New Coordination Modes of an Oxime Ligand in a Triosmium Cluster. Stabilization by Intra- and Intermolecular C−H···O Hydrogen Bonds

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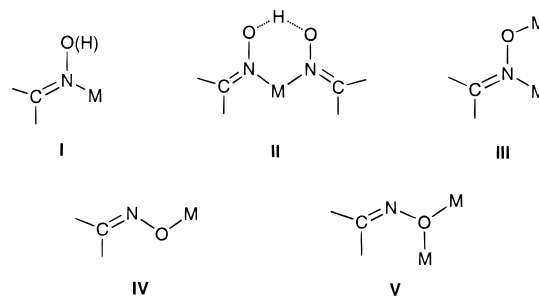
Summary: Reaction of the hydroxyamine 7-chloro-4-(hydroxyamino)quinoline with the triosmium cluster Os₃-(CO)₁₀(NCMe)₂ gave the complex (μ-H)Os₃(CO)₁₀(μ₂-η¹-O-C₉H₆N₂Cl) (3), in which a new mode of μ₂-η¹-O-oximato ligand bridged two osmium centers by an oxygen atom. This complex was slowly converted to (μ-H)Os₃-(CO)₁₀(μ₂-η²-ON-C₉H₆NCl) (4), where an aromatic C−H moiety in the μ₂-η²-ON-oximatoquinoline group formed an unusual short intramolecular C−H···O−N hydrogen bond and an intermolecular C−H···O=C hydrogen bond simultaneously. The formation of the intramolecular hydrogen bond may provide a stabilization effect for the generation of the η²-ON complex 4 and a driving force for the transformation of 3 to 4.

Introduction

Reaction of metal complexes with a hydroxyamine or an oxime could lead to new compounds with versatile structure and significant biological activity.[1−4] Often hydroxyamino and oximato groups act as a bi- or polydentate ligand that are attached to a single metal atom. The oxime group may coordinate to metals through a nitrogen or an oxygen atom or both as shown in I−IV.[2] A few examples exist for dinuclear or trinuclear metal complexes containing a bridging oximato ligand.[4] To the best of our knowledge, coordination mode type V has never been reported.

In view of our continuous efforts in the development of new hydroxyamine-incorporated organometallics,[5] we

report herein the first example containing the coordination mode of a μ₂-η¹-O-oximato group (V) in a triosmium complex (i.e., 3). It was prepared by oxidative addition of the hydroxyamine 7-chloro-4-(hydroxyamino)quinoline (2) to Os₃(CO)₁₀(NCMe)₂ (1). A new coordination mode of the oximato group was found in the triosmium complex 3. Nevertheless, it was not stable and gradually converted to complex 4 by formation of an intramolecular C−H···O−N hydrogen bond and an intermolecular C−H···O=C hydrogen bond. These two bonds shared the same aromatic C−H unit in the μ₂-η²-ON-oximatoquinoline ligand. The C−H···O interaction has been well recognized to play an important role in crystal engineering and organometallic architecture.[6] One feature of this report is that the intramolecular hydrogen bond is very short in the final product 4.

Results and Discussion

We treated the "lightly stabilized" complex Os₃(CO)₁₀-(NCMe)₂ (1) with 7-chloro-4-(hydroxyamino)quinoline (2) in CH₂Cl₂ and acetone at room temperature to produce (μ-H)Os₃(CO)₁₀(μ₂-η¹-O-C₉H₆N₂Cl) (3) as the major product and (μ-H)Os₃(CO)₁₀(μ₂-η²-ON-C₉H₆NCl) (4) as the byproduct. Aromatic hydroxyamine 2 was chosen as the ligand because of its importance in medicinal chemistry.[3a] We found that the new complex 3 was unstable and completely converted to 4 in acetone at room temperature within 2 days (eq 1). The ¹H NMR spectrum of 3 exhibited a hydride signal at δ −12.01 ppm, a broad HN peak at δ 10.02 ppm, and four sets of aromatic protons between δ 6.22 and 7.81 ppm. The

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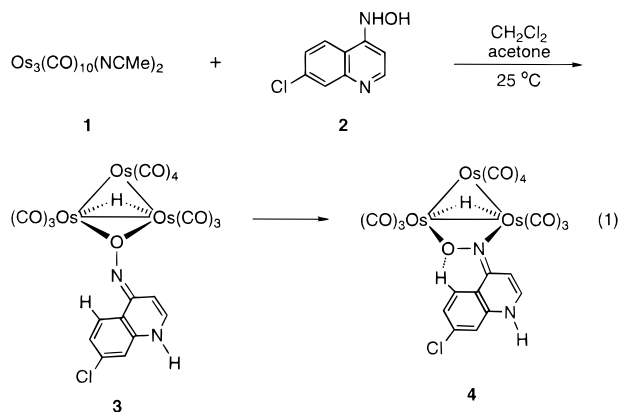
FAB mass spectrum of **3** presented a molecular ion peak at m/z 1052. These data indicate that the hydroxyquinoline ligand was coordinated to the osmium centers as a result of an oxidative addition with cleavage of the O–H bond.

We used the single-crystal X-ray diffraction method to determine the structure of **3**. Its ORTEP drawing is shown in Figure 1, and the pertinent crystallographic data are listed in Tables 1 and 2. The three Os atoms defined an isosceles triangle, in which the Os(2) and the Os(3) atoms were bridged by a hydride and an oximato ligand. The bridging oximato ligand coordinated to two Os centers through the oxygen atom alone. Such a μ_2-η^1-O coordination mode with the unique bridging oxygen is unprecedented in oximato-containing metal complexes.[7] We suggest that the coordination mode came from the oxime tautomer **2a**, instead of the parent hydroxylamine (eq 2). The bond distances of Os(2)–
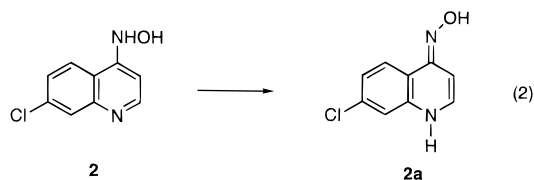
O(11) and Os(3)–O(11) therein were 2.218(7) and 2.105(8) Å, respectively, which are about the same length as those in the related hydroxy complexes[4a,5b,8] of Os3(CO)10 and slightly longer than those in the alkoxy derivatives of Os3(CO)10.[7,9,10] In complex **3**, the bond length was 1.30(2) Å for N(1)–C(18); thus it possessed substantial π-bonding character.[11] The O(11)–N(1) formed a single bond with a length of 1.47(1) Å. Nitrogen-containing heterocycles can react with Os3(CO)10(NCMe)2 at their nitrogen center, such as pyridine reported by Johnson, Lewis, et al.[12] and quinoline reported by Rosenberg et al.[13] Nevertheless, we found that the oximato moiety, in preference to the
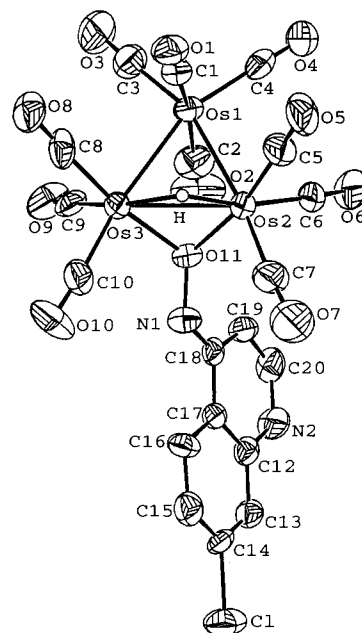
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Figure 1. ORTEP diagram of (μ-H)Os3(CO)10(μ_2-η^1-O-C9H6N2Cl) (**3**).

Table 1. Crystal and Intensity Collection Data for (μ-H)Os3(CO)10(μ_2-η^1-O-C9H6N2Cl) (3) and (μ-H)Os3(CO)10(μ_2-η^2-ON-C9H6NCl) (4)

	3	**4**
formula	C19H7ClN2O11Os3	C19H7ClN2O11Os3
fw	1045.31	1103.38
α, deg	78.13(1)	
β, deg	89.36(1)	100.488(9)
γ, deg	84.38(3)	
space group	$P\bar{1}$	$P2_1/n$
a, Å	7.946(1)	16.397(2)
b, Å	11.679(2)	7.7232(5)
c, Å	13.463(2)	22.664(3)
V, Å^3	1216.7(3)	2822.1(5)
D_{calc}, g cm^{-3}	2.853	2.597
Z	2	4
cryst dimens, mm	0.19 × 0.25 × 0.31	0.26 × 0.24 × 0.14
abs coeff, μ(Mo Kα), mm^{-1}	15.81	13.65
temp	room temperature	room temperature
radiation	Mo Kα	Mo Kα
2θ (max)	50.0	44.9
scan type	$\omega/2\theta$	$\omega/2\theta$
total no. of reflns	4614	3868
no. of obsd reflns $F_o > 2.5\sigma(F_o)$	3006	2719
no. of obsd variables	326	362
R	0.032	0.034
$wR(F^2)$	0.036	0.036
$\Delta(\rho)$, e Å^{-3}	1.010	1.500
Δ/σ_{max}	0.0001	0.003
GOF	1.32	1.47

pyridine nitrogen center, of heterocycle **2a** coordinated to the metal atoms.

Complexes **3** and **4** have very similar mass and infrared spectra but have significantly different ^{1}H NMRs. Complex **4** exhibited a more downfield proton signal at δ 9.17 ppm than δ 7.81 ppm for complex **3**. We believe that C^5-H interacted strongly with the

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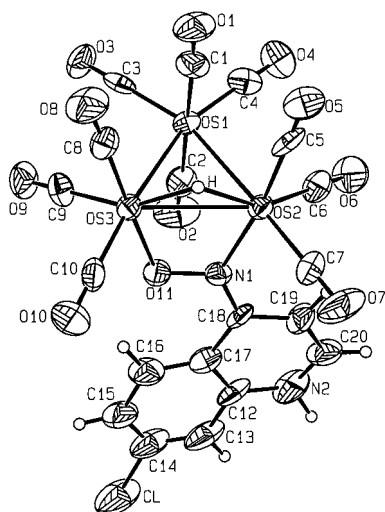
Figure 2. ORTEP diagram of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}ON\text{-}C_9H_6NCl)$ (**4**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3

Bond Distances			
Os(1)–Os(2)	2.8189(8)	N(1)–O(11)	1.47(1)
Os(1)–Os(3)	2.8171(8)	N(1)–C(18)	1.30(2)
Os(2)–Os(3)	2.7901(8)	N(2)–C(12)	1.40(2)
Os(2)–O(11)	2.218(7)	N(2)–C(20)	1.36(2)
Os(3)–O(11)	2.105(8)		

Bond Angles			
Os(2)–Os(1)–Os(3)	59.35(2)	Os(1)–Os(3)–Os(2)	60.36(2)
Os(1)–Os(2)–Os(3)	60.29(2)	Os(2)–O(11)–N(1)	111.0(6)
Os(3)–O(11)–N(1)	111.4(6)	Os(2)–O(11)–Os(3)	82.5(3)
O(11)–N(1)–C(18)	110.6(9)	N(1)–C(18)–C(17)	115.4(11)
N(1)–C(18)–C(19)	126.9(11)	C(17)–C(18)–C(19)	117.7(10)
C(12)–N(2)–C(20)	119.5(10)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4

Bond Distances			
Os(1)–Os(2)	2.8748(8)	N(1)–O(11)	1.38(2)
Os(1)–Os(3)	2.8462(8)	N(1)–C(18)	1.34(2)
Os(2)–Os(3)	2.8725(8)	N(2)–C(12)	1.37(3)
Os(3)–O(11)	2.08(1)	N(2)–C(20)	1.35(3)
C(16)–O(11)	2.71(2)	C(11)–H(16)	2.045(9)
C(16)–O(6)	3.42(2)	H(16)–O(6)	2.80(1)

Bond Angles			
Os(2)–Os(1)–Os(3)	60.28(2)	Os(1)–Os(3)–Os(2)	60.36(2)
Os(1)–Os(2)–Os(3)	59.37(2)	Os(1)–Os(2)–N(1)	88.4(3)
Os(2)–Os(3)–O(11)	70.1(3)	Os(2)–N(1)–O(11)	111.1(8)
Os(3)–O(11)–N(1)	110.7(7)	Os(2)–N(1)–C(18)	132.8(10)
O(11)–N(1)–C(18)	116.0(11)	N(1)–C(18)–C(19)	118.7(14)
N(1)–C(18)–C(17)	125.9(13)	C(17)–C(18)–C(19)	115.3(13)
C(16)–H(16)–O(11)	123.2(11)	C(16)–H(16)–O(6)	121.4(11)

oxygen atom of the oximato ligand in **4**.[14] Similar to **3** was that complex **4** also exhibited a bridging hydride peak at δ −11.52 ppm and a molecular ion at m/z 1052. These results indicate the isomerism between complexes **3** and **4**.

We confirmed the structure of **4** by the X-ray method. Its ORTEP drawing is shown in Figure 2, crystallographic data are given in Table 1, and selected bond distances and angles are listed in Table 3. The three Os atoms defined a triangle, in which the Os(2) and the Os(3) atoms were *edge-bridged* by a hydride (located) and an oximato ligand at the semiaxial sites. The bond

lengths of N(1)−O(11) and N(1)−C(18) were 1.38(2) and 1.34(2) Å, respectively, which indicate their partial double-bond character.[11] The sp² hybridization associated with the N(1) and C(18) centers was corroborated by the sum of the bond angles at N(1) (359.9°) and at C(18) (359.9°). The coordination mode of the oximato ligand is similar to that in the cluster $Os_3(\mu\text{-}H)(\mu_2\text{-}Me_2C{=}NO)(CO)_{10}$.[4a,15]

The six atoms O(11), N(1), C(18), C(17), C(16), and H(16) in complex **4** held a hexagonal arrangement. The internal angles of this hexagon ranged from 116.0(11)° to 125.9(13)°. An intramolecular C−H···O−N hydrogen bond existed in the hexagon with H(16)−O(11) of 2.045(9) Å and C(16)−O(11) of 2.71(2) Å, the latter being unusually short. In addition, this C(16)−H(16) bond also interacted with O(6)−C(6) to form an intermolecular hydrogen bond. The bond distances of C(16)−O(6) and H(16)−O(6) were 3.42(2) and 2.80(1) Å, respectively, which are in the range of a normal C−H···O hydrogen bond.[16−18] The intra- and intermolecular hydrogen bonds occurring in the same C(16)−H(16) unit exhibit an unusual phenomenon. As a consequence, the bond angles were 123(1)° for ∠C(16)−H(16)−O(11) and 121(1)° for ∠C(16)−H(16)−O(6). This long-range nature of the C−H···O interaction has been found to play an important role in crystal engineering and organometallic architecture, as reviewed by Brga and Desiraju.[6] Several types of C−H···X hydrogen bond are observed, where X = O, N, O=C, O_2N, etc.[6,16,17] Nevertheless, a type of C−H···O−N interaction as shown in complex **4** has never been reported to the best of our knowledge. Such a strong hydrogen bond interaction for C(16)−H(16) with oxygen atom O(11) was confirmed by the downfield proton signal (δ 9.17 ppm) in the ¹H NMR spectrum of **4**, which was 1.36 ppm downfield from that (δ 7.81 ppm) of complex **3**.[14] The short intramolecular C−H···O hydrogen bond interactions may help stabilize the η^2-ON complex **4** with respect to the η^1-O-bridged complex **3** and could provide a driving force for the transformation of **3** to **4**.

Furthermore, we treated the complex $Os_3(CO)_{10}(NCMe)_2$ (**1**) with the stable 7-chloro-4-(hydroxyamino)-quinoline hydrochloride salt (**2b**) in dichloromethane and acetone at room temperature for 24 h. Upon purification, we isolated the complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}ON\text{-}C_9H_6NCl)$ (**4**) in 12% yield and the known compound $(\mu\text{-}H)(\mu\text{-}Cl)Os_3(CO)_{10}$ (**5**) in 27% yield.[19] These results indicate that the hydrochloride in the reaction matrix competed with **2** to react with $Os_3(CO)_{10}(NCMe)_2$ (**1**). As a consequence, complex **4** was obtained in a low yield and complex **5** was produced as the major product.

In summary, a new coordination mode was observed for the $\mu_2\text{-}\eta^1\text{-}O$-oximato ligand in the triosmium complex **3**. Rearrangement gradually took place in **3** to give $\mu_2\text{-}\eta^2\text{-}ON$-oximato-containing complex **4**. The C(16)−H(16) bond in complex **4** exhibited an unusual short intramolecular C−H···O−N hydrogen bond and a

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C−H···O=C intermolecular hydrogen bond simultaneously.

Experimental Section

General Comments. Reagents were used as received. All manipulations, except for thin-layer chromatography (TLC), were performed under a nitrogen atmosphere using standard Schlenk techniques. Acetone, acetonitrile, dichloromethane, and hexane were dried over CaH_2 and were freshly distilled before use. 7-Chloro-4-(hydroxyamino)quinoline and $Os_3(CO)_{10}$-$(NCMe)_2$ were prepared by the methods reported.[20,21] Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. Mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed by use of a Perkin-Elmer 2400 CHN elemental analyzer.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ (1) with 7-Chloro-4-(hydroxyamino)quinoline (2). To a solution of $Os_3(CO)_{12}$ (103 mg, 0.114 mmol) in CH_2Cl_2 (100 mL) and CH_3CN (5.0 mL) was added a solution of Me_3NO (19 mg, 0.25 mmol) in a mixture of CH_3CN and CH_2Cl_2 (1:5, 5.0 mL). The mixture was stirred at room temperature for 1.0 h and passed through a short pad of silica gel. The solvent was removed under reduced pressure to give a yellow residue, $Os_3(CO)_{10}(NCMe)_2$ (1), which was redissolved in CH_2Cl_2 (100 mL). A solution of 7-chloro-4-(hydroxyamino)quinoline (22 mg, 0.11 mmol) in dry acetone (5.0 mL) was then introduced to the above stirring solution for a period of 5 min and allowed to react at room temperature for another 2.0 h. The solvent was removed under reduced pressure, and the residue was separated on a silica gel TLC plate. Compound $(\mu$-H$)Os_3(CO)_{10}(\mu_2$-η^1-O-$C_9H_6N_2$Cl$)$ (3, 44 mg, 0.042 mmol, 37%) and compound $(\mu$-H$)Os_3(CO)_{10}(\mu_2$-η^2-ON-C_9H_6NCl$)$ (4, 27 mg, 0.026 mmol, 23%) were eluted with a mixture of hexane and CH_2Cl_2 (5:1). For 3: Anal. Calcd for $C_{19}H_7ClN_2O_{11}Os_3$: C, 21.83; H, 0.68; N, 2.68. Found: C, 22.16; H, 0.64; N, 2.69. ^1H NMR (acetone-d_6): δ 10.02 (s, broad, 1 H, NH), 7.81 (d, J = 8.7 Hz, 1 H, aromatic, H^5), 7.39 (m, 1 H, aromatic, H^2), 7.33 (d, J = 2.1 Hz, 1 H, aromatic, H^8), 7.16 (dd, J = 8.7, 2.1 Hz, 1 H, aromatic, H^6), 6.22 (d, J = 7.8 Hz, 1 H, aromatic, H^3), −12.01 (s, 1 H, μ-H). IR (CH_2Cl_2): $\nu_{(CO)}$ 2105 (w), 2070 (s), 2058 (m), 2016 (vs), 2005 (sh), and 1980 (w) cm^{-1}. MS (FAB, ^{192}Os, ^{37}Cl): m/z 1052 (M$^+$), 987 (M$^+$ − Cl − CO), 959 (M$^+$ − Cl − 2CO). For 4: Anal. Calcd for $C_{19}H_7ClN_2O_{11}$-Os_3: C, 21.83; H, 0.68; N, 2.68. Found: C, 22.23; H, 0.73; N, 2.43. ^1H NMR (acetone-d_6): δ 9.77 (s, broad, 1 H, NH), 9.17 (d, J = 9.2 Hz, 1 H, aromatic, H^5), 7.23 (m, 1 H, aromatic, H^2), 7.17 (d, J = 2.3 Hz, 1 H, aromatic, H^8), 6.92 (dd, J = 9.2, 2.3 Hz, 1 H, aromatic, H^6), 5.96 (d, J = 7.7 Hz, 1 H, aromatic, H^3), −11.52 (s, 1 H, μ-H). ^{13}C NMR (acetone-d_6): δ 183.17, 182.49, 178.29, 177.80, 177.76, 177.63, 177.52, 176.36, 175.89, 174.80 (CO), 149.69 (C=N), 142.01, 136.65, 132.95, 131.66, 121.36, 119.83, 116.19, 104.37 (aromatic). IR (CH_2Cl_2): $\nu_{(CO)}$ 2106 (w), 2066 (s), 2057 (m), 2017 (vs), 1997 (sh), and 1975 (w) cm^{-1}. MS (FAB, ^{192}Os, ^{37}Cl): m/z 1052 (M$^+$), 1015 (M$^+$ − Cl), 987 (M$^+$ − Cl − CO), 959 (M$^+$ − Cl − 2CO).

Study on the Interaction of $Os_3(CO)_{10}(NCMe)_2$ (1) with 7-Chloro-4-(hydroxyamino)quinoline (2) by ^1H NMR Spectrometry. A ^1H NMR spectrometer was used to monitor the reaction of $Os_3(CO)_{10}(NCMe)_2$ (1), obtained from $Os_3(CO)_{12}$ (25 mg, 0.029 mmol), with 7-chloro-4-(hydroxyamino)quinoline (6.0 mg, 0.028 mmol) in acetone-d_6 (0.50 mL) in an NMR tube. Complex $(\mu$-H$)Os_3(CO)_{10}(\mu_2$-η^1-O-$C_9H_6N_2$Cl$)$ (3) was produced as the initial product, which was then slowly transformed to $(\mu$-H$)Os_3(CO)_{10}(\mu_2$-η^2-ON-C_9H_6NCl$)$ (4) with a yield of >95%. An independent study showed that pure complex 3 was slowly converted to 4 in acetone-d_6 at room temperature in 2 days, as observed by ^1H NMR spectroscopy.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ (1) with 7-Chloro-4-(hydroxyamino)quinoline Hydrochloride (2b). A suspension of 7-chloro-4-(hydroxyamino)quinoline hydrochloride (51 mg, 0.22 mmol) in dry acetone (25 mL) was introduced to a solution of $Os_3(CO)_{10}(NCMe)_2$ (1) in CH_2Cl_2 (200 mL), obtained from $Os_3(CO)_{12}$ (201 mg, 0.222 mmol). This mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was separated on a silica gel TLC plate. Complex $(\mu$-H$)(\mu$-Cl$)Os_3(CO)_{10}$ (5, 53 mg, 0.059 mmol, 27%) was obtained by elution with hexane. Spectral data of 5 are consistent with those reported.[22] Continuous elution with a mixture of hexane and dichloromethane (7:3) afforded compound 4 (27 mg, 0.026 mmol) in 12% yield.

Crystallographic Analysis. Crystals of $(\mu$-H$)Os_3(CO)_{10}$-$(\mu_2$-η^1-O-$C_9H_6N_2$Cl$)$ (3) and $(\mu$-H$)Os_3(CO)_{10}(\mu_2$-η^2-ON-C_9H_6NCl$)$ (4) were grown by vapor diffusion of hexane into a dichloromethane solution at −5 °C. Specimens of suitable quality were mounted in a thin-walled glass capillary and used for measurement of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by use of graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). Unit cell parameters were obtained by a least-squares fit to the automatically centered settings for 25 reflections. Intensity data were collected by use of $\omega/2\theta$ scan mode. The centrosymmetric space group was initially assumed and later confirmed by the results of refinement for 3. The systematic absences in the diffraction data of 4 unambiguously established the space group as $P2_1/n$. All intensity data were corrected for Lorentz−polarization and absorption (empirical ψ corrections). The structures of 3 and 4 were solved by direct methods using SOLVER.[23] All remaining non-hydrogen atoms were located from the difference Fourier maps, and they were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement factors. Calculations and full-matrix least-squares refinements were performed by utilization of the NRCVAX program package.[24]

Supporting Information Available: A listing of all refined and calculated atomic coordinates, all the anisotropic thermal parameters, and full bond lengths and angles for compounds 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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