

and aromatic reagents. We would like to report here the adducts with 1,3-butadiene since they appear to be unique in the literature of organometallic compounds. The products are tris(butadiene)tungsten(0) and tris(butadiene)molybdenum(0).

Tungsten and molybdenum atoms are generated by resistive heating of the respective wires, employing essentially the same apparatus and conditions as for previous reports of metal atom reactions.¹ Cocondensation of the atoms with 1,3-butadiene (1:100 molar ratio) at liquid nitrogen temperature produces a yellow matrix in both instances. After warm-up the yellow-brown liquid was siphoned from the flask under an inert atmosphere and the excess 1,3-butadiene was pumped off, leaving a residue which could be purified by sublimation (10^{-3} Torr, 50–60°) or by recrystallization from heptane. Yields are 50–60% based on the amount of metal deposited in the butadiene matrix. A typical 1 hr run yields about 200 mg of pure product.

Tris(butadiene)tungsten: the pure crystalline material is white, is in the hexagonal system, decomposes at 135°,² is soluble in organic solvents, and is stable in air (slight darkening noticeable after 2 weeks). The infrared spectrum (CCl_4) showed complexed carbon-carbon double bond stretching frequencies at 1485 (vw) and 1440 cm^{-1} (w). The ^1H nmr (C_6D_6) exhibited multiplets at τ 5.72, 8.50, and 9.62, of equal intensities. The following major ions with their respective masses were observed (70 eV, 75°): $(\text{C}_4\text{H}_6)_3\text{W}^+$ (m/e 346, relative intensity 85%), $(\text{C}_4\text{H}_6)_2\text{W}^+$ (m/e 292, relative intensity 100%). The high resolution mass spectrum provided the following mass for the ^{186}W isotope: calcd, 348.0951; found, 348.0959.

Tris(butadiene)molybdenum: the pure crystalline material is yellow, is in the hexagonal system, decomposes at 130°,² is stable in air (darkening after 1 week), and is soluble in organic solvents. Complexed carbon-carbon double bond stretching appeared at 1437 cm^{-1} (w, CCl_4). The ^1H nmr showed multiplets at τ 5.27, 8.32, and 9.46 of equal intensities. These major ions with their respective masses were observed (70 eV, 75°): $(\text{C}_4\text{H}_6)_3\text{Mo}^+$ (m/e 260, relative intensity 41%), $(\text{C}_4\text{H}_6)_2\text{Mo}^+$ (m/e 206, relative intensity 50%), $(\text{C}_4\text{H}_6)\text{Mo}^+$ (m/e 152, relative intensity 19%). The high resolution mass spectrum provided the following mass for the ^{98}Mo isotope: calcd, 260.0463; found, 260.0450.

While there have been many attempts to stabilize tungsten(0) and molybdenum(0) with ligands other than $\text{C}\equiv\text{O}$,³⁻⁶ these have usually resulted in only partial substitution or at best difficult and extended reactions. King^{4,5} has reported that substitution reactions with $(\text{CH}_3\text{CN})\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$) can be carried out. In only one case, however, was he able to obtain complete substitution, that of methyl vinyl ketone. He found that cyclic conjugated dienes would only replace some of the ligands while butadiene would not react at

all. Fischer *et al.*,⁷ have shown that the photochemical addition of butadiene to $\text{Mo}(\text{CO})_6$ produced only bis(butadiene) $\text{Mo}(\text{CO})_2$ after extended irradiation. The addition of metal atoms to organic substrates offers a useful route to organomolybdenum and tungsten complexes previously unobtainable by conventional routes.

An octahedral symmetry characteristic of the group VI transition metals is presumed for both complexes. The crystallographic structure⁸ of the related tris(methyl vinyl ketone)tungsten has recently been shown to be the unusual trigonal prismatic type. X-Ray studies are presently underway in this laboratory to determine the structure of these tris(diene)metal(0) complexes.

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(7) E. O. Fischer, H. P. Koegler, and P. Kuzel, *Chem. Ber.*, **93**, 3006 (1960).

(8) R. E. Moriarty, R. D. Ernst, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 1242 (1972).

P. S. Skell,* E. M. Van Dam, M. P. Silvon

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

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Bis(1,4-cyclohexadiyl)-1,2-dioxetane and Bis(1,4-cyclohexadiyl)oxirane from Photooxidation of 7,7'-Binorbornylidene

Sir:

2,2'-Biadamantylidene (**8**) has become a compound of particular interest since its photooxidation affords a dioxetane of unusual stability.¹ Recently, the photooxidation of **8** in pinacolone^{2a} has been interpreted as indicating the stripping of a perepoxide intermediate^{2b} by a Baeyer-Villiger process.^{2c} In view of the increasing interest in hindered alkenes of this type, we undertook the synthesis of 7,7'-binorbornylidene (**3**). The preparative method used for **3** also provided a way of making **8** in improved yield.

A solution of 2.91 g of 7-norbornanone (**1**)³ in 15 ml of petroleum ether was stirred with 22.9 g of phosphorus(V) bromide⁴ and heated to 70° for 40 hr. The work-up procedures are identical with those for 2,2-dibromoadamantane.^{5a} Recrystallization from petroleum ether gave 5.63 g (84%) of 7,7-dibromonorbornane (**2**): mp 89–90°; ir (KBr) 2940, 1450, 1300, 1180, 1150, 1020, 988, 952, 888, 876, 825, and 760 cm^{-1} ; nmr (CDCl_3)⁶ δ 1.10–1.50 (m, 4 H, endo), 1.90–2.30 (m, 4 H, exo), 2.40–2.60 (m, 2 H, bridgehead); mass spectrum m/e 256, 254, and 252 (P, 1:2:1); 214, 212, and 210 (1:2:1); 175 and 173 (base, 1:1).

(1) J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972).

(2) (a) A. P. Schaap and G. R. Faler, *J. Amer. Chem. Soc.*, **95**, 3381 (1973); (b) D. B. Sharp, Abstracts of the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, No. 79P. (c) P. R. Story, E. A. Whited, and J. A. Alford, *J. Amer. Chem. Soc.*, **94**, 2143 (1972).

(3) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(4) C. E. Kaslow and M. M. Marsh, *J. Org. Chem.*, **12**, 456 (1947).

(5) (a) H. W. Geluk, *Synthesis*, 652 (1970); (b) A. P. Schaap and G. R. Faler, *J. Org. Chem.*, **38**, 3061 (1973).

(6) The assignments of chemical shifts are based on the reported nmr spectra of 7-anti-2-exo-dibromonorbornane and 7-syn-2-exo-dibromonorbornane: D. R. Marshall, P. Reynolds-Warnhoff, and E. W. Warnhoff, *Can. J. Chem.*, **49**, 885 (1971).

(1) (a) For preceding metal reaction paper see P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Amer. Chem. Soc.*, **95**, 3337 (1973). (b) Apparatus used similar to that first described in P. S. Skell, L. D. Wescott, Jr., J. P. Golstein, and R. R. Engel, *ibid.*, **87**, 2829 (1965).

(2) Sealed tube under N_2 .

(3) E. O. Fischer, F. Scherer, and H. O. Stahl, *Chem. Ber.*, **93**, 2065 (1960).

(4) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

(5) R. B. King, *J. Organometal. Chem.*, **8**, 139 (1967).

(6) M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 301 (1973).

Anal. Calcd for $C_7H_{10}Br_2$: C, 33.10; H, 3.98. Found: C, 33.12; H, 3.88.

A solution of 1.85 g of **2** in 5 ml of anhydrous ether was added dropwise to a suspension of 0.75 g of magnesium turnings in 4 ml of anhydrous ether with stirring under nitrogen at room temperature. After refluxing for 24 hr, the solution was decanted into water, the aqueous layer was separated and extracted with ether. Recrystallization from petroleum ether and methanol gave 0.23 g (33%) of colorless crystals: mp 137–138°; ir (KBr) 2940, 1450, 1290, 1175, 1140, 870, 840, and 805 cm^{-1} ; nmr ($CDCl_3$) δ 1.00–1.80 (m, 16 H, endo + exo), 2.40 (broad s, 4 H, bridgehead); mass spectrum m/e 188 (P), 160 (base), 145, 131, 117, and 91.

Anal. Calcd for $C_{14}H_{20}$: C, 89.27; H, 10.73. Found: C, 89.18; H, 10.80.

Biadamantylidene (**8**),⁵ mp 184–185° (lit.^{5a} 184–187°) was prepared in 83% yield from 5.03 g of 2,2-dibromoadamantane^{5a} and 1.86 g of magnesium according to the procedures for the preparation of **3**.

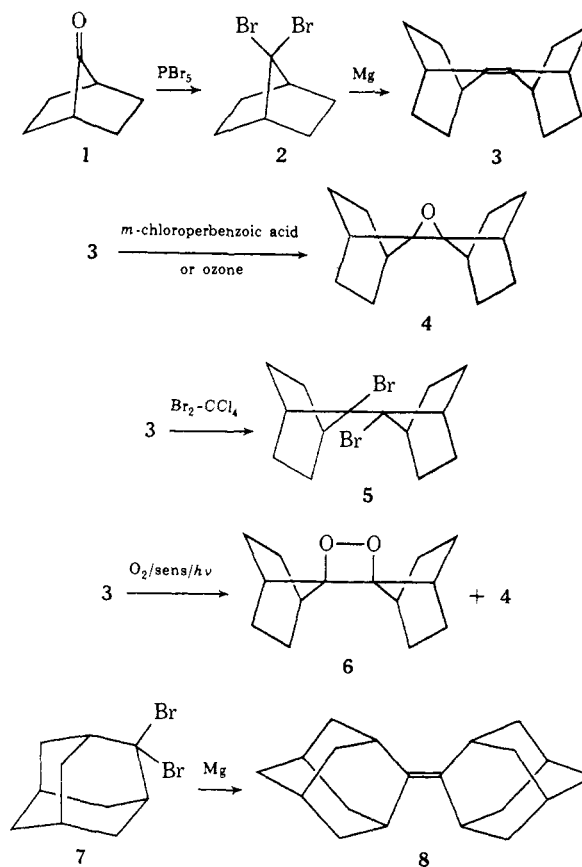
Bis(1,4-cyclohexadiyl)oxirane (**4**) can be obtained by the reaction of **3** with either *m*-chloroperbenzoic acid at 0° or ozone at –78°. Recrystallized from methanol, **4** formed colorless crystals: mp 140–141°; ir (KBr) 2940, 1540, 1450, 1305, 1295, 990, 877, 845, and 785 cm^{-1} ; nmr ($CDCl_3$) broad multiplet δ 1.20–2.20; mass spectrum m/e 204 (P), 175, 150, 123 (base), and 95.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.29; H, 9.89. Found: C, 82.22; H, 9.97.

Stirring **3** in a 5% Br_2-CCl_4 solution at room temperature for 17 hr gave 7,7'-dibromo-7,7'-binorbornyl (**5**). Recrystallization from petroleum ether gave yellow tinted crystals: mp 144–147°; ir (KBr) 2940, 1480, 1470, 1450, 1300, 1220, 1175, 1100, 1040, 900, 878, 835, 810, 788, 763, and 692 cm^{-1} ; nmr ($CDCl_3$) δ 1.20–1.90 (m, 12 H), 2.17 (m, 4 H), and 2.63 (m, 4 H); mass spectrum m/e 350, 348, and 346 (P, 1:2:1), 322, 320, and 318 (1:2:1), 269 and 267 (base, 1:1), 214 and 212 (1:1), 201 and 199 (1:1), and 188. The solubility and hence nonionic character of the product, indicated also by the parent peak in the mass spectrum, are in contrast to the bromonium tribromide of 2,2'-biadamantylidene.⁷

The behavior of **3** toward photooxidation is unusual in that the epoxide **4** and the dioxetane **6** are both isolated in all seven solvents used. In a typical experiment, 10–20 mg of **3** is dissolved in the solvent with 0.5–2.0 mg of sensitizer. The solution, maintained at room temperature and continuously saturated with oxygen, is irradiated with two 500-W tungsten filament lamps through a Corning uv-cutoff filter. Quantitative vpc analysis, with 7,7'-binorbornyl as internal standard, indicates the amount of **3** consumed and the amounts of **4** and **6** produced. High-pressure liquid chromatography at room temperature separates **4** from **6**. **4** isolated from the photooxidation reactions is identical in all respects with the epoxide prepared from **3** and *m*-chloroperbenzoic acid or ozone. The dioxetane **6** has mp 129–130°; heated slowly to 200°, **6** decomposes to give **1**: mp 74° (lit.³ 77–79°); ir of **6** (KBr) 2940, 1470, 1325, 1300, 1180, 1150, 1050, 1020, 872, and 847 cm^{-1} ; nmr ($CDCl_3$) δ 1.10–2.00 (m, 16 H, endo + exo), 2.30–2.50 (m, 4 H, bridgehead); mass spectrum

(7) J. Strating, J. H. Wieringa, and H. Wynberg, *Chem. Commun.*, 907 (1969).



m/e 220 (P), 192, 166, 140, 123, 112, 111, 110 (base), 109, 95, 92, 83, 82, and 81.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.31; H, 9.17. Found: C, 76.32; H, 9.15.

The results of the photooxidation of **3** with various sensitizers and solvents are summarized in Table I.

Table I. Products from Photosensitized Oxidation of **3** at Room Temperature

Concn [3], M	Sens ^a	Solvent	Irradiation period	% re-action	% di-oxetane	% epoxide
0.0037	TPP	CH_2Cl_2	500 min	100	60.3	39.7
0.0036	MB	CH_3CN	450	100	54.0	46.0
0.0035	MB	CH_2Cl_2	600	100	46.4	53.6
0.0037	RB	CH_3OH	500	45	44.4	55.6
0.0037	TPP		600	97	25.9	74.1
0.0036	TPP		500	77	24.8	75.2
0.0037	TPP	PhH	600	97	18.2	81.8
0.0037	TPP		400	99	16.4	83.6
0.00019	TPP	PhH	330	56	6.8	93.2
0.00019	TPP	PhH	660	84	5.1	94.9

^a Sensitizers: TPP, tetraphenylporphine, MB, Methylene Blue, RB, Rose Bengal.

Several control experiments have been carried out to verify that the epoxide is indeed formed by photooxidation. Bubbling oxygen through a solution of **3** in the

dark or irradiation of **3** in the absence of the sensitizer or in the presence of equimolar 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher,⁸ yielded no detectable dioxetane or epoxide. Addition of 2,6-di-*tert*-butyl-*p*-cresol, a free radical inhibitor, has no effect on the rate of oxidation of **3** nor on the ratio of **4** and **6**. **4** and **6** are both stable under photooxidation conditions and are not interconverted, nor is the epoxide formed from the irradiation of **3** + **6** + TPP in the absence of oxygen. Neither **4** nor **6** is produced from the vpc standard, 7,7'-binorbornyl, under the conditions of the photooxidations.

The extent of formation of epoxide in the experiments of Table I varies from 40% in methylene chloride (0.0037 *M* **3**) to 95% in benzene (0.00019 *M* **3**). This is a 28.5-fold range in the ratio of epoxide to dioxetane. Though concentration and solvent dependent, this ratio is not parallel to the polarity of the solvent, and certainly not to its capability as a substrate for the Baeyer-Villiger reaction,^{2a,c} since more epoxide was formed in benzene than in pinacolone. Hypotheses suggested by these results are under active investigation in this laboratory.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation and the National Institutes of Health.

(8) J. C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

Paul D. Bartlett,* Margaret S. Ho

Converse Memorial Laboratory, Harvard University
Cambridge, Massachusetts 02138

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On the Appropriateness of Assigning Spin Labels to Excited States of Inorganic Complexes¹

Sir:

Recently there has been a surge of interest in the photochemistry and spectroscopy of transition metal complexes of the heavier transition elements. The tris(2,2'-bipyridine)ruthenium(II) ion is playing a key role because of its unusual luminescence properties. In most of these studies it is either explicitly stated or tacitly assumed that the excited state(s) responsible for the luminescence, energy transfer, or photochemistry possesses a well-defined multiplicity.²⁻⁶ The purpose of this communication is to point out that reliance upon a spin-based language may lead to erroneous conclusions regarding excited-state properties, mechanisms of energy transfer, and photochemical reactivity in inorganic systems.

A spin labeled state is defined theoretically as a state whose eigenket satisfies the equation $S^2|\psi\rangle = S(S +$

$1)\hbar^2|\psi\rangle$, and the existence of states with this property is contingent upon the commutation of S^2 with \mathcal{H} , the total Hamiltonian of the system. Such states are found (to a high degree of approximation) in organic molecules. The total Hamiltonian always contains terms of the form $\sum(\xi r_i)_i \cdot s_i$, however. Such terms are relatively unimportant for systems containing only light atoms but may become dominant for states of molecules containing even a single atom with high atomic number. Spin-orbit ξ values (cm^{-1})⁷ are high for atoms such as cobalt (517), rhodium (968), and ruthenium (878) and become enormous for 5d elements (Os, 3500; Ir, 3600; W, 2089; Pt, 4052). In contrast, that for carbon is only 30. Thus for compounds containing 4d or 5d elements and also some 3d elements, certain state eigenkets may not satisfy the above equation, even approximately, and a spin label is no longer meaningful.

Studies of luminescent transition metal complexes containing metals of (nd)⁶ configurations have led to a correlation between the orbital nature of an excited state and the degree of appropriateness of a singlet or triplet designation. For the well-studied complexes containing π -conjugated ligands, we recognize three main classifications of excited states.

First, there are $\pi\pi^*$ states that have properties approximating those observed for organic molecules. When such an excited state lies lowest, one usually observes (77°K) a long-lived phosphorescence (>msec) and an emission band structure closely resembling that of the phosphorescence of the ligand itself. The emitting manifold spans a narrow energy range (<10 cm^{-1}). States of this nature have been observed for the tris(2,2'-bipyridine)rhodium(III), tris(1,10-phenanthroline)rhodium(III), and *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) ions.^{8,9} Their low-lying $\pi\pi^*$ states can be described, to first order, as triplets, although the emitting levels of the latter species are approaching an intermediate character (*vide infra*).

Second, we observe dd states that possess an intermediate character. An example is the low-lying (emitting) excited state of $[\text{Co}(\text{CN})_6]^{3-}$, formally a 3T_1 .^{10,11} The emission displays (77°K) a broad structureless band and has an intermediate decay time (~ 700 μsec). The excited manifold spans a wide energy range (~ 600 cm^{-1}). For this "state" it is useful to use the 3T_1 formalism only as a starting point. To fit the observed level manifold theoretically we have been forced to resort to perturbation theory involving higher excited states of various multiplicities.^{12,13} For molecules containing metals of higher atomic number the situation will be worse.

The third type of state is that for which any spin label at all is apparently not justified either experimentally or

(7) Value for carbon (zerovalent) calculated from ground term [C. E. Moore, *Nat. Bur. Stand. (U. S.) Circ.*, No. 467 (1949)]; osmium estimated for Os^{3+} [R. Dingle, *J. Mol. Spectrosc.*, **18**, 276 (1965)]; iridium (zerovalent) estimated [J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, England, 1971, p 113]; all others (zerovalent metal) [J. S. Griffith, *ibid.*, Appendix 6].

(8) D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970).

(9) R. J. Watts, G. A. Crosby, and J. L. Sansregret, *Inorg. Chem.*, **11**, 1474 (1972).

(10) G. A. Crosby, *J. Chim. Phys. Physicochim. Biol.*, **46**, 160 (1967).

(11) M. Mingardi and G. B. Porter, *J. Chem. Phys.*, **44**, 4354 (1966).

(12) K. W. Hipps and G. A. Crosby, unpublished work.

(13) M. L. Ellzey, private communication.

(1) Research supported by AFOSR (NC)-OAR, USAF Grant No. 72-2207.

(2) (a) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 2841 (1971); (b) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 4336 (1971).

(3) H. D. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

(4) P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 3635 (1972); **95**, 2470 (1973).

(5) D. A. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Petersen, D. P. McDonald, and P. C. Ford, *J. Amer. Chem. Soc.*, **94**, 6665 (1972).

(6) J. N. Demas, D. Diemente, and E. W. Harris, *J. Amer. Chem. Soc.*, **95**, 6864 (1973).