ORGANOMETALLICS

Volume 10, Number 3, March 1991

Communications

Reactivity of Permethylscandocene Derivatives with Acetylene. Structure of Acetylenediylbis(permethylscandocene), $(\eta^5\text{-}C_5Me_5)_2Sc{-}C{\equiv}C{-}Sc(\eta^5\text{-}C_5Me_5)_2$[†]

Martin St. Clair,[1] William P. Schaefer, and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received June 27, 1990

Summary: Excess acetylene reacts with $Cp^*{}_2Sc{-}R$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = H, alkyl, aryl, alkenyl, alkynyl, amide) below −78 °C to yield R—H and $Cp^*{}_2Sc{-}C{\equiv}CH$; the latter then reacts with excess C_2H_2 to form polyacetylene. $Cp^*{}_2Sc{-}C{\equiv}CH$ cleanly decomposes to $Cp^*{}_2Sc{-}C{\equiv}C{-}ScCp^*{}_2$, most likely via σ bond metathesis involving the Sc–acetylide and terminal C–H bonds for two molecules of $Cp^*{}_2Sc{-}C{\equiv}CH$. The structure of this unusual acetylenediyl-bridged dimer has been determined by X-ray diffraction methods. It crystallizes with a half-molecule of toluene per scandium dimer in the tetragonal system, space group $P\bar{4}2_1c$ (No. 114), with a = 15.057 (3) Å, c = 18.617 (6) Å, V = 4220.7 (18) Å^3, and z = 4.

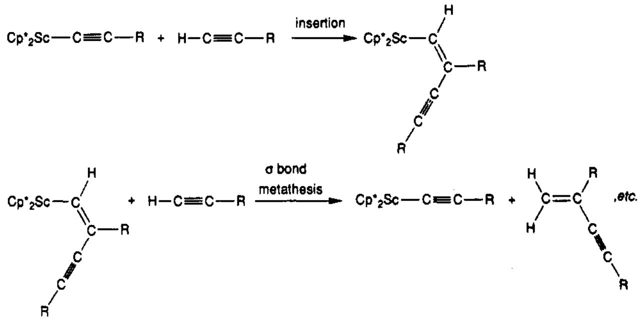
Permethylscandocene hydrido and alkyl derivatives, $Cp^*{}_2Sc{-}R$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$), are effective catalysts for the polymerization of ethylene, and we have recently investigated the chain-propagating and -transfer steps for this system.[2] With other olefins (e.g. $CH_2{=}CHR'$) σ bond metathesis to generate relatively unreactive scandocene alkenyls prevails (eq 1). Terminal alkynes react similarly (eq 2).[3] Moreover, with excess terminal acetylene catalytic dimerization to the gem enyne is observed, and the mechanism shown in Scheme I has been proposed.[3] Simple (stoichiometric) insertion of internal alkynes occurs for $Cp^*{}_2Sc{-}R$ (R = H, CH_3) to yield alkenyl derivatives that do not undergo further insertion reactions even with excess internal alkyne (eq 3).[2]

$$Cp^*{}_2Sc{-}R + CH_2{=}CHR' \rightarrow Cp^*{}_2Sc{-}CH{=}CHR' + R{-}H \quad (1)$$

$$Cp^*{}_2Sc{-}R + HC{\equiv}CR' \rightarrow Cp^*{}_2Sc{-}C{\equiv}CR' + R{-}H \quad (2)$$

$$Cp^*{}_2Sc{-}R + R'C{\equiv}CR'' \rightarrow Cp^*{}_2Sc{-}CR'{=}CRR'' \quad (3)$$

Scheme I



Since permethylscandocene alkyls readily polymerize ethylene, but *not* higher olefins,[4] it occurred to us that the parent acetylene, HC≡CH, would be the alkyne most likely to undergo oligomerization or polymerization. We report herein our studies of the reactivity of acetylene with

---

[†] Contribution No. 8148.

(1) Current address: 120 Engineering Research Facility, University of Iowa, Iowa City, IA 52242.

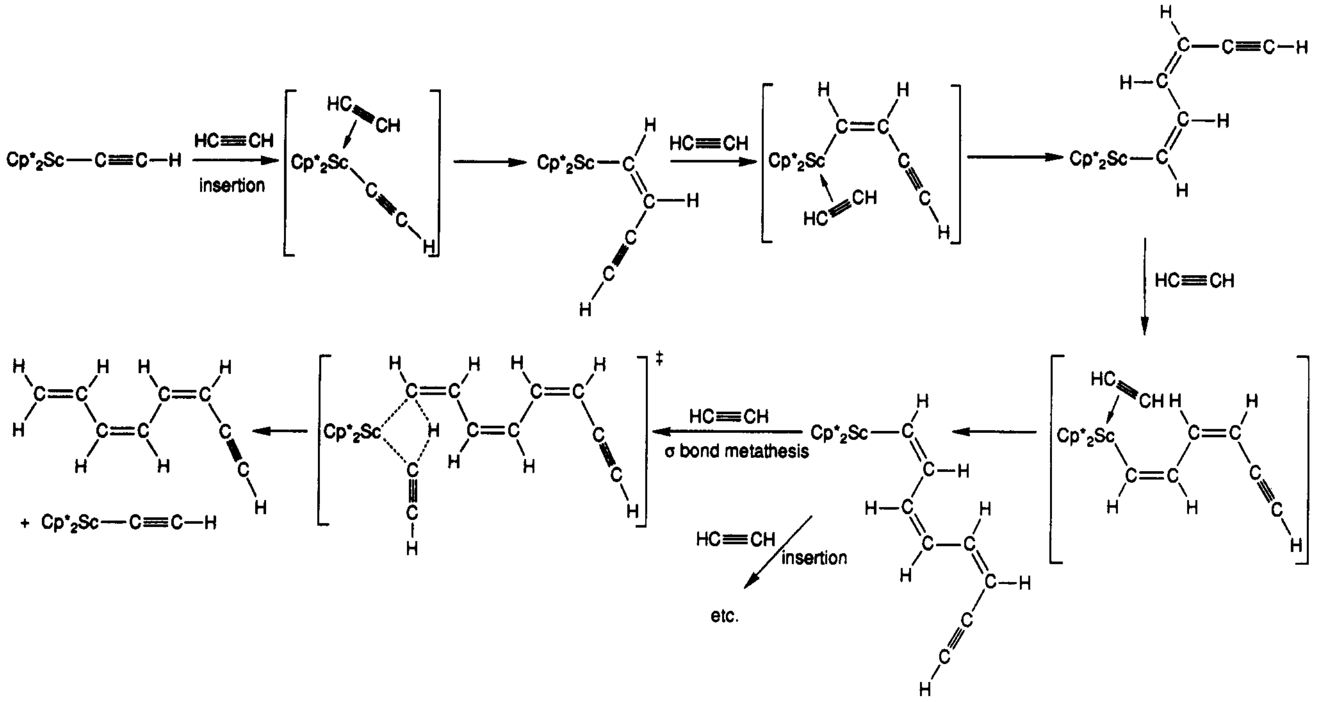
(2) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577.

(3) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, 4109, 203.

(4) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74–84.

0276-7333/91/2310-0525$02.50/0 © 1991 American Chemical Society

Scheme II



permethylscandocene derivatives, together with the structure of a novel acetylenediyl-bridged dimer, $(\eta^5\text{-}C_5Me_5)_2Sc{-}C{\equiv}C{-}Sc(\eta^5\text{-}C_5Me_5)_2$.

Addition of excess acetylene[5] to a frozen benzene solution of $Cp^*_2ScCH_3$ yields on thawing a black precipitate, CH_4 (0.95 equiv/Sc, Toepler measurement), and a single organometallic compound identified as $Cp^*_2Sc{-}C{\equiv}CH$ (vide infra). Vinylic ^1H NMR signals (δ 5–6) suggest the presence of soluble acetylene oligomers that are formed in addition to the polyacetylene precipitate. Monitoring the reaction in toluene-d_8 at low temperature by ^1H NMR spectroscopy revealed that σ bond metathesis between $Cp^*_2Sc{-}CH_3$ and $H{-}C{\equiv}CH$ is complete within minutes below −80 °C (eq 4). No further reaction occurs until ca.

$$Cp^*_2Sc{-}CH_3 + H{-}C{\equiv}CH \xrightarrow[\text{toluene-}d_8]{\le -80\ ^\circ\mathrm{C}} Cp^*_2Sc{-}C{\equiv}CH + CH_4 \quad (4)$$

10 °C, at which point free C_2H_2 is consumed and vinyl signals appear. The mechanism shown in Scheme II accommodates these features. As in the dimerization of monosubstituted alkynes, termination occurs by σ bond metathesis, but in the case of $HC{\equiv}CH$ it competes with additional insertions into the Sc–alkenyl bonds of the growing oligoacetylene chains. Observation of $Cp^*_2Sc{-}C{\equiv}CH$ as the principal organoscandium compound during and after consumption of acetylene monomer suggests that the initiation (insertion of $HC{\equiv}CH$ into the $Sc{-}C{\equiv}CH$ bond) is slow relative to both propagation (subsequent insertions of $HC{\equiv}CH$ into the scandium–carbon bonds of $Cp^*_2Sc{-}CH{=}CH(CH{=}CH)_nC{\equiv}CH$) and termination ($\sigma$ bond metathesis).

The poly- and oligoacetylenes formed in these reactions have not been fully characterized. No conditions could be found that resulted in formation of a film. The basic structure is assumed to be that shown in Scheme II. A cis geometry for the carbon–carbon double bonds seems most likely on the basis of the exclusive cis insertion observed for insertions of alkynes into Sc–C bonds,[2] and an s-trans arrangement for the C–C single bonds appears necessary to avoid formation of rings that close on themselves. Other conjugated structures may arise from insertions of $C{\equiv}C$ or σ bond metathesis of H—C of the product oligomers $(H{-}C{\equiv}C(CH{=}CH)_nCH{=}CH_2)$ with the propagating scandium–alkenyl intermediates, if these compete effectively with the corresponding processes for the smaller acetylene monomer.

$Cp^*_2Sc{-}C{\equiv}CH$ has been characterized by ^1H and ^{13}C NMR and IR data but could not be isolated (vide infra).[6] It may also be generated by reaction of a variety of permethylscandocene derivatives with C_2H_2 (eq 5). Attempts

$$Cp^*_2Sc{-}Y + H{-}C{\equiv}CH \rightarrow Cp^*_2Sc{-}C{\equiv}CH + H{-}Y \quad (5)$$

$$Y = N(CH_3)_2,\ C_6H_5,\ C(CH_3){=}C(CH_3)_2,\ CH_2Si(CH_3)_3,\ C{\equiv}CCH_3$$

to isolate $Cp^*_2Sc{-}C{\equiv}CH$, for example by crystallization from concentrated solutions, invariably gave another compound. An X-ray structure determination revealed the identity of this dimer: $Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2$. Presumably, concentration of solutions of $Cp^*_2Sc{-}C{\equiv}CH$ accelerates its binuclear decomposition to $Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2$ via σ bond metathesis involving the terminal C–H and Sc–C bonds (eq 6). An alternative preparation in-

$$2Cp^*_2Sc{-}C{\equiv}C{-}H \rightarrow Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2 + H{-}C{\equiv}C{-}H \quad (6)$$

---

(5) *Caution*! Acetylene, in its free state under pressure, may decompose violently. The higher the pressure, the smaller the initial force required to cause an explosion. Acetylene should therefore *never* be used as the free gas outside the cylinder at pressures in excess of 103 kPa (15 psig). See: Chien, J. C. W. *Polyacetylene Chemistry, Physics, and Material Science*; Academic Press: Orlando, FL, 1984.

(6) $Cp^*_2Sc{-}C{\equiv}C{-}H$ could not be isolated but was prepared and characterized in situ by condensing 34.3 Torr × 33.5 mL of $^{13}C_2H_2$ (25 °C) (0.06 mmol) into a frozen benzene-d_6 solution of 20 mg of $Cp^*_2ScCH_3$ (0.06 mmol) in an NMR tube, which was then sealed with a torch. After thawing and thorough mixing, NMR spectra were recorded. ^1H NMR: $[C_5(CH_3)_5]$ δ 1.93 s; $Sc^{13}C{\equiv}^{13}C{-}H$ δ 2.87 dd ($^1J_{C-H}$ - 215 Hz, $^2J_{C-H}$ = 32 Hz). $^{13}C\{^1H\}$ NMR: $[C_5(CH_3)_5]$ δ 121.2; $[C_5(CH_3)_5]$ δ 12.4; $Sc^{13}C{\equiv}^{13}C{-}H$ δ 99.0 ($^1J_{C-C}$ = 99 Hz). IR (benzene-d_6, NaCl windows): 3265 (m), 2907 (s), 2861 (s), 2267 (m), 1928 (w), 1489 (w), 1436 (m), 1380 (m), 1025 (m) cm^{-1}.

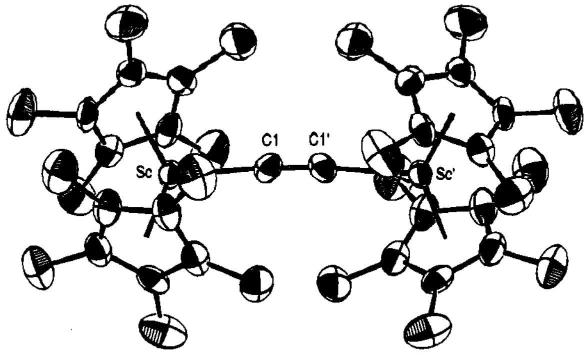


Figure 1. ORTEP drawing of $\mathrm{Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2}$ with 50% probability ellipsoids. Hydrogen atoms have been omitted.

volves reaction of $\mathrm{Cp^*_2ScCH_3}$ with $^1/_2$ equiv of acetylene (eq 7).[7]

$$\mathrm{2Cp^*_2ScCH_3 + H{-}C{\equiv}C{-}H \rightarrow Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2 + 2CH_4} \quad (7)$$

An ORTEP drawing of $\mathrm{Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2}$ is shown in Figure 1. The molecule crystallizes at a 2-fold symmetry axis that relates one $\mathrm{[Cp^*_2Sc]}$ and half the bridging acetylenediyl unit to the other half-molecule. Notable features are the $\mathrm{C{\equiv}C}$ bond length and the staggered conformation of $\mathrm{[Cp^*_2Sc]}$ moieties. The C1–C1′ bond length (1.224 (9) Å) is short, similar to that found in $\mathrm{CaC_2}$ (1.195 Å),[8] and only slightly longer than that in acetylene itself (1.21 Å). The Sc–C1 bond length (2.194 (7) Å) is only marginally shorter than the scandium–carbon bond length for $\mathrm{Cp^*_2Sc{-}CH_3}$ (2.243 (11) Å),[2] so that multiply bonded resonance structures such as

$$\mathrm{Sc^-{=}C{=}C^+{-}Sc \leftrightarrow Sc{-}C^+{=}C{=}Sc^-}$$

resulting from donation of $\mathrm{C{\equiv}C}$ π electrons to empty oribtals in the wedge of the scandocene units, do not appear to contribute significantly to the $\mathrm{Sc{-}C{\equiv}C{-}Sc}$ bonding. The nearly linear Sc-C1-C1′ angle (175.1 (6)°) and the dihedral angle between the two centroid–Sc–centroid planes of nearly 90° are as expected, since the fully staggered arrangement minimizes steric interactions between Cp* rings across the dimer. The other features of the structure (e.g. d(Cp*(centroid)–Sc) = 2.171, 2.172 Å; Cp*(centroid)–Sc–Cp*(centroid) = 143.1 (1)°) are much like those for other permethylscandocene derivatives.

Although the $\mathrm{M{-}C{\equiv}C{-}M}$ linkage is common for M = alkali and noble metals, where it generally results in extended polymeric structures,[9] this structural unit does not appear to have been reported for early and middle transition metals.[10] There has been some interest in incorporating μ-acetylide bridges for polymeric backbones of the type $\mathrm{(M{-}C{\equiv}C{-}M{-}C{\equiv}C{-})_n}$, where M = Ni, Pd, Pt.[11] While the structure of the first simple μ_2-η^1,η^1-acetylenediyl compound, *trans,trans*-$\mathrm{(PMe_3)_2Pt(I){-}C{\equiv}C{-}Pt(I)(PMe_3)_2}$, has recently been reported,[12] the only other examples of structurally characterized compounds containing $\mathrm{[M{-}C{\equiv}C{-}M]}$ units show additional π coordination of $\mathrm{C{\equiv}C}$ to another metal as well.[13]

Table I. Characteristic Spectroscopic and Structural Features of Compounds Containing the μ-Acetylenediyl Ligand

	$\nu(\mathrm{C{\equiv}C})$,[a] $\mathrm{cm^{-1}}$	δ,[b] ppm	$d(\mathrm{C{\equiv}C})$, Å	ref
$\mathrm{C_2H_2}$	1947	71.6	1.21	16
$\mathrm{Li_2C_2}$	1885	75.0		17
$\mathrm{Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2}$	1899	179.4	1.224 (9)	this work
$\mathrm{(PMe_3)_2(I)Pt{-}C{\equiv}C{-}Pt(I)(PMe_3)_2}$	2022	101.9[c]	1.179 (8)	12
$\mathrm{(Ph_3P)Au{-}C{\equiv}C{-}Au(PPh_3)}$	2040			18
$\mathrm{(PMe_2Ph)_2Pt(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}C_2)\text{-}W_2(OCMe_3)_5}$[d]		233.9	1.33	13a
$\mathrm{Ru_4(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}C_2)(PPh_2)\text{-}(CO)_{12}}$[e]			1.28	13b

[a] $\nu(\mathrm{C{\equiv}C})$ measured by Raman spectroscopy. [b] ^{13}C NMR shift (relative to TMS) for acetylenediyl carbons. [c] $\delta(^{13}\mathrm{C})$ reported is for $\mathrm{(PMe_3)_2(I)Pd{-}C{\equiv}C{-}Pd(I)(PMe_3)_2}$; ^{13}C NMR data not reported for $\mathrm{(PMe_3)_2(I)Pt{-}C{\equiv}C{-}Pt(I)(PMe_3)_2}$. [d] Bridging acetylenediyl is σ bonded to Pt and one W and π bonded to the other W. [e] Bridging acetylenediyl is σ bonded to two Ru and π bonded to the other two Ru.

Thus, the structural and spectroscopic features of $\mathrm{Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2}$ and *trans,trans*-$\mathrm{(PMe_3)_2Pt(I){-}C{\equiv}C{-}Pt(I)(PMe_3)_2}$ distinguish them from polynuclear transition-metal complexes having additional metals π bonded to the μ_n-$\mathrm{C{\equiv}C}$ moiety (Table I), as well as from the two other types of [MCCM]-bridged binuclear compounds: e.g. $\mathrm{(silox)_3Ta{=}C{=}C{=}Ta(silox)_3}$ (silox = $\mathrm{(Me_3C)_3SiO{-}}$; $\mathrm{C{=}C}$ distance 1.32 Å)[14] and binuclear complexes having bridges of the type $\mathrm{[M{\equiv}C{-}C{\equiv}M]}$ reported by Schrock and co-workers.[15]

Acknowledgment. This work was supported by the USDOE Office of Energy Research, Office of Basic Energy Science (Grant No. DE-FG03-85ER13431), and by Shell Companies Foundation, which are gratefully acknowledged. We thank the NSF (Grant No. CHE-8219039) for funds to purchase the X-ray diffractometer.

Supplementary Material Available: Details of the structure determination, including listings of crystal and intensity collection data, the final atom coordinates, thermal parameters, and bond distances and angles (9 pages); a listing of structure factors (6 pages). Ordering information is given on any current masthead page.

---

(7) $\mathrm{Cp^*_2Sc{-}C{\equiv}C{-}ScCp^*_2}$ is prepared as follows: With use of a swivel frit assembly on a vacuum line $\mathrm{Cp^*_2ScCH_3}$ (420 mg, 1.3 mmol) dissolved in 30 mL of petroleum ether was treated with 292 Torr × 42.2 mL (0.65 mmol) of acetylene at −78 °C for 40 min. The product was filtered off while cold to yield 312 mg (71%) of an off-white powder. Anal. Calcd: C, 77.03; H, 9.24. Found: C, 76.51; H, 9.08. IR (Nujol mull): 2716 (w), 1460 (s), 1379 (s), 1165 (w), 1064 (w), 1025 (m) cm^{-1}. ^{1}H NMR: δ 2.05 s ($\mathrm{C_5(C\mathit{H}_3)_5}$). ^{13}C{^{1}H} NMR: δ 12.6 ($\mathrm{C_5(\mathit{C}H_3)_5}$); δ 120.7 ($\mathrm{\mathit{C}_5(CH_3)_5}$); δ 179.4 ($\mathrm{Sc{-}\mathit{C}{\equiv}\mathit{C}{-}Sc}$).

(8) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1986; p 320.

(9) Green, M. L. H. *Organometallic Compounds: The Transition Elements*; Methuen: London, 1968; Vol. 2, p 275.

(10) The compound "$\mathrm{(Cp_2TiC{\equiv}CTiCp_2)_n}$" is reported as the product of the reaction of acetylenediylbis(magnesium bromide) with $\mathrm{Cp_2TiCl}$: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: London, 1974; p 220. However, the reference given is to "unpublished work", and no characterization is given.

(11) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromolecules* 1977, *10*, 879–880.

(12) Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamasaki, H. *Organometallics* 1988, *7*, 2257–2260.

(13) (a) Bruce, M. I.; Snow, M. R.; Tiekink, E. R. T.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* 1986, 701–702. (b) Blau, R. J.; Chisholm, M. H.; Folting, K.; Wang, R. J. *J. Chem. Soc., Chem. Commun.* 1985, 1582–1584.

(14) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* 1986, *108*, 6382–6384.

(15) Listemann, M. L.; Schrock, R. R. *Organometallics* 1985, *4*, 74–83.

(16) Morrison, T. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon: Boston, 1980; p 250.

(17) Rauscher, G.; Clark, T.; Poppinger, D.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 276–278.

(18) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* 1986, 411–414.