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Synthesis and Reactivity of Ruthenium Hydride Complexes Containing Chelating Triphosphines. 6. Reactions of Ruthenium Hydride Complexes with CO_2-like Molecules[1]

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Introduction

Activation of CO_2 by transition-metal complexes has been attracting increasing attention, presumably due to the interest in utilizing inexpensive and abundant CO_2 as a feedstock for organic compounds.[2] Insertion of CO_2 into M–H or M–C bonds constitutes one of the important steps in the production of carbon-containing compounds from CO_2.[2] In this connection, ruthenium hydride complexes such as $RuH_2(PPh_3)_4$ and $RuHCl(PPh_3)_3$ are active for the catalytic production of formates or formic acid from CO_2.[3-6] The formate complex $RuH(O_2CH)(PPh_3)_3$ could be synthesized by the insertion of CO_2 into a Ru–H bond in $RuH_2(L)(PPh_3)_3$ ($L = H_2, N_2, PPh_3$).[7,8] Insertion of CO_2-like molecules, such as CS_2,[7,8b,9-13] carbodiimides,[14,15] isothiocyanates,[16] and isocyanates[17] into Ru–H bonds in several monophosphine ruthenium hydride complexes has also been reported. We herein report the reactions of CO_2 and CO_2-like molecules with the chelating triphosphine complexes $RuH_2(H_2)(Cyttp)$ and $RuHCl(Cyttp)$ ($Cyttp = PhP(CH_2CH_2CH_2P(C_6H_{11})_2)_2$).

Experimental Section

All manipulations were performed under an argon atmosphere by using standard Schlenk techniques, unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Solutions were transferred by use of syringes that were flushed with argon before use. Air-sensitive solids were handled and transferred in a Vacuum Atmospheres HE43 inert-atmosphere box equipped with a Mo-40 catalyst system. Minute traces of oxygen and water were removed from commercially available argon by passing the gas through two columns packed with hot (180 °C) BASF active copper catalyst and Drierite, respectively.

Reagent grade chemicals were used as purchased from Aldrich Chemical Co., Inc., unless stated otherwise. Ruthenium trichloride hydrate was loaned by Johnson Matthey Inc. $RuCl_2(Cyttp)$ and RuHCl(Cyttp)[18] were prepared by literature methods.

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 4000 to 200 cm^{-1}, as pressed potassium bromide pellets, as Nujol mulls, or in solution. Spectra were calibrated against the sharp 1601-cm^{-1} peak of polystyrene film. A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz) and phosphorus-31 (101.25 MHz) NMR spectra in 5-mm tubes. Residual solvent proton resonances were used as internal standards for the ^1H spectra. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. The ^{31}P NMR and selected ^1H NMR data are collected in Tables I and II, respectively. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

$RuH_2(H_2)(Cyttp)$. In a typical experiment, a mixture of 0.30 g of $RuCl_2(Cyttp)$ (0.40 mmol) and 0.20 g of NaH (8.3 mmol) in 30 mL of THF was stirred overnight at ca. 40–50 °C under H_2 atmosphere to give a light yellow solution. The solvent was then removed completely, and the residue was extracted with ca. 40 mL of benzene, which was removed subsequently to give a light yellow solid. The reactivity of the compound was studied by adding appropriate amounts of other reagents to the extract.

Table I. ^{31}P NMR Data for the Ru(Cyttp) Complexes from Reactions of CO_2 and CO_2-like Molecules[a]

compd	δ_{P_1}	δ_{P_2}	$^2J(P_1P_2)$
$RuH(O_2CH)(Cyttp)$ (**1**)	52.1	25.7	38.7
RuH(*p*-TolNCHN-*p*-Tol)(Cyttp) (**2**)	36.2	19.6	40.5
RuH(CyNCHNCy)(Cyttp) (**3**)	39.6	24.0	40.4
$RuH(S_2CH)(Cyttp)$ (**4A**)	39.8	22.4	41.4
$RuH(S_2CH)(Cyttp)$ (**4B**)	28.6	28.2	38.7
"$Ru(S_2CH_2)(Cyttp)$" (**4C**)	46.0		49.8
$RuCl(S_2CH)(Cyttp)$ (**5**)	15.4	4.4	37.6

[a] Spectra were obtained in benzene. Chemical shifts are in δ with respect to external 85% H_3PO_4 (δ 0.0); positive values are downfield; coupling constants are in hertz. P_1 is the central phosphorus atom, and P_2, the two terminal phosphorus atoms in Cyttp.

Table II. Selected ^1H NMR Data for the Ru(Cyttp) Complexes from the Reactions of CO_2 and CO_2-like Molecules[a]

compd	δ_{Ru-H}	$^2J(P_1H)$	$^2J(P_2H)$	δ_{X_2CH}
$RuH(O_2CH)(Cyttp)$ (**1**)	−23.02 (dt)	39.1	20.1	8.57
RuH(*p*-TolNCHN-*p*-Tol)(Cyttp) (**2**)	−21.32 (dt)	33.0	21.3	8.90
RuH(CyNCHNCy)(Cyttp) (**3**)	−20.30	29.4	24.6	8.20
$RuH(S_2CH)(Cyttp)$ (**4A**)	−13.91 ("q")	18	23	11.85
$RuH(S_2CH)(Cyttp)$ (**4B**)	−15.69 ("q")	23.8	23.8	11.60
"$Ru(S_2CH_2)(Cyttp)$" (**4C**)				6.08
$RuCl(S_2CH)(Cyttp)$ (**5**)				11.45 (dt)[b]

[a] Spectra were obtained in benzene. Chemical shifts are in δ with respect to Me_4Si (δ 0.0); coupling constants are in hertz. P_1 is the central phosphorus atom, and P_2, the two terminal phosphorus atoms in Cyttp. d = doublet; q = quartet; t = triplet. [b] $J(P_1H) = 5.4$ Hz; $J(P_2H) = 3.4$ Hz.

$RuH(O_2CH)(Cyttp)$. A mixture of 1 g of dry ice (CO_2) and $RuH_2(H_2)(Cyttp)$ (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2(Cyttp)$ with

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excess NaH) in 15 mL of benzene was stirred until all the dry ice chunks disappeared (ca. 5 min) to give a yellow solution. The solvent was then removed completely, and 6 mL of hexane was added to give a yellow powder. The powder was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.17 g, 79%. Anal. Calcd for $C_{37}H_{63}O_2P_3Ru$: C, 60.56; H, 7.86. Found: C, 60.37, H, 7.73.

RuH(*p*-TolNCHN-*p*-Tol)(Cyttp) (*p*-Tol = *p*-Tolyl). A mixture of 0.10 g of *p*-TolN=C=N-*p*-Tol (0.45 mmol) and $RuH_2(H_2)$(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2$(Cyttp) with excess NaH) in 30 mL of benzene was stirred at room temperature for 30 min to give a yellow solution. The solvent was then removed completely, and 5 mL of MeOH was added to give a yellow precipitate. The precipitate was collected on a filter frit, washed with MeOH, and dried under vacuum overnight. Yield: 0.20 g, 83%. Anal. Calcd for $C_{51}H_{77}N_2P_3Ru$: C, 67.15; H, 8.51; N, 3.07. Found: C, 66.98; H, 8.57; N, 3.05.

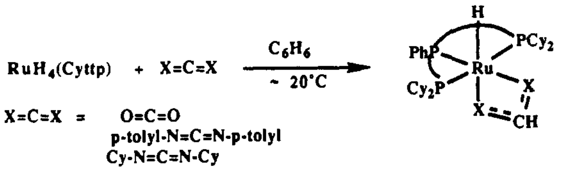
RuH(CyNCHNCy)(Cyttp) (Cy = Cyclohexyl). A mixture of 0.10 g of CyN=C=NCy (0.48 mmol) and $RuH_2(H_2)$(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2$(Cyttp) with excess NaH) in 25 mL of benzene was stirred at room temperature for 15 min to give a yellow solution. Then the solvent of the reaction mixture was removed completely, and the solid was dried under vacuum for 2 days. NMR data were collected on the residue. The product is extremely soluble in common organic solvents such as ether and hexane and reacts with MeOH to form RuH_2(CO)(Cyttp). Thus, it is difficult to obtain a pure solid.

RuH(S_2CH)(Cyttp). A 0.5-mL quantity of CS_2 (8 mmol) was added to a solution of $RuH_2(H_2)$(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of $RuCl_2$(Cyttp) with excess NaH) in 5 mL of benzene. The reaction mixture became red immediately. The liquids of the reaction mixture were then removed completely, and 5 mL of hexane was added to give a small amount of red powder. The mixture was set in a freezer for 3 days to precipitate more red solids, some of which were crystalline. The solid was collected on a filter frit, washed with cold hexane, and dried under vacuum overnight. Yield: 0.09 g, 50% (the product is extremely soluble and reacts with MeOH to form RuH_2(CO)(Cyttp)). Anal. Calcd for $C_{37}H_{63}S_2P_3Ru$: C, 58.01; H, 8.29; S, 8.37. Found: C, 57.97; H, 8.17; S, 8.47.

RuCl(S_2CH)(Cyttp). A mixture of 0.10 g of RuHCl(Cyttp) and 1.0 mL of CS_2 (16 mmol) in 15 mL of benzene was refluxed for 1 h to give a deep red solution. The liquids of the reaction mixture were then removed completely, and 15 mL of Et_2O was added to give a red powder. The powder was then collected on a filter frit, washed with Et_2O, and dried under vacuum overnight. Yield: 0.07 g, 60%. Anal. Calcd for $C_{37}H_{62}ClS_2P_3Ru$: C, 55.18; H, 7.81; Cl, 4.42. Found: C, 54.94; H, 7.69; Cl, 4.61.

Results

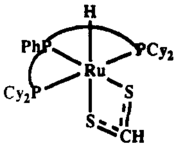
The hydride complex $RuH_2(H_2)$(Cyttp) reacts readily with dry ice (CO_2), presumably via the RuH_2(Cyttp) intermediate,[18] to give $RuH(O_2CH)$(Cyttp) (**1**), along with a trace amount of RuH_2(CO)(Cyttp) (eq 1). In the ^1H NMR spectrum, the hydride resonance appears at -23.02 ppm (dt, $^2J(PH)$ = 39.1, 20.1 Hz). The small phosphorus–hydride coupling is in agreement with a structure where the hydride is cis to the three phosphorus atoms of the triphosphine.[19] A singlet at 8.57 ppm is observed for the formate proton. This chemical shift is comparable to the values of 8.71 ppm in $MoH(O_2CH)(CO_2)(dmpe)_2$[20] and 8.55 ppm in $Cu(O_2CH)(PPh_3)_2$.[21] In the infrared spectrum of $RuH(O_2CH)$(Cyttp), the asymmetrical ν(OCO) stretching frequency is observed at 1575 cm^{-1}. This value is lower than that for a monodenate formate ligand, for example, 1614 cm^{-1} in $Mo(O_2CH)_2(dmpe)_2$,[20] but very close to the value of 1565 cm^{-1} in $RuH(O_2CH)(PPh_3)_3$,[7] which contains a bidentate formate ligand as confirmed by X-ray diffraction. Thus the formate group in $RuH(O_2CH)$(Cyttp) is bidentate. Other bands associated with the formate group[7,8,20] are observed at 2805, 1365, and 1315 cm^{-1}. The ^{31}P NMR spectrum shows a doublet at 25.7 ppm for the two terminal phosphorus atoms and a triplet at 52.1 ppm for the cnetral phosphorus atom; this pattern is consistent with a structure where the central phosphorus atom is trans to an oxygen ligand in a meridional arrangement.[22]



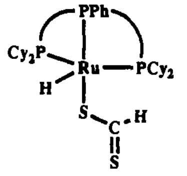
(1)

The hydride complex $RuH_2(H_2)$(Cyttp) also reacts instantly with carbodiimides RN=C=NR (R = *p*-Tol, Cy) to give the corresponding insertion products RuH(RNCHNR)(Cyttp) (**2**, R = *p*-Tol; **3**, R = Cy). The structure of RuH(RNCHNR)(Cyttp) is similar to that of $RuH(O_2CH)$(Cyttp), as indicated by spectroscopic data. The presence of formamidinate ligands is established by the presence of low-field resonances in the ^1H NMR spectra, i.e. 8.90 ppm in RuH(*p*-TolNCHN-*p*-Tol)(Cyttp) and 8.20 ppm in RuH(CyNCHNCy)(Cyttp), assignable to the central protons of the formamidinate ligands. The chemical shifts for such protons were reported to range from 6.80 to 9.32 ppm.[14,15] The formamidinate ligands in RuH(RNCHNR)(Cyttp) are probably bidentate, since the characteristic infrared bands[14,15] for chelating formamidinate ligands are observed, for example at 1550, 1500, and 1260 cm^{-1} in RuH(*p*-TolNCHN-*p*-Tol)(Cyttp).

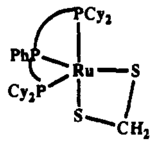
The reaction between $RuH_2(H_2)$(Cyttp) and excess CS_2 is complicated compared with the reactions described above. If the reaction time was long (over several hours), a black solid precipitated from the reaction mixture in benzene. The solid was insoluble in common organic solvents; thus no characterization was carried out. If the reaction time was short (several minutes), a red solid could be isolated from cold hexane in low yield (due to high solubility). Elemental analyses indicate that the composition of the red powder is $RuH(S_2CH)$(Cyttp) (**4**). Spectroscopic data suggest that the red powder is a mixture of three compounds: **4A**, **4B**, and **4C**. It was observed that **4A** and **4B** are unstable in benzene solution and slowly isomerize into **4C**. The proposed structures for **4A**–**4C** are as follows: Isomers **4A** and **4B** have similar proton NMR parameters, and both contain one hydride with small phosphorus–hydride coupling constants, as listed in Table II, and one dithioformate ligand. The chemical shifts for the RuH proton are -13.91 ppm in **4A** and -15.69 ppm in **4B**. The signals for the thioformate protons appear at 11.85 ppm in **4A** and 11.60 ppm in **4B**. The previously reported chemical shifts for such protons range from 9.5 to 14 ppm.[9,10,23] Compound **4A**, however, has ^{31}P NMR parameters (Table I) different from those of **4B**. For **4A**, the phosphorus resonances appear at 39.8 ppm (t, $J(PP)$ = 41.4 Hz) for the central phosphorus atom of the triphosphine and 22.4 ppm (d, $J(PP)$ = 41.4 Hz) for the two terminal PCy_2 groups. The ^{31}P NMR spectral pattern is similar to that for RuH(RNCHNR)(Cyttp) (R = *p*-Tol, Cy) and $RuH(O_2CH)$(Cyttp). Thus isomer **4A** might have a structure similar to those for the formamidinate and formate complexes. For **4B**, the chemical shifts for the central phosphorus atom (28.6 ppm) and the two terminal phosphorus atom (28.2 ppm) are very close. To be consistent with the NMR data (presence of an S_2CH ligand, similar chemical shifts for the three phosphorus atoms, and a hydride with small phosphorus–hydride coupling constants), structure **4B** is proposed. The facial arrangement for Cyttp and ttp (ttp = $PPh(CH_2CH_2CH_2PPh_2)_2$) is known.[24-26] In a facial



4A



4B



4C

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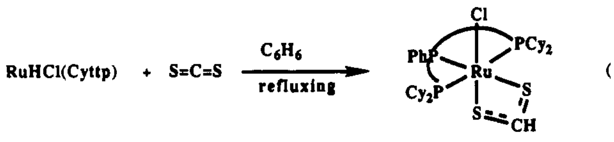
complex of ttp or Cyttp, the central and terminal phosphorus atoms could have very similar chemical shifts. In fact, the ^{31}P NMR spectrum for **4B** is very similar to that of *fac*-$Ru(O_2CMe)_2(ttp)$.[26] In structure **4B**, the coupling between the hydride and the two terminal phosphorus atoms could be similar in magnitude to that between the hydride and the central phosphorus atom, since P–H coupling constants are angular dependent[27] and cis,trans P–H coupling constants usually have opposite signs in metal complexes.[28]

The structure of **4C** is unclear on the basis of the spectroscopic data. The ^1H NMR spectrum shows no hydride resonance. In the aromatic region, besides the signal associated with the triphosphine ligand, there is a singlet at 6.08 ppm, corresponding to two protons per Cyttp on the basis of integration. The integration and absence of a hydride resonance suggest that **4C** might be $Ru(S_2CH)_2(Cyttp)$. The formation of $Ru(S_2CH)_2(PR_3)_3$ (PR_3 = PPh_2Me, $PPhMe_2$) from the reactions of CS_2 with $RuH_2(PR_3)_4$ is known. However, the value 6.08 ppm is too low for the chemical shift value for coordinated dithioformate protons (usually in the range 9.5–14 ppm).[9,10,23] This formulation is also inconsistent with the analytical data. The formulation of the compound as $Ru(S_2CH_2)(Cyttp)$ (structure **4C**) seems plausible. This formulation is consistent with analytical data and ^1H NMR integration. The signal at 6.08 ppm could be assigned to the S_2CH_2 protons. The value of 6.08 ppm is comparable with 6.25 ppm for the italic proton in S_2C*H*$-PMe_2Ph$ in the compound $[Ru(S_2CHPMe_2Ph)(PMe_2Ph)_3]PF_6$.[13] It has also been reported that the signals for bridged S_2CH_2 were observed at 6.31 ppm for $(CpMo)_2(S_2CH_2)(S_2CHCO_2Me)_2$ and 5.41 ppm for $(CpMo)_2(S_2CH_2)(S_2CH_2CO_2Me)_2$ in their ^1H NMR spectra.[29]

In contrast to $RuH_2(H_2)(Cyttp)$, the monohydride complex RuHCl(Cyttp) failed to react with CO_2, RN=C=NR (R = *p*-Tol, Cy). However, RuHCl(Cyttp) reacts with CS_2 smoothly in refluxing benzene to give $RuCl(S_2CH)(Cyttp)$ (**5**) (eq 2). The



(2)

^{31}P NMR spectrum of $RuCl(S_2CH)(Cyttp)$ shows a doublet at 4.4 ppm for the two terminal phosphorus atoms and a triplet at 15.4 ppm for the central phosphorus atom. In the ^1H NMR spectrum, the resonance for the dithioformate proton was observed at 11.45 ppm (dt, $^3J(PH)$ = 5.4, 3.4 Hz). Thus both the ^{31}P and ^1H NMR data are consistent with the triphosphine being meridional around ruthenium. In the infrared spectrum, the bands assignable to the coordinated dithioformate were observed at 1210 and 910 cm^{-1}. The dithioformate group in $RuCl(S_2CH)(Cyttp)$ is probably bidentate, to give an 18-electron complex.

Both $RuH_2(H_2)(Cyttp)$ and RuHCl(Cyttp) are reactive toward RNCS (R = Me, Ph, *p*-Tol). The products usually are mixtures and are soluble in common organic solvents. Thus it is difficult to separate and isolate pure compounds. The compounds formed in these reactions are most likely insertion products. Insertions of isothiocyanate into Ru–H bonds have been reported previously.[16]

Discussion

It was reported previously that $RuH_2(L)(PPh_3)_3$ (L = H_2, N_2, PPh_3)[7,8] reacted with CO_2 to give insertion product $RuH(O_2CH)(PPh_3)_3$, while $RuH_2(L)_4$ (L = PPh_2H, PPh_2Me, $PPhMe_2$)[8b] failed to react with CO_2. The failure was attributed to the unavailability of an unsaturated intermediate from dissociation of phosphines. This study shows that $RuH_2(H_2)(Cyttp)$ is more reactive than the 16-electron monohydride complex RuHCl(Cyttp) toward CO_2-like molecules. Thus the electronic property of an unsaturated metal center is also important to initiate CO_2 insertion.

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Hydrazinophosphine Complexes of Iron: Metallacycle Formation via Attack on Coordinated Carbon Monoxide

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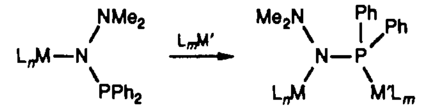
The polyfunctional ligand $Me_2NN(PPh_2)Li$ (**1**) has numerous possible coordination modes—amino, amido, and phosphino—which are capable of bonding in a monohapto fashion individually or in combination to produce chelated or bridged complexes. This variability in the nature of coordination, i.e., in both type and degree, makes these compounds attractive frameworks for the preparation of catalytically active compounds containing transition metals with complementary properties, such as early and late transition metals. Complexes of this type are of interest in catalytic reactions involving unsymmetric substrates such as the reduction of carbon monoxide.[2]

Initial investigations were designed to prepare hydrazinophosphine complexes of a single metal center such that the sole attachment of the ligand to the metal is a metal–nitrogen σ bond, thus leaving the phosphino fragment pendent (eq 1). Species of this type could then be used to prepare heterobimetallic compounds via coordination of a different metal to the phosphine.



(1)

The cyclopentadienyliron dicarbonyl fragment (Fp) was our first choice, due to its robust nature that would hopefully allow us to avoid oligomer formation via phosphine coordination by displacement of CO from other molecules of the complex.[3] Reaction of FpI with 1 equiv of **1** in THF at −80 °C produced a deep red solution that turns yellow-orange upon warming to room temperature. Removal of the volatile material from the reaction followed by extraction with methylene chloride and subsequent recrystallization from methylene chloride/ether yielded an orange crystalline material, **2**, in ca. 60% yield. Compound **2** displays a single resonance in the $^{31}P\{^1H\}$ NMR at δ 116 (relative to external H_3PO_4) indicating that the phosphorous is coordinated.[4]

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[2] For a recent review of heterobimetallic systems, see: Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

[3] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 98.

[4] The $^{31}P\{^1H\}$ chemical shift for the free hydrazidophosphine, $Me_2NN(PPh_2)H$ is δ 38.5 relative to external H_3PO_4. The chemical shift for phosphine virtually always shifts downfield upon coordination. See: Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Complexes*; Springer Verlag: Berlin, 1979.

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