(eluent petroleum ether/diethyl ether (8:2)).

Two fractions were recovered: unreacted compound 1 (51%) and compound 8 (25%, red crystals). Analytical and spectroscopic data are reported in Tables I-IV.

Oxidation of Carbenes 3n,p to Lactones 9n,p. A solution of carbene **3n** (3.63 mmol) in 70 mL of diethyl ether was irradiated with sunlight under a slight air flow. After 36 h, the reaction mixture was filtered over Celite and the solvent was evaporated under reduced pressure. Compound **9n**: oil, yield 71%; $[\alpha]_D = -31.9°$ (T = 65%; c = 0.908, CH_2Cl_2) (lit.[18b] $[\alpha]_D = -29.6°$ (c = 1.29, CH_2Cl_2)).

A similar procedure for carbene **3p** gave a crude reaction mixture, from which recrystallization from benzene/n-hexane gave product **9p**: mp 145-147 °C (84%); $[\alpha]_D = -44.1°$ (T = 65%; c = 0.39, $CHCl_3$).

Oxidation of Carbene 3o to Lactone 9o. To a solution of carbene **3o** (0.68 mmol) in 8 mL of dichloromethane was added 1.36 mmol of pyridine oxide in 3 mL of dichloromethane; the mixture was allowed to react at room temperature, with magnetic stirring, for 3 h. The solvent was evaporated, the residue was taken up with diethyl ether (100 mL), and the solution was washed with 80 mL of 10% HCl and then with water. The organic layer was separated, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography (eluent petroleum ether/diethyl ether (7:3)). Two fractions were recovered: the chromium pentacarbonyl pyridine complex (35%) and (+)-3-phenyl-5-oxotetrahydrofuran (**9o**). Data for **9o**: white crystals, mp 58-60 °C (79%); $[\alpha]_D = +50.9°$ (T = 60%; c = 1.03, chloroform) (lit.[18a] $[\alpha]_D = +52°$ (c = 0.4, chloroform)).

Synthesis of (−)-2-((*p*-Nitrobenzoxy)methyl)-5-oxotetrahydrofuran (9p). To a solution of (2*R*)-(−)-5-oxo-2-tetrahydrofuranoic acid (3.84 mmol) in 7 mL of anhydrous tetrahydrofuran was slowly added 2.2 mL (4.4 mmol) of a 2 M solution of borane-dimethyl sulfide at room temperature. After 4 h, 5 mL of methanol was added and the solvent distilled off at atmospheric pressure. The addition of methanol and the distillation were repeated until a colorless oil was obtained. The crude alcohol was dissolved in 10 mL of pyridine, and p-nitrobenzoyl chloride (3.84 mmol) was added to the solution; the mixture was heated to 75 °C for 30 min and then left at room temperature for 16 h. The solution was poured into 40 mL of 10% HCl and the white precipitate extracted with dichloromethane. The organic layer was washed with 120 mL of a saturated solution of $NaHCO_3$ and then with water to neutral pH, separated, dried over Na_2SO_4, and evaporated under reduced pressure. The residue crystallized from benzene/n-hexane, yielding compound **9p**: mp 145-147 °C (85%); $[\alpha]_D = -45.4°$ (T = 60%; c = 0.39, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.9-2.2 (m, 2 H, $CH_2C{=}O$), 2.3-2.8 (m, 2 H, $CH_2CH_2C{=}O$), 4.3-4.7 (m, 2 H, CH_2O), 5.0-5.8 (m, 1 H, CH), 8.1-8.4 (m, 4 H, arom); IR (Nujol) 1770 (CO of lactone), 1730 (CO of ester), 1530, 1350 (NO_2) cm^{-1}.

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Notes

Heterosilsesquioxanes: Synthesis and Characterization of Group 15 Containing Polyhedral Oligosilsesquioxanes

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Summary: The reactions of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (**1**) with PCl_3, $AsCl_3$, and $SbCl_3$ give high yields of the corresponding pnictite esters, $[(c\text{-}C_6H_{11})_7Si_7O_{12}M]$, M = P (**2**), As (**3**), Sb (**4**). The bismuth congener, $[(c\text{-}C_6H_{11})_7Si_7O_{12}Bi]$ (**5**), was prepared by the reaction of **1** with $(t\text{-}BuO)_3Bi$. A single-crystal X-ray diffraction study of **2** reveals an interesting molecular structure with 1 of the 12 framework oxygen atoms lying inside the cube defined by the Si and P atoms. Phosphite **2** forms a 1:1 adduct with Me_3Al and is quantitatively oxidized to phosphate $[(c\text{-}C_6H_{11})_7Si_7O_{12}PO]$ (**7**) by ozone.

We recently reported practical syntheses of several incompletely condensed polyhedral oligosilsesquioxanes as part of our efforts to develop homogeneous models for silica surfaces.[1] The focal point of most of our research has been trisilanol 1, which exhibits many geometric similarities to potential sites of coordination available on idealized surfaces of known SiO_2 polymorphs (e.g., (111) cristobalite and (0001) tridymite).[1a] Since trisilanol 1 is formally derived from the hydrolytic removal of one silicon atom from a stable octameric "T_8" silsesquioxane, it exhibits a strong tendency to undergo reactions to fill the vacant vertex. Alkyltrichlorosilanes, alkyltrichlorogermanes, and alkyltrichlorostannanes,[1a] as well as a variety of main-group[1c,d] and transition-metal complexes,[1e] all undergo high-yield "corner-capping" reactions with 1. In this paper, we report the synthesis of polyhedral heterosilsesquioxanes, where the vacant vertex presented by 1 is occupied by group 15 representative elements.

Results and Discussion

The reactions of 1 with PCl_3, $AsCl_3$, and $SbCl_3$ in Et_3N/C_6H_6 afford virtually quantitative (NMR) yields of the expected pnictite esters (i.e., 2-4). All of these compounds give molecular ions in the electron impact mass spectrum and exhibit ^1H, ^{13}C, and ^{29}Si NMR spectra that are characteristic of cyclohexyl-substituted silsesquioxanes with apparent C_{3v} molecular symmetry. Bismite 5 can be prepared by the reaction of 1 with $(t\text{-}BuO)_3Bi$.[2] It is

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[†] Recipient of a Fannie and John Hertz Predoctoral Fellowship.

(1) (a) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741-8. (b) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931-6. (c) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288-9. (d) Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638-40. (e) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850-2.

(2) Evans, W. J.; Hain, J.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1628-9.

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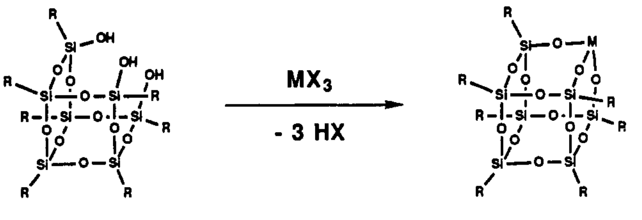

1 R = c-C_6H_{11}

2 M = P
3 As
4 Sb
5 Bi

apparently stable in the solid state but appears to decompose in solution ($t_{1/2} \sim$ 12 h at 25 °C) to give a complex mixture of insoluble products.

The highly symmetric nature of **3** and **4** extends to the solid state. Both complexes crystallize as well-formed colorless crystals in trigonal space groups ($R3$ or $R\bar{3}$). The heterosilsesquioxane frameworks of **3** and **4** clearly possess 3-fold rotational symmetry, but severe disordering of the cyclohexyl groups in both molecules has thus far prevented satisfactory completion of either structure.[3] In contrast, phosphite **2** crystallizes with an interesting asymmetric structure with major deviations from 3-fold symmetry.

The ORTEP diagram from a single-crystal X-ray diffraction study of **2** is shown in Figure 1a. The molecule possesses approximate C_s symmetry, with a pseudomirror plane bisecting the [Si_7PO_{12}] framework through P, Si3, Si4, and Si7. For the most part, interatomic distances and angles around P and between Si and O atoms within the [Si_7PO_{12}] framework are normal. The structure does, however, exhibit one very interesting feature. Unlike all other T_8 silsesquioxanes that have been structurally characterized,[1e,4,5] where the 12 framework oxygen atoms lie outside the cube defined by the 8 T atoms, 1 of the oxygen atoms in **2** is bent toward the center of the cube. As illustrated in Figure 1a, O3 is displaced inward along the pseudomirror plane with a P–O3–Si3 bond angle of 171.1 (6)°. Although somewhat unexpected, this unusual structure can presumably be adopted without significantly distorting an otherwise stable T_8 heterosilsesquioxane framework because P has a smaller covalent radius than Si and prefers interbond angles of 90–100° in trivalent PX_3 molecules.[6]

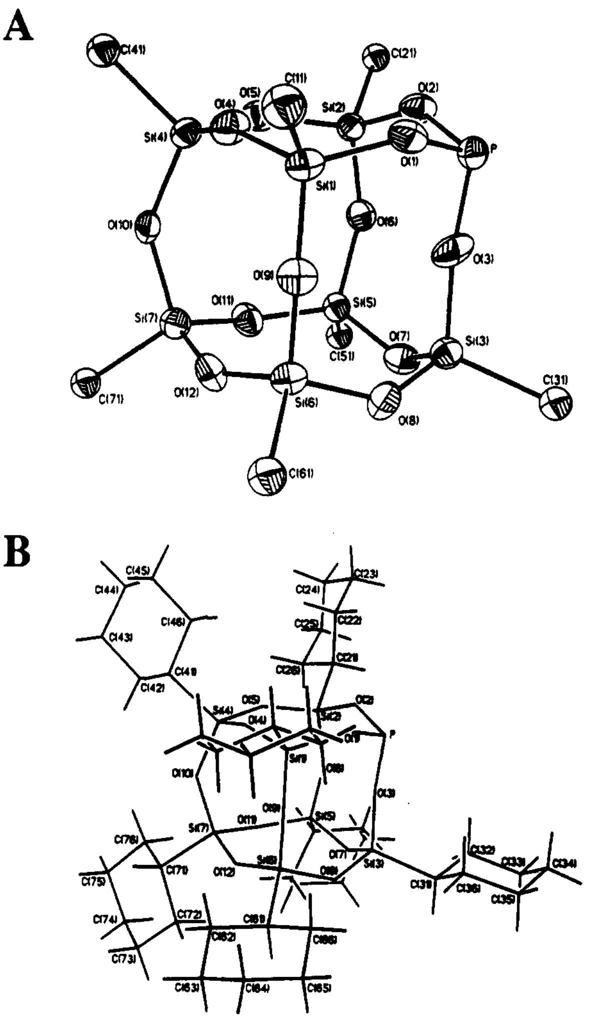

Figure 1. (A) Perspective ORTEP plot of **2**. For clarity, only C's attached to Si are shown and thermal ellipsoids are plotted at the 50% probability level. (B) Stick diagram of **2** showing atom labels for non-hydrogen atoms. For clarity, atom labels for C11 through C16 have been omitted. H atoms have the same numeric label as the carbon atoms to which it is bonded. For example, H23a and H23b are bonded to C23. Selected distances (Å) and angles (deg) are as follows: P–O1, 1.605 (9); P–O2, 1.609 (8); P–O3, 1.584 (8); Si1–O1, 1.630 (10); Si2–O2, 1.632 (9); Si3–O3, 1.624 (8). Other Si–O bond distances vary from 1.600 to 1.637 Å. P–O1–Si1, 143.0 (6); P–O2–Si2, 143.7 (5); P–O3–Si3, 171.1 (6); O1–P–O2, 101.5 (4); O1–P–O3, 101.3 (4); O2–P–O3, 100.0 (4). Other Si–O–Si angles vary from 136 to 155°.

One final aspect of the structure that merits comment concerns the steric demands of phosphite **2** as a ligand for transition-metal ions. The Tolman cone angle[7] for **2** is approximately 167°,[8] suggesting that **2** would substantially limit access to a metal atom by many potential substrates. This cone angle does not, however, accurately reflect the steric properties of **2** because the effective cone angle

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(3) Arsite **3** crystallizes from a number of solvents as poorly diffracting crystals in a trigonal space group (R and $R\bar{3}$) with a = 16.701 (2) Å and c = 17.549 (4) Å (−90 °C) and Z = 3. Stibite **4** also crystallizes in a trigonal space group with a = 16.810 (2) Å and c = 17.762 (4) Å (−90 °C). Intensity statistics (SHELXTL-PLUS, XPREP) favor the centrosymmetric space group $R\bar{3}$ for both molecules. This space group selection would, however, place the crystallographic origin at the center of each molecule, leading to disorder between the body diagonal $C_6H_{11}Si$ and As or Sb moieties. This would also increase the likelihood for disorder between the remaining symmetry-related cyclohexyl groups. Such disorder may explain the poorly diffracting nature of these otherwise beautiful, well-formed crystals. Whatever the case, all attempts to completely solve the structures in either $R3$ or $R\bar{3}$ have failed to locate any of the carbon atoms in the cyclohexyl groups.

(4) For an excellent review of oligosilsesquioxanes: Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199–236.

(5) Cf.: (a) Olsson, K.; Gronwall, C. *Ark. Kemi* **1961**, *17*, 529–40. (b) Voronkov, M. G.; Martynova, T. N.; Mirskov, R. G.; Belyi, V. I. *Zh. Obsch. Khim.* **1979**, *49*, 1328. (c) Kovrigin, V. M.; Lavrentyev, V. I.; Moralev, V. M. *Zh. Obsch. Khim.* **1987**, *56*, 2049–53. (d) Beer, R.; Burgy, H.; Calzaferri, G.; Kamber, I. *J. Electron Spectros. Relat. Phenom.* **1987**, *44*, 121–30. (e) Martynova, T. N.; Korchov, V. P.; Semyannikov, P. P. *J. Organomet. Chem.* **1983**, *258*, 277–82. (f) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Miller, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262.

(6) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984; Chapter 19 and references cited therein.

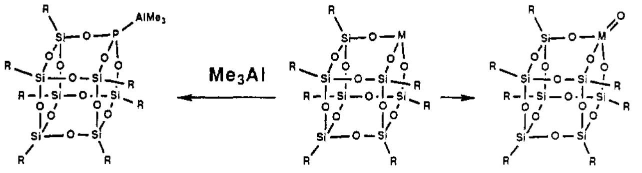
(7) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Clark, H. C. *Israel J. Chem.* **1976/77**, *15*, 210.

(8) The cone angle, θ, was calculated from the final structure according to Tolman.[7a] An imaginary metal atom was placed at a tetrahedral site 2.28 Å away from the phosphorus atom. The metal was then linked to various atoms, X, from 4 to 7 bonds away and θ calculated according to the equation

$$\theta = \frac{2}{3}\sum_{i=1}^{3}\frac{\theta_i}{2}$$

where θ_i are the individual M–P–X bond angles. The largest cone angle (165°) was found when hydrogen atoms that were seven bonds away (H13a,b; H23a,b; H34a,b) were used in the calculation. For atoms within 4–6 bonds of the phosphorus center, calculated cone angles vary from 103° (C11, C21, C31) to 124° (C12, C22, C32/36(ave)) to 147° (C13, C23, C33/35(ave)).

within the immediate coordination sphere of a metal ion (i.e., 2–4 atoms) should be much smaller.[8] Consequently, it should be possible to utilize the large overall size of **2**, **3**, and perhaps **4** to strictly limit the number of donor ligands attached to a metal ion without seriously obstructing access to the metal by medium-sized substrates. Although we have not examined the donor properties of these potentially interesting ligands, we have observed that **2** forms a stable 1:1 adduct with Me_3Al (i.e., **6**).



6 **2** M = P **3** As **4** Sb **7** M = P **8** As **9** Sb

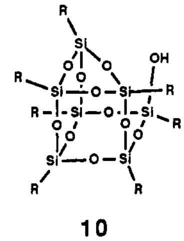
The ready availability of **2–5** provides a logical starting point for the syntheses of other group 15 heterosilsesquioxanes. We were therefore interested to see whether the relative chemical inertness and sterically demanding nature of trisilanol **1** could be exploited to stabilize **7–9**, which should, in principle, be available from the oxidation of **2–4**. Although silyl phosphates such as **7** are commonplace, structurally analogous arsates and stibates are unknown.[9]

Pnictite esters **2–4** are all air-sensitive, but only **2** can be oxidized by molecular oxygen. (Compounds **3** and **4** are water sensitive.) The reaction of **2** with dry O_2 is, however, slow at 25 °C and produces very complicated mixtures of phosphate-containing products (by ^{31}P NMR). The reagent of choice for the oxidation of **2** is ozone (2% in O_2), which reacts instantaneously (C_6H_6, 25 °C) to afford quantitative (NMR) yields of **7**.

Phosphate **7** was unambiguously identified on the basis of multinuclear NMR (^1H, ^{13}C, ^{29}Si, ^{31}P), mass spectral, and combustion analysis data. Quite remarkably, the ^1H decoupled ^{13}C NMR spectrum of this complicated molecule is completely resolved at 125 MHz: the three sets of chemically equivalent cyclohexyl groups (3:3:1) give rise to nine distinct methylene resonances (6:6:6:6:3:3:2:2:1) and three methine resonances (1 (s): 3 (s): 3 (d, J_{CP} = 3.6 Hz). As expected, the ^{31}P resonance for **7** (δ −44.95) is shifted approximately 130 ppm upfield from the resonance for **2** (δ 86.12) and is observed upfield from the region where most acyclic phosphate esters are observed (δ 10 to −20).[10] Other oxidizing agents can be used to oxidize **2** to **7**, but none are as convenient as ozone.

It is interesting to note that an obvious route to **7**, the reaction of **1** with $POCl_3/Et_3N$, does not give high yields of the expected phosphate. Instead, the major product (~50%) from this reaction is **10**, which results from the cyclodehydration of **1**.[11] A number of other unidentified products also form, including modest amounts (~20%) of **7**.

The oxidations of **3** and **4** with ozone also occur rapidly in benzene or CH_2Cl_2, but do not appear to afford simple analogues of **7**. At room temperature, arsite **3** is quickly oxidized to an extremely complex mixture of unidentified products. When the ozonolysis is performed at low temperature (−78 to −40 °C) in CD_2Cl_2, a ^{13}C NMR spectrum (−40 °C) of the reaction mixture exhibits at least five overlapping resonances in the methine region. Since the relative intensities of these resonances change dramatically with the onset of gross decomposition at −20 °C, there must be at least two compounds present in solution at −40 °C. In light of the instability of $AsOCl_3$ (T_{decomp} ~ −25 °C), which can be prepared by the ozonolysis of $AsCl_3$ at −78 °C,[12] it is tempting to propose that one of the metastable ozonolysis products is indeed **8**. There is, however, no direct evidence for the formation of **8**. The ozonolysis of **4** at −78 °C to 25 °C produces a fine white powder that is completely insoluble in common organic solvents.



10

In conclusion, we have described the syntheses and characterization of several interesting group 15 containing heterosilsesquioxanes. We have also demonstrated that the flexible silsesquioxane framework of **1** is capable of chelating atoms as small as P and as large as Bi (covalent radii = 1.1 and 1.52 Å, respectively).[13] Although the steric requirements and oxidation resistance of **1** were not able to stabilize molecules such as **8** and **9**, the versatile ligating ability of trisilanol **1** offers a number of interesting possibilities in both main-group and transition-metal chemistry.

Experimental Section

General Data. General experimental protocol and procedures for the sytnhesis of **1** are described in ref 1a. $POCl_3$ (Gold label, Aldrich), PCl_3 (Gold label, Alfa Products), $AsCl_3$ (reagent grade, J. T. Baker), and $SbCl_3$ (reagent grade, Mallinckrodt) were used without further purification. All manipulations were performed under an atmosphere of dry nitrogen by using either standard Schlenk techniques or a Vacuum Atmospheres Corp. Dri-Lab. Ozone (~2% in O_2) was generated by an electric discharge with a Welsbach ozonator and dried by passage through a calcium chloride drying tube.

NMR spectra were recorded on a General Electric GN-500 (^1H, 500.10 MHz; ^{13}C, 125.76 MHz; ^{29}Si, 99.35 MHz; ^{31}P, 202.44 MHz) spectrometer. Most ^{29}Si spectra were recorded with inverse-gated proton decoupling in order to minimize nuclear Overhauser effects. Electron impact mass spectral analyses were conducted on a VG 7070e high-resolution mass spectrometer. Melting points were measured in sealed capillaries under dry nitrogen with a Mel-temp melting point apparatus and are uncorrected.

X-ray Diffraction Study of 2. Crystals suitable for an X-ray diffraction study were obtained by allowing acetonitrile to slowly diffuse into a benzene solution of **2** over several days. Crystal data for **2** [$C_{42}H_{77}O_{12}PSi_7$ (fw 1001.6)] are as follows: orthorhombic $Pca2_1$, a = 18.449 (3) Å, b = 21.672 (3) Å, c = 13.330 (3) Å; V = 5329.5 (15) $Å^3$; D_{calc} = 1.248 g/cm^3 (Z = 4). A total of 3382 unique reflections with 4.0 ≤ 2θ ≤ 45.0° were collected on a Syntex $P2_1$ diffractometer at −90 °C with use of graphite monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS). Full-matrix least-sqaures refinement of positional and thermal parameters (anisotropic for Si, O, C, P) led to con-

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[9] (a) The bismuth congener should be an extremely powerful oxidant and almost certainly would not be stable.[9b] (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; pp 673–4.

[10] (a) Verkade, J. G., Quin, L. D., Eds.; *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; VCH Publishers: Deerfield Beach, FL, 1987, and references cited therein. (b) Verkade, J. G.; King, R. W. *Inorg. Chem.* **1962**, *1*, 948–9.

[11] The synthesis and characterization of **10** has been previously described.[1a]

[12] Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 766–7.

[13] Dean, J. W., Ed. *Langes's Handbook of Chemistry*; McGraw-Hill: New York, 1985; pp 3-121–3-126.

Organometallics **1991**, *10*, 815–817

vergence with a final R factor of 0.061 for 348 variables refined against 2693 data with $|F_o| > 4.0\sigma|F_o|$. All other details regarding the crystal structure are reported in the supplementary material.

Syntheses of 2–4. One equivalent of the appropriate trichloride (i.e., PCl_3, $AsCl_3$, $SbCl_3$) was added with vigorous stirring to a solution of **1** (200 mg, 0.205 mmol) and triethylamine (75 mg, 0.743 mmol) in benzene (10 mL). After stirring at 25 °C for 1 h, solid Et_3NHCl was removed by vacuum filtration, and then the volatiles were evaporated (0.1 Torr, 25 °C). Hexane extraction of the residue, filtration (to remove Et_3NHCl or any unreacted **1**), and evaporation of the volatiles (0.1 Torr, 25 °C) afforded the respective pnictites (**2–4**) in virtually quantitative yield (by ^{13}C NMR). Analytically pure samples were obtained by the slow diffusion of acetonitrile in benzene solutions of **2–4**.

Characterization Data for 2. ^1H NMR (25 °C, $CDCl_3$): δ 1.78 (br m, 35 H), 1.24 (br m, 35 H), 0.80 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.49, 27.46, 27.42, 26.90, 26.88, 26.79, 26.67, 26.56, 26.40 (s, CH_2), 23.25, 23.20 (s, 3:4 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −66.95 (s, 3 Si), −67.99 (s, 1 Si), −71.44 (d, 3 Si, $^2J_{Si\text{-}P}$ = 35.8 Hz). $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6): δ 86.12 ($^2J_{P\text{-}Si}$ = 35.8 Hz for ^{29}Si satellites). MS (65 eV, 200 °C; relative intensity): *m/e* 1000 (M^+, 100%), 918 ($M^+ - C_6H_{10}$, 40.2%), 836 ($M^+ - 2C_6H_{10}$, 8.5%). Anal. Calcd for $C_{42}H_{77}O_{12}PSi_7$ (Found): C, 50.36 (50.45); H, 7.75 (7.52). Mp 258–265 °C (dec).

Characterization Data for 3. ^1H NMR (25 °C, $CDCl_3$): δ 1.73 (br m, 35 H), 1.23 (br m, 35 H), 0.75 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.53, 27.49, 26.90, 26.85, 26.73, 26.64, 26.58 (s, CH_2), 23.80, 23.27, 23.17 (s, 3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −67.65, −67.84, −70.48 (s, 3:1:3). MS (65 eV, 200 °C; relative intensity): 1044 (M^+, 0.2%), 961 ($M^+ - C_6H_{10}$, 100%), 879 ($M^+ - 2C_6H_{10}$, 52%). Anal. Calcd for $C_{42}H_{77}AsO_{12}Si_7$ (Found): C, 48.25 (48.49); H, 7.42 (7.47). Mp 249–252 °C.

Characterization Data for 4. ^1H NMR (25 °C, $CDCl_3$): δ 1.74 (br m, 35 H), 1.22 (br m, 35 H), 0.75 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.67, 27.55, 27.05, 26.95, 26.67 (s, CH_2), 24.26, 23.44, 23.24 (s, 3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −67.76, −68.53, −69.65 (s, 1:3:3). MS (65 eV, 200 °C; relative intensity): 1008 ($M^+ - C_6H_{10}$, 100%), 926 ($M^+ - 2C_6H_{10}$, 32%). Anal. Calcd for $C_{42}H_{77}O_{12}SbSi_7$ (Found): C, 46.18 (46.67); H, 7.10 (7.13). Mp 266–69 °C.

Synthesis of 5. A solution of $(t\text{-}BuO)_3Bi^2$ (88 mg, 0.205 mmol) in ~3 mL of benzene was added to a suspension of **1** (200 mg, 0.205 mmol) in 5 mL of benzene. Stirring for 2 min at 25 °C produced a homogeneous solution, which was evaporated to give a virtually quantitative yield of **5**. ^1H, ^{13}C, and ^{29}Si NMR spectra of the crude product indicate that the purity is >95%. Unfortunately, the compound decomposes on standing in solution to a complex mixture of unidentified products, and could not successfully recrystallized under a variety of conditions. ^1H NMR (25 °C, C_6D_6): δ 2.17, 1.78, 1.65, 1.37, 1.29 (br m, 70 H); 1.07 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 28.31, 28.14, 27.93, 27.87, 27.54, 27.50, 27.40, 27.32 (s, CH_2); 26.21, 24.33, 23.97 (s, 3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6/C_7H_8): δ −67.83, −67.88, −69.27 (s, 1:3:3).

Reaction of 2 with Me_3Al: Synthesis of 6. Neat $AlMe_3$ (19.4 μL, 14.6 mg, 0.200 mmol) was added via syringe to a solution of **2** (200 mg, 0.200 mmol) in 5 mL of benzene. After stirring for ~10 min at 25 °C, the volatiles were removed in vacuo to afford a quantitative yield of **6** as a white powder. The material obtained in this manner is spectroscopically pure. Unfortunately, all attempts to recrystallize the complex failed because of its extremely high solubility in all organic solvents with which it does not react. ^1H NMR (25 °C, C_6D_6): δ 2.05–1.10 (br m, 70 H), 1.02 (m, 7 H), −0.094 (s, 9 H). $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6): δ 27.63, 27.58, 27.42, 27.15, 27.11, 27.04, 26.98, 26.88, 26.59 (s, 6:6:6:6:3:3:2:2:1 for CH_2), 23.59, 23.46, 23.27 (s, 1:3:3 for CH), −8.88 (br s). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −66.97, −67.91 (s 3:1 Si), −70.76 (d, 3 Si, $^2J_{Si\text{-}P}$ = 35.6 Hz). $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6): δ 62.89 (s).

Oxidation of 2 to 7. Dry ozone (~2% in O_2) was introduced at a rate of 8 mL/min into a solution of **2** (200 mg, 0.200 mmol) in 5 mL of benzene. After 10 min, the solvent was removed in vacuo (0.1 Torr, 25 °C) to afford a quantitative yield of analytically pure **6**. ^1H NMR (25 °C, $CDCl_3$): δ 1.73 (br m, 35 H), 1.24 (br m, 35 H), 0.929 (m, 3 H), 0.83 (m, 4 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.34, 27.68, 27.68, 27.09, 26.74, 26.68, 26.48, 26.46, 26.34, 25.87 (s, 6:6:6:6:3:3:2:2:1 for CH_2), 22.87, 22.62 (s, 1:3 for CH), 22.32 (d, 3 CH, $^3J_{C\text{-}P}$ = 3.6 Hz). $^{29}Si\{^1H\}$ NMR (25 °C, $CDCl_3$): δ −67.21, −68.27 (s, 3:1), −69.18 (d, 3 Si, $^2J_{Si\text{-}P}$ = 10.2 Hz). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$): δ −44.95 (m). MS (65 eV, 200 °C; relative intensity): 1016 (M^+, 100%), 934 ($M^+ - C_6H_{10}$, 89%), 852 ($M^+ - 2C_6H_{10}$, 11%), 770 ($M^+ - 3C_6H_{10}$, 5%). Anal. Calcd for $C_{42}H_{77}O_{13}PSi_7$ (Found): C, 49.57 (49.50); H, 7.63 (7.50).

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Supplementary Material Available: X-ray crystal data for **2** including experimental procedures and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (9 pages); a listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

Isotopic Exchange Studies on the Cluster Anion $[HRu_3(CO)_{11}]^-$ in Solution: Direct Evidence for Intramolecular Fluxionality in Clusters

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Summary: Variable-temperature ^{13}C NMR studies on a 1:1 mixture of $[K(18\text{-crown-}6)][HRu_3(CO)_{11}]$ (^{13}C enriched) and $[K(18\text{-crown-}6)][DRu_3(CO)_{11}]$ (nonenriched) in CD_2Cl_2–$CHFCl_2$ reveal that the ligand mobilities in the cluster anions are indeed *intramolecular* fluxional processes.

Fluxional processes are a common feature of transition-metal carbonyl clusters in solution. The coalescence phenomena in the variable-temperature ^{13}C NMR spectra of a vast number of polynuclear metal carbonyl complexes have been interpreted in terms of an *intramolecular* stereodynamic behavior based on either ligand migration within the cluster or metal rearrangement within the ligand envelope.[1-3] While this interpretation provides a con-

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