A Planar Tetracoordinate Carbon and Unusual Bonding in an Organodimetallic Propynylidene Complex Arising from Double C−H Activation of an Allene Ligand

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Alkylidenes are important in organic and organometallic chemistries and cosmochemistry because of their structures, reactivities, and interstellar/circumstellar presence. Propynylidene **1** (HCCCH) is the simplest alkynylcarbene that, along with abundant interstellar[1−3] cyclopropenylidene **2** and propadienylidene **3** (Scheme 1), has attracted substantial interest. Propynylidene is a proposed intermediate in interstellar C_3H[4,5] formation since photoisomerization between **1**, **2**, and **3** is facile.

Experimental[6−9] and recent computational[5,9,10] studies show that **1** has a triplet ground state and a C_2 geometry, although that geometry is only 0.1−0.2 kcal mol^{-1} lower than the C_s and C_{2v} geometries.[5] The conformational potential energy of singlet **1** (ca. 11 kcal mol^{-1} above the triplet[10]) is similarly flat.[10−12]

Among the successes of organotransition metal chemistry is the stabilization of reactive species. Double C−H activation of allene represents a possible route to a C_3H_2 ligand, which could complex in several ways (Chart 1, M = metal and ancillary ligands). Examples are known[13−17] for many of these, but not for **12** or **13**.

Here, we report preparation and characterization of a propynylidene organodimetallic. MO calculations on free (MCSCF) and complexed (RHF, DFT) HCCCH were used to understand the bonding of this new organometallic ligand.

The reaction of allene with the d^2-d^2 organoditantalum(III) (η-$C_5Me_4R)_2Ta_2(\mu$-X)$_4$ (R = Me (Cp*), Et; X = Cl, Br)[18] leads to complexation[19] rather than C−H activation.[20] An agostic C−H interaction in (η-$C_5Me_4R)_2Ta_2(\mu$-X)$X_3(\mu$-η^1,η^3-$C_3H_4)$ (**14**) may be antecedent to C−H activation. Reduction of **14** gives **15** (eq 1),

(1)
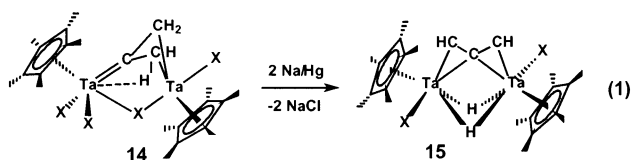
via a *double* 1,3-C−H activation, with C_3H_2 and two μ-hydride ligands instead of an allenyl hydride.[21] Product **15** is dinuclear by mass spectrometry, with high symmetry based on NMR spectroscopies. C_3H_2 ligand NMR data (X = Cl) are unusual, with downfield resonances for the hydrogen (δ 11.4), terminal carbons (δ 215.6, $^1J_{CH}$ = 189), and central carbon (δ 161.4). These data, consistent with Ta=C bonding to the HCCCH carbons, could not differentiate complexed **1** (i.e., **12**) from **2** (**9** or **10**).

Single-crystal diffractometry[22] revealed a μ-propynylidene coplanar with two Ta atoms (Figure 1). Selected bond distances and angles are listed in Table 1. The molecule has crystallographically imposed C_2 symmetry. The HCCCH ligand is related to **1** rather than the μ-alkylidene form (**13**). The HCCCH hydrogen was refined, but H(1) was not as this led to an unacceptably small Ta(1)−H(1) distance. The C(2)−C(1)−C(2A) angle (153.7(13)°) is smaller than
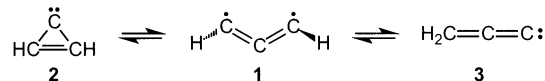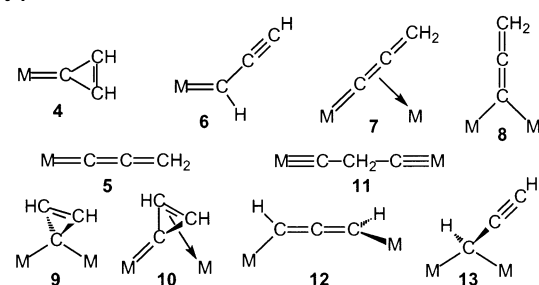
Scheme 1

Chart 1

Table 1. Experimental and Calculated Distances and Angles for **15**[a]

distance (Å)/angle (deg)	experimental	theory
Ta(1)−Ta(1A)	2.8817(7)	2.930
Ta(1)−C(1)	2.194(9)	2.203
Ta(1)−C(2)	1.970(9)	1.966
C(1)−C(2)	1.370(8)	1.385
Ta(1)−H(1)−Ta(1A)	97.9	100.0, 99.8
Ta(1)−C(1)−Ta(1A)	82.1(4)	83.4
C(2)−C(1)-C(2A)	153.7(13)	144.5
C(1)−C(2)−H(2)	139(5)	128.7
Ta(1)−C(1) −C(2)	62.1(5)	61.6, 61.6
Ta(1)−C(2)−C(1)	79.9(6)	80.3, 80.1
Ta(1)−C(2)−H(2)	139(5)	151.0, 151.2

[a] No C_2 symmetry was imposed in the calculations. Transformation for experimentally equivalent atoms: A, $-x$, $-y$, $-z + 3/2$.
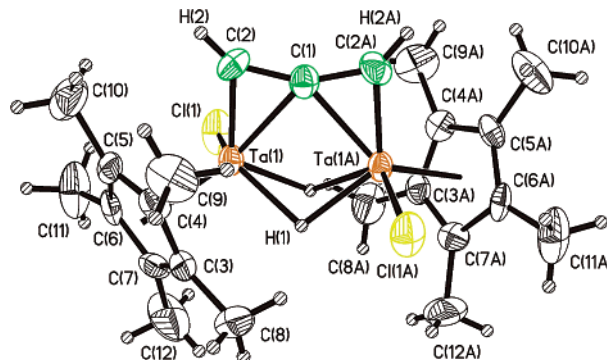
Figure 1. Thermal ellipsoid plot of **15**.

that predicted[9] (172−4°) for **1**, and the HCCCH ligand adopts a curved conformation that maximizes Ta−C bonding. The C(2)−C(1) distance (1.370(8) Å) is longer than that in allene (1.308 Å)[23] or predicted for **1** (1.273−1.279 Å).[9] Tetracoordinate C(1) is planar,
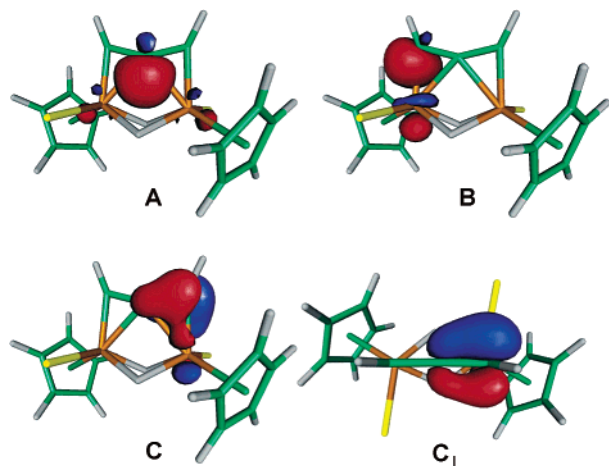
Figure 2. MOLDEN[27] plots of key MOs for **15** (with C_5H_5 in lieu of Cp*): (**A**) three-center, two-electron Ta–C(1)–Ta' bond; (**B**) Ta–C(2) σ-bond; (**C**) orthogonal views of Ta–C(2)–C(1) π-bond.

with surrounding angles totaling 360°; C(2) is planar (angle sum 358°), so H(2) is coplanar with the C and Ta atoms. The Ta–Ta distance is in the single bond range, suggesting a d^1–d^1, Ta(IV)$_2$ complex and a formally dianionic HCCCH. However, the Ta–C(2) distance is consistent with a Ta=C double bond, leading to an allenediylidene(4−)/Ta(V)$_2$ description with no Ta–Ta bonding. We turned to calculations in order to address this ambiguity.

Geometry optimizations of **15** (C_5H_5 in place of Cp*) were performed at the RHF/SBK(d) level.[24,25] Selected parameters are listed in Table 1, and agreement with the solid-state structure is quite good. Important localized[26] MOs are displayed in Figure 2. The MOs in Figures 2A and 2C are best described as three-center, two-electron σ and π bonds connecting Ta–C(1)–Ta and Ta–C(2)–C(1), respectively. There is **no** net Ta–Ta bonding MO, and the total electron density shows no evidence of a Ta–Ta bond. This suggests the following formal bonding picture with a three-center, two-electron bridge bond.
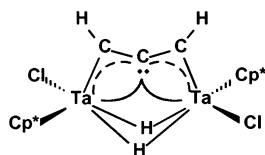
Organodimetallics with planar tetracoordinate μ-carbon atoms are rare.[28] A three-center, two-electron bond involving a carbon-based lone pair has been examined theoretically.[29]

When conceptually removed from **15** in the observed geometry, triplet HCCCH is 56.7 kcal mol^{-1} higher than the W-shaped C_2 minimum.[30] The two structures are connected by a steepest descent path with no barrier, indicating that the C_2 geometry is the closest minimum on the triplet PES.

We have examined the reactivity of this new organometallic functional group. Surprisingly for a complex with valence electron count < 18 and Ta=C bonding, **15** is unreactive (<65°, C_6D_6) toward H_2, CO, and C_2H_4. This nonreactivity may reflect the lack of a suitable LUMO for nucleophilic attack. The products from reactions with electrophiles are being characterized. We have not yet found conditions that liberate HCCCH from **15**, although photolysis appears promising.

While conversion of **14** to **15** is a formal double C–H activation, the mechanism remains to be examined by crossover experiments. We have yet to observe reaction intermediate(s) (e.g., an allenyl hydride) during the C–H activation.

These results show that propynylidene can be generated as an organodimetallic ligand in solution by double C–H activation of allene and that it can adopt a curved structure. Calculations show that the HCCCH ligand is best described as an allenediylidene(4−) with a planar tetracoordinate carbon.

Supporting Information Available: Tables of crystallographic data parameters, distances and angles, and MO calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Cp*$_2$Ta$_2$Cl$_3$(μ-Cl)(C$_3$H$_4$) (0.30 g, 0.34 mmol) and Na/Hg (2.4 equiv) in PhMe (18 mL) were shaken (3 h) via vortex mixer. The filtrate was concentrated and dark amber Cp*$_2$Ta$_2$Cl$_2$(μ-H)$_2$(C$_3$H$_2$) (0.17 g, 65%) obtained by filtration. Anal. Calcd for C$_{23}$H$_{34}$Cl$_2$Ta$_2$: C, 37.17; H, 4.61; Cl, 9.54. Found: C, 37.39; H, 4.51; Cl, 10.37. ^{1}H NMR (δ, C$_6$D$_6$): 1.99 (s, 30H, Me), 4.54 (s, 2, μ-H), 11.40 (s, 2, C$_3$H$_2$). ^{13}C NMR (δ, gated {^{1}H}): 11.5 (Me), 116.5 (*C*$_5$Me$_5$), 161.4 (s, HC*C*CH), 215.6 (d, $^1J_{CH}$ = 189 Hz, HCC*C*H). MS (EI, *m/e*): M$^+$, Cl$_2$ isotopomers. Br analogue, 49% ^{1}H NMR, 2.03 (Me), 4.01 (μ-H), 11.60 (C$_3$H$_2$); ^{13}C NMR (δ, gated {^{1}H}), 11.8 (Me), 116.5 (*C*$_5$Me$_5$), 164.5 (s, HC*C*CH), 220.4 (d, $^1J_{CH}$ = 189 Hz, HCC*C*H).
(22) Monoclinic, *C2/c*, dark red, *a* = 16.819(3) Å, *b* = 13.426(2) Å, *c* = 10.997(2) Å, β = 101.04(2)°, *T* = 293 K, *Z* = 4, *R* = 0.0435, GOF = 1.079.
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(30) Relative energy was calculated at the MCQDPT/cc-pVDZ level [Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983] via GAMESS. The curved geometry is optimized (RHF/SBK(d)) while the C_2 geometry is the MCSCF(5,4)/cc-pVDZ minimum. Significant nonintegral occupation numbers for some MOs demonstrated the need for MCSCF. The intrinsic reaction coordinate (IRC) was performed at the MCSCF(5,4)/cc-pVDZ level.

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