side of the highest field peak.

(23) (a) We determined that a similar shift of the nitrogen pattern occurred when we used our protohemin compounds dissolved in THF–chloroform solvent but with *no* tetrabutylammonium halide present. In the absence of $[Bu_4N]^+Br^-$ a magnetic hyperfine constant $|A_{zz}|$ of 7.34 MHz was obtained for the protohemin bromide. This value is slightly larger than the average value quoted in Table I for samples with $[Bu_4N]^+Br^-$ present, but the value is almost within experimental error of that average value. In the absence of $[Bu_4N]^+Cl^-$ a magnetic hyperfine coupling of 7.51 MHz was measured for the protohemin chloride; this value is slightly smaller than the average value quoted in Table I but is again within experimental error of it. Quadrupole couplings showed no change from the numbers in Table I. (b) Control experiments were done using the THF–chloroform solvent system with tetrabutylammonium halide but with washed, freshly distilled, *ethanol-free* chloroform. These controls showed no change from the tabulated ENDOR and EPR parameters.

(24) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Metal Ions", Clarendon Press, Oxford, 1970, Chapter 4.

(25) C. P. Scholes, R. A. Isaacson, and G. Feher, *Biochim. Biophys. Acta*, **244**, 206–210 (1971).

(26) We have omitted terms such as $\eta(I_x^2 - I_y^2)$ which could contribute to second-order ENDOR frequency shifts. The upshot of such terms is that ENDOR lines would no longer be separated by twice the known Zeeman energy.

(27) D. F. Koenig, *Acta. Crystallogr.*, **18**, 663–673 (1965).

(28) For ^{35}Cl and ^{37}Cl the respective values of the nuclear magnetic moments in nuclear magnetons are: 0.820 91 and 0.668 33. The corresponding values for the nuclear quadrupole moments in barns are -7.89×10^{-2} and -6.21×10^{-2}. "Handbook of Chemistry and Physics", 55th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1974, p E-69.

(29) The Zeeman splitting of these two lines agrees well within experimental error with the expected Zeeman splitting for ^{35}Cl of 2.7 MHz at the field used.

(30) For ^{35}Cl $g_n\beta_nH$ was 1.35 MHz for the magnetic field used in conjunction with the cavity which resonated near 9.0 GHz; while $g_n\beta_nH$ was 1.40 MHz for the magnetic field which was used in conjunction with the cavity which resonated near 9.4 GHz.

(31) A nonaxial term such as $P_{zz}(I_xI_z + I_zI_x)\cos\psi\sin\psi$ (see formula 3.61, Chapter 3, ref 24) would contribute to these second order ENDOR frequency shifts.

(32) There should be a ^{37}Cl peak at about 14 MHz; such a peak is predicted to occur at twice the ^{37}Cl nuclear Zeeman energy above the 11.7-MHz peak. The expected peak may lie close enough to the bulk free proton frequency (13.7 MHz in Figure 3a) to suffer interference from protons and to undergo spin cross relaxation with the bulk protons. Such an ENDOR-diminishing cross relaxation with the bulk protons has been seen with the ^{57}Fe ENDOR in metmyoglobin.[1c] When we were using the higher frequency (9.4 GHz) cavity we also saw that the ^{35}Cl line at 14.7 MHz was reduced. With this cavity the proton frequency lies at 14.3 MHz and is close enough to the ^{35}Cl line at 14.7 MHz to cause interference and loss of ENDOR intensity.

Structure of Lithium Dimethylcuprate and Mechanism of the Corey–Posner Reaction

Ralph G. Pearson* and Carl D. Gregory

Contribution from the Chemistry Department, Northwestern University, Evanston, Illinois 60201.

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Abstract: The structure of lithium dimethylcuprate has been investigated using vapor pressure depression, ^1H NMR, and solution x-ray scattering methods. It is found to exist as a dimer in ether solution $[LiCu(CH_3)_2]_2$ with a cyclic structure having approximate D_{2h} symmetry. The kinetics of reaction of this reagent with methyl iodide have been investigated. The reaction appears to involve slow oxidative addition to copper, followed by rapid reductive elimination. From the results of other workers, the oxidative addition step is a nucleophilic substitution and the reductive elimination is concerted. The role of the dimeric structure in facilitating these steps is discussed.

The reaction of lithium diorganocuprates with alkyl halides

$$LiCuR_2 + R'X \rightarrow R\text{-}R' + LiX + CuR \qquad (1)$$

to form carbon–carbon bonds (the Corey–Posner reaction[1]) has been extensively investigated. These studies have been largely concerned with the products of the reaction, from a synthetic point of view.[2-4] Thus, the mechanism of the reaction is still relatively unknown. This is due in large part to the extreme instability of the diorganocuprates, and the consequent difficulty in determining their structures. Without knowledge of the structure of the reagent in reaction 1 it is difficult to postulate any convincing mechanism for the reaction.

This paper considers the structural and mechanistic problem for the case of lithium dimethylcuprate. The most likely structure for this complex has now been determined. Some new kinetic evidence is also presented, and a mechanism is suggested which is consistent with structural, kinetic, and synthetic results.

Experimental Section

Since organocopper reagents are extremely air and water sensitive, all procedures involving them were carried out in an atmosphere of dry, prepurified nitrogen. Standard benchtop techniques[5] employing Schlenk tubes, fritted funnels, side-arm flasks, and syringes with valves were used for synthesis, storage, and kinetics. Nmr tubes with rubber septum caps (Wilmad Glass Co.) were also used. Most of the other copper(I) compounds were also air sensitive, to a lesser degree, and these were handled similarly.

Organic reagents were obtained from Aldrich Chemical Co. (reagent grade) or Eastman Organic Chemicals (White Label Grade) and were used as obtained unless otherwise indicated. Inorganic reagents were from Mallinckrodt or Baker and Adamson, and were analytical reagent grade throughout.

Except as noted, ^1H NMR spectra were obtained on a Varian T-60, ir spectra on a Perkin-Elmer 337, and uv-visible spectra on a Cary 14. Low temperature pmr spectra were obtained using a Perkin-Elmer R20B.

Diethyl ether was refluxed over CaH_2 in a nitrogen atmosphere, then distilled and stored under nitrogen.

Methyl iodide for kinetic studies was washed with aqueous sodium bisulfite and dried over P_2O_5 prior to distillation, then stored under nitrogen in the dark.

(2-Toluenesulfonyloxy)propionic acid ethyl ester was prepared according to Kenyon et al.[6] and distilled under vacuum.

Methyllithium was obtained as an ethereal solution from several suppliers: Foote Mineral Co., Apache Chemical Co., and Matheson Coleman and Bell. Concentrations were determined by hydrolysis, followed by titration, and were typically 1.5–1.6 M. Various samples contained different amounts of halide ion contamination of the order of 5% or less. Some samples were slightly discolored. However, all samples gave the same ^1H NMR spectrum and the reproducibility of both kinetic runs and syntheses did not depend on the sample used, or the supplier. Solutions appearing to be most free of contaminants were used for vapor pressure and x-ray studies. The reagent was stored under dry nitrogen.

Methylsodium was prepared according to Schlenck and Holtz.[7] It was noted that stirring the reaction mixture led to the formation of an undesirable black precipitate, so stirring was avoided. Three days appeared to be the optimum reaction time at 65 °C.

All reagents were identified by ^{1}H NMR, ir, melting point, or other properties as appropriate.

Preparation of Copper Complexes. CuI was prepared from $CuSO_4$ and KI in aqueous solution. The excess I_2 was removed by successive washes of dilute KI solution, water, alcohol, and ether. (The procedure[8] of using $Na_2S_2O_3$ to reduce I_2 gives a pure white product, which will not react with methyllithium, so this procedure was not used.) The resulting off-white product was dried in vacuo to remove water which might cause decomposition of methyllithium. CuCl was obtained as a pure white precipitate upon dilution of a solution of CuCl in concentrated HCl.[9]

Phenylethynylcopper was prepared by the method of Castro et al.[10] and dried in vacuo for use with methyllithium. Tetrakis[chloro(triphenylphosphine)copper] was made by the method of Cariati and Naldini.[11]

Lithium Dimethylcuprate. Solutions of this reagent free of contaminants were prepared for X-ray, NMR, and molecular weight experiments, while kinetic studies used reagent generated in situ. All procedures were carried out under an atmosphere of pure dry nitrogen.

Cuprous iodide was reacted with methyllithium to produce methylcopper (reaction 2). The yellow solid was filtered at low temperature (or centrifuged and decanted) and washed with dry ether.

$$\mathrm{CuI} + \mathrm{LiCH_3} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} (\mathrm{CuCH_3})_x + \mathrm{LiI} \qquad (2)$$

The precipitate was then dissolved in less than a stoichiometric amount of methyllithium solution, leaving excess methylcopper:

$$\mathrm{LiCH_3} + \mathrm{CuCH_3} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \mathrm{LiCu(CH_3)_2} \qquad (3)$$

The solution was then syringed into a clean dry container. These solutions will keep for a few weeks at room temperature in the absence of oxygen.

An alternative procedure began with methyllithium and excess CuCl. The mixture was stirred at 0 °C for several hours to ensure complete reaction, and cooled to −78 °C to precipitate as much LiCl as possible, before being decanted from the residual CuCl and LiCl.

A procedure based on the insolubility of dioxane complexes of lithium salts as a means of removing these by-products was tried. Unfortunately a yellow precipitate of methylcopper was obtained, evidently due to the removal of lithium from the cuprate complex. (This procedure is similar to one used by Whitesides et al.[12] in their preparation of lithium halide free solutions of *n*-butyl (tributylphosphine)copper. However, the phosphine seems to stabilize the copper in these latter complexes, preventing the alkylcuprate from precipitating. An attempt to prepare the analogous methyl complex produced only insoluble methylcopper.)

These solutions were analyzed for copper by hydrolysis and visible spectrophotometry of the blue complex formed in concentrated ammonia solution. Halide analysis, by hydrolysis, neutralization with HNO_3, and precipitation of silver halide indicate the presence of small amounts of residual halide ion (<5% of Cu concentration) in all cases. This is not an important quantity in terms of the measurements being made.

Several attempts to produce dimethylcuprates containing a cation other than lithium were made. These were unsuccessful, but will be described briefly.

A suspension of methylsodium in ether was substituted for methyllithium in an attempt to obtain reaction 4.

$$\mathrm{NaCH_3} + \mathrm{CuI} \rightarrow [\mathrm{NaCu(CH_3)_2}]_n + \mathrm{NaI} \qquad (4)$$

A small amount of yellow compound formed on the surface of the CuI particles (probably methylcopper) but decomposed rapidly, and no further reaction occurred. After 5 h of reaction at 0 °C, and then 2 h at room temperature, no copper was present in the ethereal layer.

Attempts to replace lithium in the complex by more direct methods also failed. Thus CsF failed to precipitate LiF via reaction 5.

$$\mathrm{LiCu(CH_3)_2} + \mathrm{CsF} \xrightarrow{\mathrm{ether}} \mathrm{LiF} + \mathrm{CsCu(CH_3)_2} \qquad (5)$$

The addition of dicyclohexyl-18-crown-6 as a phase transfer catalyst to enhance the solubility of CsF also failed. CsF dissolved, but no precipitate of LiF formed, and the NMR spectrum of the complex was unchanged.

Both dioxane and dicyclohexyl-18-crown-6 caused precipitation of methylcopper when added to solutions of the cuprate. The use of dioxane as a means of introducing alkali metal ions such as Na^+ or K^+ by reactions such as (5) failed due to the insolubility of salts of these ions in ether or ether–dioxane mixtures.

Lithium dimethylaurate(I)[13] was prepared from chloro(triethylphosphine)gold for comparison with the copper complex in the x-ray experiments. The gold concentration was determined by combustion and weighing the gold residue. The complex cannot be isolated, but probably there is one molecule of free phosphine in solution.[13]

Molecular Weight Measurement. The vapor pressure depression method was used. Samples of $[\mathrm{LiCu(CH_3)_2}]_n$ in ether were compared with pure ether at the same temperature. Complete degassing of the solutions was accomplished by freezing the liquid, evacuating the container, and thawing the solution again. This was repeated for three or more cycles. Pressure was measured by means of a mercury manometer and a cathetometer. The concentration of solute molecules is given approximately by:

$$C = \frac{d(\Delta P/P^0)}{M}1000 \qquad (\mathrm{I})$$

P^0 is the pressure of pure solvent vapor, while ΔP is the depression due to solute. M is the solvent molecular weight and d is the solvent density, required to convert concentration to units of molarity. The approximation is valid only if Raoult's law holds, and if the concentration of solute is small enough relative to that of the solvent so that the relation between molarity and molality is linear. The experimental concentration of copper (maximum solute concentration) was typically 0.5 M, while the concentration of ether is about 10 M, so the latter condition is satisfied.

Comparison of the solute concentration determined in this manner with the concentration of copper determined spectrophotometrically yields the value of n in the molecular formula, and thus the molecular weight. Note that a few percent of some contaminant will not change the result by more than a few percent. Thus the extra lithium iodide present in the solutions typically introduces less error than the precision of measurement of ΔP, which is about 5%.

Ideally, one should vary the solute concentration over a range, to see if Raoult's law is valid. A change in the calculated value of the molecular weight with concentration would indicate that the degree of aggregation was not constant. Because of experimental difficulties, it is not easy to vary the concentration over a wide range and still obtain good vapor pressure data. Instead the molecular weight was found at two temperatures, 0 and 25 °C. If several species of different degrees of aggregation were present at 0 °C, it is reasonably certain that the relative proportions would change with temperature (ΔH would not be zero for the equilibria). Hence the value of n should change.

Kinetics of Reaction of $[\mathrm{LiCu(CH_3)_2}]$ with $\mathrm{CH_3I}$. The rate of reaction 6 was studied.

$$[\mathrm{LiCu(CH_3)_2}] + \mathrm{CH_3I} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{ether}} \mathrm{C_2H_6} + \mathrm{LiI} + \mathrm{CuCH_3} \qquad (6)$$

Since the product is ethane, it is conveniently followed by the change in volume of the gas above the reaction mixture. The apparatus used consists of a thermostated constant-pressure gas buret connected by a short length of Tygon tubing to a thermostated reaction vessel (Schlenk tube) containing a magnetic stirring bar, and equipped with a rubber septum cap for injection of solutions.

For each run, two solutions were made in ether. One contained a cuprous salt and excess methyllithium, plus lithium iodide, or any other reagent. The excess methyllithium ensures that any $CuCH_3$ produced is immediately reconverted to the cuprate. Thus, the limiting reagent is methyl iodide, and the cuprate concentration is maintained constant throughout the reaction period. The second solution contained methyl iodide.

At the outset, the reaction tube was purged of air, and the former solution was added by syringe through the septum (5.5 ml). After a suitable period (about 1 h, or until no further volume change occurred) had elapsed for equilibration of the ether solvent with its vapor, the methyl iodide solution (1.0 ml) was injected. The gas volume was then recorded as a function of reaction time, indicated by a stopwatch. Total

Table I. Vapor-Pressure Depression Due to $[LiCu(CH_3)_2]_n$ in Diethyl Ether

T, °C	[Cu],[a] M	P^0 (mm)[b]	ΔP (mm)	C, M[c]	n
0.0 ± 0.1	0.53 ± 0.02	183.9 ± 0.1	5.5 ± 0.2	0.285	1.86
0.0 ± 0.1	0.53 ± 0.02	186.5 ± 0.1	5.8 ± 0.2	0.299	1.77
23.0 ± 0.1	0.47 ± 0.02	492.3 ± 0.1	13.3 ± 0.2	0.255	1.84

[a] Spectrophotometrically determined copper concentration. [b] Vapor pressure of pure ether. [c] Apparent solute concentration.

volume changes of about 4 ml were obtained by appropriate choice of methyl iodide concentration. Errors due to the solubility of ethane in ether were shown to be negligible.

The same method was used to study the reaction of the cuprate derived from phenylacetylide, and to observe reaction 6 with methyl tosylate substituted for methyl iodide. The effects of added phosphine, variation of methyllithium concentration, variation of copper concentration, and the influence of a free radical trap (triphenylmethane) were studied.

X-Ray Scattering. Scattering patterns of diethyl ether and of ether solutions of lithium dimethylcuprate(I) were obtained in order to determine the metal-metal distance in the complex.

A GE XRD-5 diffractometer using Ni-filtered Cu Kα radiation was used. The detector was a Picker scintillation counter equipped with a pulse height analyzer, counter, printer, and strip-chart recorder. The beam was defined by a 0.1° divergence slit and a well-shielded 0.2° receiving slit.

The sample was maintained perpendicular to the incident beam and was thermostated to 10 ± 1 °C, as well as being sealed to prevent entry of oxygen. The sample cell maintains a flat sample geometry with a thickness of 0.794 mm. Aluminum windows were used, each 1.78×10^{-3} cm thick. Al foil was found not to react with these solutions over a period of 24 h. These windows are not as rigid as windows made from Ni, but the latter material fluoresces strongly under Cu irradiation, and must therefore be avoided. Because of the flexibility of Al foil, some error is introduced into the absorption correction.

Data were obtained by counting continuously for 30 s at each scattering angle. The scattering angle was incremented by 0.2° (2θ) between counting periods. Three runs were made for each sample: empty cell (baseline); solvent only; and solution sample.

Absorption corrections were made using the method described by Cullity.[14] Sample densities were determined by weighing the transfer syringe, in the case of the air-sensitive solutions. Absorption coefficients were from the International Tables.[15] No correction was made for polarization or for Compton scattering, as these corrections were found to be so minor that they do not shift the peak positions.

Further discussion of the x-ray method, together with the raw data, appears in the Appendix.

Free-Radical Reaction of Tosylates with $Co(CN)_5^{3-}$. The reactions of some organic tosylates with pentacyanocobaltate(II) ion were studied. The procedure of Halpern and Maher[16] was used. Solutions of the reaction mixture were protected from oxygen in a sealed cell with a septum cap, in which their uv-visible spectra could be recorded. The sample cell was thermostated to 25.0 ± 0.1 °C. Data were analyzed in the usual manner.

The sulfonate esters did not appear to react at concentrations of 10^{-2}–10^{-3} M (Co(II) was typically 3×10^{-4} M) in water, over a period of 24 h, after which there was evidence of considerable hydrolysis of the esters in their uv spectra. Alkyl halides react completely under similar conditions in much shorter times. It is possible that no reaction of the tosylates with the cobalt(II) occurs at all.

Results

Although the empirical formula of the diorganocuprates was established by Gilman and Straley[17] to be $LiCuR_2$, the proposed structures for these reagents suggest that they may be dimers. Therefore, the degree of aggregation was determined by the vapor-pressure depression method in ether. The results are shown in Table I. Measurements at two temperatures yield similar results. The slight variation between the two determinations at 0 °C may be due to imperfect temperature control.

Table II. Heavy-Atom Distances from Solution X-Ray Scattering

Compd	Concn, M	X-X	θ_{max}, deg	R_{exptl}[a]	R_{calcd}[b]
CH_2Br_2	1.25	Br-Br	14.5	3.8	3.22
m-$C_6H_4Br_2$	1.11	Br-Br	11.0	5.0	5.65
$[LiCu(CH_3)_2]_2$	0.57	Cu-Cu	12.5	4.4	
$LiAu(CH_3)_2$	0.36	Au-Au	None		

[a] Calculated from this experiment. [b] Calculated from literature data based on crystal structures: L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958).

Since the solutions were slightly contaminated with lithium halide, the value of C (total solute concentration) will be larger than the true cuprate concentration, resulting in low values of n. Allowing 5% for this error, the result is $n = 1.8 \pm 0.2$, with the larger value more likely. ^1H NMR experiments (vide infra) show that only one compound is present, so an integral value of n is required. Thus, the molecular formula is $(LiCu(CH_3)_2)_2$.

The ^1H NMR spectra of ether solutions of lithium dimethylcuprate were measured at various temperatures from −60 to +35 °C at concentrations of about 0.2 M. In each case only a single peak was found, upfield from TMS, at $\delta = -1.46$ (ether was the internal standard). Thus, either all the methyl groups are equivalent, or else a rapid exchange process scrambles them.

From the x-ray scattering pattern of solutions of the dimethylcuprate in ether, the Cu-Cu distance may be calculated, assuming all of the copper to be present in the dimeric species. The Cu-Cu distance is estimated to be 4.4 ± 0.7 Å, the large error being due to interference from the solvent.

The error limits were assessed by calibrating the method with two molecules of known structure. Dibromomethane and m-dibromobenzene were selected as examples of molecules with two heavy atoms. Table II shows the experimental Br-Br distances found, together with the known values from the literature.

Lithium dimethylaurate(I) was selected as a test for another reason. Since gold(I) is normally two coordinate and linear in its complexes, this compound should be monomeric though probably ion paired. In fact no peaks due to a fixed Au-Au distance were found for this compound by the x-ray method (Table II).

The reaction of lithium dimethylcuprate with methyl iodide was studied as the prototype of reaction 1. Conditions were chosen such that the cuprate was present in catalytic amounts. This is possible since the methylcopper which would be produced by the reaction is immediately consumed by the large excess of methyllithium which is present, thus regenerating the cuprate. That this reaction is indeed rapid is shown by the rate of exchange between cuprate and alkyllithium, which is fast on the NMR time scale. Similar catalytic conditions have been reported in the literature.[18]

Since the cuprate concentration remains constant during a given run, the order with respect to methyl iodide may be easily determined. Plots of $\ln (v_\infty - v)$ vs. t are linear. Thus the reaction is first order in CH_3I. Variation of copper concentration permits evaluation of the order in copper or cuprate. Results are shown in Table III and a plot of the observed pseudo-first-order rate constant, k_{obsd}, vs. the copper concentration in saturated LiI solution is shown in Figure 1. Since the latter plot is a straight line (as opposed to a parabolic curve) the order with respect to copper (and hence cuprate) is 1. The overall rate law is then:

$$d(C_2H_6)/dt = k_2[\text{cuprate}][CH_3I] \qquad (7)$$

Table III. Kinetic Data for Reactions of $[LiCu(CH_3)_2]_2$ with CH_3X in Ether at 0.00 ± 0.05 °C

Cu source	10^3[Cu], M	$[LiCH_3]$,[a] M	$10^3[CH_3I]$, M	$10^3 k_{obsd}$, s^{-1}	k_2,[b] M^{-1} s^{-1}
None	0.0	0.23	73.1	7.1×10^{-2}	3×10^{-4} [d]
CuI	1.29	1.30	14.3	1.09	0.84
	2.58	1.30	14.3	2.02	0.79
	2.74	1.30	57.3	1.45	0.53
	2.74	1.30	57.3	2.47	0.90
	5.02	1.30	14.3	3.65	0.73
	5.89[c]	1.30	14.3	2.62	0.47
	5.90	1.30	14.3	5.06	0.86
	5.90	1.30	57.3	5.18	0.88
	5.90	1.30	57.3	4.73	0.80
	6.70[e]	0.69	14.3	2.10	0.34
	7.08	1.30	14.3	5.24	0.72
	7.08	1.30	14.3	5.54	0.77
	7.08	1.30	14.3	4.35	0.65
	8.07	1.30	14.3	2.78	0.44
	8.42[e]	0.23	14.3	3.46	0.43
	4.16×10^{-2}	1.30	0.124[f]	3.82	91.9
	4.16×10^{-2}	1.30	0.124[f]	3.68	88.6
$(Ph_3P\text{-}CuCl)_4$	4.52[g,e]	0.23	73.1	2.16	0.48
	4.65[h,e]	0.23	73.1	3.12	0.67
	3.75[i,e]	0.23	73.1	2.75	0.73
	4.27[j,e]	0.23	73.1	4.56	1.07
	4.68[k,e]	0.23	73.1	6.93	1.48
CuC_2Ph	11.70[e]	0.23	73.1	3.39	0.29

[a] Based on $LiCH_3$ monomers. [b] $k_2 = k_{obsd}/[Cu] = 2k_{obsd}/[cuprate]$. [c] Triphenylmethane added. $[Ph_3CH] = 0.44$ M. [d] Rate $= k_2[LiCH_3][CH_3I]$. [e] No LiI added to these runs; all other runs with saturated LiI. [f] CH_3OTs. [g] Ph_3P added. $10^3[Ph_3P] = 4.52$. [h] Ph_3P added: $10^3[Ph_3P] = 29.5$. [i] Ph_3P added: $10^3[Ph_3P] = 53.1$. [j] Ph_3P added: $10^3[Ph_3P] = 80.3$. [k] $n\text{-}Bu_3P$ added: $10^3[n\text{-}Bu_3P] = 31.2$.

This result agrees with that found earlier for alkyl tosylates and lithium dimethylcuprate.[3]

It should be noted that the rate law (eq 7) definitely excludes a rate-determining step of the alkyl halide with a monomeric copper(I) species, or any other aggregate other than the dominant dimer. For example, if a monomer were the reactant, the rate would depend on the square root of the cuprate concentration.

From the graphs and the table, k_2 may be evaluated for both methyl iodide and methyl tosylate. The values are $k_2 = 180$ M^{-1} s^{-1} (CH_3OTs) and $k_2 = 1.46$ M^{-1} s^{-1} (CH_3I). Both values are good only to ±10%. (The large amount of scatter in the data is not surprising in view of the extreme sensitivity of the cuprate reagent to traces of air and water.)

The large excess of methyllithium does not affect the rate significantly, since methyllithium itself reacts only slowly with methyl iodide (see Table III). Further, variation of the methyllithium concentration does not affect the rate significantly, supporting the assumption of rapid regeneration of the catalyst.

The addition of triphenyl- or tri-*n*-butylphosphine to the reaction mixture causes a slight acceleration of the rate. Similarly, iodide, added as lithium iodide, or generated during the course of the reaction, causes the same result. For this reason, most of the runs were carried out with solutions saturated in LiI to prevent a change in the rate observed during a run. The acceleration, however, is small in all cases. The effect could be caused by complexation of phosphine or iodide to copper increasing the nucleophilicity of the reagent.

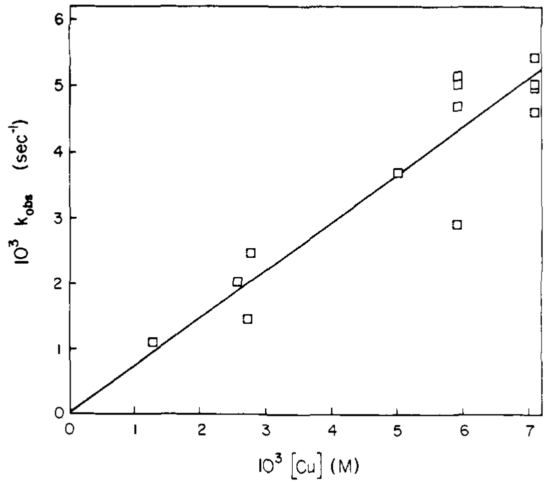

Figure 1. Dependence of k_{obsd} on copper concentration for reaction of $Li_2Cu_2(CH_3)_4$ with CH_3I.

Table IV. Rate Constants for Reaction of $Co(CN)_5^{3-}$ with RX in Water[a]

RX	k_2, M^{-1} s^{-1}	RX	k_2, M^{-1} s^{-1}
CH_3I	2.9×10^{-1}	$ICH_2CO_2CH_3$[b]	8.8×10^4
$CH_3OSO_2\text{-}C_6H_5$	$<10^{-5}$ [c]	$CH_3CH(OTs)CO_2\text{-}C_2H_5$	$<10^{-4}$ [c]

[a] At 25.0 ± 0.1 °C. All values ±10%. [b] Reference 19. See text.

It is interesting to note that the rate of the reaction is essentially independent of the source of copper. This suggests that a similar reagent is generated in each case.

Low-valent transition-metal complexes can react with alkyl halides by abstraction of a halogen atom, releasing a free alkyl radical.[16,19a] Intuitively it would seem that such a mechanism will not occur for alkyl sulfonates, because of the low affinity of the metals for the oxygen donor atom.[19b] However, there is no definite evidence in the literature. Therefore, alkyl iodides and sulfonates were reacted with pentacyanocobaltate(II), a reagent which is known to react with halides by a radical mechanism.[16] The relative rates of reaction of the two types of compound should shed some light on the question of whether sulfonates can undergo radical reactions.

$$Co(CN)_5{}^{3-} + RX \rightarrow Co(CN)_5X^{3-} + R\cdot \qquad (8)$$

$$R\cdot + Co(CN)_5{}^{3-} \rightarrow RCo(CN)_5{}^{3-} \qquad (9)$$

No reaction was observed between the cobalt complex and the tosylate or benzenesulfonate over a period of 24 h and this permits an upper limit on the rate of reaction to be established. These limits, together with the actual rate constants for some alkyl iodides, are shown in Table IV. The secondary tosylate was chosen because its iodide counterpart should react even faster (due to increased stability of a secondary radical) than the primary compound whose rate is shown. Therefore, it appears that the ratio k_I/k_{OTs} is greater than 10^9. This makes the relative reactivity of iodides and tosylates or sulfonates an ideal test for free-radical mechanisms due to direct abstraction of a group by a metal atom.

Discussion

Three possible structures may be considered for the lithium dimethylcuprate molecule. These are shown in Figure 2. Figure 2a shows a linear monomeric ion. Such a structure might be expected if copper(I) were satisfied with two coordination. Figure 2b shows the tetrahedral structure of methyllithium[20]

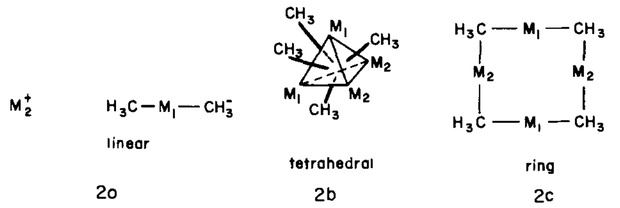

Figure 2. Possible structures for lithium dimethylcuprate and related species.

Table V. Relative Reactivities of Various Species with Dimethylcuprate[a]

RX	k_2, M^{-1} s^{-1} [b]	k_{rel}
CH_3I	1.46	1.0
n-$C_8H_{17}I$	4.8×10^{-4}	3.4×10^{-4}
CH_3OTs	1.8×10^2	1.2×10^2
n-$C_8H_{17}OTs$[c]	4.5×10^{-1}	3.1×10^{-1}

[a] Ether solvent, 0 °C. Data from Table III and ref 3. [b] k_2 from eq 7. [c] Estimated from data in ref 3.

($M_1 = M_2 = Li$). It has been proposed[21] that the cuprate is derived from this structure by replacement of two lithium atoms by copper. Note that these two atoms must be adjacent to one another. This structure, with a copper-copper contact, is likely to have a Cu-Cu distance similar to that in methyllithium (Li-Li, 2.6 Å) or slightly smaller, since the copper metallic radius (1.3 Å) is smaller than that of lithium (1.5 Å).[22] Copper-copper distances in the metal (2.56 Å), and in $(Ph_3PCuH)_6$ (2.54 Å),[23] provide additional indications that the copper-copper distance in structure 2b can be expected to be about 2.5-2.6 Å.

The ring structure shown in Figure 2c is like that found by x-ray methods for crystalline tetrakis[(trimethylsilylmethyl)copper].[24] In this compound, the copper-copper spacings are 3.39 and 2.42 Å for the trans ring and adjacent pairs, respectively. A similar structure has been proposed for the compound bis[o-(dimethylaminomethyl)phenyl]copper lithium.[25] The ^1H and ^{13}C spectrum of the latter compound requires it to have the approximate D_{2h} symmetry shown in the figure, with $M_1 = Cu$ and $M_2 = Li$. Thus, for the lithium dimethylcuprate of Figure 2c, the Cu-Cu distance is likely to be at least 3.4 Å (or greater, allowing for the increased radius of lithium relative to copper). Finally, the molecule R_4Cu_4, where R is 5-methyl-2-[(dimethylamino)methyl]phenyl, has a structure intermediate between planar and tetrahedral.[25b] The copper-copper distances are all nearly equal at 2.38 Å.

The dimeric nature of the reagent is indicated by the vapor pressure depression data, ruling out structure of Figure 2a. On the basis of the x-ray scattering data, the Cu-Cu distance is too long for the tetrahedral structure but is consistent with the structure of Figure 2c. This structure is also supported by an argument based on the ^1H NMR spectra of the complex.[26a]

Methyllithium, $[LiCH_3]_4$, has been reported to show coupling between ^{13}C and ^7Li at temperatures as high as −45 °C.[26b] This means that inter- and intramolecular processes which might cause exchange of methyl groups are absent or slow on the NMR time scale at these temperatures in this molecule. Since one of the postulated structures for the dimethylcuprate (Figure 2b) is obtained by replacement of two lithium atoms in the methyllithium structure by copper, one might expect to observe similar behavior in the cuprate. Thus the cuprate should not have exchanging methyl groups at temperatures below about −45 °C if it indeed has the tetrahedral structure.

However, the methyllithium structure for the cuprate should have two nonequivalent types of methyl groups: those with two copper atoms adjacent, and those with only one. Since no nonequivalence is observed, it can be concluded that the methyllithium structure is incorrect for the cuprate. This is based, of course, on the assumption of similar kinetic behavior for the cuprate and methyllithium, if the structures are similar.

Additional evidence for the absence of exchange of methyl groups in the cuprate at low temperature can be given. The addition of methyllithium ($\delta = -1.89$) to ether solutions of the cuprate causes the appearance of a single peak at an intermediate chemical shift position, at room temperature. This is indicative of rapid intermolecular exchange. As the temperature is lowered, the peak begins to broaden, due to a decreased rate of exchange. At −40 °C, the peak divides, and at −60 °C two peaks due to $[LiCH_3]_4$ and $[LiCu(CH_3)_2]_2$ are clearly observable. It may be argued that the absence of intermolecular exchange between the two unlike species at the same temperature at which inter- and intramolecular exchange in methyllithium are both inhibited is evidence for the absence of intramolecular exchange in the cuprate also, since similar processes should be involved (particularly if the structures are similar). But, once again, if intramolecular exchange at low temperature does not occur, all four methyl groups in the cuprate are required to be equivalent.

The ^1H NMR evidence, while not conclusive, is thus at least suggestive of the correctness of the cyclic structure 2c for the dimethylcuprate. We were unable to obtain evidence for ^{13}C-^7Li coupling, though this was seen in the case of the dimethylaminomethylphenyl analogue.

Mechanism of Reaction of Dimethylcuprate with Methyl Iodide. Any mechanism for the Corey-Posner reaction must explain not only the experimental results obtained here, but also the kinetic and stereochemical results of Whitesides et al.[2] and of Johnson and Dutra,[3] and be consistent with the many synthetic results in the literature.

The important results from the first two groups are principally stereochemical. The first is the stereochemistry of reaction at carbon in the alkyl halide. Both groups have reacted optically active alkyl halides with the cuprate reagent, and obtained essentially complete inversion of configuration at the optically active carbon atom. The second point is the stereochemistry of the alkyl carbanion (from alkyllithium, involved in formation of the cuprate). This moiety has been shown by Whitesides et al.[2] to retain its configuration during the reaction.

Some kinetic evidence is available from Whitesides' work. This shows qualitatively that the reactivity of various carbon centers toward the cuprate is methyl > primary > secondary > tertiary. Table V shows some quantitative comparisons from the work of Johnson and Dutra and the data reported above which show the same trend.

The greater reactivity of alkyl tosylates with the cuprate reagent, the small effect of the free radical trap, triphenylmethane, and the order of reactivity mentioned above all mitigate against a free-radical mechanism in these reactions. This leaves as the favored mechanism the sequential oxidative addition-reductive elimination process suggested by earlier workers.[2,3] From the stereochemical results, the rate-determining oxidative-addition step occurs by a nucleophilic substitution mechanism giving inversion. The fast reductive elimination step occurs by a concerted process giving retention.[27]

It is probable that the dimeric structure of $Li_2Cu_2(CH_3)_4$ is important in the oxidative addition step, assuming that the two copper atoms are coupled by way of overlapping orbitals including the lithium atoms. The Cu-Cu distance is too long for a direct metal-metal bond. Each copper atom can contribute one electron to the necessary two-electron change in nucleophilic substitution, eq 10.

$$Li_2Cu_2{}^{I}(CH_3)_4 + CH_3I \rightarrow Li_2Cu_2{}^{II}(CH_3)_5{}^+ + I^- \quad (10)$$

$$Li_2Cu_2{}^{II}(CH_3)_5{}^+ \rightarrow C_2H_6 + Li_2Cu_2{}^{I}(CH_3)_3{}^+ \quad (11)$$

$$Li_2Cu_2(CH_3)_3{}^+ + LiCH_3 \rightarrow Li_2Cu_2(CH_3)_4 + Li^+ \quad (12)$$

This circumvents the need for the formation of the very unstable Cu(III) oxidation state.

Evidence for this point of view comes from a comparison of the rates of reaction of $LiAu(CH_3)_2{\cdot}PR_3$ and $Li_2Cu_2(CH_3)_4$. From data presented by Tamaki and Kochi,[13] it can be seen that both complexes would react with CH_3I in ether at very nearly the same rate, at the same temperature. But the product in the case of Au(III) is stable, $Au[CH_3]_3PR_3$, whereas the copper alkyl formed is immediately unstable. In other words soft ligands such as $CH_3{}^-$ favor the formation of the higher oxidation state in the case of gold but not in the case of copper.

This can also be seen in the effect of attached soft ligands on the potentials of various gold and copper couples.[28] Figure 3 shows these potentials in the form of free-energy plots. The coordination of soft ligands such as Br^- or SCN^- makes it easier to oxidize Au(I) to Au(III). Comparable data are not available for Cu(I) and Cu(III). But this is precisely because these ligands do not stabilize the higher oxidation state, and the necessary reference compounds do not exist. It can be seen in Figure 3 that soft ligands do not make it easier to oxidize Cu(I) to Cu(II). In alternate language, Cu(I) is soft and Cu(III) is hard, whereas both Au(I) and Au(III) are soft Lewis acids.

In summary, the unusual reactivity and usefulness of the lithium cuprate reagent is probably a result of its dimeric structure. It may be recalled that activation of molecular hydrogen by cuprous salts requires the cooperative reaction of two copper atoms.[29] This process is also an oxidative addition. The general utility of cuprous salts in such coupling reactions as the Ullman reaction, the Sandmeyer reaction, etc.,[30] is no doubt connected with the polymeric structures almost invariably found for cuprous complexes.

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Appendix

Determination of Structure in Solution by X-Ray Scattering. Structures of metal complexes in aqueous solution have been determined by x-ray scattering with some success.[31] The problem presented here, however, is considerably more complex. First, the solutions contain species which are quite sensitive; hence data collection must be for as short a period as possible. Second, the solvent, unlike water, has a number of interatomic distances, and thus the solvent might be expected to obscure the structural information needed for the solute. Therefore, the approach used here must be different from the usual one of obtaining a radial distribution function from a scattering curve, and then attempting to interpret it.[32]

Consider the Debye equation:

$$I = \sum_{ij} f_i f_j \frac{\sin kr_{ij}}{kr_{ij}} \quad (A1)$$

$$(k = 4\pi \sin \theta/\lambda)$$

where f_i and f_j are scattering factors (tabulated in the International Tables), r_{ij} is the distance between a pair of atoms, and the summation is taken over all pairs of atoms in the sample. Note that the structure factors are approximately proportional to the atomic number Z of each atom. In a solution containing first-row or later transition-metal atoms in an organic matrix (C, H, N, O) the most important terms in eq A1 will be those in which both i and j represent metal atoms, since $f_i f_j$ will then be larger than for any other pairs (e.g., 29 × 29 for Cu–Cu vs. 29 × 6 for Cu–C and 6 × 6 for C–C). For this to be true, of course, the concentration of metal ions must be reasonably large; otherwise the contribution due to the metal ions will be swamped by the more numerous but smaller contributions due to the matrix. Of course, if the metal atoms are from the second or third transition series, the M–M contributions will be even larger.

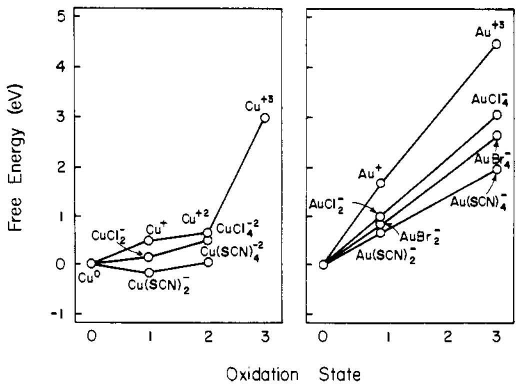

Figure 3. Oxidation state–free energy diagrams for copper and gold with various ligands. Data from ref 28.

If the concentration condition is satisfied, then eq A1 may be replaced by those terms in which only metal atoms appear as i and j, since these terms will dominate the expression. Each term of eq A1 is an expression for a strongly damped sine curve, with argument kr_{ij}. Such a curve has one strong maximum (other than that at the origin) at $kr_{ij} = 7.725$ (ignoring the slowly varying structure factors when differentiating with respect to kr_{ij}).

If the solution contains many random metal–metal (intermolecular) distances, these will all give rise to peaks in the scattering curve at different values of $k = 4\pi \sin \theta/\lambda$. Thus the random distances do not give any distinct peak. This will be the case for mononuclear complexes. On the other hand, polynuclear complexes will have several fixed (intramolecular) distances which occur repeatedly. These will give rise to peaks in identical positions for each molecule, and will thus reinforce one another to produce a large peak in the total scattering pattern.

Unfortunately, it is difficult in practice to achieve large enough concentrations of complex to cause the large terms in eq A1 to overcome the enormous number of smaller terms due to solvent. Even if one were able to do this, the complex would be so concentrated that intermolecular distances between complex molecules would begin to be significant in the scattering pattern. However, it seems possible to overcome this difficulty by merely subtracting the scattering due to the solvent from that due to the solution. The justification for this is that, once again, the intermolecular distances are relatively random.

This, then, is a simple method for determining the predominant metal–metal interaction mode and distance in a solution. Scattering patterns for both solvent and solution are obtained (and corrected for absorption of the x-ray beam). These curves can then be subtracted to yield the scattering due to the solute only. The principal peak in the resulting curve is then located by inspection and the corresponding metal–metal distance determined using eq A2:

$$R = 7.725/k = 0.61\lambda/\sin \theta_{max} \quad (A2)$$

where θ_{max} is the scattering angle at which the peak occurs.

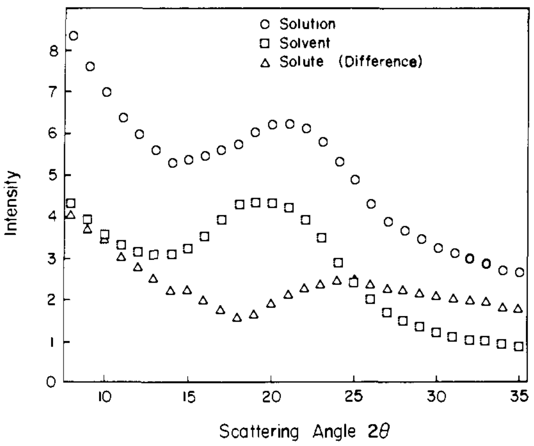

Figure 4. Experimental x-ray scattering curves for $Li_2Cu_2(CH_3)_4$ in ethyl ether solution.

The experimental curves for ether solutions of lithium dimethyl cuprate are shown in Figure 4. From the curve, $2\theta_{\max} = 25°$, so $R = 4.4$ Å. The breadth of the peak makes the determination of $\theta_{\max}$ rather inexact, so an error estimate of ± 0.7 Å is not unreasonable. This estimate is based on comparison of experimental and theoretical distances for two known compounds with similar heavy-atom spacing (see Table II). It may also be noted that $LiAu(CH_3)_2$, which is monomeric, does not give any maximum such as shown in Figure 4.

The alternative Cu-Cu distance of $R = 2.6$ Å leads to a predicted $2\theta_{\max}$ of 43°. No evidence for a maximum was found out to $2\theta = 45°$, the practical limit of our observations. Of greater significance is the fact that $\sin kr_{ij}/kr_{ij}$ has a minimum value at $kr_{ij} = 4.50$. If R were 2.6 Å, this predicts a minimum in the intensity curve at $2\theta = 25°$, in clear contradiction to our results.

Our observed minimum is at $2\theta = 18°$. This can also be used to calculate $R = 3.54$ Å. Different values of R result from use of the maximum and minimum angles because the experimental intensity curve is a composite. Presumably the maximum intensity is more reliable than the minimum.

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