β-elimination process that results in a release of the alkenyl grouping and closure of the cluster. This transformation demonstrates the existence of a relatively facile CH activation process that leads to the formation of an uncoordinated 2-propenethiolato group, such as that found in **2**. It is possible that an intermediate similar to **3** was traversed en route to **2**. Efforts to confirm this are currently in progress. This observation of the involvement of thiametallacylces in the cluster chemistry of thietane appears to contrast significantly with the proposed transformations of thietane on metal surfaces.[5,17]

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Gong Chen for help with the structural analyses.

Supplementary Material Available: Tables of crystal data, positional anisotropic thermal parameters, and bond distances and angles for the structural analysis of compounds **1** and **3** (15 pages); tables of structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

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(16) A solution of **3** (16 mg) in heptane (20 mL) was heated to reflux for 1 h. The product **4** was isolated in 60% yield by TLC on alumina. IR (ν(CO), cm^{-1}; (in hexane): 2091 m, 2051 s, 2014 vs, 1999 m, 1989 m, 1967 m, 1947 w, 1943 w. ^{1}H NMR (δ; in $CDCl_3$): 7.53–7.35 (m, 5 H), 5.73 (m, 1 H), 5.17–5.12 (m, 2 H), 2.81 (dd, 1 H, J_{H-H} = 12.7 Hz, J_{H-H} = 7.0 Hz), 2.54 (m, 1 H, J_{H-H} = 12.7 Hz, J_{H-H} = 7.0 Hz), 2.29 (d, 3 H, J_{P-H} = 10 Hz), 2.26 (d, 3 H, J_{P-H} = 10 Hz), −17.03 (d, 1 H, J_{P-H} = 26 Hz). The reverse of this reaction (CO addition) has not yet been achieved. The PPh_3 derivative of **2** was prepared by a similar sequence of insertion/ligand addition to yield the PPh_3 analogue of **3** and a subsequent decarbonylation. The PPh_3 derivative of **2** was characterized crystallographically.

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Synthesis and X-ray Crystal Structure of $[Li_2Cu_2(CH_2SiMe_3)_4(SMe_2)_2]_\infty$: The First Detailed Structural Characterization of a Lithium Dialkylcuprate Aggregate

Marilyn M. Olmstead and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

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Summary: The use of SMe_2 (dimethyl sulfide) as both ligand and solvent has allowed the first X-ray structural characterization of a lithium alkylcuprate aggregate. The title compound $[Li_2Cu_2(CH_2SiMe_3)_4(SMe_2)_2]_\infty$ (**1**) was synthesized by the reaction of 2 equiv of $LiCH_2SiMe_3$ with CuBr in SMe_2. Its structure consists of infinite chains of the dimeric units $Li_2Cu_2(CH_2SiMe_3)_4$ linked by weakly bridging SMe_2 ligands that bind to the lithium centers. The Li_2Cu_2 array is almost planar, and the α-carbons of the alkyl groups reside in alternating positions approximately 1.3 Å above and below the metal plane. The Li–S distances, 2.65–2.71 Å, are long, and the Li–C bonds, ~2.2 Å, are short. Thus, the Li atoms are relatively strongly bonded to the α-carbons of the alkyl group. The Cu–C distances are ~1.956 Å, which is close to the values in arylcuprates. The structure of **1** is significantly different, in certain details, from that predicted for $Li_2Cu_2Me_4$ on the basis of spectroscopy and theoretical calculations.

Since their introduction over 20 years ago[1] organocuprate (Gilman) reagents have proved extremely valuable in organic synthesis.[2] They are normally represented by the formula "$LiCuR_2$",[3] but they are believed to be associated into higher aggregates in solutions of ether—the solvent in which they are normally employed. For example, "$LiCuPh_2$" crystallizes as the "trimeric" ionic species $[Li_2Cu_3Ph_6]^-$ from ether or THF solution mixtures along with a countercation of solvated or complexed lithium.[4] In addition, the self-complexing cuprate $Li_2Cu_2(C_6H_4CH_2NMe_2\text{-}2)_4$ is a dimer in both solution[5] and the solid state.[6] These two structures, and that of the related species $[Li(THF)_4][LiCu_4Ph_6]$,[7] constitute the extent of the currently available detailed structural knowledge of associated lithium diorganocuprates. The scarcity of data for these compounds is further underlined by the absence of a detailed (X-ray) structure for any lithium dialkylcuprate aggregate. In addition, only two crystal structures of neutral copper(I) alkyls, the tetramer $Cu_4(CH_2SiMe_3)_4$[8] and the dimer $[(2\text{-}(Me_3Si)_2CCuC_5H_4N)_2]$,[9] have been published. Even though the structures of the separated mononuclear dialkylcuprate ions $[Cu(C(SiMe_3)_3)_2]^-$[10] and $[CuMe_2]^-$[11,12]

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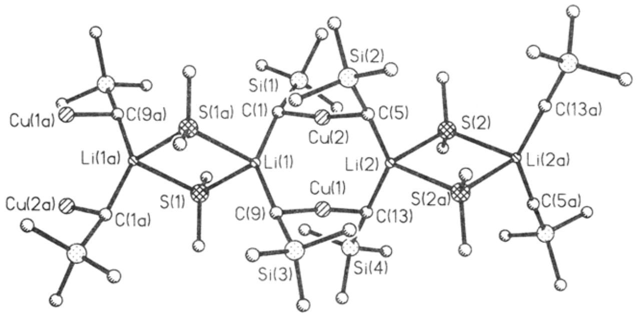

Figure 1. Computer-generated illustration of the polymeric structure of 1. Some important bond distances (Å) and angles (deg) are as follows: Cu(1)–C(9) = 1.961 (6), Cu(1)–C(13) = 1.958 (6), Cu(2)–C(1) = 1.954 (6), Cu(2)–C(5) = 1.949 (5), Li(1)–C(1) = 2.218 (13), Li(1)–C(9) = 2.205 (13), Li(2)–C(5) = 2.201 (12), Li(2)–C(13) = 2.198 (12), Li(1)–S(1) = 2.654 (9), Li(1)–S(1a) = 2.677 (9), Li(2)–S(2) = 2.679 (10), Li(2)–S(2a) = 2.709 (9); C(9)–Cu(1)–C(13) = 173.8 (3), C(1)–Cu(2)–C(5) = 171.5 (3), C(1)–Li(1)–C(9) = 142.1 (4), C(5)–Li(2)–C(13) = 140.2 (4), S(1)–Li(1)–S(1a) = 83.3 (2), S(2)–Li(2)–S(2a) = 80.8 (2).

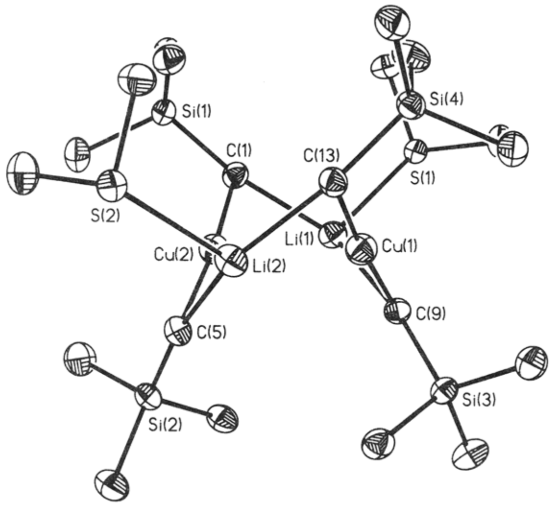

Figure 2. View of the asymmetric dimeric unit of 1. Some nonbonded distances (Å) and angles (deg) are as follows: Cu(1)···Cu(2) = 2.984 (1), Li(1)···Cu(1) = 2.637 (9), Li(2)···Cu(1) = 2.648 (9), Li(1)···Cu(2) = 2.618 (9), Li(2)···Cu(2) = 2.644 (9), Cu(1)Li(2)Cu(2) = 68.6 (2), Li(1)Cu(1)Li(2) = 110.7 (3), Li(1)Cu(2)Li(2) = 111.4 (3). Average distances of C(1), C(5), C(9), and C(13) from the Li_2Cu_2 plane are 1.26, 1.348, 1.348, and 1.28 Å, respectively.

have appeared, these are not believed to be representative of their solution structures owing to the presence of either large substituents or lithium complexing agents. Spectroscopic and theoretical data have pointed to a dimeric, approximately planar, Li_2Cu_2 array with coplanar bridging alkyl groups for $Li_2Cu_2Me_4$.[13,14] In this paper the first structure of a solvated lithium dialkylcuprate[8] aggregate, $[Li_2Cu_2(CH_2SiMe_3)_4(SMe_2)_2]_\infty$ (**1**), is now described.

The compound **1** was synthesized,[15] in a conventional manner, by the treatment of CuBr with 2 equiv of $LiCH_2SiMe_3$.[16] A key feature of its isolation involves the use of dimethyl sulfide rather than the more conventional ethers as the solvent. The advantages of using Me_2S were first recognized by Bertz,[17] who showed, inter alia, that it was possible to identify unambiguously higher order cuprates in this solvent.[18] The structure[19] of **1** consists of infinite chains in which dimeric $Li_2Cu_2(CH_2SiMe_3)_4$ units are linked by two weakly bridging SMe_2 ligands, as illustrated in Figure 1. This structure results in a very distorted tetrahedral ligand arrangement for Li^+, whereas the coppers possess almost linear coordination. Although the lithium and copper atoms are essentially coplanar, the planarity does not extend to the α-carbon atoms of the $-CH_2SiMe_3$ groups. This is illustrated by Figure 2, in which the metal-bound carbon atoms reside pairwise on opposite sides of the metal plane. Important structural information is provided in the figure captions.

The main feature of interest of **1** involves the dimeric stoichiometry of the weakly solvated $Li_2Cu_2(CH_2SiMe_3)_4$ structural motif. The relatively weak solvation of Li by SMe_2 is reflected in long[20] (2.65–2.71 Å) Li–S distances and short Li–C bonds of ~2.2 Å. The Cu–C bond lengths, ~1.956 Å, are marginally longer than those found in other lithium cuprate aggregates, although they are considerably shorter than the 2.02 Å observed in $Cu_4(CH_2SiMe_3)_4$.[4] The closest published structure related to **1** is the dimeric aryl species $Li_2Cu_2(C_6H_4CH_2NMe_2\text{-}2)_4$ (**2**).[6] This has much longer Li–C distances of about 2.385 Å due to the strong solvation of Li by the ortho $-CH_2NMe_2$ ligands. The Cu–C bonds in **2** are marginally shorter than those in **1**, perhaps owing to the different hybridization of the metal-bound carbon atoms. Other differences between the structures relate to the Cu···Cu vectors, which are 2.984 (1) Å in **1** and 2.666 (1) Å in **2**. The shorter Cu···Cu contact in **2** may be, in part, the result of some constraints imposed by the ortho donor ligand. This appears to be borne out by the structure of the aryl species $Li_2Cu_2Ph_4(SMe_2)_3$, which involves a Cu···Cu vector of 2.87 Å where these constraints are absent.[21]

The Li_2Cu_2 array in **1** is very close to planarity (mean deviation of metal atoms from the average plane 0.02 Å). When they are viewed along this plane (Figure 2), the CuC_2 units are staggered with respect to each other so that the opposite pairs of α-carbons are located approximately 1.3 Å above and below the metal plane. The structure of the dimeric unit of **1** is, in fact, remarkably similar to that found for $Li_2Cu_2Ph_4$ crystallized from SMe_2/hydrocarbon mixtures.[21] It may be described as a very distorted tetrahedron of four α-carbons in which four of the edges are bridged by the metals. In many ways the structure of the dimeric $Li_2Cu_2R_4$ species (R = alkyl, aryl) is intermediate between the cuboidal and planar forms found for Li_4R_4 and Cu_4R_4. These two contrasting structures are, in turn, the

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(19) Crystal data, obtained on a Siemens R3m diffractometer, for **1** at 130 K with Cu Kα (λ = 1.5418 Å) radiation: a = 11.337 (4) Å, b = 11.583 (5) Å, c = 15.163 (6) Å, α = 103.50 (3)°, β = 106.01 (3)°, γ = 97.49 (3)°, triclinic, space group $P\bar{1}$, d_{calc} = 1.12 g cm^{-3}, V = 1820 Å^3, 4307 data with $I > 2\sigma(I)$, R = 0.06, R_w = 0.07.

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result of the tendency of Li^+ and Cu^+ toward tetrahedral and linear coordination, respectively.

From the point of view of stoichiometry the structure of 1 is in broad agreement with the dimeric structure proposed for $LiCuMe_2$ in Et_2O. However, there are large differences in structural details. First, whereas $Li_2Cu_2Me_4$ was said to have approximate D_{2h} symmetry with coplanar Li, Cu, and Me groups, the organic groups of 1 show large deviations from the Li_2Cu_2 plane. Second, the Cu···Cu distance in $Li_2Cu_2Me_4$ was estimated to be 4.4 ± 0.7 Å,[13] which is very different from the value observed in 1. The validity of the 4.4-Å Cu···Cu distance has already been questioned and may be in error.[6,22] It is possible to argue that the deviation of the alkyl groups from the Li_2Cu_2 plane in 1 could be due to the steric effects of $-CH_2SiMe_3$. Nonetheless, it is notable that $Li_2Cu_2Ph_4$ (solvated by SMe_2)[21] also has a structure very similar to that of 1, whereas $Cu_4Ph_4(SMe_2)_2$[21] is almost planar, like $Cu_4(CH_2SiMe_3)_4$.[8] Thus, it appears that this intermediate structure in 1 may be more characteristic of $Li_2Cu_2R_4$ systems than the planar one proposed for $Li_2Cu_2Me_4$. It should also be borne in mind that, in solution, $Li_2Cu_2Me_4$ is probably solvated by ethers binding to lithium, which could play a role in its structure by imposing a nonplanar configuration on the molecule similar to that seen in 1.

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Supplementary Material Available: Tables of crystal data, data collection, and refinement, atom coordinates, bond distances and angles, and thermal parameters (10 pages); a table of structure factors (18 pages). Ordering information is given on any current masthead page.

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Articles

Synthesis and Reactivity of "MoPt" Bimetallic Systems Containing the Ligand 2-Oxacyclopentylidene

John Powell,* Eric Fuchs, and Jeffery F. Sawyer

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received June 13, 1989

Oxidative addition of P–H bonds of primary/secondary phosphines, bound to Mo–2-oxacyclopentylidene systems, to Pt(0) complexes results in the transfer of the 2-oxacyclopentylidene ligand from the Mo to the Pt center. The cationic 2-oxacyclopentylidene complexes *cis*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PPh_2H)]BPh_4$ and *trans*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(PCy_2H)]BPh_4$, obtained from the reaction of $Cp(OC)_3Mo(CH_2CH_2CH_2Br)$ with PR_2H and $NaBPh_4$, react (i) with $Pt(C_2H_4)_2(PCy_3)$ to give $[Cp(OC)_2Mo(\mu\text{-}PR_2)(\mu\text{-}H)Pt(COCH_2CH_2CH_2)(PCy_3)]BPh_4$ and (ii) with $Pt(C_2H_4)(PPh_3)_2$ to give equimolar mixtures of $[Cp(OC)_2Mo(\mu\text{-}PR_2)(\mu\text{-}H)Pt(COCH_2CH_2CH_2)(PPh_3)]BPh_4$, $Cp(OC)_2Mo(R_2PCOCH_2CH_2CH_2)$, and $[PtH(PPh_3)_3]BPh_4$. Reaction of $Cp(OC)_2Mo(COCH_2CH_2CH_2)(PCyH_2)]BPh_4$ with $Pt(C_2H_4)(PPh_3)_2$ gives a mixture of *trans(Mo),cis(Pt)*-$[Cp(OC)_2Mo(COCH_2CH_2CH_2)(\mu\text{-}PCyH)PtH(PPh_3)_2]BPh_4$ and $[Cp(OC)_2Mo(\mu\text{-}PCy(CHOCH_2CH_2CH_2))(\mu\text{-}H)Pt(PPh_3)_2]BPh_4$. The complexes $Cp(OC)_2Mo(R_2PCOCH_2CH_2CH_2)$ are readily obtained from the reaction of 7 or 8 with base (Proton Sponge). The molecular structure of $[Cp(OC)_2Mo(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(COCH_2CH_2CH_2)(PCy_3)]BPh_4\cdot CH_2Cl_2$ (**10a**) has been determined by single-crystal X-ray diffraction. Crystal data for **10a**: $C_{66}H_{76}BCl_2MoO_3P_2Pt$, fw = 1352.0, monoclinic, space group $P2_1/c$, $a = 17.920$ (3) Å, $b = 19.605$ (4) Å, $c = 18.301$ (3) Å, $\beta = 108.95$ (1)°, $V = 6081$ Å^3, $D_{exptl} = 1.48$ g cm^{-3} for $Z = 4$; $R(wR) = 0.052$ (0.051) for 5973 reflections with $F \geq 6\,\sigma(F)$. The structure of **10a** contains square-planar Pt and distorted 4:3 "piano-stool" Mo centers, which are linked by bridging diphenylphosphido and hydrido ligands with Pt–(μ-P)–Mo and Pt–(μ-H)–Mo bond angles of 81.28 (9) and 149 (7)°, respectively. The Pt···Mo separation (3.063 (1) Å) is long and weak.

Introduction

The oxidative addition of the P–H bond of a primary or secondary phosphine complex to Pt(0) complexes provides a synthetically useful route to a wide range of single-phosphido-bridged heterobimetallic complexes.[1-5] An early example involves the reaction of $(OC)_5M(PR_2H)$ (**1**; M = Cr, Mo, W) with $Pt(C_2H_4)(PPh_3)_2$ to give the μ-

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