

Cu(HMPTA)₂(ClO₄)₂ and Cu(HDMPTA)₂(ClO₄)₂ dissolve in CH₃OH, CH₃CN, DMF, or Me₂SO to produce red solutions that turn pale yellow upon standing. It is the spectra of these pale yellow solutions that are reported in Table IV. Although transitions of typical d-d intensity can be seen in the spectra at 12-14 × 10³ cm⁻¹, most detail in the visible region is obscured by the very intense peaks near 26 × 10³ cm⁻¹. The complexes are irreversibly altered by the solution process and cannot be recovered upon evaporation of the solvent, as is the case with the complexes of HDPA, HPPA, and HPTA. Further examination of the phenomenon resulted in the observation that even the ionic complexes of HDPA, HPPA, and HPTA could be made to produce red solutions in acetonitrile by merely heating the solutions. The red color is not due to perchlorate ion coordination as has been suggested⁴ because the red solutions have 1:2 electrolytic character. We now report, without elaborating on the experimental details, that the color is due to the formation of appropriate analogues of diphenylbenzidine violet,²² a well-known indicator in analytical chemistry.

The solution spectra of the neutral complexes provide an interesting contrast to those of the ionic complexes—the neutral complexes retain their pseudotetrahedral configuration in solution. There is little difference between the positions of the various d-d bands in the various solution spectra and those in the solid-state spectra, suggesting that solvent interactions are not affecting the energies of the d-d transitions. This is not true for the charge-transfer transitions and the ligand π-π* transitions, which are affected both in position and intensity. The intensities of the d-d transitions are appropriate to tetrahedral CuN₄ chromophores.

Magnetic Moments. The values of the magnetic moments (μ_{eff}) of the various copper(II) complexes are given in Table I. Because of electron spin and orbital motion, the magnetic moment of copper(II) may range from a value of 1.73 μ_{B} (no orbital contribution) to a value of 3.00 μ_{B} (full orbital contribution). Experimental values range from 1.7 to 2.2 μ_{B} . Different degrees of an orbital contribution are predicted in square-planar and tetrahedral environments. In the former geometry, no orbital moment is expected by virtue of a nondegenerate ground state. In the latter geometry, however, an orbital contribution is expected because of the ²T₂ ground state. A full contribution is not expected because the Jahn-Teller effect prevents a rigorously degenerate ground state. Moments that contain large orbital contributions have been used as evidence for pseudotetrahedral fields in bis-

(bidentate)copper(II) compounds.²³

As shown in Table I, the moments reported here have essentially spin-only values that show some degree of an orbital contribution. The large moment of Cu(MPTA)₂ is field independent, as are the others, and cannot be attributed to ferromagnetism. Basically, the moments support a pseudotetrahedral geometry for these complexes.

Registry No. Cu(HDPA)₂(ClO₄)₂, 14128-78-0; Cu(HPPA)₂(ClO₄)₂, 64682-68-4; Cu(HPTA)₂(ClO₄)₂, 64726-47-2; Cu(HMPTA)₂(ClO₄)₂, 64682-70-8; Cu(HDMPTA)₂(ClO₄)₂, 64682-72-0; Cu(DPA)₂, 19358-74-8; Cu(PTA)₂, 64728-26-3; Cu(MPTA)₂, 64682-73-1; HPPA, 64682-29-7; HPTA, 54670-80-3; HMPTA, 64728-27-4; HDMPTA, 64682-30-0; HDPA, 1202-34-2; 2-amino-pyridine, sodium salt, 40825-17-0; 2-chloro-4-methylthiazole, 26847-01-8; 2-amino-6-methylpyridine, sodium salt, 64682-28-6.

References and Notes

- Abstracted from the Ph.D. Thesis of E. M. Gouge, Clemson University, 1976.
- HL denotes the ligands and L⁻ denotes their deprotonated forms throughout this paper. DPA⁻ is the deprotonated form of HDPA, etc.
- A. W. Meibohm, S. Bellman, and A. Leth, *Proc. Indiana Acad. Sci.*, **66**, 95 (1956).
- W. R. McWhinnie, *J. Chem. Soc.*, 5165 (1964).
- W. R. McWhinnie, *Coord. Chem. Rev.*, **5**, 293 (1970).
- C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc. A*, 237 (1968).
- T. J. Hurley and M. A. Robinson, *Inorg. Chem.*, **7**, 33 (1968).
- J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc. A*, 1371 (1971).
- H. C. Freeman and M. R. Snow, *Acta Crystallogr.*, **18**, 843 (1965).
- J. Tcherniac, *J. Chem. Soc.*, **115**, 1071 (1919).
- D. St. C. Black, *Aust. J. Chem.*, **20**, 2101 (1967).
- W. K. Detweiler and E. D. Amstutz, *J. Am. Chem. Soc.*, **74**, 829 (1952).
- C. W. F. Spiers and J. P. Wibaut, *Recl. Trav. Chim. Pays-Bas*, **56**, 573 (1937).
- W. L. Johnson, Ph.D. Dissertation, Clemson University, 1976.
- L. Sobczyk and A. Koll, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **13**, 97 (1965); L. Sobczyk, A. Koll, and Z. Marlarski, *ibid.*, **13**, 403 (1965); G. C. Kulasingham, W. R. McWhinnie, and R. R. Thomas, *Spectrochim. Acta*, **22**, 1365 (1966).
- J. E. Johnson and R. A. Jacobson, *Acta Crystallogr., Sect. B*, **29**, 1669 (1973).
- R. J. Dudley, B. J. Hathaway, and R. G. Hodgson, *J. Chem. Soc., Dalton Trans.*, 882 (1972).
- L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).
- S. G. McGeachin, *Can. J. Chem.*, **46**, 1903 (1968).
- Y. Murakami, Y. Matsuda, and K. Sakata, *Inorg. Chem.*, **10**, 1728 (1971).
- L. E. Orgel, "An Introduction to Transition-Metal Chemistry", Methuen, London, 1960, p 46.
- A. Vogel, "A Text-Book of Quantitative Inorganic Analysis", 3rd ed, Longman, Green and Co., London, 1961, pp 100-101.
- R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966); R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, **14**, 241 (1971); J. E. Fergusson and C. A. Ramsay, *J. Chem. Soc.*, 5222 (1965).

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Proton Nuclear Magnetic Resonance Spectra of n-Butylcopper(I)-n-Butyllithium and Related Complexes in Diethyl Ether and Pentane^{1a}

JOSEPH SAN FILIPPO, JR.^{1b}

Received March 8, 1977

Proton magnetic resonance spectra of ether and pentane solutions of lithium di-n-butylcuprate with n-butyllithium have been examined over a range of temperatures. In ether these spectra are consistent with species of the form (R₂CuLi)₂ and R₄CuLi₃, while in pentane 1:1 and 1:2 complexes of n-butylcopper(I) with n-butyllithium are proposed. The influence of tri-n-butylphosphine and lithium iodide on the solution structure of certain lithium organocuprates has also been studied. These results suggest that copper(I)-phosphine coordination serves only to complete the coordination shell of copper(I) which, in phosphine-free donor solvents, is probably occupied by a solvent molecule. Lithium iodide is readily incorporated by solutions of n-butyl(tri-n-butylphosphine)copper-n-butyllithium. Spectral evidence is reasonable for a 1:1:2 lithium iodide-n-butyl(tri-n-butylphosphine)copper(I)-n-butyllithium complex in ether and a 1:1:1 and a 1:1:4 species in pentane.

Lithium organocuprates, (R₂CuLi)_n, rank among the most important of organometallic reagents, and considerable effort

has been extended to the study of the mechanism of their reactions with a variety of substrates. All of these studies share

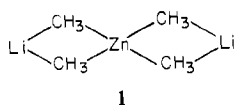


Figure 1. Proposed structure of the 2:1 complex of methyllithium with dimethylzinc(II) in diethyl ether.^{2a}

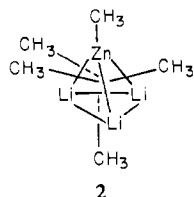


Figure 2. Proposed structure of the 3:1 complex of methyllithium with dimethylzinc(II) in diethyl ether.^{2a}

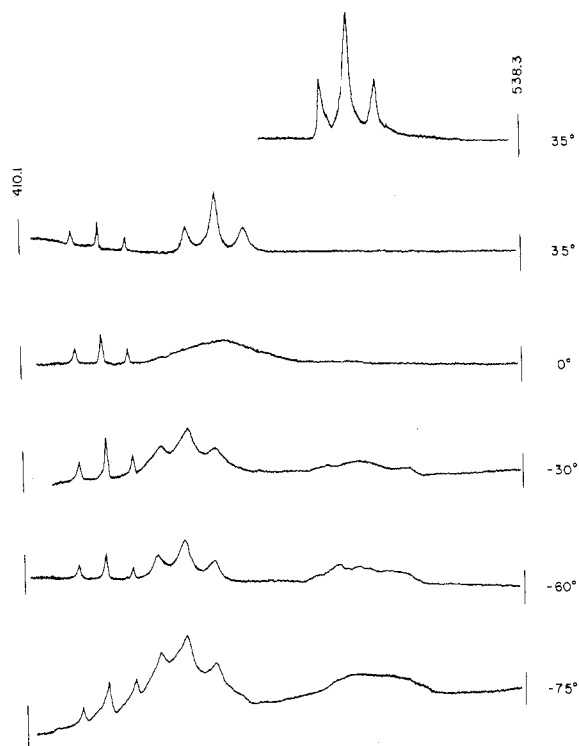


Figure 3. High-field, 60-MHz ^1H NMR spectra for $n\text{-C}_4\text{H}_9\text{Li}$ (top) and a $(n\text{-C}_4\text{H}_9)_2\text{CuLi-n-C}_4\text{H}_9\text{Li}$ (1:2) mixture in diethyl ether at various temperatures. Low-field triplet is the ^{13}C satellite for the methyl resonance of diethyl ether. Frequency markers are in hertz relative to internal benzene.

at least one factor in common: their conclusions remain premised on an assumed structure for these reagents. In an effort to shed light on the question of the structure of these important reagents, we have undertaken an extensive examination of their solution NMR spectra.

Previous ^1H NMR studies of lithium organocuprates have concentrated on the methyl species. The structure of organometallic compounds in solution is frequently influenced, often strongly, by the nature of the solvent. Such variations can be useful in interpreting the structural nature of solution-dynamic species. Because lithium dimethylcuprate cannot be prepared free of ether or other heteroatom-containing solvents, we have instead chosen to examine the no less (perhaps even more) representative species lithium di- n -butylcuprate.

Lithium Di- n -butylcuprate. In their investigations of the solution NMR of mixed organometallic complexes, Brown and his co-workers developed the concept of "local environment" to explain their observations.^{2a} Under this hypothesis the

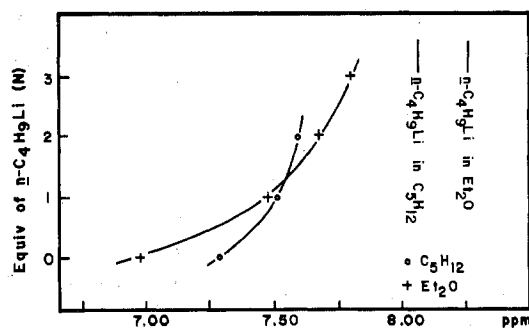


Figure 4. Effect of solvent on the chemical shift of the high-field methylene observed for lithium di- n -butylcuprate- n -butyllithium mixtures (1: N) at 30 °C (see Table I and II). Chemical shift is given relative to internal C_6H_6 .

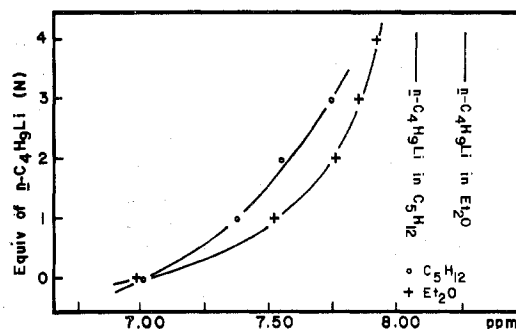


Figure 5. Effect of solvent on the chemical shift of the high-field methylene observed for n -butyl(tri- n -butylphosphine)copper(I)- n -butyllithium mixtures (1: N) at 30 °C (see Tables III and IV). Chemical shift is given relative to internal C_6H_6 .

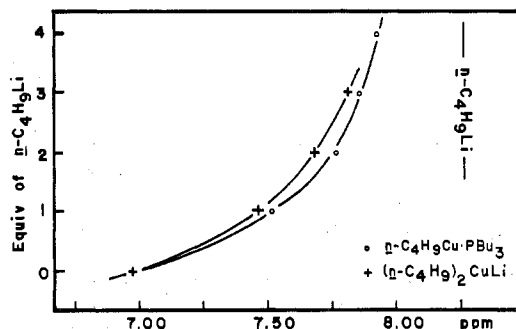


Figure 6. Comparison between the chemical shifts of the high-field methylene resonance observed for lithium di- n -butylcuprate- n -butyllithium (1: N) mixtures and n -butyl(tri- n -butylphosphine)copper(I)- n -butyllithium (1: N) mixtures in diethyl ether at 30 °C. Chemical shift is given relative to internal C_6H_6 .

chemical shift of a ligand contained in an organometallic aggregate is determined by the number and nature of the metal centers by which it is *immediately* bounded, provided intramolecular exchange within the aggregate is slow on the NMR time scale. Using this concept these investigators concluded that the 2:1 ate complex which is formed when dimethylzinc(II) is mixed with methyllithium ($\text{Li}/\text{Zn} \leq 2.0$) has structure **1** (see Figure 1). For $\text{Li}/\text{Zn} > 2$, this 2:1 complex was observed to be in equilibrium with a 3:1 complex, assigned structure **2** (see Figure 2), which can be viewed as a methyllithium tetramer in which a lithium atom has been replaced by a methylzinc(II) residue.^{2b}

Zinc(II) and copper(I) are isoelectric, and numerous complexes of these metals are isostructural. In view of this relationship, it is not unreasonable to expect an isostructural relationship between certain organolithium-organozinc(II) complexes and analogous organolithium-organocopper(I) complexes.

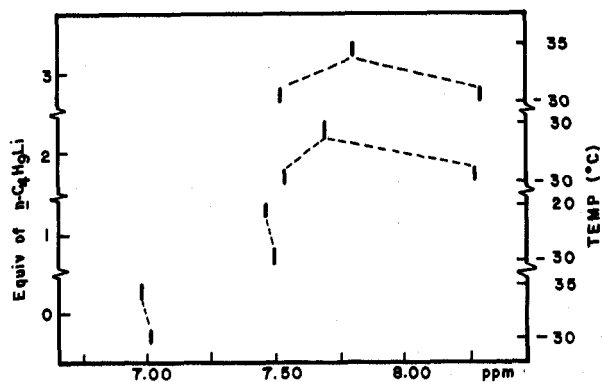


Figure 7. Effect of temperature on the chemical shift of the high-field methylene observed for lithium di-*n*-butylcuprate-*n*-butyllithium mixtures (1:*N*) in diethyl ether (see Table I). Chemical shift is given relative to internal C₆H₆.

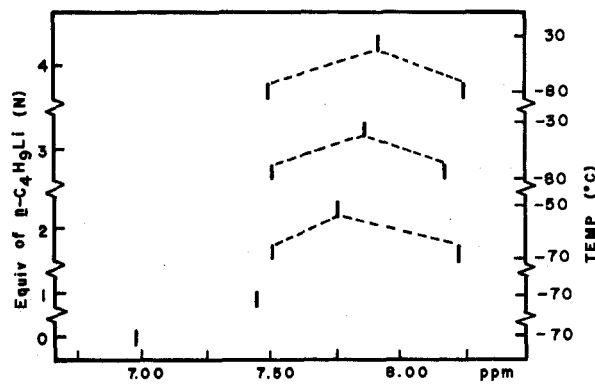


Figure 9. Effect of temperature on the chemical shift of the high-field methylene observed for *n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium mixtures (1:*N*) in diethyl ether (see Table III). Chemical shift is given relative to internal C₆H₆.

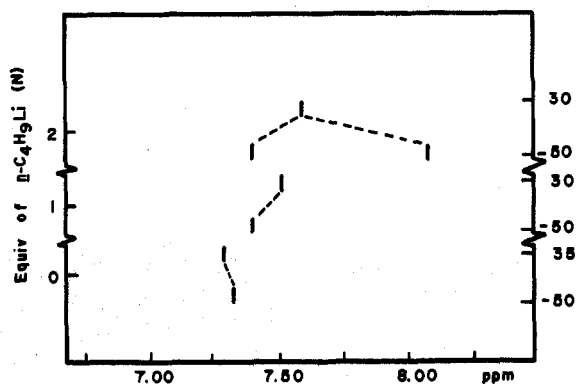


Figure 8. Effect of temperature on the chemical shift of the high-field methylene observed for lithium di-*n*-butylcuprate-*n*-butyllithium mixtures (1:*N*) in pentane (see Table II). Chemical shift is given relative to internal C₆H₆.

Figures 3-5 show the chemical shifts of the high-field methylene absorption observed for diethyl ether and pentane solutions of *n*-butylcopper-*n*-butyllithium and *n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium-lithium iodide at ambient temperatures. Figure 6 compares the chemical shifts of the high-field methylene resonance of the two complex mixtures in diethyl ether. The proton spectra for all these mixtures consists of a single triplet, $J = 7.1 \pm 0.1$ Hz, whose chemical shift depends on the ratio of *n*-butyllithium to *n*-butylcopper(I) in such fashion that, as this ratio increases, the chemical shift of the high-field triplet increases and monotonically approaches, as a limiting value, the chemical shift of pure *n*-butyllithium. These observations are consistent with a rapid exchange occurring between butyl ligands bonded to lithium and a second, less electropositive, metal.

The proton spectra of these solutions were also examined at low temperatures, and the results of these investigations are summarized in Figures 7-9 and Tables I-IV. The concept of local environment permits an interpretation of these data that is internally consistent but by no means unique.

Studies in Diethyl Ether. At low temperatures the proton spectra of 1:1 *n*-butylcopper(I)-*n*-butyllithium mixtures in ether show only those chemical shift changes and broadening anticipated for temperature changes of this magnitude. The fact that the high-field methylene absorption appears considerably downfield from that of free *n*-butyllithium suggests that the butyl ligands in a 1:1 mixture of butyllithium and *n*-butylcopper(I) are in an average environment that is less electropositive than that provided by the three lithium atoms of *n*-butyllithium. These data, as well as chemical evidence,³ support the contention that the dissolution of 1 equiv of *n*-

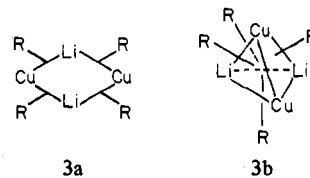
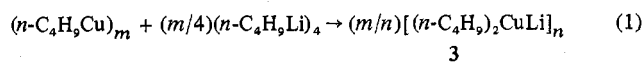


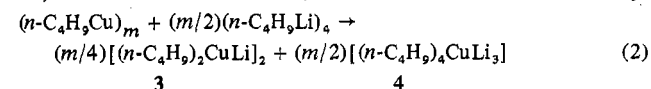
Figure 10. Suggested structures for the 1:1 complex of *n*-butyllithium with *n*-butylcopper(I) in ether. Solvent coordination has been omitted for simplicity.

butylcopper(I) in 1 equiv of *n*-butyllithium results in the formation of the solution-stable 1:1 complex lithium di-*n*-butylcuprate (3) (eq 1).



It is not possible to assign a structure to 3 with confidence; nonetheless, Figure 10 shows two likely structures for this complex based on analogy with the structure of *n*-butyllithium in ether. There is one objection to structure 3b. In terms of a local environment description, 3b would be expected to display two distinct high-field absorptions, one corresponding to the two butyl ligands bound by two copper atoms and one lithium atom and a second resonance at higher field corresponding to the two butyl ligands bound by one copper atom and two lithium atoms. However, this structure can be accommodated to the observed data if, under these conditions, intramolecular exchange remains rapid on the NMR time scale. Structure 3a is similar to one of several proposed by Brown and Kieft⁴ for [(CH₃)₃SiCH₂]₂CuLi and Pearson and co-workers⁵ for (CH₃)₂CuLi in ether.

Only a single high-field triplet appears in 2:1 mixtures of *n*-butyllithium-*n*-butylcopper(I) in ether. This absorption lies upfield from the absorption observed for the 1:1 complex 3 but is considerably downfield from the triplet observed for free *n*-butyllithium in ether. These data suggest that a 2:1 complex of *n*-butyllithium with *n*-butylcopper(I) has formed. It is difficult, however, to perceive of a reasonable structure for a 2:1 complex between *n*-butyllithium and *n*-butylcopper(I) in ether solution, based on analogy with the tetrameric nature of *n*-butyllithium in ether. Chemical evidence suggests the absence of substantial amounts of free *n*-butyllithium in a 2:1 mixture of *n*-butyllithium-*n*-butylcopper(I).³ The remaining reasonable conclusion is that a 2:1 mixture of *n*-butyllithium and *n*-butylcopper(I) in diethyl ether consists of a 1:1 mixture of the 1:1 complex 3 and the 3:1 complex 4 (eq 2) (see Figure 11). In such a 1:1 mixture, the ratio of the number of butyl



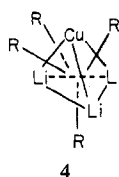


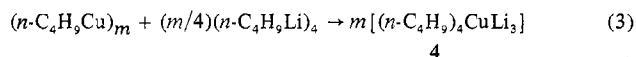
Figure 11. Suggested structure for the 3:1 complex of *n*-butyllithium with *n*-butylcopper(I) in diethyl ether. Solvent coordination has been omitted for simplicity.

ligands bound by two copper atoms and one lithium atom to the number of butyl ligands bound by three lithium atoms is 5:1. Under these circumstances, owing to the broad nature of the methylene absorption, a butyl ligand in a "three lithium atom" environment might have gone undetected, thereby accounting for the apparent failure to observe a high-field methylene with the chemical shift corresponding to free *n*-butyllithium as expected for the "one butyl" ligand in the three lithium atom environment of **4** (vide infra). For similar reasons, and also because of the occurrence of the strong ^{13}C -H satellite from the methyl group of the solvent at the expected absorption frequency, an absorption with the characteristic chemical shift of **3** could also have gone undetected.

It should be noted that these arguments assume that intramolecular exchange in **3** and **4** is slow. However, the available NMR data are equally consistent with a mixture of 3:1 and 1:1 complexes in which there is rapid intramolecular exchange.

Table I reveals that ether solutions of *n*-butyllithium and *n*-butylcopper(I) (3:1) display two distinct high-field methylene absorptions at low temperatures. The chemical shift of the first absorption is essentially that observed for the single high-field methylene displayed by a 2:1 mixture of *n*-butyllithium-*n*-butylcopper(I) at similar temperatures. The second absorption displays a chemical shift ascribable to free *n*-butyllithium. The relative integrated intensities (high to low field) of these two absorptions is 1:3.

There are two reasonable explanations for these observations. The first one is that a rapid exchange between free *n*-butyllithium and a 2:1 complex has been slowed, permitting the observation of individual species. A second possible explanation that is not inconsistent with these data is that a 3:1 complex (**4**) between *n*-butyllithium and *n*-butylcopper(I) has formed (eq 3). Only this latter explanation is in agreement



with both the undesirability of involving a 2:1 complex and the chemical evidence which indicates that there is no substantial free *n*-butyllithium in 3:1 mixtures of *n*-butyllithium and *n*-butylcopper(I).³

To accommodate the NMR data, **4** must contain one butyl ligand bound by three lithium atoms. The remaining butyl ligands must all be in equal local environments which, by virtue of their chemical shift, are less electropositive than the environments provided by three lithium atoms and similar to the environment (or averaged environments) exhibited by a 2:1 mixture of *n*-butyllithium-*n*-butylcopper(I) under similar conditions. Structure **4** as shown in Figure 11 fulfills these requirements.

One of the butyl ligands in **4** is bound by three lithium atoms; its chemical shift should therefore be similar to that of *n*-butyllithium. The remaining three butyl ligands are bound by one copper atom and two lithium atoms so that their characteristic chemical shift should be at lower field than the chemical shift characteristic of a butyl group in the environment of three lithium atoms. Furthermore, the relative

Table I. Effect of Temperature on the Chemical Shift of the High-Field Methylene Observed for Lithium Di-*n*-butylcuprate-*n*-Butyllithium Mixtures (1:*N*) in Diethyl Ether^{a-c}

Temp, °C	Chemical shift ^c (J) ^d				
	<i>N</i> = 0	<i>N</i> = 1	<i>N</i> = 2	<i>N</i> = 3	<i>N</i> = ∞
35	6.99 ^e (7.0)	7.47 (7.3)	7.70 (7.3)	7.82 (7.9)	8.29 (8.5)
0	7.02 (f)	7.50 (7.3)	7.70 (f)	7.80 (f)	g
-30	7.02 (f)	7.50 (7.2)	7.72 (7.0)	7.53 (7.0)	g
			8.29 (f)	8.30 (f)	
-50	7.10 (f)	7.54 (7.3)	g	g	g
-60	7.14 (f)	7.55 (7.3)	7.54 (7.1)	7.55 (7.0)	8.30 (f)
			8.30 (f)	8.32 (f)	

^a Lithium di-*n*-butylcuprate was prepared by dissolving halide-free *n*-butylcopper in a limiting amount of *n*-butyllithium. ^b The concentration of *n*-butyl moiety ranged between 0.5 and 0.75 M in all samples. ^c Chemical shifts are reported in ppm upfield from benzene (1%) internal standard. ^d Coupling constants are in Hz. ^e Recorded at +20 °C. ^f An accurate coupling constant could not be determined because of peak broadening. ^g Not examined.

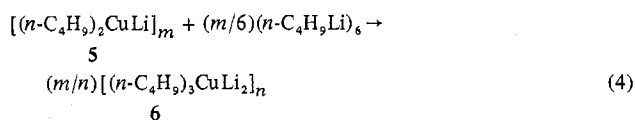
Table II. Effect of Temperature on the Chemical Shift of the High-Field Methylene Observed for Lithium Di-*n*-butylcuprate-*n*-Butyllithium Mixtures (1:*N*) in Pentane^{a, b}

Temp, °C	Chemical shift ^c (J) ^d			
	<i>N</i> = 0	<i>N</i> = 1	<i>N</i> = 2	<i>N</i> = ∞
30	7.29 ^e (7.4)	7.52 (7.5)	7.60 (7.5)	8.09 (8.5)
-30	7.32 (7.2)	7.45 (f)	g	g
-50	7.32 (7.1)	7.40 (7.0)	8.09 (f)	8.07 (f)

^a Lithium di-*n*-butylcuprate was prepared by dissolving halide-free *n*-butylcopper in a limiting amount of *n*-butyllithium. ^b The concentration of *n*-butyl moiety ranged between 0.5 and 0.75 M in all samples. ^c Chemical shifts are reported in ppm upfield from benzene (1%) internal standard. ^d Coupling constants are in Hz. ^e Recorded at +35 °C. ^f An accurate coupling constant could not be determined because of peak broadening. ^g Not examined.

integrated intensities of these absorptions should be 3:1 (low to high field). It is also noted that **4** represents the most reasonable structure for a 3:1 complex of *n*-butyllithium with *n*-butylcopper(I), based on analogy with the structure proposed for the 3:1 complex of methylithium with dimethylzinc, **2**.

Studies in Pentane. The structure and degree of association of organolithium reagents are solvent dependent. It is reasonable, therefore, to expect the structure of mixed alkylcopper(I) and -lithium aggregates also to show a solvent dependence. The chemical shift data presented in Figure 8 (Table II) are those observed for halide- and phosphine-free solutions of lithium di-*n*-butylcuprate-*n*-butyllithium in pentane. The low-temperature proton spectra of solutions which contained *n*-butyllithium and *n*-butylcopper(I) in a ratio of 2:1 or less showed only those slight changes in chemical shift and peak width which might be associated with temperature differences. The fact that only a single high-field absorption was observed for 1:1 and 2:1 solutions even down to -80 °C suggests that the butyl ligands in each complex are in similar environments. The difference between the chemical shifts of the high-field absorptions characterizing these solutions implies that an increase in the electropositive nature of the local environment of the butyl ligands occurs when 1 equiv of *n*-butyllithium is added to 1 equiv of lithium di-*n*-butylcuprate. Taken together, these observations suggest the reaction⁶



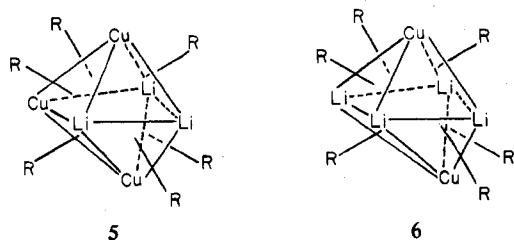


Figure 12. Tentative structures for the 1:1 and 2:1 complexes of *n*-butyllithium with *n*-butylcopper(I) in pentane.

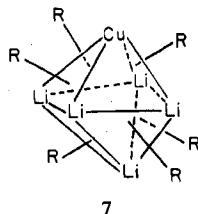
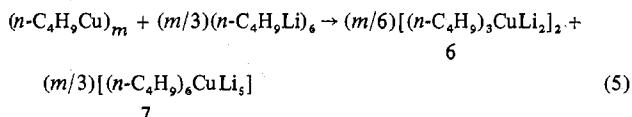


Figure 13. Proposed structure for a 5:1 complex of *n*-butyllithium with *n*-butylcopper in pentane.

Tentative structures for **5** and **6** are shown in Figure 12. These structures are suggested based on analogy with the proposed structure for *n*-butyllithium in pentane. In view of the different local environments of the butyl ligands of **5**, this structure cannot be accommodated to the NMR data in Table II unless either the chemical shifts of the two ligands in different environments are sufficiently similar so as to be indistinguishable or rapid intramolecular exchange exists. Structure **6** is consistent with the proton spectra for a solution of *n*-butyllithium-*n*-butylcopper(I) (2:1) in pentane at limiting low temperatures.

The low-temperature NMR spectra of a halide-, phosphine-free pentane solution of *n*-butylcopper-*n*-butyllithium (1:3) exhibited two high-field methylene resonances. The first triplet had a chemical shift equivalent to that of the single high-field triplet observed for a 1:2 mixture of *n*-butylcopper-*n*-butyllithium in pentane, i.e., **6**, suggesting that the *n*-butyl ligands characterized by these absorptions are experiencing equivalent local environments bounded by one copper and two lithium atoms. The second high-field triplet displayed a chemical shift ascribable to *n*-butyllithium, i.e., an environment bounded by three lithium atoms. Taken together with the nature of the reaction, these results are consistent with either of two reasonable explanations. The first explanation is that rapid intermolecular exchange is occurring in solutions of *n*-butyllithium and **6**, which at low temperatures is slowed, revealing individual components. A second likely explanation is that a pentane solution of *n*-butyllithium and *n*-butylcopper in a 3:1 ratio consists of a 1:1 mixture of 2:1 and 5:1 complexes (**6** and **7**) of *n*-butyllithium with *n*-butylcopper(I) (see eq 5). Neither of these explanations can



be discounted based on present spectroscopic or chemical evidence; however, the latter one is favored by reason of its consistency with the structure of *n*-butyllithium in pentane and by virtue of its compatibility with the concept that lithium organocuprates can be derived formally by the successive substitution of copper atoms for lithium atoms in appropriate organolithium aggregates. A reasonable structure for **7**, based on analogy with the structure of *n*-butyllithium in pentane is seen in Figure 13.

***n*-Butyl(tri-*n*-butylphosphine)copper(I)-*n*-Butyllithium**

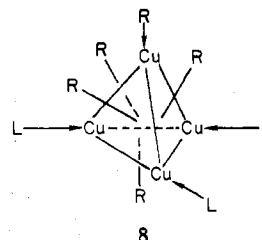


Figure 14. Proposed structure for tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] and *n*-butyl(tri-*n*-butylphosphine)copper(I) in diethyl ether, L = (*n*-Bu)₃P.

Solutions and the Influence of Lithium Iodide. An investigation into the influence of lithium iodide on the proton spectra of solutions containing *n*-butyl(tri-*n*-butylphosphine)copper(I) and *n*-butyllithium was prompted by qualitative and quantitative evidence suggesting that this halide is capable of forming complexes with organocopper(I) and -lithium reagents under a variety of conditions. For example, an examination of the product distribution from the oxidation of halide-containing solutions of *n*-butyl(tri-*n*-butylphosphine)copper(I) performed in the presence of increasing amounts of *n*-butyllithium is consistent with the view that lithium iodide is incorporated into the structures of mixed lithium(I)-copper(I) alkyls.³ A further demonstration of the ability of lithium iodide to form solution-stable copper(I)-lithium iodide complexes is seen in the facility with which many otherwise insoluble copper(I) salts dissolve in solvents containing lithium iodide. However, before attempting to interpret the NMR spectra of lithium iodide-*n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium mixtures, two questions must be considered. First, what influence does the presence of tri-*n*-butylphosphine exert on the structure of halide-free complexes of *n*-butylcopper(I)-*n*-butyllithium? Second, is the distribution of iodide statistical in a copper(I)-lithium(I) alkyl aggregate, or are there preferred sites for coordination of iodide?

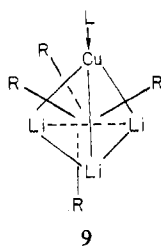
Although no direct evidence is presently available with regard to these questions, several observations pertaining to them can be recognized. First, tertiary phosphines, unlike alkyl groups and halide anions, are nonbridging ligands. Moreover, the probable structure of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] and, by analogy, that of *n*-butyl(tri-*n*-butylphosphine)copper(I) in solution⁷ (**8**, Figure 14) establish that phosphine ligands in a copper(I) cluster in which bridging ligands are involved serve to complete the coordination shell of copper(I). Second, in view of the strong affinity of tertiary phosphines for copper(I), it is reasonable to assume that in mixtures of *n*-butylcopper(I)-*n*-butyllithium-tri-*n*-butylphosphine (1:1 phosphine:copper) only the copper centers are involved in phosphine coordination. In light of these arguments, it also seems reasonable to conclude that phosphine-containing and phosphine-free complexes of *n*-butylcopper(I)-*n*-butyllithium have similar structures, the principal difference between them being one of coordinative unsaturation at copper. Finally, in view of the fact that iodide anion prefers bonding with copper(I) rather than lithium(I) (witness, e.g., the failure of copper(I) iodide to dissociate in solvents which readily dissociate lithium iodide), the problem of assigning local environments in copper(I)-lithium(I) aggregates containing both butyl and iodide is simplified by the realization that iodide anion can probably be assigned as bonding preferentially to that face which contains the greatest number of copper(I) centers. Although the above conclusions are not supported by direct evidence, the internal consistency which they provide in the interpretation of independent spectroscopic and chemical data³ argue for their correctness.

Figure 9 and Table III summarize the temperature dependence of the chemical shift of the high-field methylene

Table III. Effect of Temperature on the Chemical Shift of the High-Field Methylene Observed for *n*-Butyl(tri-*n*-butylphosphine)copper(I)-*n*-Butyllithium Mixtures (1:*N*) in Diethyl Ether^{a, b}

Temp, °C	Chemical shift ^c (δ) ^d					
	<i>N</i> = 0	<i>N</i> = 1	<i>N</i> = 2	<i>N</i> = 3	<i>N</i> = 4	<i>N</i> = ∞
30	<i>g</i>	7.53 (7.0)	7.77 (7.1)	7.87 (7.1)	7.94 (7.0)	8.30 (8.5)
-20	6.98 ^e (7.2)	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>
-50	<i>g</i>	<i>g</i>	7.52 (<i>h</i>)	<i>g</i>	<i>g</i>	<i>g</i>
			8.24 (<i>h</i>)			
-80	<i>g</i>	7.45 ^f (7.2)	7.47 (7.1)	7.52 (7.0)	7.50 (7.0)	8.25 (<i>h</i>)
			8.24 (<i>h</i>)	8.19 (<i>h</i>)	8.27 (<i>h</i>)	

^a These solutions were prepared by adding the desired number of equivalents of *n*-butyllithium to 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] dissolved in ether at -78 °C. ^b The concentration of all samples was adjusted to 0.5–0.75 M in *n*-butyl moiety. ^c Chemical shifts are reported in ppm upfield from benzene (1%) internal standard. ^d Coupling constants are in Hz. ^e Recorded at -25 °C. ^f Recorded at -70 °C. ^g Not examined. ^h An accurate coupling constant could not be determined because of peak broadening.

**Figure 15.** Proposed structure for the 1:1:2 complex between lithium iodide, *n*-butylcopper(I), and *n*-butyllithium in diethyl ether; L = P(*n*-Bu)₃.

observed for ether solutions of *n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium in the presence of lithium iodide (1:1 halide:copper). They reveal that the proton spectra of a 1:1:2 lithium iodide-*n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium mixture in ether exhibit two distinct high-field methylene absorptions at low temperatures; however, similar halide- and phosphine-free solutions of *n*-butylcopper(I)-*n*-butyllithium do not display separate high-field absorptions until a butylcopper(I) to *n*-butyllithium ratio of 1:3 is reached. The chemical shift of the higher upfield absorption displayed by these 1:1:2 mixtures is similar to the chemical shift observed for a halide-free ether solution of *n*-butyllithium; hence, it is assigned to a butyl group in the local environment provided by a face composed of three lithium atoms. The lower upfield triplet of the same solution is assigned to a local environment provided by a face bounded by one copper and two lithium atoms on the basis of a comparison of its chemical shift with the chemical shift of the high-field absorption observed for the corresponding halide- and phosphine-free, 1:3 complex of *n*-butylcopper(I)-*n*-butyllithium at -50 °C (cf. Table I, *N* = 2, and Table II, *N* = 2). The integrated relative intensity (higher to lower field) of these absorptions was ca. 0.75. These data are consistent with the suggestion that the addition of 1 equiv of lithium iodide to an ether solution of *n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium (1:2) results in the formation of a 1:1:2 complex of lithium iodide-*n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium. A structure for this complex which is consistent with the above data and the structure of the corresponding halide- and phosphine-free reagent (4) is seen in Figure 15 (9).

The high-field methylene absorptions observed in the low-temperature NMR spectra of lithium iodide containing solutions of *n*-butyl(tri-*n*-butylphosphine)copper(I) and lithium di-*n*-butyl(tri-*n*-butylphosphine)cuprate in both ether and pentane (*vide infra*) solvents never appeared as anything other than single absorptions (Table III). These results suggest that all of the butyl ligands in each of these complexes are in similar local environments. It is difficult to accommodate this suggestion with reasonable structures for 1:1 complexes of

Table IV. Effect of Temperature on the Chemical Shift of the High-Field Methylene Observed for *n*-Butyl(tri-*n*-butylphosphine)copper(I)-*n*-Butyllithium Mixtures (1:*N*) in Pentane^{a, b}

Temp, °C	Chemical shift ^c (δ) ^d				
	<i>N</i> = 0	<i>N</i> = 1	<i>N</i> = 2	<i>N</i> = 3	<i>N</i> = ∞
30	7.03 ^e (7.6)	7.39 (7.5)	7.55 (7.8)	7.76 (8.0)	8.10 (8.5)
-50	<i>f</i>	7.34 (7.6)	7.37 (7.0)	7.37 (<i>g</i>)	8.07 (<i>g</i>)
			8.00 (<i>g</i>)	8.02 (<i>g</i>)	

^a These solutions were prepared by adding the desired equiv of *n*-butyllithium to 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] dissolved in pentane at -78 °C. ^b The concentrations of all samples were adjusted to 0.5–0.75 M in *n*-butyl moiety. ^c Chemical shifts are reported in ppm upfield from benzene (1%) internal standard. ^d Coupling constants are in Hz. ^e Recorded at 0 °C. ^f Not examined. ^g An accurate coupling constant could not be determined because of peak broadening.

lithium iodide with either *n*-butyl(tri-*n*-butylphosphine)copper(I) or lithium di-*n*-butyl(tri-*n*-butylphosphine)cuprate. There are at least two possible reasons for this failure. First, the assumption used to assign the site of halide attachment to an organocopper(I)-organolithium aggregate may have failed in these solutions, specifically, intramolecular exchange may be rapid under these circumstances, and/or the factors which influence the selection of local environment may not be as decisive in these complexes as they are in a complex such as 9. Second, the higher concentration of lithium iodide present in these solutions (ca. 0.75 and 0.40 M, respectively) may have resulted in fractional crystallization of lithium iodide at low temperatures, leaving solutions of uncertain stoichiometries. On the other hand, lithium iodide-*n*-butyllithium did not appear to precipitate from 1:1:2 solutions of lithium iodide-*n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium at -78 °C as it did from more concentrated solutions. The concentration of lithium iodide in the 1:2 solutions of *n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium was 0.2 M.

The fact that tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] is readily soluble in pentane suggests that the incorporation of lithium iodide into organo(tri-*n*-butylphosphine)copper(I)-organolithium aggregates may also occur in pentane. Table IV reveals the temperature dependence of the chemical shifts of the high-field methylene absorptions for pentane solutions of *n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium containing lithium iodide (1:1, halide-copper). By contrast with halide- and phosphine-free pentane solutions of *n*-butylcopper(I)-*n*-butyllithium, which display two distinct high-field methylene absorptions only when the ratio of *n*-butylcopper(I) to *n*-butyllithium is 1:3, solutions of lithium iodide-*n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium exhibit two high-field methylene absorptions at an *n*-butyl(tri-*n*-butylphosphine)copper(I) to *n*-butyllithium ratio of 1:2.

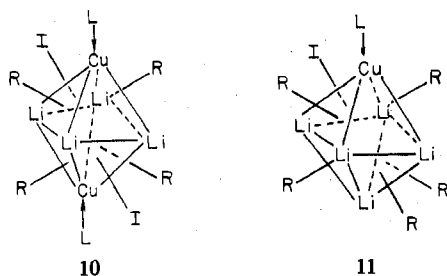


Figure 16. Proposed structures for the 1:1:1 and 1:1:4 complexes of lithium iodide, *n*-butyl(tri-*n*-butylphosphine)copper(I), and *n*-butyllithium in pentane; L = P(*n*-Bu)₃.

The integrated relative intensity (higher to lower field) of these absorptions was ca. 1.0. The chemical shift of the higher upfield absorption was the same as the chemical shift observed in the spectra of free *n*-butyllithium in pentane and is assigned to a local environment consisting of three lithium atoms. The low-field absorption is assigned to a local environment consisting of three lithium atoms. The lower upfield absorption is assigned to a local environment consisting of one copper and two lithium atoms on the basis of a comparison of its chemical shift with the chemical shift of the high-field absorption observed for the corresponding halide- and phosphine-free 1:3 complex of *n*-butylcopper(I)-*n*-butyllithium in pentane at -50 °C (cf. Table II, *N* = 2, and Table IV, *N* = 2).

These data suggest that a butyl ligand has been replaced by an iodide ligand in these mixtures. It is only speculation at this time what the structures of these halide-containing complexes of *n*-butyllithium-*n*-butyl(tri-*n*-butylphosphine)copper(I) are in pentane. However, with this in mind and based on analogy with the structures proposed for *n*-butyllithium in pentane, Figure 16 shows a proposed structure for a 1:1:1 (10) and 1:1:4 (11) complex of lithium iodide-*n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium in pentane. Chemical evidence is also consistent with the conclusion that the addition of 3 equiv of *n*-butyllithium to 1 equiv of a 1:1:1 mixture of lithium iodide-*n*-butyl(tri-*n*-butylphosphine)copper(I)-*n*-butyllithium in pentane results in the mixture being completely converted to 11.³

Finally, it was generally noted that the temperatures necessary to achieve slow exchange conditions for the halide- and phosphine-containing solutions of *n*-butylcopper-*n*-butyllithium were lower than those required for halide- and phosphine-free solutions. This observation suggests that exchange in the halide- and phosphine-free solutions is slower than exchange in the halide- and phosphine-containing solutions.

Discussion

The structures proposed above rely heavily on analogy to the solution structures of organolithium compounds, the development and formulation of which have been greatly aided by colligative property studies that revealed their degrees of association in solution. Similar data for lithium di-*n*-butylcuprate have proven experimentally difficult to obtain. Thus, the structures proposed here remain more speculative than desirable; however, they do form an internally consistent picture which is supported by chemical evidence.

Recently, other workers have presented ¹H NMR and other physical evidence related to the solution structure of lithium dimethylcuprate.^{5,10} The conclusions reached by these authors and those presented here are not in close agreement. Specifically, their method of preparing the desired lithium organocuprate differs substantially from that employed in the present study.

Pearson and Gregory⁵ have presented colligative data¹⁴ which suggest that lithium dimethylcuprate exists as a dimer

in diethyl ether solution. Using x-ray scattering techniques these authors further concluded that the Cu-Cu distance in diethyl ether solutions of [(CH₃)₂CuLi]_n is 4.4 ± 0.7 Å which, if correct, is compelling evidence against tetrahedral structure 3b and favorable evidence for 3a. This value, however, is derived from a corrected plot of intensity vs. scattering angle (2θ) for an ether solution of (CH₃)₂CuLi. The reported curve exhibited both a maximum and a minimum deflection which should yield the same Cu-Cu distance. The value of 4.4 ± 0.7 Å was calculated from an angle (2θ = 25°) derived from the maximum on this curve, a choice which the authors suggest is more reliable than the corresponding value of 3.5 ± 0.7 Å, derived from the minimum deflection value (2θ = 18°). The validity of this premise and several others used to obtain these distances and error limits is not obvious. Indeed, a consideration of this lower value, together with its rather substantial and poorly defined error limits, leads to a possible Cu-Cu distance of 2.8 Å, a value well within the range of nonbonding Cu-Cu distances observed for a variety of copper-containing tetrahedra.¹¹

Experimental Section

General Methods. All reactions involving organometallic substances were carried out under inert atmospheres of dry prepurified nitrogen or helium. Ether was distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use. All paraffinic hydrocarbon solvents were deoxygenated by scrubbing with concentrated sulfuric acid before distillation from a suspension of sodium benzophenone ketyl under a nitrogen atmosphere. Analytical GLC analyses were performed using the internal standard technique on F&M Model 810 instruments equipped with flame ionization detectors and disk integrators.

Solutions of *n*-butyllithium in hexane were purchased from Foote Mineral Co. These reagents contained less than 0.01 equiv of lithium halide per equiv of alkyl lithium reagent. The concentrations of all organolithium reagents were routinely determined by the Gilman double-titration method using 1,2-dibromoethane.

Copper analyses were performed by EDTA titration employing PAN indicator. The accuracy of this procedure in the presence of tri-*n*-butylphosphine was demonstrated by determining the copper content of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)], 8. A known quantity of 8 (0.792 g, 2.02 mmol) was treated with ~50 mL of boiling aqua regia for 20-30 min before neutralizing with concentrated ammonium hydroxide until the deep blue color of [Cu(NH₃)₄]²⁺ persisted. Analysis indicated 2.10 mmol of copper (4% error).

Iodo[bis(di-*n*-butyl sulfide)copper(I)] (12) was prepared as previously described.¹¹

Preparation of *n*-Butylcopper(I). Ether suspensions of *n*-butylcopper(I) were prepared by the following procedure. Into a 40-mL centrifuge tube, capped with a rubber septum and flame-dried under a stream of dry nitrogen, was injected 2.0 mL (2.68 g, 5.5 mol) of 12 and 30 mL of ether. Injection of 3.0 mL (4.8 mmol) of a hexane solution of *n*-butyllithium into this solution at -78 °C resulted in the immediate formation of a heavy yellow precipitate of *n*-butylcopper(I), which was compacted by centrifugation. To prevent thermal decomposition during centrifugation, the bottom of the centrifuge bucket was packed with dry ice. The centrifuge tube was then returned to a dry ice-acetone bath, and the supernatant solution was removed through a cannula employing a positive pressure of nitrogen. Fresh ether (30 mL) was again added, and the tube was shaken again and centrifuged. In all, the solid *n*-butylcopper(I) was washed five times. Insofar as possible, all procedures and manipulations were performed with the centrifuge tube chilled in a dry ice-acetone bath. *n*-Butylcopper(I) is stable indefinitely at -78 °C. The average yield of *n*-butylcopper(I) by this procedure is 70%, based on the initial number of equivalents of *n*-butyllithium employed.

GLC analysis of a hydrolyzed (dilute nitric acid) suspension of *n*-butylcopper(I) in ether indicated less than 1% of di-*n*-butyl sulfide, based on copper. Treatment of this same mixture with a 0.1 M solution of silver nitrate failed to produce a significant precipitate of silver halide (sensitivity >3% halide).

A similar procedure can be used to prepare *n*-butylcopper(I) in pentane. In this instance, the lithium iodide does not wash out but instead compacts to the bottom on centrifugation; the butylcopper(I),

Table V. Reaction of Organocopper(I) Reagents with Methanolic Hydrochloric Acid in Et₂O at -50 °C

R _n CuLi _{n-1} ·(L)	mmol of RH/mmol of copper
<i>n</i> -C ₄ H ₉ Cu ^{a,b}	0.96
(<i>n</i> -C ₄ H ₉) ₂ CuLi ^c	1.97
<i>n</i> -C ₄ H ₉ Cu·P(<i>n</i> -Bu) ₃ ^{b,d,e}	0.97
(<i>n</i> -C ₄ H ₉) ₂ CuLi·P(<i>n</i> -Bu) ₃ ^{b,e,f}	1.95

^a Uncomplexed organocopper(I) reagents were prepared by the reaction of 1 equiv of the corresponding organolithium reagent with 1 equiv of 1 in ether at -78 °C (eq 3). GLC analysis of the hydrolyzed reaction mixtures indicated that these reagents contained 1 mol % of di-*n*-butyl sulfide, based on copper.

^b A silver nitrate test for halide, sensitive to >3 mol % and performed on all reagents except where noted, indicated <3 mol % halide. ^c Prepared by dissolving 1 equiv of uncomplexed organocopper(I) compound in 1 equiv of organolithium reagent (eq 4).

^d Prepared by the addition of 1 equiv of organolithium reagent to 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] in ether at -78 °C (eq 2). ^e Prepared by the addition of 2 equiv of organolithium reagent to 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] in ether at -78 °C. ^f Lithium iodide was removed by precipitation as its ether-insoluble dioxanate on addition of 1.1 equiv of anhydrous dioxane.

which compacts in a second layer on top, can be removed by a cannula using a positive pressure of nitrogen. Analysis indicated <3% halide.

Tri-*n*-butylphosphine Complexes of Organocopper(I) Reagents. A general procedure for the preparation of the tri-*n*-butylphosphine complexes of organocopper(I) reagents is represented by the following example of the preparation of *n*-butyl(tri-*n*-butylphosphine)copper(I). A 12-mL centrifuge tube, capped with a rubber serum stopper, was flame-dried under a stream of dry nitrogen. The serum stopper was removed, and 1.6 mmol (0.628 g) of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)]⁸ was weighed into the centrifuge tube. The serum cap was replaced, and the vessel was flushed with nitrogen. Ethyl ether (ca. 5 mL) was added, and the resulting solution was chilled to -78 °C before adding 1.0 mL (1.6 mmol) of a hexane solution of *n*-butyllithium. Additional ether was added to give a yellow solution of *n*-butyl(tri-*n*-butylphosphine)copper(I) of the desired concentration.

Preparation of Lithium Di-*n*-butylcuprate. Halide-free lithium di-*n*-butylcuprate is prepared by dissolving a suspension of halide-free *n*-butylcopper(I) in an ether or pentane solution containing slightly less than 1 equiv of halide-free butyllithium. The following description represents a typical procedure. Into a 40-mL centrifuge tube capped with a rubber septum and containing ~3.5 mmol of *n*-butylcopper(I) suspended in 5–10 mL of ether at -78 °C was injected 2.0 mL (3.2 mmol) of a hexane solution of *n*-butyllithium. The centrifuge tube was shaken vigorously for 1–2 min at -50 °C before being centrifuged in a bucket with dry ice. The resulting supernatant solution was decanted by cannula into a flame-dried, nitrogen-flushed centrifuge tube capped with a rubber septum. The extremely oxygen-sensitive solution is stable indefinitely at -78 °C.

Tri-*n*-butylphosphine- and halide-containing solutions were prepared by adding the desired number of equivalents of *n*-butyllithium to 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] dissolved in the desired solvent at -78 °C. The resulting solutions ranged from colorless to pale pink, to yellow, to wine red, and they were stable indefinitely at -78 °C. These reagents, too, are extremely sensitive to oxygen.

Analysis of Organocopper(I) Reagents. The following procedures are typical of those employed in the analysis of organocopper(I) compounds.

An ether suspension of *n*-butylcopper (~2 mmol) contained in a 40-mL centrifuge tube at -50 °C was treated with 1 mL of a solution of aqueous hydrochloric acid (12 M) in methanol (1:1). After shaking the tube vigorously for several minutes while warming it to room temperature, a weighed amount of GLC internal standard was added, and the reaction mixture was analyzed without further workup using the following GLC conditions: *n*-butane analyses (internal GLC standard; *n*-pentane) were performed on a 3-ft, 3% Apiezon N on alumina (60–80 mesh) column at 90 °C. A copper analysis was carried out on the hydrolyzed reaction mixture. The results are shown in Table V.

A similar analysis on a halide-free sample of *n*-butyl(tri-*n*-butylphosphine)copper(I) was completed in the following manner. A solution of *n*-butyl(tri-*n*-butylphosphine)copper(I) (~0.5 M, 10 mL) at -78 °C was transferred by a cannula into a 12-mL centrifuge tube which had been flushed with nitrogen and which contained ~1 mL of methanolic hydrochloric acid (1:1, v/v) at -50 °C. The solution was shaken vigorously until it reached ambient temperature, and then a weighed amount of internal standard (*n*-pentane) was added and the reaction mixture was analyzed by GLC on a 3-ft, 3% Apiezon N on Alumina (60–80 mesh) column at 90%. *n*-Butane (3.49 mmol), identified by comparison of GLC retention time (peak enhancement) with an authentic sample, was the only product observed. A copper analysis performed on the remaining reaction mixture revealed 3.60 mmol of copper, giving a ratio of *n*-butane to copper of 0.97 ± 0.03 (Table V).

Preparation of NMR Samples. The above described procedures for preparing *n*-butylcopper(I) and its derivatives were modified somewhat to permit the preparation of samples sufficiently concentrated for NMR studies. A suspension of halide-free *n*-butylcopper was prepared from iodo[bis(di-*n*-butyl sulfide)]copper(I) as described above and then transferred by cannula at -78 °C to a flame-dried 12-mL centrifuge tube capped with a serum stopper. The sample was centrifuged for ca. 2 h at -78 °C. A limiting amount of *n*-butyllithium was added to the solid butylcopper(II) to produce a solution of lithium di-*n*-butylcuprate. Samples of lithium di-*n*-butylcuprate containing additional increments of *n*-butyllithium were prepared by transferring the supernatant solution of lithium di-*n*-butylcuprate by cannula to a flame-dried 12-mL centrifuge tube which was capped with a serum stopper and which contained the desired quantity of *n*-butyllithium. The samples prepared by this procedure ranged in concentration from 0.5 to 0.75 M in butyl residue. Samples containing tri-*n*-butylphosphine were more readily produced. The usual procedure was followed except that the precursor was dissolved in that quantity of a desired solvent which allowed a final concentration in the range 0.50–0.75 M in *n*-butyl residue. After preparation, the samples were transferred by cannula to flame-dried NMR tubes, capped with a serum stopper, and sealed off at -78 °C under an atmosphere of nitrogen.

NMR spectra were obtained using a Varian A-60 spectrometer. The low temperatures were obtained using the standard low-temperature accessories supplied by Varian Associates. After allowing the system to come to equilibrium at each temperature, a number of spectra were recorded with temperature measurements (methanol) before and after. All spectra were referenced with respect to internal benzene (1–3%) audio sidebands generated using a Krohn-Hite Model 450 push-button oscillator. The frequency of this oscillator was checked periodically using a Hewlett-Packard 524 electronic counter.

Registry No. *n*-C₄H₉Cu, 34948-25-9; (*n*-C₄H₉)₂CuLi, 24406-16-4; (*n*-C₄H₉)₃CuLi₂, 61288-01-5; (*n*-C₄H₉)₄CuLi₃, 64739-96-4; (*n*-C₄H₉)₅CuLi₄, 64739-97-5; *n*-C₄H₉Cu·P(*n*-Bu)₃, 26679-41-4; (*n*-C₄H₉)₂CuLi·P(*n*-Bu)₃, 24743-93-9; (*n*-C₄H₉)₃CuLi₂·P(*n*-Bu)₃, 64739-98-6; (*n*-C₄H₉)₄CuLi₃·P(*n*-Bu)₃, 64739-99-7; (*n*-C₄H₉)₅CuLi₄·P(*n*-Bu)₃, 64740-00-7; *n*-C₄H₉Li, 109-72-8; iodo[bis(di-*n*-butyl sulfide)copper(I)], 35907-31-4; tetrakis[iodo(tri-*n*-butylphosphine)copper(I)], 28132-72-1.

References and Notes

- (1) (a) This work was supported by grants from the National Science Foundation (to G. M. Whitesides) and is abstracted in part from the author's Ph.D. Thesis. (b) Address correspondence to the Department of Chemistry, Rutgers University, New Brunswick, N.J. 08903.
- (2) (a) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4141 (1966). (b) Methylithium and *n*-butyllithium are tetrameric in diethyl ether.^{12,13} The proposed structure for methyl- and *n*-butyllithium in diethyl ether is a tetrahedron of electron-deficient lithium atoms with an alkyl ligand bonded at each face through a four-center bond. *n*-Butyllithium is hexameric in aliphatic hydrocarbon solvents.^{13a} The structure of *n*-butyllithium in these solvents is proposed to be an octahedral cluster of electron-deficient lithium atoms in which each butyl ligand is attached by a four-center bond to three of the top four faces. The remaining butyl ligands are bonded to the opposite lower faces in a similar manner.
- (3) G. M. Whitesides et al., manuscript in preparation.
- (4) R. L. Kieft and T. L. Brown, *J. Organomet. Chem.*, **77**, 289 (1974).
- (5) R. G. Pearson and C. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976).
- (6) An alternative explanation is that exchange between lithium di-*n*-butylcuprate and *n*-butyllithium is very rapid. Although this possibility cannot be rigorously excluded, its likelihood at these temperatures is reduced by the fact that a very slow rate of exchange of alkyl groups

is observed for solutions of alkyllithium reagents in saturated hydrocarbon solvents: G. E. Hartwell and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4625 (1966).

- (7) This proposal is based on the fact that crystalline tetrakis[iodo(tri-*n*-butylphosphine)copper(I)], which has structure **8** ($R = I$),⁸ is also tetrameric in benzene solution.⁹
- (8) A. F. Wells, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **94**, 447 (1936).

- (9) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).
- (10) E. C. Ashby and J. J. Watkins, *J. Am. Chem. Soc.*, **99**, 5312 (1977).
- (11) J. San Filippo, Jr., L. E. Zyontz, and J. Potenza, *Inorg. Chem.*, **14**, 1667 (1975), and references therein.
- (12) P. West and R. Waack, *J. Am. Chem. Soc.*, **89**, 4395 (1967).
- (13) (a) T. L. Brown, *Adv. Organomet. Chem.*, **3**, 365 (1965); (b) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966).
- (14) See also ref 10.

Contribution from the Department of Chemistry and the Division of Engineering, Brown University, Providence, Rhode Island 02912

Crystal Growth and Characterization of the Transition-Metal Phosphides CuP_2 , NiP_2 , and RhP_3

J. P. ODILE, S. SOLED, C. A. CASTRO, and A. WOLD*

Received June 20, 1977

Single crystals of the transition-metal phosphides CuP_2 , NiP_2 , and RhP_3 were grown from a tin flux, and, for the first time, their physical properties have been well characterized. In addition, single crystals of CuP_2 were grown by the chemical-vapor transport technique, using chlorine as a transport agent. All three phosphides crystallize with structures having groups of anions bonded to one another. Although a tin content of 0.6 wt % was measured by atomic absorption in the flux-grown CuP_2 crystals, the magnetic, electrical, and optical properties of the flux and transported single crystals were very similar. From this study, CuP_2 was ascertained to be a diamagnetic p-type semiconductor with a band gap of 1.53 eV and NiP_2 a diamagnetic n-type semiconductor with a band gap of 0.73 eV. p-Type metallic conduction and diamagnetic behavior were observed for RhP_3 .

Introduction

Most of the early investigations of transition-metal phosphides have focused on metal-rich phases. The study of the phosphorus-rich transition-metal phosphides has been complicated by the formation of multiple phases during synthesis via direct combination of the elements and by difficulties in crystal growth.^{1,2} However, a recent interest in the semiconducting properties of these phases has prompted a more systematic study. Investigators from this laboratory have grown crystals of platinum diphosphide from a tin flux³ and cobalt triphosphide using the chemical-vapor transport technique.⁴ These techniques were used in the present work to prepare single crystals of the phosphorus-rich transition-metal phosphides CuP_2 , NiP_2 , and RhP_3 .

These phosphides feature different types of anion arrangements. In the CuP_2 structure, the anion framework is comprised of edge-sharing ten-membered puckered rings of phosphorus atoms lying approximately parallel to (100), that is, in a direction perpendicular to the plane of projection shown in Figure 1. Discrete pairs of copper atoms bridge these rings.

In NiP_2 , the phosphorus atoms form square rings slightly tilted from the (101) plane as shown in Figure 2 with nickel atoms situated in the center of the rings. Short P-P bonds connect the atoms in adjacent planes.

RhP_3 adopts the skutterudite⁵ structure. The phosphorus atoms cluster into planar four-membered rectangular rings, as illustrated in Figure 3. The cations are octahedrally coordinated by the anions whereas each anion is coordinated by two metal atoms and two other anions in a distorted tetrahedron. The unit cell is cubic and contains eight RhP_3 units.

Large (approximate average dimensions $2 \times 2 \times 0.5$ mm) and well-characterized single crystals have been grown in order to determine the exact physical properties of these phases.

Experimental Section

(1) **Chemical Vapor Transport.** Both copper (Johnson-Matthey, 99.999%) and nickel (Gallard-Schlessinger, 99.999%) were reduced in a dry 15% H_2 /85% Ar atmosphere for 4 h at 600 °C to remove

Table I. Experimental Growth Conditions and Results for the Tin-Flux Method^a

Nominal compn	Metal/phosphorus/tin molar ratios	Results
CuP_2	1/2/5	Good crystals
CuP_2	1/2/10	Best crystals
CuP_2	1/2/20	Good crystals
CuP_3	1/3/20	Crystals of Cu_4SnP_{10}
CuP_4	1/4/20	Crystals of Cu_4SnP_{10}
CuP_6	1/6/20	Crystals of Cu_4SnP_{10}
NiP_2	1/2/20	Good crystals
NiP_2	1/2/40	Good crystals
NiP_3	1/5/40	Crystals of NiP_2
RhP_3	1/3/40	Best crystals
RhP_3	1/3/80	Good crystals
RhP_6	1/6/10	Crystals of RhP_3

^a Soaking temperature 1150 °C; cooling rate 5 °C/h; duration 1 week.

oxygen impurities. Rhodium (Engelhard, 99.99%), red phosphorus (Leico Industries, 99.999%) and chlorine (Linde, 99%) were used as supplied.

In order to prepare single crystals of CuP_2 , stoichiometric amounts of the starting materials were introduced into silica tubes (28 cm \times 13 mm) which were then evacuated to less than 2 Torr. After the tubes were filled to a pressure of 50 Torr of chlorine, they were sealed and placed in a transport furnace. A temperature profile was maintained for 1 day with the growth zone at 835 °C and the charge zone at 815 °C to remove any potential nucleation sites from the growth zone. After thermal equilibrium was established along the tube, the charge zone was set at 810 °C and the growth zone cooled over a period of 4 days to a final temperature of 760 °C. This gradient was maintained for 3–5 days, and then the furnace was shut down and allowed to cool to room temperature. Large black, shiny crystals of CuP_2 were obtained by this method. Similar attempts to grow crystals of NiP_2 and RhP_3 were unsuccessful.

(2) **Growth from a Tin Flux.** Single crystals of CuP_2 , NiP_2 , and RhP_3 were grown from a tin flux.⁶ The tin metal (99.5%) was purified by melting under a dynamic vacuum. Stoichiometric amounts of the transition metal (Cu, Ni, or Rh) and phosphorus were placed in a silica tube and tin was added such that the resulting mixture was at