[a] Activation volume data in acetone solution, unless differences are stated. [b] From refs 25 and 26. [c] From ref 28. [d] From the second-order rate constant.[25] [e] Interpolated from Eyring plots.

easily establish solvent-assisted interactions with the inert skeleton of the complex, producing a larger compressive contribution to the activation volume.

In the same line, for the dissociatively activated systems, the differences found for the expansion on dissociation of the dimethyl sulfide ligand from complexes **1ClSMe** (20.0 cm^3 mol^{-1}) and **2ClSMe** (16.3 cm^3 mol^{-1}) has to be related with the early/late position of the transition state in the reaction coordinate for the same value of activation enthalpy (Table 1). The greater electron-withdrawing characteristics of the perchlorinated ligand in **2ClSMe** does not allow the same advance of dissociation/expansion to go to a transition state with the same enthalpic expense. Although these differences are already visible from the $\Delta S^{\ddagger}$ data, the values of $\Delta V^{\ddagger}$ are much more reliable and involve a smaller intrinsic error. $\Delta V^{\ddagger}$ is calculated from the slope of the ln k versus P plot (Figure 1, Table 1), not from the extrapolation at $T = \infty$ in classical Eyring plots. The same reasoning applies to the difference in the values on going from **2ClSMe** (16.3 cm^3 mol^{-1}) to **3FSMe** (10.3 cm^3 mol^{-1}), where perfluorination increases, even more, the electron-withdrawing effect on the Pt(IV) center. In this case, the enthalpic demands for the transition state are even smaller for the **3FSMe** complex, and this should also produce an earlier position of the transition state for the process; the limit would be the changeover to an associatively activated substitution mechanism detected for some of the reactions studied for this complex, which are discussed below.

With respect to the trends observed for the **1FSMe**, **1ClSMe**, and **1BrSMe** series of compounds, it is interesting to note that the **1ClSMe** and **1BrSMe** pair probably also are in agreement with the notion of a longer Pt−S bond for the bromo derivative in the ground state, as shown in the X-ray crystal structures of similar Cl/Br pairs (0.03 C).[27] For the **1FSMe** fluoro complex, neither the size nor the electronic characteristics of the

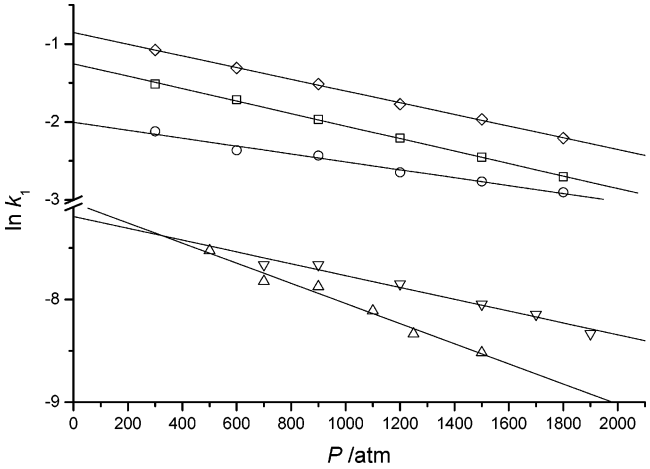


Figure 1. Pressure dependence of the value of the dissociation constant, k_1, in acetone solution: (○) **1FSMe** (39.0 °C); (□) **1ClSMe** (30.1 °C); (◇) **1BrSMe** (30.1 °C); (△) **2ClPPh** (40.0 °C); (▽) **2Clpy** (13.0 °C).

F ligand explain in a simple way the small positive value for the activation volume. For this compound, the negative values of $\Delta S^{\ddagger}$ have been tentatively associated with the formation of intramolecular interactions between the dissociating sulfide and the halogen ligand, interactions that are not assisted by the solvent.[25] In fact, the values determined for $\Delta S^{\ddagger}$ are the same in acetone and toluene solutions. Therefore, although the dissociation of the SMe_2 ligand should produce an expansion effect, the existence of the above-mentioned interactions should also create a compression effect, even for this dissociatively activated path.[36,37] Both contributions would be reflected in a less positive $\Delta V^{\ddagger}$ value than expected, as indicated in Table 1.

These general trends are evident also in the studied ionic derivatives **4MeSMe** and **4MePPh** in Chart 1, where the increase in leaving ligand size from SMe_2 to PPh_3 produces a dramatic increase of $\Delta V^{\ddagger}$ from 6.1 to 15.5 $cm^3\ mol^{-1}$, the same increment of ca. 9 $cm^3\ mol^{-1}$ as that observed for the above-described neutral **2ClSMe** and **2ClPPh** systems. Furthermore, the enthalpic demand for the process agrees very well with such a dissociative activation; the stronger $Pt^{IV}-P$ bond needs a much larger contribution of enthalpy to get to such an expanded transition state. Equilibrium constant determinations carried out on these types of complexes[28] agree with the preference of this Pt(IV) compound for phosphines versus sulfides (SMe_2, $SBzl_2$) and amines ($MeNH_2$, Me_2NH, Me_3N). The ionic nature of the complex explains the generally smaller expansion to go to the transition state; electrostriction of the solvent (acetone) should occur on the increase of the charge density produced by partial dissociation of the leaving ligand. When the reaction is carried out in toluene, the important difference in the value of $\Delta V^{\ddagger}$ is associated with the very small compressive electrostriction contribution of the solvent to the expansion on dissociation.

The negative $\Delta V^{\ddagger}$ entry for the **3FSMe**/PPh_3 system in Table 1 corroborates the previously published observation of the operation of an associatively activated

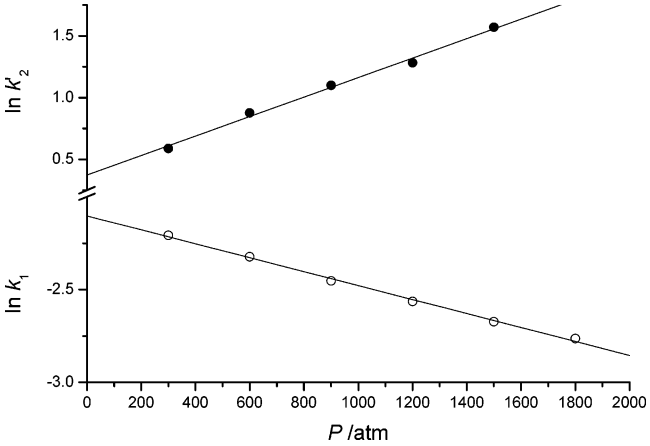


Figure 2. Pressure dependence in acetone solution of the value of k_1 (PCy_3 as entering ligand, 49.8 °C, ○) and k_2' (PPh_3 as entering ligand, 5.5 °C, ●) for **3FSMe**.

substitution mechanism on **3FSMe** with phosphines with $\theta < 165°$.[25] As seen in Figure 2, the pressure dependence of the first-order (k_1) and second-order (k_2') rate constants (Scheme 1) is the opposite, producing $\Delta V^{\ddagger}$ values of 10.3 $cm^3\ mol^{-1}$ for dissociative activation and of -18.3 $cm^3\ mol^{-1}$ for associative activation. This change is not surprising, as the aforementioned relatively low values of $\Delta V^{\ddagger}$ and $\Delta H^{\ddagger}$ for the dissociative path (k_1) point to a definitively lesser degree of dissociation in the transition state. This is especially true by taking into account the inherently stronger Pt−S bond in the complex, due to the increase of the electron-withdrawing character of the spectator ligands. Nevertheless, these differences have not produced the same effect on the **1FSMe** complex or on the same perfluorinated complex with the $SBzl_2$ ligand instead; in these cases the mechanism is fully dissociative, as found for the other systems.[25] We have prepared the equivalent SEtMe and SEt_2 derivatives of the perfluorinated complex[38] in order to tune as much as possible the associativeness/dissociativeness of the substitution processes studied. For both complexes the reactions carried out in acetone solution at 20 °C have been found to occur solely through the dissociatively activated path characterized by k_1, even with pyridine as entering ligand. The values of the first-order dissociative rate constant with PPh_3 and py entering ligands (0.027 and 0.060 s^{-1} for the SEtMe and SEt_2 derivatives, respectively) are probably too high to enable the operation, under the experimental conditions, of the associatively activated path. The extra bulkiness of the sulfide ligand makes difficult the partial association of a seventh ligand to the platinum center; in fact, an increase of 5° (165 to 170°) in the cone angle of the entering phosphine ligands has already been proved enough to produce a complete changeover in the reaction mechanism from an associatively to a dissociatively activated one, as observed

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(38) The equivalent SEtMe- and SEt_2-derived complexes have been prepared from substitution of the SMe_2 ligand in **1FSMe** with the corresponding sulfides. The complexes were characterized by their significant ^1H NMR spectra (250 MHz, $CDCl_3$, 298 K, ppm, TMS): SEtMe derivative, 1.02 (d, J(FH) = 7.7 Hz, J(PtH) = 66 Hz, Me^{ax}), 1.63 (dd, J(FH) = 9.3 Hz, J(FH) = 7.3 Hz, J(PtH) = 62 Hz, Me^{eq}), 2.00 (s, J(PtH) = 12 Hz, Me^{SEtMe}), 1.10 (t, J(HH) = 7.5 Hz, Et^{SEtMe}, (CH_3)), 2.51 (m, Et^{SEtMe}, (CH_2)), 8.65 (s, J(PtH) = 47 Hz, CH); SEt_2 derivative, 0.89 (d, J(FH) = 7.4 Hz, J(PtH) = 68 Hz, Me^{ax}), 1.58 (dd, J(FH) = 9.3 Hz, J(FH) = 7.2 Hz, J(PtH) = 63 Hz, Me^{eq}), 1.05 (t, J(HH) = 7.4 Hz, $SEt_2(CH_3)$), 2.53 (m, $SEt_2(CH_2)$), 9.17 (s, J(PtH) = 48 Hz, CH).

for other known systems.[39,40] Consequently, the expected stronger Pt−S bond for these complexes with greater σ-donor capabilities[35] cannot compensate for the difficulties in the transient entry of a seventh ligand in the coordination sphere.

Experimental Section

Compounds. 1FSMe, **1ClSMe**, **1BrSMe**, **2ClSMe**, **2ClSEt**, **2ClSBzl**, **2ClPPh**, **2Clpy**, **3FSMe**, and **4MePPh** have been prepared according to established literature methods.[20,25,26,28,41] Their characterization was confirmed via ^{1}H NMR. **4MeSMe** has been prepared by treatment of a solution of [Pt(Me)$_3$I(2,2′-bpy)] (3.8×10^{-4} mol in 25 cm^3 of acetone) with $AgCF_3SO_3$ (3.8×10^{-4} mol); after it was stirred for 15 min, the solution was filtered through Celite, 6.8×10^{-3} mol of SMe_2 was added, and the mixture was stirred for another ca. 30 min. The solvent was evaporated at reduced pressure and the solid washed several times with hexane. Yield: 72%. Anal. Calcd (found) for $C_{16}H_{23}F_3N_2O_3S_2Pt\cdot H_2O$: C, 30.7 (30.7); H, 4.0 (3.7); N, 4.5 (4.5); S, 10.3 (10.9). ^{1}H NMR (250 MHz, acetone-d_6, 298 K, ppm, TMS): 0.64 (s, ^2J(PtH) = 70 Hz, Me^{ax}), 1.13 (s, ^2J(PtH) = 68 Hz, 2 × Me^{eq}), 1.98 (s, ^3J(PtH) = 12 Hz, SMe_2). ^{195}Pt NMR (53.5 mHz, acetone-d_6, 298 K, ppm, $H_2[PtCl_6]$): −2827.

Kinetics. The reactions were followed by UV−vis spectroscopy in the 500−330 nm range, where none of the solvents absorb. At atmospheric pressure runs with $t_{1/2} > 170$ s were recorded on an HP8452A instrument equipped with a thermostated multicell transport; for runs with $t_{1/2} < 7$ s an Applied Photophysics stopped-flow instrument connected to a J&M TIDAS spectrophotometer was used. Observed rate constants were derived from absorbance versus time traces at the wavelengths where a maximum increase and/or decrease of absorbance was observed. For runs at variable pressure, a homemade stopped flow device connected to a J&M TIDAS spectrophotometer was used.[42] No dependence of the observed rate constant values on the selected wavelengths was detected, as expected for reactions where a good retention of isosbestic points is observed. The general kinetic technique is that previously described;[43] in all cases the platinum concentration was kept at $(2-6) \times 10^{-4}$ M to avoid undesired decomposition reactions.[26] For the dissociatively activated processes, given the kinetic approach taken to measure the values of the limiting rate constants indicated in eq 1, no leaving ligand was added to the reaction mixtures monitored;[27,28] in all cases the observed absorbance versus time traces behaved as first order, producing reproducible rate constants within a 5% error. Table S1 (Supporting Information) collects all the obtained k_{obs} values for all the complexes studied as a function of the starting complex, entering ligand, solvent, pressure, and temperature. The fitting of the results to the equations leading to the relevant kinetic and activation parameters was done by commercial least-squares packages; the errors quoted in Table 1 correspond to the standard deviation of the fitting.

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Supporting Information Available: k_{obs} values for all the systems studied (Table S1), a magnetization transfer experiment for the **1ClSMe** system (Figure S1), and an Eyring plot for k_1 in acetone solution for the **1ClSMe** system (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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