terized on the basis of multinuclear NMR, IR, and elemental analysis[7] and, in the case of 6, confirmed by single-crystal X-ray diffraction.

The spectral data (selected data in Table I) clearly establish the complexes to have trans stereochemistry. The ^{31}P NMR resonances are singlets with ^{195}Pt satellites, and ^1H NMR resonances are also pseudotriplets due to ^{195}Pt coupling. The aryl phosphine resonances in the ^{13}C NMR are triplets due to virtual coupling. An IR spectrum of 6 shows a weak absorption at 2112 cm^{-1} due to the C≡C stretch, and at 2102 and 2108 cm^{-1}, respectively, for 7 and 8.

The solid-state structure of 6 is illustrated in Figure 1.[8] The geometry is very close to square planar with angles about the Pt center normal at 90 ± 1°. The vinyl carbon–Pt bond length of 2.10 (1) Å and acetylide carbon–Pt bond length of 2.04 (1) Å are similar to others in comparable vinyl acetylide complexes.[9]

Although this series of compounds are not the first of their kind, they are products of a sequence of reactions that allows a systematic synthesis of bis-unsaturated *hetero* organo platinum species. The σ-vinyl group is formed via oxidative addition of the vinyl triflate and acetylide group via transmetalation of the labile triflate. These complexes, now available in a systematic fashion, are excellent models for palladium-catalyzed coupling reactions as stable analogues to the reactive palladium species. Like the palladium species, the platinum compounds in this study decompose cleanly in toluene to yield enynes. Further work is in progress and will be the subject of future reports.

Acknowledgment. Support for this work, provided by the National Science Foundation (CHE-8419099), is gratefully acknowledged. We thank Johnson-Matthey, Inc., for the generous loan of platinum. The high-field NMR spectrometers employed in this work were obtained through departmental grants from the National Science Foundation.

Supplementary Material Available: Full crystallographic data for 6 including tables of crystal data, least-squares planes, bond distances and angles, and final positional and thermal parameters (16 pages); a listing of calculated and observed structure factors (42 pages). Ordering information is given on any current masthead page.

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(7) Compound 6: mp 167–170 °C dec; IR (KBr) 3050 w, 2960 w, 2112 vw, 1572 w, 1480 m, 1431 s, 1248 m, 1093 s, 858 m, 739 s, 691 s cm^{-1}; ^1H NMR δ 0.41 (s, 9 H), 0.97 (s, $^3J(PtH)$ = 26 Hz, 3 H), 4.43 (m, $^3J(PtH)$ = 34 Hz, 1 H), 5.24 (m, $^3J(PtH)$ = 64 Hz, 1 H), 7.28–7.45 (aromatics, 18 H), 7.70–7.90 (aromatics, 12 H); ^{31}P NMR δ 22.5 (s, $^1J(PtP)$ = 3088 Hz); ^{13}C NMR δ 29.0 (s), 31.4 (s), 95.6 (t, $^2J(PC)$ = 17 Hz), 116.9 (t, $^3J(PC)$ = 3.5 Hz), 124.5 (s, $^2J(PtC)$ = 196 Hz), 127.7 (t, $^3J(PC)$ = 4.8 Hz), 130.1 (s), 132.6 (t, $^1J(PC)$ = 28 Hz), 135.6 (t, $^2J(PC)$ = 6.0 Hz), 164.8 (t, $^2J(PC)$ = 10 Hz). Anal. Calcd: C, 64.20; H, 5.27; P, 7.36. Found: C, 63.91; H, 5.37; P, 6.93. Compound 7: mp 169–170 °C dec; IR (KBr) 3048 w, 2917 w, 2102 m, 1590 m, 1574 w, 1479 m, 1431 s, 1180 w, 1082 s, 858 m, 739 s, 690 s cm^{-1}; ^1H NMR δ 0.96 (s, $^3J(PtH)$ = 25 Hz, 3 H), 4.49 (m, $^3J(PtH)$ = 33 Hz, 1 H), 5.31 (m, $^3J(PtH)$ = 64 Hz, 1 H), 6.17 (m, 2 H), 6.83 (m, 3 H), 7.30–7.50 (aromatics, 18 H), 7.75–7.86 (aromatics, 12 H); ^{31}P NMR δ 19.9 (s, $^1J(PtP)$ = 3065 Hz); ^{13}C NMR δ 31.0 (s, $J(PtC)$ = 27 Hz), 115.4 (s), 116.9 (t, $^2J(PC)$ = 17 Hz), 117.5 (br s), 124.4 (s), 127.6 (s), 128.8 (t, $^3J(PC)$ = 5.2 Hz), 129.5 (br s, $^3J(PtC)$ = 9.0 Hz), 130.4 (s), 130.7 (s), 132.2 (t, $^1J(PC)$ = 28 Hz), 135.5 (t, $^2J(PC)$ = 6.0 Hz), 163.2 (t, $^2J(PC)$ = 10 Hz). Anal. Calcd: C, 65.50; H, 4.68; P, 7.19. Found: C, 65.08; H, 4.74; P, 7.18. Compound 8: mp 166–168 °C dec; IR (KBr) 3055 w, 2920 w, 2108 m, 1572 m, 1479 m, 1431 s, 1352 m, 1183 m, 1092 s, 997 w, 892 m, 842 s, 745 s, 691 s cm^{-1}; ^1H NMR δ 0.90 (s, $^3J(PtH)$ = 25 Hz, 3 H), 2.53 (s, 3 H), 3.35 (t, $^5J(HP)$ = 1.5 Hz, $^4J(PtH)$ = 11 Hz, 2 H), 4.45 (m, $^3J(PtH)$ = 34 Hz, 1 H), 5.26 (m, $^3J(PtH)$ = 64 Hz, 1 H), 7.30–7.48 (aromatics, 18 H), 7.70–7.83 (aromatics, 12 H); ^{31}P NMR δ 23.8 (s, $^1J(PtP)$ = 3078 Hz); ^{13}C NMR δ 30.9 (s, $^2J(PtC)$ = 28 Hz), 55.6 (s), 61.7 (br s, $^3J(PtC)$ = 16 Hz), 110.1 (br s), 117.4 (br t, $^3J(PC)$ = 4.3 Hz), 127.9 (t, $^3J(PC)$ = 5.4 Hz), 130.4 (s), 132.2 (t, $^1J(PC)$ = 28 Hz), 135.5 (t, $^2J(PC)$ = 6.0 Hz), 163.1 (t, $^2J(PC)$ = 10 Hz). Anal. Calcd: C, 62.24; H, 4.86; P, 7.47. Found: C, 61.67; H, 4.88; P, 7.10.

(8) Crystal data for 6: $PtP_2C_{45}H_{44}$; colorless; crystal dimensions 0.38 × 0.25 × 0.20; monoclinic; $P2_1/n$; a = 12.724 (6) Å, b = 16.762 (5) Å, c = 18.779 (4) Å, β = 97.91 (3)°, V = 3966.9 Å^3; Z = 4; no decay correction applied; μ = 36.80 (minimum absorption correction 54.76, maximum absorption correction 99.99); Mo Kα radiation at ambient temperature; 2θ limit = 3.0–48°; reflections collected = 6198 unique, 4629 with $I > 3\sigma(I)$; R = 0.0449, R_w = 0.0567, GOF = 3.40.

(9) See ref 5. Also: Villa, A. C.; Manfredotti, A. G.; Guastini, C.; Russo, M. V. *Cryst. Struct. Commun.* **1977**, *6*, 313. E.g.: the vinyl Pt–C bond length is 2.10 (2) Å and the acetylide Pt–C is 1.99 (2) Å.

Tantalum–Ligand Bond Lengths in d^0 and d^1 Piano-Stool Complexes

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Summary: Ab initio and extended Hückel calculations on (η^5-Cp)TaCl$_3$(SiH$_3$) and (η^5-Cp)TaCl$_2$(PH$_3$)(SiH$_3$) (Cp = C$_5$H$_5$) explain why the former, d^0 complex has a longer Ta–Si bond length than the latter, d^1 complex. A spin orbital that strongly resembles the LUMO of the d^0 complex is occupied in the d^1 complex. This spin orbital has little Ta–Si bonding or antibonding character, but it has some Ta–Cl antibonding character. The presence of an electron in this level leads to longer Ta–Cl separations. Positive Mulliken charges on Ta and negative charges on the Cl's also lead to larger Ta–Cl distances when the d electron count increases. Elongation of the Ta–Cl distances allows the Ta–Si distance to decrease in the d^1 complex. d orbitals on Si have little effect on the ab initio optimized geometries or on the analysis of the electronic distribution.

Advances in silicon-based polymers and solid-state precursors are motivated by the search for new photoresists, conductors, and other materials with desireable electronic properties.[1] Exploring interactions of Si ligands with transition metals may disclose improved synthetic routes to new materials.[2] Contrasts with the transition-metal chemistry of carbon are of intrinsic interest to the organometallic chemist.[3] Understanding chemical bonding between Si and transition metals is a fundamental aspect of these research areas.

Some recent synthetic and structural studies have concentrated on piano-stool complexes containing the silyl ligand.[4] In complex A, (η^5-Cp*)TaCl$_3$(SiMe$_3$) (Cp* = C$_5$Me$_5$), the transition metal has a d^0 electron count and a Ta–Si bond length of 2.669 (4) Å. In complex B, (η^5-Cp*)TaCl$_2$(PMe$_3$)(SiMe$_3$), replacement of a chloride by a phosphine implies that the electron count is d^1. B's shorter Ta–Si bond length, 2.642 (1) Å, cannot be based on atomic radii factors because Ta(IV) has a larger radius than Ta(V). Qualitative notions of d centered molecular orbitals (MO's) suggest that they generally are nonbonding or antibonding with respect to σ-donor ligands.[5] This implies a longer,

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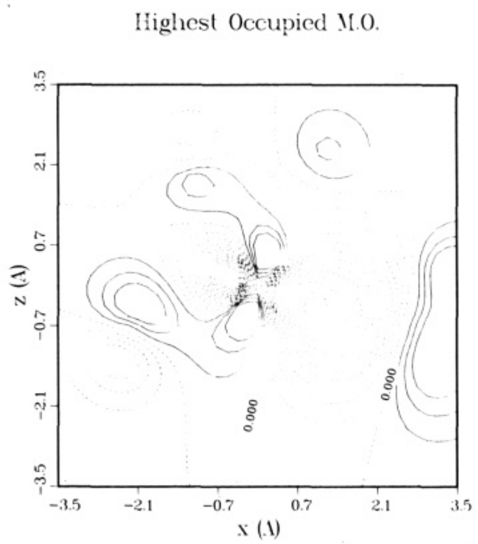

Figure 1. Contour plot of $CpTaCl_3SiH_3$'s highest occupied molecular orbital in the plane containing Ta, Si, and the Cp centroid. Dashed contours in intervals of 0.015 range from 0 to −0.21; solid contours range from 0.015 to 0.06. Approximate atomic coordinates: Ta (0, 0, 0), Si (2.47, 0, −0.90), Cl (−2.23, 0, −0.81).

not shorter, Ta–Si separation for the d^1 complex. A shorter d^1 separation can be rationalized by imagining that the extra electron is placed in a Ta-centered MO that donates to Si-centered empty orbitals with π-pseudosymmetry. A qualitative description of the latter orbitals would include Si d function and Si–H antibonding contributions.

To test the validity of these rationalizations and expectations, extended Hückel[6] and ab initio calculations were performed on models of A and B. These model compounds, called **1** and **2**, respectively, have H's in place of the original methyl groups. With use of the published crystallographic structures[4a] to freeze the C_5H_5 (Cp), Cl, and PH_3 positions, Ta–Si bond lengths were optimized to see whether reasonable structural predictions could be made.

Extended Hückel calculations on **1** were analyzed[7] in terms of the fragment MO's of $CpCl_3Ta^+$ and SiH_3^-. (No Si d functions were present in these calculations.) **1**'s HOMO (Figure 1) is composed chiefly of the HOMO of SiH_3^-, a lone pair that points at the Ta nucleus, with small stabilizing contributions from two of the d-like MO's on the Ta fragment. **1** has a mirror plane that bisects the SiH_3^- ligand, so the (C_s) symmetry label of **1**'s HOMO is a′. The a″ LUMO (Figure 2) is dominated by a Ta d orbital that is approximately parallel to the Cp plane with lobes that lie in regions between the four legs of the piano stool. Almost no energy change takes place in this MO when $CpCl_3Ta^+$ is allowed to interact with SiH_3^-. Contributions from the ligands to the LUMO are quite small. Filling this level has little effect on the Ta–Si overlap population. Calculations on **2** produce similar results, but with a single electron residing in the a″ MO.

To augment these qualitative concepts of the bonding and to calculate Ta–Si bond length changes, ab initio methods were employed. Restricted, closed-shell Hartree–Fock and unrestricted Hartree–Fock (UHF) calculations on **1** and **2**, respectively, were performed with effective core potentials (ECP's)[8] on Ta, Si, P, and Cl. Double-ζ ECP basis sets were used for Ta and Si. A basis set of similar quality was chosen for the H's attached to the Si.[9] Single-ζ ECP basis sets were used for P and Cl.[10] STO-3G basis sets were employed for the Cp ring and the phosphine H's.[11] Analytic gradient geometry optimizations[12] produced Ta–Si bond lengths of 2.752 Å for **1** and 2.738 Å for **2**. A set of five d gaussians[13] was added to the Si basis, yielding new bond lengths of 2.725 Å for **1** and 2.708 Å for **2**. By acting as polarization functions[14] that increase the flexibility of the basis set, Si d functions play a significant role in enhancing bonding between Ta and Si. The predicted difference in bond lengths is 0.017 Å and agrees reasonably well with the experimental difference of 0.02–0.03 Å.[4a]

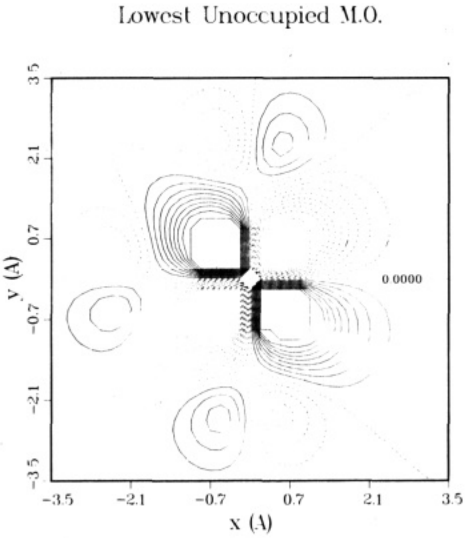

Figure 2. Contour plot of $CpTaCl_3SiH_3$'s lowest unoccupied molecular orbital in the Ta-intersecting plane that is parallel to the Cp ring. Dashed contours in intervals of 0.0075 range from 0 to −0.0675; solid contours range from 0.0075 to 0.0675. Approximate atomic coordinates: Ta (0, 0, 0), Cl (−2.23, 0, −0.80) and (0, ±2.20, −0.80).

MO's and overlap populations from the ab initio calculations were employed in an analysis of the electronic structure of these model compounds. The HOMO in **1** is a bonding combination of Ta d and Si p orbitals in approximately equal amounts. In UHF calculations on **2**, the HOMO of **1** splits into α- and β-spin orbitals. While the α-spin orbital is quite similar to **1**'s HOMO, the β-spin orbital is polarized toward Si. The LUMO of **1** and the highest occupied α-spin orbital (HOASO) of **2** are dominated by d_{xy} basis functions on Ta, where the z axis is defined by Ta and the Cp centroid. As in the extended Hückel calculations, the d function's lobes are parallel to the Cp ring and point to regions between the four piano-stool legs. There is no evidence of donation from Ta to empty Si-centered orbitals with or without Si d functions. In the d^0 and d^1 complexes, ab initio Ta–Si overlap pop-

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ulations remain constant at 0.264 for the smaller basis and at 0.280 for the larger basis. A detailed analysis of individual elements of the Mulliken overlap population matrix indicates that π-interactions between Ta and Si are insignificant. Si d functions primarily affect σ Ta–Si bonding. Most of the non-Ta contributions in 1's LUMO and 2's HOASO belong to Cl p functions that interact in a π-antibonding sense with Ta's d_{xy} functions.

An important portion of the present analysis concerns Mulliken charges, which can provide a rough summary of the electronic distribution. In all calculations, the silyl group, the phosphine, and the Cp ring have charges that are close to zero. Only the chlorine ligands are unambiguously anionic, with charges of about −0.4 for 1 and 2. Increasing the d electron count will reduce Coulomb attractions between Ta and the Cl's.

Upon changing from d^0 to d^1, a combination of electrostatic repulsions and Ta–Cl antibonding character in 2's HOASO causes the elongation of the average Ta–Cl separation from 2.343 Å in A to 2.405 Å in B. As the Ta is now less crowded in the latter structure, it is possible for Si to approach Ta more closely. (For the same reasons, the observed Ta–Cp(centroid) distance is 0.03 Å less in B). The expense of these calculations prevents a full optimization of the Ta–Si distance as a function of Ta–Cl distance or other geometric parameters. It is nonetheless possible to state how occupation of the Ta d_{xy}-like MO affects the Ta–ligand separations. Antibonding Ta–Cl character causes the Ta–Cl separation to increase, allowing the Ta–Si distance to decrease. Mulliken charges on the ligands also disclose the electrostatic origin of 2's longer Ta–Cl separation and the consequent decrease in the Ta–Si distance.

Registry No. $(\eta^5\text{-Cp})TaCl_3(SiH_3)$, 113748-18-8; $(\eta\text{-Cp})TaCl_2(PH_3)(SiH_3)$, 113748-19-9.

Dimethylsilylene: Spectroscopy, Reactivity, and Complexation in Fluid Solutions[1]

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Summary: Upon 266-nm laser flash photolysis, cyclohexane solutions of dodecamethylcyclohexasilane give rise to a transient species (λ_{max} = 465 nm) that is best assigned as dimethylsilylene. This species exhibits unusually high reactivity toward alcohols and reagents containing Si—H, C═C, and C≡C bonds (with rate constants in the limit of diffusion control) and readily forms complexes with lone-pair containing molecules (ethers, triethylamine, and acetonitrile), the latter showing considerably reduced reactivity relative to the "free" silylene.

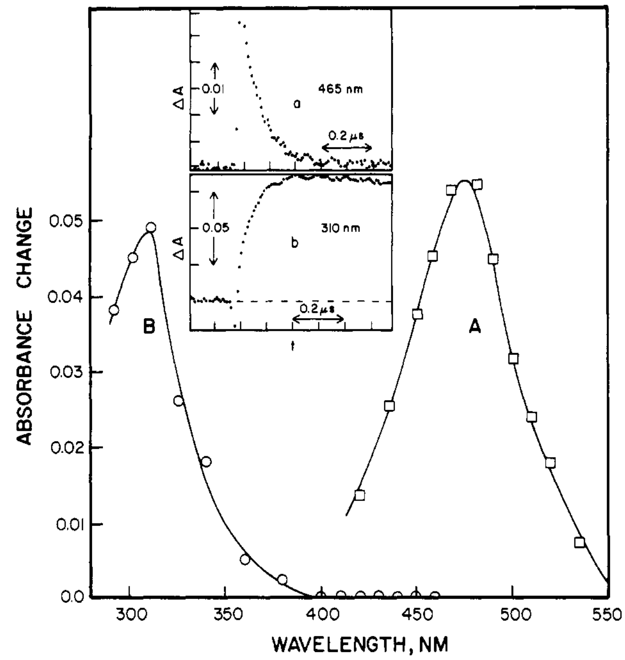

Figure 1. Transient absorption spectra following 266-nm laser flash photolysis of dodecamethylcyclohexasilane solution in cyclohexane: A, in the absence of THF and at 0.1 μs following the laser flash, and B, in the presence of 0.8 mM THF and at 1.3 μs following laser flash. Note that the two spectra were taken under different conditions of laser intensity and ground-state absorbance. Insets: kinetic traces showing (a) the enhanced decay of the 465-nm species in the presence of 0.8 mM THF and (b) the concomitant formation of transient absorption at 310 nm.

Currently, considerable interest is being shown in divalent silicon intermediates, i.e., second-row analogues of carbenes.[3] In particular, dimethylsilylene (1) has been at the center of controversy for a number of years.[4-6] This species is claimed to be formed as a bright yellow product (λ_{max} = 430–470 nm) of photolysis of various precursors (e.g., dodecamethylcyclohexasilane, 2) in low-temperature inert gas or hydrocarbon matrices[4] as well as in the course of flash pyrolysis of suitable substrates followed by isolation in low-temperature N_2 or Ar matrices.[5] In contrast, laser flash photolysis (308-nm) experiments with 2 in fluid hydrocarbon solutions at room temperature have been negative regarding the observation of the 450-nm species;

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[1] This work was supported in part by the Office of Basic Energy Sciences, Department of Energy. This is Document No. NDRL-3032 from the Notre Dame Radiation Laboratory.

[2] (a) Dow Corning Corporation. (b) Permanent address: Materials Research Department, Weizmann Institute of Science, Rehovot, Israel. (c) University of Notre Dame.

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