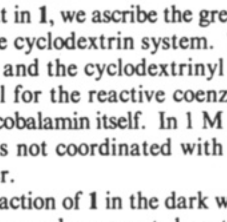
Figure 1.

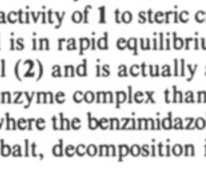
Treatment of **3** with cob(I)alamin, in a manner similar to that described[5] for the preparation of other cobalamins, yields **1** in the "base-off" form as a purified yellow powder [MS (FAB) 2447 ($M^+ + 1$); UV–vis[6] $\lambda_{max(1\ M\ HCl)}$ 340 (1.00), 405 (0.61), 450 (0.64), $\lambda_{max(pH\ 7)}$ 370 (1.00), 425 (0.61), 477 (0.81), 510 (0.81)]. The compound must be almost pure, as judged from the greater than 90% yield of reaction product **5** (vide infra). Treatment of **1** with I_2 afforded **4**.

In this form **1** may be handled briefly in air. In neutral 0.05 M phosphate buffer, however, it is quite reactive; its pseudo-first-order aerobic decomposition[7] has a half-life of 152 ± 13 min at 25 °C in the absence of light. This compares with 5 min for the same process in benzylcobalamin and 75 min for neopentylcobalamin.[7] The aerobic decomposition of adenosylcobalamin itself is too slow to be measured in the absence of the enzyme under these conditions, and dissociation requires heating or irradiation.[8] Since the bonding in adenosylcobalamin is similar to that in **1**, we ascribe the greater reactivity of **1** to steric crowding by the cyclodextrin system. Thus **1** is in rapid equilibrium with $B_{12(r)}$ and the cyclodextrinyl radical (**2**) and is actually a better model for the reactive coenzyme–enzyme complex than is adenosylcobalamin itself. In 1 M HCl, where the benzimidazole group of **1** is not coordinated with the cobalt, decomposition is much slower.

Reaction of **1** in the dark with benzyl or *tert*-butylbenzyl iodide in aqueous deoxygenated neutral 0.05 M phosphate buffer at room temperature and then quenching with air in the dark produces **4** and the corresponding benzaldehyde, probably from air oxidation of the product benzylcobalamin. Attempts to detect selective reaction for the more strongly binding 4-*tert*-butylbenzyl iodide, or bromide, were hampered by problems with solubility, hydrolysis, and radical exchange. These were overcome with the selenide (**6a**), which underwent group transfer to **2** under the above conditions and afforded a 95 ± 5% yield, based on **1**, of the cyclodextrin selenide **5**. Competition between **6a** and the weaker-binding **6b** showed a preference for reaction with **6a** of greater than 10-fold, as judged by the relative yields of **5** and of the corresponding *p*-chloro derivative. As expected, if this preference reflects binding, the addition of 20% ethanol decreased the preference to less than 2-fold by decreasing the effectiveness of hydrophobic binding to the cyclodextrin cavity. A similar decrease in selectivity between **6a** and **6b** was seen if an excess of *p*-*tert*-butylbenzoate ion, a competitive binder, was present.



3; X = Br
4; X = I
5; X = Se-Ph



6 a; X = H, R = *t*-Bu
b; X = Cl, R = H

To look for rearrangements, we examined cyclizations of the type demonstrated by Curran[9] but with substrates carrying a hydrophobic binding group. Reaction did not occur exclusively within the cavity, but there was instead a radical atom transfer chain process in free solution initiated by **1**. It is interesting that in some enzymatic reactions coenzyme B_{12} may also be serving only as a chain initiator,[10] rather than performing all the atom transfers described above. Thus we have not yet mimicked all the steps of B_{12} catalysis. However, the properties of cyclodextrin–B_{12} (**1**), with a carbon–cobalt bond labile under physiological conditions and a binding site in the resulting radical, make it a very attractive candidate for further enzyme model studies.

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Preparation of Highly Functionalized Magnesium, Zinc, and Copper Aryl and Alkenyl Organometallics via the Corresponding Organolithiums

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Received February 14, 1992

Organometallics bearing electrophilic functionalities are versatile intermediates for the synthesis of a wide range of highly functionalized organic molecules,[2,3] including important biologically active compounds.[4] The readily prepared alkyl[2] and benzylic[2d,5] organozinc halides, in particular, have found widespread applications and were shown to be compatible with most organic functionalities.[2–6] Their relatively low reactivity can be dramatically enhanced by transmetalation to copper[2–6] organometallics or by using a palladium(0) catalyst.[7] Unfortunately, the preparation of polyfunctionalized alkenyl and aryl organometallics is less straightforward, as a direct metal insertion can be troublesome. The use of highly activated metals (zinc,[3] copper[8]) or polar solvents is required to perform a metal insertion into the

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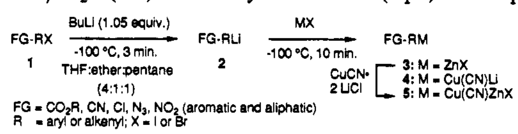
Table I. Polyfunctional Alkenes and Aromatic Compounds 6 Obtained by the Reaction of Alkenyl- and Arylzinc or -Copper Reagents 3–5 with Electrophiles

entry	organometallics 3–5[a]		electrophile	product 6[b]		yield (%)[c]
1	p-NCPhM[d]	3a	(E)-I(H)C=(H)$(CH_2)_3$OPiv	(E)-p-NCPh(H)C=C(H)$(CH_2)_3$OPiv	6a	81
2	p-NCPhM[d]	3a	m-IPhCO_2Et	p-NCPh(m-EtO_2C)Ph	6b	93
3	p-t-BuO_2CPhM[d]	3b	(E)-I(H)C=C(H)$(CH_2)_3$CN	(E)-p-t-BuO_2CPh(H)C=C(H)$(CH_2)_3$CN	6c	67
4	(E)-PivO$(CH_2)_3$(H)C=C(H)M	3c	(E)-I(H)C=C(H)Hex	(E,E)-PivO$(CH_2)_3$(H)C=C(H)(H)C=C(H)Hex	6d	72
5	(E)-NC$(CH_2)_3$(H)C=C(H)M	3d	(E)-PivO$(CH_2)_3$(H)C=C(H)I	(E,E)-NC$(CH_2)_3$(H)C=C(H)(H)C=C(H)$(CH_2)_3$OPiv	6e	86
6	p-NCPhM[d]	4a	2-cyclohexenone	3-(p-NCPh)cyclohexanone	6f	93
7	p-NCPhM[d]	5a	PhCOCl	p-NCPhCOPh	6g	82
8	(E)-PivO$(CH_2)_3$(H)C=C(H)M	5c	IC≡CBu	(E)-PivO$(CH_2)_3$(H)C=C(H)C≡CBu	6h	66
9	(E)-PivO$(CH_2)_3$(H)C=C(H)M	5c	HC≡CCO_2Et	(E,E)-PivO$(CH_2)_3$(H)C=C(H)(H)C=C(H)CO_2Et	6i	68
10	o-O_2NPhM	5e	3-iodocyclohexenone	3-(o-O_2NPh)-2-cyclohexen-1-one	6j	70
11	o-O_2NPhM	5e	H_2C=C(CO_2-t-Bu)CH_2Br	o-O_2NPhCH_2C(CO_2-t-Bu)=CH_2	6k	79
12	o-O_2NPhM	5e	PhCOCl	o-O_2NPhCOPh	6l	75[e]
13	(E)-Cl$(CH_2)_3$(H)C=C(H)M	5f	HC≡CCO_2Et	(E,E)-Cl$(CH_2)_3$(H)C=C(H)(H)C=C(H)CO_2Et	6m	70
14	(E)-Cl$(CH_2)_3$(H)C=C(H)M	5f	H_2C=C(CO_2Et)CH_2Br	(E)-Cl$(CH_2)_3$(H)C=C(H)CH_2C(CO_2Et)=CH_2	6n	81
15	(E)-$N_3$$(CH_2)_3$(H)C=C(H)M	5g	HC≡CCO_2Et	(E,E)-$N_3$$(CH_2)_3$(H)C=C(H)(H)C=C(H)$CO_2$Et	6o	81

[a] M = ZnX for all organometallics 3. M = Cu(CN)Li for all organometallics 4. M = Cu(CN)ZnX for all organometallics 5. [b] All alkenes and dienes are pure E and E,E compounds. [c] All yields refer to isolated yields of analytically pure compounds for which satisfactory spectral data (IR, ^{1}H and ^{13}C NMR, mass spectra, and high-resolution mass spectra) have been obtained (supplementary material). [d] The lithium compound was prepared from the corresponding bromide. [e] In this case, the organolithium compound was generated by treatment with PhLi in THF at −100 °C for 1 h (ref 13j).

stronger C(sp^2)–I bond, and under these conditions, the alkenyl organometallics are formed nonstereoselectively, affording a mixture of E and Z organometallics.[9] On the other hand, alkenyllithiums could be prepared stereospecifically via a halogen–lithium exchange reaction[10] but were believed to not tolerate many functionalities.[11,12] Some functionalized alkenyl and aromatic lithium[13,14] reagents have been prepared, but their high reactivity strongly limited the electrophiles that could be successfully used. We have now found that various functionalized aryl halides[13] (X = I or Br) and alkenyl iodides[14] **1** can be converted to highly functionalized organolithiums **2** by the slow addition of butyllithium (1.05 equiv, 1.5 M in hexane) to the alkenyl or aryl halide in a THF/ether/pentane mixture (4:1:1)[15] at −100 °C. After ca. 3 min, a solution of ZnI_2 in THF or CuCN·2LiCl[2a] in THF is added at −100 °C, affording *stable* solutions of organozincs FGRZnX **3** and FGRCu(CN)Li **4**, respectively. The organozincs **3** can also be converted to the copper reagents FGRCu(CN)ZnX **5** by the addition of CuCN·2LiCl in THF for aryl derivatives and in THF/Et_2S (1:1) for alkenyl derivatives (eq 1). This procedure



(1)

allows, for the first time, a convenient preparation of highly functionalized aryl- and alkenylcopper and -zinc organometallics containing an ester, cyano, chloro, azido, or nitro group (Table I). The presence of the last two functionalities in an organic halide *completely inhibits direct zinc insertion*,[16] and thus the halogen–lithium exchange reaction represents a unique approach to such organometallics[13h–j] (entries 10–12, 15). The aromatic and alkenylzincs **3a–d** can be efficiently coupled with various functionalized aromatic and vinylic iodides in the presence of a catalytic amount of $Pd(dba)_2$ (4 mol %)[17] and PPh_3 (16 mol %), affording the polyfunctional unsaturated products **6a–e** (entries 1–5) in excellent yields. The addition of CuCN·2LiCl[2a] to the organolithium **2a** gives the lithium organocuprate **4a**, which adds to cyclohexenone (0.7 equiv) in the presence of TMSCl[18] (−78 to 10 °C, 5 h; entry 6) providing the 1,4-adduct **6f** in 93% yield. The copper reagents FGRCu(CN)ZnI **5**, obtained by the transmetalation of the organozincs **3** with CuCN·2LiCl in THF, are less prone to dimerize, and they react well with various activated electrophiles such as acid chlorides (entries 7 and 12), allylic bromides (entries 11 and 14), a 1-iodoalkyne (entry 8), 3-iodo-2-cyclohexen-1-one[19] (entry 10), and ethyl propiolate (entries 9, 13, and 15).

A similar transmetalation procedure was developed for the addition of alkenyl organometallics to aldehydes. Whereas the low-temperature addition of the lithium reagent derived from **7** to an aldehyde proceeds only in moderate yields, a transmetalation to the corresponding magnesium reagent[20] ($MgBr_2$ in THF, −100 °C, 5 min), followed by the addition of an aldehyde (0.9 equiv, −90 to −50 °C, 0.5 h), cleanly furnishes the pure (E)-allylic alcohols **8a,b** in 71–77% yield (eq 2).

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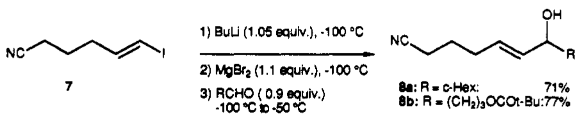

(2)

In summary, we have prepared several new classes of functionalized zinc and copper aromatic and alkenyl organometallics **3–5** which, contrary to their highly reactive organolithium precursors **2**, can be conveniently handled,[21] are relatively stable, and react chemoselectively with various classes of electrophiles with complete retention of the double bond configuration.[22] Extensions of this method allowing the preparation of other functionalized organometallics (M = Ti, Zr) are currently underway.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of the Vice President for Research of The University of Michigan for generous support of this work.

Supplementary Material Available: Typical experimental procedure and listings of characterization data for all new compounds (12 pages). Ordering information is given on any current masthead page.

(21) Typical procedure for **(2*E*,4*E*)-ethyl 8-(pivaloyloxy)-2,4-octadienoate (6i)**: A three-necked flask equipped with a thermometer, a gas inlet, and an addition funnel was charged under argon with (*E*)-5-iodo-4-pentenyl 2,2-dimethylpropanoate (0.74 g, 2.50 mmol) in a mixture of THF/ether/pentane (4:1:1; 12 mL) and cooled to −100 °C (liquid N_2, ether bath), and *n*-BuLi (2.6 mmol, 1.60 M in hexane) was added over 4 min. The resulting yellow solution was stirred for 3 min at −100 °C, and a THF (5 mL) solution of ZnI_2 (0.83 g, 2.60 mmol) was added. After the mixture was stirred for 10 min at −100 °C, a slurry of CuCN (0.23 g, 2.60 mmol) and LiCl (0.22 g, 5.2 mmol) in a mixture (10 mL) of THF and Et_2S (1:1) was added. The dark red solution was warmed to −60 °C and after 5 min was cooled back to −78 °C. Ethyl propiolate (0.20 g, 2.0 mmol) was added, and the reaction mixture was warmed to −20 °C and stirred for 2 h. After the usual workup and evaporation of the solvents, the crude residue obtained was purified by flash chromatography (hexane/ether, 19:1), yielding **6i** (360 mg, 68%) as a clear oil (100% *E,E* by GLC analysis).

(22) Presented in part at the OSCOM 6 meeting in Utrecht, The Netherlands, August 1991.

The Nature of Bonding and Stability of $(CO)_2Be–Be(CO)_2$: A Molecule with a Be–Be Double Bond

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In recent years there has been considerable interest in understanding the nature of interactions between metal atoms in polynuclear organometallic compounds where the metal atoms or ions have formally closed-shell configurations such as the d^{10} electron configuration of Cu in $[CuN_5R_2]_3$[1] (R = *p*-tosyl) and the s^2 configuration of Tl(I) or In(I) in $[(PhCH_2)_5C_5M]_2$, M = Tl or In.[2,3] An interesting feature of these molecules is that the metal–metal distances are close to the typical internuclear distance in the bulk metal, even though the metal atoms and ions have formally closed-shell configurations and hence are not expected to show metal–metal bonding. This communication reports the results of theoretical studies on the nature of the bonding and stability of $(CO)_2BeBe(CO)_2$. It is shown that as a result of hybridization the two Be atoms interact to form a double bond.

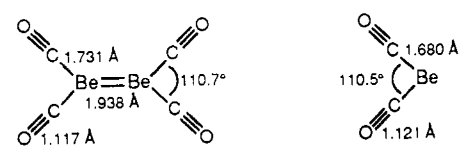
Table I. Total Energies and Dissociation Energies

	$(CO)_2BeBe(CO)_2$			$Be(CO)_2$	
		dissoc. eng[a] (kcal/mol)			
method	tot. eng (au)	a	b	tot. eng (au)	dissoc. eng[b] (kcal/mol)
HF	−480.140283	36.0	15.5	−240.057902	10.4
MP2	−481.391864	95.9	56.3	−240.651161	19.8
MP3	−481.380527	76.1	51.9	−240.648986	12.2
MP4(DQ)	−481.389015	64.1	48.4	−240.655913	7.8
MP4(SDQ)	−481.417629	68.3	50.0	−240.668907	9.00

[a] Dissociation of $(CO)_2BeBe(CO)_2$ to (a) $2Be(^1S)$ + 4CO and (b) $2Be(CO)_2(^3B_1)$. [b] Dissociation of $Be(CO)_2$ to $Be(^1S)$ + 2CO.

The computations were performed using the GAUSSIAN 86 program.[4] The geometries were determined by the Hartree–Fock (HF) self-consistent (SCF) procedure with the analytical gradient method using the 6-31G*(5d) basis set.[5] The closed- and open-shell molecules were studied in the spin-restricted and spin-unrestricted HF approximations, respectively. The nature of the stationary points on the potential energy surface was determined by computing the analytical second derivatives and determining the harmonic vibrational frequencies.[6] The contribution of electron correlation effects was determined by using Moeller–Plesset perturbation theory through partial fourth order (neglecting triple substitutions)[7] at the HF geometries. Only the valence electrons were included in the perturbation theory studies.

The geometry optimizations of $(CO)_2BeBe(CO)_2$ and $Be(CO)_2$ were carried out with the constraints of D_{2h} and C_{2v} symmetries, respectively. The computed minimum energy structures are as shown:



The D_{2h} $(CO)_2BeBe(CO)_2$ species has a ^1A_g ground state, while the ground state of $Be(CO)_2$ is $^3B_1$[8] in C_{2v} symmetry. The HF harmonic vibrational frequencies computed for both of the molecules are all positive, indicating that these molecules are true potential energy minima.

The computed structure and stability of $(CO)_2BeBe(CO)_2$ are easily rationalized in terms of the type of bonding of $Be(CO)_2$, which is hence considered first. The $^3B_1$ state of $Be(CO)_2$ is stable with respect to dissociation to $Be(^1S)$ and two CO molecules. The calculated binding energies at the various levels of theory for the HF geometry of the molecule are given in Table I. The bonding between CO and Be shows the general features of the Dewar–Chatt–Duncanson[9] model of CO binding to metal atoms: σ type bonding, involving the lone pair on the carbon atom of the CO, and π back-bonding interaction between the Be 2p and CO π^*

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