Synthesis and Characterization of the Dinuclear Copper(II) Complexes [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$X (X = O^{2-}, (OH)$_2$$^{2-}$, CO$_3$$^{2-}$, O$_2$$^{2-}$)

Nobumasa Kitajima,[*,†] **Takayuki Koda,**[†] **Shinji Hashimoto,**[‡] **Teizo Kitagawa,**[‡] **and Yoshihiko Moro-oka**[*,†]

Contribution from the Research Laboratory of Resource Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan, and Institute for Molecular Science, Okazaki National Institutes, Myodaiji, Okazaki 444, Japan. Received August 20, 1990

Abstract: The synthesis and characterization of a series of dinuclear copper(II) complexes ligated by HB(3,5-Me$_2$pz)$_3$ (hydrotris(3,5-dimethyl-1-pyrazolyl)borate) are presented. Displacement of the carbonyl group in a mononuclear copper(I) complex Cu(CO)(HB(3,5-Me$_2$pz)$_3$) (1) with PPh$_3$ affords Cu(PPh$_3$)(HB(3,5-Me$_2$pz)$_3$) (2), quantitatively. The reaction of 2 with an excess amount of PhIO results in the formation of a novel μ-oxo dinuclear copper(II) complex [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O (3). Complex 3 is readily converted to a bis(μ-hydroxo) dinuclear complex [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$(OH)$_2$ (4) in the presence of a trace amount of water. CO$_2$ reacts with 3 to give an adduct [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$(CO$_3$) (5). Treatment of 3 with H$_2$O$_2$ yields the μ-peroxo dinuclear copper(II) complex [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$(O$_2$) (6), which shows many similarities to oxyhemocyanin in its physicochemical properties: diamagnetic; UV–vis 338 nm (ϵ 20 800), 530 nm (ϵ 840); ν(O–O) 731 cm^{-1}. The resonance Raman spectroscopic study with mixed labeled hydrogen peroxide establishes that the coordination mode of the peroxide ion in 6 is symmetric as in oxyhemocyanin. Crystallography was performed on 2, 4·2C$_6$H$_6$, and 5. Compound 2 crystallizes in the monoclinic space group C2/c with a = 26.951 (4) Å, b = 18.003 (2) Å, c = 18.363 (3) Å, β = 124.53 (1)°, V = 7340 (1) Å^3, and Z = 8. The refinement converged with a final R (R$_w$) value of 8.72% (8.53%) for 4213 reflections with F$_o$ ≥ 3σ(F$_o$). Compound 4·2C$_6$H$_6$ crystallizes in the triclinic space group P$\bar{1}$ with a = 11.051 (3) Å, b = 11.296 (3) Å, c = 10.121 (2) Å, α = 103.03 (2)°, β = 103.51 (2)°, γ = 105.45 (2)°, V = 1127.0 (5) Å^3, Z = 1, and a final R (R$_w$) value of 10.83% (11.00%) for 3243 reflections with F$_o$ ≥ 6σ(F$_o$). Compound 5 crystallizes in the monoclinic space group P2$_1$ with a = 8.068 (1) Å, b = 31.008 (5) Å, c = 8.064 (1) Å, β = 113.59 (1)°, V = 1849.7 (5) Å^3, Z = 2, and a final R (R$_w$) value of 5.88% (5.18%) for 2735 reflections with F$_o$ ≥ 3σ(F$_o$).

Introduction

Spectroscopic and magnetic characterization of dinuclear copper(II) complexes has continued to receive attention during recent years.[1,2] One of the primary interests stems from their apparent biological relevance to proteins having dinuclear copper sites. Hemocyanin (Hc) and tyrosinase (Tyr) are known to contain a dinuclear copper site that can bind dioxygen in a symmetric fashion as a peroxide ion.[3] Several copper proteins[4] possess a structurally distinctive dinuclear copper site, the so-called "type III" site, in which the two copper(II) ions are strongly magnetically coupled but do not bind dioxygen as a stable adduct. Recently ascorbate oxidase, one of the proteins in this class, was characterized by a single-crystal X-ray analysis that showed the existence of a mononuclear copper(II) ion, the so-called "type II" copper, in the proximity of a dinuclear site, forming a trinuclear structure.[5]

We have been concerned with the synthesis of transition-metal complexes by use of tris(pyrazolyl)borate ligands, especially ones relevant to biological systems.[6] One of the advantages of using this ligand, particularly in preparing synthetic analogues for the dinuclear copper sites in proteins, is its rigid but flexible coordinating capability as a tripod nitrogen ligand that can mimic the coordination of three hystidyl nitrogen atoms found in the dinuclear sites in these proteins; in Hc[7] as well as in ascorbate oxidase,[5] each copper ion in the dinuclear site is coordinated with three hystidyl nitrogen atoms.

Hydrotris(3,5-dimethyl-1-pyrazolyl)borate, HB(3,5-Me$_2$pz)$_3$, was originally utilized for the synthesis of a mononuclear (thiolato)copper(II) complex as a synthetic analogue for the active site of blue copper proteins because it is highly sterically hindered.[8] The ligand was used for the syntheses of a number of other copper complexes,[9] however, there was no example of a dinuclear complex except for a dimer of the unsolvated copper(I) complex [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$.[10] During the course of our synthetic work with HB(3,5-Me$_2$pz)$_3$,[11] we found synthetic routes to derive a series of dinuclear copper(II) complexes[12] ligated by HB(3,5-Me$_2$pz)$_3$;

especially, we could isolate a remarkable μ-peroxo dinuclear copper(II) complex that bears close similarities to oxyHc and oxyTyr in its physicochemical characteristics.[13] The X-ray analysis of the analogous complex [Cu(HB(3,5-iPr$_2$pz)$_3$)]$_2$(O$_2$) established that the coordination mode of the peroxide ion is μ-η^2:η^2.[14] In the present paper, we report the details for the

(1) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834–850.
(2) (a) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219–327. (b) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 3–68. (c) Tyeklar, Z.; Karlin, K. D. *Acc. Chem. Res.* **1989**, *22*, 241–248.
(3) (a) Thamann, T. J.; Loehr, J. S.; Loehr, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 4187–4189. (b) Eickman, N. C.; Solomon, E. I.; Larrabee, J. A.; Spiro, T. G.; Lerch, K. *J. Am. Chem. Soc.* **1978**, *100*, 6529–6531.
(4) Fee, J. A. *Struct. Bonding (Berlin)* **1975**, *23*, 1–60.
(5) Messerschmidt, A.; Rossi, A.; Ladenstein, R.; Huber, R.; Bolognesi, M.; Gatti, G.; Marchesini, A.; Petruzzelli, R.; Finazzi-Agro, A. *J. Mol. Biol.* **1989**, *206*, 513–529.
(6) (a) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y. *Chem. Lett.* **1989**, 421–444. (b) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *Inorg. Chem.* **1990**, *29*, 357–358. (c) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3210–3212. (d) Kitajima, N.; Fukui, H.; Moro-oka, Y.; Mizutani, H.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, *112*, 6402–6403.
(7) Gaykema, W. P. J.; Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1985**, *187*, 255–275.
(8) (a) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *Proc. Nat. Acad. Sci. U.S.A.* **1978**, *74*, 3114–3118. (b) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180–4192. (c) Thompson, J. S.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4193–4200.
(9) (a) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522–3527. (b) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057–4059.
(10) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711–718.
(11) Fukui, H.; Ito, M.; Moro-oka, Y.; Kitajima, N. *Inorg. Chem.* **1990**, *29*, 2868–2870.
(12) (a) Kitajima, N.; Koda, T.; Moro-oka, Y. *Chem. Lett.* **1988**, *347*–350. (b) Kitajima, N.; Fujisawa, K.; Koda, T.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1357–1358.
(13) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 151–152.
(14) Kitajima, N.; Fujisawa, K.; Moro-oka, Y.; Toriumi, K. *J. Am. Chem. Soc.* **1989**, *111*, 8975–8976.

† Tokyo Institute of Technology.
‡ Institute for Molecular Science.

Dinuclear Copper(II) Complexes

J. Am. Chem. Soc., Vol. 113, No. 15, 1991 5665

synthesis and characterization of the μ-peroxo dinuclear complex ligated by HB(3,5-Me$_2$pz)$_3$ and other related dinuclear copper(II) complexes. The reactions of the peroxo complex that may be relevant to catalysis by Tyr have been reported elsewhere.[15]

Experimental Section

Instrumentation. IR spectra were recorded in KBr on a Hitatch 260-50 spectrometer. ^{1}H NMR spectra were recorded on either a JEOL-GX-270 (270 MHz) or a JEOL-GX-500 (500 MHz) NMR spectrometer. Chemical shifts are reported as values downfield from an internal standard of Me$_4$Si. ^{31}P NMR spectra were obtained with a JEOL-GX-270 spectrometer (109 MHz). ^{31}P NMR shifts were referenced relative to an external standard of PPh$_3$. Magnetic susceptibilities were determined by the Evans method.[16] Electronic spectra at room temperature were measured on a Shimazu UV-260 spectrophotometer. Low-temperature measurements of electronic spectra were carried out on a MRS-2000 spectrometer equipped with an electronic cooling apparatus at Keio University. EPR spectra were recorded on a Varian E-12 instrument for solutions frozen with liquid nitrogen in quartz tubes. Field desorption mass spectra (FD-MS) were measured on a Hitachi M-80 mass spectrometer. Raman scattering was accomplished with excitation by the 514.5-nm line of an Ar$^+$ ion laser (NEC GLG 3200) with a laser power of 80 mW at the sample point and detected with an OMA II system (PAR 1215) and an intensified diode-array detector (PAR 1420) attached to a double monochromator (Spex 1404). The sample was contained in a spinning cell (1000 rpm) and maintained at -40 °C by flushing with cold nitrogen gas. The Raman shifts were calibrated with indene. X-ray diffraction data collection and analyses were performed on a Rigaku AFC-5 four-circle diffractometer interfaced to a FACOM A-70 computer system (the AFC and CRYSTAN program package from Rigaku). Low-temperature measurements for X-ray reflections were made with a coolig apparatus purchased from Rigaku.

Materials and Methods. CH$_2$Cl$_2$ and CHCl$_3$ used for the reactions were prepurified by the literature method[17] and were distilled from P$_2$O$_5$ under argon prior to use. PhIO was synthesized by the literature method.[18] PhI^{18}O was prepared with H$_2$^{18}O (99 atom % ^{18}O from MSD-Isotopes) by the method reported by Hill et al.[19] Samples of ^{18}O$_2$ (96.5 atom % ^{18}O) and ^{18}O$_2$ (50 atom % ^{18}O; ca. 1:2:1 mixture of ^{18}O$_2$/^{18}O^{16}O/^{16}O$_2$) were purchased from MSD-Isotopes and Cambridge Isotope Laboratories, respectively. Hydrogen peroxide labeled with ^{18}O was prepared from the labeled dioxygen by the method using 2-ethylanthraquinone improved by Dr. Y. Tatsuno of Osaka University.[20] CuCl obtained from Wako (reagent grade) was washed with acetic acid on a filter several times until the filtrate became colorless. The resulting white solid was subsequently treated with distilled water, dried under vacuum, and stored in a Schlenk tube under an argon atmosphere. Other reagents were the highest grade commercially available and were used without further purification unless otherwise stated.

All reactions were performed by standard Schlenk techniques under argon. KHB(3,5-Me$_2$pz)$_3$ was obtained by the literature method.[21] Cu(CO)(HB(3,5-Me$_2$pz)$_3$) (1) was prepared by the method described by Marks et al.[10]

Cu(PPh$_3$)(HB(3,5-Me$_2$pz)$_3$) (2). Under argon, PPh$_3$ (0.67 g, 2.57 mmol) was added slowly to a solution of Cu(CO)(HB(3,5-Me$_2$pz)$_3$) (1) (1.00 g, 2.57 mmol) dissolved in 20 mL of CH$_2$Cl$_2$. Evolution of CO began immediately. After being stirred for 30 min, the solution was evaporated under vacuum to give a quantitative amount of Cu(PPh$_3$)-(HB(3,5-Me$_2$pz)$_3$) (2). The crystals suitable for X-ray diffraction were obtained by recrystallization from a CH$_2$Cl$_2$/pentane solution.

Complex 2 could also be obtained as follows. In a Schlenk flask carefully filled with argon were placed CuCl (0.99 g, 10.0 mmol), KHB(3,5-Me$_2$pz)$_3$ (3.36 g, 10.0 mmol), and PPh$_3$ (2.62 g, 10.0 mmol). To the solids was added 30 mL of CH$_2$Cl$_2$, and the mixture was stirred for 1 h. The mixture was filtered through Celite, and the resulting colorless filtrate was evaporated to dryness to afford 6.05 g of 2 (97% yield). Anal. Calcd for C$_{33}$H$_{37}$N$_6$PBCu: C, 63.62; H, 5.99; N, 13.49. Found: C, 63.92; H, 6.05; N, 13.31. ^{1}H NMR (CDCl$_3$, 25 °C, ppm): 1.68 (9 H, s, Me), 2.38 (9 H, s, Me), 5.62 (3 H, s, pz), 7.65 (15 H, m,

Ph). ^{31}P NMR (C$_6$D$_5$CD$_3$, -70 °C, external standard PPh$_3$, ppm): 11.87 (br s). IR (KBr, cm^{-1}): 2504 (BH).

[Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O (3). Under argon, to a mixture of 2 (1.00 g, 1.61 mmol) and PhIO (0.53 g, 2.41 mmol) was added 25 mL of CH$_2$Cl$_2$. The mixture was stirred for 6 h at room temperature. During the reaction, the color of the solution changed from colorless to dark green. The mixture was filtered to remove unreacted PhIO, and the filtrate was cooled overnight at -20 °C. The separated blue-green needles were collected by filtration and dried under vacuum (0.23 g, 40% yield). The crystallinity was easily lost when the crystal was exposed to air or vacuum. Anal. Calcd for C$_{30}$H$_{44}$N$_{12}$OB$_2$Cu$_2$: C, 48.86; H, 6.01; N, 22.79. Found: C, 48.41; H, 6.52; N, 23.21. ^{1}H NMR (CDCl$_3$, 25 °C, ppm): 1.86 (18 H, br s, Me), 2.45 (18 H, br s, Me), 12.62 (6 H, br s, pz). IR (KBr, cm^{-1}): 2506 (BH). FD-MS: m/e 736 (M$^+$). UV–vis (CH$_2$Cl$_2$, nm (ϵ)): 335 (2560), 660 (105). EPR (CHCl$_3$, -196 °C): silent. μ_{eff} (by the Evans method,[16] in CDCl$_3$ at 25 °C): 1.3 μ_B/mol.

[Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$(OH)$_2$·2C$_6$H$_6$ (4·2C$_6$H$_6$). Twenty milligrams (0.027 mmol) of 3 was dissolved in 1 mL of CHCl$_3$ in a glass tube of ca. 1-cm diameter. To the solution was added 5 mL of benzene slowly (reagent grade, not purified) via a syringe. The tube was sealed with a rubber cap and allowed to stand for 2 days, affording 16 mg of 4·2C$_6$H$_6$ (80% yield) as blue crystals suitable for X-ray diffraction experiments. Anal. Calcd for C$_{42}$H$_{58}$N$_{12}$O$_2$B$_2$Cu$_2$: C, 55.33; H, 6.41; N, 18.44. Found: C, 55.61; H, 6.52; N, 18.64. IR (KBr, cm^{-1}): 3620 (OH), 2506 (BH).

[Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$(CO$_3$) (5). In a Schlenk flask, 3 (100 mg, 0.136 mmol) was stirred for 1 h in 10 mL of CHCl$_3$ under pure CO$_2$. Removal of the solvent from the resultant deep green solution gave 5 quantitatively as a green powder. Crystals suitable for X-ray experiments were obtained when a CHCl$_3$ solution in a flask capped with a rubber septum was allowed to stand for 1 week at room temperature. Anal. Calcd for C$_{31}$H$_{44}$N$_{12}$O$_3$B$_2$Cu$_2$: C, 47.65; H, 5.67; N, 21.51. Found: C, 46.93; H, 5.69; N, 21.05. ^{1}H NMR (CDCl$_3$, 25 °C, ppm): 2.31 (36 H, br s, Me), 6.11 (6 H, br s, pz). IR (KBr, cm^{-1}): 2503 (BH); 1592, 1385, 749 (CO$_3$). FD-MS: m/e 784 (M$^+$). UV–vis (CH$_2$Cl$_2$, nm (ϵ)): 347 (9950), 680 (313). EPR (CHCl$_3$, -196 °C): silent. μ_{eff} (by the Evans method,[16] in CDCl$_3$ at 25 °C): 0.7 μ_B/mol.

[Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$(O$_2$) (6). Under argon, to the solution of 3 (100 mg, 0.136 mmol) in 10 mL of CH$_2$Cl$_2$ was added aqueous H$_2$O$_2$ (35 wt %, 36 μL, 0.411 mmol) at room temperature. The solution was vigorously stirred for 1 min and immediately cooled to -78 °C, resulting in precipitation of a purple solid of 6, which was collected by filtration and dried under vacuum at -20 °C (82 mg, 80% yield). Anal. Calcd for C$_{30}$H$_{44}$N$_{12}$O$_2$B$_2$Cu$_2$: C, 47.82; H, 5.89; N, 22.31. Found: C, 47.09; H, 5.78; N, 22.29. ^{1}H NMR (CDCl$_3$, -40 °C, ppm): 2.26 (18 H, s, Me), 2.37 (18 H, s, Me), 5.68 (6 H, s, pz). IR (KBr, cm^{-1}): 2504 (BH). FD-MS: m/e 751 (M$^+$). UV–vis (CH$_2$Cl$_2$, -12 °C, nm (ϵ)): 338 (20 800), 530 (840). EPR (CHCl$_3$, -196 °C): silent. μ_{eff} (by the Evans method,[16] in CDCl$_3$ at -40 °C): 0 μ_B/mol.

Oxidation of PPh$_3$ with 3. Twenty milligrams of 3 (0.027 mmol) and 43 mg of PPh$_3$ (0.163 mmol) were stirred in 0.5 mL of CDCl$_3$ for 1 h at room temperature under an argon atmosphere. ^{1}H NMR, ^{31}P NMR, and GC analyses of the resultant colorless solution established almost quantitative formation of OPPh$_3$ and 2.

Reaction of 6 with CO$_2$. Ten milligrams of 6 (0.0013 mmol) was placed in a Schlenk tube under argon and dissolved in 10 mL of CHCl$_3$ at -20 °C. After the solution was cooled to -78 °C, the atmosphere was replaced with CO$_2$, and the solution was allowed to warm to room temperature. During the warming process, the color of the solution turned from purple to deep green. The resultant solution was evaporated to dryness under vacuum, and the green solid thus obtained was characterized by IR and ^{1}H NMR spectroscopy, showing almost quantitative formation of 5. When the solution of 6 was allowed to stand below -20 °C, no reaction proceeded. The consumption rates of 6 under Ar and CO$_2$ were examined by absorption spectroscopy as described previously.[15]

X-ray Data Collection. Crystals suitable for X-ray diffraction were obtained as described above. Because of the facile removal of the benzene of crystallization, the crystallinity of 4·2C$_6$H$_6$ was lost immediately at room temperature. In order to avoid the loss of crystallinity, the crystal of 4·2C$_6$H$_6$ was sealed in a glass capillary and the data collection was carried out at -80 ± 5 °C. Unfortunately, maintenance of the constant low temperature was difficult to achieve and the fluctuation caused the data to be of low quality ($R_{\text{int}} = 4.8\%$). A Mo X-ray source equipped with a graphite monochromator (Mo Kα, $\lambda = 0.710680$ Å) was used. Automatic centering and least-squares routines were carried out for all the complexes with 25 reflections of $2\theta = $ ca. 30° to determine the cell dimensions. Data collection was made by using an ω–2θ scan. All data were corrected for Lorentz and polarization effects but not for absorption. Intensities of three check reflections monitored every 100 reflections showed no decay in any case. A summary of cell parameters, data

(15) Kitajima, N.; Koda, T.; Iwata, Y.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8833–8839.

(16) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

(17) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1990.

(18) Lucas, H. J.; Kennedy, E. R.; Formo, M. W. *Organic Syntheses*; Wiley: New York; Collect. Vol. III, pp 483–485.

(19) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563–1565.

(20) Tatsuno, Y. Personal communication.

(21) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99–105.

Table I. Crystallographic Data for Cu(PPh₃)(HB(3,5-Me₂pz)₃) (2), [Cu(HB(3,5-Me₂pz)₃)]₂(OH)₂·2C₆H₆ (4·2C₆H₆), and [Cu(HB(3,5-Me₂pz)₃)]₂(CO₃) (5)

Compound 2	
C₃₃H₃₇N₆PBCu	monoclinic, C2/c
$a = 26.951$ (4) Å	μ(Mo Kα) = 6.24 cm⁻¹
$b = 18.003$ (2) Å	$T_m = 25$ °C
$c = 18.363$ (3) Å	$2° < 2\theta < 50°$
$\beta = 124.53$ (1)°	no. of measd reflns = 6923
$V = 7340$ (1) Å³	no. of indep reflns = 4213
$Z = 8$	$R = 0.0872$
fw = 623.03	$R_w = 0.0853$
$D_c = 1.13$ g cm⁻³	

Compound 4·2C₆H₆	
C₄₆H₅₆N₁₂O₂B₂Cu₂	triclinic, P1̄
$a = 11.051$ (3) Å	μ(Mo Kα) = 9.34 cm⁻¹
$b = 11.296$ (3) Å	$T_m = -80$ °C
$c = 10.121$ (2) Å	$2° < 2\theta < 55°$
$\alpha = 103.03$ (2)°	no. of measd reflns = 5193
$\beta = 103.51$ (2)°	no. of indep reflns = 3243
$\gamma = 105.45$ (2)°	$R = 0.1083$
$V = 1127.0$ (5) Å³	$R_w = 0.1100$
$Z = 1$	$D_c = 1.34$ g cm⁻³
fw = 909.70	

Compound 5	
C₃₁H₄₄N₁₂O₃B₂Cu₂	monoclinic, P2₁
$a = 8.068$ (1) Å	μ(Mo Kα) = 11.42 cm⁻¹
$b = 31.008$ (5) Å	$T_m = 25$ °C
$c = 8.064$ (1) Å	$2° < 2\theta < 60°$
$\beta = 113.59$ (1)°	no. of measd reflns = 5847
$V = 1849.7$ (5) Å³	no. of indep reflns = 2735
$Z = 2$	$R = 0.0588$
fw = 781.48	$R_w = 0.0518$
$D_c = 1.41$ g cm⁻³	

Figure 1. ORTEP view of Cu(PPh₃)(HB(3,5-Me₂pz)₃) (2).

Table II. Bond Distances (Å) and Angles (deg) for Cu(PPh₃)(HB(3,5-Me₂pz)₃) (2)

Distances			
Cu–P	2.166 (6)	Cu–N1	2.101 (10)
Cu–N2	2.106 (14)	Cu–N3	2.086 (13)
N1–N4	1.372 (22)	N2–N5	1.369 (21)
N3–N6	1.405 (21)	B–N4	1.532 (24)
B–N5	1.572 (16)	B–N6	1.542 (20)

Angles			
P–Cu–N1	124.5 (5)	P–Cu–N2	128.2 (4)
P–Cu–N3	121.7 (4)	Cu–P–C1a	113.9 (6)
Cu–P–C1b	115.7 (7)	Cu–P–C1c	116.8 (6)
N1–Cu–N2	90.1 (5)	N1–Cu–N3	90.0 (4)
N2–Cu–N3	91.7 (5)	B–N4–N1	120.9 (1.1)
B–N5–N2	122.3 (1.5)	B–N6–N3	120.8 (1.3)
C1a–P–C1b	100.1 (7)	C1a–P–C1c	103.5 (8)
C1b–P–C1c	104.7 (6)		

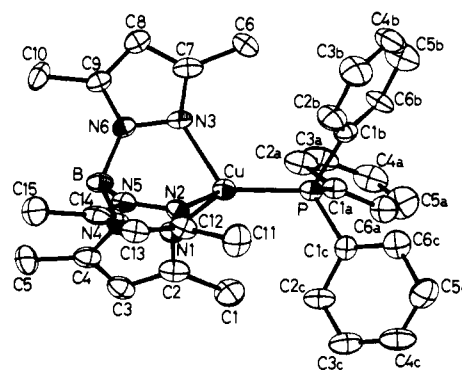collection details, and refinement results for **2**, **4·2C₆H₆**, and **5** is given in Table I.

Structure Analyses. The positional parameters for the copper atom in **2** were obtained by the direct method (SAPI 85 provided from Riga-ku). The Patterson method was applied to determine the positions of copper atoms for **4·2C₆H₆** and **5**. Subsequent difference Fourier syntheses located all non-hydrogen atoms, which were refined aniso-tropically. The hydrogen atom positions, except those for the methyl groups, were calculated and isotropically fixed for the final refinement (*d*(C–H) = 1.0 Å). The final *R* factors and refinement data are shown in Table I. The slightly high residual values of **4·2C₆H₆** result from the fluctuation of the measurement temperature and serious disorder of the C₆H₆ molecules.

Bond lengths, bond angles, and anisotropic temperature factors for non-hydrogen atoms, hydrogen coordinates, and F_o/F_c tables for **2**, **4·2C₆H₆**, and **5** are available as supplementary material.

Results and Discussion

Synthesis and Structure of the Copper(I) Triphenylphosphine Complex 2. Reaction of Cu(CO)(HB(3,5-Me₂pz)₃) (1) with PPh₃ proceeds instantaneously, resulting in displacement of CO by PPh₃ to form Cu(PPh₃)(HB(3,5-Me₂pz)₃) (2). Direct synthesis of **2** is effected by using a mixture of KHB(3,5-Me₂pz)₃, CuCl, and PPh₃. A similar method for preparing copper(I)–phosphine complexes ligated by hydrotris(pyrazolyl)borate ligands has been reported.[22] The crystal structure of **2** is presented in Figure 1, and the selected bond distances and angles are summarized in Table II. The ligand arrangement around the copper atom is described as slightly distorted tetrahedral. The bond distances between the pyrazole nitrogen and copper atoms are similar to one another, whereas the Cu–P distance is longer. A number of crystal structures of phosphine–copper(I) complexes have been reported.[23] The phosphorus–copper distances in those complexes

range from 2.15 to 2.30 Å, and thus the distance found in the present complex is not exceptional. Other bond distances and angles are also usual.

Synthesis of the μ-Oxo Dinuclear Copper(II) Complex 3 and Its Conversion to the Bis(μ-hydroxo) Complex 4. Oxidation of **2** with an excess of PhIO gives a novel μ-oxo dinuclear copper(II) complex **3**. We interpret the formation of **3** as follows. PhIO oxidizes PPh₃ easily to OPPh₃. The initiation of the reaction is thus ascribed to oxidation of coordinating PPh₃ with PhIO. Subsequent dissociation of OPPh₃ gives a coordinatively unsaturated copper(I) species that reacts with another PhIO, forming a PhIO adduct or an oxocopper(III) intermediate.[24] The intermediate couples with another coordinatively unsaturated copper(I) species immediately, resulting in the formation of **3**. The origin of the oxo group in **3** was established by labeling experiments. Figure 2A (solid lines) shows the FD-MS spectrum of **3** prepared from PhI¹⁶O. The spectrum is reasonably consistent with the one calculated from the isotope distribution. The ¹⁸O derivative synthesized by a reaction of **2** and PhI¹⁸O exhibits the spectrum shown in Figure 2B (solid lines), which clearly indicates the incorporation of an ¹⁸O atom into the sample.

Owing to its dinuclear structure, **3** shows antiferromagnetic properties. The magnetic susceptibility of **3** determined by the Evans method in CDCl₃ at 25 °C is 1.3 μ_B/mol. Accordingly, **3** is EPR silent and gives a characteristic isotropically shifted ¹H NMR spectrum, as shown in Figure 3. In the figure, only the spectra obtained at 25 and −30 °C are presented. The chemical shifts of the pyrazole proton in **1** and **3** (at 25 °C in the same solvent) are 5.60 and 5.62 ppm, respectively. Thus, the signal ascribed to the pyrazole proton of **3** (12.6 ppm at 25 °C) is shifted downfield and broadened considerably. The two distinct methyl

(22) Abu Salah, O. M.; Bruce, M. J.; Walsh, J. D. *Aust. J. Chem.* **1976**, *32*, 1209–1218.

(23) See the following papers and references cited therein: (a) Bowmaker, G. A.; Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; Papasergio, R. I.; White, A. H. *Inorg. Chem.* **1987**, *26*, 3533–3538. (b) Barron, P. F.; Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; White, A. H. *Inorg. Chem.* **1988**, *27*, 1829–1834.

(24) There is a theoretical prediction that oxocopper(III) cannot be stable.[25] Very recently, Valentine et al. demonstrated that metal-catalyzed oxo-transfer reactions with PhIO can proceed via metal–PhIO adducts and not high-valent metal–oxo intermediates.[26]

(25) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125–135.

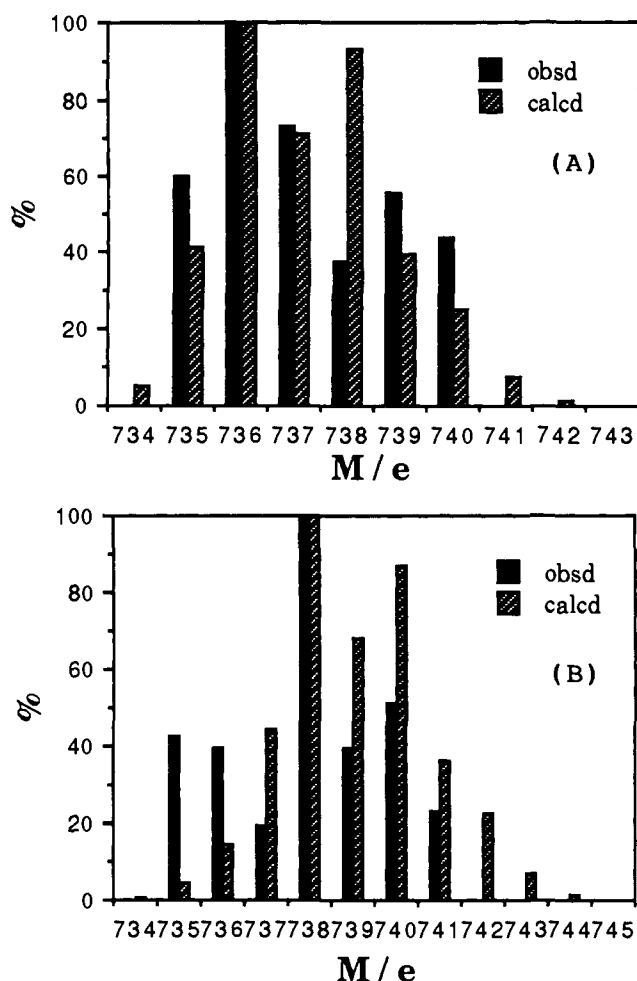(26) Yang, Y.; Diederich, F.; Valentine, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 7826–7828.

Figure 2. FD-MS spectra of ^{16}O and ^{18}O labeled **3**: (A) ^{16}O labeled **3**; (B) ^{18}O labeled **3**.
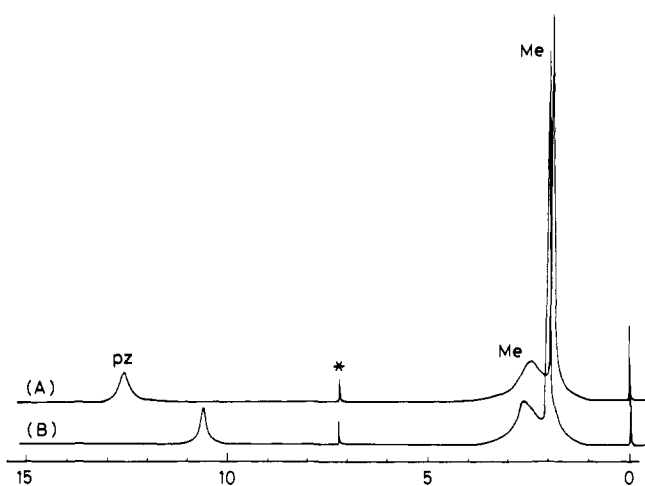

Figure 4. ORTEP view of $[Cu(HB(3,5-Me_2pz)_3)]_2(OH_2)$ (**4**). C_6H_6 molecules of crystallization are omitted.

Table III. Bond Distances (Å) and Angles (deg) for $[Cu(HB(3,5-Me_2pz)_3)]_2(OH)_2 \cdot 2(C_6H_6)_2$ (**4·2C₆H₆**)

Distances			
Cu–O	1.965 (5)	Cu–O′	1.917 (7)
Cu–N1	2.027 (7)	Cu–N2	2.277 (7)
Cu–N3	1.979 (8)	B–N4	1.596 (14)
Cu–N5	1.540 (14)	B–N6	1.543 (12)
N1–N4	1.300 (8)	N2–N5	1.375 (9)
N3–N6	1.394 (8)	Cu---Cu	3.059 (2)
Angles			
O–Cu–O′	76.0 (3)	O–Cu–N1	167.6 (3)
O–Cu–N2	102.3 (3)	O–Cu–N3	97.8 (3)
O′–Cu–N1	96.6 (3)	O′–Cu–N2	102.6 (3)
O′–Cu–N3	168.3 (3)	N1–Cu–N2	88.7 (3)
N1–Cu–N3	87.7 (3)	N2–Cu–N3	88.4 (3)
Cu–N1–N4	118.5 (6)	Cu–N2–N5	113.5 (5)
Cu–N3–N6	118.1 (5)	N4–B–N5	107.9 (8)
N4–B–N6	106.9 (7)	N5–B–N6	111.7 (7)
B–N4–N1	119.6 (6)	B–N5–N2	118.6 (6)
B–N6–N3	119.2 (7)		

high, and no oxidation was observed for dimethyl sulfide, pyridine, or cyclohexene, even under reflux in $CHCl_3$.

Although several examples of dinuclear μ-oxo copper(II) complexes are known,[28–30] no crystal structure is available to date. Therefore, extensive efforts were made to obtain a single crystal of **3**. Unfortunately, all attempts were unsuccessful because of the moderate instability of **3**. For instance, recrystallization from methanol yielded crystals of a disproportionation product Cu-$[HB(3,5-Me_2pz)_3]_2$.[31] Likewise, crystals of the dinuclear bis-(μ-hydroxo) complex **4** as the solvate with benzene were obtained when the crystallization of **3** was carried out by a layer-diffusion method with $CHCl_3$ and C_6H_6 under aerobic conditions. The structure of **4·2C₆H₆** was determined, and the ORTEP view of **4** is presented in Figure 4. A $Cu(OH)(HB(3,5-Me_2pz)_3)$ unit forms the dinuclear structure through the crystallographically imposed center of symmetry. The bond distances and angles are summarized in Table III. The bond lengths between Cu–O and Cu′–O are similar to each other and typical for Cu–OH bonds, indicating the bis(μ-hydroxo) structure. The ligand arrangement about each copper is described as square-pyramidal. One pyrazole nitrogen atom from the ligand is the apical group and the two other ligand nitrogens and the two hydroxo oxygen atoms form the basal plane. The distance between the copper and the apical nitrogen atoms (2.277 (7) Å) is considerably elongated. However, the elongation of the bond distance between the apical nitrogen and copper atoms is less than those found in the analogous complex

Figure 3. ^1H NMR spectrum of **3** in $CDCl_3$: (A) at 25 °C; (B) at –30 °C.

proton signals are also shifted and broadened. The very broad one appears further downfield and is tentatively ascribed to the methyl group on the metal side. The decrease in shift at low temperature obviously reflects the decrease in the magnetic moment of **3** due to the antiferromagnetism.[27]

Treatment of **3** with 5 equiv of PPh_3 in $CHCl_3$ results in an oxo-transfer reaction, affording a quantitative amount of **2** and $OPPh_3$. However, the propensity for oxo-transfer of **3** is not very

(27) N. M. R. of Paramagnetic Molecules; La Mar, G. N., Horrocks, W. DeW., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973.
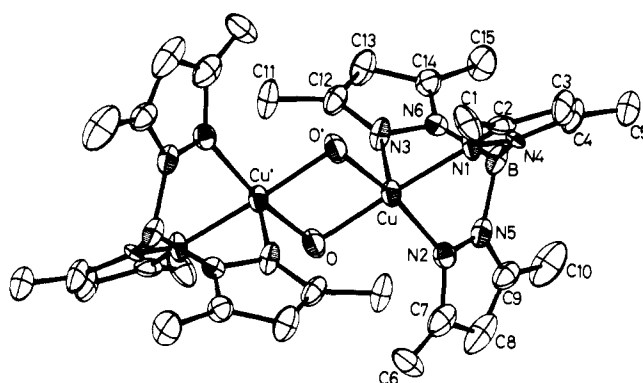
(28) Lapinte, C.; Riviere, H.; Roselli, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1109–1110.
(29) Davies, G.; El-Sayed, M. A. *Inorg. Chem.* **1983**, 22, 1257–1266.
(30) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1984**, 23, 519–521.
(31) Kitajima, N.; Moro-oka, Y.; Uchida, A.; Sasada, Y.; Ohashi, Y. *Acta Crystallogr.* **1988**, C44, 1876–1878.

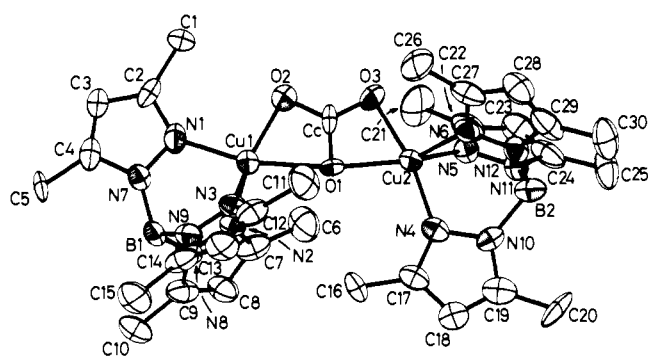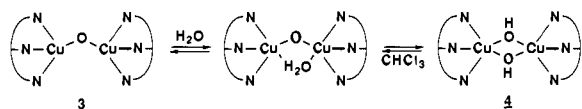**Figure 5.** ORTEP view of [Cu(HB(3,5-Me₂pz)₃)]₂(CO₃) (5).

Scheme I

[Cu(HB(3,5-iPr₂pz)₃)]₂(OH)₂[6b] (2.371 (6) and 2.640 (7) Å).

The water contaminant in the benzene used for crystallization seems to be responsible for the formation of 4·2C₆H₆ from 3. In fact, addition of a slight amount of water to the benzene promoted the formation and crystallization of 4·2C₆H₆.

The IR spectrum of the solid sample of 4·2C₆H₆ supports the existence of OH groups; a sharp band assignable to the OH groups was observed at 3620 cm⁻¹. However, the solution properties of the complex in CHCl₃ puzzled us, and it was difficult to conclude whether the bis(μ-hydroxo) dinuclear structure was preserved in the solution. No band assignable to ν(OH) was detectable in the solution samples prepared from the single crystals of 4·2C₆H₆. The FD-MS spectrum (the sample was prepared from the solution) is completely identical with that of μ-oxo complex 3. No m/e peak ascribed to 4 (M⁺, 754) was observed. The ¹H NMR spectrum at room temperature is also consistent with that of 3, whereas at −40 °C, a very broad peak was also observed at −15 ppm. The integrated intensity implies approximately one-third of a proton on the basis of the intensity of pyrazole 4-proton. Finally, treatment of the solution with 5 equiv of PPh₃ gave quantitative amounts of 2 and OPPh₃, consistent with the experimental result obtained for the reaction of 3 with PPh₃ as described above. On the other hand, in the case of [Cu(HB-(3,5-iPr₂pz)₃)]₂(OH)₂,[6b] we could obtain firm evidence that the structure is preserved in solution. For instance, the IR spectrum of the solution shows a strong band assigned to the OH group, and the complex does not oxidize PPh₃. Integration of the above experimental results leads us to the explanation that 4 is in equilibrium with 3 in CHCl₃ (Scheme I). A similar conversion and equilibrium between μ-oxo- and bis(μ-hydroxo) dinuclear copper(II) complexes have been reported.[30] We infer that the broad signal at −15 ppm observed at −40 °C is ascribed to the proton of a bridging water molecule weakly bound to the μ-oxo complex 3 ([Cu(HB(3,5-iPr₂pz)₃)]₂(OH)₂ gives the proton signal for the OH group at −51 ppm at −40 °C).

CO₂ Addition to 3, Affording the μ-Carbonato Complex 5. Formation of the μ-carbonato binuclear copper(II) complex upon treatment of CuCl with a CO₂/O₂ mixture in the presence of N-donor ligands such as N,N,N',N'-tetraethylethylenediamine was demonstrated previously.[32] The reaction was suggested to proceed via a dinuclear μ-oxo copper(II) intermediate. Hence, the reaction of 3 with CO₂ was explored. When the argon atmosphere in a Schlenk flask containing a CHCl₃ solution of 3 is replaced with CO₂, an instantaneous color change from blue-green to deep forest green is noted; and from the solution, the dinuclear μ-carbonato

Table IV. Bond Distances (Å) and Angles (deg) for [Cu(HB(3,5-Me₂pz)₃)]₂(CO₃) (5)

Distances			
Cu1–O1	2.126 (10)	Cu1–O2	1.908 (9)
Cu1–N1	1.933 (9)	Cu1–N2	2.044 (10)
Cu1–N3	2.051 (10)	Cu2–O1	2.025 (10)
Cu2–O3	1.897 (11)	Cu2–N4	1.913 (8)
Cu2–N5	2.115 (10)	Cu2–N6	2.115 (10)
N1–N7	1.359 (13)	N2–N8	1.340 (12)
N3–N9	1.350 (13)	N4–N10	1.392 (13)
N5–N11	1.359 (12)	N6–N12	1.353 (13)
B1–N7	1.524 (15)	B1–N8	1.547 (21)
B1–N9	1.545 (21)	B2–N10	1.592 (17)
B2–N11	1.585 (22)	B2–N12	1.535 (21)
Cu1---Cu2	4.140 (2)		

Angles			
O1–Cu1–O2	64.3 (4)	O1–Cu1–N1	165.2 (4)
O1–Cu1–N2	98.5 (4)	O1–Cu1–N3	98.3 (4)
O2–Cu1–N1	100.9 (4)	O2–Cu1–N2	133.3 (5)
O2–Cu1–N3	132.7 (5)	N1–Cu1–N2	91.8 (4)
N1–Cu1–N3	92.1 (4)	N2–Cu1–N3	90.8 (4)
Cu1–O1–Cc	84.1 (7)	Cu1–O2–Cc	93.8 (8)
Cu1–O1–Cu2	171.5 (4)	O1–Cu2–O3	64.2 (4)
O1–Cu2–N4	104.5 (4)	O1–Cu2–N5	133.6 (5)
O1–Cu2–N6	134.0 (5)	O3–Cu2–N4	168.7 (4)
O3–Cu2–N5	97.3 (5)	O3–Cu2–N6	97.8 (5)
N4–Cu2–N5	90.6 (4)	N4–Cu2–N6	90.4 (4)
N5–Cu2–N6	88.4 (4)	Cu2–O1–Cc	87.4 (7)
Cu2–O3–Cc	94.1 (9)	O1–Cc–O3	114.3 (1.1)
O1–Cc–O2	117.8 (1.1)	O2–Cc–O3	127.9 (1.2)
Cu1–N1–N7	115.2 (7)	Cu1–N2–N8	114.8 (8)
Cu1–N3–N9	114.2 (8)	Cu2–N4–N10	118.7 (6)
Cu2–N5–N11	115.4 (8)	Cu2–N6–N12	116.4 (8)
N7–B1–N8	108.5 (1.1)	N7–B1–N9	108.2 (1.1)
N8–B1–N9	108.9 (1.0)	N10–B2–N11	106.0 (1.2)
N10–B2–N12	108.5 (1.2)	N11–B2–N12	109.5 (1.0)
B1–N7–N1	120.8 (9)	B1–N8–N2	119.0 (1.0)
B1–N9–N3	119.6 (1.0)	B2–N10–N4	119.2 (8)
B2–N11–N5	119.8 (1.0)	B2–N12–N6	119.6 (1.0)

Scheme II
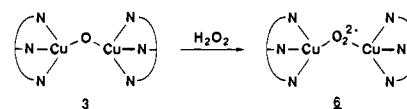
copper(II) complex 5 is isolated. Complex 5 exhibits a characteristically strong IR band at 1592 cm⁻¹ due to the bridging carbonato group. The dinuclear structure is supported by FD-MS and EPR spectra (silent). 5 shows a less isotropically shifted and sharper ¹H NMR spectrum than that of 3, implying a stronger antiferromagnetic interaction between the two copper(II) ions. In fact, the magnetic susceptibility of 5 determined by the Evans method is 0.7 μB/mol at 25 °C. The ORTEP view of 5 is presented in Figure 5. The bond angles and distances are summarized in Table IV. The carbonato group is bridged between the two copper ions in a bidentate fashion to each copper ion. One oxygen atom from the carbonato group sits approximately halfway between the two copper atoms with a Cu1–O1–Cu2 angle of 172°. A similar coordination mode for the carbonato group has been found in several dinuclear copper(II) complexes.[33,34] Although it is not simple, the coordination geometry of the each copper ion may be described as square-pyramidal with a basal plane formed by one oxygen atom bridging between the two copper ions, one other oxygen atom from the carbonato group coordinating terminally to the copper atom, and two nitrogen atoms from each tris(pyrazolyl)borate ligand. On the basis of this structural description, the strong antiferromagnetism of 5 is ascribed to the magnetic interaction between the two copper(II) ions mediated predomi-

(32) (a) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296–2300. (b) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1980**, *19*, 201–208.

(33) Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* **1978**, *100*, 6258–6260.

(34) Sletten, J.; Hope, H.; Julve, M.; Kahn, O.; Verdaguer, M.; Dworkin, A. *Inorg. Chem.* **1988**, *27*, 542–549.
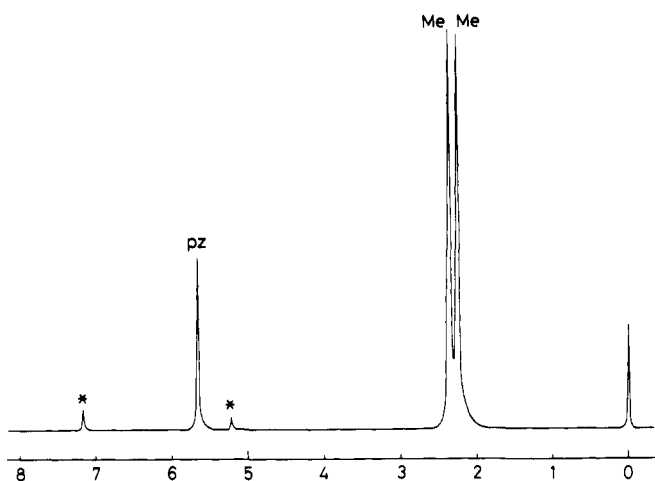
Dinuclear Copper(II) Complexes

J. Am. Chem. Soc., Vol. 113, No. 15, 1991 5669

Figure 6. ^{1}H NMR spectrum of 6 in CDCl$_3$ at -40 °C.
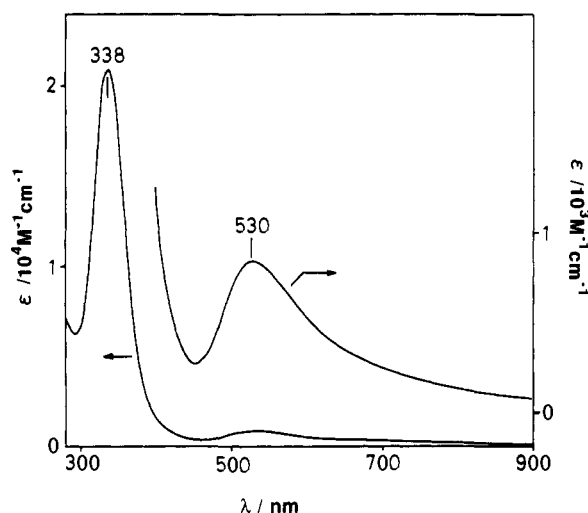
Figure 7. Electronic spectrum of 6 in CHCl$_3$ at -12 °C.

RAMAN SHIFT / cm^{-1}

Figure 8. Resonance Raman spectrum of 6 prepared from a mixture of $H_2^{16}O_2/H_2^{16}O^{18}O/H_2^{18}O_2$ (1:2:1): (A) observed at -40 °C in CHCl$_3$; (B) calculated on the basis of the assumption of a band intensity ratio of 1:2:1 with identical widths of 18 cm^{-1}.

nantly by the bridging oxygen atom.

The mechanism of the formation of **5** from **3** is explicable by the simple addition of CO$_2$ to the basic μ-oxo group, as proposed by Churchill, Davies, et al.[32] The high nucleophilicity of the oxo group in **3** is ascribed to the strong electron-donating property of HB(3,5-Me$_2$pz)$_3$.

Formation of the μ-Peroxo Complex 6 by Reaction of 3 with H$_2$O$_2$. Preparation of peroxo transition-metal complexes by treatment of the corresponding oxo metal complex with H$_2$O$_2$ is known.[35] The reaction of **3** and aqueous H$_2$O$_2$ was found to proceed smoothly to afford a μ-peroxo dinuclear copper(II) complex **6** as a thermally unstable purple solid (Scheme II). The facility of the reaction with H$_2$O$_2$, proceeding even at low temperature (ca. -40 °C), is ascribed to the high nucleophilicity of the μ-oxo group in **3**, as described above. The solubility of **6** is not very high in CH$_2$Cl$_2$; thus the isolation of **6** as a solid material from the solution is readily accomplished. Although **6** is not very stable at room temperature, it is stable below -20 °C even in solution.

The ^{1}H NMR spectrum of **6** in CHCl$_3$ is shown in Figure 6. The spectrum is reasonably sharp, and the chemical shift of the signal (5.68 ppm) assigned to the pyrazole 4-proton falls in the range for the ones of diamagnetic copper(I) complexes, indicative of the diamagnetism of **6**. The Evans method measurement indicates no detectable signal shift of a standard compound, supporting the diamagnetism of **6**.

The electronic spectrum of **6** consists of two very characteristic bands at 338 nm (ϵ 20 800) and 530 nm (ϵ 840) (Figure 7).

Although **5** shows a strong band at ca. 350 nm (assignable to a CO$_3^{2-}$ → Cu(II) LMCT), **3** does not give such a strong band around 350 nm. Accordingly, for **6** the band at 338 nm is tentatively assigned to a O$_2^{2-}$ → Cu(II) LMCT, whereas the pyrazole N → Cu(II) LMCT may also contribute to the band. The band at 530 nm is obviously assignable to a O$_2^{2-}$ → Cu(II) LMCT, since the extinction coefficient is too large for a d–d transition. However, the tailing profile of the band may be associated with the overlapping of the d–d band.

Thompson reported the synthesis of a mononuclear superoxo copper(II) complex Cu(O$_2$)(HB(3,5-Me$_2$pz)$_3$).[9b] The complex was reported to be diamagnetic and exhibit a characteristic band at 524 nm (ϵ 600); these properties are very similar to those of **6**, and at the outset of the present work, we suspected that **6** might be the superoxo complex. However, the labeling experiment gave no IR band assignable to the superoxo complex.[36] Moreover, the extensive resonance Raman study (vide infra) did not show any Raman band assigned to the superoxide ion in the 1000–1200 cm^{-1} region. Therefore, it was concluded that **6** is a peroxo and not a superoxo complex.[37]

Figure 8A shows the Raman spectrum of **6** prepared with mixed-labeled hydrogen peroxide. The spectrum was recorded in CHCl$_3$ at -40 °C with an excitation at 514.5 nm. The isotope population ratio in the mixed hydrogen peroxide was ca. 1:2:1 for $^{16}O^{16}O:^{16}O^{18}O:^{18}O^{18}O$. In the frequency region where the O–O stretching vibration of a peroxide ion was expected, a single band was observed at 731 cm^{-1} with **6** prepared from H$_2^{16}O_2$. The band was shifted to 691 cm^{-1} with ^{18}O-labeled **6** prepared from H$_2^{18}O_2$ (in CH$_2$Cl$_2$, the $^{16}O-^{16}O$ band was observed at 725 cm^{-1}, which was shifted to 686 cm^{-1} with ^{18}O-labeled **6**).[13] In spectrum A, a single additional band was observed at 712 cm^{-1}, which is

(35) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047–1054.
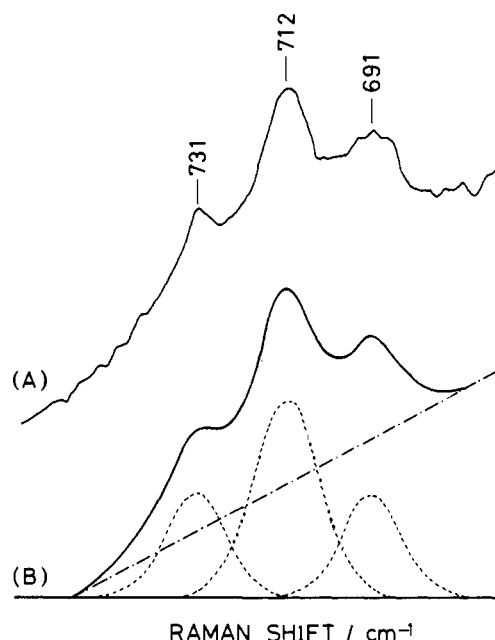
(36) The superoxo structure was identified solely on the basis of the IR band at 1015 cm^{-1} attributable to $\nu(^{18}O-^{18}O)$; the band due to $\nu(^{16}O-^{16}O)$ was not observed in the 1000–1200-cm^{-1} region because of the overlapping of the ligand bands according to Thompson.[9b]

(37) The inconsistent results of our and Thomson's experiments may be due to the similar spectroscopic properties of these two complexes obtained by the different preparation methods. Our preliminary resonance Raman studies indicated that treatment of Cu(Cl)(HB(3,5-(iPr)$_2$pz)$_3$) with 1 equiv of KO$_2$ results in formation of a complex that is not [Cu(HB(3,5-(iPr)$_2$pz)$_3$)]$_2$(O$_2$) but can possibly be described as a superoxo complex. Surprisingly, the absorption and ^{1}H NMR spectra of the complex are very similar to those of the μ-η^2:η^2 peroxo complex. This controversial problem is now under investigation.

assigned to $\nu(^{16}O-^{18}O)$. The isotopic frequency shifts for $\nu(^{16}O-^{18}O)$ $(-19\ cm^{-1})$ and $\nu(^{18}O-^{18}O)$ $(-40\ cm^{-1})$ are in reasonable agreement with the calculated values, implying that the O–O stretching vibration couples little with other vibrations of the Cu–N$_3$ moiety. Spectrum B in Figure 8 indicates a statistical combination of the background and Gaussian components of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ bands (1:2:1 ratio; half-line width 18 cm^{-1} each). The spectrum simulates spectrum A very well, suggesting the presence of only one structure for the binding of $^{16}O^{18}O$ to two Cu^{2+} ions. Accordingly, the symmetric coordination of the peroxide ion is concluded. This contrasts with the results for the dinuclear μ-peroxo copper(II) complex [Cu$_2$(XYL-O)O$_2$]$^+$ [XYL-O denotes 2,6-bis[N,N-bis(2-pyridylethyl)aminomethyl]-phenolate], which gave a broad Raman band for the $\nu(^{16}O^{18}O)$ mode and thus suggested asymmetric coordination of the peroxide ion.[42] A Raman band assignable to the Cu–O stretching vibration was not identified in the 300–500-cm^{-1} region with an excitation at 514.5 nm.

The characteristic properties of **6** described above are all comparable to those of [Cu(HB(3,5-iPr$_2$pz)$_3$)]$_2$(O$_2$) (diamagnetic; UV–vis 345 nm (ϵ 20 000), 551 (790); ν(O–O) 741 cm^{-1} with a symmetric coordination mode).[14] Therefore, it is concluded that the coordination mode of the peroxide ion in **6** is the same as in [Cu(HB(3,5-iPr$_2$pz)$_3$)]$_2$(O$_2$), in which the μ-η^2:η^2 coordination structure of the peroxide has been established by X-ray crystallography.[14]

The properties of **6** and of [Cu(HB(3,5-iPr$_2$pz)$_3$)]$_2$(O$_2$) closely mimic the characteristics of oxyHc and oxyTyr.[38] This may imply that the N$_3$Cu–O$_2$–CuN$_3$ chromophore in **6** is structurally very similar to that in those proteins. Accordingly, we propose the possibility that the coordination mode of the peroxide ion in these proteins is μ-η^2:η^2, although more adequate characterizations, especially on the solid sample of the peroxo complex, are required to confirm the conclusion. The biological relevance of this novel coordination mode of the peroxide ion will be discussed in more detail in our future publications.

Complex **6** is thermally unstable, and at room temperature in noncoordinating solvents such as CHCl$_3$ under anaerobic conditions, it decomposes to **3**. Carbon monoxide and PPh$_3$ treatment of **6** causes release of dioxygen and results in the formation of the copper(I) complexes **1** and **2**, respectively. The details of the reactions and the mechanisms have been described elsewhere.[15]

Reaction of 6 with CO$_2$. Many transition-metal peroxo complexes are known to be nucleophilic, reacting with CO$_2$ to afford carbonato complexes.[39] Treatment of **6** with CO$_2$ in CHCl$_3$ at room temperature resulted in quantitative formation of **5**. However, no reaction proceeded at –20 °C. Since **6** decomposes to **3** at room temperature, whereas it is stable at –20 °C, these results imply that the formation of **5** proceeds via **3**; **3** reacts readily with CO$_2$ to afford **5**, as described above. In order to ascertain this explanation, the consumption rates of **6** under Ar and pure CO$_2$ at 25 °C were compared. The consumption rates of **6**, determined from the time-dependent disappearance of the characteristic absorption band of **6** at 530 nm, were found to be first order with respect to the concentration of **6** under both Ar and CO$_2$. The first rate constant determined under pure CO$_2$ was identical with that of the spontaneous decomposition of **6** to **3**. This result clearly established that the rate-determining step for the formation of **5** from **6** is the spontaneous decomposition of **6** to **3**, and thereby it is conclusive that **3** is responsible for the formation of **5** and **6** at room temperature.

Karlin et al. synthesized three types of dinuclear μ-peroxo copper(II) complexes and compared their reactivities toward CO$_2$.[40] Two of the complexes (coordination mode of the peroxide ion: asymmetric terminal and trans-μ-1,2) are reactive. On the
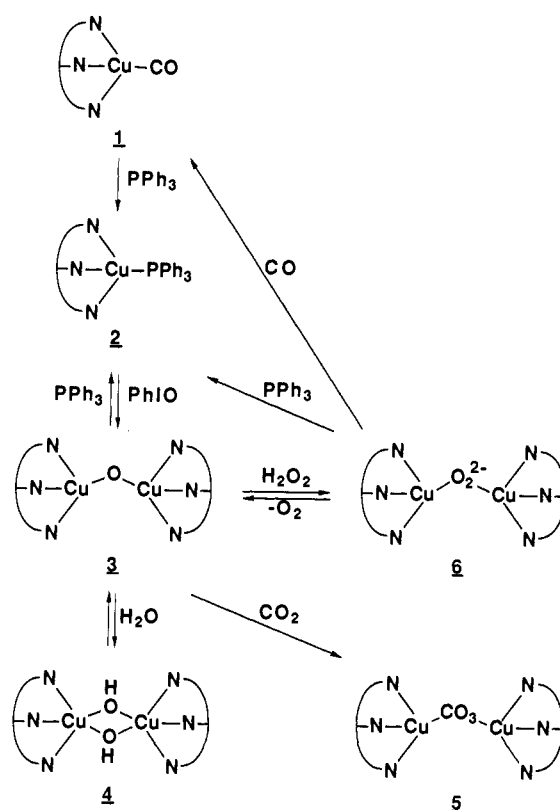

Figure 9.

other hand, the other one (the structure has not been established, but the bent μ-η^2:η^2 structure was proposed as the most likely one, whereas the possibility of cis-μ-1,2 cannot be ruled out[41]) does not react with CO$_2$. On the basis of the inertness to CO$_2$ and other reaction behavior that is unique among the three types of the complexes, they suggested that the complex is electrophilic, whereas the former two peroxo complexes are apparently nucleophilic. Given the structure of Karlin's complex as a μ-η^2:η^2, similar reactivity may be expected for **6**. In fact, **6** was found to be much less reactive to CO$_2$ than **3**. Nevertheless, this does not necessarily mean that **6** is electrophilic, because there was no such experimental implication, as we reported previously; complex **6** does not show any oxo-transfer reactivity to the substrates such as PPh$_3$ and olefin, whereas an electrophilic peroxo complex may be expected to be effective for such reactions.[15] Thus, further investigations should be required for the conclusive ascertainment of the general reactivity of μ-η^2:η^2 peroxo dinuclear copper(II) complexes.

Conclusions. The synthetic routes and reactions of **1–6** are summarized in Figure 9. The dinuclear μ-oxo copper(II) complex **3** is reasonably stable in noncoordinating solvents such as CHCl$_3$; however, in methanol, it decomposes to a disproportionation product Cu[HB(3,5-Me$_2$pz)$_3$]$_2$.[31] Because of its strong nucleophilic properties, **3** reacts with H$_2$O, CO$_2$, and H$_2$O$_2$ to give the bis(μ-hydroxo), μ-carbonato, and μ-peroxo dinuclear complexes **4–6**, respectively. These dinuclear copper(II) complexes are all antiferromagnetically coupled. ^{1}H NMR spectra provide a very useful tool to characterize these species, although the technique has been scarcely applied to copper(II) systems.

The dinuclear μ-peroxo complex **6** is thermally unstable and spontaneously decomposes to the μ-oxo complex **3**. The addition of CO and PPh$_3$ results in rapid displacement of dioxygen from **6**, affording **1** and **2**, respectively. Low-temperature treatment of **6** with CO$_2$ does not cause any reaction, while **5** is formed at room temperature, via **3**, formed by the decomposition of **6**. Thus,

(38) (a) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1–57. (b) Solomon, E. I. *Pure Appl. Chem.* **1983**, *55*, 1069–1088.

(39) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1–65.

(40) Tyeklar, Z.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 388–389.

(41) Blackburn, N. J.; Strange, R. W.; Farooq, A.; Haka, M. S.; Karlin, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 4263–4272.

(42) Pate, J. E.; Cruse, R. W.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 2624–2630.

the nucleophilic properties of **6** are weaker than those of **3**. Complex **6** shows many physicochemical similarities to [Cu-(HB(3,5-iPr$_2$pz)$_3$)]$_2$(O$_2$), which contains the μ-η^2:η^2 coordination mode of the peroxide ion, and it is concluded that **6** also has the same particular coordination structure.

Supplementary Material Available: Tables S-I–S-V, giving the summary of X-ray analyses, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2**, **4**·2C$_6$H$_6$, and **5** (26 pages); Table S-VI, listing observed and calculated structure factors for complexes **2**, **4**·2C$_6$H$_6$, and **5** (28 pages). Ordering information is given on any current masthead page.

Carbon–Hydrogen, Carbon–Oxygen, and Carbon–Carbon Bond Activation by an Electrophilic Ruthenium Complex

Deyanira Rondon, Bruno Chaudret,* Xiao-Dong He, and Daniel Labroue

Contribution from the Laboratoire de Chimie de Coordination, UPR 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205, route de Narbonne, 31077 Toulouse Cedex, France. Received December 4, 1990

Abstract: The "Cp*Ru$^+$" fragment generated by protonation of [Cp*Ru(OMe)]$_2$ with CF$_3$SO$_3$H reacts in CH$_2$Cl$_2$ or THF with cyclic C$_6$ alkenes, dienes, alcohols, ketones, enones, and diones to yield coordinated aromatic derivatives after C–H, C–O, or C–C activation. The following transformations have been performed: cyclohexene and methylcyclohexene into benzene and toluene; 1,3- or 1,5-cyclooctadiene into 1,3,5-cyclooctatriene; cyclohexanol, cyclohexanone, or cyclohexenone into benzene; methylcyclohexenone into toluene; cyclohexanedione into phenol; 4,4-dimethylcyclohexenone and isophorone into 4-methylphenol and 3,5-dimethylphenol. The byproducts of these reactions are H$_2$, H$_2$O, CH$_4$, and some C$_2$H$_6$. The conversions have been optimized and reach 100% for the three types of activation. The selectivity is better than 99% for C–H and C–O activation. In the case of *gem*-dimethyl enones, the formation of phenol derivatives is accompanied by the formation of their methyl ethers, but this problem can be circumvented. The mechanism of the reactions shows classical C–H activation and hydrogen-transfer processes to occur at the early stage of all the reactions. This is followed by H$_2$ elimination possibly through an unstable dihydrogen intermediate, H$_2$O elimination from a compound containing a coordinated OH group, or C–C bond breaking. The last process involves a radical pathway, as evidenced by the observation of C$_2$H$_6$ in the gaseous phase.

Introduction

Much interest has been devoted in the last decade to the activation of the carbon–hydrogen bond and to the functionalization of alkanes.[1] Several approaches have been used, including the utilization of electron-rich organometallic complexes able to insert into unactivated C–H bonds.[2] This approach has been used to develop a photochemical catalytic process for the selective functionalization of alkanes.[3] Early transition metals have been found to exhibit a different reactivity which has led to the novel concept of "σ-bond metathesis"[4] and recently to productive catalytic reactions.[5] A third approach has been the use of electrophilic platinum metal derivatives such as cationic complexes of platinum[1a] or palladium.[1e] In that case, methane activation and functionalization have even been possible.

Although numerous systems have been found to activate carbon–hydrogen bonds, much less is known about carbon–carbon bond activation. This process has been well documented in superacidic media,[6] but it has been much more difficult to observe in the presence of soluble tansition-metal complexes, whether electron rich or electrophilic.[7,8] Furthermore, it almost exclusively concerns strained hydrocarbons. However, Bercaw et al. recently demonstrated that highly Lewis acidic scandium complexes are able to catalytically isomerize hydrocarbons such as pentadienes through carbon–carbon bond cleavages.[8] Similar reactions have been found by Sen et al. using [Pd(MeCN)$_4$]$^{2+}$.[1e]

Concerning the carbon–oxygen bond activation, the dehydration of alcohol is a classical process in acidic media,[9] but again, C–O bond cleavage mediated by metal complexes is much more unusual. A recent example of a clean C–O bond cleavage was reported by Mayer et al.[10]

The chemistry of half-sandwich ruthenium complexes containing the pentamethylcyclopentadienyl (Cp* = η^5-C$_5$Me$_5$) ligand has

(1) (a) Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel Publishing Co.: Dordrecht, Holland, 1984; pp 142–181. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (d) Ephritikhine, M. *Nouv. J. Chim.* **1986**, *10*, 9. (e) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421.
(2) See: (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) Jones, W. A.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620.
(3) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221.
(4) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
(5) (a) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 779. (b) Guram, A. S.; Jordan, R. F. *Organometallics* **1990**, *9*, 2190.

(6) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.
(7) See for example: (a) Benfield, F. W. C.; Green, M. L. H.; *J. Chem. Soc., Dalton Trans.* **1974**, 1325. (b) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 1429, 3136; **1980**, *113*, 542, 1033, 1420, 2211. (c) Suggs, J. W.; Cox, S. D. *J. Organomet. Chem.* **1981**, *221*, 199. (d) Crabtree, R. H.; Dion, R. B.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (e) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (f) Geiger, W. E.; Salzer, A.; Edwin, J.; Von Philipsborn, W.; Piantini, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113.
(8) Bunuel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.
(9) March, J. *Advanced Organic Chemistry*; John Wiley and Sons: New York, 1985; pp 344, 345, 901.
(10) Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413.