

# Kinetic Evidence of an Arm-Off Mechanism in Complexes of Hemilabile Hybrid Ligands. Oxidative Addition of Methyl Iodide to the Rhodium(I) Complex [Rh(2,6-bis(benzylthiomethyl)pyridine)(CO)]PF<sub>6</sub> via Competitive Pathways

Mauro Bassetti,\* Alberto Capone, and Michela Salamone

*"Istituto CNR di Metodologie Chimiche", Sezione Meccanismi di Reazione, and Dipartimento di Chimica, Università "La Sapienza", 00185 Roma, Italy*

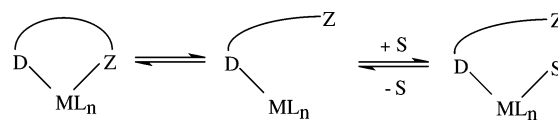
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Kinetic experiments of the oxidative addition of methyl iodide to the cationic rhodium(I) carbonyl complex [Rh(L)(CO)]PF<sub>6</sub> (**1**; L = 2,6-bis(benzylthiomethyl)pyridine) forming the observable rhodium(III) methyl species [RhI(L)(CO)Me]PF<sub>6</sub> have been performed by FT-IR. The reaction yields the isolable rhodium acyl complex [RhI(L)(COMe)]PF<sub>6</sub>. Plots of  $k_{\text{obs}}$  versus concentration of methyl iodide indicate that the reaction proceeds by two parallel pathways, one which is first order in complex **1** and zero order in MeI ( $k_1$ ) and one which is first order in complex **1** and first order in MeI ( $k_2$ ). The first-order pathway displays scarce dependence on the nature of the solvent ( $k_1$  (31 °C):  $6.7 \times 10^{-6} \text{ s}^{-1}$ , acetone;  $1.1 \times 10^{-5} \text{ s}^{-1}$ , dichloromethane;  $1.7 \times 10^{-5} \text{ s}^{-1}$ , acetonitrile), while a larger solvent effect is observed for the second-order pathway ( $k_2$  (31 °C):  $6.4 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ , dichloromethane;  $5.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , acetone;  $1.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ , acetonitrile), in agreement with the dissociative and associative character of the two routes, respectively. The  $k_{\text{obs}}$  values for the reaction in methanol exhibit a saturation behavior when plotted against the concentration of methyl iodide. <sup>1</sup>H NMR spectra of complex **1** at different temperatures in the range 208–302 K display a fluxional behavior typical of tridentate complexes of S,N,S ligands, due to pyramidal inversion at the sulfur centers. The methyl iodide independent pathway and the saturation behavior in methanol are due to reversible decoordination of one thiobenzyl arm from rhodium, yielding a transient three-coordinate bidentate N,S species which reacts rapidly with MeI. The data are discussed in terms of the concept of kinetic detection of hemilability.

## Introduction

Ligand hemilability is a peculiar feature displayed by some transition-metal complexes in which one donor atom of a polydentate system equilibrates between a coordinated, "close", and a dissociated, "open", mode, as indicated in Scheme 1.<sup>1</sup> The hemilabile property arises from the different donor strengths within the chelating system, in particular from the presence of substitutionally inert and substitutionally labile groups. Since the dissociated form is characterized by electronic and coordinative unsaturation, it may display appealing features in terms of reactivity. In fact, it can provide a free coordination site at the metal during reaction, as well as stabilize the starting complex or reactive intermediates. The intramolecular dissociation of one arm, called the "arm-off" mechanism, has been implicated in various reactions, and a variety of complexes of hemilabile ligands have been used successfully in catalysis,

## Scheme 1. Hemilabile Character of the Hybrid Bidentate Ligand D–Z



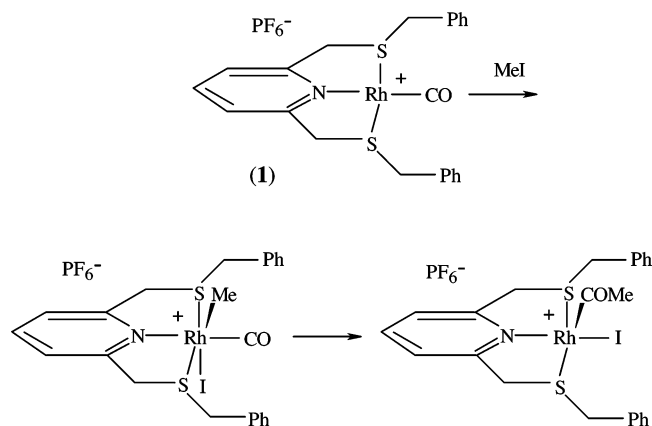
often exhibiting considerable rate enhancements.<sup>1c</sup> This field is gaining increasing importance, as testified by the extensive number of publications focused on the concept of hemilability. Only scattered examples on the synthesis and use of hybrid hemilabile ligands and derived complexes are listed here.<sup>2</sup>

Evidence of hemilability comes from ligand substitution reactions (Scheme 1), in which an entering ligand (S) has displaced the weak donor arm, from fluxional behavior due to dissociation and recoordination of weakly bonding moieties, or from the presence of monomeric as well as dimeric metal complexes.<sup>1b</sup> The hemilabile character can also be detected by spectroscopy, under conditions which have forced the equilibrium toward the "open" form.<sup>3</sup> Means of evaluating the effect of hemilability along the reaction coordinate are

\* To whom correspondence should be addressed. E-mail: mauro.bassetti@uniroma1.it.

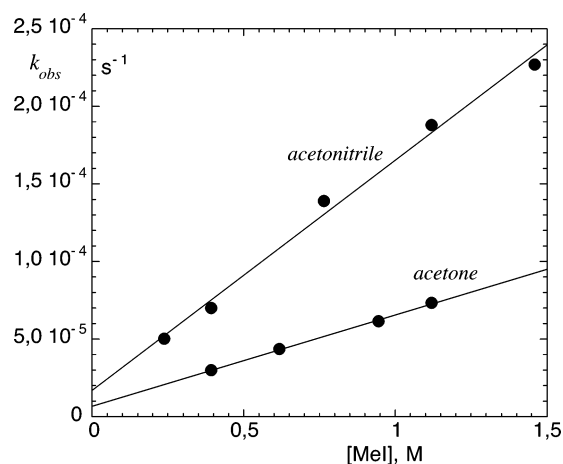
(1) (a) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680–699. (b) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233–350. (c) Espinet, P.; Soulantica, K. *Coord. Chem. Rev.* **1999**, *193–195*, 499–556. (d) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658–2666.

**Scheme 2. Sequence of Oxidative Addition–Migratory Insertion in the Reaction of Complex 1 with MeI**



missing, and the concept of kinetic detection of hemilability has not been contemplated so far.<sup>1a–c</sup>

Oxidative addition of methyl iodide to complexes of platinum metals is a fundamental process in organometallic chemistry.<sup>4</sup> We have recently reported on the reaction of the rhodium(I) carbonyl complex [Rh(L)(CO)]PF<sub>6</sub> (**1**; L = 2,6-bis(benzylthiomethyl)pyridine) with methyl iodide, as the first mechanistic study of the reaction of a cationic rhodium(I) complex and of the oxidative addition–migratory insertion sequence in a complex of a tridentate ligand (Scheme 2).<sup>5</sup> Cationic rhodium(I) carbonyl complexes of neutral 2,6-bis(substituted thiomethyl)pyridine ligands exhibit square-planar geometry, in which the ligand imposes trans-dithioether coordination to the pyridine-bound rhodium, in solution<sup>6a</sup> and in the solid state.<sup>6b</sup> We report rate studies of the oxidative addition reaction of methyl iodide to complex **1** in various solvents, which highlight the occurrence of the phenomenon of hemilability involving the thioether group. The analysis allows a



**Figure 1.** Plot of  $k_{obs}$  values vs concentration of methyl iodide for the reaction of complex **1** in acetonitrile and in acetone, at 31 °C.

quantitative evaluation of the reactivity of “closed” and “open” coordination modes of the hybrid ligand 2,6-bis((benzylthio)methyl)pyridine.

## Results and Discussion

The reaction of the complex [Rh(L)(CO)]PF<sub>6</sub> proceeds via two consecutive processes: namely, oxidative addition of methyl iodide to form easily observable intermediate rhodium(III) methyl complexes and CO migratory insertion to yield the corresponding acetyl complex [Rh(L)(COMe)]PF<sub>6</sub> (Scheme 2). In this work, we have extended the initial kinetic study carried out in neat methyl iodide and in acetonitrile to the solvents acetone, dichloromethane, and methanol and report on the results regarding the oxidative addition step. The reaction proceeds in all solvents, with quantitative transformation of complex **1**, as observed from the FT-IR spectra at the end of the kinetic runs. Therefore, no equilibration is detectable between complex **1** and the rhodium(III) methyl complexes, which are the products of oxidative addition. An NMR analysis of this reaction has revealed the formation of two isomers of the intermediate rhodium(III) methyl complex shown in Scheme 2. The runs have been performed by following the carbonyl band of **1** at 2015 cm<sup>-1</sup>, as previously described.<sup>5</sup>

A plot of pseudo-first-order rate constants ( $[MeI] \gg [1]$ ) obtained from the disappearance of complex **1**,  $k_{obs}$ , vs the concentration of methyl iodide is shown in Figure 1, for the reactions in acetonitrile and in acetone. Figure 2 shows the analogous plot for the reaction in dichloromethane. In all cases, the values of  $k_{obs}$ , reported in Table 1, show a linear dependence on the concentration of methyl iodide. The slopes of the lines correspond to the second-order rate constants in the various solvents, which are reported in Table 2 as  $k_2$  values (M<sup>-1</sup> s<sup>-1</sup>). The change of  $k_2$  with solvent (acetonitrile > acetone > neat methyl iodide  $\approx$  dichloromethane) indicates that increased solvent polarity assists the oxidative addition reaction, presumably characterized by the development of charge in the rate-determining step. The overall mechanistic information, composed of dependence on  $[MeI]$ , solvent effect, and activation parameters in acetonitrile,<sup>5</sup> conform with the classical bimolecular S<sub>N</sub>2

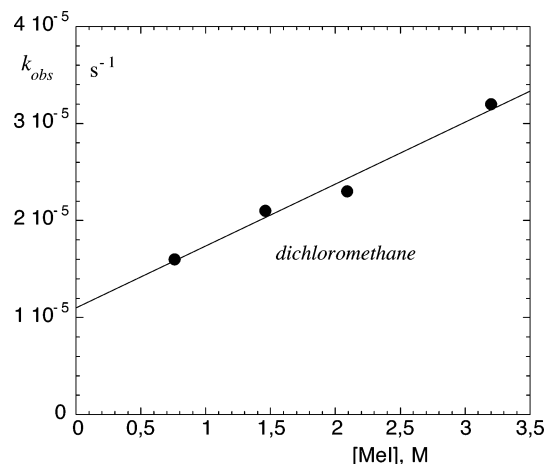
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**Figure 2.** Plot of  $k_{\text{obs}}$  values vs concentration of methyl iodide for the reaction of complex **1** in dichloromethane, at 31 °C.

**Table 1.** Values of  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) for the Reaction of the Complex  $[\text{Rh}(\text{L})(\text{CO})\text{PF}_6$  (**1**; **L** = 2,6-Bis((benzylthio)methyl)pyridine) with Methyl Iodide in Methanol, Acetone, and Dichloromethane at 31 °C<sup>a</sup>

[MeI], M	$k_{\text{obs}}$ , $\text{s}^{-1}$ in $\text{CH}_2\text{Cl}_2$	[MeI], M	$k_{\text{obs}}$ , $\text{s}^{-1}$ in $\text{CH}_2\text{Cl}_2$
0.76	$1.6 \times 10^{-5}$	2.09	$2.3 \times 10^{-5}$
1.46	$2.1 \times 10^{-5}$	3.20	$3.2 \times 10^{-5}$
[MeI], M	$k_{\text{obs}}$ , $\text{s}^{-1}$ in $\text{Me}_2\text{CO}$	[MeI], M	$k_{\text{obs}}$ , $\text{s}^{-1}$ in $\text{Me}_2\text{CO}$
0.392	$2.99 \times 10^{-5}$	0.944	$6.15 \times 10^{-5}$
0.618	$4.35 \times 10^{-5}$	1.120	$7.35 \times 10^{-5}$
[MeI], M	$k_{\text{obs}}$ , $\text{s}^{-1}$ in MeOH	[MeI], M	$k_{\text{obs}}$ , $\text{s}^{-1}$ in MeOH
0.16	$6.5 \times 10^{-6}$	1.53	$7.8 \times 10^{-5}$
0.50	$3.6 \times 10^{-5}$	2.09	$8.7 \times 10^{-5}$
1.05	$6.3 \times 10^{-5}$		

<sup>a</sup> [1] = 0.005–0.010 M.

**Table 2.** Values of Kinetic Constants for the Reaction of  $[\text{Rh}(\text{L})(\text{CO})\text{PF}_6$  (**1**; **L** = 2,6-Bis((benzylthio)methyl)pyridine) with MeI in Various Solvents, at 31 °C

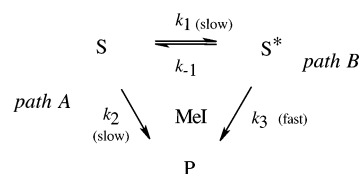
solvent	$\epsilon^a$	$k_1$ ( $\text{s}^{-1}$ )	$k_2$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$k_{-1}/k_3$
$\text{CH}_2\text{Cl}_2$	9.1	$[1.1(\pm 0.1)] \times 10^{-5}$	$[6.4(\pm 0.6)] \times 10^{-6}$	
MeCOMe	20.7	$[6.7(\pm 1)] \times 10^{-6}$	$[5.9(\pm 0.1)] \times 10^{-5}$	
MeCN	37.5	$[1.7(\pm 0.6)] \times 10^{-5}$	$[1.4(\pm 0.1)] \times 10^{-4}$	
MeOH	32.6	$[1.7(\pm 0.1)] \times 10^{-4}$		1.8 ( $\pm 0.05$ )

<sup>a</sup> Dielectric constant.

mechanism exhibited by neutral and anionic rhodium(I) carbonyl complexes, involving Rh–Me bond formation and C–I bond breaking in the rate-determining step.<sup>7</sup>

This analysis takes into account a route involving both complex **1** and MeI in the rate-determining step. However, the graphs of Figures 1 and 2 show a positive  $y$  intercept, which is more evident in dichloromethane due to the lower reactivity of the  $\text{S}_{\text{N}}2$  pathway. Plots of  $k_{\text{obs}}$  vs the concentration of one reagent characterized by a linear dependence and an intercept on the  $y$  axis are due to the presence of parallel first-order (in this

**Scheme 3**



case, first order in complex **1**, zero order in MeI,  $k_1$ ,  $\text{s}^{-1}$ ) and second-order (first order in complex **1**, first order in MeI;  $k_2$ ,  $\text{M}^{-1} \text{s}^{-1}$ ) pathways.<sup>8</sup> This is described by eq 1. In the graphs, the slope of the line represents  $k_2$  and the intercept represents  $k_1$ .

$$k_{\text{obs}} = k_1 + k_2[\text{MeI}] \quad (1)$$

Therefore, in addition to the  $\text{S}_{\text{N}}2$  pathway there is a second route in which the rate is independent of methyl iodide. A graphical representation of a chemical model satisfying eq 1 is shown in Scheme 3, where S is the substrate and P is the product. Path A represents the  $\text{S}_{\text{N}}2$  route to the oxidative addition product. The zero-order dependence on MeI implies the formation of a reactive species,  $\text{S}^*$ , via rate-determining ( $k_1$ ) rearrangement of the substrate, followed by fast reaction ( $k_3$ ) with MeI (path B). Due to the higher reactivity of  $\text{S}^*$  with respect to complex **1**, this species reacts with MeI as soon as it forms and does not accumulate in the reaction medium.

Table 2 lists the values of both  $k_1$  and  $k_2$  rate constants. The contribution of path B to the reaction can be interpolated from the plots of Figures 1 and 2, by comparing the  $k_{\text{obs}}$  value at a chosen concentration of methyl iodide with the  $k_1$  value. For instance, at  $[\text{MeI}] \cong 1$  M about 10% of the consumption of complex **1** occurs via path B in acetone and in acetonitrile, while in dichloromethane this route accounts for about 60% of the reaction. The contribution of path B is relatively large at low concentration of methyl iodide and becomes smaller with increasing  $[\text{MeI}]$ .

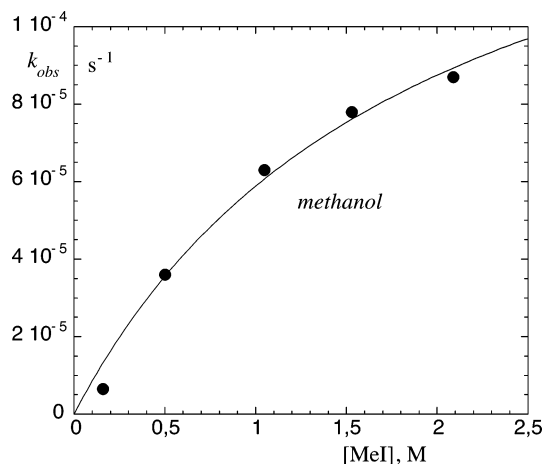
The kinetic behavior of the reaction of complex **1** with MeI appears peculiar. In fact, while the linear dependence on concentration of MeI is characteristic of oxidative addition to  $\text{d}^8$  transition-metal complexes,<sup>7a,9</sup> we have found only one case in which a plot of  $k_{\text{obs}}$  vs

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**Figure 3.** Plot of  $k_{obs}$  values vs concentration of methyl iodide for the reaction of complex **1** in methanol, at 31 °C. The solid line represents the fitting of the experimental points with eq 2.

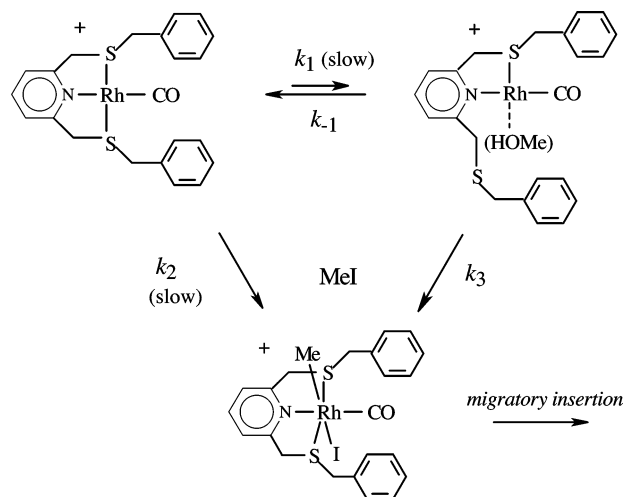
[MeI] reveals a non-zero intercept on the  $y$  axis, among the reactions of rhodium(I) complexes.<sup>10</sup> The reaction of the complex  $[Rh(\text{cupferrate})(CO)(PPh_3)]$ , coordinated by the bidentate anionic ligand  $PhNON=O$ , with methyl iodide proceeds through two competing rate-determining steps, one of which is zero order in methyl iodide. It has been proposed that this route is due to a solvent-assisted, and rate-determining, rearrangement of the square-planar rhodium(I) complex into a trigonal-bipyramidal intermediate, which reacts rapidly with MeI, and is indicated as a solvent-catalyzed pathway.

The plot of  $k_{obs}$  vs [MeI] for the reaction in the polar protic solvent methanol shows a saturation effect, in which the rate constants tend toward a limiting value at increasing concentration of the electrophile (Figure 3). This behavior, described by eq 2 as adopted to path

$$k_{obs} = \frac{k_1 k_3 [MeI]}{k_{-1} + k_3 [MeI]} \quad (2)$$

B of Scheme 3, is typical of a reaction which proceeds via an intermediate species, in equilibrium with the substrate. The formation of this species can be assisted by solvent.<sup>11</sup> Path B of Scheme 3 can account for this behavior, the saturation effect arising from competitive return of  $S^*$  to substrate S or reaction with MeI.<sup>12</sup> A linear plot obtained from a graph of  $1/k_{obs}$  vs [MeI] yields the values of  $k_1$  ( $1.7 \times 10^{-4} s^{-1}$ ) and the ratio  $k_{-1}/k_3 = 1.8$ . This kinetic analysis indicates a larger value of  $k_1$  in methanol than in the other solvents, which may explain why path B becomes dominant with respect to path A. A saturation behavior in oxidative addition reactions of methyl iodide with rhodium(I) complexes is also not common. For instance, the  $k_{obs}$  values for the reaction of the complex  $[Rh(CO)_2I_2]NBu_4$  show linear plots up to high concentrations of MeI, so that the

#### Scheme 4. Mechanism of the Reaction of Complex **1** with MeI



reaction is overall first order in rhodium complex and first order in MeI.<sup>9g</sup>

A mechanistic description which accounts for the kinetic patterns observed in acetonitrile, acetone, and dichloromethane is shown in Scheme 4. The four-coordinate complex  $[Rh(L)(CO)]PF_6$  reacts following path A via a rate-determining attack of MeI ( $k_2$ ). Reversible decoordination of one thiobenzyl arm from rhodium generates an equilibrium between the substrate and a transient three-coordinate 14-electron species, which reacts rapidly with MeI, via path B. This species forms under steady-state conditions and is therefore not detectable by spectroscopic means. The system does not remain 14e, since the novel species returns to the substrate by recoordination of the pendant arm ( $k_{-1} \gg k_1$ ), reacts with MeI ( $k_3 \gg k_1$ ), or becomes temporarily solvated before either step. Via this route, the dissociative process of the thiobenzyl group is the rate-determining step ( $k_1$ ) of the oxidative addition reaction.<sup>13</sup>

In agreement with this interpretation, the  $k_1$  values show scarce dependence on the nature of the aprotic solvent, as expected for an intramolecular dissociative step, with respect to the  $k_2$  values. Square-planar complexes of  $d^8$  transition metals are known to undergo substitution of thioether ligands via dissociative mechanisms involving coordinatively and electronically unsaturated 14-electron species.<sup>14</sup> Recently, upon studying the kinetics of ring closure of bidentate hemilabile ligands on platinum(II) metal centers, Romeo and co-workers have found that the substitution reactions of the homoditopic S–S ligand in  $[Pt(Ph)_2(\kappa^2-S-S)]$  (S–S = 1,2-bis(phenylthio)ethane, 1,3-bis(phenylthio)propane) by a diphosphine, bis(diphenylphosphino)methane or bis(diphenylphosphino)propane, in dichloromethane proceed according to eq 1; i.e., the plots of  $k_{obs}$  values as a function of diphosphine concentration afford straight

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(12) In principle, other mechanisms are compatible with saturation kinetics. See ref 8, p 15, and also: (a) Jenks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969. (b) Bassetti, M.; Monti, D. *J. Am. Chem. Soc.* **1993**, *115*, 4658–4664.

(13) Cation–anion or dimer–monomer equilibria as alternative phenomena to cause the MeI-independent pathway are unlikely, especially if considered as rate-determining events. In fact, the  $\nu_{CO}$  stretching values of complex **1** are similar both in the polar solvent acetonitrile and in dichloromethane, suggesting negligible ion pairing. Complex **1** is yellow both in the solid and in solution, while dimeric species involving Rh–Rh bonding interactions are red.<sup>6b</sup>

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lines with a  $y$  axis intercept different from zero.<sup>15</sup> In analogy to Schemes 3 and 4, this work indicates the presence of parallel pathways, one of which involves the rate-determining dissociation of one sulfur group to afford the [Pt(Ph)<sub>2</sub>( $\kappa^1$ -S-S)] transient intermediate. In the reaction of [Pt(PPh<sub>3</sub>)<sub>3</sub>] with MeI, the reactivities of [Pt(PPh<sub>3</sub>)<sub>3</sub>] and of [Pt(PPh<sub>3</sub>)<sub>2</sub>], resulting from dissociation of PPh<sub>3</sub>, have been determined by kinetic measurements.<sup>16</sup>

Less straightforward to understand is the behavior observed in methanol. In an alternative to a process proceeding via an intermediate species, a trivial effect arising from reduced polarity of the medium with increasing concentration of methyl iodide cannot be ruled out. However, it is possible that the specific coordinative ability of MeOH assists and stabilizes the formation of the transient species and increases  $k_1$  with respect to the other solvents. In this case, recoordination of the thioether arm ( $k_{-1}$ ) and oxidative addition ( $k_3$ ) compete for the intermediate and become comparable in rate. Effects arising from H-bonding interactions with the metal center<sup>7c,9g</sup> or with the free thioether arm<sup>17</sup> cannot be excluded. Peculiar behaviors of reactions carried out in methanol have been reported. For instance, it has been described that coordination of methanol molecules to a cationic rhodium(I) metal center of a hybrid tridentate P-C-O ligand is essential to create low-energy pathways for C-H and C-C bond activation.<sup>18</sup>

The proposal of a reaction pathway involving an arm-off mechanism of the ligand in complex **1** should be evaluated in the context of the known properties of transition-metal complexes coordinated by S-N-S ligands. The hemilabile character of these systems has been demonstrated by dynamic <sup>1</sup>H NMR studies carried out by Orrell et al. on [ReX(CO)<sub>3</sub>L] complexes, in which L is the bidentate (N-S) 2,6-bis(*p*-tolylthio)methylpyridine or 2,6-bis((methylthio)methyl)pyridine. An intramolecular fluxional process exchanging coordinated and uncoordinated thioalkyl or thioaryl groups as well as pyramidal inversion of sulfur in the bound moiety have been revealed by spectra at different temperatures.<sup>19a</sup> Both processes occur by loosening of the Re-S bond. Palladium(II) methyl complexes of 2,6-bis-(R-thiomethyl)pyridine ligands (L; R = Me, *t*-Bu, Ph) exist as the neutral bidentate (N-S) species [Pd(L)-MeCl] bearing a potentially coordinating arm in position 6 of the pyridine ring or as the cationic tridentate (S-N-S) species [Pd(L)Me]Cl, in which the pendant thioether arm has replaced the chloride ligand. Canovese et al. have shown that the two species can exist in equilibrium and undergo insertion of 1,1'-dimethylallene into the palladium-carbon bond at different rates, the bidentate species being more reactive.<sup>20</sup> The presence of chloride ion, which modulates the equilibrium be-

tween the two complexes, can affect the overall rate of allene insertion. A scheme analogous to Scheme 4 has been proposed. In this case, the bidentate and tridentate species are stable and different starting materials. Spectroscopic and kinetic experiments have allowed the authors to determine *directly* the equilibrium constant of the bidentate-tridentate coordination and to determine, *independently* in each case, the rates of reaction of the bidentate species and of the tridentate complex, which were found to differ by 2 orders of magnitude.

We have looked for an indication of the specific hemilabile character of complex **1**, which would be independent of the kinetic study. The methylene groups, *py*-CH<sub>2</sub>-S and S-CH<sub>2</sub>Ph, of complex **1** show an exchange-broadened <sup>1</sup>H NMR spectrum in dichloromethane-*d*<sub>2</sub> at room temperature. When the temperature is lowered, the H-4 hydrogen of the pyridine ring splits into two triplets at  $\delta$  7.75 and 7.78 ( $J = 7.9$  Hz) ppm, which are well resolved at -43 °C, and also the methylene region is increasingly resolved. At -65 °C, this region is characterized by four AB systems, two of high intensity at  $\delta$  4.36, 4.28 (2 d, 18 Hz) and  $\delta$  4.11, 4.00 (2 d,  $J = 13$  Hz) ppm and two of lower intensity, the first one at  $\delta$  4.49, 4.27 (partially hidden) (2 d,  $J = 17$  Hz) and the second at  $\delta$  4.23 ppm being unresolved. The two sets of AB systems are in 4:1 ratio, as determined by integration of the doublets at 4.00 and 4.49 ppm. The doublet at  $\delta$  4.11 shows an <sup>3</sup> $J_{\text{Rh-H}}$  coupling constant of 1.4 Hz. The two sets of signals are attributable to the diastereomeric mixture of the racemic-*dl* and meso isomers of **1**, due to the presence of the stereogenic sulfur centers. The signals become broad again upon raising the temperature, resulting in two coalesced peaks,  $\delta$  4.45 (*py*-CH<sub>2</sub>S) and 4.17 ppm (S-CH<sub>2</sub>-Ph), at 29 °C. The spectra at 29 and -65 °C are shown in Figure 4. The pyramidal inversion of the coordinated sulfur atoms causes this fluxional behavior.<sup>6c,19</sup> Therefore, the intramolecular exchange of coordinated and noncoordinated thiobenzyl groups in complex **1** is confirmed by the dynamic NMR properties.

The occurrence of a four-coordinate 16-electron and of a transient three-coordinate 14-electron species reacting in parallel toward methyl iodide represents an interesting case among oxidative addition reactions.<sup>16</sup> Although 14-electron complexes of rhodium(I) are known to be involved in various processes,<sup>18,21</sup> the oxidative addition reaction of MeI generally proceeds via the four-coordinate complex.<sup>7c,9</sup> In the context of hemilability, it should be noted that oxidative addition of methyl iodide to iridium(I) complexes of the type [IrCl(CO)(phosphine)] was found to be 100 times faster when the phosphine ligand is PMe<sub>2</sub>(*o*-MeOC<sub>6</sub>H<sub>4</sub>) than when it is PMe<sub>2</sub>(*p*-MeOC<sub>6</sub>H<sub>4</sub>) or PMe<sub>2</sub>Ph. This effect has been attributed to temporary coordination of the *o*-methoxy group on iridium, with enhanced electron density, and hence reactivity, on the metal.<sup>22</sup>

With regard to the CO migratory insertion step, which leads from the rhodium(III) methyl species to the isolable acyl complex [Rh(I)(L)(COMe)]PF<sub>6</sub> (Scheme 2),

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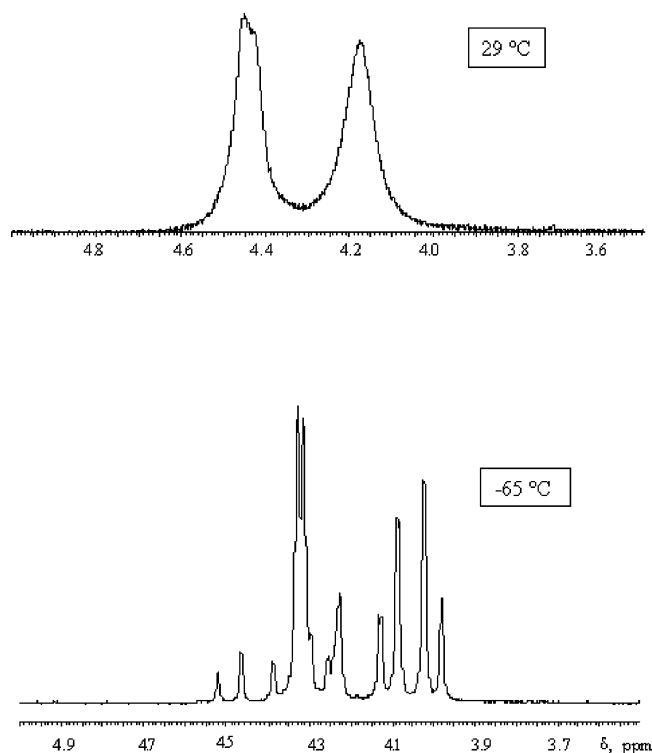
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**Figure 4.**  $^1\text{H}$  NMR spectra of complex **1** in the range  $\delta$  5–3.5 ppm at 29 and  $-65$   $^\circ\text{C}$ , in dichloromethane- $d_2$ .

we had no experimental information about the possible role played by the “opening” and “closing” of the (benzylthio)methyl arm on rhodium.<sup>5</sup> The CO migratory insertion reaction is in fact independent of methyl iodide concentration, as expected for an intramolecular step. Such opening and closing mechanisms have been inferred in the oxidative addition–migratory insertion sequence of methanol carbonylation processes catalyzed by very active rhodium(I) complexes of mixed phosphine–phosphite<sup>1a,9e</sup> or phosphine–ether bidentate

ligands.<sup>23</sup> It is interesting to note that the reaction with MeI of a complex containing a bis(oxazoline)-derived tridentate ligand,  $[\text{Rh}(\kappa^3\text{N},\text{N},\text{N}\text{-pybox})(\text{CO})]\text{PF}_6$  (pybox = 2,6-bis[4'-(*S*)-isopropylloxazolin-2'-yl]pyridine), stops at the oxidative addition product.<sup>24</sup> Due to the structural similarity with complex **1**, and since steric effects should not adversely affect the migratory insertion step in this N,N,N system, it is possible that the different behavior depends on the diversities of the ligand donor strength.

## Conclusions

This work represents the first kinetic observation of the arm-off mechanism operating along the reaction coordinate in a rhodium metal complex of a tridentate ligand. The kinetic analysis displays the intramolecular ligand dissociation step as well as its role in the reaction. Since the most relevant implication of hemilability is *reactivity*, the kinetic approach should play an important role in this field, and we expect that the concept here presented will find validation in other systems, as in the case of the ligand substitution reactions.<sup>15,25</sup>

## Experimental Section

All operations were carried out under an argon atmosphere using standard Schlenk line techniques. Methyl iodide and dichloromethane were distilled from calcium hydride, acetonitrile from phosphorus pentoxide, and methanol from magnesium turnings. Acetone was a reagent grade solvent. A Bruker AM-300 spectrometer was used for the  $^1\text{H}$  NMR spectra, and the chemical shifts are reported in values relative to tetramethylsilane. The kinetic experiments were performed as described previously.<sup>5</sup>

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