Ready formation of stable cationic Rh(I) complexes of MeCN, formamide, urea and related species via replacement of the triflate in *trans*-$(Ph_3P)_2Rh(CO)(OTf)$*

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Abstract

The weakly-coordinated trifluoromethanesulfonate (triflate) in *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ (OTf = OSO_2CF_3) can be readily replaced by ligand L to form stable ionic complexes [*trans*-$(Ph_3P)_2RhL(CO)$]OTf (L = MeCN, formamide pyrone and urea). The replacement of triflate by carbon monoxide forms an unstable species that gradually loses CO and returns the starting material. Sterically hindered ligands such as 1,1,3,3-tetramethylurea and xanthone do not react.

Introduction

The organometallic chemistry of weakly coordinating anions such as BF_4^-, PF_6^-, $CF_3SO_3^-$, ClO_4^- and FSO_3^- has been the subject of many recent studies and reviews [1–3]. These weakly-coordinated anions can be replaced by a variety of nucleophiles as well as neutral solvents to form ionic complexes, some of which are catalytically active. Recently, we reported the σ-bound cyclopropenone rhodium complexes [4] and a rhodium aqua species [5] from the reactions of *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ [6] with the corresponding ligand. Now we wish to report the replacement of triflate in *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ by MeCN, CO, and ligands that contain electron-rich carbonyl groups such as formamide, pyrone and urea resulting in stable cationic Rh(I) triflate complexes in high isolated yields.

Experimental

General

All melting points were measured on a Mel-Temp capillary apparatus and were not corrected. IR spectra (evaporated chloroform solution on a NaCl plate) were recorded on a Mattson-Polaris FT-IR spectrometer. The ^1H, ^{31}P, ^{13}C and ^{19}F NMR spectra were recorded on a Varian XL-300 spectrometer. The ^1H NMR spectra were referenced to internal tetramethylsilane ($SiMe_4$) at 0.00 ppm and the ^{31}P NMR spectra were referenced to external 85% H_3PO_4 at 0.0 ppm. The ^{19}F NMR spectra were referenced to external $CFCl_3$ at 0.0 ppm and the ^{13}C NMR spectra to the NMR solvent ($CDCl_3$ at 77.00 ppm and CD_2Cl_2 at 53.80 ppm). The fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical 750-E instrument in a matrix of 3-nitrobenzyl alcohol.

All solvents used were purified according to known procedures. All reactions were carried out in an atmosphere of nitrogen, but they were worked up in air. Commercially available compounds were used as purchased. Most of products form solvates with organic solvents. The percentage of the solvent is determined by the integrations of the ^1H NMR spectrum and has been included in the elemental analysis.

Synthesis of [trans-$(Ph_3P)_2RhL(CO)$]OTf

Complex 1 (L = MeCN)

trans-Carbonylbis(triphenylphosphine)rhodium triflate (124.3 mg, 0.155 mmol) was stirred in acetonitrile (3 ml) for 20 min. The solution was concentrated to almost dryness and addition of diethyl ether gave a yellow precipitate. It was filtered off,

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washed with ether (3×2 ml) and dried under vacuum (109.9 mg, 84%). m.p. 153–156 °C (dec.). IR (cm^{-1}) 3058, 3008, 2292 (CN), 2007 (CO), 1481, 1436, 1265, 1151, 1096, 1031, 747, 694, 637; ^1H NMR ($CDCl_3$) δ 7.74–7.43 (m, 30 H), 1.58 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$) δ 188.09 (dt, ^1J(Rh–C) = 73.5 Hz, ^2J(P–C) = 16 Hz, CO), 133.80 (t, J = 7 Hz), 131.42, 130,15 (t, J = 24.1 Hz), 129.04 (t, J = 5 Hz), 127.85 (s, CN), 120.77 (q, ^1J(F–C) = 320 Hz, CF_3), 2.26 (s, Me). ^{31}P NMR ($CDCl_3$) δ 30.6 (d, ^1J(Rh–P) = 120.0 Hz). ^{19}F NMR ($CDCl_3$) δ −78.4. MS *m/e* 655 [32, $(Ph_3P)_2RhCO$], 627 [100, $(Ph_3P)_2Rh$], 287 (84), 286 (74). *Anal.* Calc. for $C_{40}H_{33}F_3NO_4P_2SRh$: C, 56.81; H, 3.93. Found: C, 56.53; H, 3.88%.

Complex 4 (L = N,N-dimethylformamide)

A solution of *N,N*-dimethylformamide (9.4 mg, 0.129 mmol) in dry benzene (3 ml) was slowly added through a pipet to a suspension of *trans*-carbonylbis(triphenylphosphine)rhodium triflate (93.9 mg, 0.117 mmol) in the same solvent (3 ml). The mixture was stirred at room temperature for 5.5 h. Slow addition of hexane (*c.* 10 ml) while stirring gave a pale yellow precipitate. It was filtered off and washed with hexane (2×2 ml) (98.2 mg, 96%). m.p. 160–164 °C (dec.). IR (cm^{-1}) 3058, 3011, 1987 (CO), 1646 (C=O), 1481, 1435, 1376, 1263, 1224, 1151, 1096, 1031, 748, 694, 637. ^1H NMR ($CDCl_3$) δ 7.70–7.56 (m, 12 H), 7.56–7.43 (m, 18 H), 6.44 (bd s, 1 H, CHO), 2.37 (s, Me), 2.16 (s, Me). ^{13}C NMR (CD_2Cl_2) δ 189.20 (dt, ^1J(Rh–C) = 76.5 Hz, ^2J(P–C) = 17 Hz, CO), 165.13 (s, Rh−O=*C*), 134.53 (t, J = 7 Hz), 131.68, 130.25 (t, J = 23.3 Hz), 129.39 (t, J = 5.1 Hz), 121.38 (q, ^1J(F–C) = 321 Hz, CF_3), 38.85 (Me), 32.01 (Me). ^{31}P NMR ($CDCl_3$) δ 31.9 (d, ^1J(Rh–P) = 126.8 Hz); ^{19}F NMR ($CDCl_3$) δ −78.4. MS *m/e* 655 [48, $(Ph_3P)_2RhCO$], 627 [99, $(Ph_3P)_2Rh$], 307 (100), 287 (76), 286 (54). *Anal.* Calc. for $C_{41}H_{37}F_3NO_5P_2SRh \cdot 0.4C_6H_6$: C, 57.35; H, 4.37. Found: C, 57.53; H, 4.45%.

Complex 5 (L = N,N-dimethylacetamide)

This product (38.0 mg, 92%) was obtained from the reaction of *N,N*-dimethylacetamide (4.4 mg, 0.0506 mmol) and *trans*-carbonylbis(triphenylphosphine)rhodium triflate (37.5 mg, 0.0466 mmol) using the same procedure as above. m.p. 112–117 °C (dec.). IR (cm^{-1}) 3055, 3009, 1988 (CO), 1601 (C=O), 1481, 1436, 1405, 1273, 1224, 1150, 1096, 1031, 752, 695, 637. ^1H NMR ($CDCl_3$) δ 7.65–7.56 (m, 12 H), 7.56–7.45 (m, 18 H), 2.53 (s, 3 H), 2.41 (s, 3 H), 1.31 (s, 3 H, MeCO). ^{13}C NMR (CD_2Cl_2) δ 188.88 (dt, ^1J(Rh–C) = 74.7 Hz, ^2J(P–C) = 16.7 Hz, CO), 173.96 (s, Rh−O=*C*), 134.57 (t, J = 6.6 Hz), 131.73, 130.63 (t, J = 23.3 Hz), 129.30 (t, J = 5.2 Hz), 121.36 (q, ^1J(F–C) = 321 Hz, CF_3), 39.61, 36.41, 24.89 ^{31}P NMR ($CDCl_3$) δ 31.5 (d, ^1J(Rh–P) = 126.9 Hz). ^{19}F NMR ($CDCl_3$) δ −78.5. MS *m/e* 655 [46, $(Ph_3P)_2RhCO$], 627 [100, $(Ph_3P)_2Rh$], 287 (80), 286 (81). *Anal.* Calc. for $C_{42}H_{39}F_3NO_5P_2SRh \cdot 0.6C_6H_6$: C, 58.35; H, 4.58. Found: C, 58.52; H, 4.68%.

Complex 6 (L = urea)

trans-Carbonylbis(triphenylphosphine)rhodium triflate (74.9 mg, 0.0932 mmol) and urea (14.3 mg, 0.238 mmol) were stirred in dichloromethane (4 ml) at room temperature for 10 h. The mixture was filtered and the filtrate was concentrated. Addition of hexane gave a pale yellow precipitate, which was filtered off and washed with hexane (2×2 ml) (69.7 mg, 87%). m.p. 195–199 °C (dec.). IR (cm^{-1}) 3475, 3362, 3056, 3015, 1986 (CO), 1683, 1627, 1591, 1481, 1435, 1259, 1169, 1096, 1031, 745, 693, 639. ^1H NMR ($CDCl_3$) δ 7.65–7.54 (m, 12 H), 7.54–7.42 (m, 18 H); ^{13}C NMR (CD_2Cl_2) δ 188.97 (dt, ^1J(Rh–C) = 74.2 Hz, ^2J(P–C) = 16.6 Hz, CO), 162.26 (s, Rh−O=*C*), 134.45 (t, J = 6.6 Hz), 131.63, 130.84 (t, J = 23.3 Hz), 129.37 (t, J = 4.9 Hz), 120.79 (q, ^1J(F–C) = 320 Hz, CF_3). ^{31}P NMR ($CDCl_3$) δ 31.0 (d, ^1J(Rh–P) = 126.4 Hz). ^{19}F NMR ($CDCl_3$) δ −78.8. MS *m/e* 655 [51, $(Ph_3P)_2RhCO$], 627 [100, $(Ph_3P)_2Rh$], 287 (82), 286 (85). *Anal.* Calc. for $C_{39}H_{34}F_3N_2O_5P_2SRh \cdot 0.2CH_2Cl_2$: C, 53.41; H, 3.93. Found: C, 53.17; H, 3.91%.

Complex 7 (L = 2,6-dimethyl-γ-pyrone)

trans-Carbonylbis(triphenylphosphine)rhodium triflate (64.1 mg, 0.0797 mmol) and 2,6-dimethyl-γ-pyrone (11.1 mg, 0.0895 mmol) were stirred in dry benzene (5 ml) at room temperature for 4 h. Slow addition of hexane while stirring gave a pale yellow precipitate. It was filtered off and washed with 2:1 hexane/benzene (2×2 ml) (64.0 mg, 87%). m.p. 82–85 °C (dec.). IR (cm^{-1}) 3058, 3010, 1989 (CO), 1652 (C=O), 1575, 1544, 1481, 1435, 1271, 1224, 1151, 1096, 1031, 998, 906, 752, 694, 637. ^1H NMR ($CDCl_3$) δ 7.67–7.53 (m, 12 H), 7.51–7.38 (m, 18 H), 5.58 (s, 2 H), 2.07 (s, 6 H, 2 Me). ^{13}C NMR (CD_2Cl_2) δ 189.24 (dt, ^1J(Rh–C) = 74.3 Hz, ^2J(P–C) = 17 Hz, CO), 182.94 (s, Rh−O=*C*), 168.55 (=*C*−O), 134.38 (t, J = 7 Hz), 131.34, 130.38 (t, J = 23 Hz), 129.07 (t, J = 5 Hz), 121.31 (q, ^1J(F–C) = 321 Hz, CF_3), 113.01 (=*C*−C=O−Rh), 19.71 (Me). ^{31}P NMR ($CDCl_3$) δ 30.9 (d, ^1J(Rh–P) = 127.4 Hz). ^{19}F NMR ($CDCl_3$) δ −78.2. MS *m/e* 779 (4, *M*–OTf), 655 [23, $(Ph_3P)_2RhCO$], 627 [100, $(Ph_3P)_2Rh$], 287 (67), 286 (68).

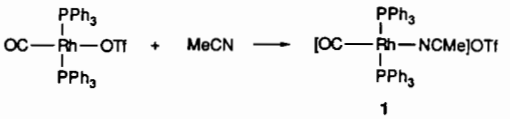
Complex 8 (L = 1-methyl-2-pyridone)

A solution of 1-methyl-2-pyridone (12.1 mg, 0.111 mmol) in dry benzene (2 ml) was added through a

pipet to a suspension of *trans*-carbonylbis(triphenylphosphine)rhodium triflate (82.3 mg, 0.102 mmol) in the same solvent (3 ml). The mixture was stirred at room temperature for 17 h. Slow addition of hexane with stirring gave a pale yellow precipitate, which was filtered off, washed with hexane (2 ml) and dried under vacuum (85.1 mg, 91%). m.p. 110–114 °C (dec.). IR (cm^{-1}) 3057, 3011, 1987 (CO), 1642, 1559, 1532, 1436, 1274, 1264, 1153, 1096, 1031, 752, 748, 694, 637. ^1H NMR (CD_2Cl_2) δ 7.75–7.54 (m, 12 H), 7.54–7.30 (m, 18 H), 7.21 (d, $J=6$ Hz, 1 H), 7.07 (t, $J=7$ Hz, 1 H), 6.32–6.18 (m, 2 H), 2.86 (s, 3 H, Me). ^{13}C NMR (CD_2Cl_2) δ 189.19 (dt, $^1J(Rh–C)=74.2$ Hz, $^2J(P–C)=16.6$ Hz, CO), 162.75 (s, Rh–O=*C*), 141.84 (C6 or C4 of Py), 140.19 (C4 or C6 of Py), 134.45 (t, $J=6.7$ Hz), 131.54, 130.71 (t, $J=23.2$ Hz), 129.14 (t, $J=5.0$ Hz), 121.34 (q, $^1J(F–C)=321$ Hz, CF_3), 119.97 (C3 or C5 of Py), 110.58 (C5 or C3 of Py), 38.87 (Me). ^{31}P NMR ($CDCl_3$) δ 32.1 (d, $^1J(Rh–P)=128.1$ Hz). ^{19}F NMR ($CDCl_3$) δ −77.6; MS *m/e* 764 (11, *M*–OTf), 655 [76, $(Ph_3P)_2RhCO$], 627 [100, $(Ph_3P)_2Rh$], 287 (66), 286 (61). *Anal.* Calc. for $C_{44}H_{37}F_3NO_5P_2SRh \cdot 0.4C_6H_6$: C, 58.98; H, 4.20. Found: C, 59.32; H, 4.37%.

Results and discussion

The reaction of *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ with acetonitrile at room temperature yields a stable yellow solid in 84% yield. The IR spectrum (Table 1) displays a CN absorption at 2292 cm^{-1}, which has been shifted to higher wavenumber compared to the CN stretching frequency of the uncoordinated acetonitrile (2250 cm^{-1}). This indicates the formation of a σ-complex (**1**) in which the coordination occurred at the nitrogen atom of the CN group, not at the CN π-bond [7]. The increased CN stretching frequency indicates that there is little π-backbonding from the filled metal d orbital to the π^* orbital of the CN group. In the ^{13}C NMR spectrum (Table 1), the CN-carbon atom in **1** resonates at 127.85 ppm, which has been shifted downfield by 10 ppm compared to the 117.7 ppm resonance for that of the free



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acetonitrile. This downfield shift probably comes from the inductive effect of the rhodium atom that acts as a Lewis acid in compound **1**. Based on these data, the CN group in complex **1** is a good σ-donor and a poor π-acceptor. The ^1H NMR spectrum of **1** displays a singlet at 1.58 ppm (Table 1) for the methyl protons, which are shifted upfield relative to the 1.94 ppm resonance for those of the free ligand. This upfield shift is probably from the coordinated MeCN in **1** being in the proximity of the phenyl groups of the phosphine ligands.

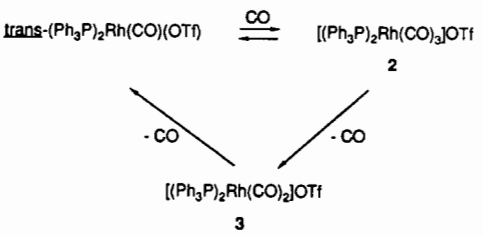
Reaction of *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ with other weakly coordinating ligands such as methanol, tetrahydrofuran and acetone does not form pure stable ionic complexes. The reaction with carbon monoxide is reversible in $CDCl_3$ as monitored by ^{31}P NMR spectroscopy. When CO is introduced into an NMR tube containing a *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ solution in $CDCl_3$, the initial doublet for *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ at 29.2 ppm ($^1J(Rh–P)=124.8$ Hz) in the ^{31}P NMR spectrum is quickly replaced by a new doublet at 33.7 ppm with a smaller ^{103}Rh–^{31}P coupling ($^1J(Rh–P)=73.5$ Hz). However, when nitrogen is introduced to remove carbon monoxide, the ^{31}P NMR spectrum shows the broadening of the doublet at 33.7 ppm and then the appearance of another doublet at 28.4 ppm ($^1J(Rh–P)=116.0$ Hz). Within a day, the ^{31}P NMR spectrum changes back to that of the starting *trans*-$(Ph_3P)_2Rh(CO)(OTf)$

TABLE 1. A comparison of IR and NMR data between the coordinated and the free ligands[a]

Ligand	IR (cm^{-1})	^{13}C NMR (ppm)	^1H NMR (ppm)
MeCN in **1**	$\nu CN=2292$ (2250[a] [8])	CN: 127.85 (117.7 [10])	Me: 1.58 (1.94[c])
$HCONMe_2$ in **4**	$\nu CO=1646$ (1670[b])	CO: 165.13 (162.4 [10])	CHO: 6.44 (7.89[c]) Me's: 2.37 (2.98[c]), 2.16 (2.81[c])
$MeCONMe_2$ in **5**	$\nu CO=1601$ (1646[b])	CO: 173.96 (169.6 [10])	MeCO: 1.31 (1.98[c]) NMe_2: 2.53 (3.01[c]), 2.41 (2.83[c])
Pyrone in **7**	$\nu CO=1652$ (1673[b])	CO: 182.94 (179.9 [10])	=CH: 5.58 (6.06[b]) Me's: 2.07 (2.25[b])

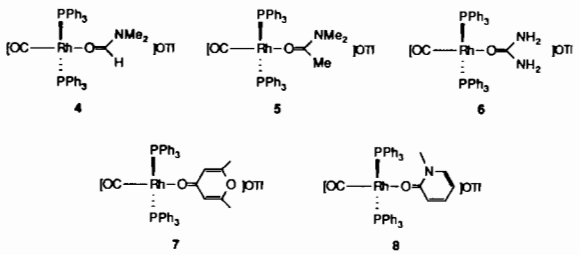
[a]Numbers in parentheses are for free ligands. [b]Recorded on authentic commercial samples. [c]The Sadtler Standard Spectra.

(29.2 ppm, $^1J(Rh-P) = 124.8$ Hz). Bases on these



data and the analogous [*trans*-$(Ph_3P)_2Ir(CO)(MeCN)]^+$ system [8a], the first observed intermediate at 33.7 ppm is assigned as a penta-coordinated species **2**, which gradually loses CO to form **3** (at 28.4 ppm) and finally returns to the starting material *trans*-$(Ph_3P)_2Rh(CO)(OTf)$. This reaction of $(Ph_3P)_2Rh(CO)(OTf)$ with CO parallels that of $[(Ph_3P)_2Rh(COD)]ClO_4$ (COD = 1,5-octadiene), which also generates [8b] a labile species $[(Ph_3P)_2Rh(CO)_3]ClO_4$. The reversible CO association is consistent with the poor nucleophilicity of carbon monoxide. It has been reported that the replacement of triflate in $Mn(CO)_5(OTf)$ by carbon monoxide is very difficult and it occurs only in superacid solutions [9].

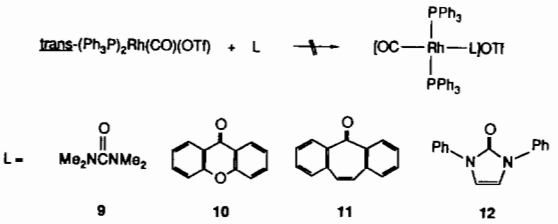
Other ligands that contain electron-rich carbonyls such as *N*,*N*-dimethylformamide and urea also replace the triflate in *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ to form ionic complexes **4–8**. All these coordinated



ligands display decreased C=O stretching frequencies in the IR spectra. For example, the carbonyls of the coordinated ligands in compounds **4**, **5** and **7** absorb in the IR spectra at 1646, 1601 and 1652 cm^{-1} (Table 1), respectively; whereas the carbonyl groups in the corresponding free ligands, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide and 2,6-dimethyl-γ-pyrone, absorb at *c.* 1670, 1646 and 1673 cm^{-1}, respectively*. Therefore, upon coordination the carbonyl stretching frequency is shifted to lower wavenumbers by *c.* 24, 45 and 21 cm^{-1} for compounds **4**, **5** and **7**, respectively. This decrease in carbonyl bond order (decreasing wavenumber) suggests the presence of π-backbonding from the filled metal d orbital to the π*orbital of the carbonyl group. However, in the ^{13}C NMR spectra all the carbonyl-carbon signals are shifted downfield relative to those in the free ligands (Table 1), indicating that the π-backbonding of the metal is not significant enough to compensate the inductive effect of the σ-bound metal. From this observation, the carbonyl groups in complexes **4–8** act more as σ-donors than as π-acceptors.

In the ^1H nMR spectra, all the protons of the coordinated ligands in **4–8** are shifted upfield compared to those in the free ligands (Table 1). The metal π-backbonding can probably cause these upfield shifts, but contribution from being in the proximity of the two phosphine ligands should also exist because the methyl protons in complex **1** are also shifted upfield although no metal π-backbonding is observed by IR spectroscopy. The mass spectra of all these compounds containing σ-bound ligands display $(Ph_3P)_2Rh$ (*m/e* = 627) as the major fragment.

Unlike urea, 1,1,3,3-tetramethylurea (**9**) shows no reactivity toward *trans*-$(Ph_3P)_2Rh(CO)(OTf)$. This must be because the introduction of the four methyls increases the steric hindrance between the two bulky phosphine and the organic ligands. Likewise, in



contrast to the pyrone molecule that forms complex **7**, xanthone (**10**) and dibenzosuberenone (**11**) do not react with *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ to form analogous ionic complexes. It is probably also due to the increased steric hindrance between the phosphine and the bulkier organic ligands. Imidazolone (**12**) also shows no reactivity toward *trans*-$(Ph_3P)_2Rh(CO)(OTf)$ in benzene, dichloromethane or more polar solvents like tetrahydrofuran.

In conclusion, we have demonstrated an easy way for the preparation of stable ionic rhodium(I) complexes by the ready replacement of triflate in *trans*-$(Ph_3P)_2Rh(CO)(OTf)$. In all these compounds, the coordinated ligands act more as σ-donors than as π-acceptors. Bulky ligands such as **9–12** do not react due to the increased steric effect with the two triphenylphosphine ligands.

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*Recorded on authentic commercial samples.

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