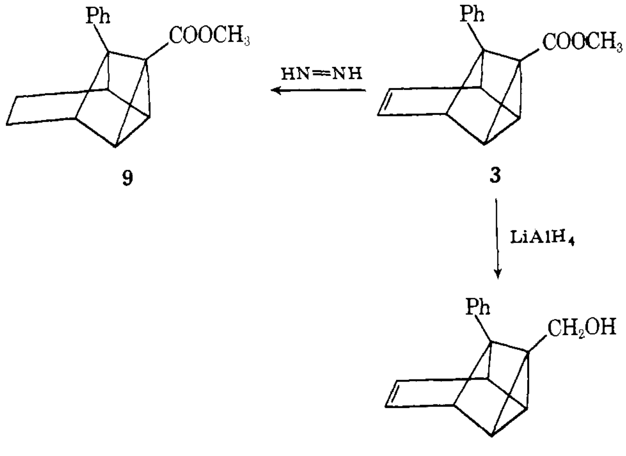
In view of the known photoreaction of tolane with naphthalene,[4] and Klumpp's reports[6] regarding $(CH)_8$ valence isomers, **3** or **7** appear to be most like alternative structures for our newly formed photoproduct, Scheme I.

Structure proof follows from spectral data as well as from the following experiments.

The position of the ester group in the unknown was conclusively established by reducing the unknown ester with $LiAlH_4$ to give corresponding alcohol **8**, a colorless oil:[5] ^1H NMR ($CDCl_3$) δ 1.62 (s, OH), 2.23 (t, 2 H, $J = 2$ Hz, H_2 and H_3), 3.76 (m, 2 H, H_1 and H_6), 3.97 (s, 2 H, CH_2O), 6.12 (t, 2 H, H_7 and H_8), and 7.23 (br s, 5 H, Ar). In the presence of the shift reagent $Eu(fod)_3$, the chemical shift of the cyclopropyl protons at δ 2.23 and bridgehead protons at δ 3.76 in the alcohol **8** shifted ~2.6 and 2.2 times as much downfield as the vinylic protons. From this, structure **7** is definitely ruled out since one would expect the opposite.

More evidence for the proposed structure **3** derived when the ester was subjected to a selective reduction of the double bond. With diimide in ethanolic solution,[8] **3** gave 95% of **9**, a colorless oil:[5] ^1H NMR ($CDCl_3$) δ 1.70 (m, 4 H, H_7 and H_8), 2.62 (m, 2 H, H_2 and H_3), 3.26 (m, 2 H, H_1 and H_6), 3.55 (s, 3 H, $COOCH_3$), and 7.25 (br s, 5 H, Ar). Furthermore, heating a solution of **3** in decalin at 183 °C for 4 h gave **2** as the only product in 80% yield.[9]



9

3

8

The formation of **3** can be shown to be a wavelength dependent phenomenon. Under conditions where only methyl phenylpropiolate is absorbing the light, i.e., through Pyrex, **3** is exclusively obtained. There is no **2**. Through quartz, however, the reaction mixture contains **2** in minor quantities and, after 56% conversion, both **2** and **3** are present in a 35:65 ratio. Control experiments established that **2** could be converted into **3** and vice versa, on irradiation through quartz. Through Pyrex, however, **3** was shown to be photostable, though **2** was converted cleanly into **3** in excellent yield under these conditions.

We interpret our results as follows. The photoaddition of methyl phenylpropiolate to benzene likely proceeds as suggested for other alkynes,[3] by way of a bicyclo[4.2.0]octatriene. In fact, such an intermediate has been isolated in the photoaddition of acetylenes to hexafluorobenzene.[2c] Formation of our product **3**, at longer wavelengths, as well as **2**, at shorter wavelengths, requires the same intermediate, 7-carboxymethyl-8-phenylbicyclo[4.2.0]octa-2,4,7-triene (**10**). The excited species leading to the formation of **10** in our experiments must be that of methyl phenylpropiolate rather than of benzene.[10]

Unless **10** rearranges to **3** by energy-transfer process, **10** must live long enough[11,12] to absorb a second photon in competition with residual **1**. This photochemical reaction of **10** must also compete with the thermal and/or photochemical ring opening leading to **2**. Therefore, **3** is the kinetically controlled photoproduct and cannot be reconverted into **2** (via **10**), in Pyrex.[13] The formation of **2** at shorter wavelengths comes from a photoreversion of **3** likely but not necessarily via **10** at these wavelengths. The formation of **2** from **3** when the latter is irradiated through quartz experimentally confirms the reverse reaction. This contention is also supported by the observation that the ratio of **2**/**3** obtained from **1** and benzene through quartz increases at higher conversions.

New product **3** is the first example of photochemical trapping of a bicyclo[4.2.0]octatriene like **10**. Whether it is occurring via a concerted symmetry allowed process, or via the most stable biradical is still unclear. We are presently pursuing the mechanistic ramifications of this unusual new reaction.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-7610893). Support of these agencies is gratefully acknowledged.

References and Notes

(1) For previous work in this area see A. H. A. Tinnemans and D. C. Neckers, *J. Org. Chem.*, **42,** 2374 (1977).

(2) (a) L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Am. Chem. Soc.*, **96,** 5806 (1974), and references herein; (b) W. Lippke, W. Ferree, Jr., and H. Morrison, *ibid.*, **96,** 2134 (1974); (c) B. Sket and M. Zupan, *ibid.*, **99,** 3504 (1977).

(3) D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Chem. Commun.*, 498 (1970).

(4) P. J. Collin and W. H. F. Sasse, *Aust. J. Chem.*, **24,** 2325 (1971), and references herein: T. Teitei, D. Wells, and W. H. F. Sasse, *ibid.*, **26,** 2129 (1973); **28,** 571 (1975).

(5) Satisfactory analyses have been obtained for all compounds reported herein.

(6) (a) G. W. Klumpp, W. G. J. Rietman and J. J. Vrielink, *J. Am. Chem. Soc.*, **92,** 5266 (1970); (b) G. W. Klumpp and J. Stapersma, *Tetrahedron Lett.*, 747 (1977).

(7) Data in parentheses refer to signal multiplicities as obtained from the off-resonance decoupled spectrum.

(8) J. M. Hoffman and R. H. Schlessinger, *Chem. Commun.*, 1245 (1971).

(9) Compound 2 was characterized by its ^1H NMR spectrum in $CDCl_3$: δ 3.55 (s, 3 H, $COOCH_3$), 6.55–5.72 (m, 5 H, H_{4-8}), 7.30 (s, 5 H, Ar), 7.35 (br s, 1 H, H_3) (cf. D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Angew. Chem., Int. Ed. Engl.*, **10,** 746 (1971)). Reaction of **2** with tetracyanoethylene in EtOAc gave 3-carboxymethyl-4-phenyl-9,9,10,10-tetracyanotricyclo-[4.2.2.$0^{2,5}$]deca-3,7-diene (**11**) in 72% yield[5] mp 246–247 °C dec; NMR (Me_2SO) δ 3.36 (t, 1 H, H_5 or H_2, $J = 5$ Hz), 3.62 (t, 1 H, H_2 or H_5, $J = 5$ Hz), 3.73 (2, 3 H, $COOCH_3$), 4.10–4.24 (m, 1 H, H_6 or H_1), 4.52–4.66 (m, 1 H, H_1 or H_6), 6.17–6.57 (ddd, 2 H, H_7 and H_8), 7.40–7.65 (m, 3 H, Ar) and 7.85–8.15 (m, 2 H, Ar).

(10) Symmetry rules predict the possibility of a concerted cis- or trans-1,2 addition of S_1 acetylene to S_0 benzene: D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **32,** 1309 (1976). However, it cannot be excluded that **10** is formed via a zwitterion: D. Bryce-Smith, R. Deshpande, A. Gilbert and J. Grzonka, *Chem. Commun.*, 561 (1970).

(11) In the present study no direct evidence was obtained for an appreciable concentration of **10**. Its half-life, however, is supposed to be comparable with that of the unsubstituted bicyclo[4.2.0]triene ($t_{1/2}$ = 14 min at 0 °C): E. Vogel, H. Keifer, and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **3,** 442 (1964).

(12) The ultraviolet spectrum of the intermediate is expected to have a considerable absorption above 280 nm. Cf. bicyclo[4.2.0]octa-2,4-diene, λ_{max} 274 nm (ϵ 3340): A. C. Cope, A. C. Haven, Jr., F. I. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74,** 4867 (1952).

(13) Under these conditions **3** is nonabsorbing. Its UV spectrum consists π–π^* λ_{max} 228 nm (ϵ 6370). There is essentially no absorption above 280 nm.

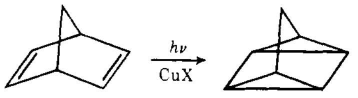
Alois H. A. Tinnemans, Douglas C. Neckers*
Department of Chemistry, Bowling Green State University
Bowling Green, Ohio 43403

Received June 6, 1977

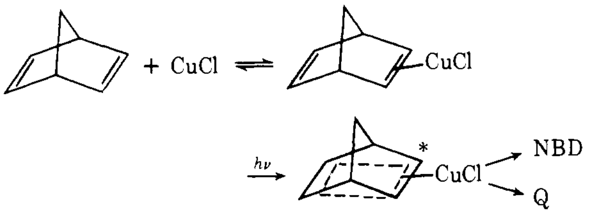
Use of Copper(I) Phosphine Compounds to Photosensitize the Valence Isomerization of Norbornadiene

Sir:

Several studies dealing with the photoassisted reactions of olefins in the presence of Cu(I) compounds have been reported,[1] and, in each system, the formation of a Cu(I)-olefin complex plays a key mechanistic role. A case in point is our recent observation[2,3] that norbornadiene (NBD) undergoes efficient valence isomerization to quadricyclene (Q) in the presence of catalytic amounts of simple CuX (X is Cl, Br, I, or $C_2H_3O_2$) salts (reaction 1). In the thoroughly studied cuprous chloride-norbornadiene system, spectral and photochemical evidence support a mechanism (eq 2) which features a 1:1 ClCu-NBD π complex as the predominant photoactive species. Minimally, the role of the complex is to facilitate the absorption of light by the otherwise weakly absorbing olefin. There is, in addition, the possibility that the complex may provide a new, low energy pathway for the production of Q.



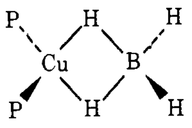
NBD Q (1)



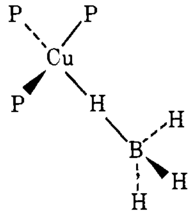
(2)

To broaden the presently limited selection of Cu(I) compounds which have been employed in photoassisted reactions of olefins, we undertook an investigation of the NBD to Q conversion in the presence of $Cu[P(C_6H_5)_3]_2BH_4$, $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$, and Cu(diphos)$BH_4$ (diphos is 1,2-bis(diphenylphosphino)ethane). These compounds are considerably less prone to air oxidation than are CuX salts and, in addition, they exist as well-defined monomeric units in solution (vide infra). Interestingly, we find that $Cu[P(C_6H_5)_3]_2BH_4$ and $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$ are ~60-90 times more effective than Cu(diphos)BH_4 in sensitizing[4] the production of Q. Furthermore, the mechanism of sensitization appears to be fundamentally different from that involving CuX salts. Our results, which provide evidence for a previously unreported mechanistic role of Cu(I) compounds in olefin photoreactions, are reported here.

Commercially available norbornadiene (Aldrich) was distilled from potassium metal under a nitrogen atmosphere. Triphenylphosphine (Eastern Chemical) and diphos (Arapahoe Chemical) were purified by repeated recrystallization from ethanol and benzene, respectively. Diphenylmethylphosphine was obtained by a literature method.[5] Samples of $Cu[P(C_6H_5)_3]_2BH_4$, $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$, and Cu(diphos)$BH_4$ which gave satisfactory elemental analyses were prepared by the general procedure of Lippard and Ucko.[6] In a typical photochemical experiment, 4 mL of a nitrogen-purged benzene solution containing 0.1 M NBD and 1×10^{-3} M Cu(I) compound was irradiated at 313 nm in a previously described merry-go-round apparatus.[3] At the concentrations employed, the Cu(I) compound absorbs ≥99% of the incident radiation. Light intensity was determined by ferrioxalate actinometry.[7] The resulting NBD-Q mixture was analyzed by gas chromatography using conditions similar to those previously reported.[3]



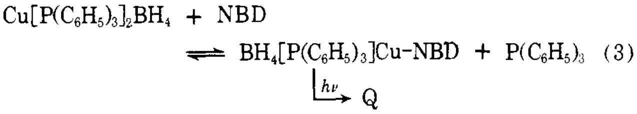
I



II

Both $Cu[P(C_6H_5)_3]_2BH_4$ and Cu(diphos)BH_4 possess structure I in the solid state and solution.[8] No dissociation of the former compound occurs in benzene solution, at least to the extent detectable by measurement of colligative properties.[9] It has recently been shown that $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$ in the solid state possesses the novel structure II, which features the copper atom in a distorted tetrahedral environment consisting of the P atoms of three $P(C_6H_5)_2(CH_3)$ ligands and a single H atom of BH_4^-.[10,11] Upon dissolution in benzene, however, the compound undergoes extensive (>78% for a 10^{-3} M solution) dissociation of one phosphine and rearranges to structure I. Phosphine lability in $Cu[P(C_6H_5)_3]_2BH_4$ and $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$ was established by ^{31}P NMR studies. Thus mixtures of each Cu(I) compound and its respective free ligand in benzene exhibit a single resonance whose chemical shift is a function of the added ligand concentration.[12]

The key photochemical observations may be summarized as follows. (1) The Cu(I) compounds containing monodentate phosphine ligands sensitize the production of Q with high quantum efficiency, the quantum yield at 313 nm in a 0.1M NBD solution being 0.18 for $Cu[P(C_6H_5)_3]_2BH_4$ and 0.27 for $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$.[13] In marked contrast, the quantum yield in the presence of Cu(diphos)BH_4 is ~0.003. (2) The quantum yield increases with increasing NBD concentration, reaching a limiting value of ~0.5 for $Cu[P(C_6H_5)_3]_2BH_4$ and ~0.6 for $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$ at NBD concentrations >0.5M. (3) Uncoordinated $P(C_6H_5)_3$ can function as a sensitizer, albeit with a quantum yield <5% of that of $Cu[P(C_6H_5)_3]_2BH_4$. (4) The photoprocess is catalytic in Cu(I) compound. Thus >10 mol of Q are formed/mol of $Cu[P(C_6H_5)_3]_2BH_4$ or $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$. (5) The quantum yield is independent of light intensity over a fivefold range in the $Cu[P(C_6H_5)_3]_2BH_4$-NBD system.



$$Cu[P(C_6H_5)_3]_2BH_4 + NBD \rightleftharpoons \underset{\downarrow h\nu \; Q}{BH_4[P(C_6H_5)_3]Cu\text{-}NBD} + P(C_6H_5)_3 \quad (3)$$

We have explored the possibility that copper-norbornadiene complexation plays a significant role in the mechanism of sensitization by $Cu[P(C_6H_5)_3]_2BH_4$ and $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$. Since tetracoordinate copper is generally considered to be coordinatively saturated,[14] complex formation would necessarily involve the replacement of one (or more) of the original ligands by NBD. Despite numerous experiments, however, we have been unable to obtain any evidence for such a ligand substitution process. For example, the addition of free $P(C_6H_5)_3$ to a solution containing NBD and $Cu[P(C_6H_5)_3]_2BH_4$ would be expected to shift the equilibrium shown in eq 3 to the left, thus decreasing the concentration of the photoactive complex. Contrary to this expectation, we find no change in the total quantum yield of Q production in the presence of a 20-90% excess of the free ligand. Likewise the single ^{31}P resonance exhibited by solutions of $Cu[P(C_6H_5)_3]_2BH_4$ or $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$ does not undergo the expected high field shift, indicative of an increased concentration of uncoordinated phosphine,[12] upon addition of excess NBD. The alternative pathway in which a copper-norbornadiene complex is formed via photochemical dissociation of a phosphine ligand, with the subsequent absorption of a second photon resulting in the production of Q, is not consonant with the light intensity independence of the quantum yield. A final possibility involves the coordination of NBD to copper at a site originally occupied by a H atom from BH_4^-. We tend to discount this pathway on the grounds that the B-H infrared stretching modes characteristic of $Cu[P(C_6H_5)_2$-

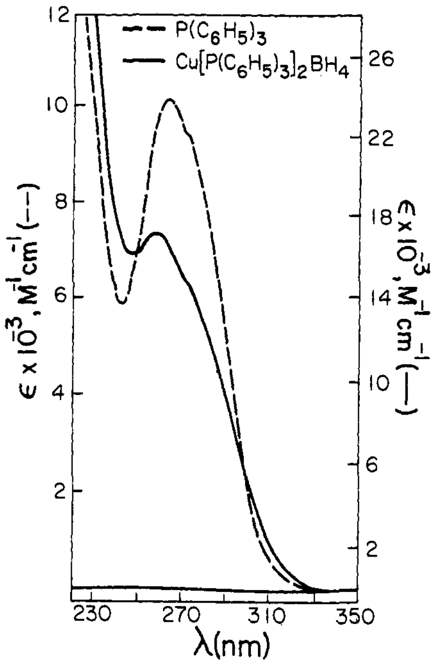
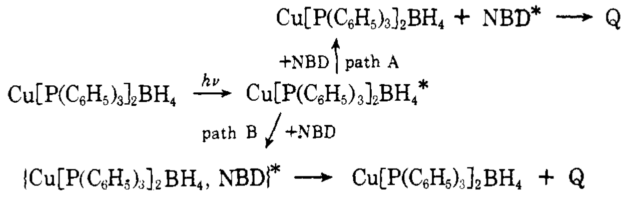


Figure 1. Electronic absorption spectra of $Cu[P(C_6H_5)_3]_2BH_4$ and $P(C_6H_5)_3$ in cyclohexane.

Scheme I



$(CH_3)]_3BH_4$ in solution are essentially unchanged upon addition of a huge excess of NBD. Formation of a photoactive, singly bridged Cu-H-BH_3 species would have produced readily detectable spectral changes.[10]

We conclude that the mechanism of sensitization by $Cu[P(C_6H_5)_3]_2BH_4$ and $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$ is fundamentally different from that exhibited by simple CuX salts in that no direct coordination of NBD to the metal occurs. The two alternative paths depicted in Scheme I thus merit serious consideration. Path A involves intermolecular electronic energy transfer from an excited state of the Cu(I) compound to the lowest π-π^* triplet state of NBD. The latter state is reported to undergo efficient conversion to Q.[15] Alternatively, path B features the formation of a complex[16] between the *photoexcited* Cu(I) compound and NBD. Relaxation of this complex may then occur by pathways which lead to NBD or Q.

Finally, we wish to note some interesting differences between the spectral characteristics of "effective" vs. "noneffective" sensitizers. The electronic absorption spectra of $Cu[P(C_6H_5)_3]_2BH_4$ and free $P(C_6H_5)_3$ are compared in Figure 1, while the corresponding spectra of Cu(diphos)BH_4 and diphos are shown in Figure 2. The intense charge transfer transition[17] in $P(C_6H_5)_3$ undergoes a relatively small perturbation upon coordination. Thus the peak maximum blue shifts by 4 nm and the low energy tail extends to slightly longer wavelengths. In contrast, the spectrum of diphos is markedly affected upon coordination of the ligand to Cu(I). The charge-transfer maximum experiences a considerable intensity reduction and develops a pronounced shoulder on the long-wavelength side. A similar pattern emerges from preliminary emission studies conducted in room temperature benzene solution. Both $Cu[P(C_6H_5)_3]_2BH_4$ and $P(C_6H_5)_3$ exhibit a broad emission

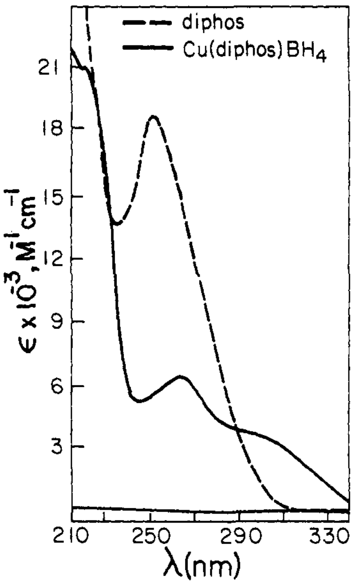


Figure 2. Electronic absorption spectra of Cu(diphos)BH_4 and diphos in cyclohexane.

which centers at 474-476 nm, indicating that the emitting levels in the two compounds are nearly isoenergetic. The 537-nm emission shown by Cu(diphos)BH_4, however, is considerably red shifted from the 500-nm band of free diphos. One inference from these spectral results is that the thermally equilibrated excited states[18] of the two Cu(I) compounds have appreciably different properties (e.g., energies, geometries, lifetimes). The extent to which such differences are related to the low sensitization efficiency of Cu(diphos)BH_4 is currently under investigation.

Acknowledgment. The authors acknowledge the support of this work by the Energy Research and Development Administration through Contract E(38-1)-893 and by the National Science Foundation through Grant No. MPS75-13752. We thank Dr. R. B. King for kindly supplying samples of the diphos and diphenylmethylphosphine.

References and Notes

(1) R. G. Salomon and M. F. Salomon, *J. Am. Chem.*, **98**, 7454 (1976), and references cited therein.
(2) D. P. Schwendiman and C. Kutal, *Inorg. Chem.*, **16**, 719 (1977).
(3) D. P. Schwendiman and C. Kutal, *J. Am. Chem. Soc.*, **99**, 5677 (1977).
(4) In the present context, a sensitizer is a compound which enhances the rate of the photoconversion of NBD to Q. The mechanism of sensitization will depend upon the nature of the sensitizer involved.
(5) M. A. Mathur, W. H. Myers, H. H. Sisler, and G. E. Ryschkewitsch, *Inorg. Synth.*, **15**, 128 (1974).
(6) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968).
(7) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A.*, **235**, 518 (1956).
(8) An x-ray determination confirms that crystalline $Cu[P(C_6H_5)_3]_2BH_4$ exists as structure I: S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967). The structure of this compound in solution, as well as the solid state and solution structures of Cu(diphos)BH_4, are inferred from infrared spectral studies.
(9) The limited solubility of Cu(diphos)BH_4 precludes an accurate molecular weight determination in benzene. However, the compound is reported to be undissociated in chloroform: F. Carlati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).
(10) J. C. Bommer and K. W. Morse, *J. Chem. Soc., Chem. Commun.*, 137 (1977).
(11) J. L. Atwood, R. D. Rogers, C. Kutal, and P. A. Grutsch, *J. Chem. Soc., Chem. Commun.*, in press.
(12) For example, a 0.14 M solution of free $P(C_6H_5)_3$ exhibits a peak at +5.8 ppm (all chemical shifts relative to external H_3PO_4), while a 0.04 M solution of $Cu[P(C_6H_5)_3]_2BH_4$ gives a single peak at +2.2 ppm. As a consequence of rapid exchange a solution mixture of 0.07 M ligand and 0.02 M Cu(I) compound exhibits a single resonance at an intermediate value of +4.8 ppm. Qualitatively similar behavior obtains for $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$.
(13) Throughout the remainder of the article we will employ the solid-state formulation, $Cu[P(C_6H_5)_2(CH_3)]_3BH_4$, as a generic label when referring to the diphenylmethylphosphine Cu(I) compound. It should be remembered, however, that the predominant species obtained upon dissolution possesses structure I.

(14) F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, **17**, 115 (1975). Only one five-coordinate Cu(I) compound has been reported, and it contains a tetradentate macrocyclic ligand: R. R. Gagné, *J. Am. Chem. Soc.*, **98**, 6709 (1976).
(15) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).
(16) Excited-state charge-transfer complexes and exciplexes have been implicated in the sensitization and quenching processes of transition metal compounds: V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
(17) W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectrosc.*, **5**, 118 (1960).
(18) A. W. Adamson, *Adv. Chem. Ser.*, **No. 150**, Chapter 12 (1976).

Paul A. Grutsch, Charles Kutal*
Department of Chemistry, University of Georgia,
Athens, Georgia 30602
Received May 31, 1977

A New Molybdoarsonate. Structure of $(PhAs)_2Mo_6O_{25}H_2{}^{4-}$ and Solution Interconversion of Heteropoly Anions That Differ by a Constitutional Water Molecule

Sir:

The mechanisms of formation and interconversion of isopoly and heteropoly oxometallate anions are not well delineated, although there is encouraging activity in this area.[1-3] A new heteropoly molybdate structure, described below, appears to be simply related to a previously determined structure by the insertion of a bridging water molecule. The solution interconversion of the two structures suggests that reaction pathways involving face sharing of MO_6 octahedra may be important in oxometallate hydrolyses.

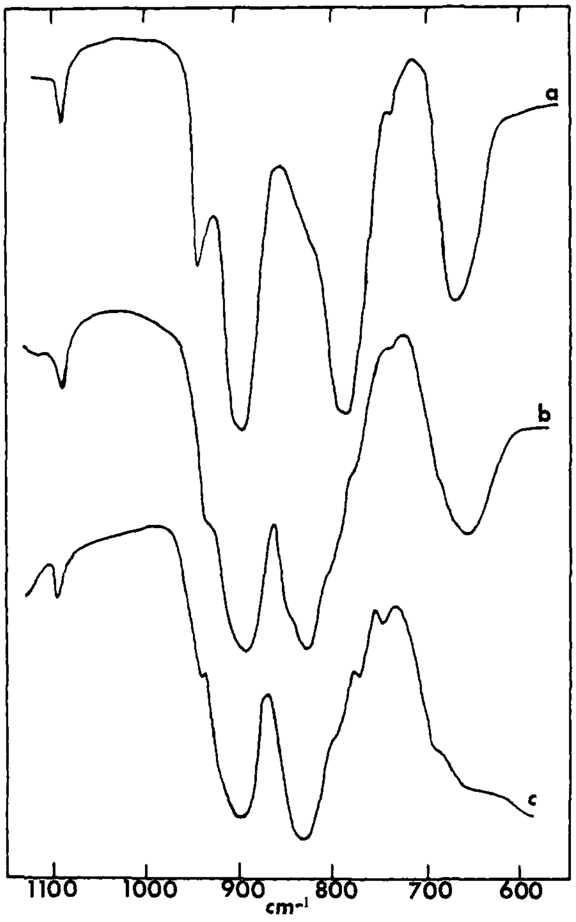


Figure 1. Infrared spectra: (a) $(CN_3H_6)_4[(PhAs)_2Mo_6O_{24}]{\cdot}6H_2O$ (A complex); (b) $(CN_3H_6)_4[(PhAs)_2Mo_6O_{25}H_2]{\cdot}4H_2O$ (B complex); (c) solution of $PhAsO_3{}^{2-}$ and $MoO_4{}^{2-}$ (1:3 molar ratio) in D_2O-DCl, pH 4.

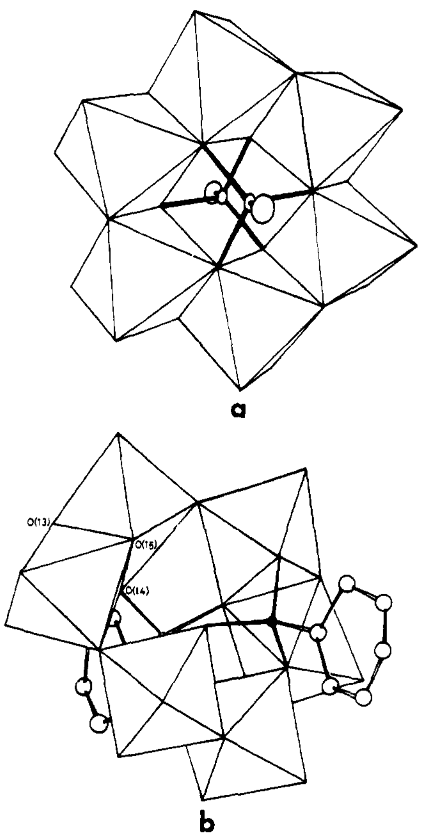


Figure 2. (a) A structure, $(MeAs)_2Mo_6O_{24}{}^{4-}$ (ref 4); (b) B structure, $(PhAs)_2Mo_{25}H_2{}^{4-}$ (this work).

We recently described the synthesis and structure of a series of hexamolybdobisorganoarsonates, $(RAs)_2Mo_6O_{24}{}^{4-}$ (A),[4,5] which are isolated from aqueous acidified solutions of $RAsO_3{}^{2-}$ and $MoO_4{}^{2-}$ (1:3 molar ratio) at pH 3-5. We now report that it is possible, reproducibly, to isolate from the same solutions salts of a second 2:6 molybdoarsonate complex (B), and that furthermore the B complexes are the predominant solute species in such solutions. The stoichiometry of the new complexes according to chemical analysis of three derivatives (R = Me, Ph, p-$C_6H_4NH_2$) is identical with that of the A complexes. Salts of the B anions can be distinguished from those of A by a consistent displacement of a strong infrared absorption band from ~795 (A) to ~825 cm^{-1} (B); see Figure 1. The corresponding Raman bands (solid samples) appear at ~790 and ~850 cm^{-1}, respectively. In aqueous or D_2O solutions at room temperature, Raman and infrared spectra show bands corresponding to the B form only, in the pH range 2.5-7.[6]

An x-ray structural investigation of the guanidinium salt of the B phenyl derivative has been carried out (K.Y.M. and Y.S.). The salt $(CN_3H_6)_4[PhAs)_2Mo_6O_{25}H_2]{\cdot}4H_2O$ crystallizes in space group $P2_1$ with a = 13.754 (8), b = 15.752 (7), c = 11.900 (5) Å; β = 115.59 (2)°; Z = 2. The x-ray intensities were measured up to 2θ = 60° on a Philips automatic four-circle diffractometer and the structure was solved by the heavy-atom method. Anisotropic temperature factors were applied to all nonhydrogen atoms and the structure was refined by the block-diagonal least-squares method. The final unweighted R value based on 4720 independent reflections was 0.066. Details of the structure determination will be published later elsewhere.[7]

The anion consists of six MoO_6 octahedra, which form a ring with one face sharing at O(13), O(14), and O(15), two corner sharings, and three edge sharings. The two tetrahedral $C_6H_5AsO_3$ groups cap the ring, one from above and the other from below, as is shown in Figure 2b.