

TRANSMETALATION. II. A CONVENIENT PREPARATION OF VINYLIC COPPER(I)  
SPECIES FROM ACETYLENES VIA ORGANOZIRCONIUM INTERMEDIATES

Masaaki Yoshifuji, Melanie J. Loots and Jeffrey Schwartz\*

Department of Chemistry, Princeton University,  
Princeton, N.J. 08540 (USA)

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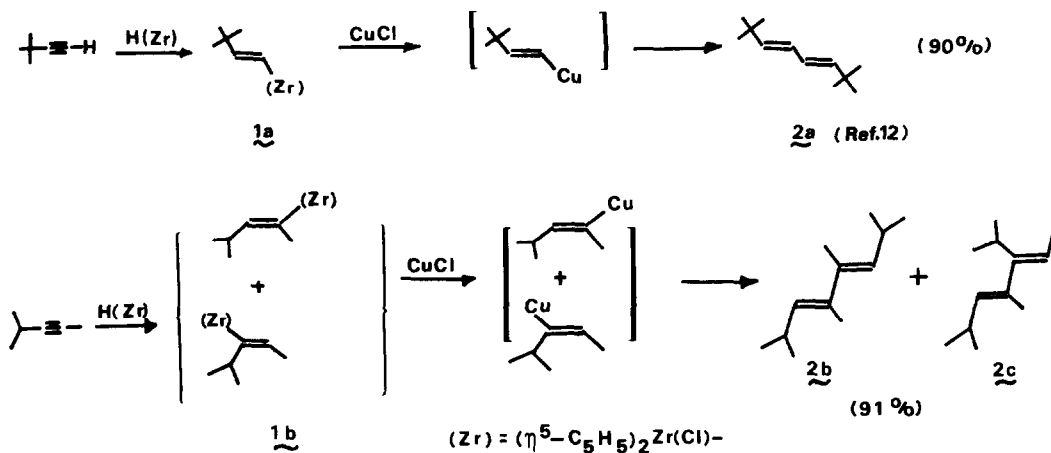
We recently noted (1) that alkyl or alkenyl complexes,  $Cp_2Zr(R)Cl$  ( $Cp = \eta^5-C_5H_5$ ; 1) (2), can give reactive organoaluminum complexes by transmetalation from Zr to Al using  $AlCl_3$ . These latter species, however, are of only limited utility in organic synthesis; we wish to report now that transmetalation of alkenyl ligands from 1 ( $R = \text{alkenyl}$ ) (3) to Cu(I) can be accomplished stereospecifically, in high yield and in straightforward fashion. Alkenylcopper(I) complexes are of demonstrated utility as synthetic intermediates in a variety of processes (4-6); implementing currently available syntheses of these reagents, however, can be tedious (5,7), and hydrozirconation-transmetalation to Cu(I) provides an alternative, convenient route to them (8,9).

Hydrozirconation of acetylenes proceeds readily by stereospecific Zr-H cis addition to the triple bond; unsymmetrical acetylenes add Zr-H with high regioselectivity (10). Transmetalation from Zr to Cu gives alkenylcopper(I) complexes in which this regio- and stereochemistry is maintained, and alkenylcopper(I) species prepared by transmetalation behave analogously to those prepared from vinylic lithium reagents and cuprous halides (7) as is illustrated below.

Addition of 174 mg (0.513 mM) 1a to a suspension of 57.3 mg (0.578 mM)  $CuCl$  in THF (11) (total volume ~ 5 ml) at  $0^\circ$  gave a yellow-green homogeneous solution. Because of the low thermal stability of alkenyl-copper compounds at  $0^\circ$ , the reaction mixture slowly decomposed over a period of 6 hrs (at  $0^\circ$ ) to give a copper mirror and a nearly colorless solution from which diene 2a was obtained in 90% yield by hydrolysis, extraction with pentane, and removal of solvent. A similar reaction performed at  $25^\circ$  instantaneously gave a dark

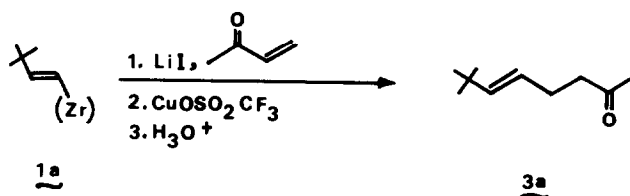
\* Author to whom correspondence should be addressed.

green solution which, on stirring at room temperature for ca. 2 hrs, became nearly colorless with concomitant deposition of a copper mirror. Work-up here, too, gave 2a (90%) (12). Similarly, treatment of 1b with CuCl gave 2b and 2c (>9:<1, 90%), a mixture which reflects the regiocomposition of 1b (13). In cases where it was feasible to quantitatively assay for the stereospecificity of this coupling reaction, for example, for Cp<sub>2</sub>Zr(Cl)-(E-1-propenyl), no loss of stereochemistry in the product diene was observable; only (E,E)-2,4-hexadiene and no (E,Z)-isomer was detected (7). We find, too, that transmetalation from Zr to Cu using CuI proceeds well in sulfolane (to give 2a from 1a in 97% yield as determined by vpc) but poorly in THF (for 2a, 16% yield by vpc); we have also observed that alkenylzirconium(IV) species 1a or 1b react with PdCl<sub>2</sub> in sulfolane to give 2a (62%) and 2b + 2c (57% combined yield) respectively and Pd metal (14).



Preliminary results indicate that alkenylcopper(I) complexes prepared by transmetalation can be captured as "ate" complexes and used subsequently in other carbon-carbon bond-forming reactions well known for these "species", such as alkylation (6) or conjugate addition to  $\alpha,\beta$ -unsaturated ketones (4). Conjugate addition, for example, was best accomplished as follows. Complex 1a (401 mg, 1.18 mmole), LiI (171 mg, 1.28 mmole) and methyl vinyl ketone (125 mg, 1.79 mmole) were dissolved in 10 ml THF. This solution was then cooled to  $-78^\circ$  and to it was quickly added a cold THF solution (at ca.  $-78^\circ$ ) of Cu(OSO<sub>2</sub>CF<sub>3</sub>) (15) (1.20 mmole). The yellow reaction mixture slowly turned orange; after being stirred for 2 hr at  $-78^\circ$  it was warmed to  $-35^\circ$  and was

kept at this temperature overnight. The resulting red reaction mixture was then warmed to room temperature. Hydrolysis, extraction with ether, drying, and removal of solvent gave 3a (73% by vpc) (16,17).



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18. One of us (M.J.L.) acknowledges support as a National Cancer Institute Trainee (1976-7).