

Figure 1. ORTEP view of **1** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) are as follows: Sn(1)-Sn(2) = 3.4192 (4), -O(10) = 2.326 (2), -O(20) = 2.045 (2), -Cl(11) = 2.354 (1), -Cl(12) = 2.290 (1), -C(122) = 2.113 (4), Sn(2)-O(10) = 2.035(2), -O(20) = 2.259 (2), -Cl(21) = 2.363 (1), -Cl(22) = 2.297 (1), -C(222) = 2.103 (5), Sn(1)-O(10)-Sn(2) = 103.1 (1), Sn(1)-O(20)-Sn(2) = 105.1 (1).

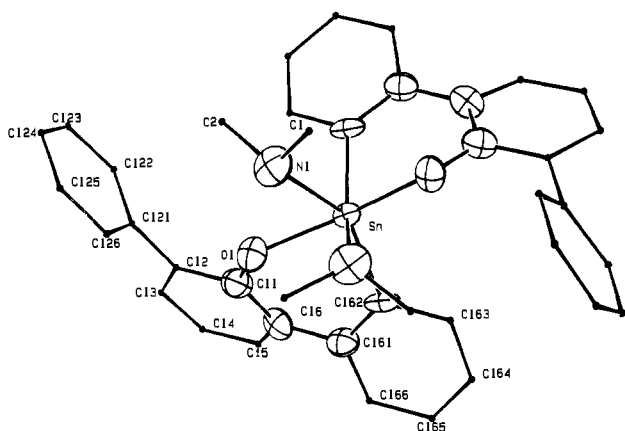


Figure 2. ORTEP view of **4** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) are as follows: Sn-O(1) = 2.091 (8), -N(1) = 2.32 (1), -C(162) = 2.12 (1), O(1)-Sn-O(1) = 157.0 (4), -N(1) = 71.2 (3), -N(1) = 89.0 (3), -C(162) = 86.5 (3), -C(102) = 105.3 (4), N(1)-Sn-N(1) = 63.3 (5), C(162)-Sn-C(162) = 118.7 (5), Sn-O(1)-C(11) = 122.8 (7).

Although an electrophilic mechanism for these aromatic CH bond activation processes seems reasonable, careful mechanistic studies are planned comparable to those both reported⁵ and underway on related d-block metal systems.¹⁵

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Supplementary Material Available: Expansions of the aromatic region of the ¹H NMR spectra of **1**, **2**, and **4** and tables of positional parameters, general temperature factors, and bond distances and angles (26 pages); tables of observed and calculated structure factors for **1** and **4** (37 pages). Ordering information is given on any current masthead page.

(15) A very minor component from the reaction of SnCl₄ with Li(OAr-2,6Ph)₂ was identified as the cage material [Li(μ-OAr-2,6Ph)₃Sn]. Hence redox chemistry is a possible mechanistic complication: Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.*, in press.

UV Laser Photochemistry of Azoalkanes: Surprising Effects of Phenyl Substitution on the Lifetimes of 1,3-Cyclopentadiyl and 1,4-Cyclohexadiyl Triplet Diradicals

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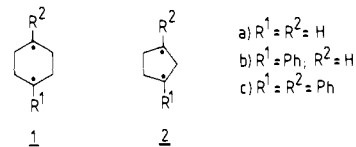
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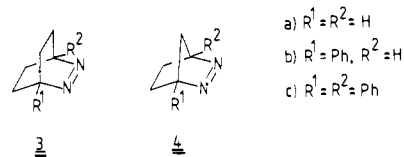
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One might intuitively expect that the lifetimes of hydrocarbon diradical intermediates tend to increase upon phenyl substitution at the radical site. Indeed, 1,4-cyclohexadiyl (**1a**), ³τ ≤ 0.1 ns,² is over 3000-fold shorter lived than its phenyl derivative **1b**, ³τ = 275 ns.³ The effect of a second phenyl group, e.g. as in **1c**,



on the triplet lifetime is difficult to anticipate because diradicals are not simply "double radicals".⁴ In fact, no systematic studies of the degree of phenyl substitution in simple hydrocarbon diradicals appear to have been reported at this time.⁵ However, an increase in lifetime has been observed with increasing chain length in phenyl-substituted polymethylene diradicals.^{5c-e} In this work we show that the effect of phenyl substitution on the lifetime of triplet 1,4-cyclohexadiyl differs dramatically from that of 1,3-cyclopentadiyl.

The azoalkanes **3^b** and **4** were chosen as precursors for the diradicals **1** and **2** in this first systematic study on the effect of phenyl substituents on triplet lifetimes. The unknown azoalkanes



4b,c were prepared by the usual triazolinedione route⁷ via the appropriate phenyl-substituted cyclopenta-1,3-dienes.⁸ The

(1) (a) Kekulé Doctoral Fellow, 1985-87, Stiftung Volkswagenwerk. (b) Liebig Postdoctoral Fellow, 1986-88, Fonds der Chemischen Industrie.

(2) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929.

(3) Adam, W.; Grabowski, S.; Wilson, R. M.; Hannemann, K.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 7572.

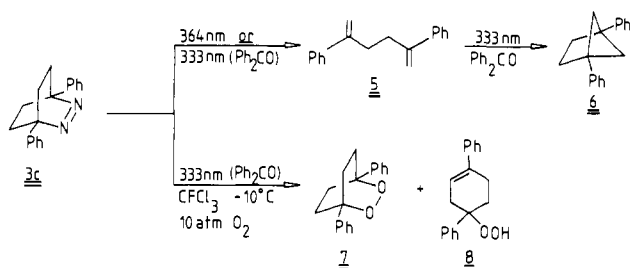
(4) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1167. (c) Wirz, J. *Pure Appl. Chem.* **1984**, *56*, 1289.

(5) (a) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (b) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1985; Vol. 7, Chapter 5. (c) Caldwell, R. A.; Majima, R.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629. Mituzono, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797. (d) Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* **1985**, *107*, 3607. (e) Zimmt, M. B.; Doubleday, D., Jr.; Gould, I.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724. Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. *J. Chem. Phys. Lett.* **1987**, *134*, 549.

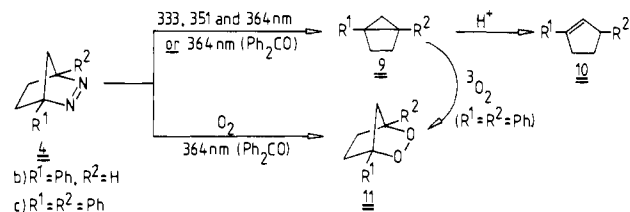
(6) Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 7102.

(7) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

Scheme I



Scheme II



azoalkane **4c** is thermally labile, having a half-life of only 30 min at 20 °C. Direct and triplet-sensitized (Ph₂CO) laser photolyses (Coherent Supergraphite CR 18 and Innova 100 System argon ion laser) of azoalkanes **3c** and **4b,c** lead to the results shown in Schemes I and II, respectively. Bicyclo[2.1.1]hexane derivative **6**⁹ in the sensitized photolysis of **3c** is a secondary photoproduct of diene **5**, and the conversion of phenyl-substituted bicyclo[2.1.0]pentanes **9b,c** to cyclopentenes **10b,c** is caused by traces of acid. In the presence of molecular oxygen (10 atm), the benzophenone-sensitized laser photolysis of azoalkane **3c** in CFCl₃ at -10 °C gave peroxides **7** (0.35%) and **8** (14%) and as remainder hydrocarbon **5**; not even traces of the corresponding bicyclo[2.2.0]hexane could be detected. Under these conditions azoalkanes **4b,c** led only to the endoperoxides **11b,c**. Peroxides **7** and **8** were isolated by means of flash chromatography on silica gel at -25 °C.⁹ An authentic sample of cyclic peroxide **7** was prepared by photooxygenation¹⁰ of 1,4-diphenyl-1,3-cyclohexadiene¹¹ and subsequent diimide reduction.¹² 1,4-Diphenylbicyclo[2.1.0]pentane (**9c**) in benzene at 25 °C rapidly reacted with molecular oxygen to yield endoperoxide **11c**.

The lifetimes of triplet diradicals **1c** and **2b,c** in degassed solution at ambient temperature were measured by flash photolysis using a XeF excimer laser (351 nm, 75–100 mJ, 25 ns).^{4c,13} No transient absorptions were observed upon direct excitation of azoalkanes **3c**, **4b**, or **4c**. At azoalkane and benzophenone concentrations in the range of 10⁻³ to 10⁻² M, most of the 351-nm radiation was absorbed by the benzophenone. The lifetime of triplet benzophenone, which was determined at 530 nm, was consistent with diffusion-controlled energy transfer to the azoalkanes. Biphasic decay curves, which fitted well to a dual exponential function, were observed in the 300- to 320-nm region: the faster decay rate was always equal to that of triplet benzophenone. The slower component was not affected by the addition of piperylene (up to 0.004 M) and was thus attributed to the triplet

Table I. Triplet Diradical Lifetimes (³τ) in Degassed Solution and Rate Constants for the Bimolecular Reaction with Molecular Oxygen (k[O₂])^a

triplet diradical	solvent	³ τ (ns)	k[O ₂] × 10 ⁻¹⁰ (M ⁻¹ s ⁻¹)
1a	CFCl ₃	<0.1 ^b	
1b	benzene	275 ± 15	1.6 ± 0.1
	benzene	280 ± 40 ^{c,d}	(1.6) ^e
	MeCN	248 ± 15	2.2 ± 0.2
1c	<i>n</i> -C ₇ H ₁₆	260 ± 60	1.2 ± 0.3
	benzene	365 ± 20	1.3 ± 0.1
	benzene	390 ^b	(1.3) ^e
2a	MeCN	310 ± 20	1.8 ± 0.2
	benzene	115 ± 20 ^{c,f}	(1.8) ^{e,f}
	<i>n</i> -C ₇ H ₁₆	93 ± 11 ^{c,f}	(1.8) ^{e,f}
2b^g	benzene	390 ± 50	1.5 ± 0.3
	MeCN	380 ± 30	1.5 ± 0.3
	MeCN	27000 ± 2000	0.75 ± 0.10

^a Determined by means of time-resolved laser flash spectroscopy. ^b Estimated by preparative oxygen trapping, ref. 2. ^c Determined by quantitative oxygen trapping, ref. 2. ^d Reference 3. ^e Assumed k(O₂). ^f Reference 14. ^g Also run in CFCl₃ at -10 °C, affording endoperoxides **11b,c**.

diradicals. Their decay rates increased linearly with increasing oxygen pressure, affording the bimolecular rate constants [k(O₂)] of their reaction with molecular oxygen. The oxygen-trapping method² provided an independent estimate for the lifetime of **1c**. These data are summarized in Table I together with previous results for **1a**,² **1b**,³ and **2a**.¹⁴

The ca. 1000-fold longer lifetime of the parent 1,3-cyclopentanediyli **2a** (³τ ca. 100 ns)¹⁴ relative to the parent 1,4-cyclohexanediyli **1a** (³τ ca. 0.1 ns)² was previously rationalized in terms of the planar geometry of **2a**, which fixes the radical lobes in a parallel arrangement (slow intersystem crossing, Salem's rule).^{4a} Our present results reveal remarkable but puzzling effects of phenyl substitution on the lifetimes of **1a** and **2a** (Table I). While the introduction of the first phenyl group causes a dramatic increase (3000-fold) in the lifetime of **1**, the effect is only moderate (4-fold) in **2**. The opposite is found upon introduction of the second phenyl group, i.e., marginal increase (1.3-fold) in **1** and a substantial rise (75-fold) in **2**. The unusual persistence of the 1,3-diradical **2c** is also revealed in its significantly slower (ca. 3-fold) trapping rate with molecular oxygen compared to congeners **2a,b** and 1,4-diradicals **1b,c**, which react essentially under diffusion control.

Several factors presumably contribute to the increase in the lifetimes upon phenyl substitution: (i) delocalization at the radical center(s) diminishes the spin densities at the radical sites in the ring and thus reduces the overlap necessary for spin-orbit coupling, (ii) benzylic conjugation introduces some rigidity against pyramidalization of the radical sites, and (iii) phenyl substitution will stabilize the diradicals thermodynamically relative to the products derived therefrom and this, on the basis of Hammond's postulate, is expected to raise their kinetic stability, irrespective of whether S → T intersystem crossing is rate determining. In fact, simple thermochemical estimates with Benson's¹⁵ heats of formation increments indicate that the ring closure reaction of 1,3-diphenyl-1,3-cyclopentanediyli (**2c**) to 1,4-diphenylbicyclo[2.1.0]pentane (**9c**) is approximately thermoneutral.¹⁶ This might explain the extended lifetime (30 μs!) of **2c**, which approaches the time domain of the long-lived non-Kekulé diradical species.^{13,17}

(8) (a) Riemschneider, R.; Nerin, R. *Monatsh. Chem.* **1960**, *91*, 829. (b) Wahren, R. *J. Organomet. Chem.* **1973**, *57*, 415. (c) Drake, N. L.; Adams, J. R., Jr. *J. Am. Chem. Soc.* **1939**, *61*, 1326.

(9) (a) All new compounds were fully characterized by elemental analyses and spectral data. (b) In the meantime the synthesis of the azoalkane **4c** and the ESR spectrum of its triplet state diradical **2c** have been reported, cf.: Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753. For a preliminary account of our results cf.: Platsch, H.; Adam, W.; Hannemann, K.; Wirz, J. *UV-Laser Photochemistry: Generation and Lifetimes of Phenyl-Substituted 1,3-Cyclopentadiyl Triplets*; XII IUPAC Symposium on Photochemistry, Bologna, Italy, July 7–12, 1988; Abstr. PK-18, pp 328–329. (10) Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

(11) Dale, J.; Kristiansen, P. O. *Acta Chem. Scand.* **1971**, *25*, 359.

(12) (a) Adam, W.; Eggelte, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 713. (b) Coughlin, D. J.; Salomon, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 655.

(13) Burnett, M. N.; Boothe, R.; Clark, E.; Gisin, M.; Hassaneen, H. M.; Pagni, R. M.; Persy, G.; Smith, R. J.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 2527.

(14) Adam, W.; Hössel, P.; Hümmer, W.; Platsch, H.; Wilson, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 7570.

(15) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. (b) Roth, W. R.; Klärner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818. (c) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (d) Doering, W. v. E. *Proc. Natl. Acad. Sci.* **1981**, *78*, 5279. (e) Doering, W. v. E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lennartz, H.-W.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.* **1988**, *121*, 1.

(16) Using the cyclopentane ring correction^{15a} in the calculation of **2c**, we estimate ΔH^o_f(298 K) ca. 91 and 92 kcal mol⁻¹ for **9c** and **2c**, respectively. (17) Borden, W. T., Ed. *Diradicals*; Wiley: New York, 1982.

Further work will be needed to establish whether 2c owes its persistence to a thermal barrier against S → T intersystem crossing or cyclization of the singlet diradical.

It is our contention that by delocalization of the radical sites and by introduction of appropriate molecular constraints still more persistent triplet diradicals can be taylor-made.

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Oxygen Atom Transfer Chemistry of Heteropolytungstate "Browns" in Nonaqueous Solvents

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The current increased interest in polyoxometalates¹ is fueled to a large extent by potential and realized applications as acid-base or redox catalysts and photocatalysts.² Hitherto, polyanion redox chemistry has been dominated by electron-transfer processes, either centered at the heteroatom (see, for example, the use of Co^{III}W₁₂O₄₀⁵⁻ as an oxidant in organic chemistry³) or at the addenda Mo or W atoms in the heteropoly blues.⁴ Atom transfer chemistry involving polyanions is much less common, although we have recently shown that lacunary polyanion fragments can mimic macrocyclic ligands and support oxygen transfer from iodobenzene in the conversion of SiMo₁₁O₃₉Cr^{III}(OH)₂⁵⁻ to SiMo₁₁O₃₉Cr^VO⁵⁻,⁵ and Hill has reported oxygen transfer from

oxygen donors to alkenes and alkanes that is catalyzed by PW₁₁(M)O₃₉⁵⁻ (M = divalent Mn, Fe, Co, Cu).^{2b,6} We now report the first general oxygen atom abstraction reactivity of reduced heteropolytungstates in nonaqueous solutions and incidentally the first examples of oxygen atom transfer to tungsten(IV). This reactivity suggests that new applications for unsubstituted heteropolyanions in synthetic and catalytic chemistry might be found.

The reduced anions in question are the heteropoly "browns" that were recently shown to contain trigonal groups of edge-shared W^{IV}O₅(OH₂) octahedra, XW^{VI}₃O₃₇W^{IV}₃(OH₂)₃ⁿ⁻ (X = H₂ (I), B (II), Si (III); n = 6, 5, 4, respectively,⁷ see Figure 1. Natural abundance ¹⁷O NMR spectra of these anions in aqueous solution show clearly resolved lines for most of the 11 different types of oxygen atoms in the C_{3v} structure.⁸ Resonances for the terminal water molecules occur at chemical shifts of -12 (I) and -10 ppm (II and III). Addition of ¹⁷O-enriched water to these solutions results in a slow enhancement of these resonances⁹ thereby demonstrating ligand exchange on W^{IV}. Approximate half-lives for exchange at ambient temperature range from 4.5 to 30 days, i.e.; 3.6 × 10⁵ s (I); 1.1 × 10⁶ s (II); 3.0 × 10⁶ s (III). These rates are comparable with that for the corresponding water molecules in the structurally related cation, W^{VI}₃O₄(OH₂)₃⁴⁺.¹⁰

Anions I-III are readily transferred into toluene or benzene solution by the phase transfer method that we have described earlier.¹¹ Excess noncoordinated water is removed by solvent-stripping, and the resulting salts are redissolved in fresh dry toluene or acetonitrile.¹² Treatment of such solutions with appropriate oxidants, XO, leads to regeneration of the oxidized heteropolyanion (identified by ¹⁸³W, ¹H, and ¹⁷O NMR, and by isolation of the tetrapropylammonium salt) and the formation of X or a successor species (¹H, ¹³C NMR, isolation). Yields of the oxidized heteropolyanion are quantitative based upon NMR.¹³ Representative yields of the organic products, based on NMR integration of unreacted substrate and product signals, are given in Table I. These yields, which are not optimized, demonstrate that on average more than one oxygen atom has been transferred per heteropolyanion.¹⁴ The overall rates of the reactions summarized in Table I are not inconsistent with the water exchange rates, except for the case of nitrosobenzene.¹⁵ That the reaction proceeds by

(1) (a) Pope, M. T. *Isopolyanions and Heteropolyanions*. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 3, Chapter 38. (b) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (c) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer Verlag: New York, 1983.

(2) Research activity is high in this area and has not been comprehensively reviewed recently. The following lists recent papers from some different research groups (alphabetically by first author) that are currently active and provides an entree to the literature. (a) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 395. (b) Ai, M. *Polyhedron* **1986**, *5*, 103. (c) Aoshima, A.; Yamaguchi, T. *Nippon Kagaku Kaishi* **1986**, 1161. (d) Baba, T.; Ono, Y. *J. Mol. Catal.* **1986**, *37*, 317. (e) Dun, J. W.; Gulari, E.; Streusand, B. *Appl. Catal.* **1986**, *21*, 61. (f) Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. (g) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347. (h) Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536. (i) Kulikov, S. M.; Kozhevnikov, I. I.; Fomina, M. N.; Krysin, A. P. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1987**, 752. (j) Misono, M.; Okahara, T.; Ichiki, T.; Arai, T.; Kanda, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5535. (k) Moffat, J. B. *Stud. Surf. Sci. Catal.* **1987**, *31*, 241. (l) Nomiya, K.; Sugie, Y.; Miyazaki, T.; Miwa, M. *Polyhedron* **1986**, *5*, 1267. (m) Papaconstantinou, E.; Argitis, P.; Dimotikali, D.; Hiskia, A.; Ionnidis, A. *NATO ASI Ser., Ser. C* **1986**, *174*, 415. (n) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219. (o) Urabe, K.; Tanaka, Y.; Izumi, Y. *Chem. Lett.* **1985**, 1595. (p) Vasilevskis, J.; De Deken, J. C.; Saxton, R. J.; Wentreck, P. R.; Fellmann, J. R.; Kipnis, L. S. PCT Int. App. WO 87 01,615 [*Chem. Abst.* **1987**, *107*, 178602p]. (q) Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107. (r) Yamase, T.; Watanabe, R. *J. Chem. Soc., Dalton Trans.* **1986**, 1669.

(3) (a) Chester, A. W. *J. Org. Chem.* **1970**, *35*, 1997. (b) Ebersson, L.; Wistrand, L. G. *Acta. Chem. Scand.* **1980**, *B34*, 349. (c) Jönsson, L. *Acta. Chem. Scand.* **1983**, *B37*, 761. (d) Ebersson, L. *J. Am. Chem. Soc.* **1983**, *105*, 3192. (e) Ayoko, M. A.; Olatunji, G. A. *Polyhedron* **1983**, *2*, 577. (f) Olatunji, G. A.; Ayoko, M. A. *Bull. Soc. Chim. Fr.* **1985**, *5*, 705. (g) Saha, S. K.; Ghosh, M. C.; Banerjee, P. *J. Chem. Soc., Dalton Trans.* **1986**, 1301. (h) Saha, S. K.; Ghosh, M. C.; Banerjee, P. *Inorg. Chim. Acta* **1986**, *126*, 29.

(4) (a) Pope, M. T. In *Mixed-Valence Compounds*; Brown, D. B., Ed.; Reidel Publishing Company: Dordrecht, 1980; p 365. (b) Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 3160. (c) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627.

(5) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186.

(6) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.

(7) Piepgrass, K. W.; Pope, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 1586.

(8) Spectra were recorded on ca. 0.15 M solutions in 0.5 M DCl/D₂O by using a Bruker AM-300WB spectrometer at 40.688 MHz with 10-mm tubes. Sweep widths were 62 000 or 83 000 Hz (acquisition times of 33 and 25 ms, respectively) with an acquisition delay of 150 μs to allow probe ringing to die out. The number of scans varied from 200 000 to 600 000. Chemical shifts are reported relative to external H₂O. Addition of Mn²⁺ at concentrations of 10⁻³ M was sufficient to remove the large solvent peak [Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders, Co.: Philadelphia, PA, 1977; p 205. Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161] and permitted observation of terminal H₂O resonances that were otherwise obscured. The presence of Mn²⁺ did affect resonances of some of the anions' terminal oxygen atoms as we discuss elsewhere [Piepgrass, K.; Barrows, J. N.; Pope, M. T. *J. Chem. Soc., Chem. Commun.*, in press] so that the complete spectra were obtained both with and without Mn²⁺.

(9) In the cases of I and II one other resonance also was enriched at about the same rate. We tentatively attribute this resonance (at ca. 400 ppm) to the oxygens (h in Figure 1) that bridge W^{IV} and W^{VI} atoms.

(10) (a) Merbach, A. E., private communication. (b) Richens, D. T.; Helm, L.; Pittet, P.-A.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *132*, 85.

(11) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

(12) Extended reflux in acetonitrile results in replacement of terminal H₂O ligands by CH₃CN.

(13) Isolated yields of the oxidized heteropolyanion salts varied from 30 to 80% depending upon solubility.

(14) With inorganic oxygen donor Bu₄NBrO₃ 1 mol was sufficient to oxidize 1 mol of I completely.

(15) In this case the product solution contained no starting material a mixture of azoxybenzene (70%) and another unidentified product (30%). The rate of this reaction excludes a mechanism in which nitrosobenzene displaces a terminal ligand on tungsten(IV), and we are investigating this further.