

Figure 1. (A) Molecular geometry of $[\text{Cu}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4]$. Important, selected, intramolecular distances (\AA) and angles (deg): Cu-Li 2.730 (5), Cu-Li(*) 2.775 (6), Cu-C(11) 1.936 (3), Cu-C(12) 1.948 (3), Li-C(11) 2.396 (6), Li-C(12) 2.374 (7), Li-N(1) 2.139 (6), Li-N(2) 2.123 (6), Li-Cu-Li(*) 122.1 (2), Cu-Li-Cu(*) 57.9 (1), C(11)-Cu-C(12), 157.7 (1), N(1)-Li-N(2) 119.6 (3). (B) Schematic structure of $[\text{Cu}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4]$.

Figure 1 shows that the structure contains an almost planar Cu_2Li_2 arrangement with $\text{Cu}\cdots\text{Li}$ distances of 2.755 \AA mean. Each aryl group bridges a $\text{Cu}\cdots\text{Li}$ pair via C(ipso) but in an asymmetric way as indicated by comparison of the long Li-C(ipso) bond of 2.385 (6) \AA (cf., this bond in $\text{Li}_2\text{Ph}_2\text{-tmeda}_2$ (**2**) of 2.21 \AA)¹⁰ with the much shorter Cu-C(ipso) bond of 1.942 (3) \AA (cf. this bond in $\text{Cu}_4(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$ (**3**) of 2.00 (2) \AA).¹¹ The tilting of the aryl plane in the direction of the lithium center indicates a better overlap of the carbon sp^2 and copper orbitals, i.e., a deviation from the symmetric three-center, two-electron bonding of aryl groups between equal metals as in, for example, **2** and **3** toward a two-center, two-electron type of Cu-C bonding.¹² This is as expected when the different orbital sizes and energies of copper and lithium are taken into account. However, the fact that in solution a $^1J(^{13}\text{C}(\text{ipso}), ^7\text{Li})$ of 7.0 Hz is still observed indicates that s electron density is present between the Li and C(ipso) nuclei.

The same asymmetric bridging configuration for the aryl bridges has been found in the $[\text{Cu}_3\text{Li}_2\text{Ph}_6]^-$ anion (Li-C(ipso) 2.240 (14) and Cu-C(ipso) 1.923 (6) \AA),⁹ and it seems reasonable to assume that this will be a general feature of bridging organo groups (e.g. alkyls, aryls, alkynyls, etc.) in cuprates. Accordingly, we propose that, for example, $\text{Cu}_2\text{Li}_2(p\text{-tolyl})_4\cdot 2\text{Et}_2\text{O}$ (**4**)^{14a} has a planar Cu_2Li_2 arrangement with the *p*-tolyl groups asymmetrically bridging between Cu and Li. Since coordinating substituents are now absent, coordination of a solvent^{14b} molecule to each of the lithium atoms is required to produce the discrete neutral cuprate species. Recent structural evidence allowing comparison of the

features of a series of aryllithium, arylcopper, and lithium cuprate compounds with and without coordinating substituents has substantiated that a major role of these heteroatom-containing groups is their functioning as well-positioned "intramolecular solvent molecules".^{2a}

Comparison of the structural features of **1** with those of the corresponding lithium diorganoaurate $\text{Au}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$ (**5**), which we recently communicated,¹³ establishes that the lithium-aryl-metal (group 11) bridges in lithium group 11 metalate complexes become increasingly asymmetric going down the series Cu(I) to Ag(I) to Au(I).¹³ This is reflected both by the increase in Li-C(ipso) bond length (for **5**, 2.50 \AA mean) as well as by the change in the planar Li_2M_2 arrangement, i.e., in **5** a regular square with equal AuAu and LiLi vectors vs. in **1** a long LiLi and a shorter CuCu vector¹⁵ of 2.6660 (8) \AA . It is interesting to note here that on the basis of liquid-phase X-ray scattering data the Cu \cdots Cu distance in $\text{Cu}_2\text{Li}_2\text{Me}_4$ in Et_2O has been estimated at 4.4 ± 0.7 \AA .¹⁶ This is not at all in agreement with the now likely structure for $\text{Cu}_2\text{Li}_2\text{Me}_4\cdot 2\text{Et}_2\text{O}$ (i.e., the same basic $\text{Cu}_2\text{Li}_2\text{C}(\text{ipso})_4$ framework as in **1** with Cu \cdots Cu amounting to 2.6 \AA) and substantiates earlier questioning¹⁷ of these X-ray scattering data.

Acknowledgment. Prof. K. Vrieze is thanked for his stimulating interest in this subject.

Registry No. 1, 94203-54-0.

Supplementary Material Available: Table of atomic coordinates, anisotropic thermal parameters, observed and calculated structure factors, bond distances (\AA), and bond angles (4 pages). Ordering information is given on any current masthead page.

(15) On the basis of ^{109}Ag and ^7Li NMR of corresponding $\text{Ag}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$ nonbonding;^{2a} Jastrzebski, J. T. B. H.; van Koten, G.; Brevard, C., unpublished results.

(16) Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098.

(17) See Stewart et. al cited in ref 2b and: Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141.

Tris(diphenylmethene)methane Dianion. Direct Evidence for Y Aromaticity

Andrzej Rajca*† and Laren M. Tolbert*

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506-0055

Received August 8, 1984

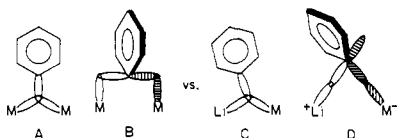
MNDO calculations¹ indicate that doubly charged conjugated systems prefer Y delocalization over cyclic delocalization. Experimental evidence is anecdotal and is limited to generation of several "dications"² and "dianions"³ with the observation that the Y-conjugated dications are formed with difficulty and the dianions with facility in contrast to the linear or cyclic counterparts. Moreover, in such systems counterion effects are difficult to determine and may dominate the relative rates that are used to evaluate stability in such systems. The use of a resonance-stabilized dianion that would be accessible in highly solvating media such as Me_2SO would simplify such an analysis. We now report the synthesis of such an example, tris(diphenylmethene)methane

(9) Hope, H.; Oram, D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1149.

(10) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3157.

(11) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *84*, 129.

(12) Compare the various bonding interactions of the aryl C(ipso) sp^2 and metal orbitals in homo (A and B, e.g., in **2** and **3**) and hetero (C and D as in **1** and **4**) bridges.^{2a,13}



(13) van Koten, G.; Jastrzebski, J. T. B. H.; Stam, C. H.; Niemann, N. C. *J. Am. Chem. Soc.* **1984**, *106*, 1880.

(14) (a) Pure $\text{Cu}_2\text{Li}_2(p\text{-Tol})_4$ made in benzene from $\text{Cu}_4(p\text{-Tol})_4$ and $\text{Li}_4(p\text{-Tol})_4$ is insoluble;^{2a} van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Organomet. Chem.* **1977**, *140*, C23. (b) Addition of Et_2O (2 equiv) affords a solution of neutral **4** in benzene; see ^1H NMR in ref 14a. With THF an ionic cuprate is formed.

* On Leave from the Technical University of Wrocław, Wrocław, Poland. (1) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1982**, *23*, 3547.

(2) Schötz, K.; Clark, T.; Schaller, H.; Schleyer, P. v. R. *J. Org. Chem.* **1984**, *49*, 733.

(3) (a) Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans 2* **1984**, 915. (b) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Buckl, K.; Boche, G. *Chem. Ber.* **1983**, *116*, 1669. (c) Mills, N. S.; Schapiro, J.; Hollingsworth, M. *J. Am. Chem. Soc.* **1981**, *103*, 1263. (d) For the parent trimethylenemethane dianion, see: Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275. (e) Mills, N. S. *J. Am. Chem. Soc.* **1982**, *104*, 5689.

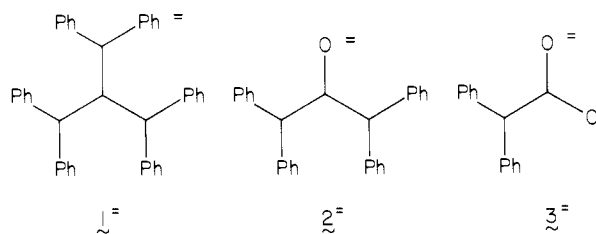


Figure 1.

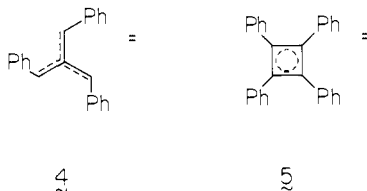
Figure 2. ^1H NMR Spectrum of $1^{2-}, 2\text{K}^+$ in 1:4 $\text{Me}_2\text{SO}/\text{THF}$.

Figure 3.

dianion (1^{2-}), and compared its properties with the anion produced by replacing each benzhydryl moiety in turn by oxygen, i.e., anions 2^{2-} and 3^{2-} (see Figure 1).

2-(Diphenylmethyl)-1,1,3,3-tetraphenylpropene (1-H_2) was prepared by treatment of tetraphenylallene with benzhydryllithium in tetrahydrofuran followed by water quench.^{4a} Treatment of the hydrocarbon with 2.5 equiv of potassium (methylsulfinyl)methide ("dmsyl") in Me_2SO or tetrahydrofuran produced a deep brown-black solution with ^1H NMR spectra bearing characteristic patterns for protons on an aromatic ring attached to a carbanionic center (see Figure 2).^{4b,5a} Similarly, diphenylacetic acid (3-H_2) yielded an orange solution having the same characteristic spectra.^{4b,6} In contrast, treatment of 1,1,3,3-tetraphenylacetone (2-H_2) under the same conditions produced monoanion only.^{4b,7} Dianion

(4) (a) 1-H_2 , NMR (CDCl_3) δ 5.39 (s, 2 H), 7.01 (s, 30 H). Anal. C, H. (b) All dianions had the characteristic pattern in aromatic region of the ^1H NMR spectra for the para, meta, and ortho protons: 1^{2-} ($\text{Me}_2\text{SO}-d_6$) δ 5.77 (t), 6.27 (t), 7.10 (d), (THF- $h_8/\text{Me}_2\text{SO}-d_6$) δ 5.75 (t), 6.32 (t), 7.19 (d); 2^{2-} ($\text{Me}_2\text{SO}-d_6$) δ 6.02 (t), 6.58 (t), 7.05–7.2 (unresolved and superimposed spectrum of the monoanion), (THF- h_8) δ 6.17 (t), 6.60 (t), 7.15 (d); 3^{2-} ($\text{Me}_2\text{SO}-d_6$) δ 6.17 (t), 6.77 (t), 7.32 (d); 2-H^- ($\text{Me}_2\text{SO}-d_6$) δ 6.42 (t, 1 H), 6.80 (t, 2 H), 7.13 (m, 15 H), 7.60 (d, 2 H). (c) Chemical shifts corrected to ppm from Me_4Si based known chemical shifts of solvent: $\text{Me}_2\text{SO}-d_6$ (δ_{H} 2.50), $\text{Me}_2\text{SO}-d_6$ (δ_{C} 39.5), THF- h_8 (δ_{H} 1.75, δ_{C} 67.96).

(5) ^{13}C NMR data of compounds ^{13}C -enriched at C-1 and C-2: (a) $1^{2-}, 2\text{K}^+$ ($\text{Me}_2\text{SO}-d_6$, 23 °C) δ 155.5 (central), 151.4 (ipso), 125.4 (meta), 124.2 (ortho), 112.5 (para), 105.0 (terminal). (b) $2^{2-}, 2\text{Li}^+$ (THF- $h_8/\text{THF}-d_6$, 40 °C) δ 175.4 (central, d, $^1J(\text{CC}) = 68.8$ Hz), 148.8 (ipso), 127.5 and 126.9 (meta and ortho), 116.5 (para), 98.2 (terminal, d, $^1J(\text{CC}) = 68.8$ Hz). (c) $2\text{-H}^-, \text{Li}^+$ ($\text{Me}_2\text{SO}-d_6$, 23 °C), formed upon dissolution of $2^{2-}, 2\text{Li}^+$ δ 169.5 (central, d of d, $^1J(\text{CC}) = 77.6$, 41.4 Hz), 103.4 (terminal, d, $^1J(\text{CC}) = 77.6$ Hz), 56.6 (terminal, m).

(6) "Dianion" 3^{2-} was generated and proved to be stable in Me_2SO , see: (a) Lambert, J. B.; Wharry, S. M. *J. Am. Chem. Soc.* **1982**, *104*, 5857. (b) Lambert, J. B.; Wharry, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 172.

(7) The dipotassium salt $2^{2-}, 2\text{K}^+$ was actually formed in small concentration but large enough to overwhelm the pale yellow color of the monopotassium salt $2\text{-H}^-, \text{K}^+$. The yellow solution of $2\text{-H}^-, \text{K}^+$ was prepared by use of a 1.5 M ratio of dmsyl anion to ketone and its structure confirmed by ^1H NMR and ^{13}C NMR spectra.

2^{2-} could be produced as its dilithium salt⁸ by treatment of 2-H_2 with *n*-butyllithium in tetrahydrofuran. However, formation of monoanion 2-H^- was instantaneous, while dianion formation proceeded more slowly (10 min at 34 °C). Removal of tetrahydrofuran solvent at -15 °C produced deep-red crystals of $2^{2-}, 2\text{Li}^+$. These, when dissolved in $\text{Me}_2\text{SO}-d_6$, underwent deuterium incorporation over 40 min to generate the monoanion.^{4b,5c} Thus we conclude that the second pK_a of 2-H_2 is above 35, the pK_a of Me_2SO , while that of 1-H_2 and 3-H_2 is below 35. In each case, quenching experiments with MeOD returned the carbon acid with the proper number of deuteria, while quenching with H_2O allowed recovery of unchanged starting material.

The greater stability of 3^{2-} over 2^{2-} is exactly what one would predict on the basis of electronegativity effects. That is, replacement of an oxo group by diphenylmethylene should increase the pK_a , a fact that is borne out by examination of reference compounds α, α -diphenylacetophenone ($\text{pK}_a = 18$ in Me_2SO) and 1,1,3,3-tetraphenylpropene ($\text{pK}_a = 26$). That replacement of the second oxo group by diphenylmethylene should reverse that order constitutes direct evidence that dianion 1^{2-} is Y aromatic.

A remaining question is the geometry of 1^{2-} . The fact that resonance stabilization appears to play a role in its stability suggests the anion has D_3 symmetry, a conclusion that is supported by MNDO calculations on the corresponding triphenyl derivative.^{3b} Moreover, 20-MHz ^{13}C NMR studies at -82 °C of $1^{2-}, 2\text{K}^+$ in tetrahydrofuran failed to remove the degeneracy of the absorptions due to the terminal carbon atoms, in contrast to similar anions, e.g., allyl or pentadienyl metal derivatives,⁹ for which conformational mobility could be inhibited. However, a conformation with lower than D_3 symmetry (e.g., C_2) cannot be unequivocally excluded because a comparison of HMO π -bond orders for the parent trimethylenemethane dianion (0.577) and allyl anion (0.707) suggests a lower barrier between conformers for Y-conjugated dianions.

Finally, we might comment on the use of charge densities as determined by ^{13}C NMR to evaluate aromaticity in dianions. Using the approach developed by O'Brien,¹⁰ Schleyer uses eq 1

$$\rho = \frac{\delta_{\text{C}} - 134.1}{153.7} \quad (1)$$

to conclude that 47% of the charge remains in the Y framework of tribenzylidenemethane dianion **4**, in contrast to 37% remaining in the cyclobutadiene framework of tetraphenylcyclobutadiene dianion **5**, an observation he attributes to the poorer electron-donating ability of the Y framework.^{3b} However, using the same equation we calculate 21% of the charge remaining on the Y framework for 1^{2-} , i.e., lower than in **5**. We suggest that the effect of phenyl groups on removing charge can be treated with a simple statistical relationship for dianionic systems. That is, the phenyl groups act as a "charge reservoir". Each phenyl group removes 22% of the charge, so that the remaining charge in each case is $(1 - 0.22)^n$, i.e., 47% for $n = 3$ (**4**), 37% for $n = 4$ (**5**), and 22.5% for $n = 6$ (1^{2-}). Our conclusion is, therefore, that to the extent that such charge density correlations are valid the resonance stabilization in 1^{2-} , **4**, and **5** is comparable.

Acknowledgment. Support by the National Science Foundation through Grant CHE-8024644 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. L.M.T. is an Alfred P. Sloan Foundation Fellow (1983–1985).

Registry No. 1-H_2 , 94234-95-4; $1^{2-}, 2\text{K}^+$, 94234-96-5; 2-H_2 , 7476-11-1; $2^{2-}, 2\text{Li}^+$, 94234-97-6; $2\text{-H}^-, \text{Li}^+$, 94234-98-7; $2^{2-}, 2\text{K}^+$, 94234-99-8; $2\text{-H}^-, \text{K}^+$, 94235-00-4; 3-H_2 , 117-34-0; $3^{2-}, 2\text{K}^+$, 94235-01-5; potassium (methylsulfinyl)methide, 15590-26-8; tetraphenylallene, 2667-02-9; benzhydryllithium, 881-42-5.

(8) For references, see: Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355.

(9) Wardell, J. L. "Comprehensive Organometallic Chemistry", 1st ed.; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 2.

(10) O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.