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# Amine Attack on the Carbonyl Ligands of the Protonated Dicyclopentadienyl-Bridged Diruthenium Complex $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}H)]^+$

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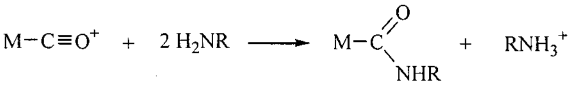
Complexes $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}H)]^+$ ($\mathbf{1}H^+BF_4^-$, $\mathbf{1}D^+TfO^-$), with a protonated Ru−Ru bond, were prepared by protonation of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4$ (**1**) with $HBF_4\cdot Et_2O$ or $CF_3SO_3D$. The bridging proton in $\mathbf{1}H^+$ is removed only very slowly by amine bases even though it is thermodynamically acidic ($pK_a^{AN} = 6.5$ ($\pm 0.2$)). This remarkable kinetic inertness of the bridging proton allows amines ($NH_3$, $NH_2CH_3$, $NH(CH_3)_2$, morpholine, piperidine, pyrrolidine) to react with $\mathbf{1}H^+$ by attacking the CO ligand to give a formamide ($HC(=O)NR_2$) and the CO-substituted product $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NHR_2)$ (**2**). Thus, protonation of the metal−metal bond in $\mathbf{1}H^+$ promotes reactions of the CO ligand that are not possible in the unprotonated **1**. A proposed mechanism for these reactions is supported by kinetic studies of the reaction of $\mathbf{1}D^+TfO^-$ with morpholine in nitromethane at 20.0 °C, as well as by deuterium-labeling experiments. The molecular structure of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NH_2CH_3)$ (**2f**), as determined by an X-ray diffraction investigation, is also presented.

## Introduction

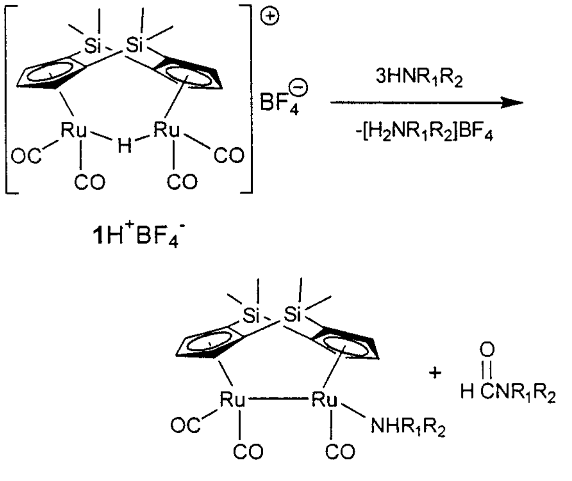
Metal-promoted nucleophilic attack on unsaturated ligands is a reaction common to a number of transition metal complexes and constitutes a transformation of synthetic importance.[1] Amines and alkoxides attack the carbon of carbon monoxide ligands in transition metal complexes if the positive charge on the complexes is sufficiently high to give C≡O stretching force constants, $k_{CO}$, that are higher than 16.5 mdyn/Å (or $\nu$(CO) values higher than approximately 2000 cm$^{-1}$).[2] A common example of such a reaction is the formation of carbamoyl complexes (eq 1).



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

Reactions of metal carbonyl complexes with amines are also known to give formamides,[3] carbamates,[4] and ureas,[5] either stoichiometrically or catalytically.

One of the simplest approaches to making a complex more positive is to add a proton ($H^+$) to the metal center.[6] However, most protonated metal carbonyl complexes either do not react with amines because their $k_{CO}$ and $\nu$(CO) values are insufficiently high or the amine bases simply deprotonate the metal to give the unreactive neutral metal complex. We recently communicated[7] the synthesis of the cationic dinuclear complex $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}H)]^+$ ($\mathbf{1}H^+$), whose carbon monoxide ligands are activated to attack by amine nucleophiles because of the positive charge on the complex, which is sufficiently high to give $\nu$(CO) values higher than 2000 cm$^{-1}$.[2] At the same time, complex $\mathbf{1}H^+$ is only slowly deprotonated by amines despite its high thermodynamic acidity.[7] Treatment of $\mathbf{1}H^+$ with 3 equiv of nucleophilic amines resulted in the formation of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(\eta^1\text{-}NHR_1R_2)$ (**2**) and the corresponding formamide in a 1:1 ratio (eq 2). This paper provides details of the earlier study[7] and



(2)

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[†] Iowa State University, Molecular Structure Laboratory.

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new results that offer some understanding of the mechanism and scope of this reaction.

## Experimental Section

**General Procedures.** All reactions were performed under an argon atmosphere in reagent grade solvents, using standard Schlenk or drybox techniques.[8] Hexanes, methylene chloride, and diethyl ether were purified by the Grubbs method[9] prior to use. All other solvents were purified by published methods.[10] Gaseous amines were dried by passing them through a BaO column. Liquid amines were distilled from Na under an Ar atmosphere. Chemicals were purchased from commercial sources or prepared by literature methods, as referenced below. Alumina (neutral, activity I, Aldrich) was degassed under vacuum for 12 h and treated with 7.5% of water. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DRX-400 spectrometer. Solution infrared spectra were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

**Synthesis of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}D)]^+CF_3SO_3^-$ ($1D^+TfO^-$).** By reacting $CF_3SO_3D$ (8 $\mu$L, 90.4 $\mu$mol) (Aldrich) with **1** (50 mg, 89.8 $\mu$mol) in $CH_2Cl_2$ (30 mL), $\mathbf{1}D^+TfO^-$ was prepared using the same method as in the preparation of $\mathbf{1}H^+BF_4^-$. Complex $\mathbf{1}D^+TfO^-$ was found to be spectroscopically ($^1H$, $^{13}C$ NMR, FT-IR) identical to $\mathbf{1}H^+BF_4^-$ except for the near absence[11] of the $\mu$-H resonance at −19.92 ppm.[7] Anal. Calcd for $C_{19}H_{18}BDF_3O_7Ru_2SSi_2$: C, 32.29; H, 2.71; S, 4.54. Found: C, 32.18; H, 2.65; S, 4.48.

**Synthesis of $\{(\eta^5\text{-}C_5H_3)_2(SiEt_2)_2\}Ru_2(CO)_4$ (3).** A solution of $Ru_3(CO)_{12}$ (200.0 mg, 312.8 $\mu$mol), $(C_5H_4)_2(SiEt_2)_2$[12] (143 mg, 475.7 $\mu$mol), and methylisobutyl ketone (1.0 mL, 10.0 mmol) in heptane (100 mL) was heated to reflux for 30 h. The mixture was cooled to ambient temperature and chromatographed on an alumina column (1 × 20 cm) first using hexanes as the eluent and then a 1:5 (v/v) mixture of $CH_2Cl_2$ and hexanes, which eluted a yellow band containing **3** (170 mg, 58%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.73 (m, 4 H, $Si(CH_2CH_3)$), 0.91 (m, 4 H, $Si(CH_2CH_3)$), 0.97 (m, 6 H, $Si(CH_2CH_3)$), 1.10 (m, 6 H, $Si(CH_2CH_3)$), 5.39 (d, $J$ = 2.2 Hz, 4 H, Cp-*H*), 5.79 (t, $J$ = 2.2 Hz, 2 H, Cp-*H*). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 5.21, 8.20, 8.23, 9.94 (Et); 87.81, 92.21, 96.04 (Cp); 204.58 (*C*O). IR (hexanes): $\nu$(CO) (cm$^{-1}$) 2025 (vs), 1967 (vs). Anal. Calcd for $C_{22}H_{26}O_4Ru_2Si_2$: C, 43.12; H, 4.28. Found: C, 43.09; H, 4.21.

**Synthesis of $[\{(\eta^5\text{-}C_5H_3)_2(SiEt_2)_2\}Ru_2(CO)_4(\mu\text{-}H)]^+BF_4^-$ ($3H^+BF_4^-$).** A solution of **3** (100.0 mg, 161.2 $\mu$mol) in $CH_2Cl_2$ (20 mL) was treated with $HBF_4\cdot Et_2O$ (24.0 $\mu$L, 174.1 $\mu$mol) at room temperature. A yellow precipitate of $\mathbf{3}H^+BF_4^-$ was obtained in nearly quantitative yield (111.0 mg, 100%) by diluting the reaction solution with a 10-fold excess of ether (200 mL). $^1H$ NMR (400 MHz, $CD_3NO_2$): $\delta$ −19.76 (s, 1 H, Ru-*H*-Ru), 0.95−1.30 (m, 20 H, $Si(CH_2CH_3)$), 6.13 (t, $J$ = 2.2 Hz, 2 H, Cp-*H*), 6.19 (d, $J$ = 2.2 Hz, 4 H, Cp-*H*). $^{13}C$ NMR (100 MHz, $CD_3NO_2$): $\delta$ 5.73, 8.05, 8.24, 9.50 (Et); 90.13, 97.41, 100.48 (Cp); 196.81, 196.86 (*C*O). IR ($CH_2Cl_2$): $\nu$(CO) (cm$^{-1}$) 2077 (vs), 2050 (w), 2027 (s). Anal. Calcd for $C_{22}H_{27}BF_4O_4Ru_2Si_2$: C, 37.72; H, 3.88. Found: C, 37.65; H, 3.95.

**Reactions of $1H^+BF_4^-$ and $1D^+TfO^-$ with Amines.** In a typical experiment, amine (3−5 equiv) was added to a mixture of $\mathbf{1}H^+BF_4^-$ (or $\mathbf{1}D^+TfO^-$) (∼10 mg) and triphenylmethane (∼3 mg, internal standard) in deuterated benzene (1 mL) in an NMR tube (gaseous amines were bubbled through the suspension for 5 min; then a stream of dry argon was bubbled through the solution in order to remove the excess amine). During the addition of amine, the reaction mixture immediately changed color from colorless to wine-red. The $\mathbf{1}H^+BF_4^-$ or $\mathbf{1}D^+TfO^-$ reacted completely, and yields of the formamides were determined by means of $^1H$ NMR spectroscopy. Yields of the formamides[13] and characterizations of **2a**−**f** are given below.

**Reactions of $1H^+BF_4^-$ and $1D^+TfO^-$ with $NH_3$:** 72% (84%).[14] $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NH_3)$ (**2a**): $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 0.29 (s, 6 H, $Si(CH_3)$), 0.36 (s, 6 H, $Si(CH_3)$), 3.54 (bs, 3 H, $NH_3$), 4.67 (d, $J$ = 2.0 Hz, 2 H), 4.78 (t, $J$ = 2.0 Hz, 1 H), 5.10 (d, $J$ = 2.4 Hz, 2 H), 5.73 (t, $J$ = 2.4 Hz, 1 H). IR (hexanes): $\nu$(CO) (cm$^{-1}$) 1974 (vs), 1903 (vs), 1879 (m).

**Reactions of $1H^+BF_4^-$ and $1D^+TfO^-$ with $NH_2CH_3$:** 84%, 88%. Isolation and characterization of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NH_2CH_3)$ (**2b**) were reported earlier.[7] Crystals of **2b** suitable for X-ray diffraction analysis were obtained by slow cooling of a saturated solution of **2b** in hexanes to −20 °C.

**Reactions of $1H^+BF_4^-$ and $1D^+TfO^-$ with $NH(CH_3)_2$:** 85%, 90%. $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NH(CH_3)_2)$ (**2c**): $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 0.30 (s, 6 H, $Si(CH_3)$), 0.36 (s, 6 H, $Si(CH_3)$), 2.03 (d, $J$ = 6.4 Hz, 6 H, $(CH_3)_2NH$), 2.90 (bs, 1 H, $(CH_3)_2NH$), 4.59 (d, $J$ = 2.0 Hz, 2 H), 4.85 (t, $J$ = 2.0 Hz, 1 H), 5.14 (d, $J$ = 2.4 Hz, 2 H), 5.73 (t, $J$ = 2.4 Hz, 1 H). IR (hexanes): $\nu$(CO) (cm$^{-1}$) 1975 (vs), 1907 (vs), 1882 (m).

**Reactions of $1H^+BF_4^-$ and $1D^+TfO^-$ with $NH(CH_2CH_2)_2O$:** 89%, 91%. $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3\{NH(CH_2CH_2)_2O\}$ (**2d**): $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 0.31 (s, 6 H, $Si(CH_3)$), 0.39 (s, 6 H, $Si(CH_3)$), 2.95 (m, 2 H, $\{O(CH_2CH_2)_2NH\}$), 3.33 (m, 2 H, $\{O(CH_2CH_2)_2NH\}$), 3.66 (m, 4 H, $\{O(CH_2CH_2)_2NH\}$), 3.71 (bs, 1 H, (N*H*)), 4.48 (d, $J$ = 2.0 Hz, 2 H), 4.81 (t, $J$ = 2.0 Hz, 1 H), 5.11 (d, $J$ = 2.4 Hz, 2 H), 5.77 (t, $J$ = 2.4 Hz, 1 H). IR (hexanes): $\nu$(CO) (cm$^{-1}$) 1981 (vs), 1909 (vs), 1889 (m).

**Reactions of $1H^+BF_4^-$ and $1D^+TfO^-$ with $NH(CH_2CH_2)_2CH_2$:** 82%, 88%. $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3\{NH(CH_2CH_2)_2CH_2\}$ (**2e**): $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 0.26 (s, 6 H, $Si(CH_3)$), 0.43 (s, 6 H, $Si(CH_3)$), 1.16 (m, 2 H, $\{CH_2(CH_2CH_2)_2NH\}$), 1.41 (m, 4 H, $\{CH_2(CH_2CH_2)_2NH\}$), 2.85 (m, 4 H, $\{CH_2(CH_2CH_2)_2NH\}$), 3.20 (bs, 1 H, (N*H*)), 4.40 (d, $J$ = 2.1 Hz, 2 H), 4.73 (t, $J$ = 2.1 Hz, 1 H), 5.01 (d, $J$ = 2.4 Hz, 2 H), 5.55 (t, $J$ = 2.4 Hz, 1 H). IR (hexanes): $\nu$(CO) (cm$^{-1}$) 1976 (vs), 1909 (vs), 1879 (m).

**Reactions of $1H^+BF_4^-$ and $1D^+TfO^-$ with $NH(CH_2CH_2)_2$:** 77%, 84%. $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3\{NH(CH_2CH_2)_2\}$ (**2f**): $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 0.32 (s, 6 H, $Si(CH_3)$), 0.40 (s, 6 H, $Si(CH_3)$), 1.26 (m, 4 H, $(CH_2CH_2)_2NH$), 2.55 (m, 4 H, $(CH_2CH_2)_2NH$), 3.10 (bs, 1 H, (N*H*)), 4.68 (d, $J$ = 2.4 Hz, 2 H), 4.84 (t, $J$ = 2.4 Hz, 1 H), 5.14 (d, $J$ = 2.4 Hz, 2 H), 5.75 (t, $J$ = 2.4 Hz, 1 H). IR (hexanes): $\nu$(CO) (cm$^{-1}$) 1973 (vs), 1907 (vs), 1887 (m).

**Reaction between $1H^+BF_4^-$ and $PhNH^-Li^+$.** A suspension of $\mathbf{1}H^+BF_4^-$ (156 mg, 0.24 mmol) in diethyl ether (50 mL) was treated with a freshly prepared ether (10 mL) solution of $PhNH^-Li^+$[15] (0.26 mmol) at −78 °C. The mixture was gradually warmed to room temperature and filtered through a short pad of Celite. Removing the solvent under reduced pressure

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(11) The $^1H$ NMR spectrum of $\mathbf{1}D^+TfO^-$ in $CD_3NO_2$ revealed a small peak for the Ru−H resonance at −19.98 ppm (s, 0.02 H), which corresponds to $\mathbf{1}H^+TfO^-$ as a ∼2% impurity.

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(13) Yield values correspond to the reactions of $\mathbf{1}H^+BF_4^-$ and $\mathbf{1}D^+TfO^-$, respectively.

(14) Yield was estimated from the yield of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NH_3)$.

gave an oily brown residue, which was found to be a mixture of **1** and formanilide (49% yield) by $^1$H NMR spectroscopy. The reaction with **1**D$^+$TfO$^-$ was conducted in a similar fashion (61% yield of formanilide).

**Synthesis of [{($\eta^5$-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}Ru$_2$(CO)$_3${NH(CH$_2$CH$_2$)$_2$}-($\mu$-H)]$^+$BF$_4$$^-$ (2fH$^+$BF$_4$$^-$).** A suspension of yellow **1**H$^+$BF$_4$$^-$ (50.0 mg, 77.6 $\mu$mol) in hexanes (25 mL) was treated with neat pyrrolidine (32 $\mu$L, 0.4 mmol). The color of the reaction mixture immediately changed to wine-red. Solvent was removed in a vacuum, and the red residue was recrystallized from hexanes (10 mL) at −25 °C to give 41 mg (85%) of **2f** as dark red, air- and moisture-sensitive crystals. A solution of **2f** (25 mg, 41.7 $\mu$mol) in CH$_2$Cl$_2$ (10 mL) treated with HBF$_4$·OEt$_2$ **(**6 $\mu$L, 43.5 $\mu$mol) immediately gave a bright red solution, which was diluted with diethyl ether (50 mL) to give **2**fH$^+$BF$_4$$^-$ (28 mg, 98%) as a red crystalline precipitate. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ −19.18 (s, 1 H, Ru-*H*-Ru), 0.38 (s, 3 H, Si(C*H$_3$*)), 0.47 (s, 3 H, Si(C*H$_3$*)), 0.51 (s, 3 H, Si(C*H$_3$*)), 0.53 (s, 3 H, Si(C*H$_3$*)), 1.71 (m, 2 H, (C*H$_2$*)), 1.86 (m, 2 H, (C*H$_2$*)), 2.33 (m, 2 H, (C*H$_2$*)), 3.19 (m, 1 H, (C*H$_2$*)), 3.34 (m, 1 H, (C*H$_2$*)), 4.96 (bs, 1 H, N*H*), 5.17 (m, 1 H, Cp), 5.64 (m, 1 H, Cp), 5.71 (m, 1 H, Cp), 5.87 (m, 2 H, Cp), 6.01 (m, 1 H, Cp). IR (CH$_2$Cl$_2$): $\nu$(CO) (cm$^{-1}$) 2050 (vs), 2002 (s), 1954 (m). Anal. Calcd for C$_{21}$H$_{28}$BF$_4$NO$_3$Ru$_2$Si$_2$: C, 36.68; H, 4.10; N, 2.04. Found: C, 36.42; H, 3.80; N, 2.06.

**Kinetic Studies of the Reaction (eq 2) of 1D$^+$TfO$^-$ with Morpholine.** In a typical NMR experiment, **1**D$^+$TfO$^-$ (3−6 mg) and triphenylmethane (~3 mg, internal standard) were dissolved in dry CD$_3$NO$_2$ (1 mL) under an argon atmosphere in an NMR tube. The tube was placed in the NMR spectrometer, and the probe temperature was set at 20.0 ± 0.5 °C. The temperature of the solution was allowed to equilibrate for at least 30 min. The tube was taken out, an amount of neat morpholine to give a $7.72 \times 10^{-2}$ to $9.40 \times 10^{-2}$ M solution was injected into the NMR tube, and the tube was returned to the NMR spectrometer. In a typical IR experiment, **1**D$^+$TfO$^-$ (30−50 mg) was dissolved in dry CH$_3$NO$_2$ (10 mL) under an argon atmosphere in a Schlenk flask equipped with a constant-temperature water jacket. The jacket was connected to a constant-temperature water circulator, and the temperature of the solution was allowed to equilibrate for at least 30 min. Then, an amount of neat morpholine to give a $4.10 \times 10^{-1}$ to $15.1 \times 10^{-1}$ M solution was added. Samples were periodically withdrawn from the flask, and their IR spectra were obtained in a constant-temperature IR cell.

The reactions were monitored by the disappearance of the 2075 cm$^{-1}$ $\nu$(CO) band in the IR spectra or the 6.11 and 6.17 ppm bands in the $^1$H NMR spectra of **1**D$^+$TfO$^-$. Rate constants were calculated from the 10−60 spectra taken during the first two (second-order conditions) or three (pseudo-first-order conditions) half-lives of the reaction. Rate data, which were obtained by the IR method under pseudo-first-order conditions, where a ~100-fold excess of morpholine was utilized, were fit to the equation[16] rate = $k_{\mathrm{obs}}$[**1**D$^+$TfO$^-$] to obtain the pseudo-first-order rate constants $k_{\mathrm{obs}}$ (s$^{-1}$). Second-order rate constants $k_2$ (M$^{-1}$·s$^{-1}$) were calculated using the expression $k_2 = k_{\mathrm{obs}}$/[morpholine]$_{\mathrm{av}}$, where [morpholine]$_{\mathrm{av}}$ is the average of the [morpholine] at the beginning and the end of the reaction.

Rate data, which were obtained by the $^1$H NMR method, when [morpholine]$_0$ was less than 30 times larger than [**1**D$^+$TfO$^-$], were fit to a second-order equation[16] by plotting ln([morpholine]$_t$/[**1**D$^+$TfO$^-$]$_t$) vs time. The second-order rate constants $k_2$ (M$^{-1}$·s$^{-1}$) were determined from the slope of the best fit straight line.

**X-ray Crystallography of {($\eta^5$-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}Ru$_2$(CO)$_3$-(NH$_2$CH$_3$) (2b).** A red crystal with approximate dimensions 0.40 × 0.18 × 0.06 mm was selected under oil under ambient conditions and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation and a diffractometer-to-crystal distance of 5.08 cm. The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about $\omega$ with an exposure time of 10 s per frame. A total of 47 reflections were obtained. The reflections were successfully indexed by an automated indexing routine in the SMART program. The final cell constants were calculated from a set of 4927 strong reflections from the actual data collection. The data were collected by using the hemisphere data collection routine. Reciprocal space was surveyed to the extent of 1.9 hemispheres to a resolution of 0.80 Å. A total of 10 630 data were harvested by collecting three sets of frames with 0.3° scans in $\omega$ with an exposure time of 60 s per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[17] Systematic absences in the diffraction data were consistent with the space groups $P\bar{1}$ and $P1$.[18] The *E*-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct method provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms except for N(1), N(2), C(7), and C(19) were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. There is occupational disorder present in the structure. One coordination site of each Ru atom is 50% occupied by a CO ligand and 50% occupied by a MeNH$_2$ ligand. The disordered groups were refined with idealized geometries. There is also half a molecule of solvate hexane per molecule of complex present in the asymmetric unit. The final least-squares refinement of 289 parameters against 4878 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for all data) of 0.0464 and 0.1107, respectively (Table 1).

## Results and Discussion

**Synthesis and Protonation of {($\eta^5$-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}-Ru$_2$(CO)$_4$ (1).** The reaction of (C$_5$H$_4$)$_2$(SiMe$_2$)$_2$[19] with Ru$_3$(CO)$_{12}$ in the presence of the hydrogen acceptor (1-dodecene or methylisobutyl ketone) furnished {($\eta^5$-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}Ru$_2$(CO)$_4$ (**1**) in 72% yield, as an air- and moisture-stable yellow solid. When the reaction was carried out in the absence of a hydrogen acceptor, a considerable amount of Ru$_4$(CO)$_{12}$($\mu$-H)$_4$[20] (15−25% based on Ru equiv) was formed and lower yields of **1** were obtained.

The hydride-bridged dinuclear Ru complex [{($\eta^5$-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}Ru$_2$(CO)$_4$($\mu$-H)]$^+$ (**1**H$^+$) was prepared in

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[17] Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

[18] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

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[20] Wilson, R. D.; Wu, S. M.; Love, R. A.; Bau, R. *Inorg. Chem.* **1978**, *17*, 1271.

**Table 1. Crystal Data and Structure Refinement for 2b**

| | |
|---|---|
| empirical formula | $C_{21}H_{30}NO_3Ru_2Si_2$ |
| fw | 602.78 |
| temperature | 173(2) K |
| wavelength | 0.71073 Å |
| crystal system | triclinic |
| space group | $P\bar{1}$ |
| unit cell dimens | $a = 8.8046(5)$ Å<br>$b = 8.9523(5)$ Å<br>$c = 16.6067(9)$ Å<br>$\alpha = 89.721(1)°$<br>$\beta = 88.199(1)°$<br>$\gamma = 66.777(1)°$ |
| volume | 1202.27(12) Å$^3$ |
| $Z$ | 2 |
| density (calcd) | 1.665 Mg/m$^3$ |
| abs coeff | 1.377 mm$^{-1}$ |
| $F(000)$ | 606 |
| cryst size | 0.40 × 0.18 × 0.06 mm |
| $\theta$ range for data collection | 2.45−26.37°. |
| index ranges | $-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $0 \leq l \leq 20$ |
| no. of reflns collected | 10 630 |
| no. of ind reflns | 4878 [$R$(int) = 0.0349] |
| completeness to $\theta$ = 26.37° | 99.0% |
| abs corr | empirical with SADABS |
| max. and min. transmn | 0.9219 and 0.6089 |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 4878/6/289 |
| goodness-of-fit on $F^2$ | 1.008 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0464, wR2 = 0.1107 |
| $R$ indices (all data) | R1 = 0.0662, wR2 = 0.1189 |
| largest diff peak and hole | 1.563 and −0.958 e Å$^{-3}$ |

quantitative yield upon addition of 1 equiv of $HBF_4{\cdot}OEt_2$ or $CF_3SO_3D$ to a $CH_2Cl_2$ solution of complex **1** at room temperature. The Ru−H resonance in the $^1$H NMR spectrum occurs as a singlet at $\delta$ −19.92 ppm. The CO stretching frequencies for $\mathbf{1}H^+$ 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] Complex $\mathbf{1}H^+$ is kinetically inert with respect to deprotonation by organic bases such as $Me_3N$. 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 $Me_3N$ or pyridine, whose conjugate acids have $pK_a^{AN}$ values of 17.61 and 12.33, respectively.[21]

In contrast, the unbridged[22a] and monobridged[22b] analogues of $\mathbf{1}H^+$, $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4(\mu\text{-}H)^+$ and $\{(\eta^5\text{-}C_5H_4)_2(SiMe_2)\}Ru_2(CO)_4(\mu\text{-}H)^+$, undergo fast and quantitative deprotonation by bases such as pyridine or diethylamine. To understand whether the slow rate of deprotonation of $\mathbf{1}H^+BF_4^-$ was caused by kinetic or thermodynamic factors, we estimated the $pK_a^{AN}$ value (6.5 (±0.2) in $CD_3CN$) for $\mathbf{1}H^+BF_4^-$ from studies of the equilibrium constant for the proton-transfer reaction between **1** and $HPPh_3^+BF_4^-$ in $CD_3CN$ at 25 °C.[7] The $pK_a^{AN}$ value for complex $\mathbf{1}H^+BF_4^-$ clearly indicates that the above-noted amine bases[21] will thermodynamically deprotonate $\mathbf{1}H^+BF_4^-$ easily. Although it is not obvious why $\mathbf{1}H^+$ undergoes slow deprotonation, it is perhaps a combination of the bulkiness of the dimethylsilyl linkers and the rigidity of the dicyclopentadienyl bridging ligand.

**Reaction of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}H)]^+BF_4^-$ ($\mathbf{1}H^+BF_4^-$) with Amines.** Complex $\mathbf{1}H^+$ reacts with 3 equiv of nucleophilic amines ($NH_3$, $NH_2CH_3$, $NH(CH_3)_2$, morpholine, piperidine, pyrrolidine) at ambient temperature to yield the complexes $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NHR_1R_2)$ (**2**) and the corresponding formamides in a 1:1 ratio (eq 2). The only other Ru-containing product was the deprotonated complex $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4$ (**1**). The yields of formamides, established for most cases by $^1$H NMR spectroscopy, vary from 72% for the reaction of ammonia with $\mathbf{1}H^+$ to 91% for morpholine with $\mathbf{1}D^+$. The only other product of these reactions was **1**, which was observed in 5−20% yields. The least bulky amine (ammonia) gave the lowest yield of formamide due to the faster rate of direct deprotonation of $\mathbf{1}H^+$ by amine to give complex $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4$ (**1**). Also, yields of the formamides were generally higher when the deuterated $\mathbf{1}D^+$ complex was used, since $\mathbf{1}D^+$ presumably undergoes slower deprotonation compared to $\mathbf{1}H^+$ because of the deuterium isotope effect. Unfortunately, we were unable to measure the magnitude of the deuterium isotope effect for proton transfer from $\mathbf{1}H^+$ because we did not find a base that will deprotonate $\mathbf{1}H^+$ without side reactions[23] at rates sufficiently fast for kinetic studies. Experiments using the deuterium-labeled $\mathbf{1}D^+TfO^-$ and amines ($NHMe_2$, morpholine) gave formamide products (D(C═O)NRR′) that are >95% deuterated at the formyl position and no other. Bulky nucleophilic amines ($Bn_2NH$, i-$Pr_2NH$, $Cy_2NH$) and weakly nucleophilic amines (aniline) failed to react with $\mathbf{1}H^+$ under the same reaction conditions.

Second-order rate constants ($k_2$) for the reaction (eq 2) of morpholine[24] with $\mathbf{1}D^+TfO^-$ were determined from rate studies conducted under pseudo-first-order conditions (∼100-fold excess of amine; $[\mathbf{1}D^+TfO^-] = (8.50-8.95)\times 10^{-3}$ M, $[\text{morpholine}] = (4.10-15.10) \times 10^{-1}$ M, by the IR method) or second-order conditions (<30-fold excess of amine; $[\mathbf{1}D^+TfO^-] = (9.09-9.89) \times 10^{-3}$ M, $[\text{morpholine}] = (7.72-9.40) \times 10^{-2}$ M, by the $^1$H NMR method) in nitromethane at 20 °C. The reactions were followed by monitoring the disappearance of the $\nu$(CO) bands in the IR spectra or the $^1$H NMR signals of $\mathbf{1}D^+TfO^-$. The rate constants $k_2$ (Table S1) were obtained either indirectly from the equation $k_2 = k_{obs}/[\text{morpholine}]_{av}$ or directly from a linear plot, $\ln([\text{morpholine}]_t/[\mathbf{1}D^+TfO^-]_t)$ vs time, for a second-order reaction. A plot (Figure 2) of $k_{obs}$ vs $[\text{morpholine}]_{av}$ gave a straight line with a near-zero intercept. Thus, the reaction follows the second-order rate law, $-d[\mathbf{1}D^+TfO^-]/dt = k_2[\mathbf{1}D^+TfO^-][\text{morpholine}]$, where $k_2 = (2.2 \pm 0.5) \times 10^{-3}$ M$^{-1}$ s$^{-1}$. Although the rate constant $k_2$ includes the rate of deprotonation of $\mathbf{1}D^+TfO^-$ by morpholine, the contribution of this concurrent reaction (≤5%) to the overall rate is smaller than the experimental error in the kinetic studies.

This rate law is consistent with the mechanism proposed in Scheme 1. Initial nucleophilic attack by the amine on a coordinated CO produces the cationic

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(23) $NMe_3$ causes slow decomposition of $\mathbf{1}H^+$ to a mixture of unidentifiable products at rates that are faster than the rate of direct deprotonation.

(24) The rate of the reaction of $\mathbf{1}D^+TfO^-$ with morpholine was the only rate suitable for kinetic studies by $^1$H NMR and FT-IR spectroscopies. More nucleophilic amines ($NH_3$, $NH_2CH_3$, $NH(CH_3)_2$, piperidine, pyrrolidine) reacted with $\mathbf{1}D^+TfO^-$ very fast ($t_{1/2}$ < 1 s).

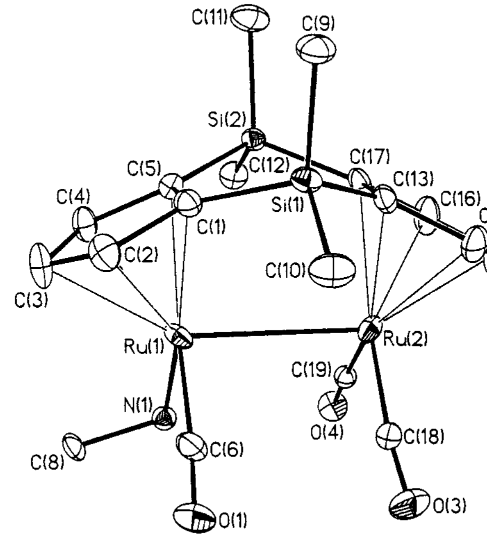


**Figure 1.** Thermal ellipsoid drawing of $\{(\eta^5\text{-}C_5H_3)_2(Me_2Si)_2\}Ru_2(CO)_3(NH_2CH_3)$ (**2b**) showing the labeling scheme at 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ru(1)−Ru(2), 2.8955(6); Ru(1)−N(1), 2.148(9); N(1)−C(8), 1.4691(10); Ru(1)−Cp(centroid), 1.887; Ru(2)−Cp(centroid), 1.889; ∠C(8)−N(1)−Ru(1), 112.5(7); ∠C(18)−Ru(2)−C(19), 99.4(4); ∠C(6)−Ru(1)−N(1), 85.3(3); ∠Ru(1)−Ru(2)−C(18), 88.50(17); ∠C(6)−Ru(1)−Ru(2), 90.94(18); ∠C(6)−Ru(1)−Ru(2)−C(18), 1.0; ∠C(6)−Ru(1)−Ru(2)−C(19), 98.4; ∠Cp−Cp fold angle, 125.9.

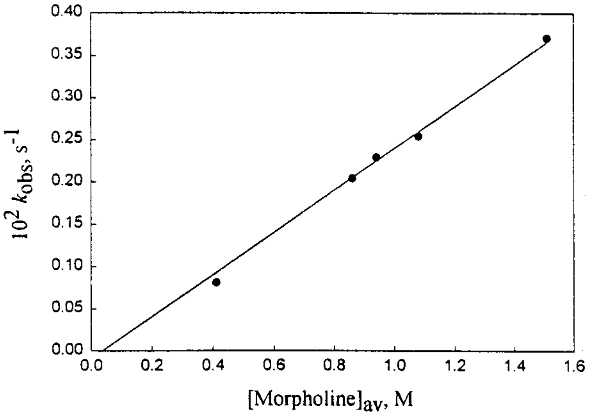
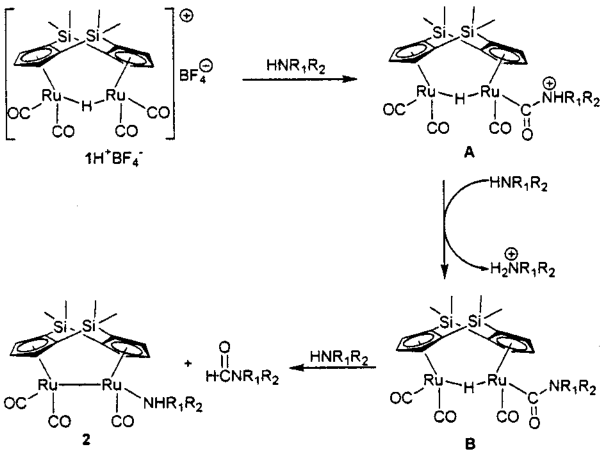


**Figure 2.** Plot of $k_{obs}$ vs $[\text{morpholine}]_{av}$ for reaction (eq 2) of $\mathbf{1D^+}TfO^-$ with morpholine at 20.0 °C.

intermediate **A**. Subsequent deprotonation of the nitrogen in **A** is likely to be fast, and reductive elimination of the formamide from **B** must be rapid because there is no spectroscopic evidence ($^1$H NMR or IR) for intermediates in the reaction. Reductive elimination of the formamide from **B** gives an unsaturated diruthenium intermediate that coordinates an amine to give **2**. The observed first-order dependence on amine concentration and the absence of measurable quantities of intermediates means that the first step, nucleophilic attack on a CO ligand, is rate-determining.

Since the bulkiness of the dimethylsilyl linkers in the $(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2$ ligand is a possible reason for the unusually low kinetic acidity of $\mathbf{1H^+}$, it is conceivable that a more bulky linker would make the proton even less kinetically acidic and presumably increase yields of the formamide products in reactions of $\mathbf{1H^+}$ with amines. We therefore synthesized the more bulky tetraethyl analogue of $\mathbf{1H^+}$, $[\{(\eta^5\text{-}C_5H_3)_2(SiEt_2)_2\}Ru_2(CO)_4(\mu\text{-}H)]^+$ ($\mathbf{3H^+}$), which was successfully characterized by elemental analysis and $^1$H NMR, $^{13}$C NMR, and IR spectroscopies. However, the reactions of amines ($NH_3$, $NH_2Me$, $NHMe_2$, morpholine) with complex $\mathbf{3H^+}$ gave essentially the same yields of formamides and **3** (the result of direct deprotonation of $\mathbf{3H^+}$ by amine) as those for the reactions of $\mathbf{1H^+}$.

**Scheme 1**

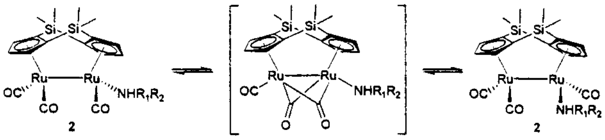


Weakly nucleophilic amines, such as aniline, with $pK_a(H_2O)$ values lower than ∼8 failed to react with $\mathbf{1H^+}$. In contrast to aniline, the corresponding lithium anilide $PhNH^-Li^+$ readily reacted with $\mathbf{1H^+}$ and $\mathbf{1D^+}$ to give formanilide (H(C=O)NHPh) in 49% and 61% isolated yields, respectively. As observed in reactions of the alkylamines with $\mathbf{1D^+}$, the formanilide product (D(C=O)NHPh) from the reaction of $\mathbf{1D^+}$ with $PhNH^-Li^+$ was found by $^1$H NMR studies to be almost completely (>95%) deuterated at the formyl position and no other. Complex **1**, rather than **2**, was observed as the only identifiable ruthenium-containing product of the reaction of $PhNH^-Li^+$ with both $\mathbf{1H^+}$ and $\mathbf{1D^+}$. The formation of **1** clearly also requires the formation of other Ru products, which were not identified. The direct deprotonation of $\mathbf{1H^+}$ by $PhNH^-Li^+$ also may lead to complex **1**.

**Characterization of Complexes $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NHR_1R_2)$ (2).** The cyclopentadienyl hydrogens of the $(\eta^5\text{-}C_5H_3)Ru(CO)(NHR_1R_2)$ fragment in **2** are observed as a well-resolved doublet and triplet, shifted approximately 0.7 ppm upfield from the cyclopentadienyl hydrogens of the $(\eta^5\text{-}C_5H_3)Ru(CO)_2$ part of the molecule. It is worth noting that at room temperature the $^1$H NMR spectra of the **2** complexes show only four signals in the cyclopentadienyl region instead of the expected six and only two singlets for the $Si(CH_3)_2$ groups instead of four, required by the structure of the molecules. The $^{13}$C NMR spectrum of **2b** exhibits only two signals for the CO ligands and six signals in cyclopentadienyl region.[7] Although these observations suggest that these compounds are fluxional, variable-temperature NMR studies of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(NH_2CH_3)$ (**2b**) in $CD_3NO_2$ at temperatures down to −25 °C did not reveal any broadening or splitting of the cyclopentadienyl resonances.

However, it is known[25] that $Cp_2Ru_2(CO)_4$ is fluxional even at low temperatures, which suggests that **2** is fluxional according to the mechanism in Scheme 2,

**Scheme 2**



which involves the pairwise exchange of two carbonyl ligands between the two metal atoms via a bridging carbonyl intermediate. This mechanism requires the movement of the $NHR_1R_2$ ligand from one side of the molecule to the other, but not from one Ru to the other; this motion accounts for the relatively simple $^1H$ and $^{13}C$ NMR spectra of the $(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2$ ligand. If CO groups on opposite sides of the Ru−Ru bond are involved in forming the carbonyl-bridged intermediate, only two of the three CO groups can participate in the exchange process, which accounts for the observation of two $^{13}CO$ signals. The IR spectra in the $\nu$(CO) region for all complexes of type **2** exhibit a medium band in the 1890 $cm^{-1}$ region and two strong bands in the 1910 and 1980 $cm^{-1}$ regions, which are typical for group 8 $Cp_2M_2(CO)_3L$ complexes without bridging CO ligands.[26]

The structure of **2b** (Figure 1), established by X-ray crystallography, shows the presence of occupational disorder. One coordination site of each Ru atom is 50% occupied by a CO (C(19), O(4)) ligand and 50% by a $NH_2Me$ ligand. The Ru−Ru distance in **2b** (2.8955(6) Å) is longer than that in **1** (2.8180(3) Å).[27] The C(6)−Ru(1)−Ru(2)−C(18) torsion angle (1.0°) confirms the eclipsed orientation of the CO ligands. Both Ru atoms of complex **2b** have pseudo-octahedral geometry, with angles of approximately 90° between adjacent carbonyls, methylamine, and the Ru−Ru bond (Figure 1). As one would expect, the Cp−Cp fold angle[28] (125.9°) is larger than in **1** (120.5(7)°) because of the longer Ru−Ru distance.

The lability of the amine ligand in complex **2** was established by observing the substitution of this ligand ($NH_3$, $NH_2Me$, $NHMe_2$) by CO in a hexanes solution of complex **2** under a flow of CO gas (1 atm) at ambient temperature ($t_{1/2} = 40-75$ min) to give $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4$ (**1**). As expected, the bulky $NHMe_2$ ligand was the most labile ($t_{1/2} = 40$ min) as compared with the less bulky $NH_3$ and $NH_2Me$. Complexes **2** are extremely air-sensitive and undergo slow decomposition in solution under inert atmosphere to give **1** as the only identifiable product.

**Protonation of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3\{NH(CH_2CH_2)_2\}$ (2f).** The Ru−Ru bond in **2f** is protonated with 1 equiv of acid ($HBF_4{\cdot}OEt_2$) to give the air-stable cationic complex $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3\{NH(CH_2CH_2)_2\}(\mu\text{-}H)]^+BF_4^-$ (**2f**$H^+BF_4^-$). The cyclopentadienyl hydrogens in **2f**$H^+BF_4^-$, appearing in the $^1H$ NMR spectrum as five sets of well-resolved multiplets, are shifted approximately 0.4 ppm downfield compared to the cyclopentadienyl hydrogens of **2f** due to the positive charge on the molecule. In contrast to **2f**, the complicated resonances in the cyclopentadienyl region of **2f**$H^+$, as well as the four separate methyl resonances of the dimethylsilyl groups, indicate the absence of fluxional behavior of the type observed for **2** (Scheme 2). The Ru−H−Ru resonance in the $^1H$ NMR spectrum occurs as a singlet at −19.18 ppm. The presence of the strongly donating pyrrolidine ligand in **2f**$H^+BF_4^-$, as one would expect, lowers the carbonyl stretching frequencies in **2f**$H^+BF_4^-$ (2050, 2002, 1954 $cm^{-1}$) as compared to those in **1**$H^+BF_4^-$ (2077, 2050, 2027 $cm^{-1}$), thereby deactivating the remaining CO ligands in **2f**$H^+BF_4^-$ to nucleophilic attack by alkylamines, which confirms the usefulness of $\nu$(CO) values for determining the reactivity of CO groups with amines. Bulky alkylamines ($NMe_3$) deprotonate **2f**$H^+BF_4^-$ ($t_{1/2} \approx 30$ min) slowly, although much faster than the deprotonation of **1**$H^+$, whereas less bulky amines ($NH_3$) deprotonate **2f**$H^+BF_4^-$ quickly ($t_{1/2} \approx 1.5$ min).

## Conclusions

We have prepared a cationic complex $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}H)]^+$ (**1**$H^+$) in which the bridging proton is removed only very slowly by amine bases even though it is thermodynamically acidic ($pK_a^{AN} = 6.5$ (±0.2)). Although it is not obvious why complex **1**$H^+$ is kinetically stable with respect to deprotonation, it may be due to a combination of the bulkiness of the dimethylsilyl linkers and the rigidity of the dicyclopentadienyl bridging ligand. The low kinetic acidity and the positive charge in **1**$H^+$ allow its CO ligands to undergo attack by alkylamines. To our knowledge, this is the only system in which protonation of metal centers in a complex activates CO ligands to nucleophilic attack. The amine reactions lead to the elimination of the $\mu$-H ligand,[29] which becomes incorporated into the formamide product, as shown in Scheme 1. Weakly nucleophilic amines (e.g., aniline) with $pK_a(H_2O)$ values lower than ~8.00[30] and bulky amines with cone angles (Θ) larger than 125° (e.g., $Bn_2NH$, i-$Pr_2NH$, $Cy_2NH$)[31] do not react with **1**$H^+$. Although aniline does not react with **1**$H^+$, its amide ($RNH^-$) does react to give the formanilide.

**Acknowledgment.** This work was supported by the National Science Foundation through Grant No. CHE-9816342.

**Supporting Information Available:** Tables giving crystallographic data for **2b** including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters; rate constants for the reaction (eq 2) of $1D^+TfO^-$ with morpholine in nitromethane at 20 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000825H

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[26] $(\eta^5,\eta^5\text{-}C_{10}H_8)Ru_2(CO)_3(PMe_3)$ in: (a) Boese, R.; Tolman, W. B.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 582. (b) Boese, R.; Cammack, J. K.; Matzger, A. J.; Pflug, K.; Tolman, W. B.; Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 6757.

[27] Ovchinnikov, M. V.; Guzei, I. A.; Angelici, R. J. Manuscript in preparation.

[28] The angle between the two cyclopentadienyl planes.

[29] For examples involving reductive eliminations involving a $\mu$-H, see: Stockland, R. A., Jr.; Anderson, G. K.; Rath, N. P. *J. Am. Chem. Soc.* **1999**, *121*, 7945, and references therein.

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

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