Scheme I

$$\mathrm{BU} + h\nu\ (254\ \mathrm{nm}) \rightarrow {}^1\mathrm{BU}^*\ (\pi,\pi^*)$$

$${}^1\mathrm{BU}^*\ (\pi,\pi^*) \rightarrow \mathrm{BU},\ \phi = 0.96$$

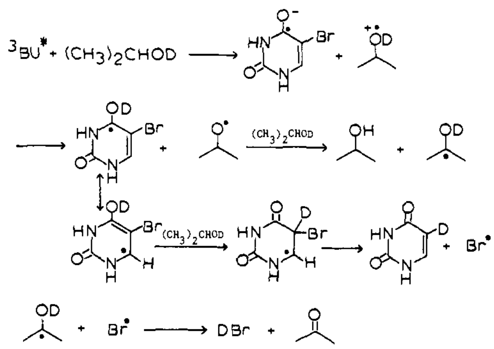
$${}^1\mathrm{BU}^*\ (\pi,\pi^*) \xrightarrow{\text{2-propanol}} \mathrm{U},\ \phi = 0.013$$

$${}^1\mathrm{BU}^*\ (\pi,\pi^*) \rightarrow {}^3\mathrm{BU}^*,\ \phi = 0.03$$

$${}^3\mathrm{BU}^* \xrightarrow{\text{2-propanol}} \mathrm{U},\ \phi = 0.20$$

$${}^3\mathrm{BU}^* \rightarrow \mathrm{BU},\ \phi = 0.80$$

Scheme II



and may also be due to the population of upper excited states.

A kinetic mechanism with quantum yields for the photoreduction of bromouracil to uracil is shown in Scheme I. The efficiency assigned to intersystem crossing of BU in the π,π^* singlet state was calculated as 0.03, assuming that energy transfer from triplet acetone occurs with unit efficiency as suggested by the data in Table II.

Deuterium incorporation in the 5 position of uracil as a function of the position of deuterium in 2-propanol suggests the following: (1) In the π,π^* singlet state BU reacts via homolysis of the vinyl carbon-bromine bond and the resulting vinyl radical is moderately selective in hydrogen atom abstraction. (2) In the reactive triplet state BU undergoes an ionic reaction with 2-propanol most likely via electron transfer. A reasonable mechanism for formation of uracil via initial electron transfer from 2-propanol to triplet BU is shown in Scheme II. The mechanism finds precedent in the photooxidation of alcohols with one-electron photooxidizing agents.[14] Reactivity of BU in the triplet manifold is dramatically sensitive to the oxidation potential or ionization potential of the solvent. Acetone-sensitized irradiation of BU in ethanol solvent leads to no reaction. The ionization potential of 2-propanol is less than the ionization potential of ethanol by 0.35 eV.[15]

The electron-transfer mechanism for the reaction of triplet BU with 2-propanol is analogous to that proposed by Ito, Saito, and Matsuura to explain the acetone-sensitized coupling of BU to tryptophan derivatives.[4] We note, however, that our results suggest that some amino acid residues less easily oxidized than tryptophan or cysteine should be reactive with triplet BU but that intimate association may be required to achieve reasonable efficiency.

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1,1-Dimetalloalkenes Containing Aluminum as Well as Titanium or Zirconium. Their Structures and Use as Novel Alkenylidene and Alkenyl Transfer Agents[1]

Tadao Yoshida and Ei-ichi Negishi*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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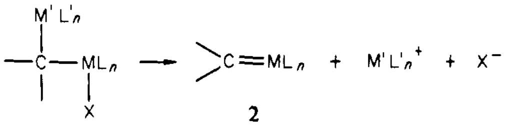
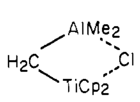
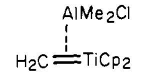
Although β elimination is one of the most commonly employed methods for the formation of the carbon-to-carbon double bond, it has not been adequately developed as a route to metal-containing double bond, i.e., metal-carbene complexes.[2] Conceptually, 1,1-dimetallo derivatives represented by **1** could undergo spontaneous or assisted syn or anti β elimination to metal-carbene complexes (**2**). Indeed, it has recently been reported that **3**



1 **2** (1)



3

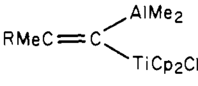


4

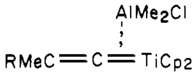
$\mathrm{Cp} = \eta^5\text{-C}_5\mathrm{H}_5$

undergoes a facile olefination reaction of carbonyl compounds and that the results can be interpreted in terms of the intermediacy of an aluminum-stabilized metal-carbene species **4**.[3]

We have previously synthesized 1,1-dimetalloalkenes (**5**) by the reaction of 1-alkynyldimethylalanes with the $\mathrm{Me_3Al\text{-}Cl_2TiCp_2}$ reagent system.[4] Attractive possibilities of probing the potential



5a, R = *n*-Pent
b, R = *n*-Pr



6

significance of hypothetical metal-carbene species **6** through investigation of the stereochemistry of **5** as well as of developing novel alkenylidene transfer agents prompted us to undertake a detailed investigation of **5**.

As briefly described earlier,[4] the reaction of 1-heptynyldimethylalane with an equimolar amount of an apparently homogeneous 1:1 mixture of $\mathrm{Me_3Al}$ and $\mathrm{Cl_2TiCp_2}$ in methylene chloride at room temperature produces **5a** in excellent yield (90-100%), as judged by ^{1}H NMR as well as GLC analysis of the hydrolysis products. Since 2-octenes are not produced in any more than 1% yield, the reaction is ≥99% regioselective. The presence of two metal groups in the terminal position was also indicated by the formation of >95% pure 1,1-dideuterio-2-methylheptene in 85-95% yield on deuterolysis of **5a** with $\mathrm{D_2O}$. Our attempts to selectively remove $\mathrm{Me_2AlCl}$ formed as a byproduct through evaporation did not succeed. However, the use of preformed $\mathrm{Cl(Me)TiCp_2}$ prepared by the method of Clauss and Bestian[5] readily solved this problem. Under these conditions the carbo-

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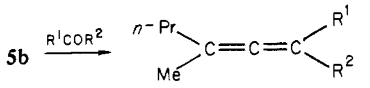
titanation reaction is as fast as when the 1:1 mixture of Me_3Al and Cl_2TiCp is used. For simplification of NMR interpretations, **5b** was prepared in essentially quantitative yield by using Cl(Me)$TiCp_2$ as a carbometalating agent and was used in all subsequent studies.[6]

To establish the relation between **3** and **5** as well as the relevance of our subsequent discussion, we reacted **5b** with cyclohexanone (30 min, 0 °C) and benzaldehyde (30 min, −30 °C) and obtained

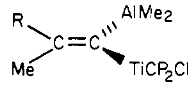


7a, $R^1, R^2 = (CH_2)_5$
b, $R^1 = Ph$; $R^2 = H$

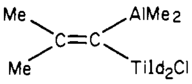
the expected allenes **7a** (bp 69 °C (4 mmHg), $n^{24}{}_D$ 1.4821) and **7b** (bp 77 °C (0.6 mmHg), $n^{19}{}_D$ 1.5409) in 83 and 67% yields, respectively. These results not only demonstrate that **5** indeed exhibits chemical properties similar to those of **3** but represent a novel alkenylidenation reaction of carbonyl compounds.

Prompted by the favorable chemical results, we then looked into the structural aspects of **5**. The compound **5b** displays the following NMR spectra, provided that they are taken immediately after the formation of **5b**:[6] ^{1}H NMR (CH_2Cl_2, Me_4Si) δ −0.67 (s, 6 H), 0.91 (t, J = 7 Hz, 3 H), 1.2–1.7 (m with a singlet at 1.34 ppm, 5 H), 1.90 (t, J = 7 Hz, 2 H) and 5.97 (s, 5 H); ^{13}C NMR[7] (C_6D_6, Me_4Si) δ 14.02, 22.06, 24.67, 41.26, 110.63, 115.64 and 142.09. Significantly, the ^{13}C NMR spectrum displays only one set of signals for **5b**, and the ^{1}H NMR spectrum shows only one relatively sharp singlet at 1.34 ppm for the allylic methyl protons. Lowering the ^{1}H NMR temperature to −110 °C does not cause any splitting. On standing **5b** for 2 h at room temperature, however, a new set of seven ^{13}C NMR peaks emerge.[7] The three new sp^2 hybridized carbon signals appear slightly upfield (0.24–1.06 ppm) relative to what appear to be the corresponding original peaks. The ^{1}H NMR spectrum taken at this time shows the emergence of a singlet at 1.79 ppm at the expense of the singlet at 1.34 ppm, the relative intensity of the latter to the former being ca. 60:40. Further examination of the compound by NMR is complicated by a slow decomposition reaction of unknown nature, but the above isomer ratio does not appear to change significantly. That the compound exhibiting a singlet at 1.79 ppm is the stereoisomer of **5b** has been established by its independent synthesis in 45% yield by the reaction of 1-propynyldimethylalane with Cl(n-Pr)$TiCp_2$. The product not only displays the same ^{1}H NMR peaks but also produces **7a** on reaction with cyclohexanone. These NMR observations indicate the following. First, **5b** is formed as a single stereoisomer which is probably the E isomer based on the known stereochemistry of the carbotitanation of simple acetylenes[4] as well as the NMR spectral data. Secondly, **5b** undergoes a relatively slow stereoisomerization leading to a ca. 60:40 mixture of the E and Z isomers. In the equilibrating mixture, however, no species other than the E and Z isomers of **5b** appears to be present in readily detectable quantities.

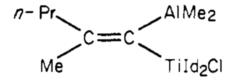
Three possible pathways for the stereoisomerization deserve our attention. One involves a trivial disproportionation via transmetalation of **5**. Disproportionation of coordinatively unsaturated organometallic species via transmetalation is a ubiquitous process. The other two more exciting possibilities involve the formation of a metal–carbene complex **4**[3] and the unimolecular rotation via **8**. Nonplanar structures similar to **8** have recently been suggested as the ground-state structures for certain 1,1-dimetallo derivatives containing two coordinatively unsaturated metal atoms.[8]



8



9 (Id = η^5-indenyl)



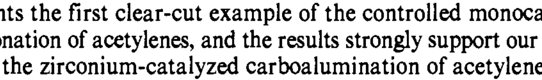
10

Cl(Me)$TiId_2$

11

The disproportionation path may be ruled out on the following ground. We prepared **9** and **10** by the carbotitanation of alkynyldimethylalanes with **11** which, in turn, was prepared by reacting Cl_2TiId_2[9] with Me_3Al in a manner similar to that reported[5] for Cl(Me)$TiCp_2$. The ^{1}H NMR signals of the allylic methyl groups of **9** appear at 1.46 and 1.60 ppm and that of **10** immediately after its generation appears at 1.48 ppm. A close examination by ^{1}H NMR of a 1:1 mixture of **5b** and **9** reveals that there is no indication for disproportionation via 1,1-dialumino and 1,1-dititano species, such as the formation of **10**. Although neither of the other two possibilities can be ruled out at this time, it seems certain that the observed stereoisomerization involves an interesting novel species, i.e., **4** or **8**.

We have also studied a related carbometalation of 1-pentynyldimethylalane with either a 1:1 mixture of Me_3Al and Cl_2ZrCp_2 or Cl(Me)$ZrCp_2$ obtained by the method of Surtees.[10] The reaction produces a single stereoisomer of **12** in essentially quantitative yield. The reaction shown in eq 2, we believe, represents the first clear-cut example of the controlled monocarbozirconation of acetylenes, and the results strongly support our view that the zirconium-catalyzed carboalumination of acetylenes reported recently by us[12] involves an aluminum-assisted carbozirconation as a crucial step.



$$n\text{-PrC}\equiv\text{CAlMe}_2 \xrightarrow{\text{Cl(Me)ZrCp}_2} n\text{-Pr(Me)C}=\text{C}\begin{matrix}\text{AlMe}_2\\ \text{ZrCp}_2\text{Cl}\end{matrix} \quad (2)$$

12

Despite the similarity in the mode of formation, **5** and **12** display a remarkable contrast. Unlike **5**, **12** is a stereochemically rigid species at room temperature (>48 h). The reaction of **12** with cyclohexanone is sluggish and does not produce **7a**. While the reaction of **5** with I_2 produces iodinated alkenes only in low yields (<20% each), the corresponding reaction of **12** with 2 equiv of I_2 cleanly gives 1,1-diiodo-2-methyl-1-pentene in 92% yield. Prompted by the stereochemically rigid nature of **12**, we have made a brief attempt to differentiate the two metal groups. Indeed, the reaction of **12** with acetyl chloride in the presence of $AlCl_3$ gives a 92:8 mixture of (Z)- and (E)-4-methyl-3-hepten-2-one in 61% yield. These results seem to point to an attractive possibility of developing novel and selective syntheses of tri- and tetrasubstituted olefins by using **12** or other related 1,1-dimetallo alkenes.

Acknowledgment. We thank the National Institutes of Health and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Professor P. von R. Schleyer for a helpful suggestion.

Supplementary Material Available: ^{1}H NMR and IR data on **5**, **7**, **9–12** (1 page). Ordering information is given on any current masthead page.

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(6) The following additional data have been obtained: IR(CH_2Cl_2) 3060 (m), 2950 (s), 2300 (m), 1560 (w), 1450 (m), 1260 (s), 1020 (m), 900 (m), 820 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{26}AlClTi$: C, 61.3; H, 7.38. Found: C, 59.1; H, 7.52. The IR absorption at 2300 cm^{-1} remains unassigned. The low value for carbon content must, in part, be due to partial oxidation during the analysis. The compound is a brown solid, but no attempt to take the melting point has been made because of its high sensitivity to air.

(7) The signal for the aluminum-bound methyl carbons is not readily discernible.

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(11) ^{1}H NMR (C_6H_6, Me_4Si) −0.31 (s, 6 H), 0.90 (t, J = 7 Hz, 3 H), 1.1–1.6 (m, with a peak at 1.42 ppm, 5 H), 2.0A (t, J = 7 Hz, 2 H) and 5.68 (s, 10 H); ^{13}C NMR[7] (C_6D_6, Me_4Si) δ 14.10, 22.45, 28.12, 44.39, 106.92, 109.59, and 153.09; IR (CH_2Cl_2) 3060 (m), 2950 (s), 2300 (m), 1560 (m), 1450 (s), 1260 (s), 1030 (s), 900 (s), 800 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{26}AlClZr$: C, 54.6; H, 6.57. Found: C, 53.8; H, 6.37.

(12) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252–2254.