Organometallics **2003,** *22,* 2535−2538

Oxidative Addition of Methyl Iodide and CO Migratory Insertion in a Cationic Rhodium Complex of a S,N,S Tridentate Ligand

Mauro Bassetti,* Alberto Capone, Lucilla Mastrofrancesco, and Michela Salamone

Istituto CNR di Metodologie Chimiche, and Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy

Received March 17, 2003

The cationic rhodium(I) carbonyl complex *mer*-[Rh(L)(CO)]PF_6 coordinated by a tridentate S,N,S donor ligand (L = 2,6-bis(benzylthiomethyl)pyridine) reacts with MeI to give the corresponding acetyl derivative [Rh(L)(COMe)I]PF_6, by consecutive oxidative addition−migratory insertion reactions *via* observable methyl−rhodium(III) intermediate complexes. Rate constants and activation parameters have been obtained for both reaction steps in MeCN, and compared with those of complexes coordinated by mono- and bidentate ligands. This is the first report on the organometallic reactivity of a rhodium(I) and carbonyl complex of S,N,S ligands.

Introduction

The oxidative addition of methyl iodide to rhodium(I) carbonyl centers is a fundamental process in organometallic chemistry, with significant implications in catalysis, especially when followed by methyl migration to give the acyl derivative.[1] Much interest is now devoted to the effects of the ancillary ligands on the rates of the oxidative addition/migratory insertion steps,[2] and in particular of bidentate versus monodentate systems.[1b,3] Information on the reaction sequence for complexes of tridentate ligands is scarce, which may influence significantly the reactivity pattern via steric and electronic effects.[4] When tridentate ligands display meridional coordination, the few reports have shown that oxidative addition of methyl iodide forming octahedral rhodium(III) methyl species is followed by spontaneous CO insertion to give the acetyl product in complexes of anionic unsymmetrical NON type ligands[5] or of unsymmetric anionic or neutral PNO type ligands.[6] In other cases, the reaction stops at the methyl derivative,[7] or CO insertion can be induced in the presence of nucleophiles.[8] Rate and mechanistic studies are not available for *mer*-tridentate systems.

Platinum metal complexes of tridentate "pincer" ligands have shown significant features in modern organometallic chemistry. Extensive chemistry has been described for complexes of chelating P,C,P,[9,10] N,C,N,[9] N,N,N,[11] and P,N,P[12] donors. Cationic rhodium(I) carbonyl complexes of neutral 2,6-bis(substituted-thiomethyl)pyridine ligands are square planar molecules in which the ligand structure imposes trans-dithioeher coordination to the pyridine-bound rhodium, in solution[13a] as well as in the solid state.[13c] Although these complexes have been known for years,[13] the organometallic reactivity has not been described so far.

We report here on the reaction sequence of the cationic rhodium(I) carbonyl complex [Rh(L)(CO)]PF_6 (**1**, L = 2,6-bis(benzylthiomethyl)pyridine) with methyl iodide, as well as the first rate studies of the consecutive steps for a meridionally tricoordinated complex.

Results and Discussion

A solution of **1** (0.05 mmoL) and MeI (0.5 mmoL) in MeOH (5 mL) at reflux changes smoothly from yellow to orange-red. After 3 h, the FT-IR spectrum of the mixture shows only one broad absorption in the acetyl region, indicating conversion of the Rh−CO moiety into

---

* Corresponding author.

[1] (a) Maitlis, P. M.; Haynes, A.; Sunley, G. J.; Howard, M. J. *J. Chem. Soc., Dalton Trans.* **1996**, 2187−2196. (b) Cavallo, L.; Solà, M. *J. Am. Chem. Soc.* **2001**, *123*, 12294−12302.

[2] (a) Baker, M. J.; Giles, M. F.; Orpen, A. G.; Taylor, M. J. *Chem. Commun.* **1995**, 197−198. (b) Rankin, J.; Poole, A. D.; Benyei, A. C.; Cole-Hamilton, D. J. *Chem. Commun.* **1997**, 1835−1836.

[3] (a) Gonsalvi, L.; Adams, H.; Sunley, G. J.; Ditzel, E.; Haynes, A. *J. Am. Chem. Soc.* **2002**, *124*, 13597−13612, and references therein. (b) Gonsalvi, L.; Gaunt, J. A.; Adams, H.; Castro, A.; Sunley, G. J.; Haynes, A. *Organometallics* **2003**, *22*, ASAP.

[4] Chauby, V.; Daran, J.-C.; Serra-Le Berre, C.; Malbosc, F.; Kalck, P.; Delgado Gonzales, O.; Haslam, C. E.; Haynes, A. *Inorg. Chem.* **2002**, *41*, 3280−3290.

[5] Louie, B. M.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1985**, *63*, 3019−3026. Cooper, A. D.; Rettig, S. J.; Storr, A. *Can. J. Chem.* **1986**, *64*, 566−574.

[6] Pelagatti, P.; Bacchi, A.; Bobbio, C.; Carcelli, M.; Costa, M.; Pelizzi, C.; Vivorio, C. *Organometallics* **2000**, *19*, 5440−5446.

[7] (a) Cuervo, D.; Díez, J.; Gamasa, M. P.; García-Granda S.; Gimeno, J. *Inorg. Chem.* **2002**, *41*, 4999−5001. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469−2476.

[8] Siegl, W. O. *J. Organomet. Chem.* **1976**, *107*, C27.

[9] Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

[10] (a) Scott Williams, B.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *Helv. Chim. Acta* **2001**, *84*, 3519−3530. (b) Rybtchinski, B.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528−4529.

[11] Nückel, S.; Burger, P. *Organometallics* **2001**, *20*, 4345−4359. Haarman, H. F.; Bregman, F. R.; van Leewen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 979−985.

[12] Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1999**, 435−440.

[13] (a) Parker, D.; Lehn, J.-M.; Rimmer, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1517−1521. (b) Constable, E. C.; King, A. C.; Raithby, P. R. *Polyhedron* **1998**, *17*, 4275−4289. (c) Helps, I. M.; Matthes, K. E.; Parker, D.; Ferguson, G. *J. Chem. Soc., Dalton Trans.* **1989**, 915−920.

10.1021/om030199z CCC: $25.00

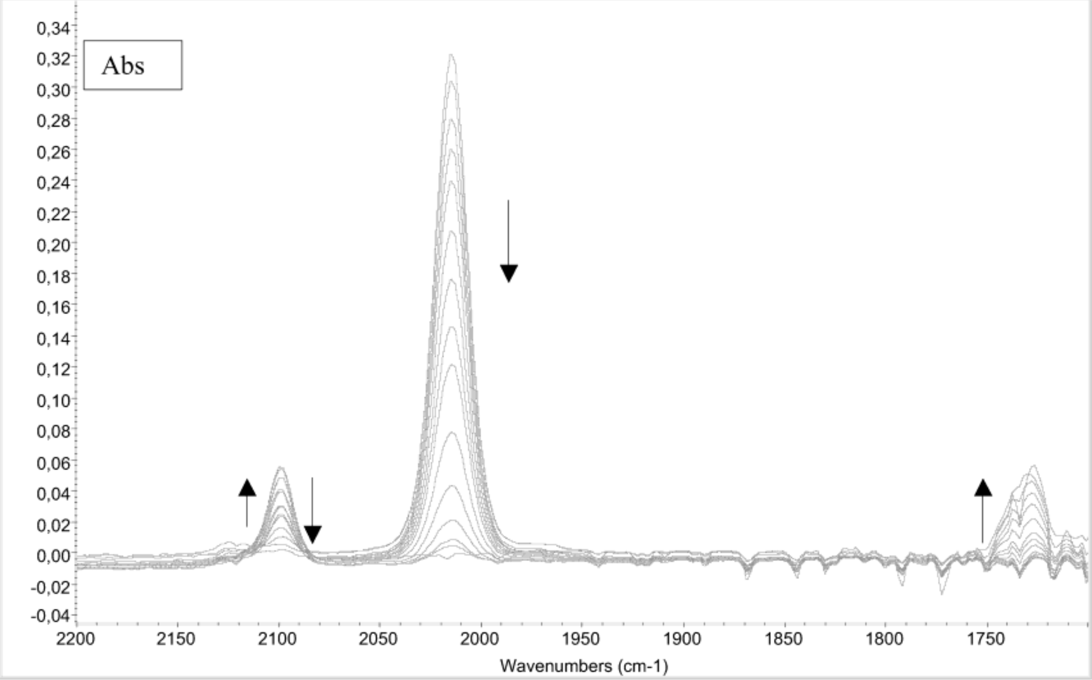
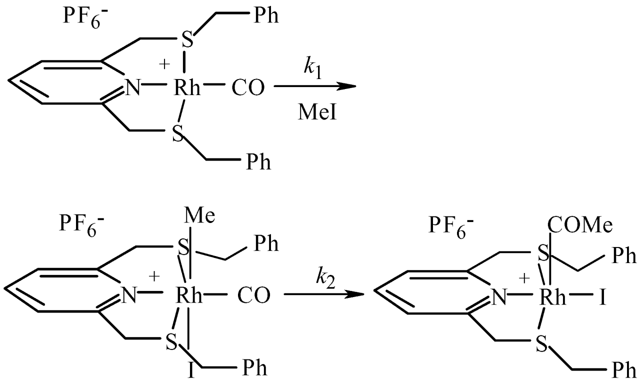


Figure 1. Series of FT-IR spectra for the reaction of **1** with MeI (in neat MeI, 31 °C). The arrows indicate the evolution of each band (from left: 2099 (***i***), 2015 (**1**), 1730 (**2**) cm^{-1}) during the progress of the reaction.

Rh−COMe of an acetyl complex. The product is isolated in 83% yield from the reaction in methanol carried out at 35 °C as a solvent adduct of formula $[Rh(L)(COMe)I(MeOH)]PF_6$ (**2**·MeOH). This implies that oxidative addition of MeI and CO migratory insertion have occurred sequentially at the metal center.[1] The fact that a cationic rhodium complex undergoes oxidative addition by an electrophilic reagent is of no surprise, since the reaction has been described for other cationic rhodium(I) complexes.[14] When the reaction is performed in neat MeI at 31 °C and monitored in situ by FT-IR, the disappeareance of the carbonyl band of **1** at 2015 cm^{-1} is accompanied by formation and then consumption of a new species (2099 cm^{-1}) and by the slow appearance of the acetyl band of **2** at 1730 cm^{-1} (Figure 1).

The frequency shift with respect to complex **1** ($\Delta\nu_{CO} = 84$ cm^{-1}) suggests that the new species is the product of oxidative addition of MeI, $[Rh(L)(Me)I(CO)]^+$. The reaction sequence can therefore be represented as in Scheme 1. The nature of the intermediate has been confirmed by NMR experiments. The ^1H NMR spectrum of a solution of complex **1** (0.018 M) and of MeI (0.76 M) in CD_3CN kept at 32 °C shows the formation of rhodium−methyl species indicated by the appearance of two doublet signals at δ 1.67 ($^2J_{Rh-H} = 2.2$ Hz) and 1.56 ($^2J_{Rh-H} = 1.9$ Hz) ppm, in approximately 2:1 ratio. A ^{13}C NMR experiment under analogous conditions shows two doublets at δ 7.2 ($^1J_{C-Rh} = 19$ Hz) and 8.1 ($^1J_{C-Rh} = 17$ Hz) due to Rh−Me, and one doublet at δ 181.7 ($^1J_{C-Rh} = 58$ Hz) ppm for the Rh−CO moiety. The latter value differs from that of complex **1**, which is found at δ 187.9 ($^1J_{C-Rh} = 69$ Hz). When these signals have disappeared, the resonance of the acetyl fragment of $[Rh(L)I(COMe)]^+$ shows up as an unresolved signal at δ 222 ppm. The presence of two ^1H and ^{13}C NMR signals for Rh−Me are indicative of a mixture of isomers, not resolved in the FT-IR spectra, which is common in the formation of octahedral transition metal complexes from square planar precursors.[3a,15] Scheme 1 shows only one of the three possible octahedral isomers of the Rh−Me intermediate, in particular the species that is productive for the subsequent coupling step, in which the methyl and carbonyl groups are mutually cis. The fact that the relative ratio of these species did not change appreciably during the reaction progress suggests that their interconversion is relatively rapid.

Scheme 1. Reactivity of Complex 1 with MeI



The infrared spectra of complex **2**·MeOH in CH_2Cl_2 and in MeCN shows two acetyl bands (ν_{COMe}), indicating the presence of conformers or isomers. This is in agreement with a broadened peak of CO*Me* in the ^1H NMR spectrum, which remains broad at −43 °C.

Rate measurements have been performed by FT-IR. The carbonyl band of **1** at 2015 cm^{-1} disappears follow-

---

[14] (a) Lindner, E.; Norz, H. *Chem. Ber.* **1990**, *123*, 459. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1980; p 942.

[15] (a) Moloy, K. G.; Wegman, R. W. *Organometallics* **1989**, *8*, 2883. (b) Ref 14b, p 1240.

Table 1. Values of k_{obs} (s^{-1}) for the Oxidative Addition Reaction of Complex $[Rh(L)(CO)]PF_6$ (1, L = 2,6-bis(benzylthiomethyl)pyridine) with MeI and Values of k_2 (s^{-1}) for the Migratory Insertion Reaction, at 31 °C

[MeI], M	k_{obs}, s^{-1} in MeCN[a]	k_2, s^{-1}	
0.237	5.03×10^{-5}	3.3×10^{-5}	
0.392	7.01×10^{-5}	3.9×10^{-5}	
0.764	1.39×10^{-4}	4.2×10^{-5}	
1.120	1.88×10^{-4}	5.2×10^{-5}	
1.460	2.27×10^{-4}	4.9×10^{-5}	
0.764	7.05×10^{-5}	1.5×10^{-5}	(22.5 °C)
0.764	2.48×10^{-4}	1.5×10^{-4}	(41.5 °C)
0.764	3.72×10^{-4}	3.2×10^{-4}	(50.9 °C)

[MeI], M	k_{obs}, s^{-1} in neat MeI
16.1[b]	1.2×10^{-4}
16.1[c]	1.3×10^{-4}

[a] [**1**] = 0.005−0.010 M. [b] [**1**] = 0.0040 M. [c] [**1**] = 0.011 M.

ing a clean exponential decay, indicating that the oxidative addition reaction is first order in **1** and yielding values of observed rate constants (e.g., $k_{obs} = 1.2 \times 10^{-4}$ s^{-1} for the experiment in Figure 1). Clean kinetic behavior was also observed in MeCN. A plot of k_{obs} versus [MeI] is linear with slope 1.4×10^{-4} M^{-1} s^{-1}, which corresponds to the second-order rate constant k_1. Values of k_{obs} are reported in Table 1.

From experiments performed in the temperature range 22.5−50.9 °C, the values of enthalpy of activation $\Delta H^{\ddagger} = 11$ (±1) kcal mol^{-1} and entropy of activation $\Delta S^{\ddagger} = -41$ (±2) cal mol^{-1} K^{-1} have been calculated for the oxidative addition reaction. The large negative value of $\Delta S^{\ddagger}$ is in agreement with a rate-determining associative step, in line with the S_N2 pathway proposed for the reaction of neutral and anionic rhodium(I) complexes.[16,17] The large solvent effect here observed for **1** (MeCN vs MeI) also supports this mechanistic pattern. The reactivity of complex **1** toward MeI is compared with that of other rhodium(I) complexes in Table 2, along with the corresponding values of ν_{CO}. The relatively high ν_{CO} frequency of **1** suggests that the reduced reactivity is due to lower electron density at the metal in this cationic complex.

The evolution of the intermediate methyl complex can be followed conveniently by FT-IR, in MeCN. Figure 2 represents the concentration changes of complex **1** and of the intermediate rhodium methyl species (***i***).

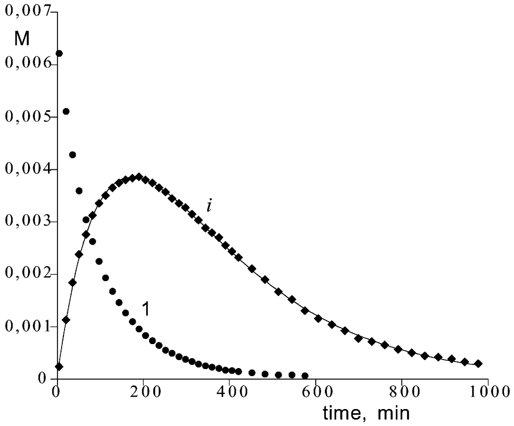


Figure 2. Graphical representation of the reaction of complex **1** (0.0074 M) with MeI (1.120 M) in MeCN, at 31 °C. The solid line applied to the concentration values of the rhodium methyl intermediate $[Rh(L)Me(CO)I]^+$ (***i***) represents the best fit with eq 1.

With the assumption that the back reactions, from the acetyl **2** to the intermediate rhodium methyl species ***i***, and from these to **1**, are negligible, the overall process can be simplified to a sequence of two consecutive first-order reactions, represented by k_1[MeI] (s^{-1}), oxidative addition of MeI to **1**, and by k_2 (s^{-1}), migratory CO insertion in the rhodium(III) complex.[18] Accordingly, the IR absorbance values of ***i*** are treated using eq 1 to obtain the value of k_2 and of the preexponential factor $(A_1)_0(\epsilon_i/\epsilon_1)$, by imposing as k_1[MeI], the k_{obs} value obtained by the first-order analysis.[19]

$$(A_i)_t = (A_1)_0(\epsilon_i/\epsilon_1)\frac{k_{obs}}{k_2 - k_{obs}}(\exp(-k_{obs}t) - \exp(-k_2 t)) \tag{1}$$

The solid line applied to [***i***] represents the best fit with eq 1, which is derived from the integrated equation describing the variation in the single concentration variable of the intermediate species and expressed with respect to absorbances ($[i] = A_i \times \epsilon_i$; $[1] = A_1 \times \epsilon_1$). Since the IR extinction coefficient of **1** has been determined experimentally ($\epsilon_1 = 2275 + 140$ M^{-1} cm^{-1}; 2014 cm^{-1} band in MeCN, 31 °C), eq 1 allows an estimate of the ϵ_i value of the rhodium(III) methyl complexes ($\epsilon_i = 700$ M^{-1} cm^{-1}, 2106 cm^{-1} band in MeCN). Experiments carried out in the concentration range of MeI 0.24−1.46 M did not show significant changes in the k_2 values, in agreement with a process that is intramolecular and as such expected to be independent of [MeI]. The values of the activation parameters for the C−C coupling step are $\Delta H^{\ddagger} = 20$ (±1) kcal mol^{-1} and $\Delta S^{\ddagger} = -13$ (±2) cal mol^{-1} K^{-1} (Table 1).

The kinetic analysis applied to the Rh(III) methyl species for the determination of the rate of migratory insertion differs from the cases reported in the literature, due to the fact that the two consecutive reactions are comparable in rate, implying substantial accumula-

Table 2. Rate Constants for MeI Oxidative Addition Reactions of Various Rh(I) Carbonyl Complexes and for Migratory CO Insertion Reactions of the Corresponding Rh(III) Methyl Complexes.

complex	ν_{CO}, cm^{-1}	k_1,[a] $M^{-1}s^{-1}$	k_2,[b] s^{-1}	$\Delta H^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}$,[b] cal mol^{-1} K^{-1}
1[c]	2015	1.4×10^{-4}	4×10^{-5}	20 (±1)	−13 (±2)
1[d]		7.5×10^{-6}			
$[Rh(CO)_2I_2](Bu_4N)$[d] [20]	2059, 1988	2.9×10^{-5}	0.054	15 (±1)	−14 (±2)
$[Rh(\eta^5\text{-}C_5H_5)CO(PPh_3)]$[e] [17]	1957	3.5×10^{-3}	fast		
$[Rh(CO)I(PEt)_2]$[2b]	1960	1.4×10^{-3}	very slow		
$[Rh(CO)I(dppms)]$[e,f] [21]	1987	1.2×10^{-3}	0.62	13 (±2)	−16 (±3)
$[Rh(k^2\text{-}Tp^*)(CO)(PMe_3)]$[e,g] [4]	1969	2.5×10^{-2}	very slow		

[a] Second-order rate constants (k_{obs}/[MeI]) for the oxidative addition step. [b] Migratory CO insertion. [c] MeCN, 31 °C. [d] Neat MeI, 31 °C. [e] CH_2Cl_2 25 °C. [f] dppms = $Ph_2PCH_2P(S)Ph_2$. [g] Tp* = tris(pyrazolyl)borate ($HB(3,5\text{-}Me_2pz)_3$).

tion of intermediate. In fact, when the C−C coupling step is rapid with respect to oxidative addition ($k_2 \gg k_1$[MeI]), the rhodium methyl complex forms only as a transient species at low concentration, it can be detected by advanced spectroscopic techniques, and it is analyzed using the kinetic steady state approximation. These are the cases of the dicarbonyl diiodide catalytic species $[Rh(CO)_2I_2](Bu_4N)$[20] and of the bidentate system [Rh(CO)(dppms)I] (dppms = $Ph_2PCH_2P(S)Ph_2$).[3a,21] Otherwise, when the coupling step is much slower with respect to MeI addition (k_1[MeI] $\gg k_2$), the rhodium methyl species forms rapidly at high concentration and rates of the migratory insertion step are obtained by analysis of its exponential decay, as in the case of [Rh(CO)(dppe)I].[3a,15a] Rate data for migratory insertion reactions of various rhodium carbonyl methyl complexes are reported in Table 2. The slower reactivity of the species ***i*** with respect to the complexes $[RhMe(CO)_2I_3]^-$ [20] and $[RhMe(CO)I_2(dppms)]$[21] is due essentially to unfavorable activation enthalpy, while $\Delta S^\ddagger$ values are similar within experimental error.

Experimental Section

General Considerations. All synthetic and kinetic manipulations were carried out under an argon atmosphere using Schlenk techniques. Methyl iodide was distilled from calcium hydride, and acetonitrile from phosphorus pentoxide. NMR spectra: Bruker AM-300 spectrometer. Chemical shifts are reported in δ values relative to tetramethylsilane; for ^{1}H NMR, $CHCl_3$ ($\delta = 7.25$) or CH_2Cl_2 ($\delta = 5.32$), and for ^{13}C NMR, $CDCl_3$ ($\delta = 77.00$) or MeCN-d_3 ($\delta = 118.2$ and 1.3 ppm) were used as internal standards. Ion electrospray mass spectra (ESI-MS): Fisons Instruments VG-Platform Benchtop LC-MS (positive ions). Elemental analyses were performed by the Servizio di Microanalisi of the Department of Chemistry, Università “La Sapienza”, Roma. $[Rh_2Cl_2(CO)_4]$ was commercially available and was sublimed before use.

2,6-Bis(benzylthiomethyl)pyridine (L). This compound has been described previously.[22] We have followed the reported procedure, except that easily attainable 2,6-bis(chloromethyl)pyridine[23] was used instead of the corresponding dibromoderivative. Yield: 83%. ^{1}H NMR ($CDCl_3$): δ 7.57 (t, 1 H, J = 7.7 Hz, H_4-py), 7.34−7.21 (m, 10 H, Ph), 7.16 (d, 2 H, J = 7.7 Hz, H_3-py), 3.72 (s, 4 H, $PyCH_2$), 3.70 (s, 4 H, benzyl). ^{13}C NMR ($CDCl_3$): δ 158.14 (C_4-py), 138.04, 137.16 (C_3,C_2-py), 129.03, 128.34, 126.91, 121.08 (Ph), 37.26, 35.79 ($pyCH_2$ and $PhCH_2$). FT-IR (CH_2Cl_2): 1591, 1574 (py) cm^{-1}.

Compound 1. $[Rh(L)CO]PF_6$ was prepared by following the procedure reported for similar complexes.[13a] $[Rh_2Cl_2(CO)_4]$ (104 mg, 0.26 mmol) was added to a solution of 188 mg (0.40 mmol) of L in MeOH (8 mL). After 15 min at room temperature the solution is filtered to remove a greenish precipitate, followed by addition of excess NH_4PF_6. Partial evaporation of the solvent under vacuum causes precipitation of an orange solid. After decanting the residual solvent, the precipitate is washed twice with MeOH and with diethyl ether (2 mL) and then vacuum-dried to leave a dark yellow powder (242 mg, 0.38 mmol, yield 72%). ^{1}H NMR (CD_2Cl_2, 29 °C): δ 7.80 (t, 1 H, J = 8.1 Hz, H_4-py), 7.40 (app d) and 7.25 (br s) (m, 12 H, Ph and H_3-py), 4.45 (br s, 4 H, $pyCH_2$), 4.17 (br s, 4 H, $PhCH_2$). ^{13}C NMR (CD_3CN): δ 187.9 (d, J_{C-Rh} = 69 Hz, CO) 159.8 (d, J_{C-Rh} = 2.6 Hz, C_2-py), 139.5, 134.3, 130.2, 128.6, 128.4, 121.4 (Ph and py), 45.5, 43.3 ($pyCH_2$ and $PhCH_2$). FT-IR: 2019 (CO), 1602 (py) cm^{-1} (CH_2Cl_2); 2009 (CO), 1603 (py) cm^{-1} (Nujol). Anal. Calcd for $C_{22}H_{21}F_6NOPS_2Rh$: C 42.12, H 3.37, N 2.23, S 10.22. Found: C 42.15, H 3.34, N 2.29, S 10.06.

2·MeOH, [Rh(L)COMe(I)(MeOH)]PF$_6$. Complex **1** (53 mg, 0.084 mmol) and MeI (0.50 mL, 8.0 mmol) in MeOH (5 mL) were allowed to react for 22 h at 35 °C. The solution changed from yellow to orange, with precipitation of a red powder, and showed an intense infrared band at 1700 cm^{-1} as the main species. The solution was decanted via cannula from the red powder, concentrated to about half volume under vacuum, cooled, separated again from a second crop of solid, and finally evaporated under vacuum to give an orange-brown powder (56 mg, 83%). FT-IR (CH_2Cl_2): 1737, 1693w (COMe), 1602 (py) cm^{-1}. FT-IR (MeCN): 1700, 1668sh (COMe), 1603 (py). ^{1}H NMR (CD_2Cl_2): δ 7.8 (m, 1 H, H_4-py), 7.4 (br s, 12 H, Ph, H_3-py), 5−4 (m, 8 H, $pyCH_2$ and $PhCH_2$), 3.74 (d, $^2J_{Rh-H}$ = 12 Hz, 1H, MeO*H*) 3.2 (s, 3H, *Me*OH), 2.0 (br s, 3 H, COMe) ppm. ^{13}C NMR (CD_3CN): δ 222 (*C*OMe). ^{13}C NMR ($CDCl_3$): 160.7 (C_2-py), 139.7, 134.9, 130.2, 129.7, 129.2, 123.2 (Ph and py), 47.6, 44.2 ($pyCH_2$ and $PhCH_2$), 49.2, 45.9 (MeOH and CO*Me*). ^{31}P NMR (CD_3CN): δ −143.5 ppm (heptet, J_{P-F} = 706 Hz, PF_6). ESI-MS (MeOH, 15 eV): positive, cluster centered at m/z 624 ($[Rh(L)(COMe)I]^+$); negative, 145 (PF_6^-). Anal. Calcd for $C_{24}H_{28}F_6INO_2PS_2Rh$: C 35.97, H 3.52, N 1.75, S 8.00. Found: C 35.43, H 3.22, N 1.97, S 8.51. The red precipitate (5 mg) contained no carbonyl species and was not further characterized. It was not observed when the reaction was performed under an atmosphere of CO. This byproduct formed extensively upon prolonged reaction times in methanol above 40 °C.

Kinetic Measurements. Complex **1** (7−10 mg) in a volumetric flask was dissolved in 2 mL of the solvent, and a known volume of MeI was added using a microsyringe. A portion of the solution was transferred into an infrared solution cell (CaF_2, 0.50 mm path length) fitted with a thermostated jacket. The reaction was monitored by FT-IR in a Nicolet 510 spectrophotometer using a macro sequence of the Omnic 4 Software. The background spectrum for each experiment was obtained using the corresponding solvent−MeI solution. Data of absorbance versus time were fitted by nonlinear least-squares regression analysis of the first-order rate equation (eq 2), which yields values of k_{obs} and A_∞.

$$A_t = A_\infty + (A_0 - A_\infty)\exp -(k_{obs}t) \qquad (2)$$

Acknowledgment. Helpful discussions and suggestions from Dr. Anthony Haynes, University of Sheffield (UK), are gratefully acknowledged.

OM030199Z

---

[16] (a) Griffin, T. R.; Cook, D. B.; Haynes, A.; Pearson, J. M.; Monti, D.; Morris, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 3029−3030. (b) Aullon, G.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3137−3144. (c) Lamprecht, D.; Lamprecht, G. J. *J. Comput. Chem.* **2000**, *21*, 692−703.

[17] Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2658−2663.

[18] Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: New York, 1985; p 282.

[19] In the hypothesis that the equilibration among the octahedral isomers of the Rh methyl intermediate involves the species in which CO and Me are mutually trans, the calculated k_2 values should be considered as apparent rate constants, involving not only the rate of the coupling step but also rates and isomeric equilibria toward the stereochemical congenial isomers. Since the experimental data in our hands do not allow the identification of the two detectable octahedral isomers, a straightforward kinetic analysis in this case would not be attainable.

[20] Haynes, A.; Mann, B. E.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 4093−4100.

[21] Gonsalvi, L.; Adams, H.; Sunley, G. J.; Ditzel, E.; Haynes, A. *J. Am. Chem. Soc.* **1999**, *121*, 11233−11234.

[22] Teixidor, F.; Escriche, L.; Rodriguez, I.; Casabò, J.; Rius, J.; Molins, E.; Martinez, B.; Miravitlles, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1381−1384.

[23] Baker, W.; Buggle, K. M.; McOmie, J. F. W.; Watkins, D. A. M. *J. Chem. Soc.* **1958**, III, 3594.