ported by other investigators. The usual methods for determination of singlet oxygen lifetimes in solution are indirect and involve monitoring the loss of a singlet-oxygen acceptor. The kinetics of this approach are often complicated and require that various simplifying assumptions be made. Lifetime values determined by using this approach are also reported in Table I.

From the observed values for the lifetime of singlet oxygen in protiated and deuterated solvents, values for the solvent isotope effect are calculated and compared to values independently determined[1] (Table II). Agreement between the values is as good as can be expected, considering the limitations of the indirect method.

In the course of this work it was discovered that high sensitizer concentrations or high laser powers can yield lifetimes that are much lower than those measured under other conditions.[12a,15] This effect is particularly important for solvents in which the lifetime of singlet oxygen is long. Values for the lifetime of singlet oxygen determined at high dye concentrations or at high laser powers can be extrapolated to zero concentration and power; values so obtained do not differ significantly from those in Table I. It seems likely that multiphoton processes (or interaction of multiple excited species) can result in the creation of species that quench singlet oxygen (e.g., the reduction of $^3O_2$ to yield $O_2^-\cdot$). For the porphyrins it is known that ionization potentials are low and that Rydberg states are readily populated.[16] Photooxygenation of dye molecules also appears to create species that quench singlet oxygen.[15] Absorption spectra of some dyes taken after irradiation show changes; in particular, extensive reaction of dyes occurred in $CHCl_3$ and CCl_4. We showed previously that species other than singlet oxygen (perhaps radical reactions) complicate the reactions in chloroform.[1] A more complete discussion is presented elsewhere.[6,17]

The large values of the deuterium isotope effect observed confirm our suggestion that the approach taken by Kearns[8b] does not provide an adequate description for the quenching of singlet oxygen by solvent interactions. In the present case, a *quantitative* correlation was not found between singlet oxygen lifetimes and the optical density of the solvent in regions that correspond to the transitions $[^1\Delta_g(v = 0) \rightarrow {}^3\Sigma_g^-]$ where $^3O_2$ is formed with varying numbers of vibrational quanta. A more complete development is presented elsewhere.[6,17]

Acknowledgment. We acknowledge the invaluable assistance of K. Stabe and R. Ponce of the UCLA Chemistry Department electronics shop in the construction of electronic equipment. We also thank Professor G. Schuster for discussion of his parallel work in this area.[11] This work was supported by National Science Foundation Grant No. CHE80 20140.

Registry No. Oxygen, 7782-44-7.

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(15) (a) Krasnovskii, A. A. *Biofizika* **1976**, *21* 748. (b) *Ibid.* **1977**, *22*, 927. (c) Krasnovskii, A. A.; Venediktov, Ye. A. *Ibid.* **1978**, *23*, 387.

(16) Dupuis, P.; Roberge, R.; Sandorfy, C. *Chem. Phys. Lett.* **1980**, *75*, 434. (b) Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407. It is reported in this paper that the extinction coefficient of the triplet state of several porphyrins far exceeds that of the ground state at 530 nm, the wavelength used to excite these dyes. Thus, even though quenching of the triplet by O_2 is extremely fast, photolysis of triplet is possible at high power levels.

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Protonation of 11-Methylene-1,6-methano[10]annulene[1]

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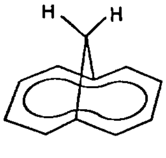
The bridged monocyclic 10-π-electron 1,6-methano[10]annulene[2] (**1**) is a classic example of Hückel aromaticity[3] despite its strong transannular interaction.[4,5,7] An important contribution to the high reactivity of **1** toward electrophiles[3b] may be the transannular interaction in the Wheland intermediate.[8] In continuation of our studies on the σ complexes of **1** under stable ion solution conditions[8,9] we now report on the protonation of 11-methylene-1,6-methano[10]annulene (**2**).[10]



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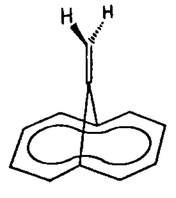

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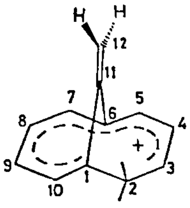

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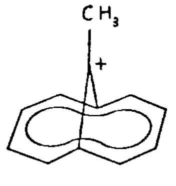

4

The intriguing aspect of **2** is that it contains a 10-π-electron aromatic system with an exocyclic, virtually noninteracting double bond. The relative reactivity of the annulene moiety and the C═C double bond in **2** may thus be investigated.

Protonation of **2** with FSO_3H in SO_2ClF at −80 °C in a NMR tube resulted in a red solution of ion **3**. The ^1H and ^{13}C NMR spectra of **3** are displayed in Figure 1, and the chemical shifts, coupling constants, and assignments are given in Table I. Quenching of the ion solution in sodium bicarbonate buffered methanol a −78 °C gives a ca. 60% recovery of **2**, demonstrating that the annulene structure remains intact and that no rearrangement has occurred.

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(2) Vogel, E.; Roth, H. D. *Angew, Chem.* **1964**, *76*, 145. Vogel, E.; Klug, W.; Breur, A. *Org. Synth.* **1974**, *54*, 11.

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(5) In the 11,11-dimethyl-**1**[6a] and 11-methyl-11-cyano-**1**[6b] the 1,6 interaction is so strong (1.62–1.81 Å) that these compounds may be regarded as bis(norcaradiene) derivatives.

(6) (a) Bianchi, R.; Morosi, G.; Mugnoli, A.; Simonetta, M. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1196. (b) Bianchi, R.; Pilati, T.; Simonetta, M. *J. Am. Chem. Soc.* **1981**, *103*, 6426; *Acta Crystallogr., Sect. B* **1978**, *B34*, 2157.

(7) For theoretical studies see: Favini, G.; Simonetta, M.; Sottocornola, M.; Todeschini, R. *J. Chem. Phys.* **1981**, *74*, 3953. Grunewald, G. L.; Uwaydah, I. M. *Tetrahedron Lett.* **1975**, *11*, 933. Burgi, H. B.; Shefter, E.; Dunitz, J. D. *Tetrahedron* **1975**, *31*, 3089.

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(9) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257.

(10) Synthesis: (*a*) Vogel, E.; Kleffner, H. W., unpublished results. Kleffner, H. W. Ph.D. Thesis, Cologne, West Germany, 1977. (b) Brinker, U. H. Ph.D. Thesis, Cologne, West Germany, 1973. Vogel, E.; Weyres, F. *Angew. Chem.* **1966**, *78*, 754.

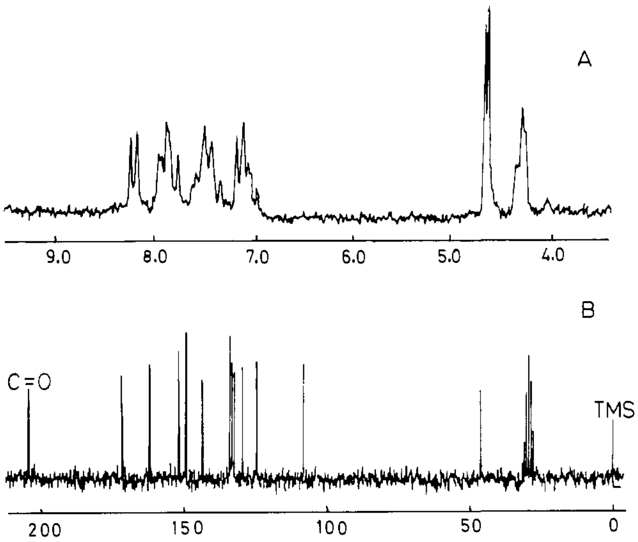

Figure 1. ^1H NMR (100 MHz) spectrum at -30 °C (A) and ^{13}C proton-noise-decoupled NMR spectrum at -80 °C (B) of ion **3** in FSO_3H-SO_2ClF.

Table I. ^1H and ^{13}C NMR Parameters of **3**[a]

position	δ ^1H	δ ^{13}C
1		151.4 (s)
2	4.25 (AB, ≈25)	47.0 (t, 135.9)
3	8.20 (m)	163.9 (d, 168.8)
4	7.35 (m)	126.5 (d, 166.5)
5	8.55 (d, 7)	173.9 (d, 165.5)
6		136.1 (s)
7	8.20 (m)	154.0* (d, 164.8)
8	7.35 (m)	131.7** (d, 165.0)
9	7.75 (m)	146.0* (d, 168.4)
10	7.75 (m)	134.7** (d, 169.2)
11		135.4 (s)
12	4.62 and 4.65	109.9 (t, 164.4)

[a] ^1H and ^{13}C chemical shifts are in parts per million from external Me_4Si (capillary). Multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet) and coupling constants (J_{HH} and $^1J_{CH}$ in hertz) are in parentheses. Resonances with an equivalent number of asterisks have interchangeable assignments.

The number and complexity of the NMR signals observed rigorously rules out the formation of the bridged protonated species **4**. The resemblance of the ^{13}C and ^1H NMR chemical shifts in the aromatic region with those of the parent 1,6-methano[10]annulenium ion is remarkable.[11,12] This suggests that the positive charge in **3** is delocalized over the whole annulenium skeleton without a significant enhancement of the 1,6-interaction. The ^1H NMR resonance of the protonated center at C(2) is centered at δ_H 4.25. The large geminal coupling between the two hydrogens of ca. 25 Hz is normal in the annulenium ions.[8,9,11] The difference in chemical shift of ca. 15 Hz is small as compared to monoprotonated **1** ($\Delta\delta_H$ = 56 Hz)[11] and diprotonated **1** ($\Delta\delta_H$ 102 Hz).[9] The C=C double bond seems to be unaffected; the carbon C(12), δ_c 109.9, carries two hydrogens $J_{^{13}CH}$ = 164.4 Hz, being unequivalent ($\Delta\delta_H$ = 3 Hz).

The protonation of **2** giving **3** shows that the annulene moiety has a higher basicity than the exocyclic double bond. In an attempt to put this observation in more quantitative terms theoretical calculations were performed on the species under consideration. Both the semiemperical MINDO/3[13a] and MNDO[13b] methods were employed with full (**3**) and partly C_{2v} symmetry[14] restricted (**4**) geometry optimizations. The MINDO/3-calculated heats of formation (ΔH_f) for **3** and **4** are 268.3 and 282.0 kcal/mol, respectively, and the MNDO ΔH_f's are 263.3 and 291.7 kcal/mol, respectively. Both sets of data confirm the preference of **3** over **4** with calculated energy differences of 13.7 kcal/mol (MINDO/3) and 28.4 kcal/mol (MNDO). The frontier orbital approach also favors formation of **3**, since the annulene moiety of **2** provides the degenerate pair of HOMO's.

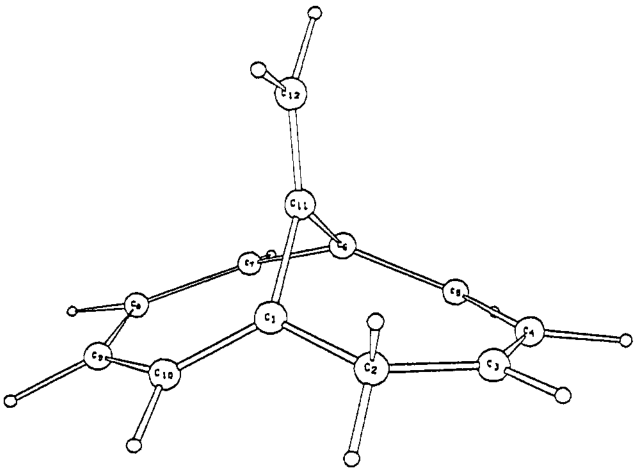

Figure 2. MNDO structure of ion **3**.

Table II. Bond Lengths (Å) and Bond Angles (Deg) in **3** (MNDO)

C(1)-C(6)	2.339	C(1)-C(10)	1.378	C(9)-C(10)	1.443
C(1)-C(11)	1.485	C(6)-C(7)	1.441	C(3)-C(4)	1.366
C(6)-C(11)	1.488	C(2)-C(3)	1.516	C(8)-C(9)	1.404
C(1)-C(2)	1.510	C(4)-C(5)	1.456	C(11)-C(12)	1.344
C(5)-C(6)	1.390	C(7)-C(8)	1.411		

C(1)-C(11)-C(6)	103.8	C(7)-C(6)-C(11)	115.4
C(1)-C(6)-C(11)	38.1	C(1)-C(2)-C(3)	114.8
C(6)-C(1)-C(11)	38.1	C(4)-C(5)-C(6)	123.3
C(2)-C(1)-C(6)	111.6	C(6)-C(7)-C(8)	121.2
C(5)-C(6)-C(1)	105.6	C(1)-C(10)-C(9)	123.7
C(10)-C(1)-C(6)	103.6	C(2)-C(3)-C(4)	131.1
C(7)-C(6)-C(1)	109.0	C(3)-C(4)-C(5)	129.2
C(2)-C(1)-C(10)	127.3	C(7)-C(8)-C(9)	126.7
C(5)-C(6)-C(7)	126.8	C(8)-C(9)-C(10)	128.3
C(2)-C(1)-C(11)	113.8	C(1)-C(11)-C(12)	128.8
C(5)-C(6)-C(11)	116.9	C(6)-C(11)-C(12)	127.4
C(10)-C(1)-C(11)	118.1		

The MNDO structure of **3** (Figure 2, Table II)[15] shows a fully delocalized annulenium moiety devoid of enhanced transannular interaction ($d(C_1-C_6)$ = 2.339 Å); the C=C double bond remains unaffected. We calculated a proton affinity for **2** of 209.7 kcal/mol (MNDO), similar to the 207.0 kcal/mol (MNDO) of the parent **1**.[16] This would suggest a comparable reactivity of **1** and **2**, contrary to observations. For example, reaction of **1** with excess of the mild reagent SO_3-dioxane results in a disulfonic acid,[3b] whereas in **2** only one sulfo group can be introduced under similar conditions.[17] Thus although bromination,[10a] formylation,[10a] and sulfonation[17] of **2** occur indeed in the annulene ring, its reactivity toward electrophiles appears to be less than the parent **1**. A possible explanation for the difference in reactivity of **1** and **2** might be the extent of transannular interaction in the σ complex. An indication might be that the parent 1,6-methano[10]annulenium ion rearranges at -60 °C, whereas **3** is stable up to -30 °C.[9]

In summary, we conclude that the annulene moiety in **2** is more reactive than the exocyclic double bond but less than the parent

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[11] Warner, P.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 7785.

[12] The ^{13}C NMR data of the 1,6-methano[10]annulenium ion will be reported in a forthcoming full paper.

[13] (a) Bisschof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

[14] C_{2v} symmetry was imposed on the annulene ring.

[15] The figure was plotted by a graphics program developed by B. Tidor and T. Clark, University of Erlangen-Nürnberg, West Germany.

[16] The calculated proton affinities (p.a.) refer to: p.a. = H_f(parent) + $H_f(H^+)$ - H_f(ion); $H_f(H^+)$ = 367 kcal mol^{-1}. The data employed are part of an extensive theoretical report on annulenes and annulenium ions currently in preparation.

[17] Lambrechts, H. J. A.; Cerfontain, H. *Recl. Trav. Chem. Pays-Bas* **1981**, *100*, 291.

1 and suggest that transannular interaction may play a significant role in the latter.

Acknowledgment. I thank Professor E. Vogel for a gift of **2** and his continuous encouragement. I also acknowledge Professors G. A. Olah and P. v. R. Schleyer for their incentive. The generous use of the laboratory facilities of the University of Amsterdam (The Netherlands) and the cooperation with the staff of the Regionales Rechenzentrum in Erlangen (West Germany) greatly facilitated the present investigation.

Registry No. 2, 10474-24-5; **3,** 81028-18-4.

Preparation and Structure of the $[Cu_5(C_6H_5)_6]^-$ Anion

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The reaction between phenyllithium and cuprous bromide in ethers has been reported to yield phenylcopper, a white, pyrophoric, and presumably polymeric solid.[1,2] When the reaction is carried out with excess phenyllithium, one gets a solution from which crystalline adducts such as $(PhCu)_4 \cdot PhLi \cdot 3.5Et_2O$ can be isolated.[1] We have investigated this system and report here the isolation and structure determination of a new pentanuclear copper cluster, $[Cu_5Ph_6]^-$, as its $[Li(THF)_4]^+$ and $[Li(PMDTA)(THF)]^+$ salts (PMDTA = pentamethyldiethylenetriamine).

$[Li(THF)_4]^+[Cu_5Ph_6]^-$ was prepared by treating a cold (−20 °C) suspension of CuBr (1 g, 7 mmol) in diethyl ether with a solution of freshly prepared phenyllithium (9.6 mL, 0.97 M in Et_2O, 9.3 mmol). The yellow suspension was allowed to warm to room temperature, when it formed first a clear yellow solution and then a pale yellow precipitate in a yellow supernatant. The precipitate was isolated and recrystallized from a THF/Et_2O mixture (50:50) to give pale yellow prisms.[3] The corresponding $[Li(PMDTA)(THF)]^+$ salt was isolated under similar conditions.[4] Salts of $[Cu_5Ph_6]^-$ are somewhat unstable, decomposing at room temperature in several days.

$[Li(THF)_4]^+[Cu_5Ph_6]^-$ crystallizes in the monoclinic space group $P2_1/n$,[5] with the following unit cell parameters: $a = 17.112$ (10) Å, $b = 13.920$ (6) Å, $c = 21.969$ (4) Å, $\beta = 105.98$ (4)°, ρ(calcd) = 1.42 g cm^{-3} for $Z = 4$. X-ray diffraction data were collected on a Syntex $P2_1$ diffractometer with Mo Kα radiation with a $\theta/2\theta$ scan mode. The positions of the five copper atoms were obtained by direct methods,[6] and the rest of the structure was solved by standard heavy-atom techniques.[7] Full-matrix least-squares refinement (with Cu atoms assigned anisotropic temperature factors) resulted in a final R factor of 0.071 for 1846 nonzero reflections $[I > 3\sigma(I)]$. The structure analysis of $[Li(PMDTA)(THF)]^+[Cu_5Ph_6]^-$ was carried out in an analogous fashion,[8] yielding a final R factor of 0.069. The $[Cu_5Ph_6]^-$ clusters in the two salts are virtually identical. In the following discussion, distances and angles quoted are averaged over both structure determinations.

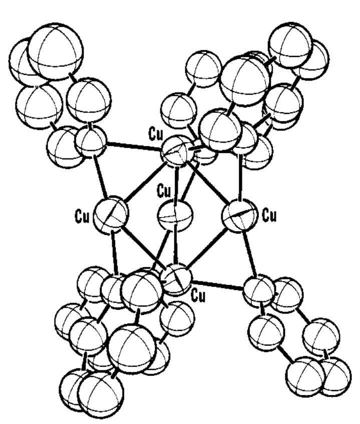

Figure 1. View of the $[Cu_5Ph_6]^-$ cluster as found in the $[Li(THF)_4]^+$ salt.

Table I. Average Distances and Angles in the $[Cu_5Ph_6]^-$ Anion

	$[Li(THF)_4]^+$ salt	[Li(PMDTA)(THF)]$^+$ salt
Cu(ax)–Cu(eq), Å	2.452 (4)	2.446 (7)
Cu(eq)···Cu(eq), Å	3.165 (4)	3.137 (8)
Cu(ax)···Cu(ax), Å	3.269 (4)	3.288 (6)
Cu(ax)–C, Å	2.19 (2)	2.14 (3)
Cu(eq)–C, Å	1.99 (2)	1.96 (4)
Cu(ax)–C–Cu(eq), deg	71.6 (7)	73.1 (12)
C–Cu(ax)–C, deg	119.1 (9)	119.5 (14)
C–Cu(eq)–C, deg	166.6 (9)	168.1 (15)

The $[Cu_5Ph_6]^-$ anion (Figures 1 and 2) has a pentanuclear skeleton that is best described as a "squashed" trigonal bipyramid, with the Cu(ax)–Cu(eq) distances [average 2.449 (9) Å] much shorter than the Cu(eq)–Cu(eq) distances [average 3.151 (6) Å]. The six phenyl groups bridge the Cu(ax)–Cu(eq) edges of the trigonal bipyramid. Distances and angles in the core of the cluster are given in Table I. The $[Li(THF)_4]^+$ cation has a normal tetrahedral geometry with an average Li···O distance of 1.93 (3) Å, while in $[Li(PMDTA)(THF)]^+$ the Li^+ ion is coordinated to one O and three N atoms in a distorted tetrahedral fashion.

The three equatorial Cu atoms in $[Cu_5Ph_6]^-$ are approximately linearly coordinated [average C–Cu–C angle = 167 (1)°], while the two axial Cu atoms are roughly trigonal planar (the axial Cu atoms are displaced by 0.2 Å from the planes of the three bridging C atoms). The bridging phenyl groups are, as expected,[9] essentially perpendicular (83°) to the Cu–Cu vectors and are situated in a slightly asymmetric position [average C–Cu(ax) = 2.17 (2) Å, C–Cu(eq) = 1.98 (1) Å]. The gross structure of the cluster is

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(1) Costa, G.; Camus, A.; Gatti, L.; Marsich, N. *J. Organomet. Chem.* **1966**, *5*, 568.

(2) Gilman, H.; Jones, R. G.; Woods, L. A. *J. Org. Chem.* **1952**, *17*, 1630.

(3) $[Li(THF)_4]^+[Cu_5Ph_6]^-$ (Anal. Calcd. for $C_{52}H_{62}O_4Cu_5Li$ (mol wt 1074.7): C, 58.1; H, 5.77. Found: C, 57.5; H, 5.25%): IR (Nujol) 3040 w, 1560 w, 1411 m, 1300 w, 1259 m, 1239 w, 1168 w, 1150 w, 1090 m, 1072 m, 1042 s, 912 w, 888 m, 798 m, 718 s, 699 s, 446 m cm^{-1}.

(4) The $[Li(PMDTA)(THF)]^+$ salt of $[Cu_5Ph_6]^-$ was prepared as follows: To a suspension of CuBr (1 g, 7 mmol) in tetrahydrofuran was added at −20 °C, dropwise with stirring, a solution of phenyllithium (14.4 mL, 0.97 M in Et_2O, 14 mmol). The suspension was allowed to warm slowly to room temperature with continued stirring, when a clear yellow solution had formed. To this solution was added dropwise pentamethyldiethylenetriamine (1 mL) with vigorous stirring. The clear yellow solution was evaporated in vacuo to dryness and the yellow tarry solid titurated with diethyl ether (30 mL) to remove LiBr. This gave a fine pale yellow powder that recrystallized from tetrahydrofuran–diethyl ether (50:50) (ca. 30 mL). Anal. Calcd. for $C_{49}H_{61}ON_3Cu_5Li$ (mol wt 1031.7): C, 57.0; H, 5.91. Found: C, 56.9; H, 5.67. IR (Nujol) 3035 w, 1680 w, 1560 w, 1412 w, 1282 m, 1261 m, 1150 w, 1120 s, 1091 m, 1030 s, 935 w, 910 w, 890 w, 857 w, 832 w, 790 m, 715 s, 698 s, 451 m cm^{-1}.

(5) Space group $P2_1/n$ is an alternative, nonstandard setting of $P2_1/c$ (No. 14) with equivalent positions (x, y, z); $(-x, -y, -z)$; $(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$; $(^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$.

(6) MULTAN: a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368].

(7) Major computations in this work were performed on the USC IBM 370/158 computer using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh's group at the California Institute of Technology.

(8) $[Li(PMDTA)(THF)]^+[Cu_5Ph_6]^-$ crystallizes in the monoclinic space group *Cc*, with $a = 13.752$ (7) Å, $b = 19.647$ (20) Å, $c = 19.797$ (10) Å, $\beta = 98.93$ (4)°, ρ(calcd) = 1.30 g cm^{-3} for $Z = 4$. As in the structure analysis of the $[Li(THF)_4]^+$ salt, the five Cu atoms were located with direct methods and the rest of the structure was solved by standard techniques. Full-matrix least-squares refinement (Cu atoms anisotropic) yielded a final R factor of 0.069 for 1570 nonzero reflections $[I > 3\sigma(I)]$.

(9) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1977**, *23*, 131.

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