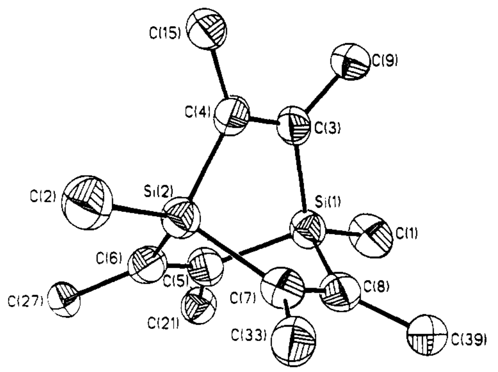
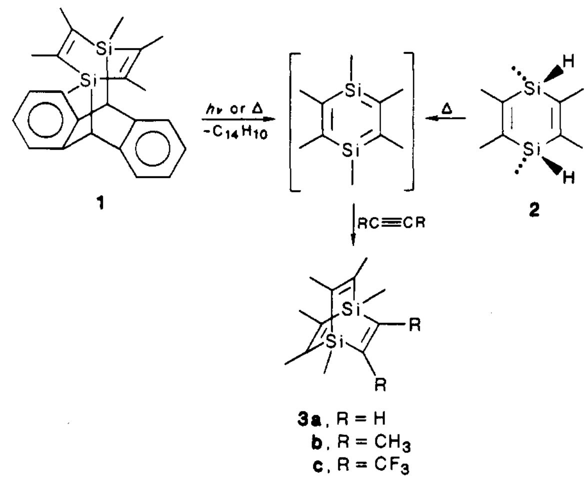


Figure 1. Crystal structure of **6a**. All atoms of the phenyl rings except the ipso carbon atoms and all hydrogen atoms have been omitted for clarity. Bond lengths (pm): 185.5 [Si(1)–C(1)], 184.9 [Si(2)–C(2)], 188.6 [Si(1)–C(3)], 188.7 [Si(2)–C(4)], 190.4 [Si(1)–C(5)], 189.7 [Si(2)–C(6)], 188.6 [Si(1)–C(8)], 190.5 [Si(2)–C(7)], 136.7 [C(3)–C(4)], 133.4 [C(5)–C(6)], 135.3 [C(7)–C(8)]. The silicon–silicon nonbonded distance is 293 pm.

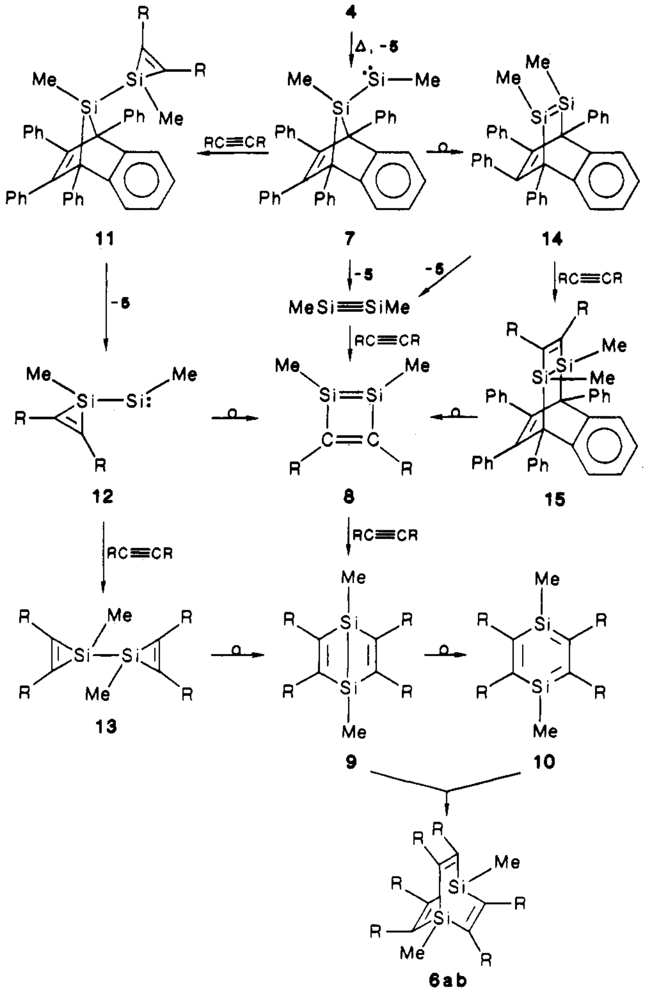
Scheme I



There are several possible mechanisms for the formation of **6ab** summarized in Scheme II, which involve intermediates of some interest. The probable initial step is loss of **5** to give silylene **7**, which might then lose a second molecule of **5** to give MeSi≡SiMe. Dimethyldisilyne would probably react rapidly with alkynes to give disilacyclobutadiene **8** followed by Dewar benzene **9**,[9] which could add a final molecule of alkyne to give disilabarrelene either directly or after rearranging to 1,4-disilabenzene **10**. An alternative route involves trapping of **7** with alkyne to give a silacyclopropene, **11**, which could lose **5** to produce the silylene **12**; the latter could add another alkyne molecule to give **13**, which could rearrange to **9**. Rearrangement of **12** to **8** is also possible. Finally, 1,2-rearrangement of **7** to give disilene **14** is conceivable; **14** could form MeSi≡SiMe, or, in two steps, **8**.

All of these and other plausible mechanisms converge at 1,4-disilabenzene, in either the open (**10**) or Dewar (**9**) form. We propose that one of these species is the immediate precursor to disilabarrelene, both in these reactions and in the syntheses from **1** and **2** mentioned above.

Scheme II



Registry No. 4, 102649-09-2; 5, 751-38-2; 6a, 113668-64-7; 6b, 113685-62-4; PhC≡CPh, 501-65-5; EtC≡CEt, 928-49-4.

Supplementary Material Available: Tables of crystal data, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, and H-atom coordinates and isotropic thermal parameters (6 pages); a listing of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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(8) A crystal of $C_{44}H_{36}Si_2$ (**6a**) (M_r 620; 0.2 mm × 0.2 mm × 0.4 mm) was found to be triclinic with a = 10.849 (3) Å, b = 16.968 (6) Å, c = 9.746 (3) Å, α = 98.76 (2)°, β = 92.51 (3)°, γ = 97.20 (3), V = 1755.84 Å^3, space group $P\bar{1}$, Z = 2, μ(Mo Kα) = 1.25 cm^{-1}, D_{calcd} = 1.173 g cm^{-3}. Data were collected on a Nicolet $P\bar{1}$ diffractometer with Mo Kα X-radiation using θ–2θ scans. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically to R = 0.073 for 3507 observed reflections ($|F_o| > 3\sigma|F_o|$; $2\theta \leq 45.770°$).

(9) 1,4-Cycloaddition of disilenes with alkynes is precedented: De Young, D. J.; West, R. *Chem. Lett.* **1986**, *6*, 883. De Young, D. J.; Fink, M. J.; Michl, J.; West, R. *Main Group Metal Chem.* **1987**, *1*, 19.

Mixed σ-Alkynyl–σ-Vinyl Bis(triphenylphosphine)platinum Complexes via a Labile σ-Vinyl Platinum Triflate Precursor

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Summary: Addition of a vinyl platinum(II) complex with a labile triflate ligand to a THF solution of selected acetylides, generated from the corresponding terminal acetylenes and LiNH$_2$, gives trans σ-alkynyl-σ-vinyl Pt(II) complexes in good yields. Key spectral features and a single-crystal X-ray structure determination are described.

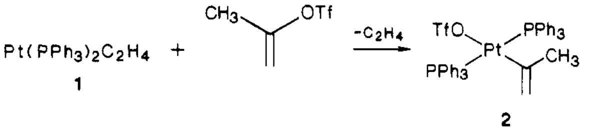
Table I. Selected NMR Data for Complexes 6–8[a]

compd	^{1}H NMR	^{31}P NMR[b]	^{13}C NMR[c]
6	0.41 (s, 9 H)	22.5 (s, ^1J(PtP) = 3088 Hz)	*d*
	0.97 (s, ^3J(PtH) = 26 Hz, 3 H)		95.6 (t, ^2J(PC) = 17 Hz)[e]
	4.43 (m, ^3J(PtH) = 34 Hz, 1 H)		116.7 (t, ^3J(PC) = 3.5 Hz)[f]
	5.24 (m, ^3J(PtH) = 64 Hz, 1 H)		124.5 (s, ^2J(PtC) = 196 Hz)[g]
			164.8 (t, ^2J(PC) = 10 Hz)[h]
7	0.96 (s, ^3J(PtH) = 25 Hz, 3 H)	19.9 (s, ^1J(PtP) = 3065 Hz)	31.0 (s, ^2J(PtC) = 27 Hz)
	4.49 (m, ^3J(PtH) = 33 Hz, 3 H)		115.4 (s)[g]
	5.31 (m, ^3J(PtH) = 64 Hz, 1 H)		116.9 (t, ^2J(PC) = 17 Hz)[e]
	6.17 (m, 2 H)		117.5 (br s)[f]
	6.83 (m, 3 H)		163.2 (t, ^2J(PC) = 10 Hz)[h]
8	0.90 (s, ^3J(PtH) = 25 Hz, 3 H)	23.8 (s, ^1J(PtP) = 3078 Hz)	30.9 (s, ^2J(PtC) = 28 Hz)
	2.53 (s, 3 H)		110.1 (br s)[g]
	3.35 (t, ^5J(PH) = 1.5 Hz, ^4J(PtH) = 11 Hz, 2 H)		117.4 (t, ^3J(PC) = 4.3 Hz)[f]
	4.45 (m, ^3J(PtH) = 34 Hz 1 H)		*i*
	5.26 (m, ^3J(PtH) = 64 Hz, 1 H)		163.1 (t, ^2J(PC) = 10 Hz)[h]

[a] All spectra were recorded in CD_2Cl_2; shifts are in ppm. [b] To external H_3PO_4. [c] Only the isopropenyl methyl and unsaturated carbons of the unsaturated ligands are reported. [d] Obscured by *tert*-butyl methyl resonance. [e] α-Carbon of acetylide. [f] β-Carbon of vinyl. [g] β-Carbon of acetylide. [h] α-Carbon of vinyl. [i] α-Carbon of the acetylide obscured by the aromatics.

Oxidative addition reactions of low-valent platinum with unsaturated substrates are well-documented[1] with some recent attention given to the reaction of vinyl substrates.[2] Little subsequent chemistry of these *σ-vinyl* Pt(II) halide compounds has been described,[3] presumably due to the unreactivity of the halide complexes toward transmetalation. The recent preparation of vinyl triflate Pt(II) complexes may circumvent this unreactivity. Due to the superior leaving group ability of the triflate group which translates to superior lability in transition-metal complexes, substitution by various nucleophiles is possible. We report here the reactions of halide-free THF solutions of selected acetylides with a labile triflate platinum complex to yield stable *trans*-Pt(II) *σ*-alkynyl–*σ*-vinyl complexes. These compounds are unique since analogous palladium complexes, which have not been isolated and characterized but only observed, have been postulated as intermediates in palladium-catalyzed cross-coupling reactions.[4] This class of compounds is very difficult to obtain by other means. To our knowledge the only examples are the compounds obtained from complex mixtures in the reactions of hydrazine, $(PPh_3)_2PtCl_2$, and acetylenes.[5]

Reaction of 1.1 equiv of 2-propenyl triflate with $(PPh_3)_2Pt(C_2H_4)$ (1) in toluene at room temperature within minutes gives as a white precipitate spectroscopically and analytically pure, 2, as a 0.5-mol toluene solvate in 84% yield (eq 1).[6] Complex 2 may be recrystallized from CH_2Cl_2/Et_2O solutions to give colorless rods. Addition of the nonrecrystallized material to THF solutions of acetylides 3–5, generated from the terminal acetylenes and $LiNH_2$, gives after stirring overnight and workup the title complexes 6–8 in 60, 68, and 38% yields, respectively (eq 2).



(1)

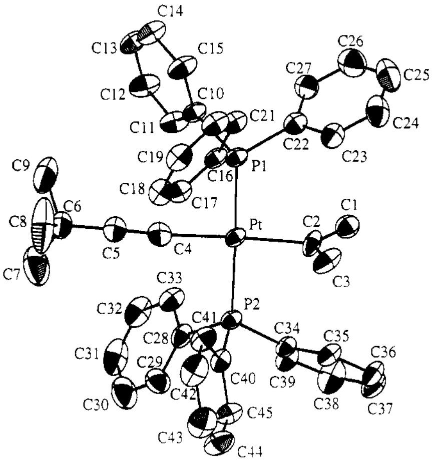
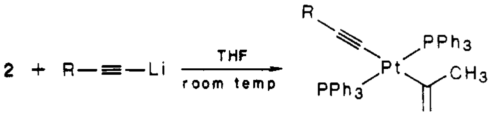


Figure 1. ORTEP representation of 6. Selected bond distances (Å): Pt–C2, 2.10 (1); Pt–C4, 2.04 (1); Pt–P1, 2.293 (3); Pt–P2, 2.296 (3); C2–C3, 1.36 (2); C4–C5, 1.21 (2); C1–C2, 1.48 (2); C5–C6, 1.46 (2). Selected bond angles (deg): P1–Pt–C2, 90.2 (3); C2–Pt–P2, 90.8 (4); P2–Pt–C4, 88.9 (4); C4–Pt–P1, 89.5 (4); C2–Pt–C4, 173.0 (4); P1–Pt–P2, 174.5 (1); C4–C5–C6, 178 (1); C3–C2–Pt, 118 (1); C1–C2–Pt, 119.8 (8).



(2)

3 R = *tert*-butyl 6
4 R = phenyl 7
5 R = methoxymethyl 8

Complexes 6–8 are stable crystalline solids (6 and 8 are colorless; 7 is pale yellow) that have been fully charac-

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(3) For palladium vinyl complexes see: Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181. Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.

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(5) Furlani, A.; Russo, M. V.; Villa, A. C.; Manfredotti, A. G.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1977**, 2154.

(6) Compound **2**: mp 142–143 °C dec; IR (KBr) 3067 w, 1585 w, 1479 m, 1429 s, 1313 s, 1200 s, 1091 s, 1005 s, 852 m, 744 s, 689 s, 620 s cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.65 (br s, ^3J(PtH) = 54 Hz, 3 H), 4.58 (br s, ^3J(PtH) = 78 Hz, 1 H), 4.77 (br s, ^3J(PtH) = 162 Hz, 1 H), 7.4–7.8 (aromatics, 30 H); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 26.9 (s, ^1J(PtP) = 3362 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 28.8 (br s, ^2J(PtC) = 57 Hz), 114.3 (br s), 128.0 (t, ^3J(PC) = 5.8 Hz), 129.4 (t, ^1J(PC) = 28 Hz), 131.1 (s), 135.2 (t, ^2J(PC) = 7.2 Hz), 135.4 (t, ^2J(PC) = 6.5 Hz). Anal. Calcd: C, 54.66; H, 4.12; P, 6.48. Found: C, 54.39; H, 4.16; P, 6.79.

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 ^{1}H 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}; ^{1}H NMR δ 0.41 (s, 9 H), 0.97 (s, ${}^{3}J$(PtH) = 26 Hz, 3 H), 4.43 (m, ${}^{3}J$(PtH) = 34 Hz, 1 H), 5.24 (m, ${}^{3}J$(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, ${}^{1}J$(PtP) = 3088 Hz); ^{13}C NMR δ 29.0 (s), 31.4 (s), 95.6 (t, ${}^{2}J$(PC) = 17 Hz), 116.9 (t, ${}^{3}J$(PC) = 3.5 Hz), 124.5 (s, ${}^{2}J$(PtC) = 196 Hz), 127.7 (t, ${}^{3}J$(PC) = 4.8 Hz), 130.1 (s), 132.6 (t, ${}^{1}J$(PC) = 28 Hz), 135.6 (t, ${}^{2}J$(PC) = 6.0 Hz), 164.8 (t, ${}^{2}J$(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}; ^{1}H NMR δ 0.96 (s, ${}^{3}J$(PtH) = 25 Hz, 3 H), 4.49 (m, ${}^{3}J$(PtH) = 33 Hz, 1 H), 5.31 (m, ${}^{3}J$(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, ${}^{1}J$(PtP) = 3065 Hz); ^{13}C NMR δ 31.0 (s, J(PtC) = 27 Hz), 115.4 (s), 116.9 (t, ${}^{2}J$(PC) = 17 Hz), 117.5 (br s), 124.4 (s), 127.6 (s), 128.8 (t, ${}^{3}J$(PC) = 5.2 Hz), 129.5 (br s, ${}^{3}J$(PtC) = 9.0 Hz), 130.4 (s), 130.7 (s), 132.2 (t, ${}^{1}J$(PC) = 28 Hz), 135.5 (t, ${}^{2}J$(PC) = 6.0 Hz), 163.2 (t, ${}^{2}J$(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}; ^{1}H NMR δ 0.90 (s, ${}^{3}J$(PtH) = 25 Hz, 3 H), 2.53 (s, 3 H), 3.35 (t, ${}^{5}J$(HP) = 1.5 Hz, ${}^{4}J$(PtH) = 11 Hz, 2 H), 4.45 (m, ${}^{3}J$(PtH) = 34 Hz, 1 H), 5.26 (m, ${}^{3}J$(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, ${}^{1}J$(PtP) = 3078 Hz); ^{13}C NMR δ 30.9 (s, ${}^{2}J$(PtC) = 28 Hz), 55.6 (s), 61.7 (br s, ${}^{3}J$(PtC) = 16 Hz), 110.1 (br s), 117.4 (br t, ${}^{3}J$(PC) = 4.3 Hz), 127.9 (t, ${}^{3}J$(PC) = 5.4 Hz), 130.4 (s), 132.2 (t, ${}^{1}J$(PC) = 28 Hz), 135.5 (t, ${}^{2}J$(PC) = 6.0 Hz), 163.1 (t, ${}^{2}J$(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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