# Synthesis and Characterization of Derivatives of a Hydroxymethyl Ruthenium Complex

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*Received March 16, 2000*

*Summary: Reaction of cis-Ru(bpy)$_2$(CO)CH$_2$OH$^+$PF$_6^-$ (**1**, bpy = 2,2′-bipyridine) with acetic anhydride yields the corresponding acetoxymethyl derivative **2**. However, reaction of **1** with a large excess of acetic acid in acetonitrile yields compound **3**, containing an acetamidomethyl ligand instead of the acetoxymethyl group. Compounds **2** and **3** have been characterized by X-ray crystallography; in the crystalline state, **3** exists as a binuclear compound held together by hydrogen bonds to a single water molecule through the acetyl carbonyl groups.*

Acylation of a hydroxymethyl metal complex provides a means to convert the relatively labile −CH$_2$OH functional group into a more stable, less base-sensitive −CH$_2$OC(O)R group while preserving the metal−carbon bond. We recently reported the acylation of *fac*-Re(bpy)(CO)$_3$(CH$_2$OH) (bpy = 2,2′-bipyridine).[1] The reaction of this compound with either acetic acid or acetic anhydride afforded the corresponding acetyl derivative in good yield. More recently, we tried to generate the acetyl derivative of *cis*-Ru(bpy)$_2$)(CO)(CH$_2$OH)$^+$PF$_6^-$ (**1**)[2] by treating it with acetic acid in acetonitrile solution since the acid is more readily removed than acetic anhydride. Treatment of **1** with 3 equiv of acetic acid afforded a 2:1 mixture of two products together with a small amount of unreacted **1** after 6 h. However, when acetic anhydride (together with acetonitrile) was used with **1**, a single product was generated which had the spectral characteristics expected for the desired acetyl derivative, *cis*-Ru(bpy)$_2$(CO)(CH$_2$OAc)$^+$PF$_6^-$ (**2**). Compound **2** was the major product from the first reaction of **1** with acetic acid. Compound **2** has been characterized by elemental analysis, spectral data, and X-ray structural determination.

As in the case of **1**, the $^1$H NMR spectrum for **2** shows doublets for each of the diasterotopic methylene protons; in **2** they appear at $\delta$ 4.83 and 5.13 in CD$_3$CN as compared with $\delta$ 4.35 and 4.45 for the methylene protons in **1**. The ORTEP diagram for **2** is shown in Figure 1; crystallographic data are shown in Table 1. Selected bond distances and bond angles are shown in Table 2. Compound **2** exhibits a slightly distorted octahedral geometry about the metal center, with a cis arrangement of the carbonyl and acetyl ligands. There are some small differences in the bond distances and bond angles around the acetyl group in **2** as compared to those in the rhenium complex studied earlier,[1] but the parameters are similar.

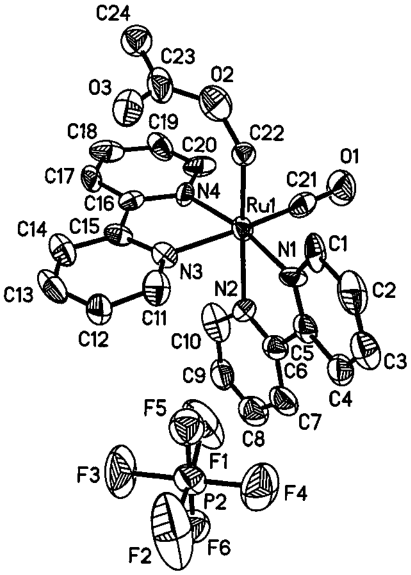

**Figure 1.** ORTEP drawing of **2** with thermal ellipsoids shown at the 45% probability level.

By using a large excess (10 equiv) of acetic acid in acetonitrile with **1**, the minor compound in the first reaction became the exclusive product in this reaction mixture. After isolation and purification, this compound, **3**, has been characterized by elemental analysis, spectral data, and X-ray crystallography also. Elemental analysis data, obtained after drying the sample under vacuum at 50 °C, are consistent with the formulation as Ru(bpy)$_2$(CO)(CH$_2$NHCOMe)$^+$PF$_6^-$ together with a half molecule of water for the composition of **3.** The

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[1] Gibson, D. H.; Sleadd, B. A.; Yin, X.; Vij, A. *Organometallics* **1998**, 17, 2689.

[2] (a) Nagao, H.; Mizukawa, T.; Tanaka, K. *Inorg. Chem.*, **1994**, *33*, 3415. (b) Toyohara, K.; Tsuge, K.; Tanaka, K. *Organometallics* **1995**, *14*, 5099.

10.1021/om000236b CCC: $19.00

**Table 1. Crystal Data and Structure Refinement for 2 and 3**

| | compound **2** | compound **3** |
|---|---|---|
| empirical formula | $C_{24}H_{21}F_6N_4O_3PRu$ | $C_{24}H_{22}N_5O_2Ru + PF_6 + 0.5H_2O +$ disordered solvent (unknown) |
| fw | 659.49 | 667.51[a] |
| temperature | 213 K | 173 K |
| wavelength | 0.71073 Å | 0.71073 Å |
| cryst syst | monoclinic | orthorhombic |
| space group | $P2(1)n$ | $Pnna$ |
| unit cell dimens | $a = 11.4842(2)$ Å<br>$b = 15.3782(3)$ Å<br>$c = 14.5218(3)$ Å<br>$\alpha = 90°$<br>$\beta = 102.428(1)°$<br>$\gamma = 90°$ | $a = 23.3634(5)$ Å<br>$b = 31.6651(7)$ Å<br>$c = 7.5768(2)$ Å |
| volume | 2504.54(8) Å$^3$ | 5605.3(2) Å$^3$ |
| $Z$ | 4 | 8 |
| density (calcd) | 1.749 Mg/m$^3$ | 1.582 Mg/m$^{3a}$ |
| abs coeff | 0.770 mm$^{-1}$ | 0.689 mm$^{-1a}$ |
| $F(000)$ | 1320 | 2680* |
| cryst size | 0.21 × 0.31 × 0.15 mm | 0.04 × 0.27 × 0.35 mm |
| $\theta$ range for data collection | 1.95−26.38° | 2.57−27.48° |
| limiting indices | $-14 \leq h \leq 13$, $-13 \leq k \leq 19$, $-17 \leq l \leq 18$ | $0 \leq h \leq 30$, $0 \leq k \leq 41$, $0 \leq l \leq 9$ |
| no. of reflns collected | 14 241 | 69 186 |
| no. of independent reflns | 5103 ($R_{int} = 0.0422$) | 6419 [$R_{int} = 0.053$] |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 3596/0/353 | 6419/0/390 |
| goodness-of-fit on $F^2$ | 1.223 | 1.027 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0417, WR2 = 0.822 | R1 = 0.0400, wR2 = 0.0811 |
| $R$ indices (all data) | R1 = 0.0706, WR2 = 0.1046 | R1 = 0.0679, WR2 = 0.0900 |
| largest diff peak and hole | 0.774 and −0.621 e Å$^{-3}$ | 0.69 and −0.43 e Å$^{-3}$ |

[a] Based on $C_{24}H_{22}N_5O_2Ru + PF_6 + 0.5H_2O$.

**Table 2. Selected Bond Distances (Å) and Angles (deg) for 2**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Ru−C(21) | 1.827(5) | Ru−N(4) | 2.074(3) |
| Ru−C(22) | 2.100(4) | C(22)−O(2) | 1.468(5) |
| Ru−N(1) | 2.092(3) | C(23)−O(2) | 1.339(6) |
| Ru−N(2) | 2.147(3) | C(23)−O(3) | 1.193(6) |
| Ru−N(3) | 2.129(3) | C(23)−C(24) | 1.511(7) |
| Bond Angles | | | |
| C(21)−Ru−C(22) | 91.4(2) | N(1)−Ru−N(4) | 170.78(13) |
| C(21)−Ru−N(1) | 93.9(2) | N(2)−Ru−N(3) | 88.36(13) |
| C(21)−Ru−N(2) | 96.1(2) | Ru−C(21)−O(1) | 176.3(4) |
| C(21)−Ru−N(3) | 171.2(2) | C(22)−O(2)−C(23) | 118.5(4) |
| C(21)−Ru−N(4) | 94.2(2) | O(2)−C(23)−O(3) | 124.4(4) |
| C(22)−Ru−N(2) | 168.6(2) | O(2)−C(23)−C(24) | 110.1(4) |
| C(22)−Ru−N(4) | 90.86(14) | O(3)−C(23)−C(24) | 125.5(5) |
| N(1)−Ru−N(2) | 77.78(13) | | |

**Table 3. Selected Bond Distances (Å) and Angles (deg) for 3**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Ru−C(21) | 1.839(3) | Ru−N(4) | 2.062(2) |
| Ru−C(22) | 2.133(3) | C(22)−N(5) | 1.455(4) |
| Ru−N(1) | 2.150(2) | C(23)−N(5) | 1.332(4) |
| Ru−N(2) | 2.088(2) | C(23)−O(2) | 1.236(4) |
| Ru−N(3) | 2.125(2) | C(23)−C(24) | 1.509(4) |
| Bond Angles | | | |
| C(21)−Ru−C(22) | 90.00(13) | N(1)−Ru−N(3) | 86.55(8) |
| C(21)−Ru−N(1) | 95.10(11) | N(2)−Ru−N(4) | 170.24(9) |
| C(21)−Ru−N(2) | 92.44(11) | Ru−C(21)−O(1) | 179.8(3) |
| C(21)−Ru−N(3) | 174.53(11) | C(22)−N(5)−C(23) | 124.3(3) |
| C(21)−Ru−N(4) | 96.48(11) | N(5)−C(23)−O(2) | 123.1(3) |
| C(22)−Ru−N(1) | 170.35(11) | O(2)−C(23)−C(24) | 120.8(3) |
| C(22)−Ru−N(4) | 89.65(10) | N(5)−C(23)−C(24) | 116.1(3) |
| N(1)−Ru−N(2) | 77.31(9) | | |

ORTEP diagram for **3** is shown in Figure 2; crystallographic data are shown in Table 1. Selected bond distances and bond angles are shown in Table 3. The ORTEP diagram, however, shows only one of the two metal complexes which are hydrogen bonded to a single water molecule through the acyl carbonyl units. Figure 3 shows a full representation of **3** (taken from the packing diagram), which shows that the water molecule is sandwiched between two ruthenium complexes and coordinated to each through hydrogen bonds involving each carbonyl oxygen; the O(3) water atom is 2.847(4) Å from the carbonyl oxygen, O(2), of the ruthenium complex shown in Figure 2. Since the water molecule sits on a crystallographic 2-fold axis, the two metal complexes are related by this symmetry operation. The packing diagram (see Supporting Information) also clearly shows this hydrogen-bonding interaction. COSY (proton−proton correlation), HSQC (proton−carbon correlation), and DEPT-135 (defining methine, methylene, and methyl carbons; quaternary carbons are absent) experiments were performed to support the structural assignment for the compound in solution. The $^1$H NMR spectrum showed a broadened singlet at $\delta$ 5.92, related to the methylene protons 1:2 (2:4); the COSY spectrum showed that this singlet is correlated with both pairs of doublets at $\delta$ 3.26 and 3.68 (assigned to the diastereotopic methylene protons in **3** that are coupled to NH also). The HSQC experiment showed that the proton resonance at $\delta$ 5.92 does not correlate with any of the carbon resonances (implying that this is due to the amide proton). The DEPT experiment shows the methylene resonance (down) at $\delta$ 28.75 and the methyl resonance (up) at $\delta$ 22.76. Furthermore, the HSQC experiment showed that both methylene protons are correlated with the carbon resonance at $\delta$ 28.75. The chemical shift of these methylene carbons is very high as compared with those in **2** ($\delta$ 65.39). Whether **3** is crystallized from solution or merely precipitated from acetonitrile the NMR spectral properties remain the same. We have not been able to establish whether the

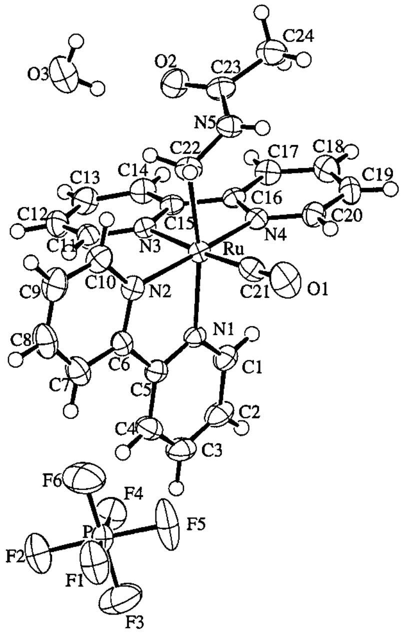

**Figure 2.** ORTEP drawing of **3** with thermal ellipsoids shown at the 50% probability level.

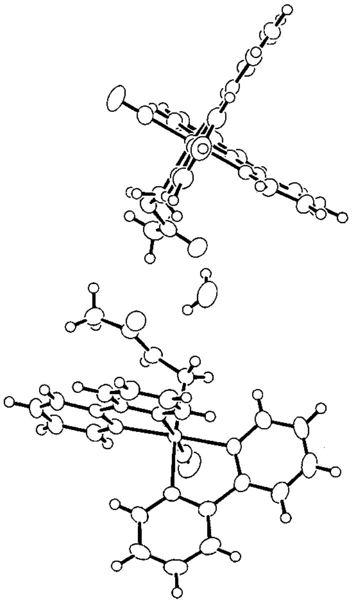

**Figure 3.** Representation of the full molecule of **3**, showing coordination of $H_2O$ to both carbonyl oxygens.

coordinated water molecule remains coordinated in solutions of **3**.

As may be seen from comparison of Figures 1 and 2, the atom numbers for the ruthenium complexes are similar, except that N(1) and N(2) are reversed. The presence of the hydrogen-bonded water molecule in **3** alters the bond distances and bond angles around the acetamidomethyl group significantly as compared with the parameters for the acetoxymethyl group in **2**. The O(2)−C(23)−C(24) angle in **3** is 120.8(3)° as compared to 125.5(5)° in **2**. The carbonyl C−O bond distance in **3** [O(2)−C(23)] is longer, at 1.236 (4) Å, than the carbonyl bond distance [O(3)−C(23)] in **2** (1.193(6) Å) because of the amido linkage and, possibly, as a result of hydrogen bonding of this oxygen to the water molecule. However, the greatest structural differences between **2** and **3** are in the orientation of the acetoxymethyl ligand in **2** as compared with the acetamidomethyl group in **3**. The dihedral angle between the least-squares plane through the bpy ligand containing N(3) and N(4) and the least-squares plane for C(22)−O(2)−C(23)−O(3)−C(24) is 98.3° for **2**, whereas the related dihedral angle involving the acetamidomethyl group in **3** is only 23.9°.

The transformation of **1** to **3** is an organometallic equivalent of the Ritter reaction,[3] in which acid-promoted dehydroxylation of an alcohol is accompanied by reaction with a nitrile and yields an amido product. When conducted with alcohols, the Ritter reaction has usually been accomplished with an excess of strong acid, such as concentrated sulfuric acid, that is capable of generating a stable carbocation as the result of dehydroxylation. Thus, allylic, benzylic, and tertiary alcohols work best; primary alcohols do not undergo the simple Ritter reaction. Since an alkylnitrilium cation is the initial product, dilution of the reaction mixture with water is usually needed to generate the amide product. Also, the reactions usually require heating or long standing for completion. The conditions used for the synthesis of **3** from hydroxymethyl complex **1** are extremely mild by comparison. Furthermore, even partial conversion of **2** into **3** can occur slowly with acetic acid/water/acetonitrile mixtures (see Experimental Section).

Interestingly, when stronger acid (10 equiv of 60% aqueous $HPF_6$) was used with **1**, compound **3** was not a reaction product (at least three other products were formed which have not been identified); **3** was produced (several unidentified products were also formed) only when a catalytic amount of this acid was used. Clearly, if the simple acetoxymethyl derivative of a hydroxymethyl complex is the one desired, acetic anhydride appears to be the preferred reagent to effect the transformation. However, the use of acetic acid/acetonitrile mixtures appears to be an effective strategy for generating acetamidomethyl complexes from hydroxymethyl complexes; to our knowledge this is the first report of this group as a ligand in metal complexes.

## Experimental Section

**General Data**. Reagent grade solvents dichloromethane, diethyl ether, acetone, and acetonitrile and HPLC-grade hexane were used as received. Acetonitrile-$d_3$ was obtained from Cambridge Isotope Laboratories. Compound **1**, *cis*-Ru(bpy)$_2$(CO)(CH$_2$OH)$^+$PF$_6^-$, was prepared as described previously.[2] NMR spectral data were obtained on Varian Unity Inova 500 spectrometers. $^1$H and $^{13}$C NMR chemical shifts were referenced to residual protons in the deuterated solvents. FTIR data were obtained by the DRIFTS method[4] on a Mattson RS1 FTIR instrument by means of a Graseby Specac Inc. "Mini-Diff" accessory as KCl dispersions. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

***cis*-Ru(bpy)$_2$(CO)(CH$_2$OAc)(PF$_6$) (2)**. To compound **1**, [Ru(bpy)$_2$(CO)(CH$_2$OH)](PF$_6$) (0.618 g; 1 mmol), in $CH_3CN$ (ca. 10 mL) was added (1.0 g; 10 mmol) acetic anhydride. The mixture was stirred for ca. 2 h; during this time, the solution became bright orange-red. The solvent and excess acetic anhydride were then pumped out under vacuum, and the red viscous

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[3] Krimen, L. I.; Cota, D. J. *Org. React.* **1969**, *17,* 213.

[4] Griffiths, P. W.; de Haseth, J. A. *Fourier Transform Infrared Spectroscopy*; Wiley: New York 1986; Chapter 5.

residue was triturated with diethyl ether, leaving a pale yellow solid. Recrystallization from $CH_2Cl_2$/hexane gave bright yellow crystals of **2** (0.50 g; 75% yield), mp 215 °C (dec). Anal. Calcd For $C_{24}H_{21}F_6N_4O_3PRu$: C, 43.70; H, 3.21. Found: C, 43.67; H, 3.29. IR (DRIFTS, KCl): $\nu_{CO}$ 1926 cm$^{-1}$; $\nu_{ester\ CO}$ 1709 cm$^{-1}$. $^1$HNMR ($CD_3CN$): $\delta$1.40 (s, 3H, $CH_2OCOCH_3$), 4.83 (d, 1H, $J$ = 8.1 Hz, $CH_2OCOCH_3$), 5.13 (d, 1H, $J$ = 8.1 Hz, $CH_2OCOCH_3$), 9.14 (d, 1H, bpy), 8.98 (d, 1H, bpy), 8.49−7.30 (m, 14H, bpy). $^{13}$CNMR($CD_3CN$): $\delta$ 203.54, 171.72, 158.48, 156.36, 155.84, 155.32, 155.17, 153.91, 150.76, 148.57, 140.16, 140.03, 139.71, 138.02, 128.12, 128.02, 127.88, 127.77, 125.21, 124.72, 124.27, 123.68, 65.39, 20.85.

***cis*-Ru(bpy)$_2$(CO)(CH$_2$NHAc)(PF$_6$)·0.5H$_2$O (3)**. To a solution of **1** (0.95 g; 1.5 mmol) in $CH_3CN$ (ca. 20 mL) was added a 10-fold excess of acetic acid (0.90 g, 15 mmol). The solution was stirred for 2 h, and then solvent and excess acetic acid were evaporated under vacuum to give a red oil. The oil was triturated with diethyl ether, leaving **3** as an orange solid (0.90 g, 88% yield). The crude product was recrystallized from $CH_2Cl_2$/acetone/hexane/ether to provide pure product, mp 260 °C).

Anal. Calcd for $C_{24}H_{22}F_6N_5O_2PRu\cdot 0.5H_2O$: C, 43.18; H, 3.47; N, 10.49. Found: C, 43.05; H, 3.51; N, 10.22. IR (DRIFTS, KCl): $\nu_{CO}$ 1930 cm$^{-1}$; $\nu_{amide\ CO}$ 1690 cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 1.26 (s, 3H, $CH_2NHCOCH_3$), 3.26 (dd, 1H, $CH_2NHCOCH_3$), 3.68(dd, 1H, $CH_2NHCOCH_3$), 5.92 (br s, 1H, NH), 9.35 (d, 1H, bpy), 9.31(d, 1H, bpy), 8.61−7.42 (m, 14H, bpy). $^{13}$CNMR ($CD_3CN$): $\delta$ 204.05, 168.25, 158.78, 156.55, 155.87, 155.60, 155.38, 154.12, 150.79, 148.59, 139.98, 139.96, 139.66, 137.58, 128.07 (2 carbons), 127.94, 127.66, 125.23, 124.86, 124.32, 123.80, 28.75, 22.76.

Before determining that a 10-fold excess of acetic acid would give **3** exclusively, various other ratios of **1** to acetic acid were used. The proportions of **2** to **3** changed, but the chemical shift positions of **2** and **3** in these mixtures did not vary.

**Reaction of 2 with Acetic Acid/Water**. Compound **2** (0.165 g; 0.25 mmol) was dissolved in $CH_3CN$ (25 mL), and acetic acid (0.30 g, 5 mmol) and a drop of water were added. An aliquot of the solution was immediately removed, and a proton NMR spectrum showed no conversion of **2** to **3**. After 2 h, the ratio of **2** to **3** was 10:1. The reaction mixture was allowed to stir at room temperature for 2 days. A portion of the reaction mixture was evaporated to dryness and then triturated with diethyl ether. The NMR spectrum of the residue showed a 2:1 mixture of **2** and **3**. No further conversion was evidenced from the remainder of the reaction mixture after 1 week (total).

**Reactions of 1 with Aqueous HPF$_6$**. (a) $HPF_6$ (60% aqueous; 0.49 mL, 3.33 mmol) was added via a syringe to **1** (0.21 g, 0.33 mmol) stirred in 20 mL of acetonitrile. Upon additon of the acid, the red solution of **1** immediately became yellow-green. Stirring was continued for 5 min, and then 10 mL of water was added. After solvent removal, proton NMR spectral analysis indicated the presence of three products (unidentified), but no **3**.

(b) A second experiment was conducted, in the same fashion, except that only a catalytic amount of aqueous $HPF_6$ was used. Examination of the crude reaction mixture by proton NMR spectroscopy showed that about 60% of it was compound **3**, but there were several other products which were not identified.

**X-ray Crystal Structure of 2.**[5] An orange block crystal was obtained by layering hexane on a solution of **2** in $CH_2Cl_2$. Data were collected on a Siemens SMART CCD area detector diffractometer at 213 K; the crystallographic data are outlined in Table 1. Selected bond distances and bond angles are shown in Table 2. Of 14 241 reflections, 3596 were considered observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$. Final $R$ indices [$I > 2\sigma(I)$]: R1 = 0.0417, wR2 = 0.0822. Programs used were standard control software and SHELXL-93 incorporated in SHELXTL-PC v5.03.[6]

**X-ray Crystal Structure of 3.**[7] A triangular orange plate was obtained by the following procedure: the crude product was dissolved in a 1:1 mixture of acetone and methylene chloride; hexane and then diethyl ether were layered on top; slow evaporation of solvent produced light orange crystals. Data were collected on a Nonius Kappa CCD diffractometer at 173 K; the crystallographic data are outlined in Table 1. Selected bond distances and bond angles are shown in Table 3. Data integration was done with Denzo,[8] and scaling and merging of data were done with Scalepack; the space group was established with the teXsan[9] package. Of the 69 186 measured reflections, 6419 are unique and 4680 satisfied the condition $I > 2\sigma(I)$. The structure was solved by direct methods in SHELXS-86[10] and refined by full-matrix least-squares on $F^2$ in SHELXL-93.[11] Neutral atom scattering factors were used and include terms for anomalous dispersion.[12] Final $R$ indices [$I > 2\sigma(I)$]: R1 = 0.0400, wR2 = 0.0811.

**Acknowledgment.** Support of this work by the United States Department of Energy, Office of Science, Office of Basic Energy Sciences, is gratefully acknowledged. The single-crystal CCD X-ray facility at the University of Idaho was established with the assistance of the NSF-Idaho EPSCoR program under NSF Grant No. OSR-930539 and the M. J. Murdock Charitable Trust, Vancouver, WA. The authors are grateful to Professor R. G. Lawler for helpful discussions about the Ritter reaction.

**Supporting Information Available:** Tables of crystallographic data, positional and isotropic thermal parameters, anisotropic displacement parameters, H atom positional parameters, bond distances and bond angles for **2** and **3**, ORTEP diagrams for **2** and **3**, and packing diagrams for **3**; also, proton and carbon spectral data for **2** and **3** as well as 2D and DEPT data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[5] The structure of **2** was solved at the University of Idaho.

[6] *SHELXTL 5.03* (PC-version); Program Library for Structure Solution and Moleular Graphics; Siemens Analytical Instruments Division: Madison, WI, 1995.

[7] The structure of **3** was solved at Ohio State University.

[8] Otwinowski, Z.; Minor, W. *Methods in Enzymology,* Vol. 276: Macromolecular Crystallography, Part A; Carter, C. W., Jr., Sweet, R. M., Eds., Academic Press: New York, 1997; pp 307−326.

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[10] SHELXS-86: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

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[12] *International Tables for Crystallography*, Vol. C; Kluwer Academic Publishers: Dordrecht, 1992.