

Figure 1. ORTEP drawing of (2-methyl-1,3,4,5- η -pentenediyl)Ru(PMe₃)(PPh₃)(CO) (**2c**). Selected bond distances and angles: Ru-C1, 2.167 (5) Å; Ru-C3, 2.290 (6) Å; Ru-C4, 2.223 (5) Å; Ru-C5, 2.237 (4) Å; C1-C2, 1.530 (10) Å; C2-C3, 1.520 (8) Å; C2-C6, 1.522 (8) Å; C3-C4, 1.383 (7) Å; C4-C5, 1.410 (9) Å; Ru-C1-C2, 97.5 (4)°; C1-C2-C6, 115.5 (6)°; C1-C2-C3, 103.8 (4)°; C3-C2-C6, 113.9 (5)°; C2-C3-C4, 123.8 (5)°; C3-C4-C5, 123.7 (5)°; C4-C5-Ru, 71.0 (2)°; C1-Ru-C5, 81.0 (2)°.

case, attack occurs with $\geq 95\%$ diastereoselectivity on the "L-side" of the pentadienyl ligand, i.e., at the internal pentadienyl carbon which resides above ligand L and opposite the bulky PPh₃ ligand. It is interesting to note that even when L is electron-withdrawing (e.g., CO or CNCMe₃) and the pentadienyl carbons trans to it (C4 and C5) are therefore relatively electron-poor,¹⁰ "L-side" attack (at C2) is still observed. Hence in this system, the site of nucleophilic attack is determined by steric factors, not by small electronic differences between the two sides of the pentadienyl ligand.

The solid-state structure of **2c**, derived from a single-crystal X-ray diffraction study, is shown in Figure 1.¹¹ As expected, attack occurs exo to the [Ru(PMe₃)(PPh₃)(CO)]⁺ fragment, displacing the attacked carbon, C2, 0.73 Å out of the C1/C3/C4/C5 plane; C2 resides 2.81 Å from the ruthenium atom. The dihedral angle between plane C1/C3/C4/C5 and plane C1/C2/C3 is 50.8 (4)°. Within the 1,3,4,5- η -pentenediyl ligand, carbon-carbon bonds C1-C2 and C2-C3 exhibit normal single-bond lengths, while C3-C4 and C4-C5 exhibit typical allylic bond distances (see caption to Figure 1).

The site of nucleophilic attack in compounds **2c** and **2d** can be unambiguously determined from their NMR spectra. Particularly diagnostic is the strong P-C coupling exhibited by pentenediyl carbon C1. This strong coupling (50 Hz in **2c** and 55 Hz in **2d**) indicates that C1 resides trans to a phosphine ligand, which, in turn, requires that nucleophilic attack must be "L-side". Inter-

pretation of **2e**'s NMR spectra is less straightforward because, in this case, C1 resides trans to a phosphine ligand regardless of the site of attack. However, a preliminary X-ray diffraction study of **2e** has confirmed "L-side" attack.¹²

In summary, we have demonstrated that electron-rich (pentadienyl)ruthenium cations undergo regioselective nucleophilic attack at internal carbon C2 of the pentadienyl ligand. The [Ru(PMe₃)(PPh₃)(L)]⁺ fragment serves as an effective chiral auxiliary, directing diastereoselective addition to the less hindered side of the pentadienyl ligand. Work currently in progress is directed toward (a) obtaining optically pure ruthenium cations and (b) effecting further transformations of the pentenediyl ligand. Results of these studies will be reported in the future.

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Supplementary Material Available: Detailed descriptions of the syntheses and spectra of compounds **1b-e** and **2c-e** and tables of structure determination summaries, final atomic coordinates, thermal parameters, bond lengths, bond angles, and significant least-squares planes for **2c** (17 pages); listing of observed and calculated structure factor amplitudes for **2c** (22 pages). Ordering information is given on any current masthead page.

(12) Blecke, J. R.; Rauscher, D. J., unpublished results.

Nucleophile-Assisted Cleavage of Silane Cation Radicals

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Nucleophilic addition to π organic cation radicals is commonly observed in many one-electron oxidation reactions.¹ In contrast, the nucleophilic cleavage of cation radical σ bonds is much less common.² This latter process is of considerable mechanistic

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(2) The photooxidative ring-opening reactions of several strained-ring compounds may involve the nucleophilic cleavage of one-electron σ bonds.^{2a-8} Also, the deprotonation of cation radicals may be viewed as the nucleophilic cleavage of a σ bond. (a) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458. (b) Mizuno, K.; Ogawa, J.; Kagano, H.; Otsuji, Y. *Chem. Lett.* **1981**, 437. (c) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741. (d) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (e) Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740. (f) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6828. (g) Mazzocchi, P. H.; Somich, C. *Tetrahedron Lett.* **1988**, *29*, 513.

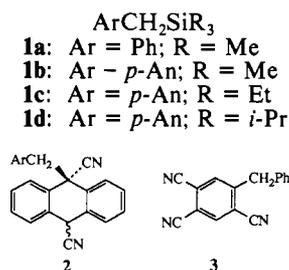
(9) Representative Synthesis of **2c**. Methylolithium (0.50 mL, 1.4 M in diethyl ether, 7.0×10^{-4} mol) was added to a stirred slurry of **1c** (0.39 g, 6.2×10^{-4} mol) in 50 mL of cold (-78°C) tetrahydrofuran. The mixture was warmed to room temperature, stirred for 1 h, and filtered. The tetrahydrofuran solvent was reduced in vacuo to yield an orange oil. The oil was dissolved in 50 mL of diethyl ether, filtered, reduced in vacuo to approximately 10 mL, and then cooled to -30°C , to precipitate **2c** as yellow-orange crystals (0.16 g, 47%).

(10) In the ¹³C NMR of [(η^5 -pentadienyl)Ru(PMe₃)(PPh₃)(CO)]⁺BF₄⁻ (**1c**), for example, C2 and C4 resonate at δ 99.1 and δ 112.7, respectively, indicating greater positive charge on C4.

(11) Crystal data for **2c**: monoclinic, space group *P2₁/n*, *a* = 15.980 (4) Å, *b* = 10.945 (3) Å, *c* = 16.541 (5) Å, β = 113.62 (2)°, *V* = 2650.7 (13) Å³, *Z* = 4, *d*_{calcd} = 1.377 g/cm³, μ = 7.15 cm⁻¹; Nicolet P3 diffractometer, Mo K α radiation, 22 °C; 6090 unique reflections with $4^\circ < 2\theta < 55^\circ$ collected, 3945 reflections with *I* > 3 σ (*I*) used in refinement; empirical absorption correction (ψ scans); *R* = 0.0352, *R*_w = 0.0381, GOF = 1.73.

interest since it can formally be viewed as the addition of a nucleophile to a one-electron bond. We describe, herein, experimental evidence for the cleavage for several benzyltrialkylsilane cation radicals by this latter reaction pathway.

Our work began with the observation that 9,10-dicyanoanthracene (DCA) photosensitized oxidation of benzyltrimethylsilane (**1a**) leads to efficient formation of adduct **2a**, as a cis/trans mixture, with a quantum yield of 0.2.³ This reaction is rationalized in terms of cleavage of the carbon-silicon bond in the silane cation radical (**1a^{•+}**) to yield a benzyl radical that adds to the DCA⁻, followed by protonation. The lifetime of **1a^{•+}** is estimated to be ca. 1 ns since the reaction is quenched inefficiently by low oxidation potential compounds such as 1,2,4-trimethoxybenzene, and the fragmentation process seems to compete with separation of the geminate ion radical pair. Accordingly, irradiations performed in the presence of 1,2,4,5-tetracyanobenzene (TCB), which undergoes secondary electron transfer with those DCA⁻ which escape the geminate pair to form TCB⁻, result in the formation of both adducts **2a** ($\Phi = 0.04$) and **3** ($\Phi = 0.16$). This indicates that 20% of the **2a** is formed within the primary geminate ion radical pair.



The extremely rapid fragmentation of **1a^{•+}** is remarkable because the one-electron bond dissociation energy of the benzylic C-Si bond is estimated to be ca. 30 kcal/mol,⁴ which precludes a unimolecular cleavage mechanism. This suggests an alternative mechanistic possibility, namely, nucleophilic participation by the solvent, as previously suggested by Mariano.⁵

This mechanism implies that the lifetime of the cation radical should increase as the steric demands at silicon increase. The lifetime of **1a^{•+}** is too short to be measured conveniently with time-resolved methods. We therefore decided to look for steric effects on the lifetimes of (*p*-methoxybenzyl)trialkylsilane cation radicals which we anticipated would be longer lived⁶ and thus be more amenable for study with nanosecond laser flash photolysis.

(3) For leading references to the photooxidative cleavage reactions of organosilanes see: (a) Mariano, P. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 9, p 1. (b) Xu, W.; Jeon, Y. T.; Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 406. (c) Mizuno, K.; Terasaka, K.; Igeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1985**, 5819.

(4) The bond dissociation energy of the benzylic C-Si bond in **1a^{•+}**, BDE(CR), was calculated from the following equation, BDE(CR) = BDE(PhCH₂-SiMe₃) - IP(PhCH₂SiMe₃) + IP(*SiMe₃). The bond dissociation energy was estimated to be 75 kcal/mol by taking the BDE for CH₂=CHCH₂SiMe₃ (73 kcal/mol)^{4a} and adding the difference between the "resonance stabilization energies" for the allyl radical (12 kcal/mol)^{4b} and the benzyl radical (10 kcal/mol).^{4b} The ionization potential (IP) of PhCH₂SiMe₃ (8.35 eV) was from ref 4c. The IP of *SiMe₃ was determined from the difference between ΔH_f° (*SiMe₃) = 147 kcal/mol^{4d} and ΔH_f° (SiMe₃) = -1 kcal/mol.^{4e} Although the estimate for BDE(CR) is for the gas phase, previous work^{4f} has shown that gas phase cation radical bond dissociation energies are often quite similar to those in solution. (a) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *202*, C65. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Pitt, C. G.; Bock, H. *J. Chem. Soc., Chem. Commun.* **1972**, 28. (d) Walsh, R. *J. Phys. Chem.* **1986**, *90*, 389. (e) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (f) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. *Chem. Phys. Lett.* **1986**, *131*, 189.

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(6) Thermodynamic cycle calculations (ref 4) suggested that the (*p*-methoxybenzyl)silane cation radicals should have stronger one-electron bonds due to the lower oxidation potentials of the silanes. The oxidation potentials (E_p) of **1a** (1.78 V), **1b** (1.31 V), **1c** (1.30 V), and **1d** (1.28 V) were obtained by cyclic voltammetry (150 mV/s) at a platinum disk electrode in acetonitrile with ca. 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte and were irreversible. The potentials were referenced to internal ferrocene (0.31 V vs SCE).

Table I. Rates of Decay of (*p*-Methoxybenzyl)trialkylsilane Cation Radicals in Acetonitrile and Rate Constants for Nucleophile-Assisted Cleavage by Alcohols

<i>p</i> -AnCH ₂ SiR ₃ ^{•+}	$(k_a)_{\text{CH}_3\text{CN}}^a$	rate constant (M ⁻¹ s ⁻¹) ^b		
		k_m	k_i	k_t
R = Me	(2.3 × 10 ⁶ s ⁻¹)	5.5 × 10 ⁶	9.7 × 10 ⁵	4.1 × 10 ⁵
R = Et	(1.3 × 10 ⁶ s ⁻¹)	3.1 × 10 ⁵	8.6 × 10 ⁴	<i>c</i>
R = <i>i</i> -Pr	(<4 × 10 ³ s ⁻¹)	<i>c</i>	<i>c</i>	<i>c</i>

^a First-order rates of decay of silane cation radicals in neat acetonitrile. ^b k_m , k_i , k_t are the second-order rate constants for reaction of the silane cation radicals with methyl, isopropyl, and *tert*-butyl alcohol, respectively. ^c Rate was too slow to measure.

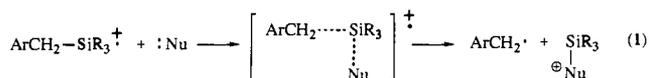
For the laser experiments, the silanes were oxidized with biphenyl cation radical as a secondary electron-transfer cosensitizer^{1a} in order to obtain a high quantum yield of "free" silane cation radicals. Furthermore, to avoid spectral interference from DCA⁻, the flash photolysis solution were purged with dioxygen. The DCA⁻ formed in these experiments reacted with dioxygen to form superoxide, which was optically transparent in the spectral region of interest.

Pulsed laser excitation (410 nm, 15 ns, 5 mJ) of a dioxygen saturated acetonitrile solution of DCA (ca. 10⁻⁵ M) in the presence of biphenyl (0.25 M) and silane **1b⁷** (10⁻³ M) resulted in rapid decay (<100 ns) of the biphenyl cation radical absorbance ($\lambda_{\text{obs}} = 650$ nm) with concomitant formation of a transient species with a λ_{max} at 500 nm. This species decayed with clean first-order kinetics ($k_a = 2.31(7) \times 10^6$ s⁻¹) and reacted rapidly with 1,2,4,5-tetramethoxybenzene (TMB) ($k_q = 9.7(5) \times 10^9$ M⁻¹ s⁻¹) and with tri-*p*-tolylamine ($k_q = 9.6(4) \times 10^9$ M⁻¹ s⁻¹) to form the corresponding aminium ion ($\lambda_{\text{max}} = 670$ nm).

Steady-state photolysis of DCA and **1b** in an argon-purged acetonitrile solution with no added cosensitizer resulted in the formation of adduct **2b**. Using TMB as a quencher gave a Stern-Volmer slope ($k_q\tau$) of 3.9(4) × 10³ M⁻¹ at 29 °C. At this temperature, k_q/k_a determined from flash photolysis was 3.7(1) × 10³ M⁻¹, in good agreement with the steady-state experiment.

The combined flash photolysis and steady state photolysis experiments strongly support the assignment of the 500-nm transient species to **1b^{•+}**.

Flash photolysis of solutions containing **1c** and **1d** produced similar transients with absorption maxima essentially the same as that attributed to **1b^{•+}**, which we thus assign to **1c^{•+}** and **1d^{•+}**. Importantly, both of these species decayed more slowly than did **1a^{•+}** (see k_a Table I). Although the effect was rather subtle for **1c^{•+}**, it was quite substantial for **1d^{•+}**. These kinetic data are consistent with cleavage of the silane cation radicals by a nucleophilic mechanism (eq 1). We presume the solvent, acetonitrile, is acting as the nucleophile in this case and that the lifetimes of the silane cation radicals increase as the steric requirements at silicon are increased.



More direct evidence for this mechanism is provided by experiments in which nucleophiles were added to compete with acetonitrile. Alcohols were effective in this regard, as the rate constants for decay of **1b^{•+}** and **1c^{•+}** both increased with added methyl alcohol. Plots of these rate constants vs methyl alcohol concentration were linear and the second-order rate constants for reaction of methyl alcohol with **1b^{•+}** and **1c^{•+}** were obtained from the slopes (k_m , Table I). Importantly, quantum yield studies demonstrated that the addition of methyl alcohol did not inhibit product formation. Thus, steady-state photolysis of **1b** in the presence of a sufficient concentration of methyl alcohol (1.0 M) to trap ca. 70% of **1b^{•+}** resulted in a quantum yield for product formation that was indistinguishable from the reaction in neat acetonitrile. These results are consistent with assisted cleavage

(7) The (*p*-methoxybenzyl)trialkylsilanes were prepared according to Coughlin, D. J.; Salomon, R. G. *J. Org. Chem.* **1979**, *44*, 3784.

of the silane cation radical by both acetonitrile and methyl alcohol after diffusional separation from the geminate ion radical pair.⁸ This conclusion is consistent with the lifetimes of **1b-d⁺** being considerably longer than those expected for the geminate pairs.⁹

The nucleophilic cleavage mechanism makes the additional prediction that the cleavage rates of the silane cation radicals should decrease as the steric demands of the nucleophile increase. This prediction is borne out by the steady decrease in the rate constants for the reaction of the silane radical cations with methyl alcohol (k_m), isopropyl alcohol (k_i), and *tert*-butyl alcohol (k_t) (Table I).

In summary, the cleavage of benzyltrialkylsilane cation radicals in acetonitrile is most consistent with a mechanism involving nucleophilic participation by the solvent. This mechanistic insight will undoubtedly be useful in more profitably utilizing silane cation radical cleavage reactions.

Acknowledgment. The authors are grateful to the National Science Foundation for a Science and Technology Center Grant (CHE-8810024).

(8) Mariano and co-workers⁵ found similar *product formation* quantum yields for a series of allyltrialkylsilane cation radicals with different substituents at silicon and concluded from this that, if a nucleophilic displacement mechanism was operating, it must be insensitive to the steric environment at silicon. Presumably their reactions, like ours, simply occur out of the geminate pair and thus the quantum yield for product formation is an insensitive probe of cation radical reactivity.

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μ - η^2 : η^2 -Peroxo Binuclear Copper Complex, $[\text{Cu}(\text{HB}(3,5\text{-iPr}_2\text{pz})_3)]_2(\text{O}_2)$

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Considerable efforts have been made in the synthesis and structural characterization of μ -1,2-peroxy binuclear copper(II) complexes, since such a moiety is known to exist in oxygen binding states of hemocyanin (Hc) and tyrosinase (Tyr).¹ Very recently, Karlin et al. have reported the crystal structure of $[\text{CuL}]_2(\text{O}_2)^{2+}$ (L = tris[(2-pyridyl)methyl]amine), which definitely established the presence of trans μ -1,2 coordination of a peroxide ion.² However, the Cu...Cu distance (4.359 (1) Å) and the electronic spectrum of the complex are significantly different from those of oxy-Hc and oxy-Tyr. On the other hand, we³ have reported the synthesis of a μ -peroxy binuclear complex, $[\text{Cu}(\text{HB}(3,5$

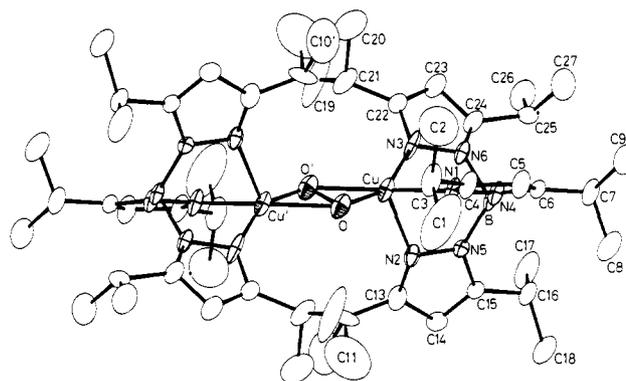
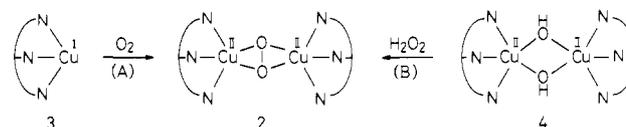


Figure 1. ORTEP view of **2** (30% probability). The molecule sits on the center of symmetry. CH_2Cl_2 molecules of crystallization were omitted. Selected bond distances (Å) and angles (deg) are as follows: Cu...Cu, 3.560 (3); Cu-O, 1.903 (11), Cu-O', 1.927 (9); O-O', 1.412 (12); Cu-N1 2.000 (8); Cu-N2, 2.258 (8); Cu-N3, 1.993 (14); O-Cu-O', 43.3 (4); Cu-O-Cu', 136.7 (5); Cu-O-O', 69.3 (6); Cu'-O-O', 67.4 (5); N1-Cu-O, 107.2 (4); N1-Cu-O', 148.8 (4); N2-Cu-O, 114.2 (4); N2-Cu-O', 111.5 (3); N3-Cu-O, 150.4 (4); N3-Cu-O', 111.3 (4); N1-Cu-N2, 88.5 (3); N1-Cu-N3, 92.7 (4); N2-Cu-N3, 87.4 (4).

Scheme I



$\text{Me}_2\text{pz}_3)]_2(\text{O}_2)$ (**1**), which shows remarkable physicochemical similarities to oxy-Hc and oxy-Tyr. In this communication, we report the crystal structure of the analogous complex $[\text{Cu}(\text{HB}(3,5\text{-iPr}_2\text{pz})_3)]_2(\text{O}_2)$ (**2**), which contains the novel coordination mode of the peroxide ion, μ - η^2 : η^2 .

2 is prepared either by direct O_2 addition to copper(I) complex $[\text{Cu}(\text{HB}(3,5\text{-iPr}_2\text{pz})_3)]$ (**3**)⁴ (method A) or by H_2O_2 treatment of $[\text{Cu}(\text{HB}(3,5\text{-iPr}_2\text{pz})_3)]_2(\text{OH})_2$ (**4**)⁵ (method B) (Scheme I). The reaction of **3** with O_2 in acetone at -78°C for 2 h gave the intensely purple colored solution of **2**. The manometric measurement of the consumed amount of O_2 conforms to the formation of **2**. The reduction of the solvent under vacuum at -20°C followed by cooling at -78°C afforded **2** as deep purple solids in an essentially quantitative yield. In a manner analogous to that for the preparation of **1**,³ **4** was reacted with an excess amount (ca. 3 equiv) of H_2O_2 (30% aqueous solution) at -20°C in CH_2Cl_2 . The solution immediately turned deep purple. **2** was also isolable from the solution. The spectroscopic characterization of **2** established that the properties of **2** are closely similar to those of **1** and also oxy-Hc (-Tyr).⁶

Slow recrystallization from the CH_2Cl_2 solution at -30°C , which was prepared by method B, gave single crystals of $2 \cdot 6\text{CH}_2\text{Cl}_2$. As shown in Figure 1, two $[\text{Cu}(\text{HB}(3,5\text{-iPr}_2\text{pz})_3)]^+$ units bridged by a peroxide ion form a binuclear complex, which sits on a center of symmetry.⁷ The O-O distance (1.412 (12) Å)

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(6) A satisfactory elemental analysis was obtained for **2** dried under vacuum at -20°C . Anal. Calcd for $\text{C}_{54}\text{H}_{52}\text{N}_{12}\text{O}_2\text{B}_2\text{Cu}_2$: C, 59.50; H, 8.51; N, 15.42. Found: C, 58.94; H, 8.54; N, 15.27. UV-vis (CH_2Cl_2 , -12°C): 349 (ϵ , 21 000), 551 nm (800). Raman (Me_2CO , -40°C) (^{16}O - ^{18}O): 741 cm^{-1} . The Raman study with the mixed-isotope dioxygen established the symmetric coordination of the peroxide ion as in oxy-Hc: (^{16}O - ^{18}O) 719, (^{18}O - ^{18}O) 698 cm^{-1} . ^1H NMR (toluene- d_8 , -10°C , δ , ppm): 1.27 (d, 36 H, Me_2CH), 1.48 (d, 36 H, Me_2CH), 3.68 (m, 6 H, Me_2CH), 3.95 (m, 6 H, Me_2CH), 6.09 (s, 6 H, pz). (The chemical shifts of the pyrazole ring proton for the copper(I) complexes are 5.7-6.1 ppm.) EPR: silent in CH_2Cl_2 at -196°C ; 0 μB by Evans method at -10°C . These properties of **2** (as well as **1**)³ closely mimic the characteristics of oxy-Hc¹ (mollusks): diamagnetic; UV-vis 345 (ϵ , \sim 20 000), 570 nm (\sim 1000); Raman (^{16}O - ^{18}O) 749, (^{16}O - ^{18}O) 728, (^{18}O - ^{18}O) 708 cm^{-1} . Further details of the preparation and properties of **2** will be reported elsewhere.

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