(acyl), 126°. Mn(CO)$_5$(COCH$_3$): MnC(CO), 1.82 Å; C–O(CO), 1.14 Å; Mn–C(acyl), 2.07 Å; C–O(acyl), 1.21 Å; C–C(acyl), 1.51 Å; C–H, 1.09 Å; O–C–C(acyl), 115°. Cp$_2$Zr(COCH$_3$)(CH$_3$): Zr–C(Cp), 2.5 Å; Zr–C(CH$_3$), 2.336 Å; Zr–C(acyl), 2.197 Å; C–O, 1.211 Å; C–C(acyl), 1.492 Å; C–H(CH$_3$), 1.1 Å; C–H(Cp), 1.08 Å; C–C(Cp), 1.40 Å; Cp–Zr–Cp, 130°; O–C–C(acyl), 120°. Cp$_2$U(COCH$_3$)Cl: U–C(Cp), 2.804 Å; U–C(acyl), 2.44 Å; U–Cl,

2.67 Å; C–O, 1.18 Å C–C(acyl), 1.47 Å; C–C(Cp), 1.42 Å; C–H, 1.09 Å; Cp–U–Cp, 138°; O–C–C(acyl), 118°.

Why the Energetic Minimum Aluminum Vinylidene Is Not Observed in Low-Temperature Aluminum + Acetylene Reactions

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Abstract: Ab initio molecular electronic structure theory has been used to investigate the Al + C$_2$H$_2$ potential energy surface. Particular emphasis was placed on resolving the apparent conflict between theory and experiment by examining the barrier to rearrangement between *cis*-AlHCCH (observed by ESR at 4 K) and AlCCH$_2$ (theoretically predicted global energy minimum). Analytic SCF gradients were employed with a double-ζ basis set to locate and characterize stationary points on the energy surface. Single point CI calculations using a double-ζ + polarization basis set have been carried out at the DZ-SCF stationary points. A DZP-CI barrier of 39.1 kcal for the *cis*-AlHCCH → AlCCH$_2$ isomerization has been found. Such a barrier is clearly prohibitive to this isomerization under the experimental conditions of 4 K. By comparing this isomerization to the bare HCCH → CCH$_2$ isomerization, the effect of the aluminum atom has been found to be significant.

The synthesis of the aluminum atom–acetylene adduct which was first reported by Kasai, McLeod, and Watanabe[1] and the more recent ESR analysis of this adduct by Kasai[2] suggest strongly the formation of a σ-bonded vinyl structure, **3**. Kasai's second paper[2] also discusses a trans → cis (**3** → **2**) conversion of this σ-bonded complex brought about by photoirradiation. A perhaps surprising feature is that no evidence was found to indicate the formation of the vinylidene complex, **1**, which has been predicted theoretically to be the global minimum on the Al–C$_2$H$_2$ energy surface.[3]
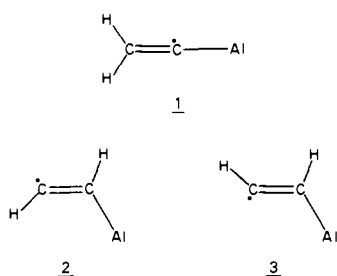
The purpose of the present research was twofold: first, to re-examine the vinylidene complex and the cis and trans (to the aluminum atom) σ-bonded vinyl radicals (structures **1**, **2**, and **3**, respectively) with analytic gradient techniques;[4] and second, to investigate the barrier to **2** → **1** rearrangement. As speculated in the previous theoretical study,[3] the presence of a large barrier to rearrangement would prohibit the formation of the low-energy vinylidene structure at the liquid helium temperatures of the ESR experiments.[1,2]

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Table I. Calculated DZ-SCF Harmonic Vibrational Frequencies (in cm^{-1}) for AlCCH$_2$ (**1**), *cis*-AlHCCH (**2**), and *trans*-AlHCCH (**3**) and the **2** → **1** Transition State[a]

AlCCH$_2$		*cis*-AlHCCH		*trans*-AlHCCH	
3360	CH$_2$ a stretch	3369	$\nu_{C_\beta-H_\beta}$	3388	$\nu_{C_\beta-H_\beta}$
3272	CH$_2$ s stretch	3238	$\nu_{C_\alpha-H_\alpha}$	3210	$\nu_{C_\alpha-H_\alpha}$
1796	ν_{C-C}	1671	ν_{C-C}	1664	ν_{C-C}
1543	CH$_2$ scissors	1286	$\delta_{Al-C_\alpha-H_\alpha}$	1270	$\delta_{Al-C_\alpha-H_\alpha}$
1109	CH$_2$ wag	1019	$\tau_{H-C-C-H}$	993	$\tau_{H-C-C-H}$
1048	CH$_2$ rock	973	$\delta_{H-C-C-H}$	928	$\delta_{H-C-C-H}$
520	ν_{Al-C}	568	ν_{Al-C}	571	ν_{Al-C}
239	$\tau_{Al-C_\alpha-C_\beta}$	565	$\tau_{Al-C_\alpha-C_\beta-H_\beta}$	522	$\tau_{Al-C_\alpha-C_\beta-H_\beta}$
183	$\delta_{Al-C_\alpha-C_\beta}$	212	$\delta_{Al-C_\alpha-C_\beta}$	192	$\delta_{Al-C_\alpha-C_\beta}$

cis-AlHCCH → AlCCH$_2$ transition state		*cis*-AlHCCH → AlCCH$_2$ transition state	
3346	$\nu_{C_\beta-H_\beta}$	513	ν_{Al-C}
3058i	$\nu_{C_\beta-H_\alpha} - \nu_{C_\alpha-H_\alpha}$	276	$\tau_{Al-C_\alpha-C_\beta-H_\alpha}$
2383	$\nu_{C_\beta-H_\alpha} + \nu_{C_\alpha-H_\alpha}$	258	$\delta_{Al-C_\alpha-C_\beta-H_\beta}$
1805	ν_{C-C}	237	$\tau_{Al-C_\alpha-C_\beta-H_\beta}$
927	$\delta_{C_\alpha-C_\beta-H_\beta}$		

[a] The carbon center bonded to aluminum is designated C$_\alpha$ and the hydrogen bonded to this carbon is designated H$_\alpha$. The remaining carbon and hydrogen are designated C$_\beta$ and H$_\beta$ respectively.

Method

All geometries were precisely optimized by using self-consistent-field (SCF) analytic gradients.[4] The contracted double-ζ (DZ) basis set of Dunning and Hay,[5] designated Al(11s 7p/6s 4p), C(9s 5p/4s 2p), and H(4s/2s), was employed for these optimizations. A series of calculations based on finite nuclear displacements from the optimized DZ-SCF geometries were carried out to obtain harmonic vibrational frequencies for all stationary points. With use of the DZ-SCF structures, single point calculations with a DZ + polarization (DZ+P) basis set and including configuration interaction (CI) were also carried out. The polarization

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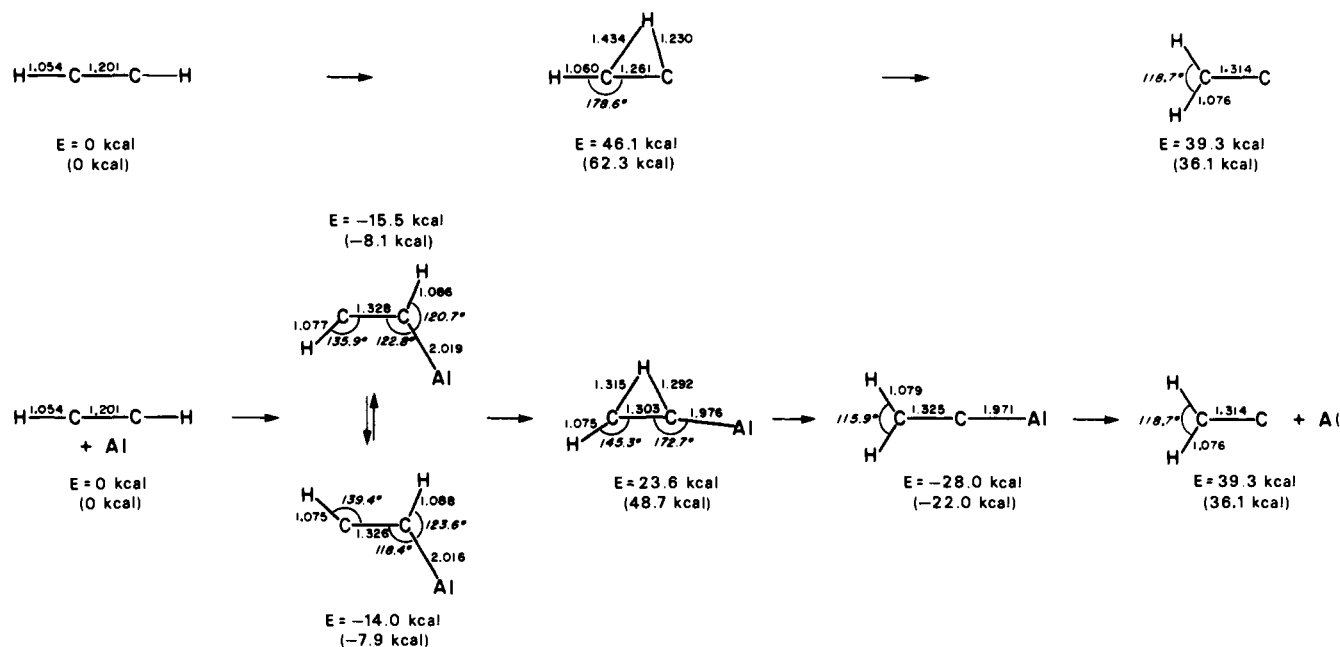
Figure 1. Comparison of the acetylene → vinylidene isomerization with the aluminum assisted acetylene → vinylidene isomerization. The single point DZP-CI energies are shown first with the corresponding DZ-SCF energies following in parentheses. Equilibrium bond lengths are in angstroms.

basis set utilized six primitive Al d-like functions (d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}, d_{yz}) with Gaussian exponent α = 0.4, an analogous set of carbon d functions (α = 0.75), and a set of hydrogen p functions (α = 0.75). The CI calculations included all single and double excitations relative to the SCF reference configuration, excepting the molecular orbitals corresponding to the aluminum and carbon 1s atomic orbitals which were held doubly occupied in all configurations and the three highest lying virtual orbitals which were deleted from the CI.

The ground-state electron configurations of the vinyl radicals and the vinylidene complex were verified as those determined by Trenary, Casida, Brooks, and Schaefer.[3] The ground-state electron configuration for the transition state of the 2 → 1 isomerization is

$$1a'^2 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2 6a'^2 7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 12a'$$
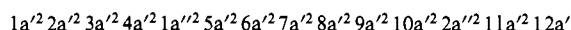
Results and Discussion

The results of our theoretical research are summarized in Figure 1 and Table I. In addition to the Al–C$_2$H$_2$ systems, the results of an analogous theoretical treatment for the bare acetylene → vinylidene isomerization are illustrated in the figure. As noted in Figure 1, the relative energies are compared to acetylene (on the top line of the figure) and to non-interacting Al + acetylene separated by 1000 bohrs (left side of bottom line of the figure). The absolute energies of these two systems are −77.1050 hartrees single point DZP-CI (−76.7992 hartrees DZ-SCF) and −319.1044 hartrees single point DZP-CI (−318.6542 hartrees DZ-SCF), respectively.

The equilibrium geometries and energies are qualitatively consistent with the earlier less precise theoretical study.[3] Comparison of the DZ-SCF aluminum–carbon bond lengths with the DZ-SCF results for the prototypical Al–C single bonds (r = 2.01 Å, Al–CH$_3$; r = 1.99 Å, Al–CH$_2$; and r = 1.97 Å, Al–CH)[6] suggests Al–C single bonds in the vinylidene complex, the 2 → 1 transition state, and the σ-bonded radicals. The slight decrease of this bond length in the Al–vinylidene complex is due to a non-zero π-overlap between the aluminum and carbon centers in the half-occupied 3b$_2$ orbital.

The harmonic vibrational frequencies presented in Table I unambiguously characterize the four stationary points. If the Al–C stretching frequencies in Table I are compared to those of Al–CH$_3$, Al–CH$_2$, and Al–CH (600, 640, and 670 cm^{-1}, respectively),[6] one notices a significant lowering of these frequencies in the Al–C$_2$H$_2$ isomers. This is not a reflection of weaker aluminum–carbon interactions in these isomers but rather a mass effect. All four

of these Al–C stretches involve significant displacement of the carbon nucleus which is not bonded to the aluminum (this effect is most prominent in the Al–vinylidene and transition-state structures). Thus, the stretching frequencies are lowered relative to those in which the motion of only one carbon is involved.

It is clear that the Al–vinylidene complex which is bound by 28.0 kcal is the most energetically favorable atomic arrangement, yet only structures 2 and 3 (bound by 15.5 and 14.0 kcal, respectively) are observed experimentally.[1,2] In spite of this, we now see that the theoretical and experimental results may be harmonized. It is structure 1 that has not yet been observed because of the prohibitive barrier (56.8 kcal with DZ-SCF and 39.1 kcal with single point DZP-CI) for the 2 → 1 isomerization. When this isomerization is compared to the acetylene → vinylidene isomerization, two important points may be made. First, the presence of aluminum stabilizes the vinylidene-like isomer, and the global energy minimum now lies on the vinylidene side of the reaction scheme. Considering that one result of the addition of the aluminum atom is to introduce an unpaired electron into the C$_2$H$_2$ system, the increased stability of Al–vinylidene is not surprising since the CCH$_2^-$ anion also exhibits this effect.[7,8] A second point to note is that the aluminum atom significantly reduces the barrier height relative to acetylene and vinylidene. The transition state between 1 and 2 is in fact lower in energy than non-interacting Al + vinylidene. The naked acetylene ⇌ vinylidene isomerization has been studied extensively,[9-13] and the most reliable studies to date give classical barrier heights of 46–48 kcal (HCCH → CCH$_2$) and 2–5 kcal (CCH$_2$ → HCCH). These results may be compared to our DZ-SCF barriers of 62.3 kcal (HCCH → CCH$_2$) and 26.1 kcal (CCH$_2$ → HCCH) and the barriers corresponding to our single point DZP-CI calculations of 46.1 kcal (HCCH → CCH$_2$) and 6.8 kcal (CCH$_2$ → HCCH). On the basis of these comparisons we predict the true barrier to

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2 → 1 isomerization to be within ±5 kcal of our single point DZP-CI result of 39.1 kcal.

It appears that aluminum, or possibly other metals, may be useful in isolating and identifying vinylidene. As discussed by Trenary,[3] the features exhibited in the energy surface of Al + C_2H_2 are likely to be important in other hydrocarbon rearrangements where a metal is introduced. A rather interesting result in this regard is found here in comparison with the naked vinylidene → acetylene rearrangement, which (as noted) has a negligible barrier. In contrast, Figure 1 shows (follow arrows in reverse direction) that the Al–vinylidene complex **1** has a substantial barrier (~52 kcal) for rearrangement to the Al–acetylene complex. Thus the

attachment of the aluminum atom, while reducing the barrier height relative to non-interacting Al + HCCH → Al + CCH_2, effectively introduces an inhibitive barrier to a reaction [**1** → **2**] which otherwise proceeds very rapidly.

Theoretical Study on the Quadruple Metal Bond in d⁴-d⁴ Binuclear Tetracarboxylate Complexes of Chromium, Molybdenum, and Tungsten by the Hartree-Fock-Slater Transition-State Method

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Abstract: Hartree-Fock-Slater calculations are presented on the metal-metal bond distance R_M^0 and metal-metal stretch force constant k_{MM}^0 for $M_2(CO_2H)_4$ (M = Cr, Mo, W) as well as the three states $^2B_{2g}$ ($\sigma^2\pi^4\delta$), ^2E_u ($\sigma^2\pi^3\delta^2$), and $^2A_{1g}$ ($\sigma\pi^4\delta^2$) of $M_2(CO_2H)_4^+$ (M = Cr, Mo, W). The three states $^2B_{2g}$, ^2E_u, and $^2A_{1g}$ corresponding to the ionization of an electron out of the δ, π, and σ metal-metal bonding orbitals, respectively, were calculated to be at lower energy than the ion states corresponding to ionizations from the ligand-based orbitals. It is shown from calculations on $W_2(CO_2CF_3)_4$ that the photoelectron spectrum of this molecule is consistent with σ, π, δ being at higher energy than the ligand-based orbitals, and a similar interpretation is offered, based on HFS calculations, for $Cr_2(CO_2CH_3)_4$ and $Mo_2(CO_2H)_4$. The ionization of an electron from δ results in a modest (0.04 Å) elongation of the metal-metal bond, whereas the increase in metal-metal bond length is more substantial (0.10 Å) for an ionization out of the π orbital. The ionization of an electron out of the strongly metal-metal bonding σ orbital does on the other hand not significantly change the metal-metal bond distance contrary to what one might have expected. This surprising result is explained in qualitative terms. It is finally shown that σ, π, δ in $M_2(PH_3)_4Cl_4$ (M = Mo, W) and σ, π in $Mo_2(OH)_6$, as for the tetracarboxylates, are at higher energy than the ligand-based orbitals, and this result is reconciled with the recorded photoelectron spectra of $M_2(PMe_3)_4Cl_4$ (M = Mo, W) and $Mo_2(OCH_2CMe_3)_6$. The change in R_M^0 on ionization of an electron from σ, π, δ in $M_2(PH_3)_4Cl_4$ (M = Mo, W) and π, σ in $Mo_2(OH)_6$ was calculated to follow the same trend as for the tetracarboxylates.

I. Introduction

The structure of the dimolybdenum tetracarboxylate complex $Mo_2(CO_2CH_3)_4$ was determined[1] shortly after the recognition of a quadruple metal-metal bond by Cotton in $Re_2Cl_8^{2-}$. Cotton accounted for the quadruple bond in $Re_2Cl_8^{2-}$ in terms of metal-metal bonding orbitals of local σ, π, δ axial symmetry, and the same bonding scheme was adopted for $Mo_2(CO_2CH_3)_4$.[3] The complex $Mo_2(CO_2CH_3)_4$ has according to Cottons bonding picture the electron configuration $\sigma^2\pi^4\delta^2$ with the same formal bond order of four as $Re_2Cl_8^{2-}$.

The neutral dimolybdenum tetracarboxylates $Mo_2(CO_2CH_3)_4$ and $Mo_2(CO_2H)_4$ have[4,5] been used widely to further our understanding of the quadruple metal-metal bond since their volatility makes them well suited for experimental investigations even in the gas phase, and $Mo_2(CO_2H)_4$ is further amiable for theo-

retical treatments.[6] One of the experimental technics with the strongest bearings on the nature of the quadruple metal-metal bond is low-energy photoelectron spectroscopy[5a] which in conjunction with theoretical calculations[6] can provide information on the states generated from ionizations of electrons out of the σ, π, δ and metal-metal bonding orbitals. Different interpretations of the recorded photoelectron spectra on $Mo_2(CO_2R)_4$ systems[5a,b] have, however, been provided by the HF ab initio[6a,b] method and the SCF–Xα–SW scheme[6c] in connection with theoretical calculations on $Mo_2(CO_2H)_4$. A recent ab initio calculation by Atha et al.[6d] seems, however, in our view, to have resolved the controversy.

The nature of the quadruple metal-metal bond has also been probed by low-energy photoelectron experiments on the homologous and equally volatile dichromium[5a] and ditungsten tetracarboxylates.[7] The interpretation of the recorded spectra of $Cr_2(CO_2R)_4$ systems by theoretical calculations[6a,8] has, however,

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