Intramolecular N−H···H−Ru Proton−Hydride Interaction in Ruthenium Complexes with (2-(Dimethylamino)ethyl)cyclopentadienyl and (3-(Dimethylamino)propyl)cyclopentadienyl Ligands. Hydrogenation of CO_2 to Formic Acid via the N−H···H−Ru Hydrogen-Bonded Complexes

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Addition of 1 equiv of HBF_4 to (η^5-$C_5H_4(CH_2)_nNMe_2$)RuH(dppm) (n = 2, 3) gave [(η^5-$C_5H_4(CH_2)_nNMe_2H^+$)RuH(dppm)]BF_4, in which the amine function was protonated. Relaxation time T_1 measurements indicated the existence of an intramolecular N−H···H−Ru hydrogen-bonding interaction in these complexes. A spin saturation transfer study and H/D exchange experiment with [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BF_4 revealed fast exchange, probably via a dihydrogen complex intermediate, between the hydride ligand and N−H. An attempt to grow single crystals of [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BPh_4 for X-ray study resulted in isolation of crystals of the complex, [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]-BPh_4, with the chelating (3-(dimethylamino)propyl)cyclopentadienyl ligand. Exposure of [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]BF_4 to 60 atm of H_2 at 60 °C gave [(η^5-$C_5H_4(CH_2)_3$-NMe_2H^+)RuH(dppm)]BF_4 within 30 min. Reacting [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]BAr'_4 (Ar′ = 3,5-$(CF_3)_2C_6H_3$) with Ph_2SiH_2 yielded [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BAr'_4; it is proposed that hydrolysis of the η^2-silane intermediate by adventitious moisture in the solvent affords an η^2-dihydrogen species, and heterolytic cleavage of the dihydrogen ligand by the pendant amino group gives the final product. Heating solutions of [(η^5:η^1-$C_5H_4(CH_2)_n$-NMe_2)Ru(dppm)]BF_4 under H_2/CO_2 (40 atm/40 atm) at 80 °C for 16 h gave formic acid in low yields (n = 2, TON = 6; n = 3, TON = 8). The formation of formic acid is best explained by a mechanism involving intramolecular heterolytic cleavage of the bound H_2 to generate [(η^5-$C_5H_4(CH_2)_nNMe_2H^+$)RuH(dppm)]BF_4, followed by CO_2 insertion into the Ru−H and then N−H protonation of the formato ligand. Carbon disulfide inserted into the Ru−H bond of [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BF_4 to give [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)Ru(η^1-SCSH)-(dppm)]BF_4.

Introduction

One of the features of dihydrogen complexes is the activation of the H_2 ligand with respect to heterolysis.[1] Intermolecular heterolytic cleavage of η^2-H_2 can be achieved by a variety of bases.[2] For example, [IrH(H_2)-(bq)(PPh_3)$_2$]$^+$ (bq = 7,8-benzoquinolinato)[2a] and [Re-(CN*t*Bu)$_3$(PCy_3)$_2$(H_2)]$^+$ [2b] can be cleaved by strong bases alkyllithium and alkoxides, respectively, [CpRu(dmpe)-(H_2)]$^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane),[2d] [Re(CO)$_2$(triphos)(H_2)]$^+$ (triphos = MeC(CH_2PPh_2)$_3$),[2g] and [Os(NCMe)$_3$(P*i*Pr$_3$)$_2$(H_2)]$^{2+}$ [2h] by mild base NEt_3, and the highly acidic dihydrogen complexes [Cp*Re-(CO)(NO)(H_2)]$^+$,[2j] [Cp*Ru(CO)(H_2)]$^+$,[2j] [Os(bpy)(CO)-(PPh_3)$_2$(H_2)]$^{2+}$ (bpy = bipyridine),[2k] [Os(dppe)$_2$(CH_3CN)-(H_2)]$^{2+}$,[2l] and [RuCl(CO)(PMP)(H_2)]$^+$ (PMP = 2,6-(Ph_2PCH_2)$_2$$C_5H_3N$)[2m] by the very weak base diethyl ether.

Intramolecular heterolytic cleavage of the H_2 ligand results from its deprotonation by the basic site on a coligand. This reaction and its reverse (eq 1) have been

(1) (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(2) (a) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794. (b) Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792. (c) Bianchini, C.; Linn, K.; Masi, D.; Peruzzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Inorg. Chem.* **1993**, *32*, 2366. (d) Chinn, M. S.; Heinekey, M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (e) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546. (f) Van Der Sluys, L. S.; Miller, M. M.; Kubas, G. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 2513. (g) Bianchini, C.; Marchi, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203. (h) Smith, K. T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473. (i) Mudalige, D. C.; Rettig, S. J.; James, B. R.; Cullen, W. R. *J. Chem. Soc., Chem. Commun.* **1993**, 830. (j) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (k) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396. (l) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270. (m) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y.-Z. *Organometallics* **1997**, *16*, 3941.

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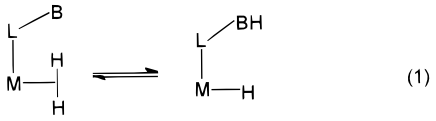


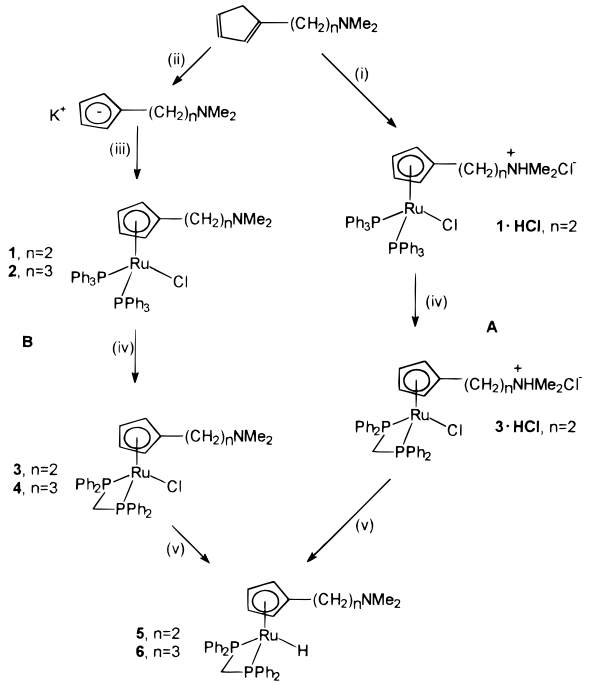
(1)

postulated to explain the H/D exchange reactions in $[IrH(H_2O)(bq)(PCy_3)_2]^+$ (bq = 7,8-benzoquinolinato),[3] $[Ir(H)_2(HS(CH_2)_3SH)(PCy_3)_2]^+$,[4] and $[IrH(X)(NH_3)_2(PEt_3)_2]^{+,2+}$ (X = Cl^-, NH_3, PEt_3).[5] Intramolecular proton transfer from the bound H_2 to, or σ-metathesis of H_2 ligand with, the neighboring organic group could be important in mechanisms of hydrogenation,[6] hydrogenolysis,[7] hydroformylation,[8] CO_2 reduction,[9] and hydrogenase reactions.[10] Recently, Crabtree's group[11] and that of Morris[12] have independently discovered complexes containing intramolecular H···H interactions of the type O−H···H−Ir and N−H···H−Ir. These compounds are regarded as intermediates in the intramolecular heterolytic splitting of dihydrogen. A dihydrogen complex, $[Os(H_2)(CO)(quS)(PPh_3)_2]^+$ (quS = quinoline-8-thiolate), was found to be in equilibrium with its coordinated thiol tautomer $[Os(H)(CO)(quSH)(PPh_3)_2]^+$.[13] We report here the synthesis and characterization of two ruthenium complexes containing intramolecular N−H···H−Ru interactions and demonstrate that existence of the equilibrium shown in eq 1 may account for the chemical properties of these complexes.

Results and Discussion

Synthesis and Characterization of (η^5-C_5H_4-$(CH_2)_n$$NMe_2$)RuH(dppm) ($n$ = 2, 3) and Related Complexes. The dppm hydride complex (η^5-$C_5H_4(CH_2)_2$-NMe_2)RuH(dppm) (**5**) was prepared according to the sequence in route A of Scheme 1. Treatment of a refluxing ethanol solution of triphenylphosphine with a $RuCl_3 \cdot xH_2O$/$C_5H_5(CH_2)_2NMe_2$ solution (in ethanol) gave (η^5-$C_5H_4(CH_2)_2NMe_2H^+Cl^-$)$RuCl(PPh_3)_2$ (**1·HCl**). The yield of this reaction was low (37%) compared to

Scheme 1[a]



[a] Legend: (i) $RuCl_3$, PPh_3, refluxed in EtOH; (ii) ^{t}BuOK, stirred in THF; (iii) $Ru(PPh_3)_3Cl_2$, stirred in THF; (iv) dppm, refluxed in toluene; (v) MeONa, refluxed in MeOH.

that of the reaction for preparation of the Cp analogue (η^5-C_5H_5)$RuCl(PPh_3)_2$ (90−95%).[14] The low yield was probably due to formation of an unidentified greenish brown side product. The amine group in the sidearm of **1·HCl** was protonated; protonation of nitrogen was confirmed by the downfield shift of the protons of the methyl groups attached to it. The ^{1}H NMR spectrum of **1·HCl** showed the *N*-methyl protons at 2.86 ppm, while those of the free ligand $C_5H_5(CH_2)_2NMe_2$ were measured at 2.27 ppm. Similar downfield shifts of the *N*-methyl protons have been observed in the titanium,[15] molydenum,[16] rhenium,[17] and rhodium[18] complexes containing similar ligands. Protonation of the amine group in **1·HCl** was also supported by observation of the broad singlet signal of N−H at 12.30 ppm in the ^{1}H NMR spectrum. Furthermore, the IR spectrum of **1·HCl** showed a broad band in the 2400−2700 cm^{-1} region, indicating nitrogen protonation. The $^{31}P\{^1H\}$ NMR spectrum of **1·HCl** showed a single resonance, consistent with the chemical equivalence of the two triphenylphosphine ligands. Substitution of PPh_3 ligands in **1·HCl** with dppm produced the dppm chloro complex (η^5-$C_5H_4(CH_2)_2NMe_2H^+Cl^-$)$RuCl$(dppm) (**3·HCl**). Its ^{1}H NMR spectrum showed the N−H signal at 11.95 ppm, and the *N*-methyl proton signal (2.62 ppm) was downfield relative to that of the free ligand. The IR spectrum

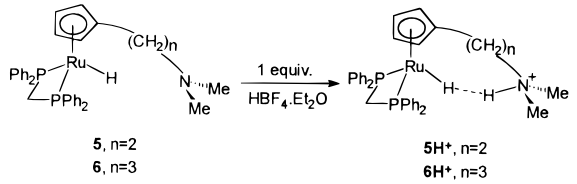
(3) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.
(4) Jessop, P. G.; Morris, R. H. *Inorg. Chem.* **1993**, *32*, 2236.
(5) Koelliker, R.; Milstein, D. *J. Am. Chem. Soc.* **1991**, *113*, 8524.
(6) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. *Organometallics* **1992**, *11*, 138. (b) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez, D. R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (c) Chan, W. C.; Lau, C. P.; Chen, Y. Z.; Fang, Y. Q.; Ng, S. M.; Jia, G. *Organometallics* **1997**, *16*, 34.
(7) (a) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65. (b) Guo, Z. Y.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1992**, *11*, 2690. (c) Albeniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242. (d) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014.
(8) Versluis, L.; Ziegler, T. *Organometallics* **1990**, *9*, 1985.
(9) Hutschka, F.; Dedieu, A.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1742.
(10) (a) Zimmer, M.; Schulte, G.; Luo, X.-L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 193. (b) Sellmann, D.; Käppler, J.; Moll, M. *J. Am. Chem. Soc.* **1993**, *115*, 1830.
(11) (a) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. *Acc. Chem. Res.* **1996**, *29*, 348. (b) Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1996**, *35*, 3007. (c) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485. (d) Lee, J. C., Jr.; Rheingold, A. L.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021.
(12) (a) Xu, W.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 1549. (b) Park, S.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 3001. (c) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (c) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201.
(13) Schlaf, M.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 625.
(14) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.
(15) (a) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140. (b) van der Zeijden, A. A. H. *J. Organomet. Chem.* **1996**, *518*, 147.
(16) (a) Wang, T.-F.; Lee, T.-Y.; Chou, J.-W.; Ong, C.-W. *J. Organomet. Chem.* **1992**, *423*, 31. (b) Wang, T.-F.; Wen, Y.-S. *J. Organomet. Chem.* **1992**, *439*, 155.
(17) Wang, T.-F.; Lai, C.-Y.; Wen, Y.-S. *J. Organomet. Chem.* **1996**, *523*, 187.
(18) Philippopoulos, A.; Hadjiliadis, N.; Hart, C. E.; Donnadieu, B.; McGowan, P. C.; Poilblanc, R. *Inorg. Chem.* **1997**, *36*, 1842.

showed the broad band of N−H at 2680 cm^{-1}. Taken together, it can be concluded that the amine group in **3·HCl** remained protonated. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at δ 15.5 ppm for the dppm ligand of **3·HCl**. The dppm hydride complex (η^5-$C_5H_4(CH_2)_2NMe_2$)RuH(dppm) (**5**) was prepared by heating the chloro complex **3·HCl** in refluxing methanol containing sodium methoxide. The same route provided an excellent synthesis of η^5-Cp iron, ruthenium, and osmium hydride complexes from their chloro precursors.[19,20] The ^1H NMR spectrum of **5** showed the hydride signal at −11.33 ppm as a triplet of doublets (^2J(HP) = 31.5 Hz, J(HH) = 3.4 Hz). The hydride is coupled to two equivalent phosphorus atoms and one of the methylene protons of dppm. Coupling of the hydride ligand with one of the methylene protons of dppm has also been observed in Cp*RuH(dppm).[20] The phosphorus atoms of the dppm ligand in **5** appeared as a singlet at δ 22.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The IR spectrum of **5** showed the Ru−H stretching frequency at 1916 cm^{-1}. It is noted that the amine group in the sidearm of **5** has been deprotonated. Deprotonation in **5** is supported by the fact that the chemical shift of its *N*-methyl protons bears strong resemblance to that of the *N*-methyl protons of the free Cp-N ligand and that the broad band in the region of 2400−2700 cm^{-1}, indicative of nitrogen protonation, is absent in its IR spectrum.

Complex **5** could also be prepared by following the sequence in route B of Scheme 1. Complexes **1** and **3** in this route are the nonprotonated forms of **1·HCl** and **3·HCl**, respectively. Unlike those of **1·HCl** and **3·HCl**, the ^1H NMR spectra of **1** and **3** do not show downfield shifts of the *N*-methyl protons in their Cp−N ligands. The overall yield of **5** by route B is higher than that by route A, because the formation of **1** in the former is near-quantitative, but the yield of **1·HCl** in route A is only 37%.

Similarly, **6** was prepared according to the sequence in route B. The hydride signal of **6** was observed at −11.26 ppm in ^1H NMR spectroscopy, also as a triplet of doublets (J(HP) = 30.8 Hz, J(HH) = 3.4 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **6** showed a singlet for the phosphorus atom of dppm at δ 23.0 ppm. The Ru−H stretching appeared as a medium to strong peak at 1929 cm^{-1} in the IR spectrum of **6**.

Acidification of (η^5-$C_5H_4(CH_2)_2NMe_2$)RuH(dppm) (5) and (η^5-$C_5H_4(CH_2)_3NMe_2$)RuH(dppm) (6). Addition of 1 equiv of HBF_4•Et_2O to **5** and **6** resulted in protonation of the pendant amine groups to give [(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)RuH(dppm)]BF_4 (**5H**$^+$) and [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BF_4 (**6H**$^+$), respectively (eq 2). Similar to those of the chloro complexes



5, n=2
6, n=3

5H$^+$, n=2
6H$^+$, n=3

(2)

1·HCl and **3·HCl**, room-temperature ^1H NMR spectra of **5H**$^+$ and **6H**$^+$ revealed downfield shifts for the methyl groups attached to nitrogen (**5H**$^+$, δ 2.56 ppm; **6H**$^+$, δ 2.82 ppm) compared to the analogous resonances for the free ligands. Observation of the N−H peaks in ^1H NMR spectra of **5H**$^+$ (δ ~3.7 ppm, partially obscured by neighboring peaks)) and **6H**$^+$ (δ 5.48 ppm) lends further support to amine group protonation.

At room temperature, the hydride signal of **5H**$^+$, which appears as a broad triplet (J(HP) = 30.6 Hz) at δ −11.47 ppm in the ^1H NMR spectrum, is slightly upfield (by 140 ppb) relative to the hydride signal of **5**. Unlike **5**, coupling of the hydride ligand in **5H**$^+$ to the methylene proton of the dppm ligand is not observed. At lower temperature (−35 °C or lower), the hydride signal of **5H**$^+$ sharpens slightly, but the H−H coupling is still undetectable. The hydride signal of **6H**$^+$ behaves similarly, showing a broad triplet (J(HP) = 30.8 Hz) at δ −11.30 ppm, which is 170 ppb upfield relative to the hydride signal of **6**; again, no H−H coupling to the dppm methylene proton is observed. Broadening of the hydride signals of **5H**$^+$ and **6H**$^+$ is probably due to H···H interaction between the hydride ligands and N−H on the pendant amine arms. Broadening and upfield shift of the hydride signal of $WH(CO)_2(NO)(PMe_3)_2$ were observed in the presence of acidic alcohol, due to the formation of intermolecular M−H···H−OR hydrogen bonding.[21] A slight upfield shift and significant broadening of hydride signals of both *cis* and *trans* isomers of $RuH_2(dppm)_2$ were also observed upon addition of exesss phenol.[22] The presence of an H···H interaction in **5H**$^+$ and **6H**$^+$ is supported by relaxation time T_1 and spin saturation transfer measurements. The relaxation time T_1 for the hydride signal of **6** was measured in THF-d_8 at room temperature and was found to be 884 ms. Upon addition of 1 equiv of HBF_4•Et_2O, **6** was converted to **6H**$^+$, and the T_1 value for the hydride signal of the latter was found to be 642 ms, which was appreciably lower than that of the hydride signal of the former. When the same experiment was performed in chlorobenzene-d_5 instead of THF-d_8, the T_1 value dropped from 966 ms for **6** to 518 ms for **6H**$^+$. Lowering of the T_1 values in the above experiments suggests some degree of hydrogen-bonding interaction between the hydride ligand and the N-bound proton in complex **6H**$^+$. A significant lowering of relaxation time T_1 for one of the hydride ligands in *trans*-[$RuH_2(dppm)_2$] was recorded in the presence of PhOH at room temperature, due to the existence of hydrogen-bonded species $(dppm)_2$HRu−H···H−OR; a dynamic equilibrium between $(dppm)_2$HRu−H···H−OR and $[(dppm)_2HRu(H_2)]^+(OR)^-$ was established at lower temperature.[22] A smaller drop of the T_1 value in THF-d_8 solution can be attributed to the presence of hydrogen-bonding interaction between the THF-d_8 molecule and the amine proton in **6H**$^+$. This N−H···THF hydrogen-bonding interaction is maintained at the expense of the N−H···H−Ru interaction. "Switching on and off" of intramolecular H···H interaction by using solvents of different hydrogen-bonding abilities has been reported.[12c]

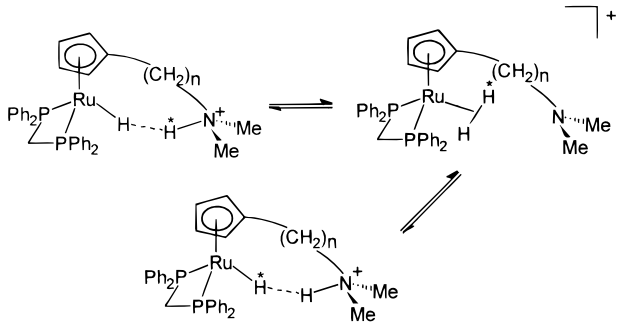
(19) (a) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(20) (a) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (b) Jia, G.; Lough, A. J.; Morris, R. H. *Orgaometallics* **1992**, *11*, 161.

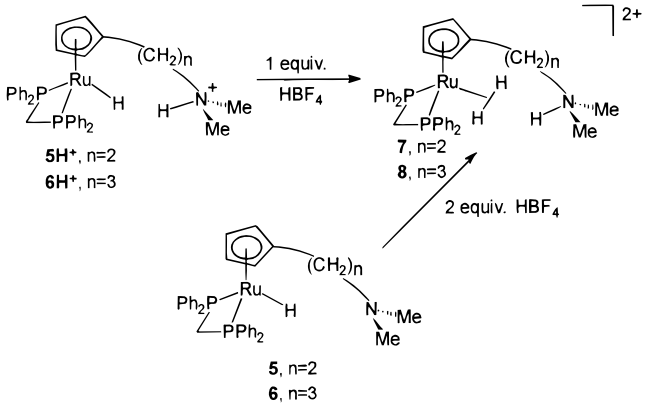
(21) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105.

(22) Ayllón, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000.

Scheme 2



Scheme 3



Similarly, T_1 values of the hydride ligand decreased substantially when **5** was protonated with 1 equiv of $HBF_4 \cdot Et_2O$ to form $\mathbf{5H}^+$: T_1 values of **5** in THF-d_8 and chlorobenzene-d_5 were 1003 and 926 ms, respectively, and those of $\mathbf{5H}^+$ in THF-d_8 and chlorobenzene-d_5 were found to be 243 and 188 ms, respectively. Unlike the case for **6** → $\mathbf{6H}^+$ conversion, the drops of T_1 values in the **5** → $\mathbf{5H}^+$ conversion in the two solvents are comparable; it is probably due to the fact that the N−H···H−Ru interaction is stronger in the latter case, so that the N−H···THF hydrogen-bonding interaction only occurs to a lesser extent. Stronger N−H···H−Ru interaction in $\mathbf{5H}^+$ than in $\mathbf{6H}^+$ is also reflected by the much smaller T_1 values (in THF-d_8 and chlorobenzene-d_5) of the hydride signal of the former.

To further confirm the presence of a hydride−proton interaction in $(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H^+)RuH(dppm)$, a spin saturation transfer experiment was carried out with the complex $\mathbf{6H}^+$. It was observed that irridation of the hydride peak at δ −11.47 ppm led to an approximately 80% decrease in intensity of the N−H signal at δ 5.48 ppm in ^{1}H NMR. This observation can be interpreted as resulting from a rapid exchange process between the metal hydride and the N-bonded proton via a η^2-H_2 complex intermediate (Scheme 2). Unfortunately, it is difficult to study spin saturation transfer on $\mathbf{5H}^+$ because the N−H signal is partially obscured by the other proton signals of the complex. The exchange process depicted in Scheme 2 was further supported by an H/D exchange reaction of $\mathbf{6H}^+$ with D_2O. We found that the metal-hydride and N−H signals of $\mathbf{6H}^+$ disappeared within 15 min after addition of D_2O to a THF-d_8 solution of the complex. It is believed that N−H first underwent H/D exchange with D_2O to give the N−D function, which then H/D-exchanged with the metal hydride. In contrast, the hydride ligand and the proton on the pyridinium ring in $[IrH(\eta^1\text{-}SC_5H_4NH)(\eta^2\text{-}SC_5H_4N)(PPh_3)_2]BF_4$ do not seem to undergo any significant exchange, although the presence of an Ir−H···H−N interaction has been ascertained.[12b]

Addition of 1 equiv of HBF_4 to $\mathbf{5H}^+$ or addition of 2 equiv of HBF_4 to **5** led to the formation of the dihydrogen complex $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)]Ru(H_2)(dppm)](BF_4)_2$ **(7)** (Scheme 3). The ^{1}H NMR spectrum of **7** showed a broad singlet, integrated to two hydrogens, at δ −6.82 ppm, assignable to $Ru(H_2)$. A variable-temperature T_1 measurement on the η^2-H_2 signal gave a minimun T_1 value of 20 ms (268 K and 400 MHz). A trace amount of *trans*-dihydride tautomer is also present, as evidenced by a very small triplet (J(HP) = 29.6 Hz) at δ −5.94 ppm. That this triplet is attributable to the *trans*-dihydride tautomer is based on its J(HP) value, which is very similar to that of the Cp* dihydride complex *trans*-$[Cp^*RuH_2(dppm)]^+$ (J(HP) = 28.8 Hz).[20] We have recently reported that the J(HP) value for *trans*-$CpOsH_2$(dppm) is 31.8 Hz; the cis isomer, *cis*-$CpOsH_2$(dppm), has a much smaller J(HP) value of 6.5 Hz.[23] Acidification of **5** with slightly over 2 equiv of DBF_4 (prepared by adding 0.1 mL of D_2O to 0.4 mL of 54% $HBF_4 \cdot Et_2O$) gave the η^2-HD isotopomer $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2D^+)Ru(HD)(dppm)](BF_4)_2$ (**7-*d*$_2$**), in which both the pendant amine function and the ruthenium hydride were deuterated. Its ^{1}H NMR spectrum shows a 1:1:1 triplet (^1J(HD) = 20.6 Hz) centered at δ −6.85 ppm, after the η^2-H_2 peak is nulled using the inversion-recovery method. The dihydrogen complex $[(\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H^+)Ru(H_2)(dppm)](BF_4)_2$ **(8)** can be generated in a similar manner (Scheme 3). The η^2-H_2 signal of **8** appears as a broad singlet at δ −6.72 ppm in the ^{1}H NMR spectrum. Like **7**, a trace amount of *trans*-dihydride tautomer is also present. A variable-temperature T_1 measurement on the η^2-H_2 signal gave T_1(min) of 20 ms at 255 K and 400 MHz. The ^{1}H NMR spectrum of the η^2-HD isotopomer $[(\eta^5\text{-}C_5H_4(CH_2)_3NMe_2D^+)Ru(HD)(dppm)](BF_4)_2$ **(8-*d*$_2$)** shows a 1:1:1 triplet (^1J(HD) = 21.5 Hz) at −6.69 ppm, after the η^2-H_2 peak is nulled using the inversion-recovery method.

X-ray Structure of $[(\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]^+$. In an attempt to grow single crystals of $[(\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H^+)RuH(dppm)]BPh_4$ for X-ray crystallographic study, single crystals of $[(\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]BPh_4$ (**10c**), which was formed by the extrusion of a H_2 molecule from $[(\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H^+)RuH(dppm)]BPh_4$, were obtained instead. Figure 1 shows the molecular structure of the cation $[(\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]^+$. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

The cation of **10c** exhibits a three-legged piano-stool geometry. The Cp ring is essentially planar, with C−C bonds in the range 1.404(6)−1.440(6) Å. The Ru−C distances range from 2.187(3) to 2.259(4) Å. The two bond distances Ru−P(1) (2.3305(8) Å) and Ru−P(2) (2.3310(8) Å) are essentially equivalent. These Ru−P distances are similar to those in $[CpRu(\eta^2\text{-dppm})(\eta^1\text{-dppm})]PF_6$[24] and $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$.[20,25] The

(23) Jia, G.; Ng, W. S.; Yao, J.; Lau, C. P.; Chen, Y. *Organometallics* **1996**, *15*, 5039.

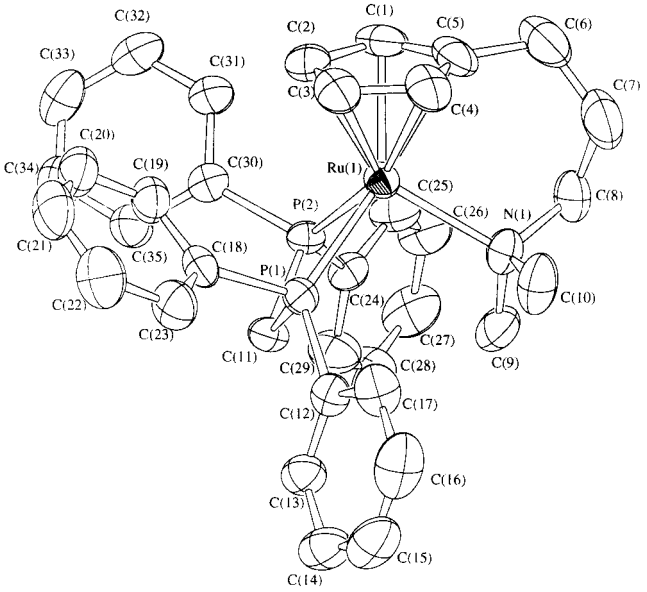


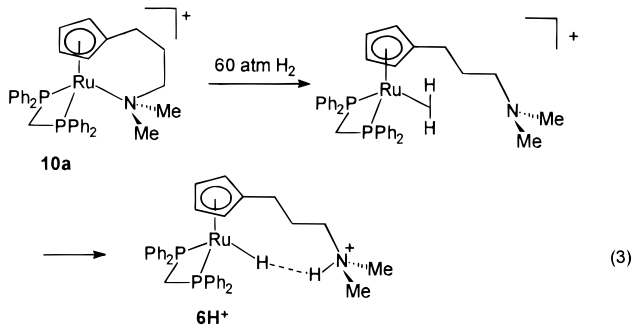
Figure 1. Molecular structure of the cation $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]^+$.

Table 1. Crystal Data and Refinement Details for $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]BPh_4$f

formula	$C_{59}H_{58}BNP_2Ru$
fw	954.94
color and habit	orange block
cryst dimens, mm	0.19 × 0.19 × 0.29
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a, Å	11.170(1)
b, Å	20.690(1)
c, Å	11.268(1)
β, deg	109.99(1)
V, Å^3	2447.2(4)
Z	2
D_{calc}, g cm^{-1}	1.296
F(000)	996
radiation	Mo Kα (λ = 0.710 73 Å)
T, °C	25.0
diffractometer	Marresearch Image Plate Scanner
$2\theta_{max}$, deg	51.3
scan type	ω
no. of rflns collected	16 719
no of unique rflns	4410
no. of obd rflns	4223 ($I > 3.00\ \sigma(I)$)
abs cor	not applied
no. of params refined	571
final R indices (obsd data), %	R = 2.4, R_w = 3.0
goodness of fit	1.20
rfln/param ratio	7.40
max peak in final diff map, e Å^{-3}	0.33
min peak in final diff map, e Å^{-3}	−0.68

Ru−N distance (2.238(3) Å) falls in the range of Ru−N distances found in the complexes Cp*Ru(κ^2-(P,N)-$Ph_2PCH_2CH_2NMe_2$)Cl (2.260(2) Å),[26] Cp*Ru(κ^2-(P,N)-$Ph_2PCH_2CH_2NMe_2$)(η^1-OSO_2CF_3) (2.256(2) Å),[26] and [Cp*Ru(κ^2-(P,N)-$Ph_2PCH_2CH_2NMe_2$)(C=C=CHPh)]$^+$ (2.217(10) Å).[26] The P(1)−Ru−P(2) angle (70.81(3) Å) is smaller than the corresponding angles reported for the three-legged piano-stool complexes with larger chelating diphosphine (for example, 82.9(1)° in CpRuCl(Ph_2-$CHMeCH_2PPh_2$),[27] 85.1(1)° in CpRu((*E*)-MeO_2CC=$CHCO_2Me$)(dppe),[28] and 83.33(7)° in Fe($CH_2C_6H_4Me$)$_2$-(dippe) (dippe = 1,2-bis(diisopropylphosphino)ethane)[29]) or monodentate phosphine ligands (for example, 93.7-(1)° in CpRu(η^2-CH_2=CHCH=CH_2)(PMe_3)$_2$,[30] 103.9(4)° in CpRuCl(PPh_3)$_2$,[31] 94.7(2)° in CpRuCl(PMe_3)$_2$,[31] and 95.8(1)° in CpRuH(PMe_3)$_2$[32]). However, it is comparable with the P−Ru−P angles in other cyclopentadienyl dppm complexes such as [CpRu(η^2-dppm)(η^1-dppm)]PF_6 (70.0(1)°),[24] [Cp*Ru(η^2-H_2)(dppm)]BF_4 (71.46 (7)°),[20,25] and CpFePh(dppm) (73.8 (1)°).[33] The P(1)−C(11)−P(2) angle (94.4 (2)°) is comparable with the correponding angles of the η^2-dppm ligands in [CpRu(η^2-dppm)(η^1-dppm)]PF_6[24] and [Cp*Ru(η^2-H_2)(dppm)]BF_4.[20,25] The amine group is bent away from the two phosphorus atoms of dppm with P(1)−Ru−N(1) and P(2)−Ru−N(1) angles of 97.19(8) and 98.77(8)°, respectively.

Reactivities of $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]BF_4$ (10a) toward H_2. The complex $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]BF_4$ (**10a**) was prepared in quantitative yield by removal of the chloro ligand of (η^5-$C_5H_4(CH_2)_3NMe_2$)RuCl(dppm) with $NaBF_4$ in methanol. Heating a C_6H_5Cl solution of $[(\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H^+)RuH(dppm)]BF_4$ (**6H**$^+$) at 90 °C for a prolonged period of time also led to the formation of **10a**. Obviously, **10a** is produced by extrusion of H_2 from **6H**$^+$. Single crystals of **10c** were grown from the solution of $[(\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H^+)RuH(dppm)]BPh_4$ after extrusion of H_2 from the latter. We are interested in studying the reversed reaction of the H_2 extrusion from **6H**$^+$, since the feasibility of this reaction provides strong evidence of intramolecular heterolytic cleavage of η^2-H_2 ligand by the amino sidearm of the Cp−N ligand. We therefore monitored the reaction of **10a** with H_2 under 60 atm in a high-pressure NMR tube by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. It was found that **10a** was completely converted to **6H**$^+$ within 30 min at 60 °C. Probably, **10a** first reacted with H_2 to form an η^2-H_2 complex intermediate which was then deprotonated by the pendant amino group to form **6H**$^+$ (eq 3). It has been reported



(3)

that the ruthenium amide complex RuCl(PPh_3)[N($SiMe_2$

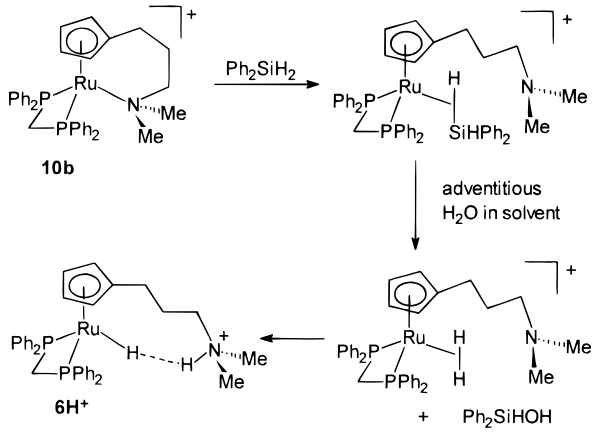
(24) Bruce, M. I.; Cifuentes, M. P.; Grundy, K. R.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1988**, *41*, 597.
(25) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677.
(26) Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 1956.
(27) Morandini, F.; Consiglio, G.; Straub, B.; Ciani, G.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2293.
(28) Bruce, M. I.; Catlow, A.; Humphrey, M. G.; Kontsantonis, G. A.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *338*, 59.
(29) Hermes, A. R.; Girolami, G. S. *Organometallics* **1987**, *6*, 763.
(30) Bruce, M. I.; Hambley, T. W.; Rodgers, J. R.; Snow, M. R.; Wong, F. S. *Aust. J. Chem.* **1982**, *35*, 1323.
(31) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398.
(32) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721.
(33) Scott, F.; Kruger, G. J.; Cronje, S.; Lombard, A.; Raubenheimer, H. G.; Benn, R.; Rufińska, A. *Organometallics* **1990**, *9*, 1071.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]BPh_4

Interatomic Distance (Å)					
Ru−C(1)	2.243(3)	Ru−C(2)	2.188(3)	Ru−C(3)	2.187(3)
Ru−C(4)	2.226(3)	Ru−C(5)	2.259(4)	Ru−N	2.238(3)
Ru−P(1)	2.3305(8)	Ru−P(2)	2.3310(8)		

Intramolecular Angles (deg)			
P(1)−Ru-P(2)	70.81(3)	P(1)−Ru-N(1)	97.19(8)
P(2)−Ru-N(1)	98.77(8)	P(1)−C(11)-P(2)	94.4(2)
Ru−P(1)−C(11)	96.4(1)	Ru−P(2)−C(11)	96.4(1)
Ru−N(1)−C(8)	111.9(2)	Ru−N(1)−C(9)	114.4(2)
Ru−N(1)−C(10)	110.9(2)	C(8)−N(1)-C(9)	106.0(3)
C(8)−N(1)-C(10)	108.1(3)	C(9)−N(1)-C(10)	105.1(3)

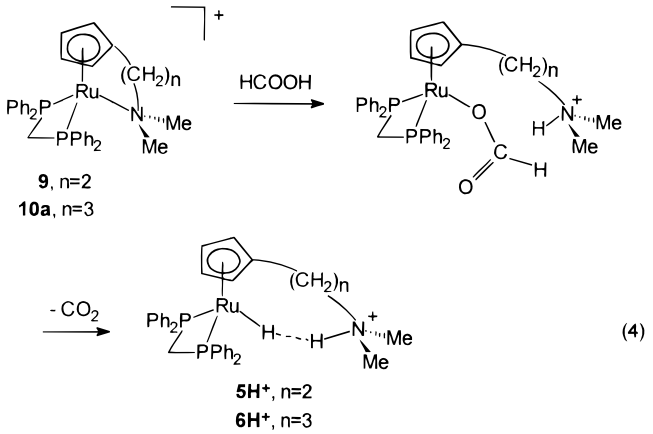
Scheme 4



$CH_2PPh_2)_2$] cleaved H_2 heterolytically to form two isomeric amine−hydride derivatives of the formula $RuHCl(PPh_3)[NH(SiMe_2CH_2PPh_2)_2]$, but the mechanism of this reaction is not clear.[34]

Reactivity of [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]-BAr'_4 (Ar′ = 3,5-$(CF_3)_2C_6H_3$) (10b) toward Ph_2SiH_2. We thought it would be interesting to study the reaction of [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]$^+$ with silane as well. It was found that the reaction of **10b** with Ph_2SiH_2 led to the formation of [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)-RuH(dppm)]BAr'_4; the reaction sequence depicted in Scheme 4 is postulated to explain the reaction. We propose that Ph_2SiH_2 first reacted with **10b** to form a cationic η^2-silane complex intermediate, which, being very sensitive to nucleophiles, was attacked by adventitious water to generate the η^2-H_2 complex intermediate, and finally the dihydrogen ligand was heterolytically cleaved by the pendant amino group to give [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BAr'_4. Brookhart et al. proposed that hydrolysis of the η^2-silane ligand in [CpFe(CO)(L)(η^2-$HSiEt_3$)]$^+$ (L = PEt_3, PPh_3) by trace moisture in the solvent was responsible for the formation of the dihydrogen complexes [CpFe(CO)(L)(η^2-H_2)]$^+$.[35]

Reactivities of [(η^5:η^1-$C_5H_4(CH_2)_nNMe_2$)Ru-(dppm)]$^+$ toward H_2/CO_2. Reactions of [(η^5:η^1-$C_5H_4(CH_2)_nNMe_2$)Ru(dppm)]$^+$ with H_2/CO_2 have also been studied. It was found that stirring a THF solution of [(η^5:η^1-$C_5H_4(CH_2)_2NMe_2$)Ru(dppm)]BF_4 (**9**) at 80 °C under H_2/CO_2 (40 atm/40 atm) for 16 h led to the production of formic acid, albeit in low yield (TON (turnover number) = 6). The same reaction had also been monitored by high-pressure $^{31}P\{^1H\}$ NMR spectroscopy, which showed that **9** was completely converted to **5H**$^+$ within 30 min, and the latter remained the only detectable metal complex in the system after heating for 24 h. Analogously, reaction of **10a** with H_2/CO_2 also gave formic acid (TON = 8); a high-pressure $^{31}P\{^1H\}$ NMR study of the same reaction showed that **6H**$^+$ was the only detectable metal-containing species throughout the experiment. It is generally true that metal complexes which effect CO_2 hydrogenation to formic acid effect the reverse reaction as well. To see whether this is true for complexes **9** and **10a**, their reactions with formic acid were studied. It was found that reactions of **9** and **10a** with formic acid in refluxing THF for 16 h led to quantitative yields of **5H**$^+$ and **6H**$^+$, respectively. Probably, HCOOH was first added across the Ru−N bond to form the transient metal formate [(η^5-$C_5H_4(CH_2)_n$-NMe_2H^+)Ru(HCOO)(dppm)]BF_4, which then extruded a CO_2 molecule to give **5H**$^+$ or **6H**$^+$ (eq 4).



(4)

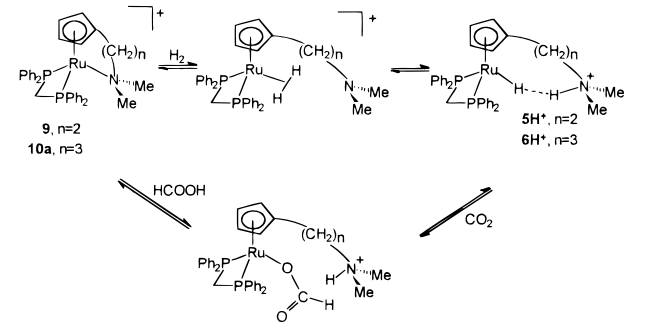
Catalytic hydrogenation of CO_2 to formic acid by transition-metal complexes has attracted much interest in recent years;[36] although normal CO_2 insertion into the metal-hydride bond to generate a metal formate complex seems to be in operation in most of the successful catalytic systems, subsequent liberation of formic acid may take a number of different routes.[36i,l] A mechanism for the hydrogenation of CO_2 to formic acid with **9** or **10a** is postulated and shown in Scheme 5. Therefore, reaction of **9** or **10a** with H_2 first forms the dihydrogen complex intermediate, which rapidly undergoes intramolecular heterolytic cleavage of η^2-H_2 to give **5H**$^+$ or **6H**$^+$. Insertion of CO_2 into the metal-hydride bond is believed to be a slow step, since **5H**$^+$ or **6H**$^+$ is the only detectable metal complex species throughout the reaction. The main feature of this scheme is protonation of the formato ligand by N−H of the pendant amine arm to generate formic acid.

(34) Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467.

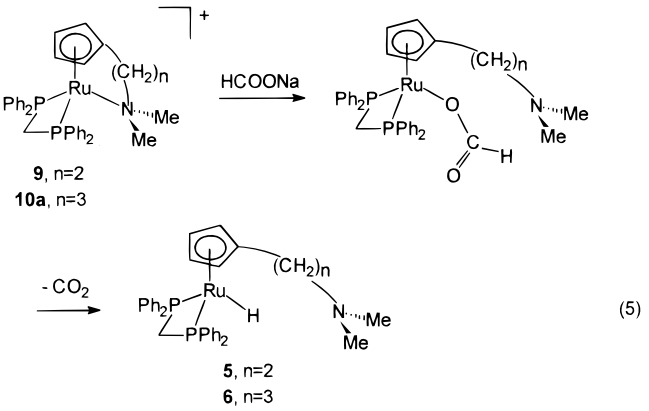
(35) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.

(36) See for example: (a) Tagui Khan, M. M.; Halligudi, S. B.; Shukla, S. *J. Mol. Catal.* **1989**, *57*, 47. (b) Tsai, J. C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117. (c) Gassner, F.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1465. (d) Leitner, W.; Dinjus, E.; Gassner, F. *J. Organomet. Chem.* **1994**, *475*, 257. (e) Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231. (f) Fornika, R.; Görls, H.; Seemann, B.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1479. (g) Lau, C. P.; Chen, Y. Z. *J. Mol. Catal. A: Chem.* **1995**, *101*, 33. (h) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Chem. Soc., Chem. Commun.* **1995**, 707. (i) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259. (j) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207. (k) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344. (l) Hutschka, F.; Dedieu, A.; Eicherger, M.; Fornika, R.; Leitner, W. *J. Am. Chem. Soc.* **1997**, *119*, 4432.

Scheme 5

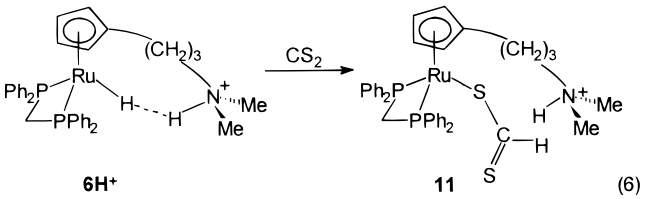


Reactions of **9** and **10a** with sodium formate in refluxing methanol gave (η^5-$C_5H_4(CH_2)_2NMe_2$)RuH(dppm) (**5**) and (η^5-$C_5H_4(CH_2)_3NMe_2$)RuH(dppm) (**6**), respectively (eq 5). Obviously, **5** and **6** were formed by expulsion of the CO_2 molecule from the metal formate intermediates.



(5)

Reaction of [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BF_4 ($6H^+$) with Carbon Disulfide. While the proposed metal formate intermediate shown in Scheme 5 remains elusive in the high-pressure NMR study, the analogous dithioformate complex **11** was easily prepared by reacting $\mathbf{6H}^+$ with excess CS_2 (eq 6).



(6)

Complex **11** was identified by IR and ^{1}H NMR spectroscopy; its IR spectrum showed the characteristic $\upsilon(CS_2)$ band of the dithioformato ligand at 1040 cm^{-1}, and its ^{1}H NMR spectrum exhibited a singlet at 11.16 ppm which is diagnostic of the dithioformato proton. The previously reported chemical shifts for unidentate and bidentate dithioformate protons range from 9.5 to 14 ppm.[37] The ^{31}P{^{1}H} NMR spectrum of **11** shows a sharp singlet at δ 17.6 ppm, indicating that the two phosphorus atoms of dppm are equivalent and probably both remain coordinated. Furthermore, the ^{1}H NMR spectrum of **11** does not show any sign of η^5 to η^3/η^1 Cp ring slippage. Where all these facts are taken together, the dithioformato ligand in **11** has to be unidentate to give a electron count of 18.

Conclusion

We have synthesized and characterized the ruthenium complexes (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)RuH(dppm) (n = 2, 3) in which the pendant amine functions are protonated. The intramolecular N−H···H−Ru proton-hydride interaction in these complexes is evidenced by the relaxation time T_1 measurements. Results of a spin saturation transfer study and H/D exchange experiment with (η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm) are consistent with the existence of a fast exchange process, via a dihydrogen complex intermediate, between the hydride ligand and the N-bound proton in the complex. The complexes [(η^5:η^1-$C_5H_4(CH_2)_nNMe_2$)Ru(dppm)]$^+$ reversibly add H_2 to give (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)RuH(dppm); the latter species are most likely formed by displacement of the coordinated amine group by H_2, followed by deprotonation of the bound H_2 by the now-pendant amine arm. This reaction is an example of Ru−N bond hydrogenolysis. We have recently reported a case of direct involvement of the dihydrogen complex in catalytic hydrogenation reactions, in which the crucial step is the intermolecular deprotonation of the dihydrogen ligand by additional base (B) to generate the metal hydride (and BH^+), and after the usual olefin coordination and insertion steps, the final alkane product is produced via alkyl group protonation by BH^+.[6c] Our present work points out that catalytic reactions can proceed by a similar mechanism, using complexes with tethered groups which can function as internal bases. The proposed mechanism of Scheme 5 provides such an example.

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All chemicals were obtained from Aldrich except dicyclopentadiene, which was purchased from BDH. The ligands $C_5H_5(CH_2)_nNMe_2$ (n = 2, 3)[38] and the complex $RuCl_2(PPh_3)_3$[39] were prepared according to published procedures. Solvents were distilled under a dry nitrogen atmosphere with appropriate drying agents (solvent/drying agent): ethanol/Mg−I_2, methanol/Mg−I_2, tetrahydrofuran/Na−benzophenone, toluene/Na−benzophenone, dichloromethane/P_2O_5, diethyl ether/CaH_2, *n*-hexane/Na. High-purity hydrogen gas was supplied by Hong Kong Oxygen.

Infrared spectra were obtained on a Nicolet Magna 750 FT-IR spectrophotometer. ^{1}H NMR spectra were obtained from a Bruker DPX 400 spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane (TMS). ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 and 100.60 MHz, respectively. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4 in D_2O. ^{13}C chemical shifts were internally referenced to the residual peak of deuterated solvent. Relaxation time T_1

(37) See for example: (a) Harris, R. O.; Hota, N. K.; Sadvoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259. (b) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1975**, *99*, C65. (c) Robinson, S. D.; Sahajpal, A. *Inorg. Chem.* **1977**, *16*, 2718. (d) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747. (e) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1985**, *24*, 932. (f) Jia, G.; Meek, D. W. *Inorg. Chem.* **1991**, *30*, 1953. (g) Albertin, G.; Antoniutti, S.; Del Ministro, E.; Gordignon, E. *J. Chem. Soc., Dalton Trans.* **1994**, 1769. (h) Albéniz, M.; Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 3746.

(38) Rees, W. S., Jr.; Dippel, K. A. *Org. Prep. Proced. Int.* **1992**, *24*, 527.

(39) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

measurements were carried out at 400 MHz by the inversion-recovery method using the standard 180°−τ−90° pulse sequence. High-pressure NMR studies were carried out in a sapphire HPNMR tube; the 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure valve was constructed at the ISSECC-CNR, Firenze, Italy. FAB MS was carried out with a Finnigan MAT 95S mass spectrometer using 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by M-H-W Laboratories, Phenix, AZ, and the Institute of Chemistry, Academia Sinica, Beijing, China.

[(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)RuCl(PPh_3)$_2$]Cl (1·HCl). A solution of $RuCl_3 \cdot 3H_2O$ (0.45 g, 1.72 mmol) in 20 mL of ethanol was refluxed for 5 min and then cooled to room temperature. To the solution was added a 0.38 g (2.80 mmol) amount of the ligand $C_5H_5(CH_2)_2NMe_2$, and the mixture was then added to a refluxing ethanol solution of PPh_3 (2.70 g, 10.00 mmol). The resulting mixture was stirred under reflux for 16 h. It was then filtered at room temperature to remove some greenish brown solids, and the filtrate was concentrated to one-third its original volume. The concentrated filtrate was stored under N_2 overnight at −20 °C to give some orange microcrystals, which were collected by filtration and dried in vacuo. Yield: 0.51 g (37%). Anal. Calcd for $C_{45}H_{45}NP_2Cl_2Ru$: C, 64.82; H, 5.44; N, 1.68. Found: C, 65.03; H, 5.52; N, 1.81. IR (KBr, cm^{-1}): ν(N−H) 2664 (br, w). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.81 (t, 2H, J(HH) = 8.1 Hz, $C_5H_4CH_2$), 2.86 (d, 6H, J(HH) = 4.6 Hz, N−CH_3), 3.27 (m, 2H, NCH_2), 3.51 (br s, 2H of Cp ring), 3.81 (br s, 2H of Cp ring), 7.10−7.35 (m, 30 H of PPh_3), 12.31 (br s, 1H, N−*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.70 MHz, 25 °C): δ 41.2 (s).

[(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)RuCl(dppm)]Cl (3·HCl). **1·HCl** (0.47 g , 0.56 mmol) and dppm (0.23 g, 0.60 mmol) were dissolved in 50 mL of toluene, and the solution was refluxed for 16 h. The solvent was then removed by vacuum; the orange residue was washed with diethyl ether (2 × 10 mL) and dried in vacuo. Yield: 0.35 g (89%). Anal. Calcd for $C_{34}H_{37}NP_2Cl_2Ru$: C, 58.88; H, 5.38; N, 2.02. Found: C, 59.02; H, 5.51; N, 2.10. IR (KBr, cm^{-1}): ν(N−H) 2680 (br, w). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.62 (s, 6H, N−CH_3), 2.86 (br s, 2H, $C_5H_4CH_2$), 3.18 (br s, 2H, NCH_2), 4.11 (br s, 2H of Cp ring), 4.39 (m, 1H, PC*H*P), 4.87 (m, 1H, PC*H*P), 4.97 (br s, 2H of Cp ring), 7.20−7.68 (m, 20 H of dppm), 11.95 (br s, 1H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.70 MHz, 25 °C): δ 15.5 (s).

(η^5-$C_5H_4(CH_2)_2NMe_2$)RuCl(PPh_3)$_2$ (1). A THF (30 mL) solution of KO^{t}Bu (0.17 g, 1.50 mmol) and $C_5H_5(CH_2)_2NMe_2$ (0.30 g, 2.20 mmol) was stirred at room temperature for 30 min. The resulting solution was then transferred to a THF (50 mL) solution of $RuCl_2(PPh_3)_3$ (1.00 g, 1.04 mmol). The solution mixture was stirred for 1 h; the solvent was then removed by vacuum to afford an orange solid, which was recrystallized from diethyl ether/hexane. Yield: 0.76 g (92%). Anal. Calcd for $C_{45}H_{44}NP_2ClRu$: C, 67.78; H, 5.57; N, 1.76. Found: C, 67.68; H, 5.51; N, 1.83. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.48 (s, 6H, NCH_3), 2.60 (m, 2H, NCH_2), 2.79 (br s, 2H, $C_5H_4CH_2$), 3.39 (br s, 2H of Cp ring), 3.91 (br s, 2H of Cp ring), 7.09−7.37 (m, 30 H of PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.70 MHz, 25 °C): δ 40.5 (s).

(η^5-$C_5H_4(CH_2)_3NMe_2$)RuCl(PPh_3)$_2$ (2). This complex was prepared by using the same procedure as for the preparation of **1**, except that $C_5H_5(CH_2)_3NMe_2$ was used in place of $C_5H_5(CH_2)_2NMe_2$. Yield: 1.31 g (88%). Anal. Calcd for $C_{46}H_{46}NP_2ClRu$: C, 68.09; H, 5.71; N, 1.73. Found: C, 67.88; H, 5.83; N, 1.89. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.83 (m, 2H, $CH_2CH_2CH_2$), 2.13 (s, 6H, NCH_3), 2.32 (t, J(HH) = 7.4 Hz, 2H, NCH_2), 2.50 (t, J(HH) = 7.3 Hz, 2H, $C_5H_4CH_2$), 4.13 (br s, 4H of Cp ring), 6.98−7.62 (m, 30 H of PPh_3), 12.30 (br s, 1H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.70 MHz, 25 °C): δ 41.3 (s).

(η^5-$C_5H_4(CH_2)_2NMe_2$)RuCl(dppm) (3). This complex was prepared by using the same procedure as for the preparation of **3·HCl**, except **1** was used instead of **1·HCl**. Yield: 0.30 g (82%). Anal. Calcd for $C_{34}H_{36}NP_2ClRu$: C, 62.14; H, 5.52; N, 2.13. Found: C, 62.32; H, 5.48; N, 2.16. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.31 (s, 6H, NCH_3), 2.47 (m, 2H, NCH_2), 2.60 2H, $C_5H_4CH_2$), 3.99 (br s, 2H of Cp ring), 4.32 (m, 1H, PC*H*P), 4.85 (br s, 2H of Cp ring), 5.26 (m, 1H, PC*H*P), 7.36−7.73 (m, 20 H of dppm). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.70 MHz, 25 °C): δ 12.4 (s).

(η^5-$C_5H_4(CH_2)_3NMe_2$)RuCl(dppm) (4). This complex was prepared by using the same procedure as for the preparation of **3·HCl**, except **2** was used instead of **1·HCl**. Yield: 0.66 g (79%). Anal. Calcd for $C_{35}H_{38}NClP_2Ru$: C, 62.63; H, 5.71; N, 2.09. Found: C, 62.42; H, 5.51; N, 2.17. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.80 (m, 2H, $CH_2CH_2CH_2$), 2.21 (s, 6H, NCH_3), 2.30 (m, 2H, NCH_2), 2.32 (m, 2H, $C_5H_4CH_2$), 4.01 (br s, 2H of Cp ring), 4.42 (m, 1H, PC*H*P), 4.84 (br s, 2H of Cp ring), 5.31 (m, 1H, PC*H*P), 7.22−7.73 (m, 20 H of dppm). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.70 MHz, 25 °C): δ 16.6 (s).

(η^5-$C_5H_4(CH_2)_2NMe_2$)RuH(dppm) (5). Complex **3·HCl** (0.16 g, 0.23 mmol) was added to 30 mL of NaOMe/MeOH (0.77 M) solution. The resulting solution was refluxed for 5 h, and then the solvent was removed by vacuum. The residue was extracted with 50 mL of toluene; and after removal of the solvent, the yellow solid was washed with hexane (2 × 5 mL). Yield: 0.09 g (62%). Anal. Calcd for $C_{34}H_{37}NP_2Ru$: C, 65.57; H, 5.99; N, 2.24. Found: C, 65.20; H, 5.97; N, 2.22. IR (KBr, cm^{-1}): ν(Ru−H) 1916 (m). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ −11.33 (td, J(HH) = 3.4 Hz, J(HP) = 31.5 Hz, 1H, Ru*H*), 2.00 (s, 6H, NCH_3), 2.16 (t, J(HH) = 7.0 Hz, 2H, NCH_2), 2.21 (t, J(HH) = 6.9 Hz, 2H, $C_5H_4CH_2$), 3.95 (m, 1H, PC*H*P), 4.78 (br s, 2H of Cp ring), 4.84 (br s, 2H of Cp ring), 4.90 (m, 1H, PC*H*P), 6.98−7.62 (m, 20 H of dppm). ^{31}P{^{1}H} NMR (THF-d_8, 161.70 MHz, 25 °C): δ 22.7 (s). Complex **5** was also prepared in 67% yield, from **3** instead of **3·HCl**, by following the same procedure.

(η^5-$C_5H_4(CH_2)_3NMe_2$)RuH(dppm) (6). This complex was prepared by using the same procedure as for the preparation of **5**, except **4** is used in place of **3·HCl** or **3**. Yield: 0.17 g (66%). Anal. Calcd for $C_{35}H_{39}NP_2Ru$: C, 66.02; H, 6.17; N, 2.20. Found: C, 65.96; H, 6.30; N, 2.14. IR (KBr, cm^{-1}): ν(Ru−H) 1929 (m). ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ −11.14 (td, J(HH) = 3.4 Hz, J(HP) = 30.8 Hz, 1H, Ru*H*), 1.64 (m, 2H, $CH_2CH_2CH_2$), 2.11−2.18 (m, 10 H, $C_5H_4CH_2$ + NCH_2 + NCH_3), 3.98 (m, 1H, PC*H*P), 4.86 (br s, 2H of Cp ring), 4.91 (br s, 2H of Cp ring), 5.13 (m, 1H, PC*H*P), 7.34−7.85 (m, 20 H of dppm). ^{31}P{^{1}H} NMR (THF-d_8, 161.70 MHz, 25 °C): δ 23.0 (s). HRMS (FAB) (m/z): 636.1622 $(M - H)^+$.

[(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)RuH(dppm)]BF_4 (5H$^+$). $HBF_4 \bullet Et_2O$ (1.8 μL, 12.8 μmol) was added to a solution of **5** (0.008 g, 12.8 μmol) in 0.4 mL of THF-d_8 in an NMR tube, and the NMR spectra were collected immediately. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ −11.47 (t, J(HP) = 30.3 Hz, 1H, Ru*H*), 2.56 (s, 6H, NCH_3), 2.71 (br s, 2H, NCH_2), 3.28 (br s, 2H, $C_5H_4CH_2$), 3.65 (br s, 1H, N*H*), 4.24 (m, 1H, PC*H*P), 4.74 (br s, 2H of Cp ring), 5.17 (m, 1H, PC*H*P), 5.22 (br s, 2H of Cp ring), 7.41−7.79 (m, 20 H of dppm). ^{31}P{^{1}H} NMR (THF-d_8, 161.70 MHz, 25 °C): δ 21.7 (s).

[(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BF_4 (6H$^+$). The procedure for **5H**$^+$ was followed exactly. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ −11.31 (t, J(HP) = 30.3 Hz, 1H, Ru*H*), 1.89 (br s, 2H, $CH_2CH_2CH_2$), 2.28 (br s, 2H, NCH_2), 2.82 (s, 6H, NCH_3), 3.09 (br s, 2H, $C_5H_4CH_2$), 4.01 (br s, 2H of Cp ring), 4.03 (m, 1H, PC*H*P), 4.84 (br s, 2H of Cp ring), 5.11 (br s, 1H, PC*H*P), 5.48 (br s, 1H, N*H*), 7.36−7.81 (m, 20 H of dppm). ^{31}P{^{1}H} NMR (THF-d_8, 161.70 MHz, 25 °C): δ 23.1 (s).

Attempts to isolate **5H**$^+$ and **6H**$^+$ from their THF solution by addition of hexane gave oily substances which failed to yield solid products. Layering of hexane on THF solutions of **5H**$^+$ and **6H**$^+$ resulted in the formation of [(η^5:η^1-$C_5H_4(CH_2)_2NMe_2$)-Ru(dppm)]BF_4 and [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]BF_4, respectively.

[(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)Ru(H_2)(dppm)][BF_4)$_2$ (7). Complex **7** was prepared in an NMR tube by addition of 1 equiv of HBF_4·Et_2O to a THF-d_8 solution of **5H**$^+$ or by addition of 2 equiv of HBF_4•Et_2O to a THF-d_8 solution of **5** under N_2. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ −6.82 (br s, 2H, Ru(H_2)), 2.75 (br s, 2H, NCH_2), 3.03 (s, 6H, NCH_3), 3.37 (br s, 2H, $C_5H_4CH_2$), 4.73 (m, 1H, PC*H*P), 5.60 (br s, 2H of Cp ring), 5.72 (m, 1H, PC*H*P), 5.79 (br s, 2H of Cp ring), 7.25−7.88 (m, 20 H of dppm), 8.99 (br s, 1H, N*H*). ^{31}P{^{1}H} NMR (THF-d_8, 161.70 MHz, 25 °C): δ 7.0 (s). Variable-temperature T_1 measurements on the H_2 signal were carried out by the inversion-recovery method using standard 180°−τ−90° pulse sequences. T_1 (THF-d_8, 400 MHz, ms): 25 (293 K), 23 (283 K), 21 (273 K), 20 (263 K), 20 (253 K), 21 (243 K), 23 (233 K) 26 (223 K). $T_{1,min}$ (20 ms at 260 K and 400 MHz) was obtained from the ln T_1 vs 1000/T plot.

[(η^5-$C_5H_4(CH_2)_2NMe_2D^+$)Ru(HD)(dppm)][BF_4)$_2$ (7-*d*$_2$). This compound was prepared in an NMR tube in THF-d_8 by reacting (η^5-$C_5H_4(CH_2)_2NMe_2$)RuH(dppm) (**5**; 0.012 g, 19.2 μmol) with DBF_4 (6 μL, 52.0 μmol), which was prepared by mixing 0.5 mL of D_2O with 0.5 mL of HBF_4·Et_2O. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ −6.85 (t, ^1J(HD) = 20.5 Hz).

[(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)Ru(H_2)(dppm)][BF_4)$_2$ (8). The complex was prepared using the same procedure as for the preparation of **7**, except that **6H**$^+$ and **6** were used instead of **5H**$^+$ and **5**, respectively. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ −6.72 (br s, 2H, Ru(H_2)), 2.03 (br s, 2H, $CH_2CH_2CH_2$), 2.32 (br s, 1H, NCH_2), 2.99 (s, 6H, NCH_3), 3.30 (br s, 2H, $C_5H_4CH_2$), 4.54 (m, 1H, PC*H*P), 5.14 (br s, 2H of Cp ring), 5.68 (m, 1H, PC*H*P), 5.77 (br s, 2H of Cp ring), 7.31−7.93 (m, 20 H of dppm). ^{31}P{^{1}H} NMR (THF-d_8, 161.70 MHz, 25 °C): δ 13.2 (s). Variable-temperature T_1 measurements on the H_2 signal were carried out by the inversion-recovery method using standard 180°−τ−90° pulse sequences. T_1 (THF-d_8, 400 MHz, ms): 23 (293 K), 23 (283 K), 21 (273 K), 20 (263 K) 20 (253 K), 21 (243 K) 24 (233 K), 26 (223 K). $T_{1,min}$ (20 ms at 255 K and 400 MHz) was obtained from the ln T_1 vs 1000/T plot.

[(η^5-$C_5H_4(CH_2)_3NMe_2D^+$)Ru(HD)(dppm)][BF_4)$_2$ (8-*d*$_2$). The procedure for **7-*d*$_2$** was followed exactly, except that **6** was used instead of **5**. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ −6.69 (t, ^1J(HD) = 21.5 Hz).

[(η^5:η^1-$C_5H_4(CH_2)_2NMe_2$)Ru(dppm)]BF_4 (9). A mixture of (η^5-$C_5H_4(CH_2)_2NMe_2$)RuCl(dppm) (**3**; 0.50 g, 0.76 mmol) and $NaBF_4$ (0.08 g, 0.76 mmol) in 20 mL of MeOH was stirred at 50 °C for 16 h, and then the solvent of the orange solution was removed by vacuum. The orange residue was washed with a few 10 mL portions of diethyl ether and dried in vacuo. Yield: 0.47 g (85%). Anal. Calcd for $C_{34}H_{36}BNF_4P_2Ru$: C, 57.64; H, 5.12; N, 1.98. Found: C, 57.96; H, 5.22; N, 1.89. ^{1}H NMR (acetone-d_6, 400 MHz, 25 °C): δ 2.45 (s, 6H, NCH_3), 2.49 (m, 2H, NCH_2), 2.73 (m, 2H, $C_5H_4CH_2$), 4.70 (m, 1H, PC*H*P), 4.35 (br s, 2H of Cp ring), 5.45 (br s, 2H of Cp ring), 5.88 (m, 1H, PC*H*P), 7.47−8.16 (m, 20 H of dppm). ^{31}P{^{1}H} NMR (acetone-d_6, 161.70 MHz, 25 °C): δ 7.5 (s).

[(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]BF_4 (10a). The procedure for **9** was followed exactly, except that **4** was used instead of **3**. Yield: 0.65 g (90%). Anal. Calcd for $C_{35}H_{38}BNF_4P_2Ru$: C, 58.18; H, 5.30; N, 1.94. Found: C, 58.23; H, 5.41; N, 1.88. ^{1}H NMR (CD_3OD, 400 MHz, 25 °C): δ 2.15 (m, 2H, $CH_2CH_2CH_2$), 2.41 (s, 6H, NCH_3), 2.47 (m, 2H, NCH_2), 2.74 (m, 2H, $C_5H_4CH_2$), 4.31 (br s, 2H of Cp ring), 5.26 (m, 1H, PC*H*P), 5.35 (br s, 2H of Cp ring), 5,74 (m, 1H, PC*H*P), 7.49−8.08 (m, 20 H of dppm). ^{31}P{^{1}H} NMR (acetone-d_6, 161.70 MHz, 25 °C): δ 7.1 (s).

[(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]BAr′$_4$ (10b; Ar′ = 3,5-$(CF_3)_2C_6H_3$). This complex was prepared by using the same procedure as for the preparation of **10a**, except that NaBAr′$_4$ was used in place of $NaBF_4$. Yield: 1.18 g (79%). Anal. Calcd for $C_{67}H_{50}BNF_{24}P_2Ru$: C, 53.68; H, 3.36; N, 0.93. Found: C, 54.13; H, 3.27; N, 0.91. ^{1}H NMR (acetone-d_6, 400 MHz, 25 °C): δ 2.05 (m, 2H, $CH_2CH_2CH_2$), 2.34 (s, 6H, NCH_3), 2.39 (m, 2H, NCH_2), 2.66 (m, 2H, $C_5H_4CH_2$), 4.26 (br s, 2H of Cp ring), 5.20 (m, 1H, PC*H*P), 5.26 (br s, 2H of Cp ring), 5.70 (m, 1H, PC*H*P), 7.39−8.16 (m, 32 H of dppm and Ar′). ^{31}P{^{1}H} NMR (acetone-d_6, 161.70 MHz, 25 °C): δ 7.5 (s).

[(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)Ru(η^1-SCSH)(dppm)]BF_4 (11). To a solution of **6** (0.08 g, 0.12 mmol) in 4 mL of THF was added HBF_4·Et_2O (1.7 μL, 0.13 mmol) and CS_2 (0.1 mL). The solution was kept at room temperature for 3 days, and then the solvent was removed by vacuum. The residue was washed with 5 mL of hexane to afford a deep red solid. Yield: 0.10 g (87%). Anal. Calcd for $C_{36}H_{40}BNF_4P_2S_2Ru$: C, 54.01; H, 5.04; N, 1.75. Found: C, 54.13; H, 5.11; N, 1.62. IR (KBr, cm^{-1}): ν(CS) 1040 (s). ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ 1.95 (quint, J(HH) = 7.8 Hz, 2H, $CH_2CH_2CH_2$), 2.28 (t, J(HH) = 7.8 Hz, 2H, NCH_2), 2.72 (s, 6H, NCH_3), 2.92 (t, J(HH) = 7.8 Hz, 2H, $C_5H_4CH_2$), 4.49 (dt, J(HH) = 14.7 Hz, J(HH) = 11.3 Hz, 1H, PC*H*P), 4.77 (br s, 2H of Cp ring), 5.22 (dt, J(HH) = 14.7 Hz, J(HP) = 10.0 Hz, 1H, PC*H*P), 5.34 (br s, 2H of Cp ring), 7.33−7.53, 7.72 (m, 20 m of dppm), 11.16 (s, 1H, SC*H*S). ^{31}P{^{1}H} NMR (THF-d_8, 161.70 MHz, 25 °C): δ 17.8 (s).

CO_2 Reduction by 9 or 10a. A solution of **9** (0.012 g, 0.016 mmol) or **10a** (0.012 g, 0.017 mmol) in 10 mL of THF was heated under 80 atm of H_2/CO_2 (1/1) in a stainless steel autoclave for 16 h. The reactor was cooled rapidly and carefully vented. The formic acid formed was analyzed by ^{1}H NMR.

Reaction of 9 or 10a with CO_2/H_2 in an HPNMR Tube. A THF-d_8 solution of **9** or **10a** in the HPNMR tube was pressurized with 80 atm of H_2/CO_2 (1/1). ^{31}P{^{1}H} spectra of the solution were taken at 60 °C every 2 h for a period of 18 h.

Reaction of 10b with Ph_2SiH_2. Ph_2SiH_2 (4 μL, 22 μmol) was added through a microsyringe to a 0.4 mL THF-d_8 solution of **10b** (18 mg, 12 μmol) in a 5 mm NMR tube sealed with a rubber septum. The solution was heated in the NMR probe at 50 °C for 2 h and ^{1}H and ^{31}P{^{1}H} spectra taken indicated that a small amount of **6H**$^+$ was formed. The tube was continuously heated at 50 °C in the probe, and the NMR spectra were recorded every 2 h for a period of 14 h. It was shown by ^{1}H and ^{31}P{^{1}H} NMR that, at the end of the period, ∼80% of **10b** had been converted to **6H**$^+$ and these two were the only metal complexes present throughout the experiment.

Crystallographic Analysis for [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)-Ru(dppm)]BPh_4 (10c). Crystals suitable for an X-ray diffraction study were obtained by layering of hexane on a THF solution of [(η^5-$C_5H_4(CH_2)_3NMe_2H^+$)RuH(dppm)]BF_4 (**6H**$^+$) containing 5 equiv of $NaBPh_4$. An orange block-shaped crystal of dimensions 0.19 × 0.19 × 0.29 mm was mounted in a glass capillary and used for X-ray structure determination. All measurements were made on a Marreserach image plate scanner with graphite-monochromated Mo Kα radiation. The crystal system is found to be monoclinic and the space group $P2_1$(No. 4) was found from the systematic absences and confirmed by successful solution and refinement. The data were collected at 25 °C using the ω-scan technique to a maximum 2θ value of 51.3°. Of the 16 719 reflections which were collected, 4410 were unique (R_{int} = 0.037); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo Kα radiation is 4.3 cm^{-1}. The structure was solved by the Patterson method and expanded using Fourier techniques with the teXsan crystallographic software package. All non-H atoms except B were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4223 observed reflections ($I > 3.00\sigma(I)$) and 571 variable parameters and converged with unweighted and weighted agreement factors R = 2.4% and R_w = 3.0% with GOF = 1.20. The data to parameter ratio was 7.41:1 and residual electron density/hole +0.33/−0.68 e$^-$Å^{-3}. Further crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, all bond lengths and bond angles, anisotropic displacement coefficients, and isotropic displacement coefficients for [(η^5:η^1-$C_5H_4(CH_2)_3NMe_2$)Ru(dppm)]BPh_4 (26 pages). Ordering information is given on any current masthead page.

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