calculations of the ZFS parameters using simple Hückel wave functions afford permissive support. For this purpose, we assume that only the dipolar coupling contributes significantly to the ZFS and that spin-orbit effects can be neglected. All the component two-center integrals of the expectation value $\langle D \rangle$ are evaluated by the point-charge approximation of McWeeny,[15] but all three- and four-center integrals are neglected.[13] We calibrate this highly approximate method by calculations of $|D|/hc$ for three known triplet biradicals, trimethylenemethane (TMM), tetramethyleneethane (TME), and 1,8-dimethylenenaphthalene (DMN) as 0.052, 0.049, and 0.040 cm^{-1}, respectively.[16] The corresponding experimental values are 0.024,[17] 0.020,[18] and 0.022[19] cm^{-1}. Clearly, the method tends to overestimate the D values by roughly a factor of 2. Since integral values obtained by the point charge method[15] agree quite well with those obtained[13] by rigorous numerical methods, the evaluation of the integrals probably is not the source of the high D estimates. A more probable origin of the discrepancies is in the use of single configuration wave functions. Other studies[13] have indicated the importance of configuration interaction in the accurate calculation of ZFS parameters.

Values of $|D|/hc$ for **3a**, **3b**, and **3d** calculated by the present approximate method are 0.070, 0.046, and 0.032 cm^{-1}, respectively. Scaling the **3b** value to the above results for TMM, TME, and DMN, we obtain a predicted value of 0.023 cm^{-1}, in good agreement with experiment. The results also suggest that the experimental $|D|/hc$ values for the triplet biradicals (**3a** and **3d**) of *m*-quinone and *m*-quinodimethane should be, respectively, larger and smaller than that of **3b**.

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(4) Satisfactory combustion analysis and mass spectrometric molecular weight.

(5) ^1H NMR (270 MHz, δ units): 7.64 (H_4, 1 H, d × d, J = 2.199, 5.133); 5.76 (H_3, 1 H, d, J = 5.133); 5.27 ($=CH_2$, 2 H, s); 3.04 (bridgehead methine, 1 H, m, including J = 2.199); 2.76 (bridgehead methine, 1 H, m). ^{13}C NMR (proton splittings by off-resonance decoupling): 27.46 (d); 30.03 (d); 99.62 (t); 128.92 (d); 145.28 (s); 160.20 (d), 204.00 (s). IR (neat film, cm^{-1}): 3100–2800, 1700, 1556.

(6) Purified by gas chromatography at 60 °C on SE-30 or OV-17 columns, injector and detector at 100 °C.

(7) Identified by NMR and mass spectroscopy.

(8) Independently synthesized from *m*-hydroxybenzyl alcohol[9] by successive methanesulfonylation, treatment with the appropriate alkoxide ($HOCH_2CH_2ONa$ or MeONa), and saponification.

(9) Aldrich Chemical Co.

(10) Using the method of P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **41,** 379 (1964), as programmed for a Wang calculator by Professor J. M. McBride, to whom we are indebted.

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(16) For $|E|/hc$ of TMM, TME, DMN, **3a, 3b,** and **3c,** we obtain 0, 0.0019, 0.0077, 0.0054, 0.0012, and 0.0047 cm^{-1}, respectively. Calculated values for E generally are less reliable than for D[13] and thus are not useful here for structural assignment.

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(18) Since our calculation treats TME as a planar (D_{2h}) structure, we give the experimental value of $|D|/hc$ for 2,3-dimethylenecyclohexa-1,4-diyl (W. R. Roth and G. Erker, *Angew. Chem., Int. Ed. Engl.*, **12,** 503 (1973)), which should be nearly planar. The value for TME itself, which could be twisted out of planarity (see D. A. Dixon, R. Foster, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100,** 1359 (1978)), is 0.012 cm^{-1} (P. Dowd, *J. Am. Chem. Soc.*, **92,** 1066 (1970)).

(19) R. Pagni, M. N. Burnett, and J. R. Dodd, *J. Am. Chem. Soc.*, **99,** 1972 (1977).

(20) Dox Graduate Fellow, 1978–1979.

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Received April 23, 1979

Rapid Selective Dimerization of Ethylene to 1-Butene by a Tantalum Catalyst and a New Mechanism for Ethylene Oligomerization

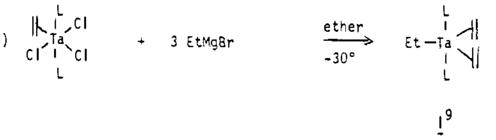
Sir:

Some time ago we found that $Ta(CH_2CMe_3)_3(CHCMe_3)$,[1] at least 2 mol of PMe_3, and ethylene (40 psi) in pentane at 25 °C produced a homogenous catalyst which rapidly dimerized ethylene selectively to 1-butene. Since such selectivity is rare,[2] we set out to find a plausible explanation. We believe the C_4 chain does not form by "insertion of ethylene into a metal-ethyl bond" but via a metallacyclopentane intermediate.

$Ta(CH_2CMe_3)_3(CHCMe_3)$ reacts with PMe_3 (L) to give $Ta(CHCMe_3)_2L_2(CH_2CMe_3)$.[3] This molecule probably has a trigonal-bipyramidal structure similar to that recently found for $Ta(CHCMe_3)_2L_2(mesityl)$[4] (axial L's and two different neopentylidene ligands which lie in the trigonal plane). It reacts rapidly with ethylene (30 psi) in pentane to give 3 mol of neopentylethylene,[5] one of two "normal" products of neopentylidene cleavage by ethylene,[6,7] and a catalyst which will dimerize ethylene to 1-butene at a rate of ~0.5 turnovers/metal·min at 0 °C; essentially no internal butenes are produced and longer chain products do not appear until 1-butene is virtually the solvent. Removing all volatiles from a typical catalytic reaction at 0 °C leaves a red-brown oil which by ^{13}C NMR (67.89 MHz) contains largely two organometallic compounds in approximately a 70:30 ratio. The same two (in a variable ratio) are seen by ^{13}C NMR in a functioning catalytic reaction in toluene-d_8 at −20 °C. They are extremely soluble in pentane and will not crystallize readily, even at −78 °C.

The reaction between blue $Ta(C_2H_4)L_2Cl_3$[8] and 3 mol of EtMgBr gives what is clearly a close relative of the major organometallic component of the catalytic reaction (**1**, eq 1). The characteristic "virtual" triplet pattern for the PMe_3 ligands in the ^1H or ^{13}C NMR spectrum suggests that **1** is also a tri-

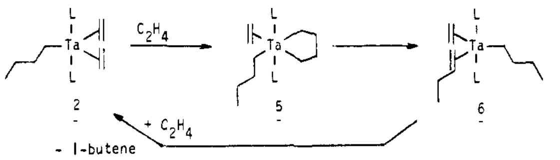
(1)



1[9]

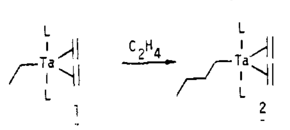
0002-7863/79/1501-5099$01.00/0

Scheme I. The Simplest Proposed Ethylene Dimerization Mechanism



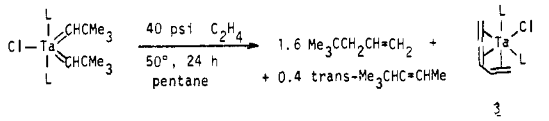
gonal-bipyramidal molecule with axial PMe_3 ligands. The equatorial ethylene ligands must not be rotating rapidly on the ^1H NMR time scale since two types of ethylene protons are found at τ 9.52 and 10.29 at 25 °C. However, the ^{13}C NMR spectrum at −25 and 25 °C shows only one type of ethylene carbon atom. Consequently (barring an unlikely accidental degeneracy) the ethylenes' C═C axes must be oriented perpendicular to the trigonal plane. This is what would be expected since an olefin ligand's MC_2 plane must orient perpendicular to an alkylidene ligand's MCHR plane in an equivalent coordination site in order to utilize the same metal π orbitals.[10] The reaction of **1** with ethylene gives the dimerization catalyst mixture containing the same two organometallic components. We propose that the major component is the analogous *n*-butyl complex, **2** (eq 2), based on the similarity of its ^{13}C NMR spectrum[11] to that of **1**; the minor component still has not been identified.

(2)



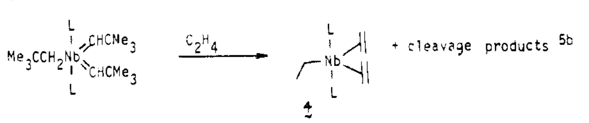
$Ta(CHCMe_3)_2L_2Cl^3$ reacts much less readily with ethylene than $Ta(CHCMe_3)_2L_2(CH_2CMe_3)$ to give the butadiene complex, **3** (one possible structure is shown; eq 3).[12] 1-Butene and some 2-butene are formed catalytically but at a rate which is *at least* 10^2 times slower than that of the system containing **2**.

(3)



$Nb(CHCMe_3)_2(PMe_3)_2(CH_2CMe_3)^3$ reacts immediately with ethylene to give cleavage products[5b] and a solution which does not dimerize ethylene rapidly. This solution contains largely, if not solely, **4** by ^1H and ^{13}C NMR (eq 4). It can be isolated from this mixture and also can be prepared by other routes.[13]

(4)



We know that tantalum-metallacyclopentane complexes[6,14] can form from olefin complexes[15] and that double β-hydride eliminations therefrom yields butadiene complexes.[16] Therefore we propose that the butyl and butadiene ligands in **2** and **3**, respectively, are formed via metallacyclopentane intermediates, and that **2** also reacts with ethylene to give a metallacyclopentane intermediate. We have evidence that niobacyclopentane complexes do not form nearly so readily as tantallacyclopentane complexes[6] and we believe this is why **4** is formed instead of the butyl derivative analogous to **2**.

The mechanism that we propose for dimerizing ethylene is shown in Scheme I. (One involving monophosphine intermediates is also possible[17] but, we feel, less likely.) We suggest a necessary but not sufficient condition for forming a metallacyclopentane from two ethylene ligands is that the angle between their two coordination sites be 80–90° in order that the C_α–M–C_α angle in the resulting metallacycle (e.g., **5**) be on that order.[15,18] (A metallacycle cannot readily form in **2** unless one L and one ethylene exchange positions.) Stable relatives of **5** are known (*trans,mer*-$Ta(C_2H_4)(PMe_3)_2Cl_3$[8] and $Ta(C_2H_4)(PMe_3)_2(C_2H_5)_2Cl$[19]) but $Ta(C_2H_4)(PMe_3)_2(C_2H_5)_3$, a plausible intermediate in the reaction to give **1** (eq 1), decomposes readily. Therefore a β hydrogen should transfer readily from the butyl ligand in **5** to one metallacycle α-carbon atom; the alternative, transfer from the metallacycle to the butyl or ethylene ligand, should be relatively slow.[20] (The rates of olefin dimerization reactions where β-hydrogen transfer from the metallacycle is the rate-determining step are in fact slow ($k \approx 10^{-4}$ s^{-1} at 30 °C)[14,21] compared with the rate of dimerization found here.) Finally, we know that ethylene can displace less strongly bound olefins without forming a metallacycle in complexes of the type $Ta(\eta^5\text{-}C_5Me_5)Cl_2(\text{olefin})$.[15] Therefore we propose **6** → **2**. Since **2** is observed under catalytic conditions, the step **2** → **5** must be the slowest. We believe it is this type of step which is prohibitively slow when the metal is niobium.

The metallacycle mechanism proposed here is a plausible alternative to direct insertion of ethylene into a metal-ethyl bond whenever such insertion is not expected to be fast and/or when metals in lower oxidation states can be formally "oxidized" by forming a metallacyclopentane complex.[22] If 1-butene is *not* displaced, but forms a "mixed" (1-butene-ethylene) metallacycle,[15] then the next higher olefin can form. If each mixed metallacycle is α substituted, then only linear terminal α olefins will form and, in the extreme, polyethylene.

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(2) (a) Later transition metals such as Co[2b] or Rh[2c] will dimerize ethylene to 1-butene, but they rapidly isomerize the 1-butene to a mixture of *cis*- and *trans*-2-butene under the reaction conditions.[2d] Therefore these dimerizations are "selective" for C_4 but not for any isomer. Early transition metals, perhaps the most successful of which has been Ti,[2e,1] will dimerize ethylene to 1-butene (and will not subsequently isomerize the 1-butene) sometimes quite selectively.[2d,e] More often significant amounts of higher boiling products (1-hexene, 1-octene, etc.) or polyethylene are formed. (b) Pu, L. S.; Yamamoto, A; Ikeda, S. *J. Am. Chem. Soc.* **1968,** *90*, 7170–1. (c) Cramer, R. *J. Am. Chem. Soc.* **1965,** *87*, 4717–27. (d) Lefebvre, G.; Chauvin, Y. In "Aspects of Homogeneous Catalysis", R. Ugo, Ed.; Carlo-Manfredi: Editore-Milano, 1970; pp 107–201, Vol. I, and references therein. (e) Farina, M.; Ragazzini, M. *Chem. Ind.* (*London*) **1958,** *40*, 816. (f) Bestian, H.; Clauss, K.; Jensen, H; Prinz, E. *Angew. Chem., Int. Ed. Engl.* **1963,** *2*, 32–41.

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(5) (a) How the neopentyl group is converted into neopentylethylene is a subject that we will treat elsewhere. We believe the neopentyl group at some point donates an α proton to some acceptor (ethylene or the α carbon of a metallacyclobutane) and is thereby converted into a neopentylidene ligand, a process which is related to the β-hydrogen transfers that we will be talking about here. Consistent with this postulate (but not definitive) is the finding that $Ta(CHCMe_3)_2(PMe_3)_2(CD_2CMe_3)$ yields a 1:1 mixture of neopentylethylene-d_0 and -d_1 containing <5% (if any) neopentylethylene-d_2. (b) $Nb(CHCMe_3)_2L_2(CH_2CMe_3)$ and C_2H_4 give 2.11 equiv of $Me_3CCH_2CH{=}CH_2$, 0.07 equiv of *trans*-$Me_3CHC{=}CHMe$, 0.54 equiv of neopentane, and 0.15 equiv of *trans*-$Me_3CHC{=}CHCMe_3$. The last is a common decomposition product of neopentylidene complexes.

(6) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977,** *99*, 3519–20.

(7) The other common product is the internal olefin, *trans*-4,4-dimethyl-2-pentene. This isomer predominates (~90%) when octahedral neopentylidene complexes of the type *trans,mer*-$Ta(CHCMe_3)Cl_3(PMe_3)_2$ react with ethylene (G.A.R., unpublished results).

(8) *trans,mer* $Ta(C_2H_4)(PMe_3)_2Cl_3$ is the organometallic product of the reaction described in note 7. Anal. Calcd for $TaC_8H_{22}P_2Cl_3$: C, 20.56; H, 4.74. Found: C, 20.64; H, 4.08.

(9) Anal. Calcd for $TaC_{12}H_{31}P_2$: C, 34.46; H, 7.46. Found: C, 34.58; H, 7.68.

$^{13}\mathrm{C}$ NMR (ppm from $\mathrm{Me_4Si}$, $\mathrm{C_6D_6}$, +10 °C, 67.89 MHz): 36.9 (t, $J_{\mathrm{CH}} = 128$ Hz, $\mathit{C}\mathrm{H_2CH_3}$), 36.4 (tt, $J_{\mathrm{CH}} = 150$, $J_{\mathrm{CP}} = 7.3$ Hz, $\mathrm{C_2H_4}$), 14.1 (qt, $J_{\mathrm{CH}} = 128$, $J_{\mathrm{CP}} = 9.5$ Hz, $\mathrm{PMe_3}$), −2.3 (q, $J_{\mathrm{CH}} = 123$ Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$). $^1\mathrm{H}$ NMR (τ, $\mathrm{C_6D_6}$, 270 MHz): 8.85 (t, 18, $J_{\mathrm{PH}} = 2.4$ Hz, $\mathrm{PMe_3}$), 9.13 (qt. $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, $J_{\mathrm{PH}} = 23.8$, $J_{\mathrm{HH}} = 8.0$ Hz), 9.48 (m, $\mathrm{C_2}\mathit{H}_2\mathrm{H_2'}$), 10.29 (m, $\mathrm{C_2H_2}\mathit{H}_2'$), 11.00 (t, $\mathrm{CH_2C}\mathit{H}_3$, $J_{\mathrm{HH}} = 8.0$ Hz). Mol wt (cyclohexane): calcd, 418; found, 372.

(10) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenburger, L. J. *J. Am. Chem. Soc.* **1978,** *100*, 3793–3800, and references therein.

(11) $\mathrm{Ta(C_2H_4)_2(}n\mathrm{\text{-}butyl)(PMe_3)_2}$ $^{13}\mathrm{C}$ NMR (ppm from $\mathrm{Me_4Si}$, toluene-d_8, −20 °C, 67.89 MHz): 52.6 (tt, $J_{\mathrm{CH}} = 118$, $J_{\mathrm{CP}} = 4.4$ Hz, $\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 39.4 (tt, $J_{\mathrm{CH}} = 145$, $J_{\mathrm{PC}} = 7.3$ Hz, $\mathrm{C_2H_4}$), 33.5 (t, $J_{\mathrm{CH}} = 124$ Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 28.2 (t, $J_{\mathrm{CH}} = 124$ Hz, $\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 14.7 (qt, $J_{\mathrm{CH}} = 128$, $J_{\mathrm{CP}} \approx 11$ Hz, $\mathrm{PMe_3}$), 12.7 (q, $J_{\mathrm{CH}} = 124$ Hz, $\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$).

(12) $\mathrm{Ta(C_2H_4)(C_4H_6)Cl(PMe_3)_2}$ $^{13}\mathrm{C}$ NMR (ppm from $\mathrm{Me_4Si}$, toluene-d_8, −30 °C, 67.89 MHz): 94.9 (d, $J_{\mathrm{CH}} = 160$ Hz, $\mathrm{CH_2{=}}\mathit{C}\mathrm{HCH{=}CH_2}$), 92.6 (d, $J_{\mathrm{CH}} = 163$ Hz, $\mathrm{CH_2{=}CH}\mathit{C}\mathrm{H{=}CH_2}$), 51.8 (tt, $J_{\mathrm{CH}} = 147$, $J_{\mathrm{CP}} = 5.6$ Hz, $\mathit{C}\mathrm{H_2{=}CH_2}$), 43.4 (ddd, $J_{\mathrm{CH}} = 156$, $J_{\mathrm{CH'}} = 148$, $J_{\mathrm{CP}} = 5.7$ Hz, $\mathit{C}\mathrm{H_2{=}CHCH{=}CH_2}$), 34.8 (ddd, $J_{\mathrm{CH}} = 141$, $J_{\mathrm{CH'}} = 149$, $J_{\mathrm{CP}} = 7.8$ Hz, $\mathrm{CH_2{=}CHCH{=}}\mathit{C}\mathrm{H_2}$), 30.2 (td, $J_{\mathrm{CH}} \approx 150$, $J_{\mathrm{CP}} = 8.2$ Hz, $\mathrm{CH_2{=}}\mathit{C}\mathrm{H_2}$), 14.9 (qd, $J_{\mathrm{CH}} \approx 130$, $J_{\mathrm{CP}} = 21.6$ Hz, $\mathrm{PMe_3}$), 13.5 (qd, $J_{\mathrm{CH}} \approx 130$, $J_{\mathrm{CP}} = 23.3$ Hz, $\mathrm{PMe_3}$).

(13) $\mathrm{Nb(C_2H_4)_2(PMe_3)_2(C_2H_5)}$ can be prepared in low yield by reacting $\mathrm{MgEt_2}$ (dioxane) (2.5 equiv) with $\mathrm{NbCl_5}$ (1 equiv) and $\mathrm{PMe_3}$ (2.1 equiv) in $\mathrm{Et_2O}$ at −78 °C. A better yield is obtained when $\mathrm{Nb(CH_2CMe_3)_2(C_2H_5)_3}$ decomposes in ether in the presence of 2.1 equiv of $\mathrm{PMe_3}$. $^{13}\mathrm{C}$ NMR (ppm from $\mathrm{Me_4Si}$, toluene-d_8, −10 °C, 15 MHz): 35.1 (tt, $J_{\mathrm{CH}} = 149$, $J_{\mathrm{CP}} = 7.3$ Hz, $\mathrm{C_2H_4}$), 30.8 (br t, $J_{\mathrm{CH}} = 134$ Hz, $\mathit{C}\mathrm{H_2CH_3}$), 14.2 (qt, $J_{\mathrm{CH}} = 127$, $J_{\mathrm{CP}} = 7.3$ Hz, $\mathrm{PMe_3}$), −0.97 (q, $J_{\mathrm{CH}} = 121$ Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$).

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(16) Heating $(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Me_2}\overline{\mathrm{TaCH_2CH_2CH_2CH_2}}$[15] in pentane under $\mathrm{C_2H_4}$ to 50 °C for 6 h yields $(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{butadiene})\underline{\mathrm{TaCH_2CH_2CH_2CH_2}}$: S. J. McLain, unpublished results.

(17) We have shown that free L exchanges with coordinated L at 25–100 °C on the NMR scale in all such five-coordinate molecules (bisneopentylidene–tantalum complexes included) and that the rate is fastest in more crowded molecules of a given type. In relatively uncrowded $\mathrm{Ta(C_2H_4)_2L_2Et}$, however, the exchange rate is fast at 25 °C. We are presently investigating these exchange reactions in more detail.

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(19) Green $\mathrm{Ta(C_2H_4)(PMe_3)_2(C_2H_5)_2Cl}$ (probably trans,trans) can be prepared readily from *trans,mer*-$\mathrm{Ta(C_2H_4)(PMe_3)_2Cl_3}$ and 2 mol of EtMgCl at −78 °C in ether. So far this complex has not been obtained pure; it is mixed with 5–10% of the monoethyl analogue.

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(22) It is almost certainly true that ethylene can rapidly insert into a Ti–alkyl bond[21] (the Cossee mechanism[23]) and probably into other metal–alkyl bonds (V and Cr). (It is interesting, however, to note that V and Cr catalysts are believed to be most active in the +2 oxidation state.[24]) Variations of this metallacyclopentane proposal are possible. For example, the crucial intermediate in Cramer's ethylene dimerization system[2c] could well be $[\mathrm{Cl_3(C_2H_4)}\overline{\mathrm{RhCH_2CH_2CH_2CH_2}}]^{2-}$ and $[\mathrm{Rh(butyl)Cl_3(C_2H_4)(solvent)}]^{-}$ the result of protonating the metallacycle at C_α.

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(25) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978–1983.

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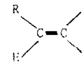
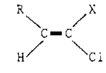
α-Chloroalkenylalanates. Their Preparation and Conversion into (*E*)-1-Chloro-1-alkenes and Mixed 1,1-Dihalo-1-alkenes

Sir:

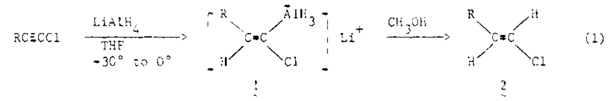
A number of years ago we revealed that preparation of the synthetically valuable α-haloalkenylboranes may be readily achieved through hydroboration of 1-halo-1-alkynes with dialkylboranes.[1] Unfortunately, attempts to synthesize the corresponding α-haloalkenylalanates via the reaction of 1-halo-1-alkynes with diisobutylaluminum hydride were unsuccessful.[2] However, since the trifunctional α-halovinylalanyl moiety represents a uniquely constituted synthon for substituted olefins, we continued to search for suitable approaches for its preparation.

Table I. Yields of (*E*)-1-Chloro-1-alkenes and (*Z*)-1-Halo-1-chloro-1-alkenes from 1-Chloro-1-alkynes[a]

RC≡CCl R=	, %	X=	, %[b]
n-$\mathrm{C_4H_9}$	(96)	Br	78
		I	85
n-$\mathrm{C_6H_{13}}$	80	Br	80
		I	86
	(93)	Br	87
		I	89
t-$\mathrm{C_4H_9}$	(76)	Br	61
$\mathrm{THPO(CH_2)_3}$	(95)	Br	86[c]

[a] The numbers in parentheses are GLC yields. [b] The NMR and mass spectral data are consistent with the assigned structures. [c] The structural assignment follows from the stereochemical results observed with the other 1-chloro-1-alkynes.

We now disclose that the lithium [(*E*)-1-chloro-1-alkenyl]-alanates **1** (eq 1) may be prepared by the highly stereo- and regioselective trans addition in tetrahydrofuran solvent of the Al-H moiety of lithium aluminum hydride to the triple bond of the readily available 1-chloro-1-alkynes.[3-5] These α-halovinylalanates represent a novel class of compounds which possess moderate stability at 0 °C and provide upon methanolysis excellent yields of the corresponding (*E*)-1-chloro-1-alkenes **2** (Table I).



1 2 (1)

The lower GLC yield of **2** (R = *t*-$\mathrm{C_4H_9}$) realized in the case of *t*-butylchloroacetylene (Table I) results from the fact that its hydroalumination produces besides **1** an appreciable amount of *tert*-butylacetylene (23%). On the other hand, 1-chloro-1-alkynes containing primary or secondary alkyl substituents on reaction with $\mathrm{LiAlH_4}$ give, after workup, <6% of the corresponding 1-alkynes. The formation of 1-alkynes can be rationalized in terms of an α-elimination of $\mathrm{LiAlH_3Cl}$ (or LiCl) from the hydroalumination product **1** with concomitant 1,2 shift of hydrogen (Fritz-Buttenberg-Wiechell rearrangement).[6]

In exploring the further scope of the α-chlorovinylalanates **1** as intermediates for organic synthesis, we next directed our attention toward their conversion into mixed 1,1-dihalo-1-alkenes of defined stereochemistry. In contrast to the 1-halo-1-alkenes whose usefulness as synthons for preparing olefins and diene has been clearly demonstrated, the 1,1-dihalo-1-ethenyl moiety has not yet played a major role in synthetic methodology. This is probably because most of the currently available methods for its synthesis are limited to the preparation of homo 1,1-dihalo olefins.[7,8] Thus, we were gratified to observe that conversion of the trihydridoalumino moiety of **1** into the triisopropoxyalumino moiety in **3** by treatment with acetone followed by addition of bromine at −78 °C and hydrolytic workup affords (*Z*)-1-bromo-1-chloro-1-alkenes (**4**, eq 2) in >97% isomeric purities and in good yields (Table I).[9] In a similar manner, treatment of **3** with a solution of iodine monochloride (1.1 equiv) in methylene chloride at −30 °C, followed by stirring of the reaction mixture at this temperature for 1 h and at ambient temperature for 2 h, produces, after hydrolytic workup, the corresponding (*Z*)-1-chloro-1-iodo-1-alkenes **5** (Table I).[10]

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