

The crystal structure of **1** is presented in Figure 1. The average V-O bond distance of 2.021 Å in **1** is 0.08 Å longer than the corresponding distance in the V^{III} analogue, **3**.⁵ In contrast to the distorted tetrahedral geometry of **3** and the nearly perfect tetrahedral coordination sphere that results when Li⁺ is taken away from **3** with 12-crown-4, the geometry of **1** approaches a square-planar configuration. From inspection of orbital diagrams for planar vs tetrahedral ML₄ species as presented by Albright et al.,¹² it follows that on electronic grounds the geometrical preference of a four-coordinate d³ complex is for the square-planar configuration.¹³ Distortion from idealized square-planar geometry is due in part to the relatively small bite angle of the [Li(DIPP)₂]⁻ bidentate ligands (79.0°). Furthermore, it is likely that the sterically bulky ligands are responsible for the nonzero (27.2°) dihedral angle between the O(1)VO(2) and O(3)VO(4) coordination planes. For comparison, the corresponding dihedral angle in W(DIPP)₄ is 17.5°.¹⁴ With the less bulky DMP ligand, more rigorously square planar complexes of W^{IV}¹⁴ and Cr^{III}¹⁵ have been obtained. Steric crowding in **1** forces the aromatic rings to be nearly perpendicular to the VO₄ plane, as is also the case with W(DIPP)₄¹⁴ and [Cr(DMP)₄][Na(TMEDA)]₂.¹⁵ In the structure of W(DIPP)₄,¹⁴ a relatively large average W-O-C angle (156°) has been taken to be indicative of π donation to the metal. The average V-O-C angle of 145° in **1** is substantially smaller than the corresponding value for W(DIPP)₄.¹⁴

The physical properties of bulk samples of **1** are consistent with a d³ electronic configuration. Taking into account a V^{III} impurity, the solid-state magnetic moment of **1** is 3.83 μ_B, as expected for an S = 3/2 ion. As mentioned above, the green V^{III} impurity often obtained in preparations of **1** has been identified as **3** by UV-vis-near IR spectroscopy.⁵ Pure samples of **1** are light yellow-green, and a hexane solution has an absorption maximum at 435 nm (ε = 168 M⁻¹ cm⁻¹), which presumably corresponds to a d-d transition. While the V^{III} complex **3** has no readily detectable EPR signals at 77 K at X-band frequencies, its V^{II} counterpart **1** displays a rhombic EPR spectrum (Figure 2) characteristic of S = 3/2 species. The g values given in Figure 2 are consistent with a rhombicity parameter (E/D) of approximately 0.07.¹⁶

Although upon inspection of Figure 1 one may conclude that substrate molecules should have access to the vanadium center, space-filling molecular models make it clear that the metal atom is very effectively shielded from attack. The same structural effect was noted for W(DIPP)₄.¹⁴ In contrast to the relative stability of W(DIPP)₄, which was ascribed to this steric shielding, **1** is quite reactive toward a variety of substrates. For example, **1** will react at room temperature with CO, CO₂, acetylenes, epoxides, ketones, aldehydes, and alcohols. Ligand redistribution and redox chemistry are observed in the reaction with excess CO, such that the principle products obtained are **3** and [V(CO)₆]⁻. Compound **1** behaves as an oxygen atom acceptor in its reaction with cyclohexene oxide to form cyclohexene along with a dimeric V^{IV} complex.¹⁷ The greater reactivity of [V(DIPP)₄Li(THF)]₂

compared to W(DIPP)₄ is attributed to principally two factors: (1) the greater reducing power of the V^{II} complex and (2) the relative ease of loss of Li(DIPP) from **1** compared to the loss of DIPP⁻ from W(DIPP)₄.

In conclusion, the first example of a four-coordinate V^{II} complex has been isolated. Attainment of a rigorously square planar geometry as predicted for a four-coordinate d³ ion is prevented by coordination to the Li⁺ ions and the sterically bulky phenolate ligands. Compound **1** displays reactivity toward molecules with a variety of functional groups. Products from the reaction of **1** with CO and with cyclohexene oxide have been identified. Further definition of several other of the aforementioned reactions is in progress.

Note Added in Proof. Rhenium(IV) phenoxides have been reported recently: Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. A. *Inorg. Chem.* **1989**, *28*, 3688-3695. This work was supported by University of California, Berkeley Biomedical Research Grant No. 88-4 and 89-6 and by National Science Foundation Grant No. CHE-8857455.

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Supplementary Material Available: A fully labeled ORTEP drawing and tables of positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for compound **1** (8 pages). Ordering information is given on any current masthead page.

Isolation and X-ray Structure of a Dinuclear Copper-Nitrosyl Complex

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We have recently described three types of copper-dioxygen complexes, {Cu₂-O₂}ⁿ⁺ (n = 1 or 2), which are formed reversibly by the addition of O₂ to either mono- or dinuclear copper(I) complexes (**1-3**, Scheme I, PY = 2-pyridyl) at -80 °C in solution.¹ These {Cu₂-O₂}ⁿ⁺ species are best described as peroxo dicopper(II) complexes which are formed through the formal oxidative addition of O₂ to **1-3**.² However, they have substantially different spectroscopic properties and reactivity characteristics.³ In order to better understand the nature of this oxidative process and to explore the chemistry of the copper(I) precursor compounds, we are studying reactions of **1-3** (Scheme I) with a variety of elec-

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(1) (a) Tyeklár, Z.; Karlin, K. D. *Acc. Chem. Res.* **1989**, *22*, 241-248 and references cited therein. (b) Jacobson, R. R.; Tyeklár, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690-3692. (c) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196-1207. (d) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668-2679.

(2) This assignment is based on a variety of criteria obtained from a combination of resonance Raman, X-ray absorption, and UV-vis spectroscopic studies.¹

(3) For example, the dioxygen complex derived from **2** is relatively unreactive toward stoichiometric amounts of protic acids, whereas those species derived from **1** and **3** react with H⁺, liberating hydrogen peroxide in high yield. See: Tyeklár, Z.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 388-389.

(12) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley and Sons: New York, 1985; p 304.

(13) A distorted tetrahedral Cr^{III} complex, [Cr{OCH(CMe₃)₂Li(THF)}], has been reported. However, in this case the bulky alkoxide ligand may prevent planar coordination on steric grounds. Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1863-1871.

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(15) Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Spek, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 2142-2147.

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(17) The purple dimeric V^{IV} complex [V₂O₂(μ-OH)₂(DIPP)₄Li(THF)]₂ was crystallized from the reaction mixture and characterized by X-ray crystallography. A complex with the same core structure was reported by Wieghardt and co-workers.¹⁸

(18) Wieghardt, K.; Bossek, U.; Volckmar, K.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 1387-1389.

Scheme I

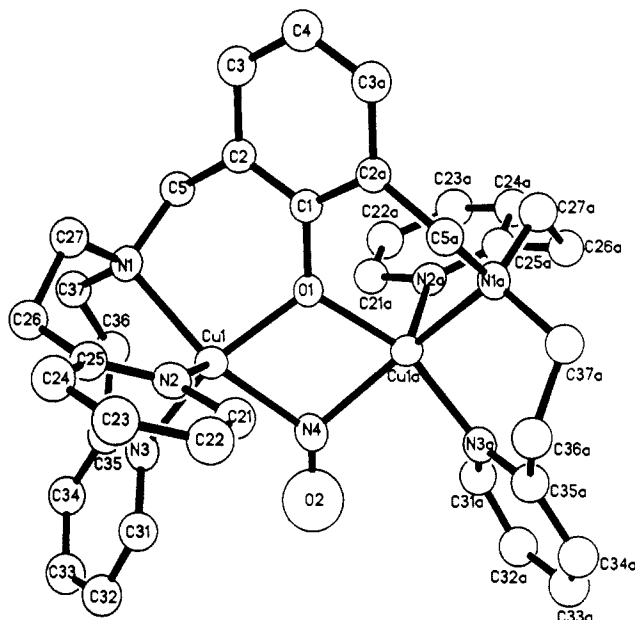
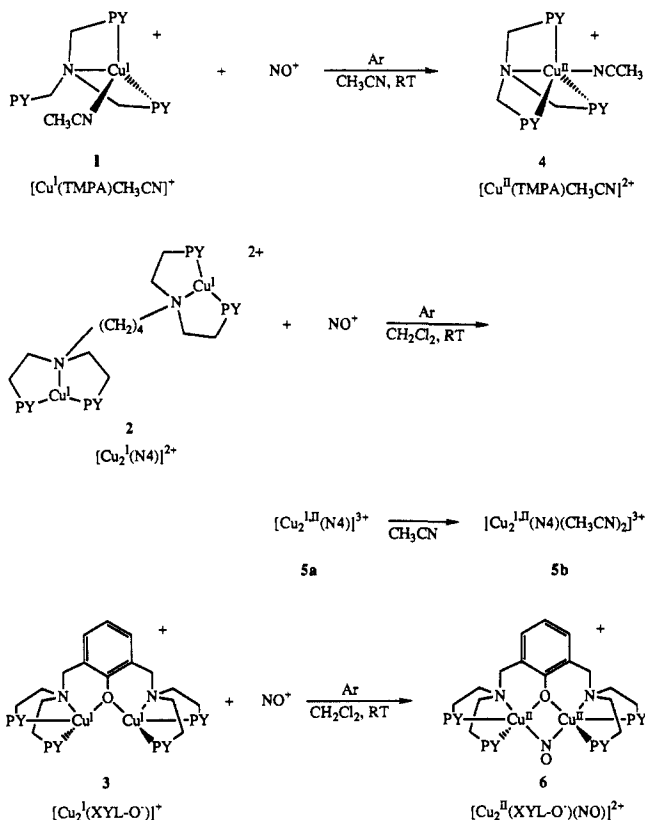


Figure 1. ORTEP diagram of $[Cu_2(XYL-O)(NO)]^{2+}$, showing the atom-labeling scheme. Selected bond lengths (Å) and angles (degrees) are as follows: Cu1...Cu1a, 3.140 (1); Cu1—O1, 1.935 (6); Cu1—N1, 2.079 (10); Cu1—N2, 2.189 (8); Cu1—N3, 1.959 (9); Cu1—N4, 2.036 (10); N4—O2, 1.176 (1); O1—Cu1—N1, 94.4 (3); O1—Cu1—N2, 97.3 (3); O1—Cu1—N3, 159.5 (3); O1—Cu1—N4, 75.1 (2); N1—Cu1—N2, 94.4 (4); N1—Cu1—N3, 97.4 (4); N1—Cu1—N4, 151.3 (2); N2—Cu1—N3, 98.4 (3); N2—Cu1—N4, 113.2 (3); N3—Cu1—N4, 86.6 (3); Cu1—N4—O2, 129.5 (1); Cu1—O1—Cu1a, 108.6 (5).

trophiles. Here, we report preliminary results for the reactions of 1–3 with the nitrosonium ion (NO^+). While NO^+ acts as a simple one-electron oxidant toward compounds 1 and 2, $[Cu_2XYL-O]^{2+}$ (3) reacts by oxidative addition to give $[Cu_2(XYL-O)(NO)]^{2+}$ (6) (Scheme I). We have been able to crystallize and characterize this product by X-ray crystallography, thus providing the *first* structurally determined example of a copper–nitrosyl complex.⁴

Complex 1– PF_6^- reacts rapidly with 1 equiv of NO^+ in acetonitrile to give a blue solution, from which the Cu(II) monomeric complex $[Cu(TMPA)(CH_3CN)]^{2+}$ (4– $(PF_6)_2$) was isolated in 69% yield.^{5,6} Complex 2– $(PF_6)_2^{1c}$ reacts rather slowly with NO^+ in dichloromethane to give an intensely purple precipitate, formulated as $[Cu_2(N_4)]^{3+}$ (5a– $(PF_6)_2(BF_4)$) (65% yield).⁷ It can be recrystallized from CH_3CN/Et_2O to give a 54% yield of a blue complex $[Cu_2(N_4)(CH_3CN)_2]^{3+}$ (5b– $(PF_6)_2(BF_4)$).⁸ Complexes 5a and 5b are mixed-valence species, based on their magnetic properties and their formulations as 3:1 electrolytes in solution (5b).^{8,9}

By contrast to these simple oxidations by NO^+ , reaction of 1 equiv of NO^+ with the phenoxo-bridged dicopper(I) complex

$[Cu_2(XYL-O)]^+$ (3– (PF_6^-)) in CH_2Cl_2 results in the addition of a nitrosyl ligand to the dinuclear center to give the brown colored complex $[Cu_2(XYL-O)(NO)]^{2+}$ (6– $(PF_6)_2$) in 71% yield.^{10,11} A structural determination^{12,13} (Figure 1) reveals that the complex is similar to that found for the phenoxo- and hydroxo-bridged dicopper(II) analogue, $[Cu_2(XYL-O)(OH)]^{2+}$, where the two Cu(II) ions are found in a square-based pyramidal (SP) environment with $Cu...Cu = 3.08$ (1) Å.¹⁴ In 6– $(PF_6)_2$, the Cu(II) ligation is a bit distorted from SP geometry,¹⁵ resulting in an elongated Cu...Cu distance of 3.140 (1) Å. The N–O bond length is 1.176 Å, which is typical and characteristic of a bridging NO^-

(10) $[Cu_2(XYL-O)(NO)](PF_6)_2 \cdot 2CH_2Cl_2$ (6– $(PF_6)_2$): Anal. Calcd for $C_{38}H_{43}Cl_4Cu_2F_{12}N_7O_2P_2$: C, 38.39; H, 3.64; N, 8.24. Found: C, 39.67; H, 3.76; N, 8.33. The low value found for C is due to the unavoidable loss of dichloromethane solvate from crystalline material; this point has been confirmed by NMR analysis and integration. UV-vis (CH_2Cl_2): $\delta_{max} = 382$ ($\epsilon = 5300$), 545 ($\epsilon = 2200$), 730 sh ($\epsilon \sim 500$) nm. $\mu_{RT} = 0.59 \mu_B/Cu$. The complex is EPR silent.

(11) Other examples of oxidative addition of NO^+ to dinuclear transition-metal complexes include the following: (a) Fjeldsted, D. O. K.; Stobart, S. R.; Zavorotko, M. K. *J. Am. Chem. Soc.* **1985**, *107*, 8258. (b) Rabinowitz, H. N.; Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 1420. (c) Connelly, N. G.; Payne, J. D.; Gieger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 295–299.

(12) $[Cu_2(XYL-O)(NO)](PF_6)_2 \cdot 2CH_2Cl_2$ (6– $(PF_6)_2$) crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.924$ (2) Å, $b = 11.352$ (3) Å, $c = 18.347$ (4) Å, $\beta = 108.45$ (2)°, $V = 2356$ (1) Å³, and $Z = 2$ ($T = 233$ K). A Nicolet R3m/V diffractometer was used in the θ -scan mode to collect 3441 unique reflections, of which 2097 reflections with $F_o \rightarrow 6\sigma|F_o|$ were used in the solution and refinement. The positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were calculated and fixed at 0.96 Å from carbon. All non-hydrogen atoms in the cation, anion, and disordered dichloromethane molecule were refined anisotropically; one molecule of lattice CH_2Cl_2 was identified and located in the final stages of refinement. The structure was refined to the current residual values of $R = 0.0874$ and $R_w = 0.0963$ (Mo K α , $\lambda = 0.71073$ Å). (13) Supplementary material.

(14) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Cruse, R. W.; McKown, J.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121–2128.

(15) A structural criterion described by Addison, Reedijk, and co-workers was used to analyze the deviation from ideal SP geometry: Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

(4) (a) The term M-nitrosyl is the general term usually given to a complex containing a coordinated NO moiety, regardless of the oxidation state of the metal or ligand. (b) Here, the NO unit is best described as a coordinated NO^- anion, the conjugate base of nitroxy, i.e., HNO. See also footnote 18.

(5) $[Cu^I(TMPA)(CH_3CN)](PF_6)_2 \cdot CH_3CN$ (4– $(PF_6)_2$) (69% yield): Anal. Calcd for $C_{22}H_{24}CuF_{12}N_6P_2$: C, 36.40; H, 3.33; N, 11.57. Found: C, 36.95; H, 3.34; N, 11.00. IR (Nujol): $\nu(CN) = 2285$ (s), $\nu(PF) = 825$ (s, br) cm^{-1} .

(6) The complex 4– $(ClO_4)_2$ has been previously synthesized and structurally characterized: Jacobson, R. R. Ph.D. Dissertation, State University of New York at Albany, 1989.

(7) $[Cu_2(N_4)](PF_6)_2(BF_4)$ (5a– $(PF_6)_2(BF_4)$): Anal. Calcd for $C_{32}H_{40}BCu_2F_{16}N_6P_2$: C, 37.95; H, 3.98; N, 8.30. Found: C, 37.55; H, 3.92; N, 8.28. IR (Nujol): $\nu(PF) = 835$ (s), $\nu(BF) = 1095$ (s, br) cm^{-1} .

(8) $[Cu_2(N_4)(CH_3CN)_2](PF_6)_2(BF_4)$ (5b– $(PF_6)_2(BF_4)$): Anal. Calcd for $C_{36}H_{44}BCu_2F_{16}N_8P_2$: C, 39.49; H, 4.20; N, 10.24. Found: C, 39.96; H, 4.11; N, 10.47. UV-vis (CH_3CN): $\lambda_{max} = 690$ ($\epsilon = 240$) nm. IR (Nujol): $\nu(CN) = 2265$ (s), $\nu(BF) = 1075$ (s, br), $\nu(PF) = 835$ (s) cm^{-1} . $\mu_{RT} = 1.93 \mu_B/Cu_2$. $\Delta_m(CH_3CN) = 425 \Omega^{-1} cm^{-1} mol^{-1}$.

(9) A frozen-solution EPR spectrum of 5b indicates that the copper ions are magnetically isolated (to be discussed elsewhere).

ligand.^{4b,11,16} The observation of a new strong IR absorption (Nujol mull) at 1536 cm⁻¹ is also consistent with the formulation of **6**-(PF₆)₂ as having a coordinated NO⁻ ligand, thus affirming the conclusion that the nitrosonium cation has been reduced by the dicopper(I) center in **3**.^{4b,11,16-18}

As was found for the reactions of the {Cu₂-O₂}ⁿ⁺ complexes with various reagents such as H⁺ and CO₂, the present investigation indicates that the ligands in **1-3** are exerting pronounced differential effects upon the reactivity of these species. While vacant coordination sites potentially exist in all of these complexes,¹⁹ only **3** reacts with NO⁺ to give a coordinated nitrosyl ligand. Of course, copper-nitrosyl intermediates cannot as yet be ruled out in the cases where simple oxidation of Cu(I) by NO⁺ occurs in **1** and **2**.

There are a number of reasons that compound **6** is of interest. The nitrosyl moiety is a very common ligand in inorganic chemistry, and it readily forms complexes with most transition metals. Yet, there are only a few examples of systems where evidence for a copper-nitrosyl moiety exists,^{20,21} and until this study there were no structurally characterized synthetic examples. There is a biological relevance as well, since nitric oxide (NO) adducts of a number of copper proteins apparently do exist.^{20,22,23} Most importantly, Averill and co-workers²⁰ have recently proposed that a copper-nitrosyl intermediate (Cu⁺-NO⁺ or equivalent) is present in the copper-containing nitrite reductase of *Achromobacter cycloclastes* (catalysis of NO₂⁻ → N₂O). Since NO⁺ ion is an oxidation-state equivalent of NO₂⁻,²⁴ our reaction of nitrosonium ion with the dicopper(I) complex may represent a model for an early step in copper ion mediated nitrite reduction. Interconversions of nitrogen oxide species such as NO₂⁻, NO, and N₂O have previously been shown to be effected by polynuclear copper centers in enzymes such as hemocyanin, tyrosinase, and laccase.^{22,23} A nitrous oxide reductase (N₂O → N₂), possibly containing a dinuclear copper site, has also been recently characterized.²⁵ Further investigations in our laboratories will be directed toward the development of the redox and atom-transfer chemistry of nitrogen oxides with copper complexes.

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Supplementary Material Available: Listing of crystallographic data, atomic coordinates and temperature factors, bond lengths,

bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for complex [Cu₂(XYL-O⁻)(NO)](PF₆)₂·2CH₂Cl₂ (6 pages); observed and calculated structure factors for complex [Cu₂(XYL-O⁻)(NO)](PF₆)₂·2CH₂Cl₂ (12 pages). Ordering information is given on any current masthead page.

Oxidation of Coordinated Thiophene: The Preparation of Cp*Rh(tetramethylthiophene S-oxide)

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The coordination chemistry of thiophene is an active area of research¹ that is relevant to a molecular-level understanding of metal-catalyzed fossil fuel desulfurization.²⁻⁵ Previous research in this area has emphasized the role of the metal in promoting the reduction of the heterocycle. We have discovered a pathway whereby metals facilitate the *oxidation* of coordinated thiophene.

η⁴-Thiophene complexes have been described very recently.^{6,7} Our studies⁷ have focused on Cp*Rh(η⁴-TMT), [1]⁰ (TMT is 2,3,4,5-tetramethylthiophene), prepared by the cobaltocene reduction of [Cp*Rh(η⁵-TMT)]²⁺, [1]²⁺. The present communication is based on the following experiment: when a toluene solution of [1]⁰ is stirred under a dry oxygen atmosphere for 24 h, we observe a clean conversion to the corresponding thiophene S-oxide complex Cp*Rh(TMTO), **2**⁸ (Figure 1). Thiophenes are completely unreactive toward oxygen under normal laboratory conditions. 2,5-Di-*tert*-butylthiophene S-oxide and 2,5-di-*tert*-octylthiophene S-oxide, the only known examples of thiophenic sulfoxides, are prepared by peroxy acid oxidations of the corresponding bulky thiophenes.⁹

The oxygenation reaction of [1]⁰ is accompanied by a color change from red to orange and reproducibly affords >90% isolated yields after removal of solvent. The ¹H NMR spectrum of **2** consists of three singlets in the ratio 6:15:6. The formulation has been confirmed by the observation of a parent ion in its field desorption mass spectrum (FDMS). The ¹³C NMR spectrum of **2** shows three resonances in the range for ring carbon atoms, each of which shows coupling to ¹⁰³Rh. Compared with the data for [1]⁰, ¹³C NMR resonances¹⁰ for the carbon centers adjacent to

(16) Tiripicchio, A.; Lanfredi, A. M. M.; Ghedini, M.; Neve, F. *J. Chem. Soc., Chem. Commun.* **1983**, 97.

(17) (a) Assignment of the ν(NO) IR band was made by the observation of the strong absorption observed for **6**, but not seen either in the precursor **3** nor in [Cu₂(XYL-O⁻)(OH)](PF₆)₂. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; p 309.

(18) The formulation of **6** as a Cu(I)-NO⁺-Cu(I) complex is unlikely due to (a) the low energy of the ν(NO) IR stretch, (b) the presence of a d-d absorption (>600 nm) indicative of Cu(II) and not the d¹⁰ Cu(I) ion, and (c) the pentacoordination found in **6**, which is untypical of Cu(I).

(19) Copper(I) complexes with TMPA always are isolated as adducts, [Cu(TMPA)(L)]⁺ (L = RCN, CO, or PPh₃),^{1b} and compound **2** readily reacts with the same ligands L to give [Cu₂(N₄)(L)₂]²⁺.^{1c}

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(24) Protonation and dehydration of nitrite can produce NO⁺. See: Glidewell, C. *J. Chem. Educ.* **1989**, *66*, 631-633 and references cited therein.

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(8) Anal. Calcd for C₁₃H₂₇ORhS: C, 54.82; H, 6.90. Found: C, 54.80; H, 6.86. ¹H NMR: benzene-d₆ solution, 1.55 (s, 6 H), 1.41 (s, 15 H), 1.39 (s, 6 H); acetone-d₆ solution, 1.81 (s, 6 H), 1.77 (s, 15 H), 1.57 (s, 6 H). ¹³C NMR: acetone-d₆ solution, 95.4 (s), 88.71 (d, J = 88.7 Hz), 75.46 (d, J = 13.3 Hz). IR (KBr): ν_{SO} = 1011, ν_S = 976 cm⁻¹.

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