the hydride or alkyl ligand at the CO_2 carbon atom.[3,12-14] The few examples in which dissociative mechanisms appear are found for complexes with enhanced ligand lability or where the metal–ligand bond is cleaved photochemically prior to the insertion step.[15,16]

Acknowledgment. We wish to acknowledge the Gas Research Institute for generous funding.

Registry No. *fac*-Re(bpy)$(CO)_3$H, 94241-40-4; *fac*-Re(bpy)$(CO)_3$C(O)H, 100229-21-8; *fac*-Re(4,4′-Cl_2-2,2′-bpy)$(CO)_3$H, 100229-22-9; *fac*-Re(4,4′-Me_2-2,2′-bpy)$(CO)_3$H, 100229-23-0; *fac*-Re(4,4′-*t*-Bu_2-2,2′-bpy)$(CO)_3$H, 100229-24-1; *fac*-Re(4,4′-OMe_2-2,2′-bpy)$(CO)_3$H, 100229-25-2; D_2, 7782-39-0; CO_2, 124-38-9.

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The Electronic Structure of a Methylated Polysilane Chain: Trans H–$(SiMe_2)_5$–H

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Summary: CNDO/2(S + DES CI) computations on trans H–$(SiMe_2)_5$–H are shown to yield energies and transition intensities which parallel experiment. The nature of the levels contributing to excitation is discussed.

Electronically saturated aryl- and alkyl-substituted silane chains and their cyclic counterparts have been found to exhibit a wide range of properties generally associated with π-electron frameworks.[1] Of interest is elucidation of the nature of the strong and conformationally dependent electronic absorption observed in the near UV for longer chain systems.[2-5] Although several computational efforts have addressed silane chain ground-state conformational properties,[6] the nature of the lower lying excited states is not well understood.

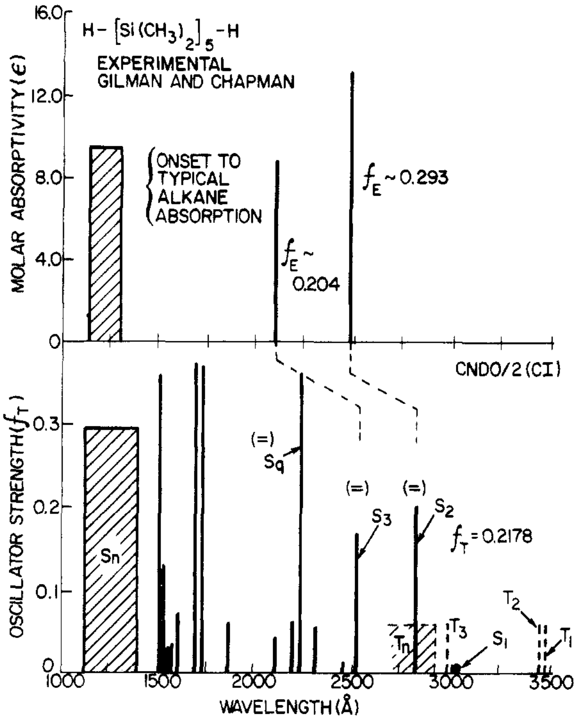

Figure 1. Comparison of the experimental[9] and calculated silane chain absorption spectrum. The experimental oscillator strengths were estimated from the molar absorptivities[9] in accord with the approximately of H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules* (Academic: New York 1967), p 9, assuming $(\Delta\bar{\nu})_{1/2} = 5.0 \times 10^3$ cm^{-1}. Polarizations relative to the long chain axis are given in parenthesis. T_n denontes a dense manifold of triplets at $\sim S_2$, suggesting efficient intersystem crossing. For comparison to typical alkane absorption, see Robin.[5c]

This communication reports the results of semiempirical CNDO/2(S + DES CI) computations[7] on the ground and selected singlet and triplet excited-state properties of trans H–$(SiMe_2)_5$–H using an Si 3s, 3p, C 2s, 2p + H1s minimal basis set.[8] Si–Si bond stabilization due to methyl substitution is discussed and attributed in part to ionic bonding enhancements.

Figure 1 compares the computational results with the optical absorptions.[9] Although S_2 and S_3 are considerably below the observed transition energies, their separation and relative oscillator strengths reflect the experimental splitting and intensity pattern. Furthermore, the calculated intense transition ~0.6 eV above S_3 (S_9 in Figure 1) is in accord with expectations based on the spectra of closely related system.[1b,5c] The lower lying CI wave functions have dominant singly excited components in-

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(8) The molecular geometry was approximated (C_{2v}) using Si–Si and Si–H bond lengths of 2.280 and 1.430 Å, respectively, with slightly distorted tetrahedral Si–Si–Si bond angles of 120°—see (a)–(c) below for *optimized* Si–Si–Si bond angles near 120°; Si–C and C–H bond lenghs of 1.850 and 1.119 Å, respectively, with C–Si–C and Si–Si–C bond angles of 120° and standard tetrahedron bond angles for the methyl groups. (a) Dewar, M. J. S.; Lo, D. H.; Ramdsen, C. A. *J. Am. Chem. Soc.* **1975**, *97* 1311–1318. (b) Teramae, H,; Yamabe, T.; Imamura, A., Theoret. Chim. Acta **1983**, *64*, 1–12. (c) Takeda, K.; Matsumoto, N.; Fukuchi, M., *Phys. Rev. B: Condens. Matter* **1984**, 30, 5871–5876.

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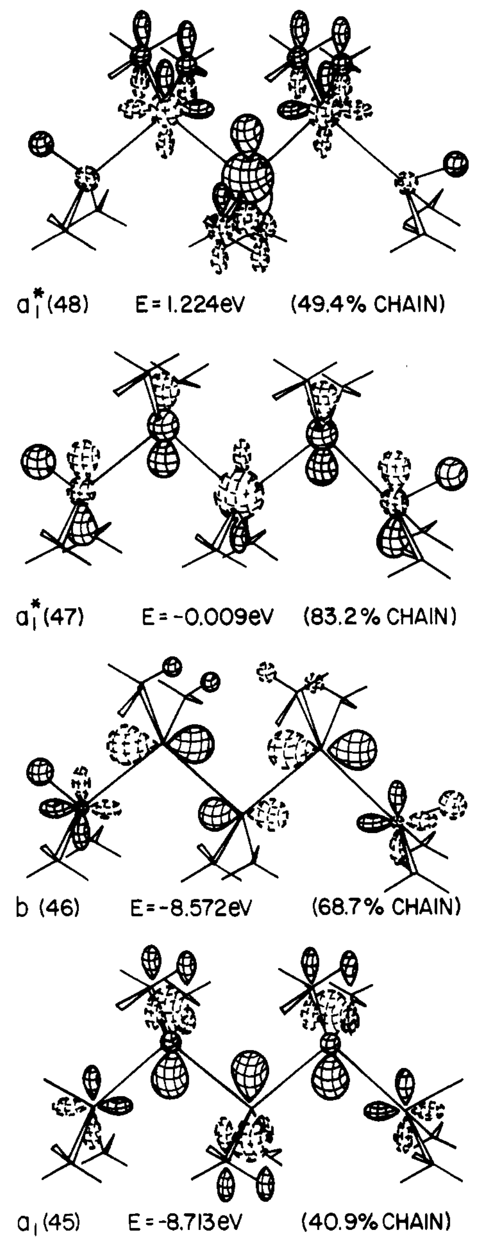

Figure 2. The highest occupied and lowest unoccupied molecular orbitals of trans H–(SiMe$_2$)$_5$–H (C_{2v}). Only Si and C s and p orbitals with coefficients greater than or equal to |0.100| are included. The b$_1$(45) and a$_1$*(48) levels have significant out-of-plane carbon p orbital contributions. In the interest of clarity only the s and in-plane p orbital coefficients are shown.

volving the two highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, Figure 2. S$_2$ and S$_3$ involve HOMO → LUMO ± HOMO → 2nd LUMO transitions (~72.0/11.0 and 4.0/64.0%, respectively), whereas T$_2$ is ~90.3% pure HOMO → LUMO. S$_1$ and T$_1$ are primarily excitations from the 2nd HOMO level (93.0 and 72.2%, respectively). The qualitatively different nature of the HOMO and LUMO levels imply a weak optical absorption. As found previously for the trans models of hydrogenated silane chains,[6d,10] the –SiMe$_2$– repeat unit transition moment terms are relatively small for excitation from the b$_1$ (σ) HOMO level. These terms constructively sum due to a highly favorable phase relationship to yield one-electron b$_1$(46) → a$_1$*(47) and b$_1$(46) → a$_1$*(48) transition moments which are too large to reflect experiment. For example, pure HOMO → LUMO excitation occurs with an oscillator strength of $f_T = 0.536$. Configuration mixing yields net transition moments reduced from the one-electron values due to partial destructive interference between the interacting terms.

Much of the intensity contained in the one-electron HOMO → LUMO transition comes from the $\langle s|\Delta x|s\rangle$ transition moment components associated with the end groups: Si and H(Si). The 30 methyl hydrogen atoms collectively contribute only approximately one-third of the in-phase transition strength of the two H(Si) end atoms! The carbon contributions are negligible. The ZDO approximation is relaxed in the transition moment analysis, and origin-independent single-center cross-terms of the type $\langle s|\bar{r}_i|p\rangle$ are considered.[7b,11] The one-center Si $\langle s|\Delta x|p_x\rangle$ cross-terms also constructively sum to a moderate value but are out-of-phase with the larger diagonal $\langle s|\Delta x|s\rangle$ and $\langle p|\Delta x|p\rangle$ elements. A considerable portion of the HOMO → LUMO transition intensity is due to coefficients so small as to be neglected in Figure 2.

$^1\Psi(S_0)$ is stabilized only 0.064 eV from the SCF value. Enhanced Cl due to doubly excited configurations appears relatively unimportant at lower energies. The full-scale Cl results indicate S$_0$ → S$_2$ yields a methyl → chain charge transfer (CT) of +0.1814e or a 0.5995e net gain by the Si 3s orbitals. Again, the methyl CT character collectively arises from terms neglected in Figure 2. The substituent → chain CT is in marked contrast to the chain → hydrogen CT of 0.2437e calculated for S$_0$ → S$_1$ excitation of trans H–(SiH$_2$)$_5$–H.[10] S$_0$ → T$_1$ and S$_0$ → T$_2$ involves CT to the silicon chain of +0.4101 and +0.1306e, respectively. Methyl substitution destablizes the HOMO level by ~1.4 eV, in good agreement with the observed decrease of ~1.56 eV from UPS studies.[6a] The intense optical absorption, however, shifts only ~0.78 eV (~1.0 eV calculated).[9,12] The ~0.6–0.7 eV splitting between the 1st and 2nd ionization potentials of both hydrogenated and methylated silane chains ($n = 5$),[6a] and the compelling analysis in terms of conformational mixtures,[6a] indicates that transitions from the 2nd HOMO level (S$_1$ and T$_1$ in Figure 1) are probably too low in energy by ≥ 0.5 eV. However, S$_0$ → S$_1$ is very weakly allowed and does not enter into interpretation of the absorption spectrum.

The silane chain ($n = 5$) becomes 0.426e more positive in going from the hydrogenated to the methylated species. In accord with such enhanced chain/substituent polarization, the CNDO/2 Wiberg indices and Mulliken population and Cohen bond-order analyses[13] indicate that the Si–Si covalent bond strength is decreased by methylation. This is consistent with computations which show a 0.027 Å Si–Si bond lengthening in disilane due to a single methyl substitution.[14] Experiment, however, indicates an increase in Si–Si bond dissociation energy upon methylation.[15] The above three-bond analysis schemes correctly reflect the relative bond dissociation energies between hydrogenated silicon and carbon chains ($n = 5$),[15] and the relative strengths of the internal and external bonds of each system.[15] It is important to consider that the –SiMe$_2$– repeat units are highly polarized: –Si$^{\delta+}$ – (C$^{\delta-}$ – H$_3^{\delta+}$)$_2$ of ~+0.384, –0.432, and +0.048e compared to –Si$^{\delta+}$ – (H$^{\delta-}$)$_2$ of ~+0.298 and –0.298e. The added charge separation following methylation is likely to increase the Si–Si bond dissociation

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energies due to the overall stronger ionic bonding forces. Excited-state methyl → chain CT could effectively weaken or neutralize such ionic bonding contributions, thus facilitating easy scission as observed experimentally.[16]

In summary, CNDO/2 (Cl) minimal basis set computations on trans $H-(SiMe_2)_5-H$ were shown to yield transition energy and intensity profiles paralleling the observed optical spectrum. The likely importance of d orbital contributions to higher lying excitations of hydrogenated and methylated silane chains has been most recently addressed computationally by Halevi and co-workers.[17]

Registry No. *trans*-$H(S;Me_2)_5H$, 7514-96-7.

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Synthesis and Substitution Reactions of Tris- and Tetrakis(trimethyl phosphite)-Substituted Carbyne Complexes of Chromium, Molybdenum, and Tungsten

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Summary: Methods for the synthesis of $X(CO)[P(OMe)_3]_3M{\equiv}CPh$ (M = Cr, X = Br; M = Mo, W, X = Cl) and $Cl[P(OMe_3)]_4M{\equiv}CPh$ (M = Mo, W) starting from the acyl complexes $[NMe_4][(CO)_5M-C(O)Ph]$are described. Substitution of two or all four trimethyl phosphite ligands in $Cl[P(OMe)_3]_4W{\equiv}CPh$ by bis(diphenylphosphino)ethane is demonstrated. The crystal structure of $Cl[P(OMe)_3]_4Mo{\equiv}CPh$ is reported.

Disubstituted carbonylmetal carbyne, or alkylidyne, complexes $X(CO)_2L_2M{\equiv}CR$[1a] (X = halide; L = donor ligand; M = Cr, Mo, W; R = alkyl, aryl) have become easily accessible through recently developed synthetic methods.[2] The chemistry of these compounds is strongly influenced by the presence of the two carbonyl ligands. For example, reaction of $Cl(CO)_2(py)_2W{\equiv}CR$ (py = pyridine) with anionic bidentate ligands leads to carbonyl–carbyne coupling,[3] a process which has also been observed for other carbonylmetal carbyne complexes.[4] With alkenes $Cl(CO)_2(py)_2W{\equiv}CR$ reacts to give stable tungsten alkene carbyne complexes but only when the alkenes are highly activated.[5] Presumably, the two carbonyl ligands stabilize the occupied metal d orbitals to such an extent that normal olefins cannot compete effectively for π-bonding. For a general investigation of the reactivity of carbyne ligands it therefore seemed desirable to have access to systems containing only one or no carbonyl ligand. However, such compounds are not easily available. The first monocarbonyl derivatives of *trans*-halotetracarbonylmetal carbyne complexes, such as $Cl(CO)$(maleic anhydride)$(py)_2W{\equiv}CPh$, have been prepared only recently.[5] Cyclopentadienyl-substituted monocarbonyl carbyne complexes $(\eta^5-C_5H_5)(CO)(PMe_3)M{\equiv}CC_6CH_3$-(4) had been described previously as byproducts in the formation of ketenyl complexes.[6] Carbonyl-free derivatives have been prepared only by routes other than carbonyl substitution. The complex $Cl(PMe_3)_4W{\equiv}CCMe_3$ has been synthesized by reduction of $Cl_3(PMe_3)_3W{\equiv}CCMe_3$ in the presence of trimethylphosphine and $Cl(PMe_3)_4W{\equiv}CH$ by reaction of $Cl_2W(PMe_3)_4$ with $Al(CH_3)_3$.[7] Reaction of the dinuclear molybdenum complex $Br(Me_3SiCH_2)_2Mo{\equiv}Mo(CH_2SiMe_3)_2Br$ with phosphines leads to formation of $Br(PR_3)_4Mo{\equiv}CSiMe_3$.[8] $Me(PMe_3)_4W{\equiv}CMe$ resulted from the reaction of WMe_6 with PMe_3.[9] Complexes of the type $(\eta^5-C_5H_5)[P(OMe)_3]_2M{\equiv}CCH_2R$ (M = Mo, W; R = CMe_3, $SiMe_3$) have been generated by isomerization of η^2-vinyl complexes.[10] Thermolysis of the ketenyl complex $(\eta^5-C_5H_5)(CO)(Me_2PCH_2CH_2PMe_2)W[C(CO)C_6H_4CH_3-(4)]$ led to $(\eta^5-C_5H_5)(Me_2PCH_2CH_2PMe_2)W{\equiv}CC_6H_4CH_3$-(4).[11] Since tetracarbonyl carbyne complexes $X(CO)_4M{\equiv}CR$ are very easily accessible,[2] facile routes for their conversion into monocarbonyl and carbonyl-free derivatives would be of considerable interest. Here we describe simple methods for the synthesis of tris- and tetrakis(trimethyl phosphite)-substituted carbyne complexes of Cr, Mo, and W and demonstrate further substitution of the phosphite ligands.

The *trans*-chloro(tetracarbonylmetal) benzylidyne complexes of molybdenum and tungsten, $Cl(CO)_4M{\equiv}CPh$, **5** and **6**, react with trimethyl phosphite easily to give the tris(phosphite) complexes $Cl(CO)[P(OMe)_3]_3M{\equiv}CPh$, **11** and **12**, respectively. In the presence of excess ligand (5–10-fold) the substitution of three carbonyl ligands proceeds to completion (eq 3) (5 h at room temperature for M = Mo; 24 h at 55 °C for M = W). Since solutions of the tetracarbonylmetal carbyne complexes are conveniently prepared[2] by reaction of the tetramethylammonium salts of the pentacarbonylmetal acyl complexes,[1b] **2** and **3**, with oxalyl halide at low temperatures (eq 1), compounds **11** and **12** are accessible in simple overall procedures (eq 1 and 3) in 85 and 82% yield, respectively.[12]

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[12] Approximately 0.1 M solutions (suspensions) of $[NMe_4][(CO)_5M-C(O)Ph]$ and oxalyl halide in CH_2Cl_2 are combined at −78 °C, the reaction mixtures are warmed briefly to −10 °C (M = Cr, W) or −40 °C (M = Mo), and recooled to −78 °C for filtration. (Recooling and filtration can be omitted.) After addition of a five- to tenfold excess of trimethyl phosphite or pyridine, the solutions are allowed to warm to room temperature. The solvent is removed, and the respective products are freed from excess ligand by washing with cold pentane. The bis(pyridine)-substituted complexes (7;[1a] 8, ν_{CO} 1992, 1914 cm^{-1}; 9[2]) are used without further purification.

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