Oxidative Addition of Iodomethane to Charge-Tuned Rhodium(I) Complexes

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The zwitterionic Rh^I monocarbonyl complex [Rh(EtSNS)(CO)] (1, EtSNS = EtNC(S)Ph₂P= NPPh₂C(S)NEt⁻) was reacted with iodomethane in dichloromethane, yielding the stable acetyl-Rh^{III} complex [Rh(EtSNS)(COCH₃)I] (4). Complex 4 was characterized in solution and in the solid state by X-ray diffraction analysis. The rate constant of the reaction $[5.48 (7) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} \text{ at } 25 \text{ °C CH}_2\text{Cl}_2]$ and the activation parameters ΔH^{\ddagger} [28(3) kJ mol⁻¹] and ΔS^{\ddagger} [-173(10) J mol⁻¹ K⁻¹] were determined, confirming a nucleophilic addition mechanism. The rate constant was obtained by monitoring the acetylic product by ¹H NMR, under second-order conditions ($[Rh]/[CH_3I] = 1$). Complex 1 can be mono- and biprotonated with HX (X = PF₆, OTf, NO₃), forming [Rh(HEtSNS)(CO)]X (2·X) and $[Rh(H_2EtSNS)(CO)]X_2$ (3 · X₂), respectively. A decrease of the calculated DFT Mulliken atomic population on the Rh atom is observed along the series $1 \ge 2 \ge 3$ in accordance with the variation of the coordinated CO stretching frequency. Compounds 2.X were also reacted with iodomethane, forming complexes $[Rh(HEtSNS)(COCH_3)I]X$ (5·X), stable in solution for a short time, that transform by deprotonation into 4 and into unidentified decomposition products. The rate constants were determined under pseudofirst-order conditions due to the lower reactivity $[2 \cdot NO_3 = 24.6 (6) \times 10^{-5} M^{-1} s^{-1}; 2 \cdot OTf = 12.7 (3)$ $\times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$; **2**·PF₆ = 2.50 (6) $\times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$]. The activation parameters for **2**·PF₆ were also determined. The influence of the counterion could be explained assuming that the different non-metalcoordinated anions form hydrogen bonding with the NH group of $2 \cdot X$, which in turn causes a variation of the electron density on the Rh center. A good correlation between the CO stretching frequencies and the rate constants was observed. The experimental rate constant for complex 1 is 1 order of magnitude higher than the one calculated using the linear regression function obtained for the $2 \cdot X$ series (experimental = 5.48 \times 10⁻² M⁻¹ s⁻¹; calculated = 1.29 \times 10⁻³ M⁻¹ s⁻¹), pointing out that the monoprotonated complexes react more slowly than expected. Both steric and electronic effects were examined and held responsible for this reduced reactivity. Complexes $3 \cdot X_2$ reacted too slowly, yielding complex 4 and unidentified decomposition products, hindering the determination of the rate constants.

Introduction

It is established, by experiment and calculation, that oxidative addition of methyl iodide to square-planar rhodium(I) carbonyl complexes proceeds via a nucleophilic mechanism, where the rate-determining step shows a S_N2 transition state.¹ Consequently, if the reactivity is not strongly moderated by steric effects, due to bulky substituents or ligand orientation that hinders the space above *and* below the Rh coordination plane,²

higher reaction rates are found for complexes with high electron density on the Rh center, which behaves as a nucleophile toward the carbon atom of CH₃I. The value of the IR stretching frequency of coordinated CO is taken as an indicative measure of the electron density on the Rh atom, and a qualitative correlation between the electronic density, the CO frequency, and the reaction rate is possible (as a rule of thumb, faster kinetics are observed for complexes with a CO frequency of about 1990 cm⁻¹ or lower). However, Haynes et al.³ suggest that similar complexes with sensibly different CO stretching frequency, namely, trans-[Rh(CO)(PPh₃)₂I] and [Rh(CO)-(dppe)I] [dppe = 1,2-bis(diphenylphosphino)ethane; ν (CO) = 1981 and 2011 cm⁻¹, respectively], might be expected to have similar electron density on the Rh center. In our opinion, this shows that the Rh electron density is dependent not only on the kind of donor atoms in the ligands but also on their orientation and geometry and that this density is indeed reflected by the CO stretching frequency. A calculation on the cis and trans isomers of [Rh(CO)(PPh₃)₂Cl] that we performed (vide *infra*) apparently supports that coordination geometry might indeed influence both the CO stretching and the Mulliken

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population on the Rh atom. Nonetheless, in different complexes with the same donor atoms and the same coordination geometry, the CO stretching frequency can be used, with confidence, as a measure of the electronic densities.

The rhodate complex $[Rh(CO)_2I_2]^-$ (the "Monsanto" catalyst)⁴ is taken as reference in comparing kinetic constant values; until now, the highest ones have been determined for carbonyl complexes containing bis(imino)carbazolide⁵ and N-heterocyclic carbene⁶ ligands. It can be assumed that for geometrically analogous complexes whose CO stretching frequencies are equal, the electron density on the Rh atom is the same and the variation of the sterics of ligand substituents allows the observation of steric effects alone.⁷ For Rh^I carbonyl complexes, the oxidative addition is often followed by the migratory CO insertion, forming an acetyl complex. This reaction seems faster when steric demand is high^{8,9} but slower for high electron density complexes.¹⁰ Apparently, rate-enhancing electronic effects in the migratory CO insertion are observed when strong π -donor ligands are used.¹¹ In this paper we report kinetic and thermodynamic studies of the oxidative addition of iodomethane to the zwitterionic metalate¹² [Rh(EtSNS)(CO)]¹³ (1) and its protonated derivatives:¹⁴ [Rh(HEtSNS)(CO)]X ($2 \cdot X$) and $[Rh(H_2EtSNS)(CO)]X_2 (\mathbf{3} \cdot X_2) [X = PF_6, OTf, NO_3; EtSNS =$ EtNC(S)Ph₂P=NPPh₂C(S)NEt⁻].¹⁵ In the case of [Rh(EtSN-S)(CO)], ¹H NMR was useful to obtain real second-order kinetic parameters, while in most literature cases, pseudo-first-order rate constants were determined.¹⁶ In the case of the monoprotonated compounds 2 · X, a quantitative correlation between their CO

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Scheme 1. Formation of the Mono-cationic Complex 2 and the Di-cationic Complex 3 by Protonation of the Zwitterionic Metalate 1



stretching frequency with different counterion and the kinetic constant was observed, showing a long-range electronic effect due to the different hydrogen-bonding acceptor properties of the anion. The biprotonated complexes were found, as expected, to react very slowly.

Results and Discussion

As previously reported, ^{13,14} the $S, N, S - \kappa^3$ complex [Rh(EtSN-S)(CO)] (1) can be prepared by reaction of HEtSNS with $[Rh(CO)_2Cl]_2$ in the presence of *t*-BuOK or by bubbling CO in a solution of the *S*,*S*- κ^2 complex [Rh(EtSNS)(cod)] (cod = 1,5cyclooctadiene). During these reactions, the unstable $S_{1}S^{2}-\kappa^{2}$ intermediate [Rh(EtSNS)(CO)₂] was observed, monitoring the solution reaction by FTIR (ν CO: 2075, 2009 cm⁻¹). The coordination of the nitrogen atom raises the electron density of the Rh, as inferred from the lower CO stretching frequency of 1 [ν CO (CH₂Cl₂): 1967 cm⁻¹]. Compound 1 is a biprotic base and can be protonated, affording cationic species [Rh(HEtSN-S(CO)⁺ (2) and $[Rh(H_2EtSNS)(CO)]^{2+}$ (3), in which protons bind to the nitrogen atoms of the thioamidyl functions $[pK_a]$ in $CH_2Cl_2 = 6.5(3)$ and 4.8(4)¹⁴ (Scheme 1). Compound **3** can be conveniently prepared by using an excess of acid, while 2 is obtained by mixing 1 and 3 in 1:1 molar ratio.

The electronic distribution varies dramatically, as evidenced by the C–S and C–N bond distances¹⁴ and by the ³¹P{¹H} NMR chemical shift values (Table 1). In the case of $2 \cdot X$ (X = PF₆, OTf, NO₃), two ³¹P resonances are present,¹⁴ suggesting that proton exchange is very slow (exchange can be fast, i.e., when X = CF₃COO⁻; δ = 27.9 ppm, unpublished results). In turn, protonation influences the electron density on the Rh(CO) system, as reflected by the infrared CO stretching frequencies (Table 1).

The Mulliken populations for the Rh atom were calculated at the BS-0 level for 1, 2, and 3 in the gas phase and varies from -0.338 to -0.263 au (Table 2), showing that the protonation of one thioamidic function induces a 13% decrease in the electronic population for the monoprotonation and a 22% decrease for the biprotonation (a decrease of 8% and 16%, respectively, has been found in solution simulation). This decrease in the calculated population is in agreement with the trend found experimentally for the CO stretching frequencies. A more detailed calculation has been carried out at the BS-I level, in both the gas and solution phase, to confirm the BS-0 data. The results are consistent with the above-mentioned trend (see Table S1 of the Supporting Information).

As suggested by a referee of this paper, it would be of great interest to understand if two complexes with essentially the same electron density at the metal could have different CO stretching frequencies if the strength of back-donation to CO differs (for example depending on whether a π -acceptor or π -donor ligand

Table 1. vCO Stretching (CH₂Cl₂ solution and HATR-ZnSe crystal) and Relevant ¹H NMR, ³¹P{¹H} NMR, and ¹⁰³Rh NMR Chemical Shifts of 1, $2 \cdot X$, and $3 \cdot X_2$ (X = PF₆, OTf, NO₃)

			= (\$)	,			
	1	$2 \cdot NO_3$	2 •OTf	$2 \cdot PF_6$	$3 \cdot (NO_3)_2$	$3 \cdot (OTf)_2$	$3 \cdot (PF_6)_2$
ν CO (HATR, ZnSe, cm ⁻¹)	1953	1968	1977	1979	2006	2011	2013
$\nu CO (CH_2Cl_2, cm^{-1})$	1967	1989	1992	1994	2008	2013	2017
¹ H NMR (NH, CD ₂ Cl ₂ , ppm)		10.5	10.8	11.0	10.4	10.6	11.1
${}^{31}P{}^{1}H}$ NMR (CD ₂ Cl ₂ , ppm)	16.6	35.2-25.1	36.7-22.1	36.7-19.9	41.1	39.3	38.2
¹⁰³ Rh NMR (CD ₂ Cl ₂ , ppm)	-6886			-6888			-6901^{a}

^a:In CD₂Cl₂/CD₃OD (1:1 ratio).

Table 2. Mulliken Populations (au) for Selected Atoms, in the Gas Phase and in Solution (PCM, CH₂Cl₂) for 1, 2, and 3^a

Gas Phase									N ₁		
	Rh	S1	S2	N1	N2	N3	С	0	P1	P2	
1	-0.338	-0.055	-0.055	-0.381	-0.381	-0.820	0.313	-0.271	0.937	0.937	, ^{C1} S1
2	-0.294	0.087	0.0095	-0.409	-0.373	-0.823	0.315	-0.229	0.899	0.922	Pí ['
3	-0.263	0.137	0.134	-0.417	-0.417	-0.825	0.311	-0.188	0.905	0.903	N
	CH ₂ Cl ₂									/ 00	
	Rh	S1	S2	N1	N2	N3	С	0	P1	P2	P ₂
1	-0.395	-0.120	-0.116	-0.376	-0.358	-0.835	0.302	-0.280	0.940	0.939	C_2^{-1}
2	-0.361	0.097	-0.074	-0.420	-0.348	-0.836	0.324	-0.264	0.904	0.934	1
3	-0.331	0.123	0.132	-0.413	-0.402	-0.827	0.337	-0.239	0.912	0.908	N ₂

^a For compound **2**, the protonation is on the N1 atom [B3LYP/BS-0//B3LYP/BS-0; BS-0 = 6-31G** + Lanl2DZ(Rh)].



is situated trans to the CO). Given that the measure of the electronic density is a difficult task and can be performed by electron density studies on very good, low-temperature, singlecrystal X-ray diffraction data, DFT calculation were performed on the cis and trans isomers of [Rh(CO)(PPh₃)₂Cl] (the cis isomer cannot be obtained by synthesis due to its higher energy with respect to the trans isomer). Both the calculated gas-phase CO stretching frequencies and the electronic populations on the Rh atom differ significatively [Mulliken population (au): cis -0.421, trans -0.485; calculated vCO (cm⁻¹): cis 2093, trans 2062]. Noteworthy, the difference between the stretching frequency of these two isomers ($\Delta \nu$ CO = 31 cm⁻¹) is very similar to the difference between the experimental frequencies of trans-[Rh(CO)(PPh₃)₂I] (1981 cm⁻¹) and cis-[Rh(CO)(dppe)I] [dppe = 1,2-bis(diphenylphosphino)ethane, 2011 cm⁻¹; $\Delta\nu$ CO $= 30 \text{ cm}^{-1}$].³ We are aware that this result can be a coincidence and that other studies are needed to clarify if the CO stretching frequency can be directly correlated to the Rh electronic population.

The ¹⁰³Rh NMR chemical shifts are very similar for **1**, **2** · PF₆, and **3** · (PF₆)₂ (Table 1). Nevertheless, ¹⁰³Rh shielding seems to be mainly dependent on the kind of coordinated atoms and on the coordination geometry, both identical in our case.¹⁷

The ν CO stretching in complexes **2** · X and **3** · X₂ (X = PF₆, OTf, NO₃) is slightly different (Table 1). As shown by the value of the ¹H NMR (CD₂Cl₂) chemical shift of the NH group, the

anion interacts with the cation through hydrogen bonding (Table 1). The NH values of mono- and diprotonated complexes move, as expected, downfield along the series NO₃ (coordinating), OTf (less coordinating), and PF₆ (noncoordinating) in good correlation with the variation of the CO stretching. The more coordinating anion lowers the positive charge on the Rh center through the hydrogen bonding, causing a decrease of the CO stretching value and suggesting that the Rh electron density can be fine-tuned by changing the anion.

Reaction of [Rh(EtSNS)(CO)] (1) with CH₃I. Treatment of **1** with a stoichiometric amount of CH₃I in CH₂Cl₂ at 25 °C resulted in the quantitative formation of the stable Rh^{III} acetylcomplex [Rh(EtSNS)(COCH₃)I] (4) characterized in solution and in the solid state (Scheme 2).

The FTIR spectrum of the reacting solution (Figure 1) showed the decay of the intensity of the ν CO stretching of 1 at 1967 cm⁻¹, accompanied by the formation of a new absorption at 1712 cm⁻¹, assigned to the acetyl complex 4 (for ca. 30 mg of complex 1 the reaction was completed in ca. 8 min).

The intensity of the ν CO band of the methyl-carbonyl Rh^{III} intermediate **A** (2065 cm⁻¹, observed as a shoulder of the CH₂Cl₂ absorption at 2055 cm⁻¹) was very weak and absent at the end of the reaction. Another weak band started to form at 1736 cm⁻¹ and then decayed after ca. 5 min, finally disappearing at the end of the reaction. This band can be possibly assigned to the speculative isomer **B**. The methyl intermediate **A** and the acetyl isomer **B** were not evidenced in the ¹H NMR spectra at room temperature. The complex **A** could be observed by ¹H NMR only by slowing the reaction at 250 K ($\delta = 1.92 \, {}^{2}J_{Rh,H} =$ 2 Hz, integral = 3% with respect to the integral of the CH₃

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Figure 1. Superimposed FTIR spectra of the reaction of 1 with CH_3I in 1:1 ratio in CH_2Cl_2 at rt.



Figure 2. View of the (a) CH_2 , (b) $COCH_3$, and (c) CH_3 ¹H NMR signals after 28 min of reaction at 280 K, evidencing the presence of two sets of peaks.

signal of the ligand ethyl groups). When the reaction was performed at 280 K, two sets of peaks with very close chemical shifts and different intensities were present (Figure 2). They were assigned to the ethyl groups of **4** and, possibly, to the acetyl isomer **B** [**4** = 1.208 (t, $-CH_2CH_3$), 3.699 (m, $-CH_2CH_3$); **B** = 1.214 (t, $-CH_2CH_3$), 3.800 (m, $-CH_2CH_3$)]. The acetyl groups of **4** and **B** are overlapped, apparently resonating at the same chemical shift (δ = 2.80 ppm, Figure 2).

The solution was then warmed from 280 to 300 K, and only the peaks of **4** were present. At rt the presence of the CO absorptions of **A** and **B** in the infrared spectra, at low relative concentrations not detectable by ¹H NMR, is probably due to a high infrared absorbitivity of these Rh^{III} complexes. The ³¹P{¹H} NMR spectrum of the reacting solution shows the formation of only one singlet at 27.4 ppm (**4**), and the complete decay of the signal of **1** (16.6 ppm).

Crystals of 4 were obtained at -20 °C by layering hexane on a CH₂Cl₂ solution. The ORTEP plot of the structure of 4 is depicted in Figure 3. Selected structural parameters are given in Table 3.

The complex shows a slightly distorted square-pyramidal coordination geometry with the acetyl group occupying the apical position. The coordination around the metal involves the S1, N3, and S2 atoms of the ligand, in a $S,N,S-\kappa^3$ coordination fashion, the carbon atom of the acetyl, and the iodine atom. The Rh atom lies at 0.24(1) Å from the mean plane defined by



Figure 3. ORTEP plot of the structure of **4**. Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

Table 3. Se	lected Bond	Lengths	(A) a	nd Angle	es (deg)	for (Complex	4
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2.340(1)	C1-S1	1.743(4)
2.322(1)	C2-S2	1.721(4)
2.619(4)	C1-N1	1.278(5)
2.128(3)	C2-N2	1.271(5)
1.950(4)	P1-N3	1.622(3)
1.194(5)	P2-N3	1.626(3)
1.475(6)		
133.8(1)	S2-Rh1-C31	91.5(1)
89.8(1)	S1-Rh1-S2	168.0(1)
89.7(1)	C31-Rh1-I1	98.9(1)
101.4(1)	C31-Rh1-N3	91.8(1)
91.8(1)	C32-C31-O1	122(4)
86.2(1)	I1-Rh1-N3	169.1(1)
	$\begin{array}{c} 2.340(1)\\ 2.322(1)\\ 2.619(4)\\ 2.128(3)\\ 1.950(4)\\ 1.194(5)\\ 1.475(6)\\ 133.8(1)\\ 89.8(1)\\ 89.7(1)\\ 101.4(1)\\ 91.8(1)\\ 86.2(1) \end{array}$	$\begin{array}{llllllllllllllllllllllllllllllllllll$

I1–S1–S2–N3. The oxidation to Rh^{III} causes a slight variation of the bond lengths and angles of the EtSNS[–] ligand with respect to the Rh^I complex **1**. In particular the Rh1–N3 [2.128(3) Å], Rh1–S1 [2.340(1) Å], and Rh1–S2 [2.322(1) Å] bond distances are slightly shorter than those observed in **1**.¹³ The bond distances Rh1–I1 [2.619(4) Å] and Rh1–C31 [1.950(4) Å] are among the shortest found in the Cambridge Structural Database for similar fragments.¹⁸ The acetyl group adopts a conformation that minimizes steric interactions with the close phenyl group of the EtSNS ligand, directing the methyl group between the I1 and S2 atoms (I1–Rh1–C31–C32 torsion angle 48.9°).

The ${}^{1}\text{H}-{}^{1}\text{H}$ 2D NOESY NMR spectrum of 4 (CD₂Cl₂ at 25 °C) displays cross-peaks between the acetylic CH₃ group and some of the phenylic hydrogens. This is consistent with the square-pyramidal coordination geometry with an apical acetyl ligand as found in the solid state (Figure 3).

In the solid state, **4** seems to partially transform in the methyl complex **A** as evidenced by FTIR-HATR. In the spectrum, a weaker ν CO band at 2049 cm⁻¹ is present, together with the stronger one at 1709 cm⁻¹ assigned to the acetyl complex. When the solid is dissolved on the HATR crystal, by addition of few μ L of dichloromethane, the spectrum shows only one band at 1712 cm⁻¹. By evaporating the solvent on the crystal, the band at 2049 cm⁻¹ reappears. A similar behavior was already reported in the literature, with the acetyl complex undergoing reductive elimination, re-forming the parent Rh^I complex.^{2,19} A CP-MAS ¹³C solid-state NMR was collected on **4**, in order to verify the presence of **A**. Only the peaks of **4** were present, probably due to the very low concentration (<3%) of **A** in the solid [spectra are reported in Figure S1 (1) and S2 (4) of the Supporting Information].

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Scheme 3. Reactivity of $2 \cdot X$ (X = PF₆, OTf, NO₃) with CH₃I in CH₂Cl₂



Reaction of the Monoprotonated Complexes [Rh(HEtSNS)-(**CO**)]**X** (**2**•**X**, **X** = **PF**₆, **OTf**, **NO**₃) with **CH**₃**I**. The reaction of complexes **2**•X with CH₃I in 1:100 ratio (CH₂Cl₂ at 25 °C, Scheme 3) was monitored by FTIR, ¹H NMR, and ³¹P{¹H} NMR. In the infrared spectrum of the reacting solution of **2**•OTf (Figure 4, the same discussion applies for X = PF₆ and NO₃; see superimposed spectra in Figures S3 and S4 of the Supporting Information), the presence of a very weak band at 2066 cm⁻¹ (PF₆ = 2068 cm⁻¹, NO₃ = 2061 cm⁻¹) indicated the formation of the methyl-Rh^{III} intermediate **A**'.

The change in the intensity of this band was in agreement with a steady-state intermediate, and the band disappeared at the end of the reaction (after 48 h). The formation of the acetyl complex [Rh(HEtSNS)(COCH3)I]OTf (5 · OTf) was evidenced by the appearance of a band at 1721 cm⁻¹ ($PF_6 = 1725$ cm⁻¹, $NO_3 = 1717 \text{ cm}^{-1}$). After ca. 50 min, for all three anions, a shoulder band at 1712 cm⁻¹ was evident in the spectra and was ascribed to the deprotonated acetyl-complex 4. At the end of the reaction, only this band was present (Figure S5 of the Supporting Information for X = OTf). During the reaction, a weak shoulder band at 2013 cm⁻¹ formed and then disappeared $[2017 \text{ cm}^{-1} \text{ for } \mathbf{3} \cdot (\text{PF}_6)_2 \text{ and } 2009 \text{ cm}^{-1} \text{ for } \mathbf{3} \cdot (\text{NO}_3)_2]$. It could be due to the formation of the diprotonated complex $3 \cdot (OTf)_2$ by protonation of 2 · OTf.¹⁴ In the ¹H NMR spectrum of the CD_2Cl_2 reacting solution, the methyl group of intermediate A' is not observable, due to the strong excess of CH₃I, whose peak resonates in the same region. The $-CH_2CH_3$ groups of 2 · X and $5 \cdot X$ (X = PF₆, OTf, NO₃) are broad, probably due to proton exchange, and resonate in the same range, being undistinguishable. Moreover, only one peak attributed to the acetyl complexes is present.

In the ³¹P{¹H} NMR spectrum of the reacting solution, a similar situation was observed. The intensity of the two peaks



Figure 4. Superimposed FTIR spectra of the reaction of $2 \cdot \text{OTf}$ with CH₃I (1:100 ratio) in CH₂Cl₂ at rt.

of 2•OTf (Table 1) decreased along with the formation of two new absorptions at lower field (44.6, 23.7 ppm), which were attributed to complex 5•OTf. The methyl-Rh intermediate A' was not evidenced in the spectra. After ca. 50 min, a new band at 27.4 ppm was starting to form and was attributed to complex 4, obtained by deprotonation of 5•OTf (see Figure S6 of the Supporting Information). After two days, the peak of 4 was still present in the ³¹P{¹H} NMR spectrum. Other unidentified decomposition products, which were not observed in the carbonylic region of the FTIR spectrum, were also formed (see Figure S7 of the Supporting Information). The decomposition of the protonated complexes 5•X can be due to the strong excess of CH₃I present in solution or to the intrinsic incompatibility of the acid with the acetyl group.^{1d}

Compounds 5•OTf and 4 could be separated by preparative TLC (in a test reaction that was stopped before completion, using silica plates and CH₂Cl₂/hexane (8:2) as eluent). The ³¹P{¹H} NMR spectra of the separated compounds confirmed the assignment. In the ¹H NMR spectrum, the acetyl group of complexes $5 \cdot X$ and 4 resonates at the same chemical shift. We were unable to better characterize complexes $5 \cdot X$ due to their instability. They could be observed in solution only (by means of ³¹P{¹H} NMR), by protonation of complex 4 with equimolar amounts of the corresponding acids, and they underwent subsequent decomposition to 4 and the unidentified products.

Reaction of the Diprotonated Complexes [Rh(H₂EtSNS)-(CO)]X (3 \cdot X_2, X = PF₆, OTf, NO₃) with CH₃I. The diprotonated complexes 3 \cdot X_2 reacted very slowly with CH₃I in 1:100 ratio, the band of the starting reagents disappearing from the solution FTIR spectra only after 5 days. No Rh-methyl complexes were evidenced in the FTIR spectra, and only the formation of the acetyl complex 4 was observed (FTIR absorption at 1712 cm⁻¹ for all three complexes). This complex was separated by TLC, as in the case of the reactions of compounds 2 \cdot X, and identified by {}^{31}P{}^{1}H{} NMR. Unidentified decomposition compounds were also evidenced in the {}^{31}P{}^{1}H{} NMR spectrum of the crude product, but no further investigation was performed.

Kinetics of the Reaction of 1 and $2 \cdot X$ with CH₃I. At the concentrations employed for the kinetic measurements for the oxidative addition of CH₃I on 1 and $2 \cdot X$ (X = PF₆, OTf, and NO₃), ¹H NMR spectra obtained by a single FID collection were of good resolution and good signal-to-noise ratios and prompted us in the use of this technique for the determination of the reaction rates. For the $2 \cdot X$ complexes, the experiments were performed in order to evaluate the effect of protonation and the role of the counterion.

In the case of 1 the reaction with CH₃I is quite fast and its constant could be determined at different temperatures under second-order conditions ($[CH_3I]/[Rh] = 1-5$). The calculation was performed by processing the integral of the signals of the



Figure 5. ¹H NMR stack plot spectra for the reaction of 1 with $CH_{3}I$ (ratio 1:1) at 280 K in $CD_{2}Cl_{2}$.

 Table 4. Second-Order Rate Constants for the Reaction of 1 with CH₃I at Different Temperatures^a

temperature (K)	$k (M^{-1} s^{-1})$	σ^{b}
273.16	$1.53(3) \times 10^{-2}$	1.23×10^{-3}
278.16	$2.31(3) \times 10^{-2}$	1.64×10^{-3}
286.16	$3.56(7) \times 10^{-2}$	1.39×10^{-3}
298.16	$5.48(7) \times 10^{-2}$	1.38×10^{-3}

^{*a*} Standard deviations are given in parentheses. The corresponding least-square sample standard deviations (σ) are also reported. ^{*b*} $\sigma = [\sum_i (I_i^o - I_i^c)^2/(n - m)]^{1/2}$, where I_i^o , I_i^c are the observed and calculated integral values, *i* is the number of the spectrum, *n* is the number of observations, and *m* is the number of parameters refined.

 CH_3 groups of CH_3I and $-C(O)CH_3$ as a function of time (Figure 5), using nonlinear least-squares fitting functions.

On these grounds, their integrals could be related to the concentrations of the species, making use of appropriate equations as reported in the Experimental Section. At 25 °C the migratory CO insertion is a very fast reaction compared with the oxidative addition of CH₃I. Only at 250 K was the methyl intermediate A detected, but its relative concentration was too low for the determination of the migratory CO insertion rate. Thus, it was not possible to determine the kinetic rate constants for both reaction steps, but only the reaction rate of the slowest one (oxidative addition), which was then approximated to the overall rate for the reaction $1 + CH_3I \rightarrow 4$ with $v = k[1][CH_3I]$. The rate constants determined at different temperatures for this reaction are reported in Table 4. They were employed for the calculation of the activation parameters ΔH^{\ddagger} $[28(3) \text{ kJ mol}^{-1}]$ and $\Delta S^{\ddagger} [-173(10) \text{ J mol}^{-1} \text{ K}^{-1}]$ by means of the nonlinearized Eyring function and using the least-squares procedure (see Figure S8 of the Supporting Information). As expected, the nucleophilic attack by the Rh complex on CH₃I on the Rh to reach the transition state is endothermic, which corresponds to a negative activation entropy, confirming an associative mechanism.¹⁶

For the monoprotonate complexes $2 \cdot X$ (X = PF₆, OTf, and NO₃) the reaction is slower than for **1**, and pseudo-first-order conditions were used ([CH₃I]/[Rh] = 100). Under these conditions, both a second-order treatment and a pseudo-first-order treatment gave the same values for the second-order rate constants. With CH₃I in large excess, the decrease in its ¹H NMR peak integral could not be observed, and only the increase of the CH₃ signal of the Rh acetyl complex **5** · X was considered

Table 5. Second-Order Rate Constants for the Reaction $2 \cdot X$ (X = PF₆, OTf, and NO₃) with CH₃I at 298.16 K^a

counterion	$k (M^{-1} s^{-1})$	σ^{b}
PF_6	$2.50(6) \times 10^{-5}$	7.66×10^{-3}
OTf	$12.7(3) \times 10^{-5}$	2.88×10^{-2}
NO_3	$24.6(6) \times 10^{-5}$	1.67×10^{-2}

^{*a*} Standard deviations are given in parentheses. The corresponding least-square sample standard deviations (σ) are also reported. ^{*b*} $\sigma = [\sum_i (I_i^o - I_i^o)^2/(n - m)]^{1/2}$, where I_i^o , I_i^c are the observed and calculated integral values, *i* is the number of the spectrum, *n* is the number of observations, and *m* is the number of parameters refined.

in the calculations. We decided to take into account only the integral values at t < 15 min. During this time, as observed in the FTIR and ³¹P{¹H} NMR spectra, **A'** and **5** · X are the only product observed. Taking into account a single reaction step under pseudo-first-order conditions, a very good fitting of the intensity of the acetyl ¹H NMR signal versus time was obtained, as evidenced by the very low standard deviations of the calculated rate constants, at 298.16 K (Table 5). This suggested that, although in the steady state, under this approximation the concentration of the methyl complex **A'** is very low, as supported by the ³¹P{¹H} NMR spectrum and as also found for the reaction of complex **1**.

The ΔH^{\ddagger} and ΔS^{\ddagger} activation parameters were determined for the **2**•PF₆ complex and were 45(7) kJ mol⁻¹ and -180(30) J mol⁻¹ K⁻¹, respectively (see Table S1 of the Supporting Information for kinetic rate costants at different temperature for **2**•PF₆). The ΔH^{\ddagger} value is markedly higher than that determined for **1**, indicating, as expected, that the activation process for an oxidative addition of CH₃I on a positively charged complex is more endothermic. The ΔS^{\ddagger} value is similar to that of the neutral complex (-175 J mol⁻¹ K⁻¹), but, due to the high standard deviation, any clear discussion on the entropic activation change during the reaction is not possible. It seems clear that the decreased reaction rate for the monoprotonate complexes might be due to enthalpic factors associated with the oxidative addition step.

A similar cationic tridentate $S,N,S-\kappa^3 \text{ Rh}^1$ monocarbonyl complex, namely, [Rh(L)CO]PF₆ [ν CO (CH₃CN) = 2015 cm⁻¹; L = 2,6-bis(benzylthiomethyl)piridine] was reported to react with CH₃I.^{16h,n} In this case, the kinetic costants of both the oxidative addition step $(1.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1})$ and the migratory CO insertion $(4 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1})$ were determined in CH₃CN at 31 °C. Under these conditions, the rate-determining step of the reaction is apparently the migratory insertion, while, in our case, it is the oxidative addition. Nevertheless, the observed rate contant in CH₂Cl₂ is very close^{16h} (5.9 × 10⁻⁵ M⁻¹ s⁻¹; see Table 4 for **2**•X rate constants).

As expected taking into account the ν CO stretching frequency of the complexes, the reactivity decreases in the order $1 \gg 2 \cdot \text{NO}_3 > 2 \cdot \text{OTf} > 2 \cdot \text{PF}_6 \gg 3 \cdot \text{X}_2$. The effect of the protonation can be also seen in the energy of the gas-phase DFT-calculated MOs. Assuming that the suitable MO for the nucleophilic attack of the Rh atom on the CH₃ group must be the one at the highest energy with a σ -symmetry, the energies found for these MOs in **1**, **2**, and **3** were -0.167, -0.278, and -0.393 au, respectively (see Figure S10 of the Supporting Information for the orbital drawings).

A similar situation can be found in the literature for β -aminovinylketonato complexes of formula {Rh[R¹C(O)-CHC(NH)R²](PPh₃)(CO)}, where the R groups can be CH₃ or CF₃: it was observed that the presence of one or two electron-attractive fluorinated substituents in the ligand retard the





Figure 6. Linear regression function of the correlation between the CO stretching frequencies and the rate kinetic constants of the monoprotonated complexes $2 \cdot X$.

oxidative addition. In this case, however, quantitative kinetic parameters were not determined. $^{\rm 20}$

A correlation between the ν CO stretching and the rate constants for 1 and 2·X (X = PF₆, OTf, NO₃) should be possible. This is only true for the 2·X series, as depicted in Figure 6.

The experimental rate constant for complex 1 is 1 order of magnitude higher than the calculated one (using the linear regression function obtained for the 2.X series: experimental = $5.48 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$; calculated = $1.29 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$), pointing out that the monoprotonated complexes react more slowly than expected. Two simultaneous effects could be responsible for this behavior. A steric effect can be due to the variation in the geometry of the two penta-atomic chelation rings (Rh-S-C-P-N) when complex 1 is protonated, causing one axial phenyl ring to move toward the Rh metal center [the distance of the Rh atom from the phenyl carbon atoms directly bonded to the P atoms of the PNP group are 3.92 for 1 and 3.75 and 3.86 for $2 \cdot PF_6$]. A superposition of the solid-state structures of 1^{13} and $2 \cdot PF_6^{14}$ is depicted in Figure 7 (the atoms used for superposing the structures were the Rh and the coordinated S, S', N, and C).

This higher steric hindrance would lower the rate of the oxidative addition but enhance the rate of the migratory insertion. As previously reported,^{3,9-11} the migratory CO insertion rate can be higher when a π -donor ligand is present, forming a molecular orbital of suitable energy in which the contribution of the methyl ligand is not negligible and is inphase with Rh and CO(π^*), thus generating a continuous lobe that contains the three atoms involved in migratory CO insertion. A DFT calculation was performed to optimize the possible Rh^{III}-CH₃ intermediate for the reaction of complex 1 and complex 2 with $CH_{3}I$ (A and A', respectively). An octahedral geometry for the Rh-CH₃ complex was adopted, with the CH₃ group and the I atom in trans axial positions with respect to the S, N, S, C, Rh plane. Only in the case of the neutral complex A did we find one MO spreading on the atoms involved in the migratory CO insertion (Figure S11 of the Supporting Information), whereas no similar orbital was present in the cationic A'. These two effects, one reducing the oxidative addition rate and

Figure 7. Superposition of the structures of 1 (red) and $2 \cdot PF_6$ (blue).

the other reducing the migratory CO insertion rate, could be responsible for the lower than expected reactivity of $2 \cdot X$ (X = PF₆, OTf, and NO₃).

Conclusion

The zwitterionic Rh^I monocarbonyl complex [Rh(EtSN-S)(CO)] (1) can be mono- and biprotonated, affording cationic complexes [Rh(HEtSNS)(CO)]X (2·X) and [Rh(H₂EtSNS)-(CO)] X_2 (3 · X_2) (X = PF₆, OTf, NO₃). In these compounds, the electron density on the Rh atom varies, as pointed out by the change of the IR stretching frequency of the coordinated CO, and confirmed by the DFT-calculated Mulliken atomic populations. The effect of the protonation was studied in the reaction with iodomethane. In the case of 1 and $2 \cdot X$ the oxidative addition of CH₃I was followed by the migratory CO acetyl-Rh^{III} insertion, forming the complexes [Rh(EtSNS)(COCH₃)I] (4) and [Rh(HEtSNS)(COCH₃)I]X (5), respectively. Complex 4 was characterized in solution, and its solid-state structure was determined by X-ray diffraction methods. Compounds 5 · X are stable in solution for a short time, undergoing deprotonation, forming complex 4, and also decomposing to unidentified products. The rate constants of the reaction were determined by means of ¹H NMR spectroscopy; in the case of complex 1, second-order conditions ([CH₃I]/[Rh] = 1) could be employed. The reactivity decreases in the order 1 $[5.48(7) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}] \gg 2 \cdot \text{NO}_3 [24.6 \text{ (6)} \times 10^{-5} \text{ M}^{-1}]$ s^{-1}] > 2 · OTf [12.7 (3) × 10⁻⁵ M⁻¹ s⁻¹] > 2 · PF₆ [2.50 (6) × $10^{-5} \text{ M}^{-1} \text{ s}^{-1} \gg 3 \cdot X_2$ at 25 °C in CH₂Cl₂. Complexes $3 \cdot X_2$ reacted too slowly, hindering the determination of the rate constants. The activation parameters ΔH^{\ddagger} and ΔS^{\ddagger} were determined for 1 and $2 \cdot PF_6$, confirming the nucleophilic mechanism. Calculations addition showed that the suitable MO for the nucleophilic attack of the Rh atom on the CH₃ group of iodomethane (that must be the one at the highest energy with a σ -symmetry) displayed a variation of its energy that paralleled the reactivity trend of 1, 2, and 3. A good correlation was found between the rate constants, along the series $2 \cdot NO_3$, $2 \cdot OTf$, and $2 \cdot PF6$, with the corresponding CO stretching frequency values. This correlation could be explained assuming that the different non-metal-coordinated anions form a hydrogen bonding with the NH group of 2 (as evidenced by its ¹H NMR chemical shift), which in turn causes a variation of the electron density on the Rh center (as observed by the change in the CO stretching frequency). In conclusion, the reactivity

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of complex 1 toward iodomethane could be tuned by protonation and fine-tuned by changing the counterion.

Experimental Section

Materials. All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Methyl iodide (Aldrich) and dichloromethane were distilled from calcium hydride. [Rh(EtSNS)(CO)],¹³ [Rh(HEtSNS)(CO)]X, [Rh(H₂EtSNS)(CO)]- $(X)_2$ (X = PF₆, OTf),¹⁴ and [Rh(CH₃CN)₂(CO)₂]NO₃²¹were prepared as described elsewhere. HNO3 (65%) and [Rh(CO)2Cl]2 (Aldrich) were used as supplied. Elemental analysis was carried out with a Carlo Erba EA1108 microanalyzer. FTIR spectra (4000-400 cm⁻¹) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond or ZnSe crystal); IR cell: CaF₂ windows, 0.5 mm path length. ¹H NMR (300.13 MHz, TMS) spectra were recorded on a Bruker 300 Avance, and ³¹P{¹H} NMR (161.98 MHz, external reference 85% H₃PO₄) and ¹⁰³Rh NMR (12.65 MHz, the absolute ¹⁰³Rh frequency was determined by relating it to the reference frequency $\Xi = 3.16$ MHz) spectra were recorded on a Bruker AMX400, using deuterated solvents (CDCl₃, CD₂Cl₂, and CD₃OD). All solid-state NMR spectra were acquired on a Bruker Avance II 400 operating at 400.23 and 100.65 MHz for ¹H and ¹³C, respectively, at room temperature with a spinning speed of 12-14 kHz. Cylindrical 4 mm o.d. zirconia rotors with a sample volume of $120 \,\mu\text{L}$ were employed. A standard ramp cross-polarization pulse sequence was used with a contact time of 5 ms, a ¹H 90° pulse of 3.35 ms, recycle delays of 10 s, and 264-1000 transients. A two-pulse phase modulation (TPPM) decoupling scheme was used with an rf field of 75 kHz. ¹³C chemical shifts were referenced via the resonance of solids HMB (hexamethyl benzene, methyl signal at 17.4 ppm). A Micromass Quattro LC triple quadrupole instrument equipped with an electrospray interface (Masslynx v. 3.4 software) was used for ESI-MS data collection and processing. The nebulizing gas (nitrogen, 99.999% purity) and the desolvation gas (nitrogen, 99.998% purity) were delivered at a flow rate of 80 and 500 L/h, respectively. ESI-MS analyses were performed by operating the mass spectrometer in positive ion (PI) mode, acquiring mass spectra over the scan range m/z 100–2800, using a step size of 0.1 Da and a scan time of 2.7 s. The interface operating parameters were source temperature 70 °C, desolvation temperature 70 °C, ESI(+) capillary voltage 3.0 kV, cone voltage 15 V, rf lens 0.3 V.

X-ray Data Collection, Structure Solution, and Refinement. The intensity data of compound 4 were collected at room temperature on a Bruker AXS Smart 1000 single-crystal diffractometer equipped with an area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystallographic and experimental details of the structure are summarized in Table 6. An empirical correction for absorption was made. The structure was solved by direct methods and refined by full-matrix least-squares procedures (based on F_o^2)²³ first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms.

Preparation of [Rh(CO)(HEtSNS)]NO₃ ($2 \cdot NO_3$). A solution of [Rh(CH₃CN)₂(CO)₂]NO₃ (0.200 g, 0.26 mmol) in CH₂Cl₂ (10 mL) was added under nitrogen to a solution of HEtSNS (0.148 g, 0.26 mmol) in CH₂Cl₂ (15 mL). Stirring was continued for 2 h,

Table 6. Summary of Crystallographic Data for 4

	•	
	formula	$C_{32}H_{33}IN_3OP_2RhS_2$
	fw	831.52
	crystal system	monoclinic
	space group	$P2_1/n$
	Т, К	293
	<i>a</i> , Å	10.220(1))
	b, Å	17.102(2)
	<i>c</i> , Å	19.943(2)
	β , deg	99.151(2)
	$V, Å^3$	3441.5(6)
	Ζ	4
	$D_{\rm calcd}$, g cm ⁻³	1.605
	F(000)	1656
	cryst size, mm ³	$0.11 \times 0.13 \times 0.10$
	μ , cm ⁻¹	16.37
	rflns collected	42 555
	rflns unique	8298
	rflns obsd $[I > 2\sigma(I)]$	5383
	parameters	379
	\overline{R} indices $[I > 2\sigma(I)]$	R1 = 0.0372 (wR2 = 0.0902)
	R indices (all data)	R1 = 0.0670 (wR2 = 0.0998)
а	$P_1 = E - E /S E - P_2 = P_2 $	$\sum \sum E_{1} (E_{1}^{2}) = E_{1}^{2} (\sum E_{1}^{2}) (\sum E_{1}^{2}) (E_{1}^{2}) (E$

^a R1 = $||F_0| - |F_c|| / \Sigma |F_0|$. wR2 = $[\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2]]$.

and the solution color turned to red. Evaporation of the volatiles afforded compound [Rh(CO)(HEtSNS)]NO₃ (**2**•NO₃) as a red microcrystalline powder (yield 87%). Anal. Calcd for C₃₁S₂H₃₁O₄-N₄P₂Rh (*M* = 752.59): C 49.47; H 4.15; N 7.44; S 8.52. Found: C 49.30; H 4.12; N 7.40; S 8.49. ¹H NMR (CD₂Cl₂): δ 10.5 (s, br, 1H, N–H); 7.7–7.4 (m, 20H, Ph); 3.67 (m, br, 4H, –*CH*₂CH₃), 1.16 (t, 6H, –*CH*₂*CH*₃, ³*J*_{H,H} = 7.2 Hz) ppm. ³¹P{¹H} NMR (CD₂Cl₂): δ 35.2 (s), 25.1 (s) ppm. ESI-MS [MeOH solution: *m/z* (rel int, formula)]: 690.6 (100%, [Rh(CO)(HEtSNS)]⁺). FTIR (Diamond crystal HATR, cm⁻¹): ν_{CO} = 1968s; (CH₂Cl₂, cm⁻¹): ν_{CO} = 1989s.

Preparation of [Rh(CO)(H₂EtSNS)](NO₃)₂ [3 · (NO₃)₂]. In a Schlenk tube and under nitrogen, a solution of [Rh(EtSNS)(CO)] (0.200 g 0.29 mmol) in 10 mL of CH₂Cl₂ was treated with 10 mL of a water solution of HNO₃ (5 M) in large excess with respect to the rhodium precursor and the yellow solution turned orange. The two liquid phases were separated, and the organic one dried, giving an orange red solid. The solid was recrystallized from hot methanol affording compound [Rh(CO)(H₂EtSNS)](NO₃)₂ [3 · (NO₃)₂] as an orange microcrystalline powder (yield 92%). Anal. Calcd for C31H32N5O7P2RhS2 (815.61): C 45.65, H 3.95, N 8.57, S 7.86. Found: C 45.48, H 3.91, N 8.52, S 7.83. ¹H NMR (CD₂Cl₂): δ 10.4 (s, br, 2H, N-H); 7.7-7.4 (m, 20H, Ph); 3.82 (m, 4H, -CH₂CH₃, ${}^{3}J_{\text{H,H}} = 7.2 \text{ Hz}$, 1.27 (t, 6H, $-\text{CH}_2CH_3$, ${}^{3}J_{\text{H,H}} = 7.2 \text{ Hz}$) ppm. ³¹P{¹H} NMR (CD₂Cl₂): δ 41.1 (s) ppm. ESI-MS [MeOH solution: m/z (rel int, formula)]: 691.6 (100%, [Rh(CO)(H₂EtSNS)]²⁺). FTIR (Diamond crystal HATR, cm⁻¹): $\nu_{CO} = 1986s$; (CH₂Cl₂, cm⁻¹): $v_{\rm CO} = 2008 {\rm s.}$

Reaction of [Rh(EtSNS)(CO)] with CH₃I. Methyl iodide (0.014 g, 0.98 mmol) was added to a solution of [Rh(EtSNS)(CO)] (0.068 g, 0.98 mmol) in CH₂Cl₂ (10 mL). The resulting red reaction mixture was stirred for 3 hs. Evaporation of the solvent afforded compound [Rh(EtSNS)(COCH₃)I] (4) as a red powder (yield: 91%). The complex could be recrystallized by layering hexane onto a CH₂Cl₂ solution of crude product at -20 °C affording red crystals of [Rh(EtSNS)(COCH₃)I] (4). Anal. Calcd for C₃₂H₃₃IN₃OP₂RhS₂ (*M* = 831.51): C 46.22; H 4.00; N 5.05; S 7.71. Found: C 46.12; H 3.97; N 4.99; S 7.66. ¹H NMR (CD₂Cl₂): δ 7.60–7.30 (m, 20H, Ph); 3.79 (m, br, 4H, -CH₂CH₃), 2.80 (s, 3H, COCH₃); 1.23 (t, 6H, $-CH_2CH_3$, ${}^{3}J_{H,H} = 7.1$ Hz) ppm. ${}^{31}P{}^{1}H}$ NMR (CD₂Cl₂): δ 27.4 (s) ppm. CP-MAS ¹³C NMR: $\delta = 210.8$ (s, CO), 181.5 (d, ${}^{1}J_{C,P} =$ 151 Hz, C=N), 175.9 (d, ${}^{1}J_{C,P} = 161$ Hz, C=N), 137.2-120.9 (m, Ph), 51.8 (s, -*CH*₂CH₃), 49.1 (s, -*CH*₂CH₃ + COCH₃), 15.0 (s, -CH₂CH₃), 12.1 (s, -CH₂CH₃) ppm. FTIR (Diamond crystal HATR, cm⁻¹): ν CO = 1709s [Rh^{III}C(O)Me]; (CH₂Cl₂, cm⁻¹): ν CO = 1712s [Rh^{III}C(O)Me].

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Reaction of [Rh(HEtSNS)(CO)]X (X = PF₆, OTf, NO₃) with CH₃I. Methyl iodide was added to a solution of [Rh(HEtSN-S)(CO)]X (X = PF₆, OTf, NO₃) ([CH₃I]/[Rh] = 100) in CH₂Cl₂ (10 mL). The reactions were monitored by FTIR spectrophotometry (CaF₂ windows, 0.5 mm path length) until the absorption of the ν CO of the starting materials were completely absent. The crude solutions were chromatographed by preparative TLC silica plate (CH₂Cl₂/hexane, 8:2), affording the monoprotonated Rh^{III}-acetyl complexes [Rh(HEtSNS)(COCH₃)I]X (5 · X, X = PF₆, OTf, NO₃), **4** and unidentified products. 5 · PF₆: ³¹P{¹H} NMR (CD₂Cl₂): δ = 44.5 (s), 23.2 (s) ppm. FTIR (CH₂Cl₂, cm⁻¹): ν CO 1725s [Rh^{II}.r(C)Me]. 5 · OTf: ³¹P{¹H} NMR (CD₂Cl₂): δ 44.3 (s), 23.6(s) ppm. FTIR (CH₂Cl₂, cm⁻¹): ν CO = 1721s [Rh^{III}C(O)Me]. 5 · NO₃: ³¹P{¹H} NMR (CD₂Cl₂): δ 44.1 (s), 23.9(s) ppm. FTIR (CH₂Cl₂, cm⁻¹): ν CO = 1717s [Rh^{III}C(O)Me].

Kinetic Experiments. The kinetics of the oxidative addition of CH_3I to the complexes **1**, **2** · PF₆, **2** · OTf, and **2** · NO₃, were studied by ¹H NMR in CD_2Cl_2 . For the complexes **1** and **2** · PF₆, the reaction rates of the oxidative addition were determined at different temperatures.

Samples of the complexes ([Rh] = $(1.57-1.98) \times 10^{-2}$ M) were prepared by dissolving in CD₂Cl₂ (ca. 0.6 mL in a sealed NMR tube) an appropriate weighted amount of the recrystallized complex. Second-order conditions for 1 complex ($[CH_3I]/[Rh] = 1-5$) were obtained by adding a proper amount $(20-60 \,\mu\text{L})$ of a ca. 1 M CH₃I solution in CD₂Cl₂ to the complex solution. Pseudo-first-order conditions for $2 \cdot X$ (X = PF₆, OTf, NO₃) complexes ([CH₃I]/[Rh] = 100) were obtained by adding a proper amount (ca. 80 μ L) of neat CH₃I to the complex solution. The precise concentration of CH₃I in the tube was obtained by referencing the integrals of the CH₃ group of CH₃I and the acetyl complex to the integral of the CH₃ groups of the complex (used as internal standard) in the first collected spectrum. Spectra were collected as single FID acquisition at intervals of 30-60 s(1) and $45-180 \text{ s}(2 \cdot \text{X})$ making use of a dedicated Bruker MULTIZG program. Time zero offsets $(t_{\text{first spectrum}} - t_{\text{reactants mixing}})$ for any kinetic run were 90-120 s. Spectra collection lasted up to 2 h.

For each kinetic run, the NMR spectrum collected prior to CH_3I addition was used as reference spectrum. Measurements were performed in the temperature range 273.16–298.16 K for 1 (4 experiments), and 280.16–298.16 K for 2•PF₆ (3 experiments). Temperature was controlled by the Bruker TopSpin software function.

Processing of the spectra (30-50 for each kinetic run) was performed by using MestreNova, and all integrals were normalized using the TMS or solvent peaks (CDHCl₂ in CD₂Cl₂). Calculations of the kinetic constants were performed processing the integrals of the signals of the reactants and the products vs time using the SPECFIT 32 software.²⁴ For 1, both the variations of the acetyl CH₃ signal (2.80 ppm) and CH₃I signal (2.20 ppm) were taken into account in the calculations while, for the monoprotonate complexes, only the appearance of the acetyl CH₃ signal (2.80 ppm) was considered. Integrals were correlated to the CH₃I and acetyl complex concentrations considering that $I_{\text{MeI or complex}} = I^*[CH_3I \text{ or complex}]$, where I^* is the calculated integral for a CH₃ group at 1 M concentration as obtained from the spectrum collected prior to CH₃I addition {I* = $I_{2x(Me)}/(2 \times [Rh])$ }. A second-order and both a second-order and a pseudofirst-order fitting functions were used to process the spectra for 1 and $2 \cdot X$ (X = PF₆, OTf, NO₃), respectively.

For 1, best fit was obtained using a second-order reaction function. For the monoprotonate complex, best fit was obtained using either one second-order or one pseudo first-order functions. For the latter complex, a good fitting was obtained only using the spectra collected within 15 min after reagents mixing. After this time, a marked deviation from the calculated fitting function was obtained, indicating the occurrence of a second subsequent reaction after this reaction time. For all complexes, the fitting for the acetyl complex signal was obtained with a single function, indicating that the migratory CO insertion is faster than the oxidative addition step.

The second-order rate constants determined for complexes 1 and $2 \cdot \text{PF}_6$ as a function of the temperature were processed to obtain the activation ΔH^{\ddagger} and ΔS^{\ddagger} parameters by means of the Eyring function $k = (\kappa \text{T/h}) \exp(-\Delta H^{\ddagger}/\text{RT}) \exp(\Delta S^{\ddagger}/R)$, where k is the rate constant at temperature T, κ is the Boltzmann's constant, h the Planck's constant and R the gas constant. A nonlinear least-squares algorithm implemented in SPSS 14.0 software was used for the calculations.

Each kinetic run was repeated at least twice to check reproducibility; the k (for 1) and k_{obs} (for $2 \cdot OTf$, $2 \cdot PF_6$, and $2 \cdot NO_3$,) given values were averaged, with the component measurements deviating from each other by $\leq 5\%$. The error in the temperature was assumed to be 1 K.

Computational Details. The geometries of all minimums were optimized in the gas phase at density functional theory (DFT) level by means of hybrid B3LYP functional.²⁵ The geometries were optimized in gas phase with 6-21G** basis set on H, C, N, Cl, O, P, and S atoms and Lanl2DZ basis and pseudopotential on Rh developed by Hay and Wadt (BS-0). The latter uses a semicore double- ξ contraction scheme for the heavy elements such as Rh. A more wide basis set has been used to evaluate the pseudopotential effects on some molecular properties, substituting the Lanl2DZ functions and potential with complete dgdzvp functions (BS-I).²⁶ All the simulations were performed both in the gas phase and solution by means of the polarizable continuum model (PCM). The continuum were built in CH2Cl2 environment and standard PCM energies were computed with UA0 cavity model. Thermochemical analysis has been performed on all the minimum and no imaginary frequencies were found. Accurate energy calculation has been performed at the same level with tight SCF criteria on the wave function. Mulliken population analysis²⁷ were performed at each calculation level. The MO rendering was performed with the cubegen utility provided in the Gaussian03 package. All the calculations were performed with Gaussian03 and gdv package.²⁸

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Charge-Tuned Rh(I) Complexes

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Supporting Information Available: CIF file of the complex 4, Mulliken populations in the gas phase and solution for 1, 2, and 3, CP-MAS ¹³C solid-state NMR of 1 and 4, superimposed FTIR spectra in CH₂Cl₂ solution of $2 \cdot PF_6 + CH_3I$ and $2 \cdot NO_3 + CH_3I$, superimposed FTIR spectra in CH₂Cl₂ solution of $2 \cdot OTf + CH_3I$ at the beginning and at the end of the reaction, ³¹P{¹H} NMR spectrum of the reaction of $2 \cdot \text{OTf} + \text{CH}_3\text{I}$ in CD_2Cl_2 after 2 h and after 2 days, linearized Eyring plot for the reaction of 1 with CH₃I, table of second-order rate constants for the reaction $2 \cdot \text{PF}_6 + \text{CH}_3\text{I}$ at different temperatures, drawings of the highest energy σ -symmetry MOs for 1, 2, and 3, and drawing of the optimized structure of the [Rh(EtSNS)(CO)(CH₃)I] complex with continuous in-phase MO. This material is available free of charge via the Internet at http://pubs.acs.org.

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