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Notes

Synthesis and Characterization of Triazacyclononane-Ligated Iridium Dihydride Complexes

Masanori Iimura, Daniel R. Evans, and Thomas C. Flood*

Department of Chemistry, University of Southern California,
Los Angeles, California 90089-0744

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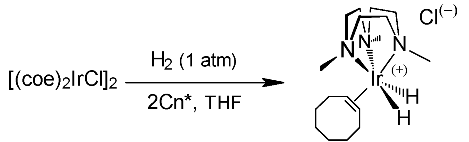
Summary: Unexpectedly stable [(tacn)Ir(H)$_2$(coe)]$^+$ and its tri-N-methyl analogue are prepared from [(coe)$_2$IrCl]$_2$ and the triamine ligand under hydrogen atmosphere.

Unexpectedly stable [(tacn)Ir(H)$_2$(coe)]$^+$ and its tri-*N*-methyl analogue are prepared from [(coe)$_2$IrCl]$_2$ and the triamine ligand under hydrogen atmosphere.

Relative to the amount of organometallic chemistry known of group 9 metals containing “soft” ancillary ligands (Cp, CO, PR$_3$, etc.), that of the “hard” ligated systems (amines, pyridines, alkoxides, tris(pyrazolyl)-borate, etc.) still remains scarce. Our laboratory has been investigating the organometallic chemistry of group 9 metals in the environment of the hard ancillary ligands 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane, for convenience abbreviated here as Cn and Cn*, respectively. We have developed a significant amount of synthetic chemistry of organometallic (Cn*/Cn)Rh complexes,[1] but have found that the same methods do not tend to work for the iridium analogues. We have previously reported the preparation of [(Cn*/Cn)Ir(1,5-cyclooctadiene)]X.[2] We report here the preparation of [(Cn*/Cn)Ir(H)$_2$(coe)]X, **1** and **3** (coe = cyclooctene and X = Cl or OTf (trifluoromethanesulfonate)).

[Cn*Ir(H)$_2$(coe)]Cl (**1**·Cl) is obtained by treating [(coe)$_2$IrCl]$_2$ with 2 equiv of Cn* under 1 atm of H$_2$ pressure in THF (eq 1). Concentration of the reaction mixture, followed by precipitation by addition of pentane, leads to isolation of light brown **1**·Cl in excellent yield (97%). Salts with other anions can be generated from **1**·Cl via anion metathesis reactions. For example, [Cn*Ir(H)$_2$(coe)][OTf], **1**·OTf, is isolated as a brown oil by treating **1**·Cl with 1 equiv of NaOTf.



1·Cl

(1)

Complex **1**·Cl was characterized by standard methods. The ^{1}H and ^{13}C spectra are consistent with the proposed formulation having C_s symmetry. The presence of hydride ligands was confirmed by the ^{1}H NMR two-proton peak at δ −23.8 ppm and two infrared bands at high metal hydride frequency, 2209 and 2148 cm^{-1}. Presumably, the latter correspond to the symmetric and antisymmetric stretching modes of the cis dihydride. Metal hydrides are reported to have characteristic infrared absorption bands in the range 2100−1800 cm^{-1}, and for some other late transition metal polyhydride systems two bands are reported, as for example with TpIr(H)$_2$(PPh$_3$) at 2179 and 2139 cm^{-1}.[3a] In general, however, most seem to exhibit only one band, as in the case of **3** (below), TpIr(H)$_2$(PMe$_3$), 2143 cm^{-1},[3a] Tp^{Me_2}Ir(H)$_2$(PMe$_3$), 2138 cm^{-1},[3a] Cp*Ir(H)$_2$(PMe$_3$), 2099 cm^{-1},[3b] and Tp^{Me_2}Ir(H)$_4$, 2163 cm^{-1}.[3c] The expected shift is evident in the IR spectrum of [Cn*Ir(H)$_2$(coe)]Cl-d_n, prepared using the above method substituting D$_2$ for H$_2$; two weak peaks are observed at 1550 cm^{-1} along with the two stronger ones at the normal Ir−H frequencies. Consistent with this IR spectrum, the ^{2}H NMR spectrum reveals a significant amount of deuterium incorporation into the coe ligand as well as the hydride position in the partially deuterated molecule.

Slow diffusion of pentane into a concentrated solution of **1**·Cl in benzene afforded single crystals amenable to X-ray crystallographic study. Two unique molecules were found in the unit cell. An ORTEP drawing of molecule A is depicted in Figure 1, along with selected metric data. As expected, cation **1** adopts an octahedral structure, assuming two sites for the hydrides that were not located crystallographically. A pronounced struc-

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[1] (a) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (b) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999. (c) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647. (d) Wang, L.; Wang, C.; Bau, R.; Flood, T. C. *Organometallics* **1996**, *15*, 491. (e) Wang, L.; Sowa, J. R., Jr.; Wang, C.; Lu, R. S.; Gassman, P. G.; Flood, T. C. *Organometallics* **1996**, *15*, 4240. (f) Zhou, R.; Wang, C.; Hu, Y.; Flood, T. C. *Organometallics* **1997**, *16*, 434. (g) Zhen, H.; Wang, C.; Hu, Y.; Flood, T. C. *Organometallics* **1998**, *17*, 5397. (h) Flood, T. C.; Janak, K. E.; Iimura, M.; Zhen, H. *J. Am. Chem. Soc.* **2000**, *122*, 6783.

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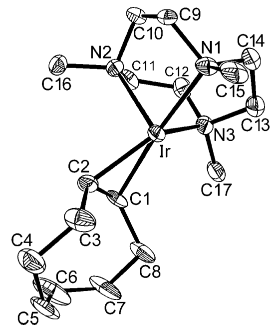
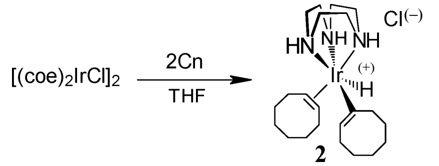


Figure 1. ORTEP drawing of $[Cn^*Ir(H)_2(coe)]^+$ (**1**) at 30% probability. Selected bond lengths (Å) and angles (deg): Ir−N(1) 2.143(7), Ir−N(2) 2.234(6), Ir−N(3) 2.216(8), Ir−C(1) 2.163(8), Ir−C(2) 2.151(8), C(1)−C(2) 1.383(13), N(1)−Ir−N(2) 81.4(2), N(2)−Ir−N(3) 79.3(3), N(1)−Ir−N(3) 80.5(3), C(1)−Ir−C(2) 37.4(4), Ir−C(1)−C(2) 70.8(5), Ir−C(2)−C(1) 71.8(5), N(1)−Ir−C(1) 172.7(3), N(1)−Ir−C(2) 149.8(4), N(2)−Ir−C(1) 100.0(3), N(2)−Ir−C(2) 96.9(3), N(3)−Ir−C(1) 92.6(3), N(3)−Ir−C(2) 129.0(3).

tural feature is that the two Ir−N bonds trans to the two hydrides are longer, 2.234(6) and 2.216(8) Å, than the one trans to the cyclooctene ligand, 2.143(7) Å. (For molecule B the corresponding lengths are 2.275(8), 2.243(6), and 2.101(7) Å.) This presumably is due to a combination of the hydride being a strong trans-influence ligand and the cyclooctene ligand being a π-acceptor.

Preparation of the Cn analogue was attempted in the same manner as for **1**·Cl. While a peak corresponding to a hydride was observed in the ^1H spectrum, the presence of three distinct NH resonances indicates that the metal center is chiral, in contrast to the C_s symmetryof the desired product. Further analysis of the ^1H and ^{13}C spectra was consistent with the assignment of [CnIr(H)(η^1-cyclooctenyl)(η^2-cyclooctene)]Cl, **2**. Indeed, treatment of $[(coe)_2IrCl]_2$ with 2 equiv of Cn under inert atmosphere without H_2 present also afforded complex **2** in 65% yield (eq 2). Oro has previously reported formation of TpIr(H)(η^1-cyclooctenyl)(η^2-cyclooctene) from reaction of $[(coe)_2IrCl]_2$ and sodium tris(pyrazolyl)borate.[4]



(2)

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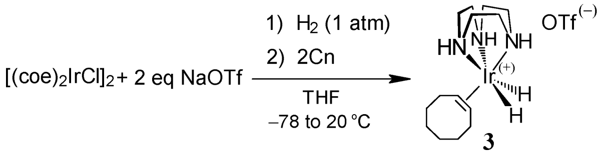
A slight modification of the procedure for preparation of **1** led to formation of $[CnIr(H)_2(coe)]^+$ (**3**). Addition of 2 equiv of Cn to a rapidly stirred mixture of $[(coe)_2IrCl]_2$ and 2 equiv of NaOTf in THF under an atmosphere of H_2, followed by filtration and removal of volatiles, yielded a brown solid assigned the structure $[CnIr(H)_2(coe)]$OTf, **3**, in 60% yield (eq 3). Simply adding the H_2 before the Cn apparently accounts for the formation of **3** rather than **2**.



(3)

3

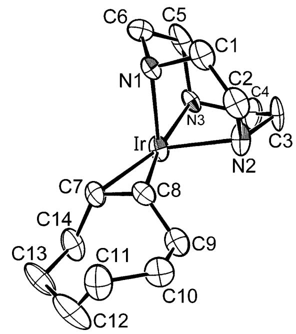


Figure 2. ORTEP drawing of $[CnIr(H)_2(coe)]^+$ (**3**) at 30% probability. Selected bond lengths (Å) and angles (deg): Ir−N(1) 2.187(13), Ir−N(2) 2.173(12), Ir−N(3) 2.101(12), Ir−C(7) 2.20(2), Ir−C(8) 2.15(2), C(7)−C(8) 1.40(2), N(1)−Ir−N(2) 80.5(5), N(2)−Ir−N(3) 81.1(5), N(1)−Ir−N(3) 80.9(5), C(7)−Ir−C(8) 37.5(6), Ir−C(7)−C(8) 69.1(9), Ir−C(8)−C(7) 73.4(10), N(1)−Ir−C(7) 101.0(5), N(1)−Ir−C(8) 95.1(6), N(2)−Ir−C(7) 122.8(6), N(2)−Ir−C(8) 85.3(6), N(3)−Ir−C(7) 156.1(6), N(3)−Ir−C(8) 166.3(5).

^1H and ^{13}C NMR spectra, very similar to those of **1**, are consistent with this proposed formulation. The infrared spectrum of **3** exhibits the hydride stretching band at 2142 cm^{-1}, for unknown reasons, a single peak in this molecule. Deuterium gas was used in place of H_2 in the preparation of **3** in an attempt to generate $[CnIr(D)_2(coe)]^+$ (**3**-d_2). ^2H NMR revealed the deuterium to be located mostly in the cyclooctene ring with little in the metal hydride position.

An X-ray diffraction study was carried out on a single crystal of **3** isolated from THF/pentane solution. An ORTEP drawing is depicted in Figure 2, along with selected metric data. Again, an octahedral geometry with *fac* coordination of the triamine ligand is observed. As expected, for reasons described above, the two Ir−N bonds trans to the two hydrides are much longer (2.187 and 2.173 Å) than the Ir−N bond trans to the coe ligand (2.101 Å).

Comparing the structures of **1** and **3**, it is clear that the methyl groups have some effect on the Ir−N bond distances, with those of **1** being about 0.044(8) Å longer. In addition, the N−Me groups of **1** appear to protrude significantly below the equator of the complex and are presumed to cause considerably more crowding at the base of the molecule compared to **3**. We attribute much of the observed differences in the stability and the reactivity of Cn*Ir and CnIr complexes to this steric congestion in the Cn*Ir system.

Both **1** and **3** are indefinitely stable as solids at room temperature in the absence of oxygen. Both are soluble in polar organic solvents such as THF and DMSO and are not soluble in alkanes, but **1**·Cl is somewhat soluble in benzene. Heating of a benzene solution of **1**·Cl at 70 °C for several hours left the complex unaltered. A benzene solution of **1**·Cl in a borosilicate NMR tube that had been irradiated by a medium-pressure mercury arc for 30 min also showed no change. Even photolysis in the presence of PMe_3 revealed no replacement of H_2 or cyclooctene. For comparison, Ferrari et al. reported that

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[4] Fernandez, M. J.; Rodriguez, M. J.; Oro, L. A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2073. See also: Alvarado, Y.; Boutry, O.; Gutierrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Perez, P. J.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860.

photolysis of $Tp^{Me2}Ir(H)_2(coe)$ in benzene in the presence of $P(OMe)_3$ results in formation of $Tp^{Me2}Ir(Ph)H[P(OMe)_3]$ presumably via the five-coordinated $Tp^{Me2}Ir(H)_2$.[5] While the reason is still unclear, we have been continuing to find that the organometallic species of group 9 containing these "hard" ligands are, in general, much more stable than those with conventional π-acidic "soft" ligands and even more stable than Tp-ligated complexes.

Experimental Section

General Comments. All reactions and manipulations involving organometallic compounds were carried out using standard vacuum-line, Schlenk, and glovebox techniques, under an atmosphere of purified N_2. All glassware was flamed out immediately prior to use or dried overnight at 160 °C. All solvents were purified and dried using standard procedures and were distilled immediately prior to use. Deuterated solvents were stored over 3 Å molecular sieves. THF-d_8 was dried and stored over Na metal. NMR chemical shifts are referenced to tetramethylsilane for ^1H, ^2H, and ^{13}C. Long relaxation delays (~10 s) were applied to ensure accurate integrals. Photolysis was carried out using an ACE-Hanovia medium-pressure Hg arc lamp. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Cn and Cn* were prepared using our modifications of published procedures.[1d] A literature preparation of $[(coe)_2IrCl]_2$ was used.[6] Trimethylphosphine was dried over Na metal, vacuum transferred, and stored over 3 Å molecular sieves. Unless otherwise noted, all other reagents were purchased from commercial suppliers and were used without further purification.

To minimize H/D exchange with adventitious proton sources, all glassware (i.e., Schlenk flasks and NMR tubes) and spin bars used for deuterium-labeling experiments were washed with and then soaked in D_2O for 2 days. They were then rinsed with acetone-d_6 before oven drying them at 160 °C overnight prior to use.

Synthesis of [Cn*Ir(H)$_2$(coe)]Cl, 1·Cl. A Schlenk flask equipped with a spin bar was charged with 0.36 g (0.40 mmol) of $[(coe)_2lrCl]_2$, 10 mL of THF, and 5 mL of CH_2C1_2. The solution was cooled to −78 °C, and 0.18 mL (0.93 mmol) of Cn* was added by a gastight syringe. This mixture was degassed by three freeze−pump−thaw cycles and was again brought to −78 °C, and then 1 atm of H_2 was introduced. After stirring 1 h, the reaction mixture was slowly warmed to ambient temperature, during which the orange suspension turned to a homogeneous wine-red solution. After stirring for another hour, the solution was concentrated to ca. 5 mL under vacuum and 50 mL of pentane was added. The resulting precipitate was washed with pentane and dried under vacuum. The light brown powder was isolated in 97% yield (0.40 g). IR (KBr): 2209, 2149 cm^{-1}, Ir−H stretch. ^1H NMR (DMSO-d_6): δ 4.30−2.58 (m, 12H, NCH_2), 3.78 (m, 2H, CH=), 3.14 (s, 3H, NCH_3), 2.40 (s, 6H, NCH_3), 2.14−1.29 (m, 12H, coe), −23.68 (s, 2H, Ir−*H*). ^{13}C NMR (DMSO-d_6): δ 63.36 (*C*H=), 62.97 (N*C*H_3), 61.73, 58.11, 53.34 (N*C*H_2), 34.33, 33.38, 26.69 (coe). Anal. Calcd for $C_{17}H_{37}N_3ClIr$: C, 39.94; H, 7.30; N, 8.22. Found: C, 40.06; H, 7.47; N, 7.91.

Synthesis of [Cn*Ir(D)$_2$(coe)]Cl, 1·Cl-d_2. This compound was prepared using the method described above, substituting D_2 in place of H_2. Spectra clearly show partial equilibration into the coe ligand. IR (KBr): 2209, 2149 cm^{-1} (Ir−H stretch), and 1587, 1550 cm^{-1} (Ir−D stretch). ^1H NMR (DMSO-d_6): δ −23.68 (s, Ir−*H*), the remainder as for **1**. ^2H NMR (DMSO): δ 3.8 (br, C*D*=), 2.2−1.2 (br m, coe-*d*), −23.7 (br s, Ir−*D*).

Synthesis of [Cn*Ir(H)$_2$(coe)]OTf, 1·OTf. A flask was charged with 0.55 g (1.07 mmol) of **1**·Cl and 0.24 g (1.39 mmol) of NaOTf. Fifteen millliliters of benzene was added, and the mixture was allowed to stir overnight at room temperature. The solution was filtered through Celite, and volatiles were removed in vacuo, yielding an oil. ^1H and ^{13}C NMR solution spectra of this oil were the same as those of **1**·Cl.

Synthesis of [CnIr(H)(η^1-cycloocten-1-yl)(η^2-cyclooctene)]Cl, 2(Cl). A flask charged with 0.22 g (0.25 mmol) of $[(coe)_2IrCl]_2$ and 20 mL of THF was cooled to −78 °C, a solution of Cn (0.62 g, 0.62 mmol) in 10 mL of THF was added by cannula, and the mixture was stirred for 15 min. The mixture was allowed to warm slowly to ambient temperature, during which the suspension turned to an orange homogeneous solution, soon followed by formation of a white precipitate. The supernatant was decanted by cannula, and the precipitate was washed with Et_2O and dried under vacuum. Product **2** was obtained as an off-white powder in 65% yield (0.17 g). ^1H NMR (DMSO-d_6): δ 6.80, 6.40, 5.07 (3br s, 1H each, N*H*), 4.90 (m, 1H, IrC=C*H*), 3.37−2.42 (m, 12H, NCH_2), 3.20 (m, 2H, C*H*=C*H*), 2.22−1.06 (m, 24H, coe CH_2), −18.15 (s, 1H, Ir*H*). ^{13}C NMR (DMSO-d_6): δ 130.07 (IrC=CH), 126.69 (Ir−C=CH−), 58.78, 55.43, 53.33, 50.58, 48.94, 48,75 (N*C*H_2), 54.07, 48.47 (*C*H=*C*H), 32.53, 31.75, 31.15, 31.04, 28.02, 27.97, 26.49, 26.45, 26.33, 25.80, 25.75, 25.63 (coe). Anal. Calcd for $C_{22}H_{43}N_3ClIr$: C, 45.77; H, 7.51; N, 7.28. Found: C, 45.44; H, 7.51; N, 7.51.

Synthesis of [CnIr(H)$_2$(coe)]OTf, 3(OTf). A Schlenk flask charged with 0.63 g (0.70 mmol) of $[(coe)_2IrC1]_2$, 0.24 g (1.39 mmol) of NaOTf, and 20 mL of THF was degassed with three freeze−pump−thaw cycles, and H_2 was then introduced. Since no rapid reaction was observed, H_2 was continuously bubbled through the mixture. After a few minutes the mixture turned to a dark wine-red solution. This was cooled to −78 °C, and a THF solution of Cn (0.25 g, 1.93 mmol) was added dropwise. After 1 h of stirring, the solution was allowed to warm slowly to ambient temperature. Stirring was continued another hour, the solution was filtered through a plug of Celite, the filtrate was concentrated to ca. 5 mL, and 40 mL of Et_2O was added. The supernatant was decanted by cannula, and the precipitate was washed with Et_2O and dried under vacuum. Brown powder **3** amounted to 0.49 g (60%). ^1H NMR (DMSO-d_6): δ 7.62 (s, 1H, N*H*), 5.88 (s, 2H, N*H*), 2.88 (d, 2H, C*H*=), 2.96−2.58 (m, 12H, NCH_2), 2.20−1.28 (m, 16H, coe). ^{13}C NMR (DMSO-d_6): δ 53.48 (*C*H=), 53.09, 50.95, 50.33 (N*C*H_2), 33.31, 32.78, 25.99 (coe). IR (KBr): 2142 cm^{-1} (νIrH_2). Anal. Calcd for $C_{15}H_{31}N_3F_3SO_3Ir$: C, 30.92; H, 5.36; N, 7.21. Found: C, 30.62; H, 5.33; N, 7.53.

X-ray Crystal Structural Determinations. [Cn*Ir(H)$_2$(coe)]C1, 1·Cl. Single crystals of **1**·Cl were obtained by slow diffusion of pentane into a saturated solution of **1**·Cl in benzene with exclusion of light. Diffraction data were acquired at room temperature using Mo Kα radiation ($\lambda = 0.71073$ Å). Solution and refinement of the structure were carried out using SHELXL-97 in the WinGX program package.[7] The unit cell contains eight molecules (two unique) of **1**·Cl, four molecules of water, and two molecules of benzene. For $\{[Cn^*Ir(H)_2(coe)]Cl\}_2\cdot(H_2O)\cdot{}^1/_2(C_6H_6)$ (**1**·Cl): $C_{37}H_{77}C1_2Ir_2N_6O$, $M = 1077.41$ g/mol; monoclinic; space group $P2_1/n$; $a = 10.596(5)$ Å, $b = 25.381(5)$ Å, $c = 16.470(4)$ Å, $\beta = 105.77(3)°$; $V = 4263(2)$ Å^3; $Z = 4$; D(calcd) = 1.672 g/cm^3; absorption coefficient = 6.398 mm^{-1}; $F(000) = 2132$. Crystal size 0.67 × 0.52 × 0.35 mm. Reflections collected = 9289 and 5435 independent reflections with R(int) = 0.0967. Data/restraints/parameters = 5439/0/

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249; goodness-of-fit on $F^2 = 1.068$; $R(I > 2\sigma(I)) = 0.0461$, $wR_2 = 0.1167$; R(all data) = 0.0711, $wR_2 = 0.1361$; largest difference peak and hole = 0.885 and −1.275 e Å^{-3}. Figure 1 shows an ORTEP diagram and gives selected bond lengths and angles.

[CnIr(H)$_2$(coe)]OTf, 3(OTf). Single crystals of **3** were obtained by slow diffusion of pentane into a saturated solution of **3** in THF with the exclusion of light. Diffraction data were acquired at −100 °C using Cu Kα radiation ($\lambda = 1.54178$ Å). For [CnIr(H)$_2$(coe)]OTf (**3**): $C_{15}H_{31}F_3IrN_3O_3S$, $M = 582.69$ g/mol; monoclinic; space group $P2_1/n$; $a = 13.222(2)$ Å, $b = 9.227(2)$ Å, $c = 16.917(3)$ Å, $\beta = 98.83(1)$°; $V = 2039.4(6)$ Å^3; $Z = 4$; D(calcd) = 1.898 g/cm^3; absorption coefficient = 14.056 mm^{-1}; $F(000) = 1144$. Crystal size 0.3 × 0.25 × 0.4 mm. Reflections collected = 2548 and 1866 independent reflections with R(int) = 0.0788. Data/restraints/parameters = 1866/0/235; goodness-of-fit on $F^2 = 0.637$; $R(I > 2\sigma(I)) = 0.0593$, $wR_2 = 0.1526$; R(all data) = 0.0677, $wR_2 = 0.1593$; largest difference peak and hole = 2.913 and −2.283 e Å^{-3}. Figure 2 shows an ORTEP diagram and gives selected bond lengths and angles.

Acknowledgment. We thank Prof. Robert Bau for assistance with the X-ray structure determinations, and NSF for support of this research (CHE 97-08356).

Supporting Information Available: Full information on the structure determinations for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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