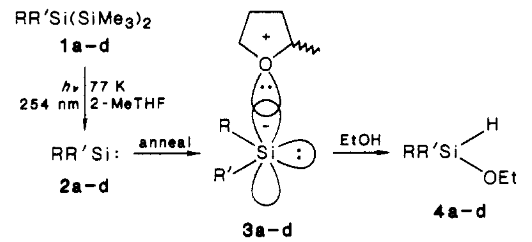
Scheme I



a, R = mesityl, R′ = *t*-Bu; **b**, R = mesityl, R′ = 2,6-diisopropylphenoxy; **c**, R = mesityl, R′ = 1-adamantyl; **d**, R = R′ = mesityl

Table II. Product Ratios for Competitive Trapping of Silylene 2a at Room Temperature

	MeOH/EtOH	MeOH/IPA	EtOH/IPA
pentane	1.2	2.0	1.8
Et_2O	1.4	5.4	3.0
2-MeTHF	1.6	6.4	4.4

Quite different results were obtained when **1a–d** were irradiated in pure 2-MeTHF. For **1c**, the electronic spectra are shown in Figure 1. Photolysis again produces a band at 530 nm,[8] assigned to free silylene, as well as a band at 350 nm. When the matrix is annealed, the 530-nm band diminishes as the 350-nm band grows. Similar behavior was observed for trisilanes **1a,b,d** (for **1d** only the band at 350 nm was observed). All of the samples showed only the band at 350 nm after the matrix was annealed (Table I).

Melting of the matrix gave, in each case, a solution with no bands having $\lambda_{max} > 300$ nm, indicating that no disilene was formed. Analysis of the photolysate by GC–MS showed the only volatile products to be four different isomers of a compound with a molecular ion corresponding to $(RR'Si + 2\text{-}MeTHF)^+$.[9] When ethanol was present as a silylene trap,[10] the O–H insertion compounds **4a–d** were produced. All of these data are consistent with the assignment of the 350-nm absorption bands to silylene–2-MeTHF complexes **3a–d** (Scheme I).

To provide further evidence for silylene complexes a series of competitive trapping experiments similar to those described by Weber[3] were done utilizing **1a** as the silylene precursor. In these studies methanol, ethanol, and 2-propanol, present in 20-fold molar excess, were used as trapping reagents in the solvents pentane, diethyl ether, and 2-MeTHF. All of the trapped products were characterized by GC–MS and by comparison to authentic samples.[11] The selectivity for insertion of silylene **2a** into the O–H bond of the less hindered alcohol increases in ether solvents (Table II). These results agree with those obtained by Weber and Steele; moreover the selectivity is distinctly greater for **2a** than for dimethylsilylene, probably reflecting the larger steric bulk of **2a**.

A final experiment indicates that silylene–ether complexes may also have a reasonable lifetime in solution at low temperatures. Irradiation of **1c** in 2-MeTHF solution at −135 °C for 2 h followed by freezing in liquid N_2 yielded a matrix whose UV spectrum contained only the band at 350 nm. Addition of ethanol to the matrix after the UV spectrum was obtained gave a small yield of the insertion product **4c**. The complex therefore has a short, but significant lifetime in solution, estimated to be 1 min based on measurement of the decay rate of the 350-nm band at −135 °C.

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. F49620-86-0010 and National Science Foundation Grant No. CHE-8318820-02. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation thereon.

Registry No. **1a**, 88526-27-6; **1b**, 111060-23-2; **1c**, 111060-24-3; **1d**, 79184-72-8; **2a**, 89486-28-2; **2b**, 111060-25-4; **2c**, 111060-26-5; **2d**, 79184-71-7; **3a**, 111060-27-6; **3b**, 111060-28-7; **3c**, 111060-29-8; **3d**, 111060-30-1; **4a**, 111060-31-2; **4b**, 111060-32-3; **4c**, 111060-33-4; **4d**, 51525-38-3; 2-MeTHF, 96-47-9; 3-MP, 96-14-0; MeOH, 67-56-1; IPA, 67-63-0; EtOH, 64-17-5; Mes(*t*-Bu)SiHCl, 111060-34-5.

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(8) The 4-nm shift of the silylene absorption maximum in going from 3-MP to 2-MeTHF is probably due to a matrix effect.

(9) Attempts to isolate these compounds as single isomers have been unsuccessful. These compounds are probably the products of insertion into the C–O bond of 2-MeTHF. Each regioisomer would have two stereoisomers, leading to the observation of four isomers by GC–MS. Data from a high-resolution mass spectrometry study of the mixture of isomers are consistent with this assignment.

(10) Gu, T-Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7–11.

(11) Authentic samples of the products of silylene insertion into alcohols were prepared by reacting Mes(*t*-Bu)SiH(Cl) with the desired alcohol in dry hexane in the presence of triethylamine as an HCl scavenger. The average yield of these reactions was 85%. Mes(*t*-Bu)SiH(OMe): ^1H NMR ($CDCl_3$) δ 1.21 (s, *t*-Bu), 2.42 (s, para Me), 2.69 (s, ortho Me), 3.66 (s, OMe) 5.22 (s, SiH), 6.99 (s, ArH); ^{29}Si NMR ($CDCl_3$) δ +3.40, +5.54 ($J_{Si-H} = 213.4$ Hz); MS, *m/e* (relative intensity) 239 (M^+, 17.2), 179 ($M^+ - t$-Bu, 100). Mes(*t*-Bu)SiH(OEt): ^1H NMR ($CDCl_3$) δ 1.25 (s, *t*-Bu), 1.43 (t, CH_3), 2.48 (s, para Me), 2.69 (s, ortho Me), 3.94 (q, OCH_2), 5.30 (s, SiH), 6.98 (s, ArH); ^{29}Si NMR ($CDCl_3$) δ −0.39, 1.63 ($J_{Si-H} = 200.4$ Hz); MS, *m/e* (relative intensity) 250 (M^+, 6.6), 193 ($M^+ - t$-Bu, 100). Mes(*t*-Bu)SiH(O-iPr): ^1H NMR ($CDCl_3$) δ 1.26 (s, *t*-Bu), 1.45 (d, CH_3CH), 2.49 (s, para Me), 2.74 (s, ortho Me) 4.2 (sep, OCH), 5.37 (s, SiH), 7.05 (s, ArH); ^{29}Si NMR ($CDCl_3$) δ −3.91, −1.94 ($J_{Si-H} = 196.7$ Hz); MS, *m/e* (relative intensity) 264 (M^+, 6.0), 207 ($M^+ - t$-Bu, 100). Satisfactory analyses were obtained for all three compounds.

Intermediates in the Direct Synthesis of Rhenium Carbide Clusters from Rhenium Carbonyl. Crystal Structure of $[Et_4N]_2[HRe_5(\mu_5\text{-}C)(CO)_{16}]$

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Summary: The reaction of $Re_2(CO)_{10}$ with a 1.2:1 mole ratio of sodium in triglyme at 200 °C yields the new rhenium carbido clusters $[HRe_6C(CO)_{18}]^{3-}$ and $[HRe_5C(CO)_{16}]^{2-}$. The latter cluster consists of a square-based pyramid of rhenium atoms with a μ_5-carbido atom 0.10 Å below the basal plane and a semibridging carbonyl on one basal–apical edge. This compound is the first example of such a M_5C complex outside of the iron triad elements.

The reduction of $Re_2(CO)_{10}$ with sodium at elevated temperatures in glyme solvents is an efficient synthetic pathway to the high-nuclearity clusters $[H_2Re_6C(CO)_{18}]^{2-}$, $[Re_7C(CO)_{21}]^{3-}$, and $[Re_8C(CO)_{24}]^{2-}$.[1,2] These clusters have been prepared by different routes and crystallographically characterized by Ciani et al.[3-5] In order to probe for

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(1) Hayward, C. M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816.

(2) (a) Hayward, C. M. T. Ph.D. Thesis, University of Illinois, Urbana, 1984. (b) Hayward, C. M. T.; Shapley, J. R. *Organometallics*, accepted for publication.

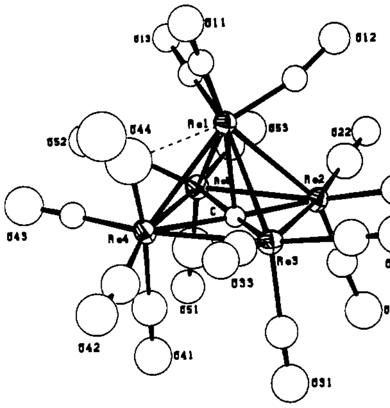

Figure 1. The molecular structure of $[HRe_5C(CO)_{16}]^{2-}$. Selected bond lengths (Å): Re1–Re2, 3.044 (3); Re1–Re3, 3.006 (3); Re1–Re4, 2.996 (3); Re1–Re5, 2.976 (3); Re2–Re3, 2.983 (3); Re3–Re4, 2.977 (3); Re4–Re5, 2.964 (3); Re5–Re2, 2.947 (3); Re1–C, 2.26 (5); Re2–C, 1.99 (5); Re3–C, 2.22 (4); Re4–C, 2.20 (5); Re5–C, 1.99 (4). All metal–metal–metal angles are within 3.0° of the angles expected for a regular square-based pyramid.

possible intermediates in the direct synthesis, we have examined variations in the $Re_2(CO)_{10}$/Na ratio. We now report that pyrolyzing a mixture of sodium and $Re_2(CO)_{10}$ (1.2:1) in triglyme at 200 °C generates a mixture of rhenium carbonyl carbido cluster anions from which we have crystallized, after metathesis with $[Et_4N][Cl]$, the new clusters $[Et_4N]_3[HRe_6C(CO)_{18}]$ (46%) and $[Et_4N]_2[HRe_5C(CO)_{16}]$ (5%), together with traces of $[Et_4N]_3[Re_7C(CO)_{21}]$.[2,4]

$[Et_4N]_3[HRe_6C(CO)_{18}]$ has been fully characterized by spectroscopic and analytical means.[6] Since only one carbonyl ^{13}C NMR signal is observed, the single hydride ligand apparently scrambles rapidly over the entire metal framework. The complex can also be prepared by deprotonation of the previously known[3] dihydride complex $[H_2Re_6C(CO)_{18}]^{2-}$ with potassium hydride or potassium *tert*-butoxide, an observation which suggests an analogous M_6C octahedral structure.[7]

The spectroscopic and analytical data for $[Et_4N]_2[HRe_5C(CO)_{16}]$[8] do not fully establish its structure; however, an X-ray diffraction study provides the necessary information. An ORTEP diagram of the molecular structure is shown in Figure 1.[9] The dianion consists of a square-based pyramid of rhenium atoms,[10] with a carbon atom lying 0.10 (5) Å below the mean basal plane. Comparison of this value with those in the isoelectronic species $[M_5C(CO)_{14}]^{2-}$ (M = Fe, Os)[11,12] and $M_5C(CO)_{15}$ (M = Fe, Ru, Os),[11,13,14] reveals that the displacement in $[HRe_5C(CO)_{16}]^{2-}$ is about half of that observed in the dianions but roughly equal to that seen in the neutral compounds. The carbide atom in the rhenium complex lies much closer to two of the basal atoms (Re2 and Re5, average 1.99 (5) Å) than to the other two basal atoms and the apical atom (average 2.23 (5) Å). This type of M_5C complex has previously been viewed as characteristic of iron triad elements,[11,15] although complexes of the composition $[Fe_4C(CO)_{12}ML_n]^{y-}$ (y = 1,2) have been characterized.[16] The only other known rhenium cluster with an exposed carbon atom is the recently characterized $[Re_4C(CO)_{15}I]^-$.[17]

A striking feature of $[HRe_5C(CO)_{16}]^{2-}$ is the arrangement of the carbonyl ligands. Three of the basal atoms and the apical atom are each bonded to three carbonyls; the remaining basal atom is bonded to four carbonyls. Of all closo clusters containing more than three rhenium atoms, only two are known which have four carbonyls bonded to one metal atom. In $[H_4Re_4(CO)_{13}]^{2-}$ all the carbonyl ligands are strictly terminal;[18] in $[Re_7C(CO)_{22}]^-$ one carbonyl symmetrically bridges a rhenium–rhenium bond.[19] $[HRe_5C(CO)_{16}]^{2-}$ is intermediate between these two cases: one carbonyl (C44 in Figure 1) is bent significantly over toward the apical rhenium atom (d(Re1–C44) = 2.52 (10) Å, ∠(Re4–C44–O44) = 150 (9)°, α^{20} = 0.31). To our knowledge this structure contains the first example of a

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(6) Anal. Calcd. (Found) for $C_{43}H_{61}N_3O_{18}Re_6$: C, 25.50 (25.53); H, 3.04 (2.82); N, 2.07 (2.13). IR (CH_3CN): ν_{CO} 1963 (vs), 1948 (s), 1898 (w, sh), 1870 (m) cm^{-1}. ^1H NMR (acetone-d_6, 20 °C): δ 3.42 (q, 24 H, CH_3CH_2N), 1.36 (tt, 36 H, CH_3CH_2N), −20.9 (s, 1 H, hydride). ^{13}C NMR (acetone-d_6, 20 °C): δ 418.4 (s, 1 C, carbide), 201.7 (s, 18 C, CO). (No change to −80 °C). FAB-MS (negative ion): m/z (^{187}Re) 1768 (M − 2Et_4N), 1638 (M − 3Et_4N).

(7) A single-crystal X-ray diffraction study of $[HRe_6C(CO)_{18}]^{3-}$ could not be successfully completed because of disorder; however, the octahedral metal framework was resolved. Rheingold, A. L., University of Delaware, personal communication.

(8) Anal. Calcd (Found) for $C_{33}H_{41}N_2O_{16}Re_5$: C, 23.98 (24.27); H, 2.50 (2.22); N, 1.70 (1.78). IR (acetone): ν_{CO} 2067 (w), 2019 (m), 1990 (vs), 1977 (s), 1930 (m), 1912 (m), 1897 (m), 1887 (m, sh), 1864 (w) cm^{-1}. ^1H NMR (acetone-d_6, 20 °C): δ 3.49 (q, 24 H, CH_3CH_2N), 1.39 (tt, 36 H, CH_3CH_2N), −15.2, −16.9, −19.4 (all s, relative ratio 1.00/0.64/0.58, hydrides of various isomers). FAB-MS (negative ion): m/z (^{187}Re) 1367 ($HRe_5C(CO)_{15}$).

(9) $[Et_4N]_2[HRe_5C(CO)_{16}]$ crystallized in the unambiguous orthorhombic space group $P2_12_12_1$ with a = 11.829 (6) Å, b = 15.480 (3) Å, c = 23.569 (3) Å, V = 4316 (5) Å^3, and ρ_{calcd} = 2.542 g/cm^3 for Z = 4. The transparent, red, octahedral data collection crystal was roughly equidimensional (0.05-mm radius). Diffraction data: Enraf-Nonius CAD4 diffractometer, Mo radiation ($\lambda(K\bar{\alpha})$ = 0.71073 Å), range $2.0 < 2\theta < 46.0°$ (+h,+k,−l), 3378 unique data (R_i = 0.022), 1815 observed ($I > 2.58\sigma(I)$), corrected for anomalous dispersion, absorption (maximum and minimum transmission factors, 0.347 and 0.247), Lorentz, and polarization effects. The structure was solved by direct methods (SHELXS-86) and difference Fourier syntheses. One of the cations was disordered and refined as a rigid group in two positions (relative occupancy 0.26 (2) for group "A"). Rhenium atoms were refined with anisotropic thermal coefficients, and the remaining atoms were isotropically refined. Hydrogen atoms were not included in structure factor calculations. Final agreement factors were R = 0.054 and R_w = 0.053. An enantiomer test did not improve agreement factors. The final difference Fourier map (range $+1.4 < e/Å^3 < -1.3$) located maximum residual electron density in the vicinity of the disordered cation.

(10) A square-pyramidal arrangement of rhenium atoms has also been observed in $Re_5(CO)_{14}(\mu_4\text{-}PMe)(\mu\text{-}PMe_2)(\mu_3\text{-}P[Re(CO)_5])$. Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1985**, 478.

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semibridging CO ligand in a rhenium cluster.

The hydride ligand was not located crystallographically. In solution, the observation of three ^{1}H NMR signals for the hydride suggests the presence of isomers differing in terms of the hydride location. If the Re1–Re3 bond distance of 3.006 (3) Å and the Re1–Re3–C32 bond angle of 113 (2)° are compared to analogous Re–Re bond lengths (average 2.984 (3) Å) and Re1–Re–C(radial) bond angles (average 107 (2)°), it seems likely that the hydride bridges the Re1–Re3 edge over the Re1–Re2–Re3 face (i.e., away from the semibridging carbonyl). A potential energy calculation[21] supports this assignment as the probable hydride site; however, these calculations suggest that a basal edge-bridging site (specifically, along the Re2–Re3 edge) and/or a face-bridging site (e.g., above the Re1–Re2–Re3 face) may be only slightly higher in energy. We note a similar distribution of sites in the structure of $Ru_5C(CO)_{13}(NO)Au(PEt_3)$:[22] two geometric forms of this molecule, μ_2-Au(PEt_3) (basal–apical edge-bridging) and μ_3-Au(PEt_3), exist in the same crystal.

Reaction of $[HRe_5C(CO)_{16}]^{2-}$ with 3 equiv of $Re_2(CO)_{10}$ in triglyme at 200 °C affords $[Re_8C(CO)_{24}]^{2-}$ quantitatively. It therefore seems reasonable that $[HRe_5C(CO)_{16}]^{2-}$ is an intermediate on the way to higher nuclearity clusters in the reductive pyrolysis of $Re_2(CO)_{10}$. Efforts to isolate other intermediates in this reaction are currently underway.

Acknowledgment. This work was supported by National Science Foundation Grants DMR 86-12860 to the Materials Research Laboratory and CHE 84-07233 to J. R.S.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths and angles for $[Et_4N]_2[HRe_5C(CO)_{16}]$ (6 pages); a listing of structure factor amplitudes for $[Et_4N]_2[HRe_5C(CO)_{16}]$ (10 pages). Ordering information is given on any current masthead page.

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CpZr(allyl)$_3$: The Molecular Structure of a π- and σ-Dynamic Allyl Transition Metal Complex

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Received September 24, 1987

Summary: CpZr(allyl)$_3$ (**2**), prepared by reacting $CpZrCl_3$ (**1**) with excess allylmagnesium chloride at low temperature, is characterized by rapidly occurring intramolecular allyl rearrangement and scrambling even at very low temperature in solution. In the solid state **2** features three differently bonded allyl ligands and a Cp group around zirconium in a distorted (pseudo) tetrahedral geometry (X-ray crystal structure analysis at −173 °C: space group $P2_12_12_1$; a = 8.603 (3) Å, b = 18.520 (5) Å, c = 8.033 (4) Å, Z = 4). One allyl group is σ-bonded. A slightly distorted π-allyl ligand and a η^3-allyl moiety whose bonding features are approaching those of a σ,π-allyl type complement the coordination sphere of this zirconium(IV) complex of a formal 16-electron count.

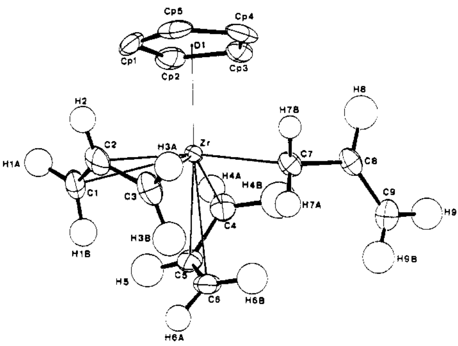

Figure 1. A view of the molecular geometry of CpZr(allyl)$_3$ (**2**) as determined by X-ray diffraction.

Allyl transition-metal complexes are of enormous practical importance as active catalysts and catalyst precursors as well as stoichiometric reagents in organic synthesis.[1] Metal allyl species have been divided into six different groups according to their IR features and NMR behavior.[2] Many representative examples of five of these groups have also been carefully examined in the solid state by X-ray diffraction.[3] To our knowledge, detailed structural information on the most interesting type, i.e. the π- and σ-dynamic allyl complexes, surprisingly, seemed to be lacking.

CpZr(allyl)$_3$ (**2**)[4] was prepared by treating a suspension of $CpZrCl_3$ (**1**)[5] in ether with excess (4 equiv) allylmagnesium chloride at −40 °C. After low-temperature workup (<−35 °C), large, dark red crystals of **2** were obtained by crystallization from pentane at −80 °C. The CpZr(allyl)$_3$ thus obtained is thermally rather sensitive; it slowly decomposes at temperatures above −10 °C even in the solid state. In solution **2** exhibits two different types of allyl ligands as judged by IR spectroscopy [alkane solvent: ν 1595 cm^{-1} (η^1-allyl); 1535 cm^{-1} (η^3-allyl)]. These rapidly equilibrate on the NMR time scale [toluene-d_8: ^{1}H (60 MHz, −78 °C) δ 5.10 (s, 5 H, Cp), 5.27 (m, 3 H), 2.95 (d, 12 H, dynamic allyl); ^{13}C (100.6 MHz, −30 °C) δ 106.4 (Cp), 135.3 (allyl-CH), 71.9 (allyl-CH$_2$)]. At temperatures

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