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NMR spectrum showed that the two downfield peaks split into doublets and the four upfield peaks into triplets. Anal. Calcd for $C_6H_{10}BrCl$: C, 36.36; H, 5.44. Found: C, 36.38; H, 5.26.

The *trans*-1-bromo-2-chlorocyclohexane obtained from the surface reaction was identical with authentic material prepared by the reaction of cyclohexene with Br_2/HCl in carbon tetrachloride.

Technique Used To Determine the Br_2 Adsorption Isotherm. A standard plot of bromine concentration (in carbon tetrachloride) versus absorbance (at 410 nm) was prepared using solutions from 0.0001 to 0.01 M in Br_2. The absorbance was determined using a Bauch and Lomb Spec 21 visible spectrometer.

Brockmann activity I neutral grade alumina was dehydrated as previously described. The dehydrated alumina was transferred to an inert atmosphere and added in 20-g samples to 100-mL solutions of bromine in carbon tetrachloride. The concentrations ranged from 0.02 to 0.001 M Br_2 in carbon tetrachloride. The solutions were stoppered, and the flasks were covered with aluminum foil to avoid contact with light. After 3 days, aliquots of each solution were removed and the absorbance of Br_2 was determined. By comparing the absorbance of each solution to the standard plot of absorbance versus concentration, the equilibrium concentration of Br_2 for each sample was determined. By determining the difference between the initial and equilibrium concentrations, the amount of bromine adsorbed on alumina was determined.

A plot of p_a/V, where p_a equals the equilibrium Br_2 concentration and V equals the moles of Br_2 adsorbed per gram of Al_2O_3, versus p_a yields a straight line with a slope equal to $1/V_\infty$ and an intercept equal to $1/KV_\infty$.[19,20] Thus, V_∞, which corresponds to a monolayer coverage of Br_2, equals 3.8×10^{-5} mol of Br_2/gram of Al_2O_3 or 2.3×10^{19} molecules of Br_2/gram of Al_2O_3 and K, the equilibrium constant, is 5.2×10^2. If one eliminates one point, which deviates substantially from the straight line, one get $V_\infty = 3.7 \times 10^{-5}$ mol of Br_2/gram of Al_2O_3 and $K = 8.3 \times 10^2$ with a correlation coefficient of 0.994. Most reactions were run with Br_2 concentrations $\leq V_\infty$.

Determination of Bromo Chloride Formation Site. A solution of 0.2 mL of bromine in 10 mL of CCl_4 was adsorbed onto 100 g of alumina. Twenty grams of this alumina was washed with 50 mL of CCl_4, and the resulting liquid was mixed with 5 mL of cyclohexene, which was allowed to stand for 10 h at room temperature. After most of the CCl_4 was removed by rotoevaporation, the resulting liquid was found to contain cyclohexene and *trans*-1,2-dibromocyclohexane.

pH and pCl Measurements. Hydrogen ion and chloride ion concentrations were determined with a pH meter (Fisher Scientific Co., Accument Model 810) with pH and chloride electrodes.

Preparation of NaCl Aluminas. An aqueous solution of NaCl was added to alumina and mixed. The water was removed first on a rotoevaporator and then by heating under vacuum at 400 °C. Typical concentrations were 6×10^{-4} mol of NaCl/gram of Al_2O_3. Once the NaCl had been adsorbed in this fashion, Br_2 and cyclohexene were adsorbed as previously described. CCl_4 was adsorbed prior to the adsorption of NaCl.

Adsorption of Br_2 on Silica Gel and Its Reaction with Cyclohexene/Silica Gel. One hundred grams of silica gel were dehydrated by the same method used to dehydrate alumina, after which 3.5×10^{-5} mol of Br_2/gram of silica gel was adsorbed along with 1 mL of CCl_4. The Br_2/SiO_2 was reacted with cyclohexene/SiO_2 for 24 h. The mixture was extracted with CCl_4, and the solution was analyzed by gas chromatography. Only *trans*-1,2-dibromocyclohexane was detected.

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Registry No. 1, 7429-37-0; **2**, 13898-96-9; benzene, 71-43-2; iodobenzene, 591-50-4; toluene, 108-88-3; *o*-iodotoluene, 615-37-2; *m*-iodotoluene, 625-95-6; *p*-iodotoluene, 624-31-7; phenol, 108-95-2; *o*-iodophenol, 533-58-4; *p*-iodophenol, 540-38-5; anisole, 100-66-3; *o*-iodoanisole, 529-28-2; *m*-iodoanisole, 766-85-8; *p*-iodoanisole, 696-62-8; aniline, 62-53-3; acetanilide, 103-84-4; *N*,*N*-dimethylaniline, 121-69-7; *p*-iodo-*N*,*N*-dimethylaniline, 698-70-4; bromobenzene, 108-86-1; naphthalene, 91-20-3; 1-iodonaphthalene, 90-14-2; azulene, 275-51-4; 1-iodoazulene, 76279-71-5; 1,3-diiodoazulene, 36044-42-5; azobenzene, 103-33-3; nitrobenzene, 98-95-3; cyclopentene, 142-29-0; cyclopentyl iodide, 1556-18-9; cyclohexene, 110-83-8; cyclohexyl iodide, 626-62-0; cycloheptene, 628-92-2; cycloheptyl iodide, 2404-36-6; cyclooctene, 931-88-4; cyclooctyl iodide, 1556-10-1; 1-octene, 111-66-0; 2-iodooctane, 557-36-8; 3,3-dimethyl-1-butene, 558-37-2; 2,3-dimethyl-2-iodobutane, 594-59-2; 2,3-dimethyl-2-butene, 563-79-1; alumina, 1344-28-1; norbornene, 498-66-8; *trans*-stilbene, 103-30-0; styrene, 100-42-5; 1-hexyne, 693-02-7; (*E*)-1,2-diiodo-1-hexene, 115482-64-9; 3-hexyne, 928-49-4; (*E*)-3,4-diiodo-3-hexene, 87161-05-5; phenylacetylene, 536-74-3; (*E*)-α,β-diiodostyrene, 71022-74-7; 5-chloro-1-pentyne, 14267-92-6; (*E*)-5-chloro-1,2-diiodo-1-pentene, 115482-65-0; 3-hydroxypropyne, 107-19-7; (*E*)-α,β-diiodoallyl alcohol, 71264-49-8; propiolic acid, 471-25-0; (*E*)-diiodoacrylic acid, 14092-48-9; dimethyl acetylene dicarboxylate, 762-42-5; dimethyl diiodofumarate, 20697-49-8; iodophenol, 30587-23-6.

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Preparation of Aryl, Alkynyl, and Vinyl Organocopper Compounds by the Oxidative Addition of Zerovalent Copper to Carbon–Halogen Bonds

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A highly reactive copper slurry can be prepared by the reduction of CuI·PEt_3 with 1 equiv of lithium naphthalide. The highly reactive copper is found to undergo rapid oxidative addition to alkyl, aryl, alkynyl, and vinyl halides under mild conditions. The aryl, alkynyl, and vinyl organocopper compounds are stable at room temperature. These organocopper compounds can be prepared with a variety of functional groups such as nitro, nitrile, ester, and ketone.[3,4] The arylcopper compounds can be cross-coupled in moderate to high yields with acid chlorides and with alkyl halides. A comparison of different methods for producing activated copper is presented, and the scope and limitations are discussed.

Organocopper and lithium alkyl cuprate reagents are finding ever increasing usage in organic synthesis. Normally, these reagents are produced from the reaction of an organolithium or Grignard reagent with an appropriate

Table I. Reaction of C_6F_5I with Various Preparations of Copper[a]

no.	copper source	reduction method	temp, °C	time	% yield C_6F_5I	 C_6F_5H	 $C_{12}F_{10}$	ref
1	copper bronze		300	10 h			72	11
2	CuI	A	85	1 h	0	17	83	10
3	CuCl	B	85	1 h	0	8	92	
4	CuCl	B	25	1 h	63	34	4	
5	$CuCl·S(CH_3)_2$	C	25	1 min	20	49	31	
6	$CuI·P(Et)_3$	D	25	1 min	0	98	2	8c

[a] Entries 2–6 were run in dimethoxyethane. Yields were determined by GC analysis.

Table II. Organic Halide Reactions with Copper Prepared by Method A

no.	RX	RX/Cu	solvent	temp, °C	time, h	% yield RX	 RH	 RR
1	p-$NO_2C_6H_4I$	1/1	DME	25	48	33	36	3
2	$CH_2{=}CHCH_2Br$	1/1	DME	85	0.5	0	15	85
3	n-BuI	1/1	DME	85	24	100	0	0
4	C_6F_5Br	1/1	DME	85	24	47	20	2

Table III. Organic Halide Reactions with Copper Prepared by Method B

no.	RX	RX/Cu	solvent	temp, °C	time, h	% yield RX	 RH	 RR
1	$CH_2{=}CHCH_2Br$	1/1	THF	25	2	0	13	87
2	$CH_2{=}CHCH_2Cl$	1/1	THF	65	24	81	13	6
3	$PhCH_2Br$	1/1	THF	65	24	28	1	71
4	n-$C_7H_{15}I$	1/1	dioxane	101	24	72	21	0

Table IV. Organic Halide Reactions with Copper Prepared by Method C

no.	RX	RX/Cu	solvent	temp, °C	time, h	% yield RX	 RH	 RR
1	$PhCH_2Br$	1/2	THF	25	1	44	0	31
2	o-$NO_2C_6H_4Br$	1/2	dioxane	101	24	1	12	87
3	o-BrC_6H_4CN	1/2	dioxane	101	18	90	0	0

copper(I) salt.[5] Accordingly, the types of functional groups that can be tolerated are highly limited. However, once formed these reagents will tolerate a wide range of functionality.[6] We have previously demonstrated that highly reactive metal powders can be prepared by the reduction of metal salts with a variety of reducing agents.[7–9] In this paper, we would like to describe the preparation of a highly reactive zerovalent copper slurry, which readily undergoes oxidative addition to aryl, vinyl, alkynyl, and alkyl halides.[8] The corresponding aryl, alkynyl, and vinyl organocopper reagents are stable and undergo the usual types of homo- and cross-coupling reactions. Moreover, we have demonstrated that these reagents can be prepared with a variety of functional groups present.

Results and Discussion

Previous reports from our laboratories have shown that highly reactive metal powders can be prepared by the reduction of anhydrous metal salts with a variety of reducing agents.[9] In an earlier paper, we reported on the preparation of a reactive form of copper powder.[10] Even though this copper was far more reactive than any other form of copper powder available at that time, it still was of limited synthetic value. In order to extend the usage of the active copper, several new approaches leading to a much more reactive copper were developed. A convenient probe for comparison of the various metal's reactivities is their oxidative addition to pentafluoroiodobenzene.[11] Table I contains reaction conditions for the active copper prepared by four different methods as well as for standard copper bronze. Both copper bronze and the copper prepared by method A require high enough temperatures to effect oxidative addition that the intermediate arylcopper species reductively couples to give decafluorobiphenyl. In contrast, the more reactive forms of copper react readily at room temperature or lower to generate (pentafluorophenyl)copper, which upon hydrolysis yields pentafluorobenzene.[10] It is clear that the most reactive copper is that prepared by method D.

Method A. Entry 2 represents the initial method used to produce reactive copper powder. This preparation shows a large increase in reactivity over entry 1. The metal was produced by reducing CuI with a stoichiometric

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Table V. Reactions of Aryl Halides[a]

no.	aryl halide	temp, °C	time	% yield Ar H	coupling conditions	time, h	% yield Ar–Ar
1	PhI	25	10 min	98	85 °C	24	66
2	PhBr	25	1 h	50			
3	PhCl	25	1 h	48			
4	o-$IC_6H_4NO_2$	0	1 min	60	85 °C	1	87
5	o-BrC_6H_4CN	0	1 h	90	0 °C, O_2	1	76
6	C_6F_5I	25	1 min	97	151 °C[b]	24	91
7	p-$CH_3O_2CC_6H_4Br$	0	3 min	62			
8	p-$BrC_6H_4COC_6H_5$	0	1 min	42			
9	p-$CH_3C_6H_4Br$	25	10 min	47			

[a] Copper prepared by method D. [b] Refluxing mesitylene.

amount of potassium in a 10 mol % solution of naphthalene in dimethoxyethane (DME) under an inert atmosphere of argon.[10] The reduction requires 8 hours and produces a gray-black granular solid. Excessive stirring sinters the powder into copper-colored beads with a resulting loss in reactivity. Table II illustrates the extent of the reactivity of this copper preparation.

Method B. To combat the sintering produced by 8 h of stirring, we sought to accelerate the reduction by the addition of the copper salt to 1 equiv of a preformed solution of lithium naphthalide in DME. By use of this procedure, it was found that CuCl produced the most reactive copper. The reduction of the CuCl requires only 0.5 h and results in a less sintered copper powder. Entries 3 and 4 in Table I show the increase in reactivity from this preparation. Table III shows some of the reactions of this copper preparation.

Methods C and D. Since a strong correlation was noted between particle size and reactivity, it seemed reasonable to expect that the reduction of a soluble copper salt by a solution of 1 equiv of preformed lithium naphthalide would result in a rapid reduction and would produce a very finely divided metal powder. Of the several salts examined, $CuCl{\cdot}S(CH_3)_2$[12] (method C) and $CuI{\cdot}P(Et)_3$[13] (method D) yielded the most reactive copper. Either of these salts may be dissolved in ethereal solvents and, when rapidly mixed with a cooled solution of lithium naphthalide (1 equiv), produced a very reactive zerovalent copper. Subsequent experiments showed that the reduction of the phosphine complex produces the more reactive metal. Entries 5 and 6 in Table I shows the resulting increase in reactivities. Table IV represents some of the reactions that the reduced $CuCl{\cdot}S(CH_3)_2$ complex will undergo.

Copper Activation Summary. While copper prepared by methods A and B will undergo reactions with reactive organic halides such as C_6F_5I, allyl bromide, and benzyl bromide, it is not useful with less reactive systems such as vinyl bromides or other alkyl halides such as *n*-heptyl iodide. Only method C and D preparations allow reactions with these latter compounds. To date, the copper produced by methods C and D has not been physically characterized. It is, however, interesting to note that the powders formed by methods A and B would settle to the bottom of the reaction flask within 1 h of formation, leaving a clear supernatent. Method C preparations settle very slowly in the course of 24 h and method D preparations show no evidence of settling within 24 h and are possibly colloidal suspensions. Additional studies on the nature of the copper are in progress.

Arylcopper Formation. The reactions of several aryl halides with activated copper are shown in Table V. The column headed "% yield Ar H" indicates the amount of reduced product formed by quenching the organocopper intermediate with water.

Phenyl iodide reacts within 10 min to produce a nearly quantitative yield of phenylcopper. Treatment of the organometallic intermediate with H_2O or D_2O gave a quantitative conversion to the respective products ArH and ArD. A D_2O quench of the C_6F_5I reaction, entry 6, yielded a 97% conversion to C_6F_5D according to mass spectra analysis. Heating the phenylcopper in refluxing DME produced the homocoupled biphenyl in good yield.

Chlorobenzene and bromobenzene do not completely react with the copper under similar conditions. Half of the starting material was recovered in both cases.

Withdrawing groups on aryl halides activate these compounds toward the Ullmann reaction.[14] The same effect is observed with these compounds in their reactions with the activated copper. The o-$NO_2C_6H_4I$ is so reactive that it is completely consumed within 1 min. However, o-$NO_2C_6H_4Cu$ decomposes quickly at room temperature, and an aqueous quench at 1 min produces only a 60% yield of nitrobenzene. To effect a high conversion to the coupled 2,2′-dinitrobiphenyl, the starting material is added directly to a flask of the hot activated copper solution. An aryl ketone and ester (entries 7 and 8) could also be tolerated. It is interestingly to note that p-$CH_3O_2CC_6H_4Cu$ is quite stable even in refluxing THF. Attempts to carry out a thermal homocoupling were not very successful. Also, oxidative homocoupling with oxygen did not yield the corresponding biphenyl but instead gave a moderate yield of the corresponding phenol p-$CH_3O_2CC_6H_4OH$.

The organocopper species produced from o-BrC_6H_4CN also decomposed slowly at room temperature but was stable at 0 °C. To effect homocoupling the organocopper intermediate was maintained at 0 °C, and then molecular oxygen was bubbled through the reaction mixture, oxidatively coupling the reagent to form 2,2′-dicyanobiphenyl.

C_6F_5I reacts with activated copper to produce a nearly quantitative yield of (pentafluorophenyl)copper. This intermediate is very stable and will not couple thermally until heated to 151 °C in refluxing mesitylene.

Scheme I provides a plausible mechanism to explain the formation of arylcopper intermediates and their subsequent thermal coupling. Step 1 consists of the oxidative addition of copper to the aryl halide producing the arylcopper and copper(I) halide. In an earlier study of the reaction of C_6F_5I with copper produced by method A,[10] C_6F_5Cu was isolated as a tan solid. Hydrolysis of the solid

Scheme I

$$RX + 2Cu^0 \rightarrow RCu + CuX \qquad (1)$$

$$2RCu \rightarrow RR + 2Cu^0 \qquad (2)$$

$$RCu + RX \rightarrow RR + CuX \qquad (3)$$

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Table VI. Reactions of Vinyl Halides

no.	compound	Cu/RX	temp, °C	solvent	product[a]	% yield 1 min	% yield 10 min	% yield 1 h
1	$\mathrm{CH_3CH{=}CHBr}$	2/1	25	DME	S	30	0	0
					C	0	0	0
					R	20	50	55
2	$\mathrm{PhCH{=}CHBr}$	2/1	25	DME	S	34	0	0
					C	0	0	0
					R	44	53	53
3	$\mathrm{PhCH{=}CHI}$	2/1	25	DME	S	0	0	0
					C	23	36	47
					R	23	44	52
4	$\mathrm{PhCH{=}CHBr}$	2/1	0	THF	S	48	42	14
					C	4	5	5
					R	37	51	52
5	$\mathrm{PhCH{=}CHBr}$	4/1	25	THF	S	0	0	0
					C	37	35	32
					R	59	57	51
6	$\mathrm{PhCH{=}CHBr}$	4/1	0	THF	S	0	0	0
					C	0	1	2
					R	78	82	63

[a] S = $\mathrm{PhCH{=}CHX}$, C = $\mathrm{PhCH{=}CHCH{=}CHPh}$, R = $\mathrm{PhCH{=}CH_2}$.

Table VII. Reactions of $\mathrm{PhC{\equiv}CBr}$ at 25 °C in DME

product[a]	% yield 1 min	% yield 10 min	% yield 1 h	% yield 18 h	coupling conditions	product	% yield, 2 h
R	0	25	29	42	O_2, 25 °C	R	0
C	13	13	15	19		C	30

[a] R = $\mathrm{PhC{\equiv}CH}$, C = $\mathrm{PhC{\equiv}CC{\equiv}CPh}$.

produced pentafluorobenzene. Thermal decomposition of the solid under argon yielded decafluorobiphenyl and copper metal (step 2).

Arylcopper compounds are well-known species.[15] Phenylcopper, which has been formed by several different methods, is stable up to 80 °C;[16] it has been isolated and characterized.[17] The compound is known to self-couple at temperatures above 80 °C to produce biphenyl and elemental copper (step 2) and to react with other aryl halides to give the cross-coupled product and a copper(I) halide (step 3).[18] Thus, there is strong evidence to support the plausibility of these three steps. Scheme I, in fact, constitutes one of the mechanisms put forth for the traditional Ullmann biaryl coupling.[14]

For the highly reactive preparations of copper, step 1 occurs readily at 25 °C or below. At these temperature steps 2 and 3 proceed very slowly or not at all. Since many simple arylcopper compounds are stable in this temperature range, the result is a buildup of the arylcopper intermediate. The intermediate can then be self-coupled according to step 2 as the temperature is raised.

With less reactive preparations of copper, such as commercial copper bronze, the initial oxidative addition does not take place until the temperature is suitably elevated. At these higher temperatures, the rates of steps 2 and 3 become significant and the primary product of the reaction becomes the homocoupled dimer, often with no detectable trace of any organometallic intermediate.

Alkenylcopper Formation. Vinyl halides parallel the reactivities of aryl halides as shown in Table VI. For example, β-iodostyrene was completely consumed in 1 min whereas, under the same conditions, β-bromostyrene was only about 50% consumed.

By combining the low-temperature effect from entry 4 with the effect of excess copper in entry 5, we were able to achieve a much higher (82%) conversion to the β-styrenylcopper intermediate (entry 6). A D_2O quench showed an 80% conversion of the β-styrenylcopper intermediate to $\mathrm{PhCH{=}CHD}$ by mass spectral analysis.

Homocoupling to produce 1,4-diphenyl-1,3-butadiene was best achieved through the use of the vinyl iodide (entry 3). However, only a moderate yield of 36% could be produced by replacing THF, after the formation of the organometallic, with higher boiling DMF and then refluxing for 2 h. Homocoupling could not be induced through the use of molecular oxygen. This reluctance to couple is consistant with the increased stability of vinylcopper phosphine complexes reported by Whitesides and co-workers.[19]

Alkynylcopper. The reaction of 1-bromo-2-phenylacetylene with the activated copper produced a moderate yield of phenylacetylene upon quenching. Bubbling molecular oxygen through the reaction mixture produced a low yield of the homocoupled 1,4-diphenylbutadiyne.

The reactivity of the alkynyl bromide is less than that of the analogous alkenyl bromide, with the former giving a 42% yield of intermediate in 18 h while the latter produced a similar yield of organocopper in 10 min. Heating the alkynylcopper intermediate to 85 °C in DME did not induce homocoupling. Interestingly, (2-phenylethynyl)copper would homocouple when molecular oxygen was bubbled through the reaction mixture. This method of coupling was not successful with the vinylcopper intermediates.

Reaction with Alkyl Halides. Primary alkyl iodides and allyl and benzyl halides readily reacted with the active copper at room temperature to give the homocoupled product in high yields.[8,20] In contrast, primary alkyl

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Table VIII. Reactions of Arylcopper with Acid Chloride To Form Ketones

no.	organocopper	RC(O)Cl	solvent	temp, °C	time, h	product	% yield
1	PhCu	PhC(O)Cl	DME	85	8.5	PhC(O)Ph	60
2	*o*-NCC_6H_4Cu	PhC(O)Cl	DME	0	2	*o*-$NCC_6H_4C(O)Ph$	71
3	*o*-NCC_6H_4Cu	$CH_3C(O)Cl$	DME	0	1	*o*-$NCC_6H_4C(O)CH_3$	41
4	C_6F_5Cu	PhC(O)Cl	mesitylene	165	18	$C_6F_5C(O)Ph$	25

Table IX. Reactions of Arylcopper Reagents with Alkyl Halides[a]

						% yield		
no.	reagent	halide	solvent	temp, °C	time	AA	AB	BB
1	PhCu	$PhCH_2Br$	THF	25	10 min		20	20
2	2PhCu	$PhCH_2Br$	THF	25	10 min		70	20
3	PhCu	$2PhCH_2Br$	THF	25	1 h		84	15
4	PhCu	$CH_2{=}CHCH_2Br$	THF	25	10 min		35	66
5	*o*-NCC_6H_4Cu	$PhCH_2Br$	THF	0	3 h	16	46	12
6	PhCu	*n*-$CH_3(CH_2)_5CH_2I$	DME	25	10 min	4	62	21
7	PhCu	CH_3I	THF	25	10 min	0	23	
8	*p*-$PhCOC_6H_4Cu$	*n*-iodobutane	THF	25	90 min		32	
9	*p*-$CH_3O_2CC_6H_4Cu$	*n*-iodobutane	THF	25	18 min		58	

[a] Yields are based on the limiting reagent.

bromides with β-hydrogens produce mixtures of the alkane and the alkene even at temperatures as low as −60 °C. Apparently for the alkyl bromides the alkylcopper species undergoes β-hydride elimination to generate CuH faster than it homocouples. The CuH then reacts with another mole of RCu to generate the alkane. This mechanism was postulated by Whitesides et al. in their studies on the decomposition of *n*-butylcopper.[21] It is apparent that under these conditions the primary alkylcopper species cannot be stabilized. However, it must be emphasized that new methods have been developed that lead to stable primary alkylcopper reagents. A preliminary report has been made.[3] A full report on the stable primary alkylcopper reagents will be made in the near future.

Cross-Coupling Reactions. The arylcopper compounds were found to readily cross-couple with acid chlorides to yield the corresponding ketones in moderate to high yields (see Table VIII). An exception is entry 4, which required extensive heating due to the high thermal stability of $C_6F_5Cu{\cdot}P(Et)_3$.

Table IX contains the results of a series of cross-coupling reactions with alkyl halides. While the majority of yields are in the 60–80% range, some cross-coupling reactions are not nearly as effective.

Conclusions

A highly reactive copper slurry can be prepared by the lithium naphthalide reduction of $CuI{\cdot}P(Et)_3$. The reactivity of the copper is, in fact, highly dependent on the solubilizing ligand used. The resultant copper slurry undergoes rapid oxidative addition to aryl, vinyl, and alkynyl halides under very mild conditions. This approach allows the formation of stable aryl- and vinylcopper reagents containing a wide spectrum of functionality including nitro, nitrile, ester, and ketone. The organocopper species were found to undergo the traditional reactions, including homocoupling and cross-coupling with alkyl halides and acid chlorides.

Experimental Section

General Data. Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer neat between NaCl plates or as KBr disks. ^1H NMR spectra were recorded on a Varian EM-390 (90 MHz), Varian XL-200 (200 MHz), or Varian VXR-200 (200 MHz) spectrometer. Proton-decoupled ^{13}C NMR spectra were recorded at 50 MHz on a Varian VXR-200 or a Varian XL-200 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in ppm (δ) with Me_4Si as internal shift reference. High-resolution mass spectra were performed by the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln on a Kratos MS-80 mass spectrometer.

All manipulations were carried out on a dual manifold vacuum/argon system. The Linde prepurified grade argon was further purified by passing it through a 150 °C catalyst column (BASF R3-11) and then through a column of phosphorus pentoxide followed by a column of granular potassium hydroxide. 1,2-Dimethoxyethane (DME) and THF were freshly distilled under argon from sodium/potassium alloy.

Experimental Setup. All reactions were carried out in 50-mL two-necked round-bottom flasks equipped with a reflux condenser and a rubber septum. The top of the condenser was fitted with a tubing connector, containing a stopcock, connected to an argon/vacuum dual manifold.

Chemicals for Copper Reduction. CuI and CuCl were purchased from CERAC Inc. (99% pure). The salts were used as received but were opened and transferred within the glovebox. Lithium metal was purchased from Alfa Chemical Co. as sticks of metal under mineral oil. The oil was removed with several washings of hexane, and then the metal was transferred immediately into the glovebox. Naphthalene was purchased from Aldrich Chemical Co. (reagent grade) and used as received. Biphenyl was purchased from Matheson, Coleman, and Bell (reagent grade) and used as received.

Chemicals for Reaction with Activated Copper. All chemicals were reagent grade or better and used as received unless otherwise stated.

Gas Chromatography Analysis. GC analyses were performed on a Varian Model 920 Aerograph equipped with a thermal conductivity detector and a laboratory-built temperature programmer of Hewlett-Packard 5890A instrument.

The columns used were as follows: Column I consisted of 5% SE-30 (Perkin-Elmer) on Chromosorb-P (Analabs) support packed in a $^1/_8$ in. × 10 ft stainless steel column. Column II consisted of a 3% OV-17 (Altech Asso) liquid phase on Chromosorb-W (Analabs) support packed in a $^1/_8$ in. × 10 ft stainless steel column. Column III consisted of a 5% Carbowax-20M (Perkin-Elmer) liquid phase on Chromosorb-W (Analabs) support packed in a $^1/_8$ in. × 10 ft stainless steel column. These same packing were also used in $^1/_4$ in. × 10 ft stainless steel preparative columns.

Workup and Isolation Procedures. The contents of the reaction flask (typically 20–45 mL) were poured into HCl (0.01 M, 50 mL). Methylene chloride (25 mL) was added, and the mixture was stirred. The organic layer was washed three times with distilled water and dried with $MgSO_4$. Relatively volatile components were isolated either by fractional distillation or preparative GC. For the isolation of higher boiling components,

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(21) Whitesides, G. M.; Stedronsky, E. R.; Casey, C. P.; SanFilippo, J., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1426.

the solvent and lower boiling compounds were removed through the use of a rotary evaporator. The remaining components of the mixture were then separated by flash chromatography.[22]

Standard Reaction Procedure. To a flask containing activated copper (20 mmol) prepared by methods B, C, or D was added an internal standard compound (4 mmol) and the organic halide (10 mmol). The temperature was adjusted and stirring commenced. One-milliliter aliquots were removed via syringe at timed intervals and quenched with HCl (0.01 M, 0.5 mL). The organic layer from the quenched aliquot was analyzed by GC. The remaining contents of the reaction flask were subjected to the workup and isolation procedure to obtain the individual products for spectroscopic identification and characterization.

Homocoupling of Stable Organocopper Intermediates. For thermal coupling: The standard reaction procedure was followed with the following modification. The temperature of the reaction vessel was raised to the refluxing temperature of the solvent after the formation of the activated copper and the addition of the internal standard. The organic halide was then added to the refluxing copper solution. The standard procedure was followed from this point. **For oxidative coupling:** The standard procedure was followed, and the reaction progress was monitored by GC analysis until the maximum yield of organocopper was obtained. Then a 50-mL syringe was purged and filled with oxygen from a supply tank, and the contents were slowly injected through the septa into the reaction vessel with the syringe needle below the surface of the mixture. The addition of oxygen was repeated. The reaction flask often warmed slightly, and the coupling was usually complete in 30 min. From this point, the standard analysis and workup procedure was followed.

Cross-Coupling with Stable Organocopper Intermediates. The standard procedure was followed, and the progress of the reaction was monitored by GC until the maximum yield of stable organocopper intermediate was obtained. Then an excess (3/1) of the cross-coupling reagent was added, and the standard procedure was followed from this point.

Activated Copper Produced by Method A. This procedure has been published by Rieke and Rhyne.[10]

Formation of Lithium Naphthalide. Typically, oven-dried glassware was placed in the glovebox and charged with lithium metal (22 mmol) and either naphthalene or biphenyl (23 mmol). The glassware was attached to the manifold, freshly distilled THF or DME (15–20 mL) was syringed into the flask, and stirring was commenced. At 25 °C the reduction takes approximately 2 h in THF and 3 h in DME. The reduction was judged complete when no solid lithium could be found. The finished reduction was dark green when naphthalene was used and deep blue with biphenyl. The solution should be used as soon as possible.

Activated Copper Produced by Method B. Lithium naphthalide was performed as described previously. The septa was removed from the reaction flask, CuCl (20 mmol) was added under a positive argon flow, and the reaction vessel was resealed. The slurry was stirred until the reduction was complete, 30 min to 1 h. The reaction was judged complete by the following procedure. A small aliquot of the reduction mixture was injected into a small test tube containing distilled water. The reduced copper formed a fine black precipitate and the naphthalene a white precipitate. If the reduction was not complete, the fine yellow precipitate of CuCl was also present. The resulting activated copper should be used as soon as possible.

Activated Copper Produced by Methods C and D. Both $CuCl{\cdot}S(CH_3)_2$[12] and $CuI{\cdot}P(Et)_3$[13] were prepared by literature methods, recrystalized once, dried under vacuum, and stored in tightly stoppered bottles under refrigeration until needed. Both complexes were kept for several months under these conditions. The complex salt was weighed out (20 mmol) and placed in a reaction flask. The reaction vessel was filled with argon, and freshly distilled THF or DMF (5–10 mL) was syringed in. For the $CuI{\cdot}P(Et)_3$ complex, a gentle swirling of the flask for a few seconds dissolved the salt, leaving a clear solution. For the $CuCl{\cdot}S(CH_3)_2$ complex, the flask was warmed and stirred, and additional dimethyl sulfide (5–15 mL) was added to effect total dissolution. In another reaction flask, lithium naphthalide was preformed according to the procedure previously given and then cooled in an ice bath. The complex salt solution was drawn up into a syringe and quickly injected into the cooled, stirring solution of lithium naphthalide. The ice bath was removed after 1 min, and the reaction was allowed to warm to room temperature. The brown suspension/solution of activated copper was now ready for subsequent reactions. The activated copper can be kept for a few hours and used with only a slight loss in reactivity, but for best results the preparation should be used as soon as possible.

Reaction of Pentafluoroiodobenzene with Activated Copper. Pentafluoroiodobenzene (10 mmol) was reacted with activated copper (20 mmol). Toluene (3 mmol) was added as an internal standard. For the precise reaction times, temperature, and yields for the various copper preparations, see Table I. To produce the highest yield of homocoupled $C_{12}F_{10}$, activated copper was prepared by method D in THF. The solvent was removed by vacuum and replaced with freshly distilled mesitylene. The temperature was raised to 151 °C, after which the C_6F_5I was added (see entry 1 of Table V). The reaction was analyzed by GC (column I).

Reaction of *o*-Nitroiodobenzene with Activated Copper. The *o*-nitroiodobenzene (10 mmol) was reacted with activated copper (20 mmol) prepared by method D in THF. At 0 °C the 1-min quench of the reaction showed a 60% yield of (*o*-nitrophenyl)copper. To maximize the yield of homocoupled 2,2′-dinitrobiphenyl, the reaction was run in refluxing DME for 1 h, producing an 87% yield of coupled product. The reaction was quite exothermic. Toluene (3 mmol) was added as an internal standard, and the reaction was analyzed by GC (column I).

Reaction of *o*-Nitrobromobenzene with Activated Copper. The *o*-nitrobromobenzene (10 mmol) was reacted with activated copper (20 mmol) produced by method C in THF. After the formation of the copper, the THF was removed by vacuum and replaced with freshly distilled dioxane. The temperature was increased to 101 °C, and the starting material was added. At the end of 24 h, the yield of nitrobenzene was 12% and 2,2′-dinitrobiphenyl 87%. Toluene (3 mmol) was added as an internal standard, and the reaction was analyzed by GC (column I).

Reaction of *o*-Bromobenzonitrile with Activated Copper. Activated copper (20 mmol) produced by method D was generated in a reaction vessel and cooled to 0 °C. *o*-Bromobenzonitrile (10 mmol) was added along with decane (3 mmol) as an internal standard. The reaction was stirred for 1 h. The GC analysis (column II) of a quenched sample showed a typical yield of *o*-CuC_6H_4CN to be 80–90%. The maximum yield of homocoupled product was obtained by injecting 90 mL of molecular oxygen into the reaction vessel after the initial hour of reaction. The temperature was maintained at 0 °C for an additional 0.5 h for the coupling to be complete. GC analysis showed the yield of 2,2′-dicyanobiphenyl to be 87%.

Reaction of Halobenzene with Activated Copper. Activated copper (20 mmol) produced by method D in DME was generated in a reaction flask at 25 °C. Halobenzene (10 mmol) was added along with with toluene (3 mmol) as an internal standard. For the maximum yields of phenylcopper produced from the different halobenzenes, see Table V. The maximum yield of biphenyl (66%) was produced by refluxing the reaction mixture for 24 h. The yields of benzene and biphenyl were determined by GC analysis (column III) as described previously.

Reaction of Vinyl Halides with Activated Copper. Activated copper produced by method D was allowed to react with various vinyl halides. The internal standard for these reactions was decane (3 mmol). For the specific Cu/RX ratio, reaction temperature, solvent, reaction time, and product ratio for the various vinyl halide reactions, see Table VI. The product yields were determined by GC analysis (column II). β-Iodostyrene was prepared by the method of Zweifel and Whitman.[23]

Reaction of (2-Bromophenyl)acetylene with Activated Copper. Activated copper (20 mmol) produced by method D in THF was generated in the reaction flask at 25 °C. Decane (3 mmol) was added as an internal standard. (2-Bromophenyl)acetylene (10 mmol) was added, and the solution was stirred for 18 h. GC analysis (column II) showed the products to be phe-

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[22] Still, W. C.; Kahn, M.; Nitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[23] Zweifel, G.; Whitman, C. *J. Am. Chem. Soc.* **1967**, *89*, 2753.

nylacetylene (42%) and 1,4-diphenylbutadiyne (19%). To maximize the yield of homocoupling, molecular oxygen (90 mL) was bubbled through the solution for 0.5 h. The yield of 1,4-diphenylbutadiyne was 30%.

Benzophenone. Activated copper (20 mmol), produced by method D in DME, was generated in the reaction flask and brought to 25 °C. Iodobenzene (10 mmol) was added along with toluene (3 mmol) as an internal standard. After 10 min, benzoyl chloride (30 mmol) was added and the temperature was raised to 85 °C for 8.5 h. GC analysis (column II) showed a 60% yield of benzophenone.

***o*-Cyanobenzophenone.** Activated copper (20 mmol) produced by method D in DME was cooled to 0 °C. *o*-Bromobenzonitrile (10 mmol) was added along with decane (3 mmol) as an internal standard. The solution was stirred for 1 h, benzoyl chloride (30 mmol) was added, and the solution stirred for 2 h while the temperature was maintained at 0 °C. The reaction mixture was put through the standard workup procedure, and the components of the mixture were separated by flash chromatography as described previously. The flash column was packed with 60-mesh silica gel and eluted with toluene to give *o*-cyanobenzophenone (71%): mp 83–84 °C (lit.[24] mp 83.5 °C); IR 1665, 2230 cm^{-1}.

***o*-Cyanoacetophenone.** This reaction was identical with the synthesis of *o*-cyanobenzophenone except for the substitution of acetyl chloride (30 mmol) for benzoyl chloride. The isolated yield was 41%: mp 39–42 °C (lit.[25] mp 48 °C); IR 1690, 2218 cm^{-1}. The phenylhydrazine derivative[26] was prepared: mp 198–200 °C (lit.[25] mp 205–207 °C).

2,3,4,5,6-Pentafluorobenzophenone. Activated copper (20 mmol) was generated by method D in DME and brought to 25 °C. Pentafluoroiodobenzene (10 mmol) was added along with toluene (3 mmol) as an internal standard. After 5 min the solvent was removed by vacuum with gentle warming of the flask (30 °C) and replaced with 20 mL of freshly distilled mesitylene. Benzoyl chloride (30 mmol) was added, and the reaction mixture was heated to reflux (165 °C) for 18 h. The reaction mixture was put through the standard workup and flash chromatography isolation procedure. The flash column was packed with 60-mesh silica gel and eluted with toluene to give 2,3,4,5,6-pentafluorobenzophenone (25%): mp 29–30 °C (lit.[27] mp 30–31 °C); bp 92–94 °C (0.2 mmHg) [lit.[28] bp 93 °C (0.2 mmHg)]; IR 1495, 1520 cm^{-1}.

***o*-Benzylbenzonitrile.** Activated copper (20 mmol) was produced by method D in THF and cooled to 0 °C. *o*-Bromobenzonitrile (10 mmol) was added along with decane (3 mmol) as an internal standard, and the mixture was stirred for 1 h. Benzyl bromide (30 mmol) was added, and the mixture was stirred for 1 h at 0 °C. The temperature was increased to room temperature, and the mixture was stirred for an additional 2 h. The reaction mixture was put through the standard workup procedure, and the components of the mixture were separated by flash chromatography. The flash column was packed with 60-mesh silica gel and eluted with toluene to give *o*-benzylbenzonitrile (46%) as a green liquid: bp 162 °C (4 mmHg) [lit.[29] bp 158–160 °C (2 mmHg)]; IR 2227 cm^{-1}.

4-*n*-Butylbenzophenone. 4-Bromobenzophenone (1.332 g, 5.10 mmol) in THF (5 mL) was added via cannula to activated copper (22.79 mmol, produced by method D and containing *n*-hexadecane (0.427 g, 1.89 mmol) as an internal gc standard) at 0 °C, and the solution was stirred for 40 min. The solution turned greenish black within 1 min. 1-Iodobutane (3.88 g, 21.08 mmol) was added neat via syringe, and the mixture was stirred at 0 °C for 40 min (reaction is complete at this time) and then at room temperature for 25 h until workup. The reaction mixture was quenched with HCl (3%, 50 mL) and extracted with three portions (50 mL each) of chloroform. The chloroform extracts were washed with water, filtered, and dried over anhydrous sodium sulfate. Removal of the chloroform gave an oil, which was chromatographed on silica gel (gradient elution: hexanes–methylene chloride). The oil was extracted several times with hexanes to give 4-*n*-butylbenzophenone (32%) as a yellow oil: ^{1}H NMR (90 MHz, $CDCl_3$) 0.80–1.80 (m, 7 H), 2.60 (t, J = 8 Hz, 2 H), 6.6–8.1 (m, 9 H); IR (neat) 2930, 2915, 2830, 1660, 1605, 1450, 1310, 1275, 1175 cm^{-1}; mass spectrum, m/e 238.1355, calcd for $C_{17}H_{18}O$ 238.1356; m/e (relative intensity) 238 (35), 161 (100), 105 (83).

Methyl 4-*n*-Butylbenzoate. Methyl 4-bromobenzoate (2.231 g, 10.37 mmol) in THF (5 mL) was added via syringe to active copper (23.13 mmol, produced by method D and containing dodecane (0.597 g, 3.50 mmol) as an internal GC standard) at room temperature and the solution was stirred for 40 min. 1-Iodobutane (5.77 g, 31.36 mmol) was added neat via syringe, and the mixture stirred at room temperature for 18 h. The reaction mixture was quenched with HCl (3%, 50 mL) and then extracted with three portions (50 mL each) of dichloromethane. The dichloromethane extracts were washed with several portions of water, which were in turn reextracted. The dichloromethane layer was filtered, dried over anhydrous sodium sulfate, and filtered again, and the CH_2Cl_2 was removed to give an oil, which was chromatographed on silica gel (gradient elution: hexanes–methylene chloride). Column fractions that contained product were distilled at reduced pressure to give methyl 4-*n*-butylbenzoate (58%): bp 69–70 °C (0.13 mmHg); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.80–1.80 (m, 7 H), 2.60 (t, J = 10 Hz, 2 H), 3.80 (s, 3 H), 7.1 (d, J = 10 Hz, 2 H), 7.85 (d, J = 10 Hz, 2 H); IR (neat) 2930, 2920, 2835, 1730, 1605, 1440, 1420, 1280, 1180, 1110 cm^{-1}; mass spectrum, m/e 192.1156, calcd for $C_{12}H_{16}O_2$ 192.1154; m/e (relative intensity) 192 (50), 161 (77), 150 (80), 149 (100).

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Registry No. C_6F_5I, 827-15-6; C_6F_5H, 363-72-4; $C_{12}F_{10}$, 434-90-2; *p*-$NO_2C_6H_4I$, 636-98-6; $CH_2{=}CHCH_2Br$, 106-95-6; *n*-BuI, 542-69-8; C_6F_5Br, 344-04-7; $NO_2C_6H_5$, 98-95-3; $CH_2{=}CHCH_3$, 115-07-1; $CH_2{=}CHCH_2CH_2CH{=}CH_2$, 592-42-7; $CH_2{=}CHCH_2Cl$, 107-05-1; $PhCH_2Br$, 100-39-0; *n*-$CH_3(CH_2)_5CH_2I$, 4282-40-0; $PhCH_2CH_2Ph$, 103-29-7; *n*-C_7H_{16}, 142-82-5; *o*-$NO_2C_6H_4Br$, 577-19-5; *o*-BrC_6H_4CN, 2042-37-7; *o*-$NO_2C_6H_4C_6H_4NO_2$-*o*, 2436-96-6; PhI, 591-50-4; PhBr, 108-86-1; PhCl, 108-90-7; *p*-$CH_3O_2CC_6H_4Br$, 619-42-1; *p*-$BrC_6H_4COC_6H_5$, 90-90-4; *p*-$CH_3C_6H_4Br$, 106-38-7; $CH_3CH{=}CHBr$, 590-14-7; $PhCH{=}CHBr$, 103-64-0; $PhCH{=}CHI$, 101349-79-5; $PhCH{=}CHCH{=}CHPh$, 886-65-7; $PhCH{=}CH_2$, 100-42-5; $PhC{\equiv}CBr$, 932-87-6; $PhC{\equiv}CH$, 536-74-3; $PhC{\equiv}CC{\equiv}CPh$, 886-66-8; PhCu, 3220-49-3; PhC(O)Cl, 98-88-4; PhC(O)Ph, 119-61-9; *o*-NCC_6H_4Cu, 93684-09-4; *o*-$NCC_6H_4C(O)Ph$, 37774-78-0; $CH_3C(O)Cl$, 75-36-5; *o*-$NCC_6H_4C(O)CH_3$, 91054-33-0; C_6F_5Cu, 18206-43-4; $C_6F_5C(O)Ph$, 1536-23-8; *p*-$PhCOC_6H_4Cu$, 115591-50-9; *p*-$CH_3O_2CC_6H_4Cu$, 115591-51-0; CH_3I, 74-88-4; $PhCH_2Ph$, 101-81-5; $PhCH_2CH{=}CH_2$, 300-57-2; *o*-$NCC_6H_4CH_2Ph$, 56153-61-8; *n*-$CH_3(CH_2)_5CH_2Ph$, 1078-71-3; $PhCH_3$, 108-88-3; *p*-$PhCOC_6H_4(CH_2)_3CH_3$, 55363-57-0; *p*-$CH_3O_2CC_6H_4(CH_2)_3CH_3$, 20651-69-8; *n*-$CH_3(CH_2)_{12}CH_3$, 629-59-4; lithium naphthalide, 7308-67-0; *o*-nitroiodobenzene, 609-73-4; (*o*-nitrophenyl)copper, 61625-12-5; 2,2′-dicyanobiphenyl, 4341-02-0.

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