6130 *J. Am. Chem. Soc.* **2000,** *122,* 6130−6131

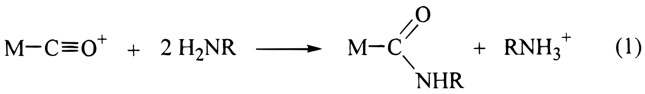
A Kinetically Inert Proton on a Metal−Metal Bond in [{(η^5-C_5H_3)$_2$($SiMe_2$)$_2$}$Ru_2(CO)_4$(μ-H)]$^+$ that Promotes Reactions with Amines

Maxim V. Ovchinnikov and Robert J. Angelici*

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received March 13, 2000

Unsaturated ligands in transition metal complexes can be activated to nucleophilic attack by creating a positive charge on the complex.[1] Carbon monoxide ligands are activated to attack by amine nucleophiles when the positive charge on a complex is sufficiently high to give C≡O stretching force constants, k_{CO}, that are higher than 16.5 mdyn/Å (or ν(CO) values higher than approximately 2000 cm^{-1}).[2] These reactions lead to carbamoyl complexes (eq 1), and some reactions give formamides and ureas



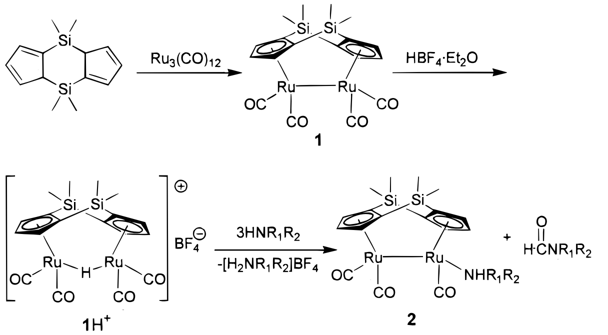
$$M{-}C{\equiv}O^+ + 2\,H_2NR \longrightarrow M{-}C(=O)NHR + RNH_3^+ \qquad (1)$$

catalytically.[3] One approach to making a complex more positive is to add a proton (H^+) to the metal (eq 2). While numerous metal carbonyl complexes have been protonated,[4] the CO ligands in

$$M(L)_x(CO)_y + H^+ \rightarrow H{-}M(L)_x(CO)_y^{\,+} \qquad (2)$$

these complexes either do not react with amines because their k_{CO} and ν(CO) values are insufficiently high or the amine bases simply deprotonate the metal to give the unreactive neutral complex $M(L)_x(CO)_y$. This rapid deprotonation occurs for a wide range of cationic metal hydride complexes $H{-}M(L)_x(CO)_y^{\,+}$.[5,4b] Neutral $H{-}M(L)_x(CO)_y$ complexes often undergo deprotonation much more slowly,[6] but their k_{CO} and ν(CO) values are not sufficiently high to promote attack by amines. Di- and polynuclear metal complexes with M−H−M bridging hydrides also undergo rapid deprotonation with bases.[7,8] In this communication we describe a cationic dinuclear complex [{(η^5-C_5H_3)$_2$($SiMe_2$)$_2$}Ru_2-$(CO)_4$(μ-H)]$^+$ (**1**H^+) whose high ν(CO) values promote amine attack but is only slowly deprotonated by amines. The bridging dicyclopentadienyl (η^5-C_5H_3)$_2$($SiMe_2$)$_2$ ligand[9] with two $SiMe_2$ groups linking the cyclopentadienyl rings is a key contributor to the slow rate of deprotonation of **1**H^+ thereby allowing nucleophilic attack on a CO ligand.

Scheme 1



The reaction of $(C_5H_4)_2(SiMe_2)_2$[10] with $Ru_3(CO)_{12}$ in the presence of the hydrogen acceptor 1-dodecene furnished {(η^5-C_5H_3)$_2$($SiMe_2$)$_2$}$Ru_2(CO)_4$ (**1**) in 72% yield, as an air- and moisture-stable yellow solid (Scheme 1).[11] The hydride-bridged dinuclear Ru complex[12] **1**H^+ was formed in quantitative yield upon addition of 1 equiv of $HBF_4{\cdot}OEt_2$ or CF_3SO_3D to a solution of complex **1** in CH_2Cl_2 at room temperature. The Ru−H resonance in the ^1H NMR spectrum occurs as a singlet at δ −19.92 ppm. The CO stretching frequencies for **1**H^+ are approximately 67 cm^{-1} higher than those for **1** and fall within the range where amine attack on the CO groups is expected to occur.[2] An X-ray diffraction study of **1**$H^+BF_4^-$ reveals an eclipsed orientation of the terminal CO ligands on the two Ru atoms. The Ru−Ru distance is substantially longer in **1**$H^+BF_4^-$ (3.1210(5) Å) than in **1** (2.8180(3) Å).[13]

Compound **1**H^+ is exceptionally stable with respect to deprotonation by strong organic bases such as Et_3N, quinuclidine, or pyridine. Less than 2% of the complex was deprotonated after 1 h in CD_3NO_2 or CD_3CN solution in the presence of 10-fold excesses of these amines. Moreover, the deuterated complex **1**D^+TfO^- in wet acetone solution (~10% H_2O) did not undergo measurable H−D exchange after 5 days at 25 °C. In contrast to **1**H^+, the unbridged and monobridged complexes (η^5-C_5H_5)$_2$$Ru_2$-$(CO)_4$($\mu$-H)$^+$ [14a] and {(η^5-C_5H_4)$_2$($SiMe_2$)}$Ru_2(CO)_4$(μ-H)$^+$ [14b] were deprotonated instantly and quantitatively by bases such as pyridine or diethylamine. The acidity of **1**$H^+BF_4^-$, estimated as pK_a^{AN} from studies of the equilibrium constant for the proton-transfer reaction

---

(1) Bush, R. C.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 2735.

(2) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

(3) (a) McCusker, J. E.; Logan, J.; McElwee-White, L. *Organometallics* **1998**, *17*, 4037. (b) McCusker, J. E.; Abboud, K. A.; McElwee-White, L. *Organometallics* **1997**, *16*, 3863. (c) McCusker, J. E.; Grasso, C. A.; Main, A. D.; McElwee-White, L. *Org. Lett.* **1999**, *1*, 961. (d) Dombek, B. D.; Angelici, R. J. *J. Catal.* **1977**, *48*, 433.

(4) (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 52. (b) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiments*; Dedieu, A., Ed.; VCH: New York, 1991; Chapter 10. (c) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (d) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (e) Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1.

(5) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 582.

(6) (a) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945. (b) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (c) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(7) (a) Nataro, C.; Thomas, L. M.; Angelici, R. J. *Inorg. Chem.* **1997**, *36*, 6000. (b) Nataro, C.; Angelici, R. J. *Inorg. Chem.* **1998**, *37*, 2975.

(8) (a) Weberg, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1105. (b) Kristjánsdóttir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983.

(9) For recent examples of (η^5-C_5H_3)$_2$($SiMe_2$)$_2$ complexes, see: (a) Sun, H.; Teng, X.; Huang, X.; Hu, Z.; Pan, Y. *J. Organomet. Chem.* **2000**, *595*, 268. (b) Cano, A. M.; Cano, J.; Cuenca, T.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Inorg. Chim. Acta* **1998**, *280*, 1.

(10) (a) Siemeling, U.; Jutzi, P.; Neumann, B.; Stammler, H. G.; Hursthouse, M. B. *Organometallics* **1992**, *11*, 1328. (b) Hiermeier, J.; Koehler, F. H.; Mueller, G. *Organometallics* **1991**, *10*, 1787.

(11) In a typical procedure, a solution of $Ru_3(CO)_{12}$ (50.0 mg, 78.2 μmol), $(C_5H_4)_2(SiMe_2)_2$ (28.6 mg, 117.0 μmol), and 1-dodecene (260.0 mg, 2.4 mmol) in heptane (30 mL) was heated to reflux for 18 h. The mixture was chromatographed on an alumina column (1 × 20 cm) first with hexanes and then with a 1:10 (v/v) mixture of CH_2Cl_2 and hexanes which eluted a yellow band containing **1** (47 mg, 72%). ^1H (400 MHz, $CDCl_3$): δ 0.26 (s, 6 H, Si(C*H*$_3$)), 0.46 (s, 6 H, Si(C*H*$_3$)), 5.37 (d, J = 1.6 Hz, 4 H, Cp-*H*), 5.78 (t, J = 1.6 Hz, 2 H, Cp-*H*). ^{13}C (100 MHz, $CDCl_3$): δ −2.25 (*C*H_3), 4.53 (*C*H_3), 87.72, 93.95, 95.57 (Cp), 204.57 (*C*O). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2015 (vs), 1952 (vs). Anal. Calcd for $C_{18}H_{18}O_4Ru_2Si_2$: C, 38.84; H, 3.26. Found: C, 39.05; H, 3.32.

(12) **1**$H^+BF_4^-$): ^1H (400 MHz, CD_2Cl_2): δ −19.92 (s, 1 H, Ru-*H*-Ru), 0.47 (s, 6 H, Si(C*H*$_3$)), 0.62 (s, 6 H, Si(C*H*$_3$)), 5.99 (d, J = 2.0 Hz, 4 H, Cp-*H*), 6.02 (t, J = 2.0 Hz, 2 H, Cp-*H*). ^{13}C (100 MHz, CD_2Cl_2): δ −2.57 (*C*H_3), 2.86 (*C*H_3), 88.97, 98.56, 98.81 (Cp), 195.19 (*C*O). IR (CH_2Cl_2): ν-(CO) (cm^{-1}) 2077 (vs), 2050 (w), 2027 (s). Anal. Calcd for $C_{18}H_{19}BF_4O_4$-Ru_2Si_2: C, 33.55; H, 2.97. Found: C, 33.19; H, 2.90.

(13) Details of the X-ray diffraction studies of **1**, **1**$H^+BF_4^-$, and **2**a will be published separately: Ovchinnikov, M. V.; Guzei, I. A.; Angelici, R. J. Manuscript in preparation.

(14) (a) Ovchinnikov, M. V.; Angelici, R. J. Unpublished results. (b) Froehlich, R.; Gimeno, J.; Gonzalez-C. M.; Lastra, E.; Borge, J.; Garcia-G. S. *Organometallics* **1999**, *18*, 3008.

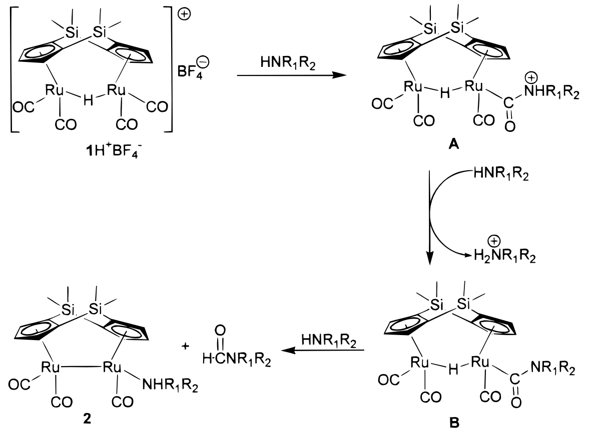
10.1021/ja000883u CCC: $19.00

between **1** and $HPPh_3^+BF_4^-$ in CD_3CN at 25 °C,[15] is 6.5(±0.2) in CD_3CN. This pK_a^{AN} value clearly indicates that the above-noted amine bases will thermodynamically deprotonate **1**$H^+BF_4^-$ easily. Although it is not obvious why the $(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2$ bridging ligand causes the bridging proton to be so slowly removed, it may be due to a combination of the bulkiness of the dimethylsilyl linkers and the rigidity of the molecule. The donor ability of the $(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2$ ligand to the Ru atom is probably similar to that of the Cp ligand based on average ν(CO) values[16] for **1**$H^+BF_4^-$ (2044 cm^{-1}) and $Cp_2Ru_2(CO)_4(\mu\text{-}H)^+$ [7a] (2046 cm^{-1}).

Reactions of **1**H^+ with secondary amines (Me_2NH, Et_2NH, morpholine, pyrrolidine), primary amines ($MeNH_2$, $EtNH_2$, $BnNH_2$), or ammonia furnished $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NHRR')$ (**2**) complexes and the corresponding formamides in a 1:1 ratio (Scheme 1). Complexes of type **2**[17] were isolated in 78−94% yield as air- and moisture-sensitive dark-red solids. The other Ru-containing product in these reactions was the deprotonated complex **1** observed in 5−20% yields as a result of direct deprotonation of **1**H^+ by amine. The yields of **1** appear to depend on the steric properties of the amine as less bulky amines (e.g. NH_3) give higher yields of **1**. Also, the yields of **1** were lower when the deuterated **1**D^+TfO^- complex was used. Using a variety of amines, we determined that **1**H^+ reacts when the amine has a pK_a value equal to or greater than 8.33 (morpholine)[18] and a cone angle Θ that is equal to or less than 125° (diethylamine).[19] Bulky amines (Bn_2NH, i-Pr_2NH, Cy_2NH) and weakly nucleophilic amines (aniline) failed to react with **1**H^+.

On the basis of studies described below, the amine reactions are proposed to occur by the mechanism shown in Scheme 2. This involves initial nucleophilic attack by the amine on a coordinated CO to produce the cationic intermediate **A**, which is rapidly deprotonated to **B**.[2,20] Reductive elimination of the formamide from **B** gives an unsaturated diruthenium intermediate that coordinates an amine to give **2**. No intermediates were observed by FT-IR or NMR spectroscopy during the course of the reaction. Experiments using the deuterium-labeled **1**D^+TfO^- gave formamide products (D(C=O)NRR′) that are completely deuterated at the formyl position and no other. When **1**D^+TfO^- rather then **1**$H^+BF_4^-$ was used in the reaction, substantially less deprotonation to **1** was observed, as expected for a deuterium isotope effect.

Scheme 2



Rates of the reaction of **1**D^+TfO^- ([**1**D^+TfO^-] = 8.34×10^{-3}–11.12×10^{-3} M^{-1}) with morpholine ([morpholine] = 8.56×10^{-1} to 10.82×10^{-1} M^{-1}) in nitromethane solvent to give $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3\{NH(CH_2CH_2)_2O\}$ were followed by monitoring the disappearance of the ν(CO) bands in the IR spectra or ^1H NMR signals of **1**D^+TfO^-. The reaction was shown to follow the second-order rate law, $-d[\mathbf{1}D^+TfO^-]/dt = k_2[\mathbf{1}D^+TfO^-][\text{morpholine}]$, where $k_2 = (2.3 \pm 0.5) \times 10^{-3}$ M^{-1} s^{-1} at 20 °C. This rate law is consistent with the first step in the mechanism (Scheme 2) being rate-determining. The subsequent deprotonation of the nitrogen in **A** is likely to be fast and the reductive elimination of the formamide from **B** must be rapid because there is no spectroscopic evidence for intermediates in the reaction. Such a facile reductive elimination is surprising because removal of the bridging H^+ by bases is so slow. Reductive eliminations involving a μ-H have only recently been characterized, e.g. in the formation of alkanes and arenes from $Pd_2R_2(\mu\text{-}H)(dppm)_2^+$.[21]

In conclusion, we have discovered that protonation of the Ru−Ru bond in **1** gives a cationic complex (**1**H^+) in which the bridging proton is removed only very slowly by bases even though the proton is thermodynamically acidic ($pK_a^{AN} = 6.5(\pm 0.2)$). The low kinetic acidity of **1**H^+ allows it to react with alkylamines, which attack a CO ligand that is activated to such an attack by the cationic nature of the complex. These amine reactions lead to the elimination of the μ-H which becomes incorporated into the formamide product. Mechanistic studies support the pathway shown in Scheme 2. Further studies of reactions of **1**H^+ with nucleophiles are in progress.

Acknowledgment. We appreciate the support of the National Science Foundation through Grant No. CHE-9816342.

JA000883U

---

[15] A solution of **1** (18.6 mg, 31.9 μmol) and $HPPh_3^+BF_4^-$ (11.2 mg, 32.0 μmol) in CD_3CN (1 mL) was sealed in an NMR tube under an argon atmosphere. After following the reaction for 8 days, the ^1H NMR spectrum indicated a [**1**]/[**1**$H^+BF_4^-$] ratio of 2.35, and the ^{31}P NMR spectrum established a $[HPPh_3^+BF_4^-]/[PPh_3]$ ratio of 2.47. From these two ratios and the pK_a^{AN} of $HPPh_3^+$ (8.0), the pK_a^{AN} of **1**$H^+BF_4^-$ was calculated to be 6.5(±0.2) in acetonitrile.

[16] Jolly, W. L.; Avanzino, S. C.; Rietz, R. R. *Inorg. Chem.* **1977**, *16*, 964.

[17] In a typical procedure, gaseous CH_3NH_2 was slowly bubbled through a suspension of yellow **1**$H^+BF_4^-$ (50.0 mg, 77.6 μmol) in hexanes (25 mL) for 5 min at ambient temperature. The color of the reaction mixture immediately changed to wine-red. Solvent was removed in a vacuum, and the red residue was recrystallized from hexanes (10 mL) at −25 °C to give 39 mg (83%) of **2**a as dark-red, air- and moisture-sensitive crystals. ^1H (400 MHz, C_6D_6): δ 0.24 (s, 6 H, $Si(CH_3)$), 0.38 (s, 6 H, $Si(CH_3)$), 1.58 (bs, 2 H, CH_3NH_2), 1.67 (t, $J = 6.4$ Hz, 3 H, CH_3NH_2), 4.52 (d, $J = 2.0$ Hz, 2 H), 4.77 (t, $J = 2.0$ Hz, 1 H), 5.11 (d, $J = 2.4$ Hz, 2 H), 5.76 (t, $J = 2.4$ Hz, 1 H). ^{13}C (100 MHz, C_6D_6): δ −1.88 (CH_3), 5.38 (CH_3), 41.39 (CH_3NH_2), 79.20, 83.59, 90.10, 92.98, 94.37, 95.52 (Cp), 209.07 (CO), 211.98 (CO). IR (hexanes): ν(CO) (cm^{-1}) 1973 (vs), 1907 (vs), 1884 (m). Anal. Calcd for $C_{18}H_{23}NO_3Ru_2Si_2 \cdot {}^1/_4C_6H_{14}$: C, 40.30; H, 4.60; N, 2.41. Found: C, 40.77; H, 4.57; N, 2.95.

[18] Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworth: London, 1972.

[19] For amine cone angles, see: Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520.

[20] Semmelhack, M. F. *J. Organomet. Chem., Libs.* **1976**, *1*, 361.

[21] Stockland, R. A., Jr.; Anderson, G. K.; Rath, N. P. *J. Am. Chem. Soc.* **1999**, *121*, 7945.