to b. (3) The dipole moments of **3** ($X = CH_2$, O) are larger than those of **2**. An exception is the case of *cis*-**3** (X = NH), which reveals a small value. This is due to the trans orientation of the lone pairs with respect to the PN σ-bonds. The substituent attached to the phosphorus atom exerts a considerable effect on the ∠NPN bond angle.

Appendix

Qualitative considerations were drawn from EH calculations.[19] The H_{ij} matrix elements were computed with the Wolfsberg–Helmholtz approximation.[20] The parameters are listed in Table VIII. The ab initio calculations were carried out at a SCF level, utilizing the following basis sets: (1) Minimal basis set calculations were carried out with the STO-3G basis developed by Pople et al.[21] (2) Basis I consists of Gaussian lobe functions.[22] It is of double-ζ quality, constructed from the following Huzinaga[23] bases: C, (7/3) in the contraction (4,3×1/2,1); N, (8/4) in the contraction (4,4×1/2,2×1); O, (8/4) in the contraction (4,4×1/2,2×1); P, (10/6) in the contraction (4,6×1/3,3×1); H, (3,1). A set of p functions ($\zeta_p = 0.65$) was added to the hydrogens. (3) Basis II consists of basis I plus one set of d functions at the heavy atoms C, N, O, and P. The various exponents were chosen as follows: C, $\zeta_d = 0.30$; N, $\zeta_d = 0.95$; O, $\zeta_d = 1.25$; P, $\zeta_d = 0.50$. Hence basis I refers to a saturated s, p basis while basis II accounts in addition for d orbital participation. Localization of the orbitals was performed at basis I and basis II level by using the Boys localization criterion.[24]

Registry No. $HPCH_2$, 61183-53-7; *trans*-HPNH, 58734-30-8; HPO, 13817-06-6; $HP(CH_2)_2$, 6569-82-0; $HP(NH)_2$, 99686-53-0; HPO_2, 99686-54-1.

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Notes

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Oligosilastyrene-Supported Bis(arene)metal and -dimetal Complexes from Metal Vapor Synthesis

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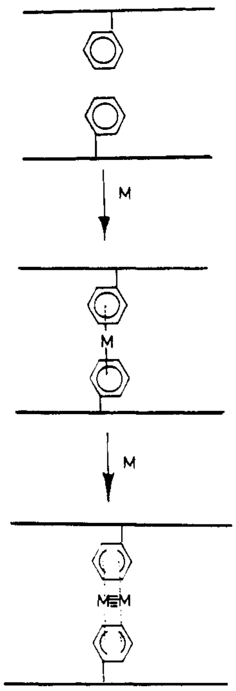
We have recently shown that organometallic polymers containing up to three different transition metals or transition-metal clusters[1-5] can be synthesized by vaporizing the atoms Ti, V, Cr, and Mo into liquid oligoalkanes, oligo(ethylene oxides) and siloxane polymers functionalized with arenes. These preparations and characterizations were carried out via metal atomization utilizing a rotary reactor for gram-scale preparation or matrix isolation techniques modified for spectroscopy on thin quiescent liquid films.[6,7] A key feature of these experiments is that the bis(arene) transition-metal complexes that are initially formed undergo subsequent reactions by direct addition of diffusing metal atoms (Scheme I), yielding metal clusters.[1-5,6b,8] In reactions with polymers, the macromolecular domain restricts metal atom clustering, under specified conditions of temperature and metal loading, to spatial regions where accretion and flocculation are prevented. Thus, the bis(arene)metal complexes act as functional loci for cluster growth, also stabilizing them against aggregation by providing a more or less rigid local environment due to polymer cross-linking. The result is a selectively doped metal-containing polymer.

Because of the current interest in organic metals and transport processes in electrically conducting dispersely filled polymeric composites, we have initiated studies involving the application of metal atom preparative methods to a class of polymers based on chains of silicon atoms. In this note we report that the transition-metal atoms Ti, V, Cr, and Mo can be trapped as bis(arene)metal complexes in fluid cyclic oligomers of a phenyl-containing polysilane.[9] In the one case examined, vanadium dimers

Scheme I



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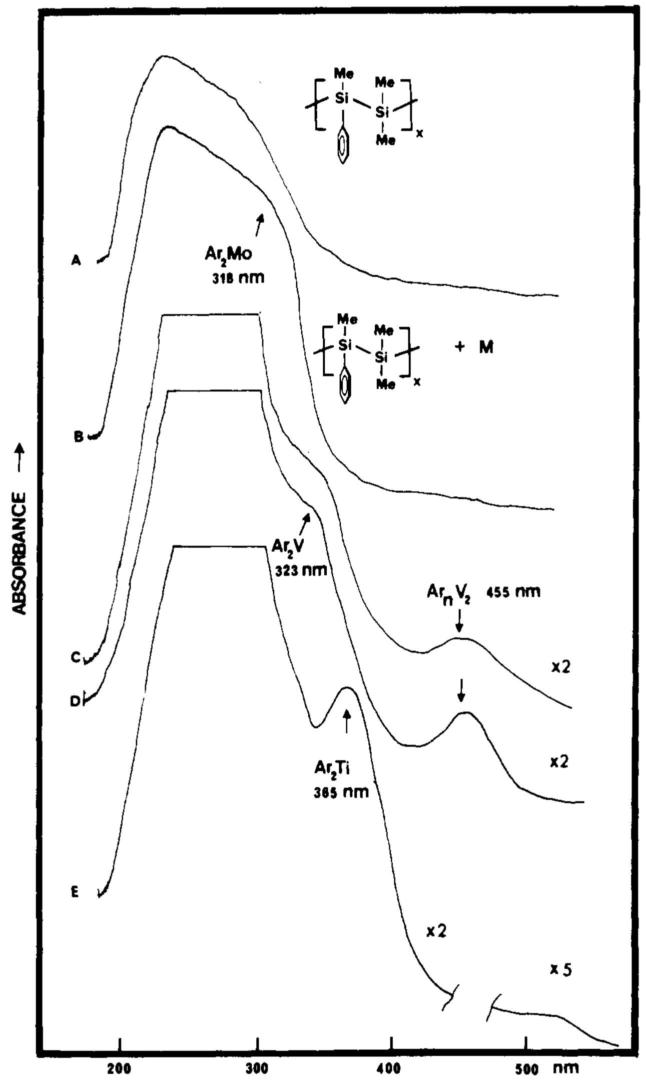

Figure 1. UV-visible absorption spectra of a liquid room-temperature 200-μm film of cyclic oligomers of phenylmethylsilylene-*co*-dimethylsilylene and products of reactions with transition-metal atoms for (A) unreacted starting material and for film containing (B) 70 μg of Mo, (C) 112 μg of V, (D) 136 μg of V, and (E) 144 μg of Ti. Metal-to-ligand charge-transfer transitions are indicated. Metal atom deposition rate = 0.7 × 10^{-3} mmol h^{-1}. Absorptions at wavelengths shorter than 220 nm have been cut off by the substrate spectroscopic window.

could also be stabilized in these materials.

The polymer employed was poly(phenylmethylsilylene-*co*-dimethylsilylene), "polysilastyrene".[10,11a] The material used in our experiments consisted of low molecular weight oligomers containing mostly cyclic species obtained as the soluble fraction after precipitating the high molecular weight polysilastyrene from THF solution by addition of 2-propanol, where $Me_2Si/PhMeSi$ = 0.5–1.5. Polysilanes are of practical import as precursors to silicon carbide and transition-metal mixed carbides and silicides,[11] as photoresist materials in microelectronics,[12] and as photoinitiators for vinyl polymerization.[13] Furthermore, they show potential for novel chemical and physical properties based on the delocalized Si–Si d-orbital system,[9] including the tendency of the polymers to become semiconducting when doped with oxidizing agents,[10] and the rather facile expulsion of the dimethylsilylene unit when the $\sigma^* \rightarrow \sigma$ transition is excited.[14]

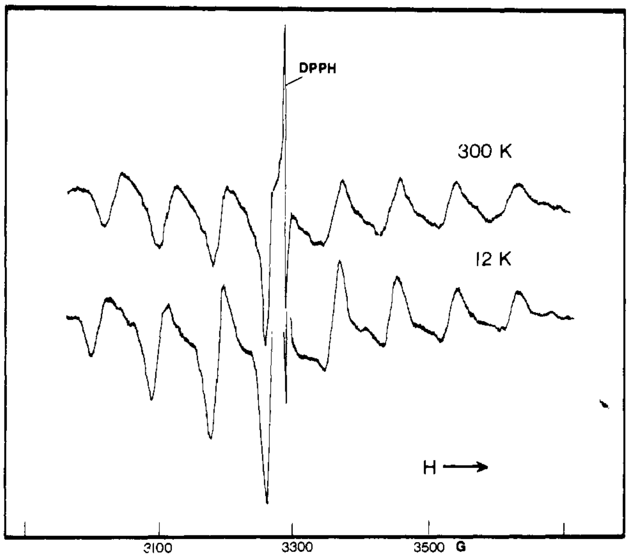

Figure 2. EPR spectrum of vanadium ($I = {}^7/_2$) supported as the bis(arene)vanadium complex in cyclic oligosilastyrenes (A) at room temperature ($\langle g \rangle = 1.988$, $\langle a(^{51}V) \rangle = 71$ G) and (B) at 12 K. Approximately 100 μg of V deposited at 0.7 × 10^{-3} mmol h^{-1}.

Results and Discussion

Microscale metal atom reactions were undertaken on thin (1–100 μm) liquid films of cyclic oligomers deposited onto the 1.5-cm^2 surface area of a quartz optical window that was housed in a variable-temperature Air Products CSW-202 cryostat. Metal atoms were quantitatively evaporated downward into the horizontal room-temperature film for UV–visible absorption spectroscopy or into samples maintained on a vertical sapphire rod for in situ EPR analysis. The results of these experiments are shown in Figures 1 and 2. Figure 1A shows the UV spectrum of the unreacted liquid oligomer containing pendant arenes, which has two shoulders at 230 and 285 nm and a possible weak shoulder near 320 nm, before the onset of an intense high-energy band (not shown) near 200 nm.

The products of the metal atom reactions, as bis(arene)metal(0) and metal dimer complexes, in most cases were identified by their characteristic metal-to-ligand charge-transfer (MLCT) and metal–metal-localized optical transitions.[1-7] Evidently there is considerable overlap of the substrate and bis(arene)metal product absorptions (Figure 1), partially obscuring the peak maxima for all but M = Ti. The product of reaction with Cr (not shown) was identified most easily by in situ oxidation with iodide ion to bis(arene)chromium(I) (λ_{max} = 336 nm).[2] In absorption (Figure 1E), reactions with Ti atoms are most informative where the MLCT band of the sandwich compound is well red-shifted (λ_{max} = 365 nm, with a weak absorption at 500–540 nm) from that of the unreacted material. The bis(arene)vanadium complex is paramagnetic and therefore amenable to EPR analysis.[6-8] An eight-line spectrum (Figure 2, $\langle g \rangle = 1.988$, $\langle a(^{51}V) \rangle = 71$ G) from the room-temperature film confirmed the existence of this complex. Its mobility is extremely restricted at room temperature in this viscous medium, as the EPR spectrum closely resembles that of the complex in the rigid limit at 12 K (Figure 2B). Reactions with vanadium atoms were carried out through high metal loadings to the dimer stage, indicated by the metal atom concentration-dependent absorption band at 455 nm (Figure 1C,D).[1-7] Here also the presence of bis(arene)vanadium is detectable in the

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shoulder (MLCT) overlapping the 270-nm band of the unreacted oligomer.

There is some motivation for pursuing the photochemistry of these systems in view of the propensity for metal-free polysilanes to cross-link. This behavior offers the possibility of supplementary immobilization of preformed metal aggregates in the polymer matrix. Initial broad-band photolysis studies of oligosilastyrene-bound Ti showed that incorporation of the transition metal as the sandwich complex, however, suppresses photochemistry.

These experiments using transition-metal vapors to form metal-containing complexes in silastyrene derivatives can be viewed as successful first steps toward the synthesis of metal-doped polysilane polymers.

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Pressure Effects in Scalar Coupling in $Co(H_2O)_6{}^{2+}$ and High-Spin-Low-Spin Equilibria in (1,4,8,11-Tetraazaundecane)nickel(II) Studied by Oxygen-17 Nuclear Magnetic Resonance

Roger M. Nielson, Harold W. Dodgen, John P. Hunt,* and Scot E. Wherland

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In a previous publication[1], we described the use of oxygen-17 NMR for studying high-spin-low-spin equilibria in nickel(II) tetraamines. To use our chemical shift approach at elevated pressures it is necessary to investigate the scalar coupling (A/h) between the paramagnetic metal ion and $^{17}OH_2$ as a function of pressure. The $Co(H_2O)_6{}^{2+}$ ion is a good species to use for this purpose as a relatively simple "fast-exchange" region is easily accessible. Merbach and co-workers[2] indicate that shifts in this region are "not strongly pressure dependent". We have undertaken a precise study of this point.

Work has appeared on some nickel(II) tetraamine systems including a ^1H NMR study by Merbach et al.[3] and an absorption spectral study by Kitamura[4] with ΔV° values ranging from +10 to ca. +1 cm³/mol for the process $Ni(H_2O)_2L \leftrightarrow NiL + 2H_2O$. Since the ΔV° values found are smaller than might have been anticipated, the systems are of considerable interest in understanding the basic factors that may contribute to volume changes.

Experimental Section

Oxygen-17 NMR was observed at ca. 12 MHz on instrumentation developed in our laboratories.[5] Purified[1] $^{17}OH_2$ was used at ca. 4-40% enrichment. Baker Analyzed $Co(NO_3)_2{\cdot}6H_2O$ (100.5%), Fisher "Purified" $NaClO_4$ and analyzed nickel(II) 1,4,8,11-tetraazaundecane perchlorate prepared by Pell[1] were used. The Co(II) solution was 0.0514 m in 4% $^{17}OH_2$. The Ni complex solutions were (1) 0.0496 m in Ni and 0.0992 m in $NaClO_4$ and (2) 0.0675 m in Ni and 4.013 m in $NaClO_4$. Both 28% and 40% $^{17}OH_2$ were used in the Ni studies. Reference solutions were made by using appropriate amounts of $Zn(NO_3)_2$ and ligand where applicable.

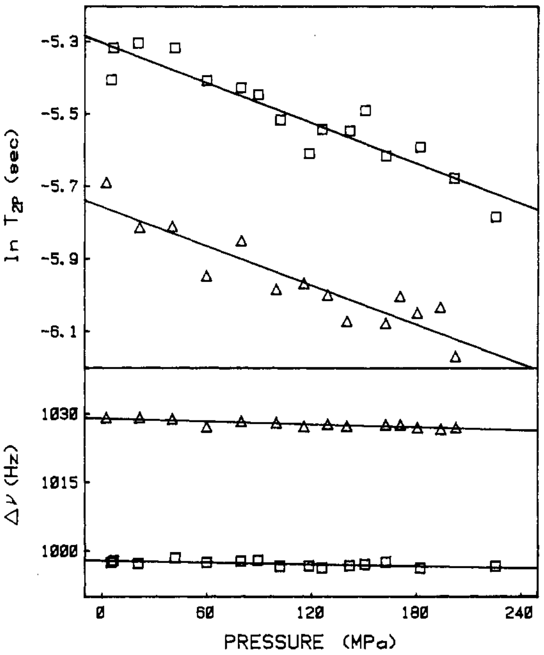

Figure 1. ln T^*_{2p} and shifts of the $^{17}OH_2$ NMR line, due to $Co(H_2O)_6{}^{2+}$, vs. pressure.

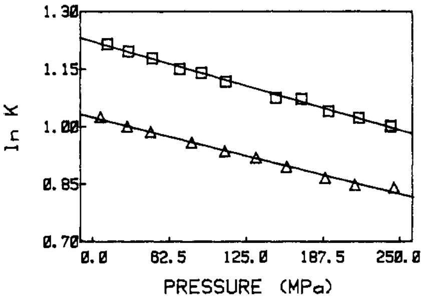

Figure 2. ln K for high-spin-low-spin equilibrium in Ni-2,3,2-tet vs. pressure: (□) data at 62 °C; (△) data at 45 °C.

Treatment of Data and Results

Figure 1 shows plots of ln T^*_{2p} and $\Delta\nu$ as a function of pressure for the Co(II) solution. We define $T^*_{2p} = [M]/[L]2\pi\Delta W$, where [M] is the metal concentration, [L] is the solvent water concentration, and ΔW is the line broadening (in Hz) relative to the Zn blank. The quantity $\Delta\nu$ is the paramagnetic shift (in Hz) in the bulk $^{17}OH_2$ line produced by Co(II), relative to the Zn blank. Both line broadenings and shifts are pressure-dependent although the shifts (which are known to better than 0.1%) are only slightly so and *decrease* with increasing pressure (ca. 0.01 Hz/MPa). The rate of exchange of H_2O can be obtained by the methods of Swift and Connick as shown by Hoggard.[6] From the relation $d \ln K/dp = -\Delta V^\ddagger/RT$ the pressure data yield $\Delta V^\ddagger = 5.5 \pm 0.6$ cm³/mol at 83.0 °C and $\Delta V^\ddagger = 5.2 \pm 0.7$ cm³/mol at 72.3 °C in good agreement with Merbach et al.[4] The observed decrease in shift with increasing pressure can be quantitatively accounted for by the fact that the water exchange rate is slowing with increasing pressure.

In the case of $Co(H_2O)_6{}^{2+}$, $1/T_{2M}$ is small and the Swift-Connick equations become

$$\Delta\nu = \Delta\nu_\infty/(1 + \tau_M{}^2\Delta\omega_M{}^2)$$

$$\Delta W = \tau_M\Delta\omega_M\Delta\nu$$

where $\Delta\nu$ is the shift of the resonance, $\Delta\nu_\infty$ is the shift when τ_M

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