

Figure 1. Tris(*N*-methylthioformohydroxamato)iron(III) viewed down the C_3 axis. Principal bond lengths (angstroms) follow: Fe-S, 2.444 (1); Fe-O, 2.010 (1); C(1)-S, 1.681 (2); C(1)-N, 1.295 (2); N-C(2), 1.458(2); N-O, 1.342 (2).

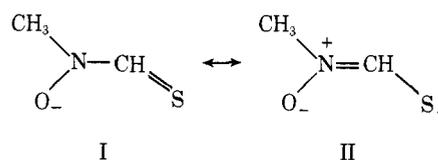
a Philips PW 1100 diffractometer using graphite crystal monochromated Mo $K\alpha$ radiation. The structure was solved by difference Fourier techniques and refined by full-matrix least squares on 1186 reflections (corrected for absorption, $\mu = 15.2 \text{ cm}^{-1}$) with $I \geq 3\sigma(I)$. On crystallization the complex is spontaneously resolved into its enantiomers, all molecules within a crystal being of the same configuration. The absolute configuration in the crystal studied here was established by the anomalous dispersion technique as Λ with final residuals R 0.0205, R_w 0.0191; the alternate Δ configuration had significantly higher residuals, R 0.0449, R_w 0.0480. Recently it has been shown that the Λ and Δ isomers of a related complex, tris(benzothiohydroxamato)iron(III), surprisingly can be resolved and stabilized in chloroform solutions.⁷

Unfortunately, it was not possible to obtain the circular dichroism spectrum of the present Λ isomer to compare with the spectra of $\text{Fe}(\text{PhC}(\text{S})\text{NHO})_3$, on account of the single crystal being too small to obtain a solution sufficiently strong to give a measurable rotation. It was also not possible to distinguish, by eye, crystals of the same chirality to obtain a more concentrated solution. Further, the low solubility of the chelate in organic solvents did not allow separation on an optically active column into the Λ and Δ enantiomers, although, if such a resolution were possible, a full structural determination would still be required on a crystal obtained from one of the solutions.

The molecular structure of the title complex, as shown in Figure 1, has exact C_3 symmetry with a Λ -cis arrangement of the ligands. Interestingly, only the cis geometric isomer has been found in all other tris chelates where the bidentate ligand has an O,S donor set. These include tris(*N,N*-dimethylthiocarbamate)iron(III),⁸ tris(benzohydroxamato)iron(III),⁹ tris(5,5-dimethyl-2-thio-4-phenyl-1-pyrrolidine 1-oxide)-iron(III),¹⁰ and iron(III) tris chelates of substituted thioacetylacetonate ligands.¹¹ It is interesting to note that the specific isomer, Λ -cis, has also been structurally characterized in ferrichrome A¹² and ferrichrysin¹³ in which the chelating groups are hydroxamates. A comparison of the absolute configuration of the naturally occurring fluopsin F with that of the present synthetic chelate would be particularly interesting.

Concerning the structural features, the Fe-S bond length, 2.444 (1) Å, is typical of those found in high-spin tris(dithiocarbamate)iron(III) complexes^{14,15} but is significantly longer than in tris(*N,N*-dimethyl thiocarbamate)iron(III),⁸ 2.413 Å, and tris(1,3-diphenyl-3-thiolprop-2-en-1-one)iron(III),¹¹ 2.368 Å, where the metal chelate rings are four- and six-membered respectively. The Fe-O bond length falls between

the values observed in the latter two complexes. The twist angle¹⁶ of the octahedron is 41.1° . The geometry of the thioformohydroxamate moiety is consistent with the canonical resonance forms I and II. In particular the C(1)-S and N-C(1)



bond lengths (Figure 1) are both indicative of substantial double bond character. In addition, the ligand is planar with the Fe atom 0.38 Å out of the plane.

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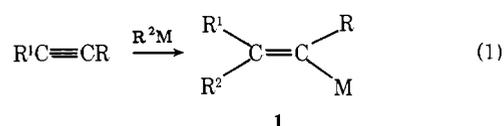
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Controlled Carbometalation. Reaction of Acetylenes with Organoalane-Zirconocene Dichloride Complexes as a Route to Stereo- and Regio-Defined Trisubstituted Olefins¹

Sir:

Over the past few decades, several hydrometalation reactions, such as those involving B,² Al,³ Si,⁴ Sn,⁵ and Zr,⁶ have provided convenient and selective routes to disubstituted olefins. On the other hand, their application to the synthesis of trisubstituted olefins via internal acetylenes is far from being general and satisfactory. An alternate and inherently more attractive approach would be to achieve controlled and selective carbometalation of acetylenes, such as the transformation represented by eq 1.



R = H or organic group; R¹ and R² = organic groups; M = a metal or metal containing group

Aside from highly special examples of much limited synthetic utility,⁷ the reaction of organocoppers of the $\text{RCu}\cdot\text{MgX}_2$ type with terminal acetylenes⁸ appears to be essentially the only known synthetically useful carbometalation of reasonable generality which is capable of converting terminal acetylenes into **1** ($\text{R} = \text{H}$) as discrete, albeit unstable, intermediates. Unfortunately, however, difficulties have been encountered in utilizing methylcopper species as carbometalation agents,⁸ although some promising results have also been reported recently.⁹

We now wish to report our finding that acetylenes react with organometallic reagents obtained by mixing organoalanes with zirconocene dichloride (Cl_2ZrCp_2) to produce selectively alkenyl metals represented by **1** in high yields according to eq 1. Although acetylenes have been polymerized or oligomerized on Ti or V containing catalysts,¹⁰ relatively little is known about the controlled monocarbometalation of acetylenes with reagents containing early transition metals,^{7c,d} and such a transformation with Zr-containing reagents appears totally unprecedented.

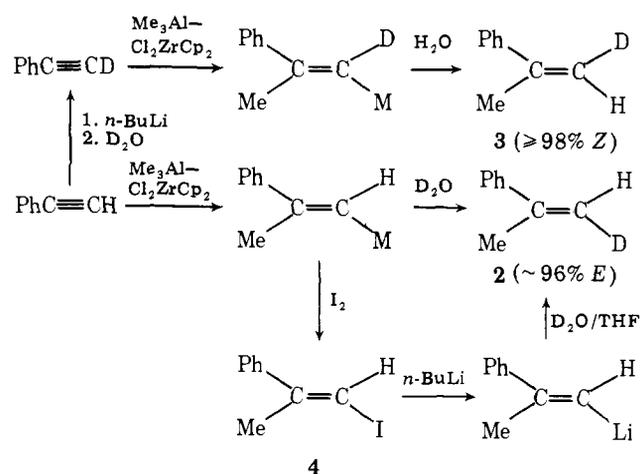
The carbometalation procedure reported here is exceedingly simple and the following is representative. To 2.92 g (10 mmol) of Cl_2ZrCp_2 suspended in 25 mL of 1,2-dichloroethane or dichloromethane was added under an atmosphere of nitrogen 1.44 g (1.92 mL, 20 mmol¹¹) of trimethylalane¹² at 20–25 °C. All of the Cl_2ZrCp_2 dissolved to give a lemon-yellow solution. To this was added at 20–25 °C 1.10 g (1.48 mL, 10 mmol) of 1-octyne. After 3 h, GLC examination of an aliquot quenched with 3 N hydrochloric acid indicated that 2-methyl-1-octene and 2-nonene were formed in quantitative combined yield, the ratio of the two products being 95:5.

If one either omits Cl_2ZrCp_2 or uses aluminum-free $\text{Cl}(\text{Me})\text{ZrCp}_2$,¹³ no more than a trace of 2-methyl-1-octene is formed even after 24 h under otherwise comparable conditions, indicating that both Al and Zr are essential in observing the facile carbometalation reaction. It is worth noting that Me_2ZrCp_2 has been reported to undergo only a slow hydrogen-abstraction reaction with phenylacetylene even in refluxing toluene.¹⁴

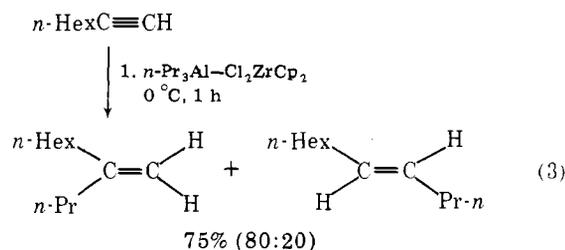
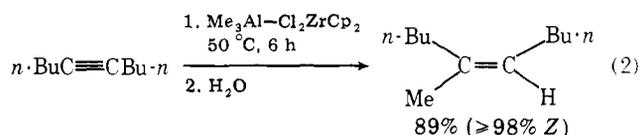
Although the exact structure of the $\text{Me}_3\text{Al}\cdot\text{Cl}_2\text{ZrCp}_2$ reaction product is not clear, the formation of an organozirconium species, which rapidly exchanges the methyl group with methylalanes, has been clearly indicated by ¹H NMR. Thus, whereas the ¹H NMR spectrum of the reaction mixture in 1,2-dichloroethane (30 °C) exhibits only two broad singlets (half-width \approx 4 Hz) for the Me and Cp groups at δ (relative to Me_4Si) -0.41 and 6.30 ppm, respectively, the THF-quenched mixture (THF/ $\text{Me}_3\text{Al} = 1$) shows three sharp Me signals (half-width \approx 1.2 Hz) at δ 0.17, -0.81, and -1.03 ppm and two sharp Cp signals (half-width \approx 1.2 Hz) at δ 6.37 and 6.14 ppm. The chemical shifts and relative intensities indicate that the quenched mixture consists of Cl_2ZrCp_2 , $\text{Cl}(\text{Me})\text{ZrCp}_2$, $\text{Me}_3\text{Al}\cdot\text{THF}$, and $\text{Me}_2\text{AlCl}\cdot\text{THF}$, the $\text{Cl}_2\text{ZrCp}_2/\text{Cl}(\text{Me})\text{ZrCp}_2$ ratio being \sim 1:2. No Me_2ZrCp_2 appears to be present.¹⁵

To establish the stereochemistry of the reaction, phenylacetylene was methyl metalated in a manner similar to that described above and quenched with D_2O . The C_9 products were obtained in 98% combined yield, the ratio of α -methylstyrene to β -methylstyrene being 95:5 in this case as well. The ¹H NMR spectrum of a distilled sample of α -methylstyrene, bp 91–92 °C (59 mm), shows that the area ratio of the β -proton peaks, which are trans and cis to the phenyl group at δ 5.0 and 5.3 ppm,¹⁶ respectively, is 0.04, indicating that the β -deuterio- α -methylstyrene (**2**) is at least 96% *E*. That the stereoselectivity of the carbometalation reaction is actually \geq 98% has been shown by the formation of \geq 98% pure (*Z*)- β -deuterio- α -methylstyrene (**3**) from $>$ 99% pure 2-deuteriophenylacetylene.¹⁷ These results are summarized in Scheme I.

Scheme I

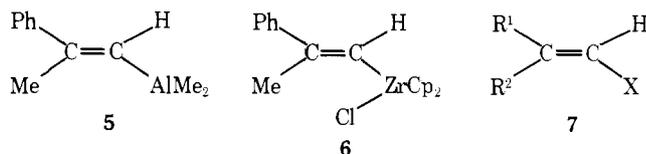


The results summarized in Scheme I not only indicate that the carbometalation reported here presumably involves a clean cis addition, but also strongly suggest that an alkenyl metal species **1** ($\text{R}^1 = \text{Ph}$; $\text{R}^2 = \text{Me}$, and $\text{R} = \text{H}$ or D) is formed as a discrete intermediate which can be transformed further in a separate step. The latter conclusion has been further supported by the preparation of (*E*)- β -iodo- α -methylstyrene¹⁸ (**4**) in 73% isolated yield via methyl metalation-iodinolysis. Essentially the same results were observed even when the iodinolysis was delayed by 24 h (20–25 °C). The carbometalated product is therefore quite stable at room temperature. The stereochemistry of **4** has been unequivocally established by converting **4** to \sim 96% pure **2** via halogen-metal exchange and deuterolysis (Scheme I). Similarly, (*E*)-1-iodo-2-methyl-1-hexene was prepared in 85% isolated yield from 1-hexyne. Another point of significance indicated by the results summarized in Scheme I is that the carbometalation reaction is not complicated by the known hydrogen-abstraction reaction of terminal acetylene with either organozirconium¹⁴ or organoaluminum¹⁹ compounds.



The scope of the carbometalation may be further indicated by the examples shown in eq 2 and 3, as well as a few additional examples in the accompanying communication.²⁰ The results shown in eq 2 indicate that internal acetylenes can also be stereoselectively carbometalated. The stereochemistry of 5-methyl-5-decene has been established by ¹³C NMR, which indicates that the isomeric purity is \geq 98%, as well as by comparing its allylic methyl chemical shift²¹ (δ 1.67 ppm) with that of the *E* isomer (δ 1.60 ppm) prepared in high yield by treating (*E*)-1-iodo-2-methyl-1-hexene, obtained earlier, with *n*-BuLi in ether ($<$ -50 °C, 15 min) followed by addition of THF.²² In the reaction of *n*-Pr₃Al-Cl₂ZrCp₂ with 1-octyne, both the yield and regioselectivity are lower than those in the corresponding reaction of $\text{Me}_3\text{Al}\cdot\text{Cl}_2\text{ZrCp}_2$ ²³ (eq 3). Formation of 1-octene in 20% yield indicates that the reaction presumably is competed by β elimination and hydrozirconation.⁶

The precise mechanism of the carbometalation reported here is not yet clear. However, our preliminary investigation has revealed that the product **1** in the reaction of phenylacetylene with $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ is largely an (*E*)-2-phenylpropenylalane species (~95%) mixed with a minor amount (~5%) of the corresponding organozirconium species. Thus, the ^1H NMR spectrum of the phenylacetylene- $\text{Me}_3\text{Al}-\text{Cl}_2\text{ZrCp}_2$ reaction mixture in CH_2Cl_2 shows two distinct allylic methyl signals at δ 2.35 and 1.93 ppm in the ratio of ~20:1. The ^1H NMR spectra of authentic samples of **5** and **6** prepared by



treating **4** with *n*-BuLi, followed by addition of Me_2AlCl and Cl_2ZrCp_2 , respectively, show their allylic signals at δ 2.35 and 1.93 ppm, respectively. These results not only support the above conclusion, but indicate the following. (1) The interconversion between the organoaluminum and organozirconium species is slow on the NMR time scale, in contrast to the methyl exchange. (2) The propenyl C-1 atom in the products is not bonded simultaneously to both Al and Zr to any detectable extent. The spectroscopic data presented above suggested that the carbometalation reaction might be catalytic with respect to Cl_2ZrCp_2 . Indeed, the reaction of 1 equiv of phenylacetylene with 2 equiv of Me_3Al in the presence of 0.1 equiv of Cl_2ZrCp_2 for 12 h at 25 °C produced, after hydrolysis, α -methylstyrene in 60% yield.

While the scope and the mechanistic details remain to be further explored, it is clear that a novel, selective, and operationally simple route to trisubstituted olefins represented by **7** via carbometalation of $\text{R}^1\text{C}\equiv\text{CH}$ is now at our disposal. Various known reactions of alkenylaluminums,²⁴ including those reported in the accompanying communication,²⁰ point to the potential utility of the alkenyl metal products obtainable by the procedure reported here in the synthesis of trisubstituted olefins.

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- Sadtler NMR Catalog No. 9908.
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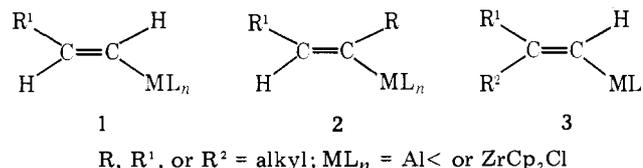
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Double Metal Catalysis in the Cross-Coupling Reaction and Its Application to the Stereo- and Regioselective Synthesis of Trisubstituted Olefins¹

Sir:

We have recently developed highly selective procedures for the synthesis of olefins which involve the reaction of alkenylalanes or alkenylzirconium derivatives (**1**) with unsaturated organic halides in the presence of a Pd^0 -phosphine or Ni^0 -phosphine complex.² While these procedures offer a facile entry into certain disubstituted olefins,² our initial attempts to apply them to the synthesis of trisubstituted olefins via **2** were unsuccessful or unsatisfactory. Particularly frustrating was the generally low reactivity of **3**, which is now readily available via carbometalation as described in the accompanying communication,¹ in the Pd-catalyzed cross-coupling.



To alleviate this difficulty, we turned our attention to a simple but little-tested possibility of doubly or multiply catalyzing the Pd- or Ni-catalyzed cross-coupling reaction³ which presumably proceeds via oxidative addition-transmetalation-reductive elimination.⁴ Since the difficulty appeared largely steric in origin, and since steric acceleration rather than steric hindrance was expected in the reductive elimination step, the difficulty appeared to lie in the transmetalation step.⁵ We further reasoned that, in the catalytic reaction of this nature, the difficulty must be kinetic rather than thermodynamic, and that such a kinetically unfavorable transmetalation process