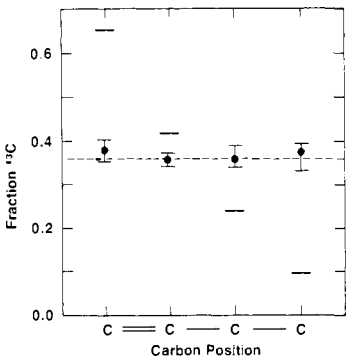

Figure 2. Fraction of ^{13}C at each position in the transiently labeled butene sample. The dashed horizontal line is the average value derived from GC/MS analysis. The short horizontal lines illustrate the anisotropy that would have resulted if only ^{13}C had been added sequentially to one end of the growing chains.

information about a major fraction of the steady-state hydrocarbon production since half the label had exchanged by the end of the collection interval. Results for 1-butene are shown here. The presence of ^{13}C at a given position in the molecule is revealed by the splitting of the proton resonance for that position. Any anisotropy seen in the positional distribution of the ^{13}C in the intermediately labeled molecules would indicate that the isotopic composition of the C_1 monomer changed appreciably fast compared to the rate of the chain propagation step. In this case, each successive carbon atom added to a given molecule after the isotope switch is significantly more likely to carry the ingrowing label. Such conditions would allow identification of the isotope exchange kinetics with chain growth kinetics. In addition, mechanisms in which carbon atoms are added to the end of the growing chain (e.g., alkyl migration[8] or CO insertion[9]) could be distinguished from mechanisms with alternative growth steps.[10]

Figure 2 shows that within experimental error the label incorporation is isotropic. The butene chains collected here must have grown in a time much shorter than the time in which the isotopic composition of their surface precursors changed appreciably.[11] Modeling calculations show that the average butene molecule must have grown in less than 1 s. Under this condition, information about the mechanics of chain growth is lost. However, the rapid chain growth rate inferred from the isotropic ^{13}C incorpration means the amount of carbon in growing chains is much smaller than the amount of "active" carbon derived from our GC/MS data. From the butene production rate and the chain growth rate calculated here, we conclude that most of the butene product comes from fewer than 5 nmol of growing chains per g of catalyst. If we assume that the chain addition rate is independent of chain length, and if we use the Flory law to extrapolate the product distribution in Table I, we can estimate that at steady state fewer than 50 nmol of growing chains per g of catalyst are responsible for over half of all the C_2^+ hydrocarbon product. Modeling calculations and additional measurements will help refine this number and will take into account the fraction of product with longer isotope exchange times.

Acknowledgment. We thank K. D. Rose and R. E. Pabst, Jr., for NMR analyses and J. J. Krajewski for technical assistance.

Registry No. Iron, 7439-89-6; CO, 630-08-0.

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(11) We have assumed that the chain integrity has not been compromised by scrambling. Our reaction conditions were chosen to limit the CO conversion to less than 1%. The fact that the reaction products are 1-olefins rather than the thermodynamically favored internal olefins suggests that secondary reactions which could scramble the position of the carbon atoms are absent.

Crystal Structure of the Neutral Diarylcuprate $Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$: The Asymmetric Bonding Configuration of Organo Groups Bridging Cu and Li

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Reaction of an organolithium reagent, RLi, with a copper salt, Cu^IX, in a 2/1 molar ratio leads to the formation of a so-called lithium organocuprate reagent which has R_2CuLi overall stoichiometry. The unique change in reactivity brought about by this partial substitution of Li by Cu is of tremendous use in organic synthesis[1] and has also led to considerable interest in the bonding of the organo groups in these reagents.[2]

After many attempts[3] we succeeded in growing single crystals of the cuprate[4] $Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$ (**1**) which were suitable for an X-ray structure determination.[5] The molecular structure of **1** is shown in Figure 1 together with some relevant bond distances and angles. To our knowledge this structure is the first example of a structural investigation of a neutral lithium organocuprate with 1/1 Cu/Li atomic ratio in the central metal core. Several other organocuprate structures have been reported which, however, all have ionic structures consisting of either mononuclear R_2Cu^- (Mes_2Cu,[6] $[(Me_3Si)_3C]_2Cu^7$) or polynuclear (i.e., $[Cu_5Ph_6]^-$)[8] anions and solvated Li cations. Anionic $[Cu_3Li_2Ph_6]^-$ is the only other structurally characterized cuprate species known that contains both Li and Cu in the same metal framework.[9]

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(3) In one crystallization from diethyl ether both yellow $Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4$ and colorless crystals were formed. According to an X-ray structure determination the latter crystals appeared to be the lithium enolate $(Li_4(2\text{-}H_2C{=}C(O)C_6H_4CH_2NMe_2)_4$, i.e., the product of an acetylation reaction at C(1): Jastrzebski, J. T. B. H.; van Koten, G., unpublished results.

(4) (a) The title compound was prepared by reacting pure $Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4$[2b] (5 mmol) with pure $Li_4(C_6H_4CH_2NMe_2\text{-}2)_4$[4b] (5 mmol) in 10 mL of benzene. (b) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. *J. Am. Chem. Soc.* **1982**, *104*, 5490.

(5) (a) Crystals of the title compound, $Cu_2Li_2C_{36}H_{38}N_4$, are monoclinic, space group $C2/c$, with four molecules in a unit cell of dimensions a = 23.824 (2) Å, b = 9.614 (2) Å, c = 17.824 (2) Å, and β = 114.77(1)°. 3040 independent reflections measured on a NONIUS CAD 4 diffractometer using graphite monochromated Cu Kα radiation. Of these 847 were below the $3\sigma(I)$ level and were treated as unobserved. An emperical absorption correction (DIF ABS)[5b] was applied (μ = 15.8 cm^{-1}; crystal dimensions 0.23 × 0.30 × 0.50 mm). The structure was solved by means of a Patterson minimum function on the basis of the four translation-independent Cu positions in the unit cell and refined by means of block-diagonal least-square calculations, anisotropic for Cu, Li, C, and N and isotropic for H. The H atoms were located in a F synthesis. The final R value was 0.039 for 2193 reflections. An extinction correction was applied and a weighting scheme $w = 1/(5.2 + F_0 + 0.009F_0^2)$ was employed. The anomalous dispersion of Cu was taken into account. (b) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

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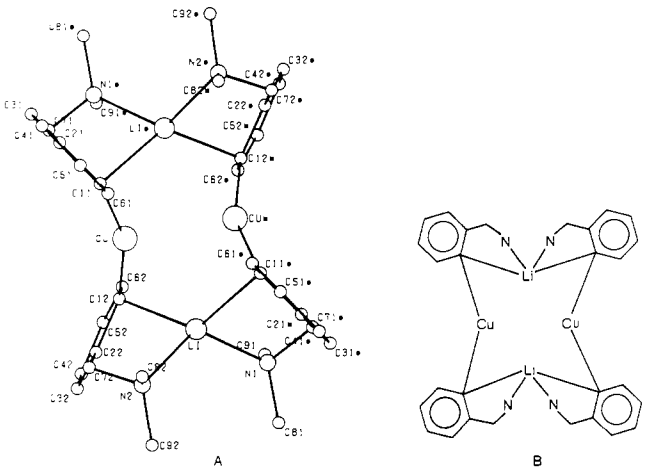

Figure 1. (A) Molecular geometry of $[Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$. Important, selected, intramolecular distances (Å) and angles (deg): Cu–Li 2.730 (5), Cu–Li(*) 2.775 (6), Cu–C(11) 1.936 (3), Cu–C(12) 1.948 (3), Li–C(11) 2.396 (6), Li–C(12) 2.374 (7), Li–N(1) 2.139 (6), Li–N(2) 2.123 (6), Li–Cu–Li(*) 122.1 (2), Cu–Li–Cu(*) 57.9 (1), C(11)–Cu–C(12), 157.7 (1), N(1)–Li–N(2) 119.6 (3). (B) Schematic structure of $[Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$.

Figure 1 shows that the structure contains an almost planar Cu_2Li_2 arrangement with Cu···Li distances of 2.755 Å mean. Each aryl group bridges a Cu···Li pair via C(ipso) but in an asymmetric way as indicated by comparison of the long Li–C(ipso) bond of 2.385 (6) Å (cf., this bond in $Li_2Ph_2\cdot tmeda_2$ (**2**) of 2.21 Å)[10] with the much shorter Cu–C(ipso) bond of 1.942 (3) Å (cf. this bond in $Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4$ (**3**) of 2.00 (2) Å).[11] The tilting of the aryl plane in the direction of the lithium center indicates a better overlap of the carbon sp^2 and copper orbitals, i.e., a deviation from the symmetric three-center, two-electron bonding of aryl groups between equal metals as in, for example, **2** and **3** toward a two-center, two-electron type of Cu–C bonding.[12] This is as expected when the different orbital sizes and energies of copper and lithium are taken into account. However, the fact that in solution a $^1J(^{13}C(ipso),^7Li)$ of 7.0 Hz is still observed indicates that s electron density is present between the Li and C(ipso) nuclei.

The same asymmetric bridging configuration for the aryl bridges has been found in the $[Cu_3Li_2Ph_6]^-$ anion (Li–C(ipso) 2.240 (14) and Cu–C(ipso) 1.923 (6) Å),[9] and it seems reasonable to assume that this will be a general feature of bridging organo groups (e.g. alkyls, aryls, alkynyls, etc.) in cuprates. Accordingly, we propose that, for example, $Cu_2Li_2(p\text{-tolyl})_4\cdot 2Et_2O$ (**4**)[14a] has a planar Cu_2Li_2 arrangement with the *p*-tolyl groups asymmetrically bridging between Cu and Li. Since coordinating substituents are now absent, coordination of a solvent[14b] molecule to each of the lithium atoms is required to produce the discrete neutral cuprate species. Recent structural evidence allowing comparison of the features of a series of aryllithium, arylcopper, and lithium cuprate compounds with and without coordinating substituents has substantiated that a major role of these heteroatom-containing groups is their functioning as well-positioned "intramolecular solvent molecules".[2a]

Comparison of the structural features of **1** with those of the corresponding lithium diorganoaurate $Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$ (**5**), which we recently communicated,[13] establishes that the lithium–aryl–metal (group 11) bridges in lithium group 11 metalate complexes become increasingly asymmetric going down the series Cu(I) to Ag(I) to Au(I).[13] This is reflected both by the increase in Li–C(ipso) bond length (for **5**, 2.50 Å mean) as well as by the change in the planar Li_2M_2 arrangement, i.e., in **5** a regular square with equal AuAu and LiLi vectors vs. in **1** a long LiLi and a shorter CuCu vector[15] of 2.6660 (8) Å. It is interesting to note here that on the basis of liquid-phase X-ray scattering data the Cu···Cu distance in $Cu_2Li_2Me_4$ in Et_2O has been estimated at 4.4 ± 0.7 Å.[16] This is not at all in agreement with the now likely structure for $Cu_2Li_2Me_4\cdot 2Et_2O$ (i.e., the same basic $Cu_2Li_2C(ipso)_4$ framework as in **1** with Cu···Cu amounting to 2.6 Å) and substantiates earlier questioning[17] of these X-ray scattering data.

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

Registry No. 1, 94203-54-0.

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

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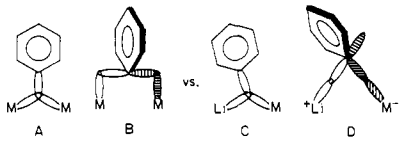
(12) Compare the various bonding interactions of the aryl C(*ipso*) sp^2 and metal orbitals in homo (A and B, e.g., in **2** and **3**) and hetero (C and D as in **1** and **4**) bridges:[2a,13]



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(14) (a) Pure $Cu_2Li_2(p\text{-Tol})_4$ made in benzene from $Cu_4(p\text{-Tol})_4$ and $Li_4(p\text{-Tol})_4$ is *insoluble*:[2a] van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Organomet. Chem.* **1977**, *140*, C23. (b) Addition of Et_2O (2 equiv) affords a *solution* of neutral **4** in benzene; see ^1H NMR in ref 14a. With THF an ionic cuprate is formed.
(15) On the basis of ^{109}Ag and ^7Li NMR of corresponding $Ag_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$ nonbonding:[2a] Jastrzebski, J. T. B. H.; van Koten, G.; Brevard, C., unpublished results.
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Tris(diphenylmethylene)methane Dianion. Direct Evidence for Y Aromaticity

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MNDO calculations[1] indicate that doubly charged conjugated systems prefer Y delocalization over cyclic delocalization. Experimental evidence is anectodal and is limited to generation of several "dications"[2] and "dianions"[3] with the observation that the Y-conjugated dications are formed with difficulty and the dianions with facility in contrast to the linear or cyclic counterparts. Moreover, in such systems counterion effects are difficult to determine and may dominate the relative rates that are used to evaluate stability in such systems. The use of a resonance-stabilized dianion that would be accessible in highly solvating media such as Me_2SO would simplify such an analysis. We now report the synthesis of such an example, tris(diphenylmethylene)methane

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