J. Org. Chem. **1981**, *46*, 5133–5139 **5133**

Comparative Studies on the Addition Reactions of the Normant Reagent ("CH_3MgBr" + CuBr) and the New Tetrahydrofuran-Soluble Magnesium Methylcuprates $Mg_mCu_n(CH_3)_{2m+n}$ with Phenylacetylene

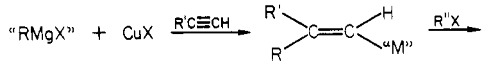
E. C. Ashby,* R. Scott Smith, and A. B. Goel

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received May 28, 1981

Reactions of phenylacetylene with the Normant reagent ("CH_3MgBr" + CuBr) and the THF-soluble magnesium methylcuprates $Mg_mCu_n(CH_3)_{2m+n}$ obtained from the reaction of $(CH_3)_2Mg$ with CuBr have been studied in detail. An attempt to determine the reactive species in Normant reagents was made by studying the rate of reaction of the Normant reagent with phenylacetylene compared to the rate observed with various magnesium methylcuprates. $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ have been shown to be the most probable candidates responsible for reactions involving the Normant reagent with alkynes. The effect of $MgBr_2$ and LiBr on the reactivity and the product selectivity has also been studied.

Applications of lithium organocuprate reagents in organic synthesis have been the subject of recent reports.[1,2] More recently, magnesium organocuprate reagents (so called Normant reagents) derived from reactions of Grignard reagents with cuprous halides, have attracted a great deal of interest and have been utilized very imaginatively in organic synthesis by Normant and others.[2-6] For instance, the stoichiometric mixture of Grignard reagent and cuprous halide is a versatile reagent for the stereoselective synthesis of trisubstituted alkenes from terminal alkynes[5] as shown below. However, the precise composition of the Normant reagent or the identification of the reactive species present in the reaction mixture has not been reported. The importance of trisubstituted alkenes in the synthesis of isoprenoid natural products,[7] and the ease with which they are formed by the above transformation make an understanding of the nature of the Normant reagent highly desirable. We have now studied the solution composition of a mixture of "CH_3MgBr" and CuBr in THF to determine (1) what compounds are formed in this reaction mixture, (2) how much of each compound formed is present at a particular time under the conditions of addition to the terminal alkynes, and (3) which compounds actually add to the terminal alkyne. Although reaction of the "methyl" copper reagent is considered somewhat anamolous[10] compared to other alkyl groups in its reaction with terminal acetylenes, we have selected the "methyl" copper reagent due to the easier interpretation of the composition of methyl–metal compounds in solution (singlet observed for the methyl group in the NMR). The determination of the exact nature of the Normant reagent possessing other alkyl groups proved to be much more complicated due to the more complex systems obtained. The details of these studies are presented here.



Results and Discussion

Preparation of Copper–Magnesium "Ate" Complexes. When "CH_3MgBr" was allowed to react with CuBr in THF, the following copper-magnesium "ate" complexes were identified: $CuMg(CH_3)_3$, $Cu_3Mg_2(CH_3)_7$, $Cu_2Mg(CH_3)_4$, $Cu_3Mg(CH_3)_5$, $Cu_4Mg(CH_3)_6$, $Cu_6Mg(CH_3)_8$.[8] These compounds were found to exist independently of $MgBr_2$ formed as a byproduct. In addition, the ate complexes were formed in a discrete manner by the reaction of $(CH_3)_2Mg$ with CuBr or CH_3Cu in the appropriate molar ratios. From a convenience standpoint,[9] these copper–magnesium ate complexes are best formed in THF via the reaction of $(CH_3)_2Mg$ with CuBr as shown in eq 1–6.

$$2CuBr + 3(CH_3)_2Mg \xrightarrow{-10\text{ to }-25\ ^\circ C} 2CuMg(CH_3)_3 + MgBr_2 \quad (1)$$

$$6CuBr + 7(CH_3)_2Mg \xrightarrow{-10\text{ to }-25\ ^\circ C} 2Cu_3Mg_2(CH_3)_7 + 3MgBr_2 \quad (2)$$

$$2CuBr + 2(CH_3)_2Mg \xrightarrow{-10\text{ to }-25\ ^\circ C} Cu_2Mg(CH_3)_4 + MgBr_2 \quad (3)$$

$$6CuBr + 5(CH_3)_2Mg \xrightarrow{-25\ ^\circ C} 2Cu_3Mg(CH_3)_5 + 3MgBr_2 \quad (4)$$

$$4CuBr + 3(CH_3)_2Mg \xrightarrow{-25\ ^\circ C} Cu_4Mg(CH_3)_6 + 2MgBr_2 \quad (5)$$

$$6CuBr + 4(CH_3)_2Mg \xrightarrow{-50\ ^\circ C} Cu_6Mg(CH_3)_8 + 3MgBr_2 \quad (6)$$

$CuMg(CH_3)_3$, $Cu_3Mg_2(CH_3)_7$, and $Cu_2Mg(CH_3)_4$ are stable at room temperature for at least 1 day and may be prepared at temperatures as high as −10 °C. However,

---

[1] J. F. Normant, *Synthesis*, **63** (1972); G. H. Posner, *Org. React.* **19**, 1 (1972); G. H. Posner *ibid.*, **22**, 253 (1975); H. O. House, *Acc. Chem. Res.*, **9**, 60 (1976).

[2] J. F. Normant, *J. Organomet. Chem. Libr.*, 1, 219 (1976).

[3] J. K. Crandall and F. Collonges, *J. Org. Chem.*, 41, 4089 (1976).

[4] D. E. Bergbreiter and J. M. Killough, *J. Org. Chem.*, 41, 2750 (1976).

[5] A. Marfat, P. R. McGuirk, and P. Helquist, *J. Org. Chem.*, **44**, 3888 (1979), and references therein.

[6] M. T. Rahman, A. K. M. M. Hogue, I. Siddique, D. A. N. Chowdhury, S. K. Nahar, and S. L. Sahar, *J. Organomet. Chem.*, 188, 293 (1980).

[7] For example, geraniol, fornesylacetone, grisofolin, and caulerpol.

[8] E. C. Ashby, A. B. Goel, and R. Scott Smith, submitted for publication.

[9] The reactions of "CH_3MgBr" + CuBr, "CH_3MgBr" + CH_3Cu, and $(CH_3)_2Mg$ + CH_3Cu were often very slow. These rates were inconvenient for the preparation of $Cu_4Mg(CH_3)_6$ which often took several hours and proved impossible for the preparation of unstable $Cu_6Mg(CH_3)_8$.

[10] (a) J. Normant, G. Cahiez, M. Bourgain, C. Chuit, and J. Villieras, *Bull. Soc. Chim. Fr.*, 1656 (1974). (b) H. Westmijze, J. Meijer, H. J. T. Box, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **95**, 304 (1976).

0022-3263/81/1946-5133$01.25/0

Table I. Reactions of Magnesium-Copper "Ate" Complexes with PhC≡CH in THF at -25 °C

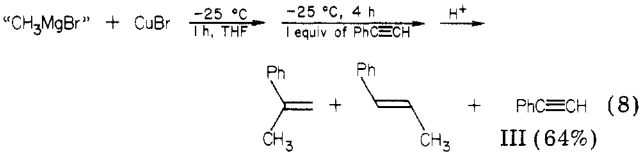
entry	reagent	ratio of PhC≡CH/ reagent	concn,[b] M	time, h	% yield of products[a]		
					I	II	III
1	$CuMgMe_3 + 0.5MgBr_2$	3	0.033	118	0	0	92[c]
2	$CuMgMe_3 + 5\ MgBr_2$	3	0.033	24	0	0	98
3	$Cu_3Mg_2Me_7 + 1.5MgBr_2$	7	0.015	119	0	0	104
4	$Cu_3Mg_2Me_7 + 17MgBr_2$	7	0.015	24	0	0	90[c]
5	$Cu_2MgMe_4 + MgBr_2$	4	0.025	119	0	0	95
6	$Cu_2MgMe_4 + 4MgBr_2$	4	0.025	24	1.5	0	98
7	$Cu_3MgMe_5 + 1.5MgBr_2$	5	0.02	118	2.4	0	96
8	$Cu_3MgMe_5 + 5MgBr_2$	5	0.02	24	6.5	1.3	91[c]
9	$Cu_4MgMe_6 + 2MgBr_2$	6	0.017	36	7.3	0	79[c]
10	$Cu_4MgMe_6 + 6MgBr_2$	6	0.017	2	10	3	86
11	Cu_6MgMe_8[d] $+ 3MgBr_2$	8	0.013	2	20	8	78
12	Cu_6MgMe_8[d] $+ 8MgBr_2$	8	0.013	2	36[e]	13	57

[a] Based on PhC≡CH. [b] Concentration of reagent. [c] Mass balance was low due to the formation of PhC≡CC≡CPh. [d] Reaction carried out at -30 °C. [e] Actually 35% $PhC(CH_3)=CH_2$ and 1% $PhC(CH_3)=CHCH_3$.

$Cu_3Mg(CH_3)_5$ and $Cu_4Mg(CH_3)_6$ cannot be prepared at temperatures above -25 °C but are stable indefinitely at this temperature. $Cu_6Mg(CH_3)_8$ is only metastable at -50 °C and is not easily prepared at lower temperatures. $Cu_6Mg(CH_3)_8$ slowly disproportionates to $Cu_4Mg(CH_3)_6$ and solid methyl copper (eq 7) over a period of several hours at -50 °C.

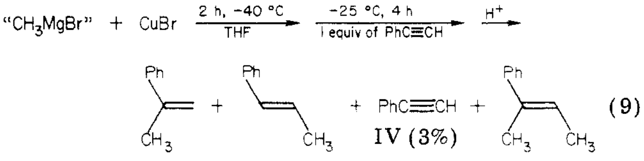
$$Cu_6Mg(CH_3)_8 \rightarrow Cu_4Mg(CH_3)_6 + 2CuCH_3 \qquad (7)$$

Reaction of a 1:1 "CH_3MgBr"/CuBr Mixture with PhC≡CH in THF. Methylmagnesium bromide and CuBr in 1:1 ratio, when allowed to react in THF solvent for 1 h at -25 °C, produced a reagent which reacted with phenylacetylene according to eq 8. The low yield of addition products can be attributed to a competing deprotonation of phenylacetylene by the reagent,[10] since the yield of addition products is maximized in 4 h or less. Interestingly, no addition products were found for this reaction according to a recent report. Also, the observed regiochemistry is unusual since β addition has been previously reported only for reactions involving *tert*-butyl Grignard reagent-cuprous halide.[10]



I (24%) II (12%) III (64%)

The reagent was also prepared by the literature procedure which involves the reaction of the Grignard reagent with CuBr for 2 h at -40 °C[11] followed by reaction with phenylacetylene according to eq 9. Except for the trisubstituted olefin, the result is identical with that represented by eq 8. The trisubstituted olefin arises from coupling of the initial addition product with a methyl reagent.[12] Again, the reaction with phenylacetylene was complete in 4 h or less. Thus, there is no advantage to preparing this reagent at temperatures less than -25 °C; however, higher temperatures should be avoided since the suspended solid slowly turns green.



I (24%) II (9%) III (64%)

Table II. Effect of Varying $MgBr_2$ Concentration on the Reaction of Cu_4MgMe_6 with PhC≡CH at -25 °C in THF

entry[b]	Cu_4MgMe_6/ PhC≡CH/ $MgBr_2$ ratio	time, h	% yield of products[a]		
			I	II	III
1	1:6:2	4	6.3	0	87
2	1:6:2	36	7.3	0	79[c]
3	1:6:2	119	12	0	80[c]
4	1:6:4	1	6	1	93
5	1:6:4	2	6	1	92
6	1:6:4	24	9.7	2.8	42[c]
7	1:6:6	0.25	3	1	65[c]
8	1:6:6	1	9	2	92
9	1:6:6	2	10	3	86
10	1:6:12	6.25	4	3	61[c]
11	1:6:12	1	10	3	81
12	1:6:12	2	10	3	87

[a] Based on PhC≡CH. No IV was found in any case.
[b] Concentration of $Cu_4Mg(CH_3)_6$ was 0.017 M in all cases.
[c] Mass balance was low due to the formation of $PhC{\equiv}CCH_3$ during the reaction and of PhC≡CC≡CPh during the workup.

Reaction of Copper-Magnesium "Ate" Complexes with PhC≡CH in THF. Entries 1, 3, 5, 7, 9, and 11 of Table I show the results for the reaction of PhC≡CH with the copper-magnesium ate complexes prepared by eq 1-6. The ratio of PhC≡CH to methyl groups was 1:1 so as to mimic the conditions of the reaction in eq 8. Only $Cu_3Mg(CH_3)_5$ (entry 7), $Cu_4Mg(CH_3)_6$ (entry 9), and $Cu_6Mg(CH_3)_8$ (entry 11) gave addition products with PhC≡CH. Only $Cu_6Mg(CH_3)_8$ gave a yield and distribution of products comparable to the Normant reagent (eq 8). However, the Normant reagent may well contain more $MgBr_2$ per mole of active reagent than the above reactions. The effect of $MgBr_2$ on these reactions was then investigated by adding $MgBr_2$ so that the ratio of $MgBr_2$ to methyl groups was at least 1:1.[13] An inspection of entries 2, 4, 6, 8, 10, and 12 shows that $MgBr_2$ has only a modest effect on the reactivity of these ate complexes. $Cu_2Mg(CH_3)_4 + 4MgBr_2$

---

[11] The temperature for preparation of this reagent in the literature varies from -60 to -30 °C (see ref 10). For preparation of this reagent in diethyl ether at -45 °C, see ref 5.

[12] The trisubstituted olefin arises via coupling of copper reagents and is not related to the addition reaction: "Cu—CH_3" + "Cu—CH=C(CH_3)Ph" → 2Cu° + Ph(CH_3)C=CH(CH_3). See G. H. Posner, *Org. React.*, 19, 1 (1972).

[13] The solutions became saturated with $MgBr_2$ at $MgBr_2/CH_3$ ratios of 0.2 or greater.

Table III. Effect of Varying $PhC\equiv CH$ Concentration while Holding the Cu_4MgMe_6 and $MgBr_2$ Concentrations Constant

entry[c]	Cu_4MgMe_6/$PhC\equiv CH$/$MgBr_2$ ratio[b]	% yield of products[a]			
		I	II	IV	III[d]
1	1:1:2	10	trace	trace	68
2	1:2:2	6	7	5	70
3	1:3:2	9.5	3	1	87
4	1:4:2	7	2	0	79
5	1:6:2	7.3	0	0	79

[a] Based on $PhC\equiv CH$. [b] Reactions carried out at −25 °C in THF. [c] The concentration of $Cu_4Mg(CH_3)_6$ was 0.017 M, and the reaction time was 36 h in all cases. [d] Mass balances were low due to the formation of $PhC\equiv CCH_3$ during the reaction and $PhC\equiv CC\equiv Ph$ during workup.

(entry 6) gave a very small yield of α-addition product. Most significant, however, is the appearance of β-addition product[14] caused by the addition of $MgBr_2$. Also, the yield of addition product for $Cu_6Mg(CH_3)_8$ + $8MgBr_2$ (entry 12) was greater than that for the Normant reagent (eq 8).

Effect of $MgBr_2$ on the Reaction of $Cu_4Mg(CH_3)_6$ with $PhC\equiv CH$. The effect of $MgBr_2$ on the addition reactions of $Cu_3Mg(CH_3)_5$, $Cu_4Mg(CH_3)_6$, and $Cu_6Mg(CH_3)_8$ was investigated in greatest detail for $Cu_4Mg(CH_3)_6$ (Table II). While the increase in yield of addition product in the presence of added $MgBr_2$ is modest and there is a change in product distribution, the rate of reaction is most profoundly affected. The rate of $Cu_4Mg(CH_3)_6$ + $12MgBr_2$ (entry 11) appears to be about 2 orders of magnitude faster than $Cu_4Mg(CH_3)_6$ + $2MgBr_2$ (entry 3). Furthermore, the rate of reaction appears to be a smooth function of $MgBr_2$ concentration with no significant breaks.

As mentioned above, the copper–magnesium ate complexes appear[15] to exist in THF solution independent of any $MgBr_2$ that may be present. Therefore, the effect of $MgBr_2$ on the addition reactions of $Cu_3Mg(CH_3)_5$, $Cu_4Mg(CH_3)_6$, and $Cu_6Mg(CH_3)_8$ cannot be ascribed to complexation of the reagent with $MgBr_2$. Although THF should be a stronger Lewis base than $PhC\equiv CH$ for $MgBr_2$, evidence for the complexation of $MgBr_2$ with $PhC\equiv CH$ was sought by infrared spectroscopy. No change in the C—H stretching vibration of $PhC\equiv CH$ in THF was observed when $MgBr_2$ was added. Unfortunately, the weak $C\equiv C$ IR band for $PhC\equiv CH$ could not be observed due to a band from a THF impurity.[16] However, no new IR bands were observed in the 2300–1800-cm^{-1} region when $MgBr_2$ was added to $PhC\equiv CH$ in THF.

Table IV. Effect of Varying Cu_4MgMe_6 Concentration while Holding the Concentrations of $PhC\equiv CH$ and $MgBr_2$ Constant

Cu_4MgMe_6/$PhC\equiv CH$/$MgBr_2$ ratio[b,c]	% yield of products[a]			
	I	II	IV	III
12:12:24	10	trace	trace	68[d]
6:12:24	9	trace	0.8	83
3:12:24	7.6	0.8	trace	82
1:12:24	11	3	1.5	83

[a] Based on $PhC\equiv CH$. [b] Reactions were carried out at −25 °C in THF. [c] The concentration of $PhC\equiv CH$ was 0.05 M, and the reaction time was 15 h in all cases. [d] Mass balance was low due to the formation of $PhC\equiv CCH_3$ during the reaction and $PhC\equiv CC\equiv CPh$ during workup.

Table V. Reaction of $PhC\equiv CH$ with Mixtures of Cu_4MgMe_6 Plus $CuMgMe_3$, Cu_3MgMe_7, Cu_2MgMe_4, or Cu_3MgMe_5 at −25 °C in THF

reagent[c]	$PhC\equiv CH$/CH_3/$MgBr_2$ ratio	% yield of products[a,d]	
		I	III
Cu_4MgMe_6 + $CuMgMe_3$	1:1:2.6	0	101
Cu_4MgMe_6 + $Cu_3Mg_3Me_7$	1:1:1.5	0	98
Cu_4MgMe_6 + Cu_2MgMe_4	1:1:3.3	1	102
Cu_4MgMe_6 + Cu_3MgMe_5	1:1:1.5	2	90[b]

[a] Based on $PhC\equiv CH$. [b] Mass balance low due to $PhC\equiv CCH_3$ formation during reaction and $PhC\equiv CC\equiv CPh$ formation during workup. [c] The concentration of $PhC\equiv CH$ was 0.1 M, and the reaction time was 24 h in all cases. [d] No $PhCH=CHCH_3$ or $PhC(CH_3)=CHCH_3$ was found in all cases.

Effect of Varying $PhC\equiv CH$ Concentration while Holding $Cu_4Mg(CH_3)_6$ and $MgBr_2$ Concentrations Constant. Neither NMR analysis of copper–magnesium ate compounds mixed with $MgBr_2$ nor infrared spectroscopy of $PhC\equiv CH$ mixed with $MgBr_2$ demonstrated any relationship between $MgBr_2$ and increased rates and yields of addition products. In the hope of better understanding the effect of $MgBr_2$ on this reaction, we varied the concentration of $PhC\equiv CH$ while holding the $MgBr_2$ and $Cu_4Mg(CH_3)_6$ concentrations constant. The information in Table III demonstrates that the yield of addition products does change with changing $PhC\equiv CH$ concentration relative to $MgBr_2$ and $Cu_4Mg(CH_3)_6$. The product distribution also changes with varying $PhC\equiv CH$ concentration. However, whether the change is due to the $Cu_4Mg(CH_3)_6$/$PhC\equiv CH$ ratio or $PhC\equiv CH$/$MgBr_2$ ratio is unclear. The yields of addition products listed in Tables I–III are based on $PhC\equiv CH$. Table III clearly shows that the yield based on $Cu_4Mg(CH_3)_6$ changes from 44% in entry 5 to 10% in entry 1.

Effect of Varying $Cu_4Mg(CH_3)_6$ Concentration while Holding $PhC\equiv CH$ and $MgBr_2$ Concentrations Constant. To study further the effect of $MgBr_2$ on the addition reactions, the concentration of $Cu_4Mg(CH_3)_6$ was varied while the $MgBr_2$ and $PhC\equiv CH$ concentration were held constant. The information in Table IV shows a small amount of variation in the yield and distribution of products with varying $Cu_4Mg(CH_3)_6$ concentration. The appearance of β-addition product increases with decreasing $Cu_4Mg(CH_3)_6$ concentration. The data in Tables II–IV do not suggest how $MgBr_2$ affects the addition reaction of $Cu_4Mg(CH_3)_6$ with $PhC\equiv CH$. While the effect of $MgBr_2$ is least pronounced with a constant $MgBr_2$/$PhC\equiv CH$ ratio of one or greater, the concentration of $Cu_4Mg(CH_3)_6$ does appear to have a minor effect.

Reaction of $PhC\equiv CH$ with Mixtures of Copper–Magnesium "Ate" Complexes. The data in Table I show that only $Cu_3Mg(CH_3)_5$, $Cu_4Mg(CH_3)_6$, and $Cu_6Mg(CH_3)_8$ are likely candidates for the reactive species in the Normant reagent responsible for addition to terminal alkynes. The reactions in Table V were carried out to ensure that $Cu_2Mg(CH_3)_4$ or $Cu_3Mg(CH_3)_5$ admixed with $Cu_4Mg(CH_3)_6$ is not the reactive species in the Normant reagent. After

---

(14) The α-addition product is $Ph(CH_3)C=CH_2$, and the β-addition product is *trans*-$PhCH=CH(CH_3)$.

(15) There was no change in the NMR signals for these compounds in the presence or absence of $MgBr_2$. The conclusion that $MgBr_2$ does not interact with the copper compounds extends to the limits of detectability and time frame.

(16) A band of medium intensity at 1900 cm^{-1} was observed in THF. The band for C—H of $PhC\equiv CH$ was at 3239 cm^{-1} with a shoulder at 3302 cm^{-1}.

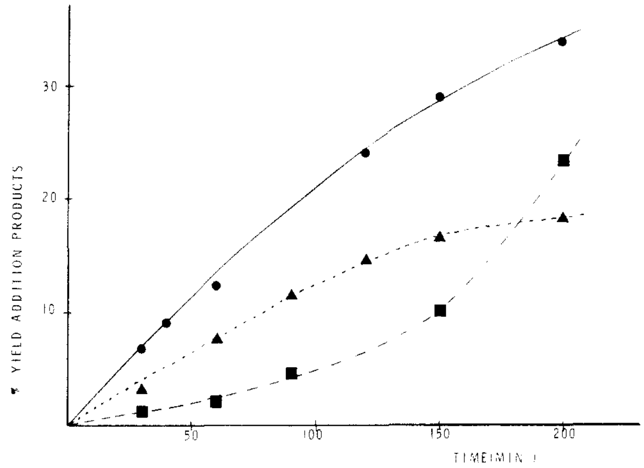


Figure 1. Percent yield of total addition products with time for the reactions of $Cu_4Mg(CH_3)_6$ + $6MgBr_2$ (▲), $Cu_6Mg(CH_3)_8$ + $8MgBr_2$ (●), and CH_3MgBr + CuBr (■) with phenyl acetylene in THF at -40 °C. The reactions were 0.1 M in phenylacetylene, and the $CH_3/PhC{\equiv}CH$ ratio was 1:1.

"CH_3MgBr" was mixed with an equimolar amount of CuBr at -40° C for 2 h in THF, $Cu_2Mg(CH_3)_4$, $Cu_3Mg(CH_3)_5$, and $Cu_4Mg(CH_3)_6$ were found to be the major components in solution in addition to $MgBr_2$ (according to NMR analysis). $CuMg(CH_3)_3$ and $Cu_3Mg_2(CH_3)_7$ are only present in the early stages of mixing CuBr with "CH_3MgBr" at -40 °C. However, in order to obtain information about cuprates formed early in the reaction, we mixed $CuMg(CH_3)_3$ and $CuMg_2(CH_3)_7$ spearately with $Cu_4Mg(CH_3)_6$ in 1:1 molar ratios and then allowed them to react with $PhC{\equiv}CH$ (Table V). The data clearly show that when either $CuMg(CH_3)_3$, $Cu_3Mg_2(CH_3)_7$, $Cu_2Mg(CH_3)_4$, or $Cu_3Mg(CH_3)_5$ are mixed in a 1:1 molar ratio with $Cu_4Mg(CH_3)_6$ and with a $MgBr_2/CH_3$ ratio of greater than 1, much less addition to $PhC{\equiv}CH$ takes place than with $Cu_4Mg(CH_3)_6$ + $6MgBr_2$ (entry 10, Table I). Therefore, the compounds $CuMg(CH_3)_3$, $Cu_3Mg_2(CH_3)_7$, and $Cu_2Mg(CH_3)_4$ do not participate at all in the addition to $PhC{\equiv}CH$ by the 1:1 "CH_3MgBr"/CuBr mixture (Normant reagent). Furthermore, $Cu_3Mg(CH_3)_5$ may also be ruled out as an active reagent for two reasons. The data in Tables I and V exclude the existence of any compound having a copper/magnesium ratio of less than 4 (i.e., $Cu_4Mg(CH_3)_6$) for the composition of the reactive component(s) of the 1:1 "CH_3MgBr"/CuBr mixture. The compounds with less than a Cu/Mg ratio of 4 either fail to give addition products with $PhC{\equiv}CH$ or cause $Cu_4Mg(CH_3)_6$ to give less addition product. In addition, a 1:1 "CH_3MgBr"/CuBr mixture after 1 h at -25 °C has a solution composition consisting of a 6:1 mixture of $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$, respectively (eq 10). The solid formed was found

$$Cu_6Mg(CH_3)_8 \rightleftharpoons Cu_4Mg(CH_3)_6 + 2\,CH_3Cu \qquad (10)$$

to be mostly CH_3Cu with some unreacted CuBr. Seventy percent of the copper starting as CuBr was contained in the solid phase. Thus, no $Cu_3Mg(CH_3)_5$ was present in this mixture which gave a 36% yield of addition products with $PhC{\equiv}CH$ (eq 8). Also worthy of note is the -25 °C temperature used for the reaction of $PhC{\equiv}CH$ with a 1:1 "CH_3MgBr"/CuBr mixture prepared at -40° C for 2 h. Thus, $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ are at least compatible candidates for the active components of the Normatn reagent.

Kinetics of the Reaction of $PhC{\equiv}CH$ with $Cu_4Mg(CH_3)_6$, $Cu_6Mg(CH_3)_8$, and the Normant Reagent. Figure 1 shows the kinetic behavior of $Cu_4Mg(CH_3)_6$ + $6MgBr_2$, $CuMg(CH_3)_8$ + $8MgBr_2$, and "CH_3MgBr" + CuBr on reaction with $PhC{\equiv}CH$. The kinetic studies were performed at -40 °C so that decomposition of $Cu_6Mg(CH_3)_8$ over the course of the reaction would be minimal. The equimolar mixture of "CH_3MgBr" and CuBr was allowed to react at -25 °C for 1 h and then cooled to -40 °C before $PhC{\equiv}CH$ was added. Both $Cu_4Mg(CH_3)_6$ + $6MgBr_2$ and $Cu_6Mg(CH_3)_8$ + $8MgBr_2$ gave a faster rate of formation of addition product initially than "CH_3MgBr" + CuBr. However, the rate of formation of addition products with $Cu_4Mg(CH_3)_6$ decreases rapidly after 120 min while the rate for "CH_3MgBr" + CuBr is increasing. The slow initial rate of the "CH_3MgBr" + CuBr reagent can be accounted for by the differences in concentration of $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ in the "CH_3MgBr" + CuBr mixture vs. that used for studying the rates independently. The rate studies were carried out at 0.1 M $PhC{\equiv}CH$ such that the $PhC{\equiv}CH/CH_3$ ratio was 1:1. As stated previously, only 30% of the copper starting as CuBr was in solution after equimolar amounts "CH_3MgBr" and CuBr were allowed to react for 1 h at -25 °C. This would place the effective concentrations of $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ at 6×10^{-3} and 1×10^{-3} M, respectively. $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ were used at 1.7×10^{-2} M and 1.3×10^{-2} M, respectively, for the independent rate assessments. The concentration of $MgBr_2$ was 0.1 M in all three rate studies and should not affect the outcome of the study.

The latter stages of the reaction of $PhC{\equiv}CH$ with "CH_3MgBr" + CuBr appear to indicate the formation of a larger concentration of reactive reagent as evidenced by the increased rate of addition. An NMR study of the "CH_3MgBr" + CuBr mixture at -30 °C shows that the amount of copper-magnesium ate complexes in solution actually decreases with time to give insoluble CH_3Cu. Therefore, in the latter stages of the reaction of $PhC{\equiv}CH$ with "CH_3MgBr" + CuBr there is an increase in rate due either to a higher concentration in $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ formed by some unknown mechanism or to an initial product[17] of the addition reaction (i.e., before hydrolysis) that is more reactive than $Cu_4Mg(CH_3)_6$ or $Cu_6Mg(CH_3)_8$.

Table VI. Reaction of Cu_4MgMe_6 with $PhC{\equiv}CH$ in the Presence of Added CuBr

entry[b]	Cu_4MgMe_6/CuBr/$PhC{\equiv}CH$/MgBr ratio	% yield of products[a] I	II	IV	III
1	2:1:12:4	25	8	2	68
2	2:2:12:4	22	7	1	58[c]
3	2:4:12:4	1	trace	1.5	86[c]
4	2:8:12:4	trace	0	0	93

[a] Based on $PhC{\equiv}CH$. [b] The concentration of $Cu_4Mg(CH_3)_6$ was 0.017 M, and the reaction time was 4 h in all cases. [c] Mass balance low due to the formation of $PhC{\equiv}CCH_3$ during reaction and $PhC{\equiv}CC{\equiv}CPh$ during workup.

Reaction of $Cu_4Mg(CH_3)_6$ with $PhC{\equiv}CH$ in the Presence of Added CuBr. Since the 1:1 "CH_3MgBr"/CuBr mixture contains both a solution and a solid phase, the effect of unreacted CuBr contained in the solid phase on the reaction of $Cu_4Mg(CH_3)_6$ + $2MgBr_2$ with $PhC{\equiv}CH$ was investigated. When up to an equimolar amount of CuBr was added to $Cu_4Mg(CH_3)_6$, the yield of addition products with $PhC{\equiv}CH$ at -25 °C after 4 h increased from

---

[17] The exact nature of the addition product before hydrolysis is not known. However, a reasonable formulation would be the substitution of a vinyl group for methyl in $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$. The product could also have $CuMgR_3$, $Cu_3Mg_2R_7$, Cu_2MgR_4, and Cu_3MgR_5 formulations.

Table VII. Reactions of Copper-Magnesium "Ate" Complexes with PhC≡CH in the Presence of Added LiBr

reagent	PhC≡CH/reagent LiBr/$MgBr_2$ ratio	concn,[b] M	time, h	% yield of products[a] I	II	IV	III
$CuMgMe_3$	3:1:1:0.5	0.033	24	0	0	0	101
$Cu_3Mg_2Me_7$	7:1:3:1.5	0.015	24	0	0	0	104
Cu_2MgMe_4	4:1:2:1	0.025	24	0	0	0	107
Cu_3MgMe_5	5:1:3:1.5	0.02	24	26	8	2	66
Cu_4MgMe_6	6:1:4:2	0.017	24	24	8	3	39[c]
Cu_6MgMe_8[d]	8:1:6:3	0.013	2	24	9	0	71
Cu_4MgMe_6	6:1:4:6	0.017	24	trace	0	3	82[c]

[a] Based on PhC≡CH. [b] Concentration of copper-magnesium ate complex. [c] Mass balance low due to formation of $PhC{\equiv}CCH_3$ during reaction and PhC≡CC≡CPh during workup. [d] At −30 °C.

6.3% (entry 1, Table I) to 35% for 0.5 equiv CuBr and 30% for 1 equiv of CuBr (entries 1 and 2, respectively, Table VI). However, with more than 1 equiv of added CuBr (entries 3 and 4, Table VI) the yield of addition products was nearly zero. The addition of 1 or <1 equiv of CuBr has a tremendous effect on the rate and yield of addition products with $Cu_4Mg(CH_3)_6$ but more than 1 equiv of added CuBr destroys the reactivity of $Cu_4Mg(CH_3)_6$. While the explanation for the increased rate of formation and yield of addition products with 1 or <1 equiv of added CuBr is not clear, CuBr probably leads to the formation of more reactive $Cu_6Mg(CH_3)_8$ (eq 11 and 12). With more than 1 equiv of added CuBr, the formation of less reactive compounds such as $(CH_3)Cu$, $Cu_3Mg_2(CH_3)_7$, $Cu_2Mg(CH_3)_4$, and $Cu_3Mg(CH_3)_5$ undoubtedly occurs (eq 13). Another explanation for the increased yield and rate for ≤1 equiv of added CuBr may involve the regeneration of $Cu_4Mg(CH_3)_6$ from the initially formed reaction product which is inactive as an addition reagent.[17,18]

$$4Cu_4Mg(CH_3)_6 + CuBr \rightarrow 3Cu_6Mg(CH_3)_8 + MgBr_2 \quad (11)$$

$$2Cu_4Mg(CH_3)_6 + 2CuBr \rightarrow Cu_6Mg(CH_3)_8 + 4CH_3Cu + MgBr_2 \quad (12)$$

$$Cu_4Mg(CH_3)_6 + 2CuBr \rightarrow 6CH_3Cu + MgBr_2 \quad (13)$$

Reaction of Copper-Magnesium "Ate" Complexes with PhC≡CH in the Presence of Added LiBr. A recent report on the addition reactions of the Normant reagent demonstrated a remarkable improvement in yield of addition product when an equimolar amount of LiBr was added to the reagent.[10b] These workers reported better than a 90% yield of addition to PhC≡CH with a two-fold excess of the reagent 2"CH_3MgCl" + CuBr + LiBr in THF. Without the addition of LiBr this reagent gave only deprotonation of PhC≡CH. Table VII presents the results of adding 1 equiv of LiBr per copper atom of the copper–magnesium ate complexes prior to reaction with PhC≡CH. $CuMg(CH_3)_3$, $Cu_3Mg_2(CH_3)_7$, and $Cu_2Mg(CH_3)_4$ gave no addition products, and both $Cu_3Mg(CH_3)_5$ (entry 4) and $Cu_4Mg(CH_3)_6$ (entry 5) showed vast improvement in yield over that observed without LiBr (Table I). The reaction with $Cu_6Mg(CH_3)_8$ (entry 6, Table VII) showed only a small improvement in yield in the presence of added LiBr (entry 11, Table I).

$MgBr_2$ and LiBr are known to form $LiMgBr_3$ in THF, and the effect of $MgBr_2$ on the reactions with LiBr was tested in entry 7 (Table VII). The action of $Cu_4Mg(CH_3)_6$ with 6 equiv of PhC≡CH and $MgBr_2$ in addition to 4 equiv of LiBr gave a poor yield of addition product. The yield from this reaction was noticeably less than that obtained for $Cu_4Mg(CH_3)_6$ + $2MgBr_2$ (Table I, entry 9, or Table II, entry 1).

The mechanism by which LiBr affects the reactions of $Cu_3Mg(CH_3)_5$, $Cu_4Mg(CH_3)_6$, and $Cu_6Mg(CH_3)_8$ is unknown. The nearly equal yields and distribution of products from all three reactions may indicate the formation of a common lithium–copper–magnesium ate complex. An infrared study of LiBr + PhC≡CH in THF, similar to that carried out for PhC≡CH + $MgBr_2$, failed to show any interaction between LiBr and PhC≡CH.

Product Distribution of the Reaction of PhC≡CH with $Cu_4Mg(CH_3)_6$, $Cu_6Mg(CH_3)_8$, and "CH_3MgBr" + CuBr. As mentioned previously, β addition to terminal alkynes for the reagent "RMgX" + CuBr has been reported only when R is *tert*-butyl.[10] However, we find that "CH_3MgBr" + CuBr in THF gives a 2:1 ratio of α- to β-addition products. When $Cu_3Mg(CH_3)_5$ and $Cu_4Mg(CH_3)_6$ are allowed to react with PhC≡CH with a PhC≡CH/$MgBr_2$/CH_3 ratio of 1:1:1, β-addition product is obtained. For $Cu_3Mg(CH_3)_5$ (entry 8, Table I) the ratio of α- to β-addition product is 6:1, and for $Cu_4Mg(CH_3)_6$ (entry 10, Table I) the ratio is 3.3:1.

A kinetic analysis of the α- to β-addition product ratio for "CH_3MgBr" + CuBr at -40 °C shows that in the first 90 min the ratio is ≥7[19] and then rapidly drops to an average value of 2.6 at 200 min. A similar behavior is also observed for $Cu_4Mg(CH_3)_6$ + $6MgBr_2$. Here the α/β ratio is 4 after 30 min at -40 °C and rapidly drops to an average ratio of 3 after 60 min. The α- to β-addition ratio of $Cu_6Mg(CH_3)_8$ could not be determined kinetically due to the formation of (*E*)-Ph(CH_3)C=CH(CH_3) in these reactions.

The mechanism controlling the regiochemistry of these reactions is unknown. The difference in regiochemistries for $Cu_4Mg(CH_3)_6$, $Cu_6Mg(CH_3)_8$, and "CH_3MgBr" + CuBr is probably due to differences in the nature of the reagents in the latter stages of reaction. $MgBr_2$ also appears to have an effect on the α/β product ratio, but for reasons that are not apparent.

Stereochemistry of Addition Reactions. The stereochemistry of addition of "RMgX" + CuY to terminal alkynes has been determined to be syn, with only R = *tert*-butyl being an exception.[1] The stereochemistry of α- and β-addition products from reaction of PhC≡CH with $Cu_4Mg(CH_3)_6$ or $Cu_6Mg(CH_3)_8$ was also determined to be syn. The stereochemistries of Ph(CH_3)C=CH(CH_3) and 2,4-diphenyl-2,4-hexadiene were not determined. However, the coupling of organocopper compounds is known to occur with retention of configuration.[10,12] Diene and trisubstituted olefin isolated from the $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ reactions (when they were present) had NMR

---

(18) While this is in opposition to an earlier suggestion, this conclusion is equally consistent with the data. Note also that deprotonation of PhC≡CH by the reagent may cause a substantial decrease in the rate of the addition reaction.

(19) The ratio was 7 at 90 min, but prior to 90 min the β-addition product was present in too small an amount to quantify.

spectra identical with those isolated from the "CH_3MgBr" + CuBr reaction.

Conclusions

The soluble components of the 1:1 "CH_3MgBr"/CuBr mixture in THF responsible for addition to PhC≡CH have been identified as $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$. Although $MgBr_2$ was not found to interact with either reagent or PhC≡CH to a detectable degree, it does exert an influence on the course of the addition reactions. The exact mechanism of $MgBr_2$ involvement was studied by varying the concentrations of $Cu_4Mg(CH_3)_6$, PhC≡CH, and $MgBr_2$. The results were inconclusive but did show that a constant ratio of PhC≡CH to $MgBr_2$ produced the least variation in addition yield and product distribution. A kinetic analysis at −40 °C of the reactions of $Cu_4Mg(CH_3)_6$, $Cu_6Mg(CH_3)_8$, and "CH_3MgBr" + CuBr with PhC≡CH revealed a complex reactivity pattern after the first few hours of reaction.

The α/β product ratio for 1:1 "CH_3MgBr"/CuBr and $Cu_4Mg(CH_3)_6$ was investigated kinetically at −40 °C. The ratio was found to be high initially, but rapidly decreased with time. The β-addition product appears to form because of an alteration of the initial reagent by the product.[17] The α/β ratio for $Cu_6Mg(CH_3)_8$ could not be studied due to the formation of (*E*)-Ph(CH_3)C=CH(CH_3).

One or fewer equivalents of CuBr added to $Cu_4Mg(CH_3)_6$ increased the rate and yield of addition products substantially. This result is important because unreacted CuBr is present in the 1:1 "CH_3MgBr"/CuBr mixture, which contains a 6:1 ratio of $Cu_4Mg(CH_3)_6$ to $Cu_6Mg(CH_3)_8$ after being mixed for 1 h at −25 °C. The unreacted CuBr may be involved in regenerating $Cu_4Mg(CH_3)_6$ from unreactive initially obtained product or in the formation of the more reactive $Cu_6Mg(CH_3)_8$ (eq 11 and 12). The addition of more than 1 equiv of CuBr to $Cu_4Mg(CH_3)_6$ almost completely stopped the addition reaction. This can be accounted for by redistribution between CuBr and $Cu_4Mg(CH_3)_6$ to form unreactive methylcopper.

The addition of LiBr to $CuMg(CH_3)_3$, $Cu_3Mg_2(CH_3)_7$, and $Cu_2Mg(CH_3)_4$ was ineffective in promoting addition to PhC≡CH. However, at a Cu/LiBr ratio of one, $Cu_3Mg(CH_3)_5$, $Cu_4Mg(CH_3)_6$, and $Cu_6Mg(CH_3)_8$ produced nearly the same yield and distribution of addition products. The yield of addition products showed a vast improvement over that of the reaction of $Cu_6Mg(CH_3)_8$ in the absence of LiBr. The results may be interpreted in terms of formation of a single compound distinctly different in nature than the starting reagents.

An investigation is in progress to determine whether the same ate complexes are the reaction intermediates when the alkyl group is other than methyl, and this work is being extended to the synthetically more useful solvent diethyl ether.[10a,11] In addition, $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$ may prove to be more useful reagents for addition reactions with less reactive terminal alkynes than the 1:1 "CH_3MgBr"/CuBr mixture.[10b,20]

Experimental Section

Materials. THF was distilled prior to use from sodium benzophenone ketyl. CuBr was prepared by the reduction of $CuBr_2$ using a known procedure.[21] $(CH_3)_2Mg$ was prepared by reaction of $(CH_3)_2Hg$ with magnesium metal. The solid $(CH_3)_2Mg$ was then dissolved in THF and standardized. "CH_3MgBr" was prepared by gaseous addition of CH_3Br to magnesium metal covered by THF. The resulting solution of "CH_3MgBr" was standardized by magnesium (EDTA), bromide (Volhard titration), and methane after hydrolysis (Toepler pump).

PhC≡CH was obtained commercially (Farchan) and distilled prior to use (bp 137–138 °C). A standard solution of PhC≡CH was prepared in THF and stored under nitrogen in the dark. α-Methylstyrene and β-methylstyrene were obtained commercially (Aldrich) and used without further purification. 2-Phenyl-2-butene was prepared by dehydration of 2-phenyl-2-butanol in refluxing benzene with a catalytic amount of *p*-toluenesulfonic acid. 2-Phenyl-2-butanol was prepared by addition of acetophenone to CH_3CH_2MgBr in diethyl ether. The 2-phenyl-2-butene was purified by chromatography on silica gel with hexane. The resulting liquid was found to contain two components by GLC (25-ft column of TCEP at 115 °C with a flow rate of 70 mL/min). The longer eluting component was collected and identified as Ph(CH_3)C=CH(CH_3).

1,4-Diphenylbutadiyne was prepared by coupling phenylacetylene with basic Cu^{II}.[22] The crude product was crystallized several times from EtOH: mp 85.5–86.5 °C (lit. mp 87–88 °C); NMR ($CDCl_3$) δ 7.7–7.2 (m); IR ($CDCl_3$) 3090, 3070, 3045, 3025, 2230, 2160 cm^{-1}; mass spectrum, *m/e* (relative intensity) 202 (100), 200 (16.4).

(*E,E*)-2,5-Diphenyl-2,4-hexadiene was prepared by reacting a 1:1 "CH_3MgBr"/CuBr mixture with phenylacetylene in THF at −25 °C for 2 h and then stirring it for 24 h at room temperature.[10] Hydrolysis with pH 8 saturated aqueous NH_4Cl and extraction with THF gave a white solid after removal of THF. This solid was crystallized five times from ethanol to give a white crystalline solid: mp 148–149 °C (cor); NMR ($CDCl_3$) δ 7.63–7.17 (m, 10 H), 6.83 (s, 2 H), 2.27 (s, 6 H); IR ($CDCl_3$) 3090, 3065, 3035, 1600 cm^{-1}; mass spectrum, *m/e* (relative intensity) 234 (63), 219 (100), 204 (45).

Typical Procedure for Preparing Copper–Magnesium "Ate" Complexes from CuBr and $(CH_3)_2Mg$. CuBr was added inside a drybox to a tared 50-mL Erlenmeyer flask equipped with a stirring bar or to a 100-mL round-bottomed flask equipped with a stirring bar which was then stoppered with a tared serum cap. The reaction vessel was reweighed and the number of moles of CuBr calculated. THF was then added via syringe to the reaction vessel in such a manner that CuBr clinging to the walls of the vessel could be washed off and included in the CuBr slurry. The reaction vessel was then cooled to the appropriate temperature given in eq 1–6. The appropriate number of moles of $(CH_3)_2Mg$ was then introduced as a solution in THF via syringe. It was critical to maintain virgorous stirring during the addition of $(CH_3)_2Mg$ to ensure a reasonable rate of reaction (usually 0.5–1 h).

$Cu_6Mg(CH_3)_8$ was prepared at −50 °C because of the metastable nature of this compound. With a vigorous rate of stirring the solid CuBr usually reacted completely in 5 min.

Typical Procedure for Reaction of PhC≡CH with Copper–Magnesium "Ate" Complexes. $CuMg(CH_3)_3$, $Cu_3Mg_2(CH_3)_7$, $Cu_2Mg(CH_3)_4$, and $Cu_3Mg(CH_3)_5$ at −25 °C were prepared as above, and any additives were added immediately after all the solid CuBr disappeared. The desired amount of PhC≡CH was then added to the reaction vessel quickly as a room-temperature THF solution with vigorous stirring. The stirring was continued for a few minutes, and the reaction vessel was maintained at −25 °C.

The reactions of $Cu_4Mg(CH_3)_6$ could also be carried out in this fashion, or, alternatively, a stock solution of $Cu_4Mg(CH_3)_6$ was prepared if several reactions were to be performed. In these instances the appropriate amount of $Cu_4Mg(CH_3)_6$ was transfered via syringe (precooled with dry ice) to a reaction vessel containing the PhC≡CH solution and additives at −25 °C. Again, the reaction mixtures were stirred vigorously for a few minutes and then placed in the freezer.

The reaction of $Cu_6Mg(CH_3)_8$ with PhC≡CH had to be carried out immediately after formation of the reagent. Even at −50 °C, a solid precipitate appeared within 5 min after complete reaction of the solid CuBr with $(CH_3)_2Mg$. The reaction mixture was then allowed to warm to −30 °C over a period of 15 min after addition

---

[20] H. Westmijze, J. Meijer, H. J. T. Box, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas* **95**, 299 (1976).

[21] W. C. Fernelius, *Inorg. Synth.*, 2, 1 (1976).

[22] I. D. Campbell and G. Eglinton, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 517.

of $PhC\equiv CH$. The reactions were maintained at −30 °C with stirring for the duration of the reaction.

The reactions with $Cu_3Mg(CH_3)_5$ and $Cu_4Mg(CH_3)_6$ took on a dark brown color 1–2 h after addition of $PhC\equiv CH$. The solutions remained homogeneous in most instances. When a black solid was obtained in the reaction mixture either $Ph(CH_3)C=CH(CH_3)$, $Ph(CH_3)C=CHCH=C(CH_3)Ph$, or $PhC\equiv CCH_3$ was present as a product after hydrolysis.

Occasionally a yellow solid was obtained from the $Cu_3Mg(CH_3)_5$ or $Cu_4Mg(CH_3)_6$ reactions. In one instance this yellow solid was analyzed and found to be $PhC\equiv CCu$.

The reactions of $Cu_6Mg(CH_3)_8$ also imparted a brown color within 0.5 h after $PhC\equiv CH$ addition, but a significant amount of solid was present every time.

The reactions of $CuMg(CH_3)_3$ and $Cu_3Mg_2(CH_3)_7$ remained colorless after $PhC\equiv CH$ addition except when LiBr was present, and then the solutions were yellowish. The reactions of $Cu_2Mg(CH_3)_4$ only imparted a brown color when addition products were present after hydrolysis. A yellow color was obtained after addition of $PhC\equiv CH$ when LiBr was present.

The mass balance of the reaction was dependent on the manner in which hydrolysis and workup were carried out. The optimum hydrolyzing solution was saturated aqueous NH_4Cl (pH 8). This solution rapidly hydrolyzed the initial addition products but did not consistently hydrolyze $PhC\equiv CCu$. It was then necessary to add THF to the reaction vessel and expose the hydrolyzed mixture to air with vigorous stirring. Usually within 15 min to 0.5 h all the yellow solid disappeared, leaving a deep blue aqueous layer and a nearly colorless THF layer. The THF layer was separated from the aqueous layer after the addition of the internal standard as a THF solution.

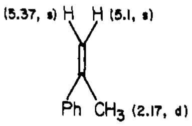
If dilute aqueous HCl (~10%) was used as the hydrolyzing solution, addition products were not reproducibly obtained. If diethyl ether was used as a solvent during oxidative workup with NH_4Cl (pH 8) hydrolysis, the time necessary for complete disappearance of the yellow solid ranged from hours to days. These long workup times allowed significant coupling of the recovered $PhC\equiv CH$ by aqueous Cu^{II}. A measurement of $PhC\equiv CC\equiv CPh$ was then required for a complete mass balance. If the yellow solid was still present when the ether layer was separated and analyzed, a mass balance could not be obtained. The use of diethyl ether did not appear to affect the analysis of addition products.

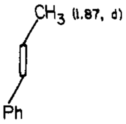
Analysis of Products. The products of the reaction of $PhC\equiv CH$ with copper–magnesium ate complexes were analyzed by GLC. The column, conditions, internal standard, and relative retention time (in parentheses) of the product versus internal standard are reported below.

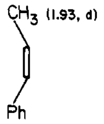
Column A: 20 ft, 15% TCEP, 115 °C with tetradecane as the internal standard for 2-phenylpropene (2.2), phenylacetylene (2.5), 1-phenylpropene (3.3), 2-phenyl-2-butene (3.9), and 1-phenylpropyne (5.0). The 1-phenylpropyne was not quantitized and appeared to account for no more than 5% of the starting phenylacetylene when it was present.

Column B: 4 ft, 8% Apiezon L, 180 °C with anthracene as the internal standard for 1,4-diphenylbutadiyne (1.9) and 2,4-diphenyl-2,4-hexadiene (2.9).

Determination of Reaction Stereochemistry. The stereochemistry of addition to $PhC\equiv CH$ was determined by hydrolysis of the reaction mixture with 2 M DO_2CCH_3, in D_2O. The products were then isolated by preparative GLC on a 18-ft, 10% TCEP column at 120 °C. The NMR assignments of the relevant protons are given below. The vinylic protons of 1-phenylpropene could not be resolved sufficiently to determine the position of deuterium substitution. The doublets due to the methyl group were sufficiently resolved to distinguish between the two isomers. The vinylic protons of 2-phenylpropene were sufficiently resolved to determine which one was substituted with deuterium.







To ensure a high deuterium incorporation in the products, the D_2O–DO_2CCH_3-hydrolyzed reaction mixture had to be stirred for at least 0.5 h under an oxygen-free atmosphere. The amount of deuterium incorporation could be determined by integration of each vinylic proton vs. the methyl group for 2-phenylpropene.

Preparation of 1:1 "CH_3MgBr"/CuBr and Reactions with $PhC\equiv CH$. Solid CuBr was added to a tared reaction vessel inside a drybox and then capped with a tared serum cap. The reaction vessel was reweighed and the number of moles of CuBr calculated. THF was added to the reaction vessel which was then cooled to either −25 or −40 °C. An equimolar amount of "CH_3MgBr" in THF at room temperature was then slowly added via syringe with stirring. The mixture was then stirred for the appropriate amount of time. Some of the CuBr dissolved, and the remainder of the solid imparted a yellow color with time. The "CH_3MgBr" + CuBr mixture was then equilibrated at the desired reaction temperature, and $PhC\equiv CH$ was then added quickly via syringe as a room-temperature THF solution. Stirring was maintained throughout the duration of the reaction. The hydrolysis and workup were identical with those used for the reaction of copper–magnesium ate complexes reported above.

Kinetics of Reaction of $Cu_4Mg(CH_3)_6$, $Cu_6Mg(CH_3)_8$, and "CH_3MgBr" + CuBr with $PhC\equiv CH$ at −40 °C in THF. The copper reagents were prepared as described previously. Phenylacetylene was added as a room-temperature THF solution to the reagents $Cu_4Mg(CH_3)_6$ and "CH_3MgBr" + CuBr which had been allowed to equilibrate to −40 °C. Vigorous stirring was maintained during addition of $PhC\equiv CH$ and throughout the course of the reactions. A separate reaction was run for each time interval, and the entire reaction was quickly hydrolyzed at the end of the time period and worked up as previously described.

Phenylacetylene was added as a room-temperature THF solution to $Cu_6Mg(CH_3)_8$ at −50 °C with stirring. The reaction vessel was then placed immediately in a −40 °C temperature bath and stirring resumed. Time zero was recorded when the reaction was placed in the −40 °C bath. A separate reaction was run for each time interval, and the entire reaction was quickly hydrolyzed at the end of the time interval.

The concentration of the copper–magnesium reagents was not the same for $Cu_4Mg(CH_3)_6$, $Cu_6Mg(CH_3)_8$, and "CH_3MgBr" + CuBr. However, the concentrations of $PhC\equiv CH$ and $MgBr_2$ was constant at 0.1 M in the kinetic studies with $Cu_4Mg(CH_3)_6$ and $Cu_6Mg(CH_3)_8$. The concentration of $PhC\equiv CH$ was 0.1 M for the kinetic study with "CH_3MgBr" + CuBr. (Note: After the "CH_3MgBr" + CuBr reagent was mixed for 1 h at −25° C, almost enough $MgBr_2$ is produced to give a 0.1 M concentration.)

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. I, 98-83-9; II, 873-66-5; III, 536-74-3; IV, 768-00-3; CuBr, 7787-70-4; $(CH_3)_2Mg$, 2999-74-8; CH_3MgBr, 75-16-1; $MgBr_2$, 7789-48-2; 1,4-diphenylbutadiyne, 886-66-8; (*E*,*E*)-2,5-diphenyl-2,4-hexadiene, 16914-12-8.