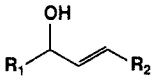
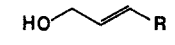
Table I. Relative Rates of Epoxidation[a]



compd	R_1	R_2	rel $k_{m\text{-CPBA}}$[b]	rel k_{ti}[c]	rel k_s[d]	rel k_f[e]	k_f/k_s
3	c-C_6H_{11}	Me	1.0	1.0	1.0	1.0	104
4	c-C_6H_{11}	t-Bu	0.93	0.31	0.43	1.25	300
5	Me	n-C_5H_{11}		0.460	0.63	0.98	160
6	Me	c-C_6H_{11}	1.15	0.44	0.45	1.44	330
7	Me	t-Bu		0.168		1.39	
2	n-C_5H_{11}	$SiMe_3$	0.174	0.052	0.040	0.268	700
8	n-C_5H_{11}	$SiEt_3$	0.144	0.036		0.149	
9	n-C_5H_{11}	$Si(i\text{-Pr})_3$	0.053	0.0120	0.010	0.029	300

[a] The relative rates are generally reproducible to within 5%. [b] Epoxidation by m-CPBA. [c] Epoxidation by $Ti(O\text{-}i\text{-Pr})_4$/TBHP. [d] Epoxidation of slow enantiomers by $[Ti(DIPT)(O\text{-}i\text{-Pr})_2]_2$/TBHP. [e] Epoxidation of fast enantiomers by $[Ti(DIPT)(O\text{-}i\text{-Pr})_2]_2$/TBHP.

Table II. Competition of Primary Allylic Alcohols[a]



compd	R	rel k_f'[b]	rel k_{ti}'[c]
10	n-C_5H_{11}	1.0	1.0
11	c-C_6H_{11}	1.80	0.91
12	1-Ad	2.2	0.74

[a] The relative rates are generally reproducible to within 5%. [b] Epoxidation by $[Ti(DIPT)(O\text{-}i\text{-Pr})_2]_2$/TBHP. [c] Epoxidation by $Ti(O\text{-}i\text{-Pr})_4$/TBHP.

not immediately apparent, and the small magnitude of it obliges caution in speculating on its origin. However, based on our understanding of the mechanism of the kinetic resolution, we expected to see acceleration of the rate of asymmetric epoxidation of primary allylic alcohols bearing bulky olefinic substituents relative to unhindered primary allylic alcohols. As shown in Table II, substrates **11** and **12** are indeed accelerated relative to **10** in epoxidation by $[Ti(DIPT)(O\text{-}i\text{-Pr})_2]_2$/TBHP.

Steric enhancement of rate is unprecedented in group transfer reactions such as epoxidation, and this selectivity cannot be rationalized in terms of inductive differences, since no such effect is manifested in the rel $k_{m\text{-CPBA}}$ experiments. However, completely analogous steric effects on the rates of epoxidation of fast and slow enantiomers had been seen previously with respect to increasing size of the tartrate ester group.[1b,d] Although the rel k_f, rel k_f' and tartrate ester results are hard to account for by conventional steric and electronic arguments, such selectivity is commonly observed in enzymic systems.[12] In fact, the observation that certain substrates react faster than smaller analogues bearing all the requisite functionality has been a primary focus in the development of modern theories of enzyme specificity.[13] Specificity for competing substrates has been shown to depend only on the relative binding of their transition states to the enzyme. The intriguing possibility then presents itself that the same types of substrate-active site interactions responsible for enzymic specificity also operate in the abiotic titanium–tartrate catalyst.[14]

Whatever the ultimate explanation for the rate acceleration of the fast enantiomer, the basic reasons for the enhanced kinetic resolution observed by Sato can now be clearly seen. Increasing steric bulk at the olefinic terminus (within the limits described above) increases the rate of epoxidation of the fast enantiomer and decreases the rate of epoxidation of the slow enantiomer. Thus the ratio k_f/k_s increases. The most efficiently resolved substrate is the one reported by Sato, **2**, with k_f/k_s = 700, an efficiency nearly five times greater than that of any substrate measured before.[15] The carbon-substituted substrates **4** and **6** are also resolved with an efficiency much greater than observed before, although not as well as Sato's compound. Compound **9** is not as efficiently resolved as **2**, due to the precipitous drop in rel k_f. In any case, the remarkable degree of selectivity documented here for the titanium–tartrate epoxidation catalyst indicates that abiotic catalysts can achieve the levels of chiral recognition formerly associated only with enzymic processes.

Acknowledgment. We thank the National Institutes of Health (Grant GM-28384) and the National Science Foundation (Grant CHE-8303355) for generous support of this work. G.S. thanks NATO for a postdoctoral fellowship.

(12) (a) Hexokinase: Jencks, W. P. In *Advances in Enzymology*; Meister, A., Ed.; John Wiley & Sons: New York, 1975; Vol. 43, p 223–224. (b) Isoleucyl-tRNA synthetase: Loftfield, R. B.; Eigner, E. A. *Biochim. Biophys. Acta* **1966**, *130*, 426. (c) Alanyl-tRNA synthetase: Tsui, W. C.; Fersht, A. R. *Nucl. Acids. Res.* **1981**, *9*, 4627. (d) Glycerophosphate acyltransferase: Kornberg, A.; Pricer, W. E. *J. Biol. Chem.* **1953**, *204*, 345. (e) Butyryl-CoA dehydrogenase: Green, D. E.; Mii, S.; Mahler, H. R.; Bock, R. M. *J. Biol. Chem.* **1954**, *206*, 1. (f) Butyryl-CoA synthetase: Mahler, H. R.; Wakil, S. J.; Bock, R. M. *J. Biol. Chem.* **1953**, *204*, 453.

(13) (a) Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W. H. Freeman and Company: New York, 1985; Chapters 12 and 13. (b) Dixon, M.; Webb, E. C. *Enzymes*, 3rd ed.; Academic Press: New York, 1979; Chapter 6, pp 231–270. (c) Reference 12a, pp 219–410.

(14) The analogy between titanium–tartrate and enzymic catalysts has been drawn before with respect to the issue of selectivity. Structurally, the catalyst has steric interaction-free pockets or grooves in which the substrates lie (see ref 1b and c), which could be considered analogous to active sites.

(15) Sato has recently reported kinetic resolutions of the iodo- and tri-*n*-butylstannyl-substituted analogues of **2**. The apparent kinetic resolution efficiencies reported for these substrates are consistent with the steric model described in this communication. (a) Kitano, Y.; Matsumoto, T.; Wakasa, T.; Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F; Miyaji, K.; Arai, K. *Tetrahedron Lett.* **1987**, *28*, 6351. (b) Kitano, Y.; Matsumoto, T.; Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F. *Chem. Lett.* **1987**, 1523.

Synthesis of Boroles and Their Use in Low-Temperature Diels–Alder Reactions with Unactivated Alkenes†

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The chemistry of boroles has not been studied extensively primarily because of the difficulty in generating these species synthetically.[1] The only known isolable monomeric boroles without annulated aromatic groups are derivatives of the sterically hindered 1,2,3,4,5-pentaphenylborole.[1,2] We have previously reported the preparation of main group heterocycles by metal-

† Contribution No. 4510.

(1) (a) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379–385. (b) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436–4437. (c) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1977**, *127*, C9–C13. (d) See, also: Killian, L.; Wrackmeyer, B. *J. Organomet. Chem.* **1978**, *148*, 137–146. (e) Schacht, W.; Kaufmann, D. *Angew. Chem.* **1987**, *99*, 682–683.

(2) (a) Herberich, G. E.; Ohst, H. *Chem. Ber.* **1985**, *118*, 4303–4313. (b) Herberich, G. E.; Buller, B.; Hessner, B.; Oschmann, J. *J. Organomet. Chem.* **1980**, *195*, 253–259.

0002-7863/88/1510-2979$01.50/0

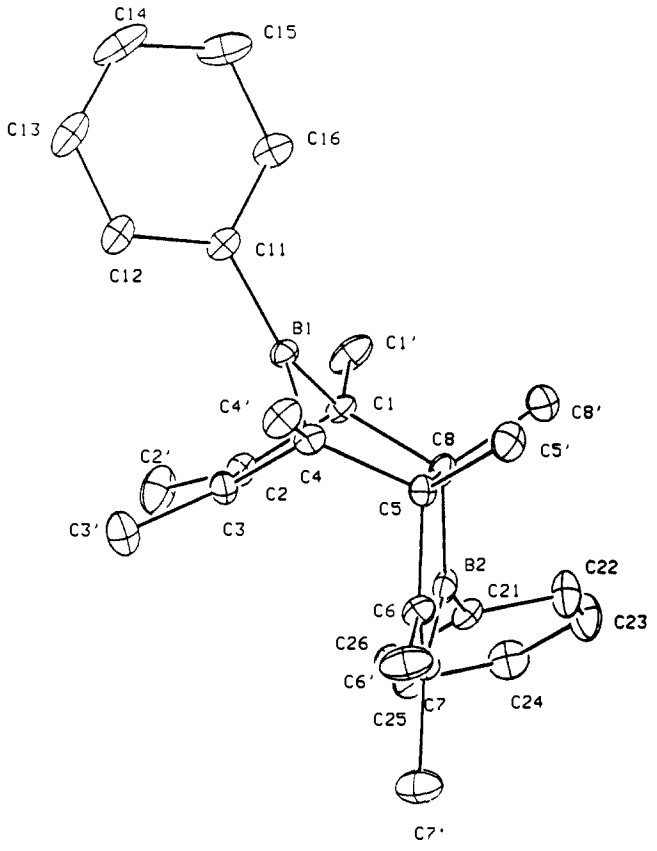
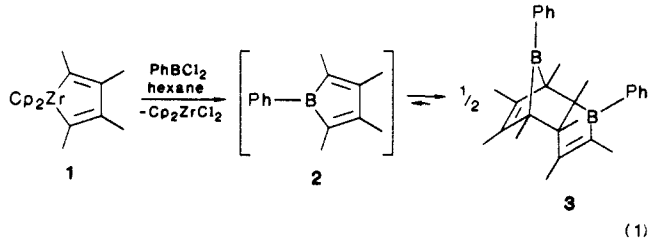


Figure 1. ORTEP drawing of **3** (H atoms omitted). Bond distances (Å): C2–C3, 1.375 (6); C3–C4, 1.488 (6); C1–C2, 1.487 (6); C11–B1, 1.568 (7); C1–C8, 1.557 (6); C4–C5, 1.573 (5); C5–C8, 1.563 (6); C5–C6, 1.510 (6); C6–C7, 1.361 (6); C7–B2, 1.520 (7); C8–B2, 1.579 (7); C21–B2, 1.570 (7).

lacycle transfer from zirconium reagents.[3] Here we report the preparation of the Diels–Alder dimer of 1-phenyl-2,3,4,5-tetramethylborole by this method. This dimer contains a "nonclassical" interaction of an electron deficient boron with a double bond as determined by a single-crystal X-ray diffraction study. In addition, we demonstrate the ability of this dimer to serve as a source of the borole monomer, which can participate in Diels–Alder reactions under mild conditions with *unactivated* alkynes and alkenes. The combination of these low-temperature Diels–Alder reactions with the well-known chemistry for functionalization of organoboranes[4] is a potentially powerful synthetic method.

Reaction of the zirconium metallacycle **1**[5] with 1 equiv of dichlorophenylborane in hexane results in precipitation of Cp_2ZrCl_2 and production of the borole dimer **3** (eq 1).[6] The

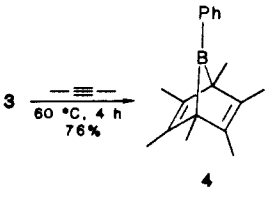


(1)

borole monomer **2** is proposed to be an intermediate in this reaction, although direct detection of **2** has not been possible. Filtration of the hexane followed by cooling (−78 °C) precipitates **3** which can then be isolated in 70% yield.[7] The results of a single-crystal X-ray analysis of **3** are presented in Figure 1.[7] The structure determination establishes that **3** is a Diels–Alder dimer of **2** and that the stereochemistry observed is a result of "endo addition" as is typical of Diels–Alder reactions.[8] There is evidence for "endo addition" in the only other known borole Diels–Alder dimer characterized spectroscopically by Herberich and co-workers.[2a] An interaction of the electron deficient bridgehead phenylboron group with the double bond C2–C3 is evident in the structure of **3**. Thus the plane defined by B1, C1, and C4 is tilted substantially toward C2–C3 making an angle of 90.1° relative to the plane defined by C1, C2, C3, and C4 (B1–C2 = 1.864 (7) Å, B1–C3 = 1.864 (7) Å; cf. B1–C1 = 1.595 (6) Å, B1–C4 = 1.589 (7) Å). This structural feature is related to the once controversial "nonclassical" structure proposed for 7-norbornenyl carbocations and supports the view of these species as having a symmetrical three-center two-electron bond.[1c,9]

The propensity of the intermediate borole **2** to dimerize despite the degree of substitution on the borole ring is indicative of a pronounced ability to participate in Diels–Alder reactions. Eisch and co-workers have noted and rationalized this tendency in the reaction of diphenylacetylene with 1,2,3,4,5-pentaphenylborole as being a consequence of the unoccupied orbital on boron.[1,10] The degree to which boroles can participate in Diels–Alder reactions with other unactivated substrates however has not been determined, and it was therefore of interest to generate and study the reactivity of **2**.

Attempts were made to trap **2** by carrying out the reaction of **1** with dichlorophenylborane in the presence of 2-butyne. It was observed that even if the reaction was carried out in neat 2-butyne under dilute conditions at room temperature, only a small amount (ca. 10%) of the expected Diels–Alder adduct **4** was formed along with the dimer **3**. The dimer **3** was then heated (60 °C, 4 h) with 2-butyne in toluene solution to test whether **2** could be produced in situ by a retro-Diels–Alder reaction. The reaction was found to proceed smoothly to yield the Diels–Alder adduct **4** (eq 2) as a colorless crystalline product after sublimation (50 °C, 10^{-4} Torr).[7] These results are good evidence for the existence of **2** as an intermediate and show that its dimerization is reversible upon mild heating.



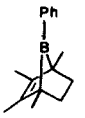
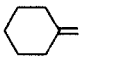
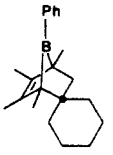
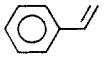
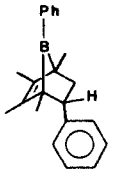
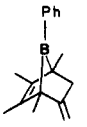
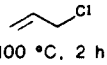
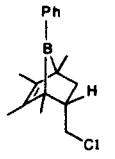
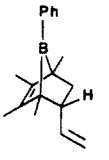
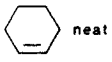
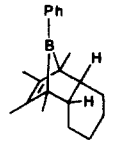
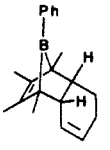
(2)

The ability to generate **2** allowed us to test its reactivity in Diels–Alder reactions with unactivated alkenes. Heating a toluene solution of **3** for 5 h under ethylene (<1 atm, 80 °C) yielded the adduct **5** as a colorless liquid after isolation by oil sublimation (60 °C, 10^{-4} Torr) (Table I).[7] These are exceptionally mild conditions for a relatively poor dienophile such as ethylene.[8] As shown in Table I, a variety of unactivated substituted alkenes will react with **3** to generate the expected Diels–Alder adducts **6–12** in high to moderate yield.[7] In the products **6**, **7**, **8**, and **12**, only

(3) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.*, in press.
(4) (a) Brown, H. C. *Organic Synthesis via Organoboranes*; Wiley-Interscience: New York, 1975. (b) Srebnik, M.; Ramachandran, P. V. *Aldrich. Acta* **1987**, *20*, 9–24. (c) Brown, H. C. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, pp 111–142. (d) Zaidlewicz, M. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, pp 143–254. (e) Negishi, E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, pp 255–364.
(5) Negishi, E.; Cederbaum, F. E.; Tamotsu, T. *Tetrahedron Lett.* **1986**, *27*, 2829–2832.

(6) The transfer from other zirconium metallacycles (e.g., $Cp_2ZrC(CH_3)=C(CH_2)_4C=C(CH_3)$ and $Cp_2ZrC(CH_3)=C(CH_2)_2C=C(CH_3)$)to phenylboron dichloride has also been accomplished.
(7) See Supplementary Material.
(8) (a) Gleiter, R.; Bohm, M. C. *Pure Appl. Chem.* **1983**, *55*, 237–244, and references therein. (b) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807, and references therein.
(9) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803–6806, and references therein.
(10) For comparison, see chemistry of siloles: Barton, T. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, pp 250–261.

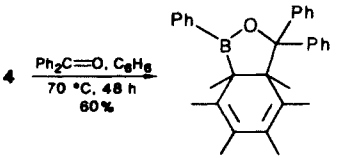
Table I. Reactions of 3 with Unactivated Alkenes

reactant	product[a]	reactant	product[a]
= 80 °C, 5 h	 5 (82%)	 80 °C, 24 h	 9 (91%)
 100 °C, 2 h	 6 (92%)	=•= 70 °C, 4 h	 10 (75%)
 100 °C, 2 h	 7 (89%)	 80 °C, 4 h	 11 (63%)
 neat 120 °C, 21 h	 8 (94%)	 100 °C, 27 h	 12 (87%)

[a] All products were isolated as colorless oils.

one of the two possible stereoisomers is observed, and the coupling constants observed for **6** and **7** in their ^{1}H NMR spectra are again consistent with endo addition of the borole **2**.[7] Preliminary results indicate that **2** can react with both double bonds of 1,3-butadiene, which accounts for the lower yield obtained in the case of **11**.

Heating the 7-boranorbornadiene adduct **4** at 120 °C in toluene solution in a sealed tube generates hexamethylbenzene and an as yet unidentified boron-containing product. Complex **4** can be reacted with benzophenone to produce the compound **13** which was isolated as a white solid from cold (−78 °C) hexane (eq 3).[7]



(3)

13

The product **13** is expected based on the known reactivity of allylic boranes.[11] These reactions demonstrate that both removal of boron or further functionalization of the Diels–Alder adducts is possible. In some respects, the chemistry of boroles is reminiscent of the electronically related cyclopentadienylcobaltacyclopentadiene fragment which is a presumed intermediate in cobalt-mediated [2 + 2 + 2] reactions.[12] An important difference is that intermolecular reactions with alkenes proceed more readily in the case of the boroles.

Acknowledgment. We thank Ronald J. Davis for capable technical assistance.

Registry No. **1**, 84101-39-3; **3**, 113668-53-4; **4**, 113668-54-5; **5**, 113668-55-6; **6**, 113668-56-7; **7**, 113668-57-8; **8**, 113668-58-9; **9**, 113668-59-0; **10**, 113668-60-3; **11**, 113668-61-4; **12**, 113668-62-5; **13**, 113668-63-6; $PhBCl_2$, 873-51-8; $Ph_2C{=}O$, 119-61-9; 2-butyne, 503-17-3; ethene, 74-85-1; styrene, 100-42-5; 3-chloropropene, 107-05-1; cyclohexene, 110-83-8; methylenecyclohexane, 1192-37-6; allene, 463-49-0; 1,3-butadiene, 106-99-0; 1,3-cyclohexadiene, 592-57-4; hexamethylbenzene, 87-85-4.

Supplementary Material Available: ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, mass spectral, and analytical data for **2–13**; X-ray data and tables of atomic positional parameters, thermal parameters, bond distances, and bond angles for **3** (9 pages); table of observed and calculated structure factors for **3** (2 pages). Ordering information is given on any current masthead page.

(11) (a) Negishi, E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, pp 358–360. (b) Mikhailov, B. M. *Pure Appl. Chem.* **1974**, *39*, 505–523.

(12) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556, and references therein.

Synthesis and Unusual Properties of a Helically Twisted Multiply Metalated Rubrene Derivative†

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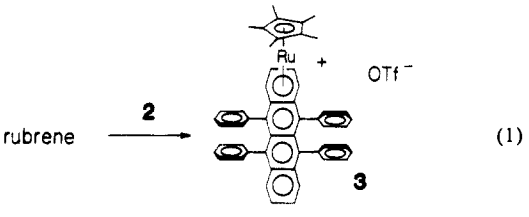
Received January 7, 1988

We have been interested in preparing organometallic complexes with specific shapes and distributions of charge for use in the rational preparation of solid-state materials.[1] For these studies, we have used the Cp^*Ru^+ ($Cp^* = \eta$-$C_5(CH_3)_5$) fragment for derivatization of aromatic hydrocarbons which serve as geometric templates to obtain a desired molecular shape and arrangement of positive charges. We report herein the properties of the complex {5,6,11,12-[$Cp^*Ru(\eta$-$C_6H_5)$]$_4$naphthacene}$^{4+}(OTf^-)_4$ (**1**$^{4+}(OTf^-)_4$; OTf = CF_3SO_3) obtained by multiple substitution of Cp^*Ru^+ on 5,6,11,12-tetraphenylnaphthacene (rubrene). Substitution of Cp^*Ru^+ on the phenyl groups of rubrene greatly distorts the structure such that the naphthacene core is helically twisted as determined by a single-crystal X-ray diffraction analysis. Despite the presence of the four ruthenium heavy atoms, **1**$^{4+}$ is intensely luminescent like rubrene itself, and although significantly perturbed, the photophysical and redox properties of **1**$^{4+}$ are essentially dominated by the naphthacene portion of the molecule.

Reaction of $[Cp^*Ru(CH_3CN)_3]^+OTf^-$ (**2**)[2] with an equivalent of rubrene at room temperature in CH_2Cl_2 leads to formation of the blue-green derivative **3** (eq 1). The ^{1}H NMR spectral data



(1)

for **3** reveal that the Cp*Ru group is bound to the outermost ring of the naphthacene functionality.[5,6] However, by repeatedly heating and removing solvent from a CH_2Cl_2 solution of rubrene

† Contribution No. 4592.

(1) (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C., to be submitted for publication. (b) Ward, M. D.; Fagan, P. J.; Johnson, D. C.; Calabrese, J. C., to be submitted for publication.

(2) Preparation of **2**: reduction of Cp^*RuCl_2[3] with 1 equiv of lithium triethylborohydride in THF precipitates orange $(Cp^*RuCl)_4$. Refluxing $(Cp^*RuCl)_4$ in CH_3CN for 2 h followed by addition of AgOTf yields a solution of **2** which was filtered, and solvent was removed from the filtrate. Addition of ether and collection by filtration yields crystalline yellow-orange **2** (94%). The PF_6^- salt of the cation $Cp^*Ru(CH_3CN)_3^+$ has previously been prepared by a photochemical route.[4]

(3) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274–278. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161–1164.

(4) Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501–3504.

(5) See Supplementary Material.

(6) Related complexes have been reported: McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519–2527.

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