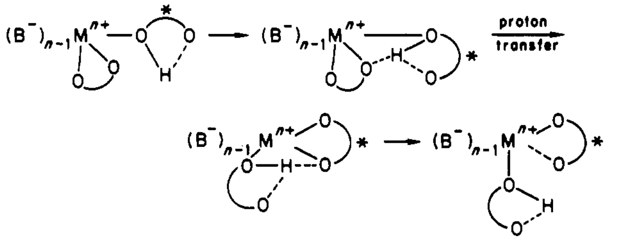
those of the present study. The retardation effect by addition of free base L can be interpreted by the decrease in concentration of $UO_2(acac)_2acacH$ with the addition of L. This interpretation is similar to that of the retardation in acac exchange in $Th(acac)_4$ but different from that in the exchange of acac in $VO(acac)_2$,[12] where the retardation is attributed to the formation of an outer-sphere intermediate with the added base.

As mentioned above, the present substitution reaction in $UO_2(acac)_2L$ and the exchange reaction of acac in $Th(acac)_4$ proceed through the type 3 mechanism, where the rate-determining step is the proton-transfer process. Although there is a similarity between the mechanisms of both systems, the reaction rates differ considerably from each other. The difference in rates of the proton-transfer processes can be understood by assuming that the process consists of three steps:



(7)

where M^{n+} is a metal ion and $HO\frown O$ represents a β-diketonate (HB) in the enol form. In the first step in eq 7, incoming HB^* and coordinated B^- come near each other to make a hydrogen bridge between HB^* and B^-. The second step is the proton transfer including the formation of the hydrogen bridge. The third step is the breaking of the hydrogen bridge between coordinated B^{-*} and leaving HB. The difference in rates is mainly attributed to the difference in $\Delta G^‡$ values for the first step, since the variation in $\Delta G^‡$ values for the proton-transfer step is expected to be relatively small. The unidentate β-diketonate as a proton donor, which was coordinated to the metal ion with a large ionic radius, rotates about a metal–oxygen bond so freely that the β-diketonate can easily orientate so as to favor proton transfer. Large negative $\Delta S^‡$ values (Tables II and III) seem to reflect the steric hindrance in the first step. Consequently, the difference in rates between $UO_2(acac)_2L$ and $Th(acac)_4$ or $U(acac)_4$[7] is explained by the difference in ionic radii of central metal ions. The steric hindrance may be responsible fin part for the difference in rates of exchange between $Th(acac)_4$ and $Th(tta)_4$[4] (tta = 2-thionyltrifluoroacetonate) because tta is more bulky than acac.

Although many studies on the intermolecular proton-transfer reaction have been repported, data on the rate of the intramolecular proton-transfer reaction, particularly in organic solvents, are not available. More detailed studies on the $UO_2(\beta\text{-diketonate})_2L$ system are in progress in order to elucidate the steric hindrance and kinetic isotope effect in the intramolecular proton-transfer process, and information on these aspects is to be considered in a future report.

Acknowledgment. W.-S.J. wishes to thank Dr. Y. Ikeda for providing uranyl complexes.

Registry No. $UO_2(acac)_2(Me_2SO)$, 71357-22-7; $UO_2(acac)_2(dmf)$, 89145-11-9; $UO_2(acac)_2(tmp)$, 102575-53-1; dbm, 19274-26-1; D_2, 7782-39-0.

Contribution from the Lash Miller Chemical Laboratories,
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Reactions of Transition-Metal Atoms with Arenes, Arene-Functionalized Alkanes, Oligo(ethylene oxides), and Polysiloxanes. 4

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New synthetic, chemical, and spectroscopic (optical, Raman, IR, EPR) experiments aimed at further elucidation of the details of the near-room-temperature reactions of metal atoms with arene-functionalized liquid polysiloxanes to produce organometallic polymers and polymer-supported metal clusters are described. By examining the reactions of V, Cr, and Mo atoms with model arenes, arene-functionalized alkanes, and arene-functionalized oligo(ethylene oxides), one is able to gain insight into the role of arene substituents, bis(arene)metal cross-links, and the solvating backbone in the mode of formation and stabilization of metal cluster sites on the polysiloxane. The chemical and physical homogeneity of the resulting polymers is also assessed.

Introduction

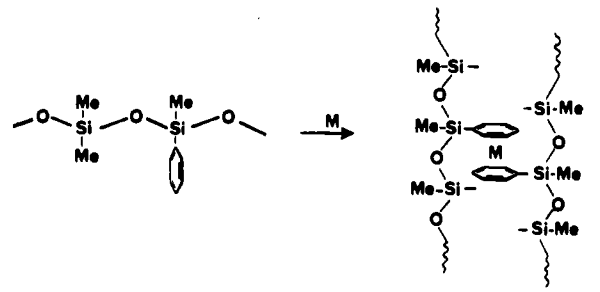
A theme running through much of our recent metal atom research has been to find ways of generating and stabilizing metal clusters at or close to room temperature in various fluid trapping media and to devise methods for investigating their physical and chemical properties within the trapping medium itself.[1] The ability to transfer the metal aggregates from the fluid intact to supports such as carbon, inorganic oxides, and zeolites emerged as a result of such investigations.[1,2]

In this paper we focus attention on a method of metal cluster formation in the liquid phase that is based on the direct sequential addition of metal atoms according to sequence 1 during the metal

$$M + M_n \rightarrow M_{n+1} \qquad (1)$$

atom deposition process. This reaction is viewed as occurring at a site preformed in the support medium, which invariably contains arene functionalities, usually linked to oligoalkanes, oligo(ethylene oxides), and oligo- and polysiloxanes. In particular, the arene substituents inhibit competing metal atom polymerization reactions by chemically trapping the atomic diffusant. In general, these liquid supports permit chemical reactions of metal atoms with ligands to occur at higher temperatures, which will result in a more favorable competitive balance between bis(arene)M complex

Scheme I



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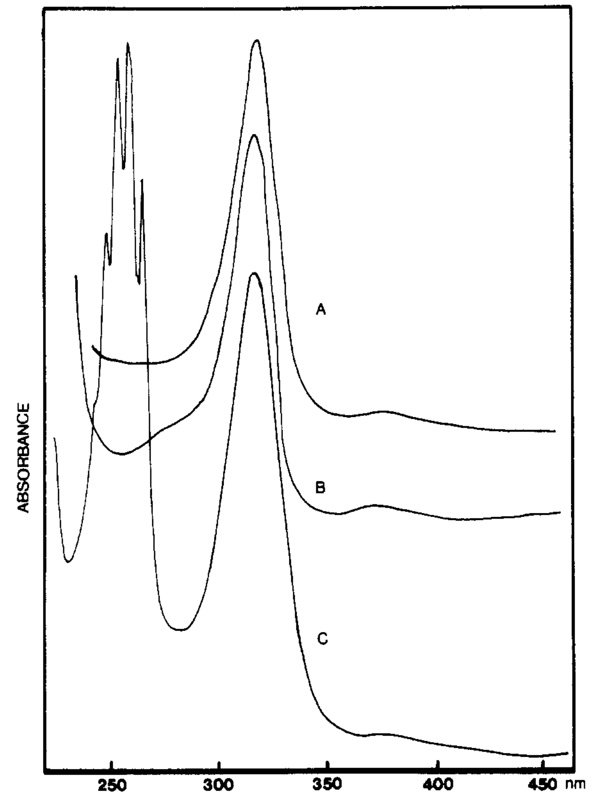

Figure 1. UV-vis spectra: A, $(C_6H_5CH_3)_2Mo$ in spectral grade pentane, 3.4×10^{-6} M ($\epsilon = 1.1 \times 10^5$, $\lambda = 318$ nm); B, $(C_6H_5CH_3)_2Mo$ in poly(dimethylsiloxane) (DC 200) fluid; C, the (arene)$_2$Mo complex prepared in situ in poly(dimethyl-*co*-methylphenylsiloxane) (DC 510) by electron-beam or resistive metal vaporization.

formation and metal atom agglomeration, other things being equal.

Francis and Timms[3] first reported that bis(arene) transition-metal complexes could be formed by cocondensing transition-metal atoms of Ti, V, Cr, Mo, and W into liquid poly(methylphenylsiloxanes, DC 510) at 273 K using metal vapor rotary reaction techniques. These reactions produce organometallic polymers as shown in Scheme I. The principle of these reactions has been extended to quantitative depositions of transition-metal atoms into thin, quiescent liquid films of these nonvolatile materials, particularly the Dow Corning 510 fluid.[4-8] The thin-film experiments form the intermediate link between the matrix-isolation experiments and the macroscale rotary reactor experiments.

The present study is organized as follows: We very briefly review published results of liquid-thin-film experiments involving reactions of transition-metal atoms with the poly(methylphenyl-*co*-dimethylsiloxane) (DC 510) system. The experiments and arguments implicating metal cluster compounds in this macromolecular support have been detailed in earlier papers from this laboratory to which the reader is referred.[4-8] In this paper, some further insight into the mode of stabilization of metal clusters in the DC 510 system is obtained from studies involving different phenyl-substituted monomers and oligomers in metal vapor reactions surveying the temperature range 12–300 K.

Experimental Section

The experimental details of metal vaporization into siloxane polymers containing pendant arenes have been described previously.[1-8] Quantitative studies of metal atom reactions in these polymers were made possible by the development of a static, liquid-thin-film microscale analogue to the macrosynthetic experiments.[9] In brief, the method exploits the characterization tools developed for matrix-isolation experiments and was thus suitably adapted for in situ microgram-scale metal vapor synthesis and spectroscopy.[4-9] In what follows we detail only those aspects of the chemical and spectroscopic procedures that are unique to the present investigation.

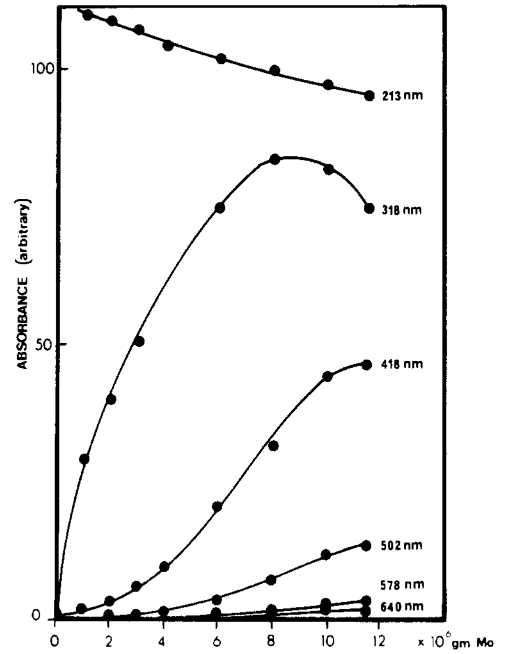

Figure 2. Graphical representation of a Mo/DC 510 reaction at 250 K of the type shown in ref 4.

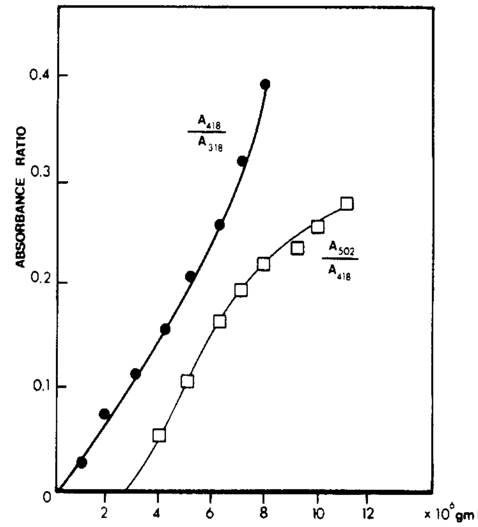

Figure 3. Plot of $A_{\mathrm{Mo}_n}/A_{\mathrm{Mo}}$ showing independent growth characteristics.

Synthetic Procedures. (a) Arene End-Functionalized Oligo(ethylene oxides). Preparations of these compounds were based on the methods of Perry and Hibbert[10] and on the method of Bomer et al.[11] For experiments symbolized by Figure 4, the α,ω-diphenyl ethers of tetra- through heptaethylene glycol were synthesized. Tetraethylene glycol was purchased from Aldrich. The remaining glycols were synthesized according to the method prescribed for hexaethylene glycol.

(i) Hexaethylene Glycol. The α,ω-dibromo derivative of diethylene glycol was synthesized according to the procedure of Dann et al.[12] in 40% yield. The monosodium salt of diethylene glycol (dried over activated

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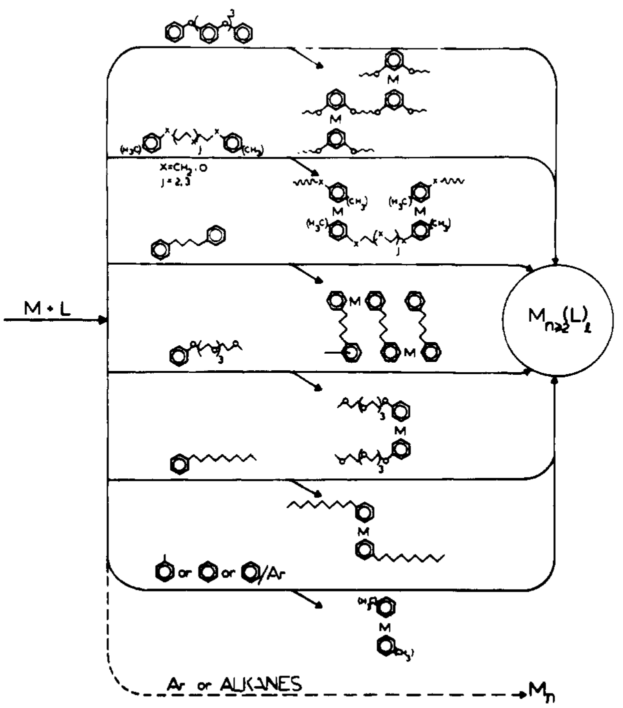

Figure 4. Matrix and macroscale metal vapor synthetic strategy used to elucidate the nature of metal cluster diffusion/agglomeration/complexation in DC 510.

4A molecular sieves) was prepared as prescribed by Bomer[11] with freshly cut sodium metal, all manipulations being made under a nitrogen atmosphere until the alkoxide formation was complete (several hours). Thus to 600 g (5.66 mol) of mechanically stirred diethylene glycol was added 184.2 g (1.88 mol) of sodium metal. The solution turned orange and became quite viscous during the room-temperature reaction. α,ω-Dibromodiethyl ether (227.7 g, 0.99 mol) was added slowly to the stirred alkoxide solution. NaBr precipitated, and the solution was heated to 75 °C until it became neutral to pH paper (ca. 20 min). The orange-brown solution was separated from the salt by vacuum filtration through a coarse sintered-glass funnel. This liquid was still contaminated with NaBr and was finally freed of the salt by liquid–liquid extraction (Et_2O) after 5 days. A pale yellow extract collected in the ether pot. The ether was removed under vacuum, and the viscous bright yellow oil distilled through a 15-cm Vigreux column (101.2 g, 178 °C (0.05 mm), lit.[10] bp 203–205° (0.03 mm)). The hexamethyldisilazane derivative of the diol was prepared and chromatographed according to the method of Calzolari et al.,[13] which indicated that the diol was pure. NMR ($CDCl_3$, 60 MHz): δ 3.01 (s, 2 H), 3.65 (s, 24 H). IR (neat): 3540 cm^{-1} (br, OH bonded).

(ii) Hexaethylene Glycol Ditosylate. Hexaethylene glycol (8.5 g, 0.03 mol) was dissolved in 25-mL dried (CaO) pyridine and cooled to −5 °C. Tosyl chloride (11.8 g, 0.062 mol) in 20 mL of pyridine was added with stirring at such a rate that the temperature of the reaction mixture did not rise above −2 °C (formation of pyridinium chloride precipitate). The reaction was stirred for $18^1/_2$ h. The reaction mixture was poured over 300 mL of crushed ice/water and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with 3 × 300 mL of ice cold 6N HCl and 250 mL of cold, saturated ammonium chloride. The organic phase was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed under vacuum to yield a faintly yellow-brown colored oil after chromatography (silica, EtOH:CH_2Cl_2 2%:98% v/v). Yield: 16.53 g, 93% NMR ($CDCl_3$, 60 MHz): δ 2.40 (br s, 6 H, $ArCH_3$), 3.57 (s, 8 H, $-OCH_2CH_2O-$), 3.61 (s, 8 H, $-OCH_2CH_2O-$), 3.5–3.8 (m, 4 H, $TsOCH_2CH_2O-$), 3.97–4.28 (m, 4 H, $TsOCH_2CH_2O-$), 7.29 and 7.72 (AA′BB′, 8 H, J_{AB} = 8 Hz, ArH).

(iii) α,ω-Diphenyl Ether of Hexaethylene Glycol. The ditosylate (11.84 g) in 10 mL of THF was added to 3.76 g (0.04 mol) of phenolate anion prepared by adding 2.3 g (0.041 mol) of KOH dissolved in 2.5 mL of H_2O to the phenol in 65 mL of THF. The solution was stirred under N_2 at 70 °C for 5 h and then at 45 °C for 16 h. When the liquid was cooled, in ice, a large mass of white crystals deposited. These were separated by vacuum filtration. The THF was removed under vacuum and the yellow oil chromatographed on alumina (Et_2O:pentane, 2:3). The product was pale yellow and could not be decolorized. NMR ($CDCl_3$, 60 MHz): δ 3.58 (s, 8 H, $-OCH_2CH_2O-$), 3.63 (s, 8 H, $-OCH_2CH_2O-$), 3.5–3.9 (m, 4 H, $ArOCH_2CH_2O-$), 3.96–4.16 (m, 4 H, $ArOCH_2CH_2O-$), 6.64–7.37 (m, 10 H, ArH).

The α,ω-diphenyl ethers of the tetra-, penta-, and heptaethylene glycols were similarly prepared.

(iv) α,ω-Diphenyltetraethylene Glycol. NMR (acetone-d_6, 60 MHz): δ 3.61 (s, 4 H, $-OCH_2CH_2O-$), 3.63 (s, 4 H, $-OCH_2CH_2O-$), 3.60–3.90 (m, 4 H, $ArOCH_2CH_2O-$), 4.0–4.23 (m, 4 H, $ArOCH_2CH_2O-$), 6.70–7.42 (m, 10 H, ArH). Lit. NMR ($CDCl_3$): δ 3.68–4.2 (m, 16 H, $-OCH_2CH_2O-$).

(v) α,ω-Diphenylpentaethylene Glycol. NMR (acetone-d_6, 60 MHz): δ 3.58–4.23 (m, 20 H, $-OCH_2CH_2O-$), 6.78–7.42 (m, 10 H, ArH).

(vi) α,ω-Ditoluylheptaethylene Glycol. NMR (acetone-d_6, 60 MHz): δ 2.23 (s, 6 H, $ArCH_3$), 3.50–4.21 (m, 28 H, $-OCH_2CH_2O-$), 6.68–7.20 (m, 8 H, ArH).

(vii) Microscale Metal Vapor Reactions of the α,ω-Diaryloligo(ethylene glycols). Reactions of these liquids were carried out at or near room temperature according to the method described in ref 4.

(b) Synthesis of α,ω-Ditoluyldecane. This compound was prepared by the Fittig reaction between *p*-bromotoluene and 1,10-dibromodecane (*Caution*! 1,10-dibromodecane is a suspected *potent* carcinogen). The product was purified by preparative GLC (support, Chromosorb W HP, 80/100 mesh, OV-101 coated, 6 ft × 2 mm, 200 °C). NMR (acetone-d_6, 60 MHz): δ 1.2–2.0 (br m, 12 H, $-CH_2$), 2.4–2.82 (m, 8 H, $Ar(CH_2CH_2-)$), 2.3 (s, 6 H, $ArCH_3$), 7.13 (s, 8 H, ArH).

(i) Microscale Metal Vapor Reactions of α,ω-Ditoluyldecane. This compound is a solid at room temperature. The following method was devised to carry out a solution-phase metal atom reaction: A 15% w/v solution of the ligand in Fischer (125/135, arene free) paraffin oil was mixed with 1 mL of spectral grade hexane and applied as a thin film, via vacuum microsyringe, to a horizontal NaCl window as described in ref 9. The hexane quickly evaporated, leaving behind an unbroken film of liquid. Vanadium or molybdenum atoms were allowed to react with the room temperature liquid. 1,4-Diphenylbutane (Aldrich) was allowed to react in the same manner.

(c) Synthesis of the Phenyl Ether of Methyltetraethylene Glycol. The compound was prepared by tosylating the monomethyl ether of tetraethylene glycol (Aldrich) and reacting the tosylate with phenolate anion as described above for the synthesis of α,ω-diphenylhexaethylene glycol.

(i) $CH_3O(CH_2CH_2O)_4Ts$. NMR (acetone-d_6, 60 MHz): δ 2.40 (br s, 3 H, $ArCH_3$), 3.23 (s, 3 H, CH_3O-), 3.45–4.35 (m, 16 H, $-OCH_2CH_2O-$), 7.30 and 7.72 (AA′BB′, 4 H, J_{AB} = 8 Hz, ArH).

(ii) $CH_3O(CH_2CH_2O)_4C_6H_5$. NMR (acetone-d_6, 60 MHz): δ 3.23 (s, 3 H, $ArCH_3$), 3.42–4.23 (m, 16 H, $-OCH_2CH_2O-$), 6.70–7.42 (m, 5 H, ArH).

Reactions of this liquid with vanadium and molybdenum atoms are described later in this paper.

Results and Discussion

To gain an appreciation of the earlier work and that which follows, we present a brief review, with some supplementary new results of data regarding Mo/DC 510 reactions obtained by the microscale metal vapor technique. This information forms a necessary basis for the subsequent presentation.

The existence of $(arene)_2Mo$ complexes in DC 510 can be considered established.[3,7] Figure 1 shows the UV–vis absorption spectra (new data) of $(C_6H_5CH_3)_2Mo$ in pentane ($\epsilon = 1.1 \times 10^5$, λ_{max} = 318 nm) (Figure 1A) and in poly(dimethylsiloxane) (DC 200) (Figure 1B) and for the complex prepared in the DC 510 polymer. In supplementary work we have synthesized these compounds on the gram scale by electron-beam evaporation of Mo accompanied by reaction with toluene or DC 510.[15] The major features of importance in the figure are the intense MLCT absorption centered at 318 nm and a weak absorption at 395 nm. On the basis of the measured peak heights, the ratio of the 318/395-nm transitions is 80:1 for the $(arene)_2Mo$ complex regardless of the solvent medium (pentane or polymer).

In Figure 2 we represent graphically the results of depositing increments of Mo into a thin (10–100 μm) 250 K film of DC 510. The initial Mo deposition represented in Figure 2 produces $(arene)_2Mo$. The absorption at 318 nm, by comparison with Figure 1, is characteristic of the MLCT transition of the molybdenum sandwich complex. Increasing the metal loading (at approximately

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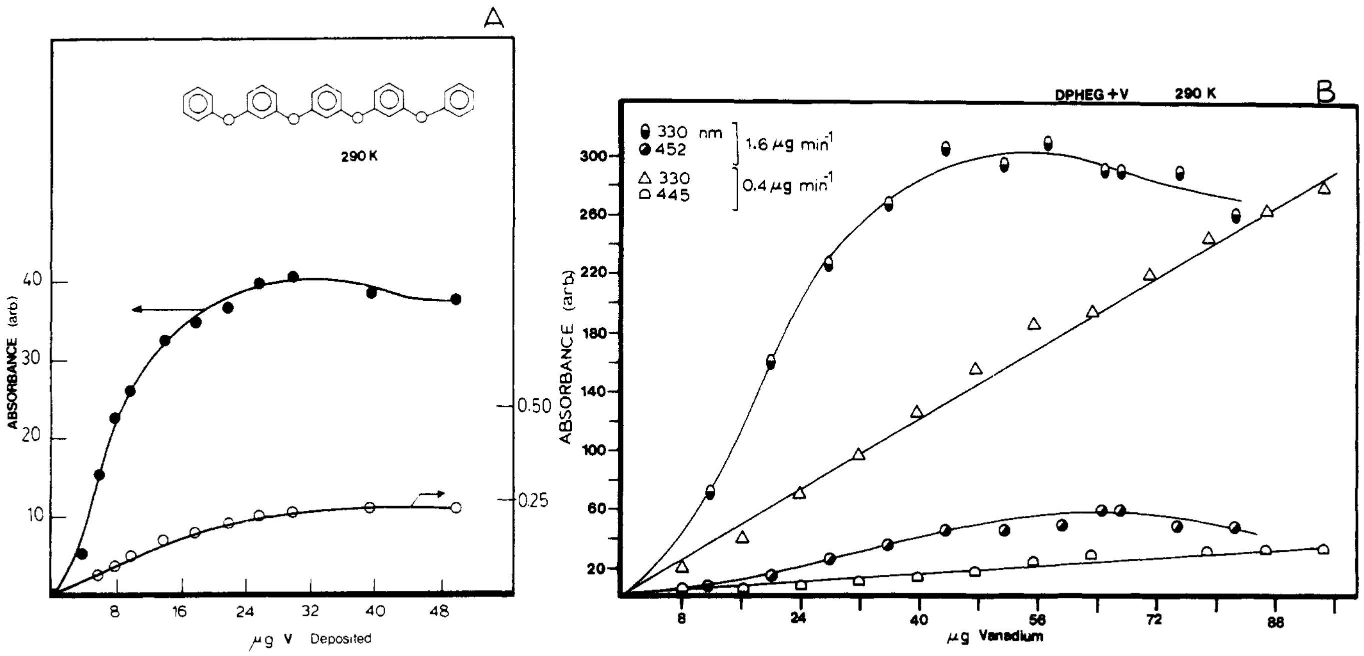

Figure 5. (A) Graphical representation of growth characteristics: (○) growth of the (arene)$_2$V complex when Santovac-5 is titrated with vanadium atoms; (●) growth of the second species, which is associated with a vanadium dimer. The peak maximum in the absorption spectrum is plotted as a function of the amount of deposited metal in each case. (B) Graphical representation as in part A above, except that the reaction occurs between V and α,ω-diphenylhexaethylene oxide. The effect of V deposition rate is shown by comparing the shape of the two growth curves.

2×10^{-4} mmol h^{-1} deposition rate) to roughly 10^{-8} mol results in the growth of a new absorption at 418 nm (Figure 2). As the amount of molybdenum in the film is gradually increased, more transitions can be observed at 502, 578, and 640 nm (Figure 2). The variation of the absorbance for each band as a function of metal loading is depicted in Figure 3 *and confirms that each band represents a separate species as shown by their independent growth characteristics.* The following extinction coefficients were estimated by using the data of Figure 2: $\epsilon_{318} = 2.7 \times 10^5$, $\epsilon_{418} = 7.4 \times 10^4$, $\epsilon_{502} = 2.2 \times 10^4$ L mol^{-1} cm^{-1}. The value for the polymer supported (arene)$_2$Mo complex is within a factor of 2 of the value given above for the metal-to-ligand charge-transfer absorption of bis(toluene)molybdenum in pentane.[7] The order of stability of the species giving rise to those bands red-shifted from the 318-nm MLCT absorption is the same as the order of production. Except for the absorption associated with the (arene)$_2$Mo complex, all other absorptions gradually disappear on warming of the polymer medium to 300 K. Furthermore, these latter absorptions are rapidly quenched on allowing $\simeq$1 torr of O_2 to diffuse into the fluid at 290 K. In contrast, the polymer bound bis(arene)molybdenum(0) complex is oxidized only slowly to the bis(arene)molybdenum(I) analogue.[7] The above data with minor modifications are essentially representative of our findings for the Ti, V, and Cr reactions with DC 510 as well as their bimetallic counterparts.[4-8]

Arguing heuristically for the existence of polymer-supported metal clusters, we note the following:

(i) The excitation energies of the multimers M_n ($n \geq 2$) in solid rare-gas matrices red shift with increasing nuclearity.[16]

(ii) The gas phase secondary ions [(arene)$_2$Cr$_2$(CO)$_3$]$^+$, [(arene)$_2$Cr$_3$(CO)$_6$]$^+$, and [(arene)$_2$Cr$_2$]$^+$ are known to exist.[17]

(iii) Concentration studies of the cocondensation of V, Cr, and Mo with C_6H_6:Ar = 1:10 at 12 K reveal bands on the low-energy side of the (η^6-C_6H_6)$_2$M MLCT band, possessing a metal concentration dependence consistent with that expected for binuclear metal species. These lower energy transitions are assigned to metal-localized excitations.[4-8,18]

(iv) Bimetallic M/M′/DC 510 studies provide additional support for the metal nuclearity and metal-localized electronic assignments.[5-7]

(v) Microsolution spectroscopy experiments on V and Cr atom titrations of bis(toluene)vanadium and bis(toluene)chromium dissolved in 140 K methylcyclohexane liquid films indicated the arene stoichiometry might be two for the binuclear species.[19]

(vi) Simple series parallel competitive kinetic schemes were devised that account for the cluster growth curves for V$_n$-, Cr$_n$-, and Mo$_n$/DC 510, up to the $n = 4$ stage for Mo (see part 2 of this series of papers).

Reactions of Transition-Metal Atoms with Arenes and Arene-Functionalized Alkanes and Oligo(ethylene oxides). In order to examine in more detail the origin of the metal concentration-dependent absorptions in DC 510 we developed the synthetic strategy sketched in Figure 4. From top to bottom the scheme shows metal vapor syntheses in matrices varying in temperature from 293 to 12 K. In common with the DC 510 polymer the benzene ring is repeated from ligand to ligand. A subset of ligands also contains ether linkages. Considering the exemplary vanadium atom, quantitative vaporization into neat liquids or solutions in every case (A–F) resulted in the production of the bis(arene)vanadium complex recognizable by its characteristic charge-transfer absorption at 330–340 nm (depending on the ligand) and its EPR spectrum. For the α,ω-diphenyl compounds, bis(arene)metal complex formation is possibly accompanied by oligomerization leading to chain lengthening. If we trace routes A and B in Figure 4 for vanadium atom reactions, in each case a band is produced at $\simeq$455 nm in addition to the intense MLCT absorption of the sandwich complex. As found for reactions of this transition metal with DC 510, the species absorbing at 455 nm shows growth characteristics independent of the bis(arene)vanadium complex,[4,5] although a rate dependence shows up at the slowest depositions (see part 2 of this series of papers). New examples of this behavior are shown in Figure 5. They can be compared with those of vanadium deposited into DC 510 at 250 K.[4,5] Since reactions of vanadium with α,ω-ditoluyldecane or 1,4-diphenylbutane lead to the development of the 455-nm absorption, we conclude that ether oxygens are not implicated in its production. Clearly the ability to establish an initial chain

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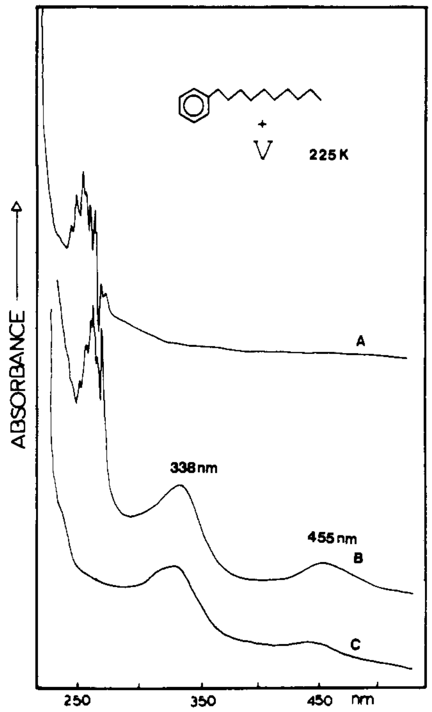

Figure 6. Microsolution reaction of vanadium atoms with 1-phenyl-*n*-decane at 255 K: spectrum A, base line; spectrum B, $\simeq 3 \times 10^{-3}$ mmol of vanadium deposited at 2×10^{-4} mmol h^{-1}; spectrum C, recorded at 300 K after removing unreacted ligand in vacuo.

propagation step via bis(arene)metal complex formation is still possible through sequences A–C. One can imagine that a medium of increasing viscosity due to increasing molecular weight might act in some physical manner to immobilize small transition-metal cluster molecules. The view here is that of a trapping medium comprising randomly interpenetrating molecules oligomerized as a result of the formation of bis(arene)metal complexes. Experiments were undertaken in which vanadium atoms were vaporized into a variety of high molecular weight poly(dimethylsiloxanes) (M_r 10^4–10^6). The optical absorption spectrum evidenced *only an unstructured absorption rising smoothly toward the ultraviolet.* This is typical behavior for absorption and scattering by colloidal metal. Arguing against the necessity of having an oligomeric or polymeric medium to stabilize the species absorbing at 455 nm, we have found that reactions of vanadium atoms with 1-phenyl-*n*-decane, which is liquid at 255 K, rapidly gave rise to the 455-nm band. This reaction is important for another reason. Figure 6B shows the result of depositing $\sim 3 \times 10^{-3}$ mmol of V (deposition rate = 2×10^{-4} mmol h^{-1}) into a thin film of phenyldecane maintained at 255 K on a 3-cm^2 quartz window. By a careful warming of the fluid to 260 K, the unreacted phenyldecane could be removed under dynamic vacuum. Spectrum C was recorded at 300 K and shows the metal–ligand charge transfer and the 455-nm absorptions coexisting. The rising baseline between 350 and 250 nm is due to scattering by the inhomogeneous residual organometallic film, interspersed with minute gray particles, which were probably colloidal vanadium. Unlike the benzene or toluene analogues, the products of the reaction of vanadium with phenyldecane are involatile under 10^{-6} torr, at room temperature. A weak spectrum showing both absorption maxima was obtainable after 13 h at 300 K.

On eliminating all substituents linked to the phenyl ring (Figure 4) we return to the metal concentration studies involving V/C_6H_6/Ar where a dimeric vanadium compound was first inferred.[18] It therefore appears likely that the species responsible for the 455-nm absorption in V/DC 510 and in the phenyl rich systems of Figure 4 can be assigned to a vanadium dimer molecule interacting in an as yet unspecified manner with the phenyl substituent(s). The results of optical absorption spectroscopy of the series of microsolution and matrix-isolation reactions represented in the scheme of Figure 4 are summarized in Table I. The position of the MLCT absorption due to (arene)$_2$V varies from 328 to 345 nm, showing a *red shift* as the ring is substituted with alkyl or ether groups and as the surrounding medium is changed from aliphatic/arene to ether/arene. The "V_2" absorption is not uniformly red-shifted, showing an average value of 455 ± 5 nm and suggesting excitations that are mainly *metal-localized.* Neither the MLCT nor the "V_2" band shows a substantial variation in the position of the peak maximum as the temperature is varied to 12 K.

Table I. Results of Optical Absorption Spectroscopy of Microsolution or Matrix-Isolation Reactions of Vanadium Atoms with Various Functionalized Arenes

substrate	abs max, nm		reacn temp, K
	(arene)$_2$V	"V_2"	
Santovac-5	340	458	290
α,ω-diphenylhexaethylene oxide	335	454	290
α,ω-ditoluyldecane	340	460	290
phenylhexaethylene oxide monomethyl ether	330	452	280
DC 510	323	455	250
1,4-diphenylbutane	345	455	245
phenyldecane	338	455	225
benzene (toluene)	328 (335)	450 (450)	77
	328 (335)	450 (450)	12
benzene:argon 1:10	328	450	12
argon or alkanes		478, 555–590, 740–840	12

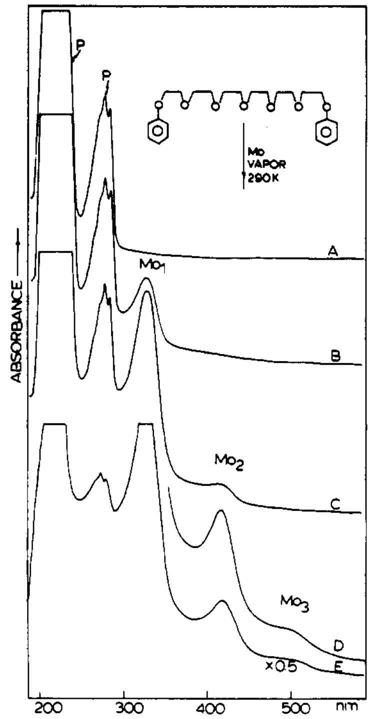

Figure 7. UV–visible absorption spectroscopic study of the reaction of Mo atoms with α,ω-diphenylhexaethylene oxide at 290 K: A, pure oligomer; B–D, increasing Mo atom concentration.

Reactions of Arenes with Mo Atoms. Returning to the scheme shown in Figure 4, a similar set of reactions was also carried out for Mo, with similar findings. Reactions with Mo gave rise to a MLCT absorption varying from 323 nm in DC 510 to 327 nm in 1,10-ditoluyldecane. A second absorption showing the familiar metal atom concentration dependence was detected at 418–422 nm in every case. A typical series of room-temperature microscale reactions between Mo atoms and the seven-oxygen α,ω-diphenylhexaethylene oxide is shown in Figure 7. This spectrum clearly displays three of the growth states encountered for reactions of Mo with DC 510 (Figure 2). Regarding the ether oligomer, the absorptions at 418 and 502 nm coincide with those detected in DC 510 fluid. Additional reasons for choosing the oligo(ethylene oxides) derive from their proven ability to complex metal

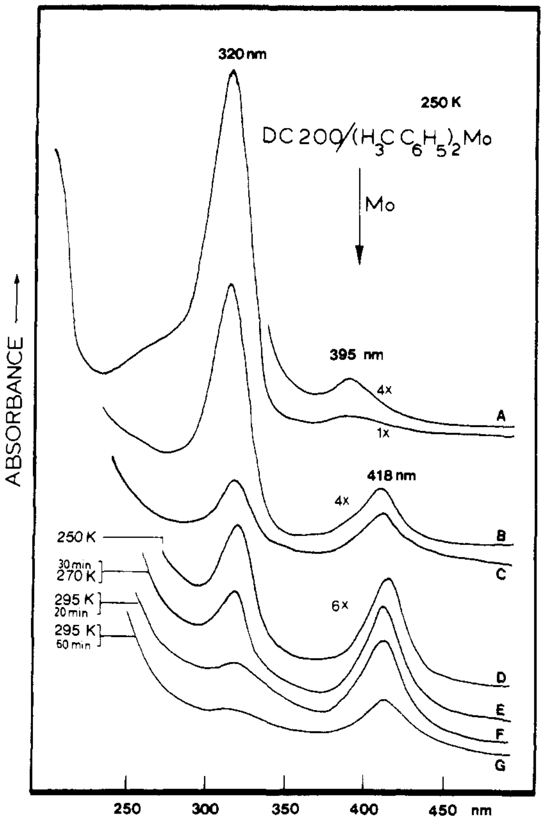

Figure 8. Results of Mo atom titration of 10^{-4} M $(C_6H_6)_2Mo$ dissolved in DC 200 at 250 K: curve A, base line; curve B, 0.5×10^{-4} mmol (corrected) of Mo deposited; curve C, an additional 0.3×10^{-4} mmol (corrected) of Mo deposited. Curves D–G represent the outcome of warming the matrix through various temperature increments.

ions, an ability that might extend to a metal atom.

To the results of the above series of reactions we can add the outcome of depositing Mo atoms into DC 200 containing dissolved bis(toluene)molybdenum. This liquid poly(dimethylsiloxane) was chosen to mimic some of the properties of DC 510 (similar viscosity and molecular weight). In this reaction matrix, the sandwich complexes are not bound to the polymer chain, but the situation provides a polymeric solvent medium similar to DC 510 and loosely represents the case in which all available phenyl groups have been converted to complexes. Figure 8 lucidly expresses the results of this experiment. Curve A represents 10^{-4} M bis(toluene)molybdenum dissolved in DC 200 (60 μL of fluid spread over an area of 3 cm^2) at 250 K in vacuo. Curves B and C represent successive increments (0.5×10^{-4} and 0.3×10^{-4} mmol (corrected)) of Mo atoms deposited at a rate of 2.4×10^{-4} mmol h^{-1} into this film. The consumption of the bis(toluene)molybdenum complex and the simultaneous growth of the absorption at 418 nm are manifest. Warming the film to 270 K (curve E) and then to 295 K (curves F and G) appears to result in the *preferential loss* of residual bis(toluene)molybdenum. There is also a simultaneous but less rapid decrease in the intensity of the 418-nm band. A subsequent experiment established that the $(C_6H_5CH_3)_2Mo$ complex gradually sublimes from the DC 200 film at 290 K ($\sim 10^{-5}$ torr). *This metal vapor experiment suggests the possibility of generating and separating the thermally unstable reaction product from the starting sandwich complex by preferential sublimation* and hence provides an opportunity for obtaining a stable product for a detailed spectroscopic and/or X-ray study on this fascinating class of (arene)metal cluster complexes. Hopefully this goal will be achieved in the near future. Interestingly, the polymer medium seems to impede the thermally activated decomposition of the species responsible for the 418-nm absorption. Reasoning from the results of our studies of vanadium and chromium, we suggest that a molybdenum dimer is the likely candidate for the origin of this band. We have carried out a molybdenum/benzene concentration study and a kinetic analysis of the type described earlier.[18] A plot of log (A_{418}/A_{320}) vs. log R_0 for the species absorbing at 320 and 418 nm gave a straight line with a slope of 0.95, implicating a molybdenum dimer as the carrier of the 418-nm absorption.

In the Mo/DC200/$(CH_3C_6H_5)_2Mo$ thin-film experiments there was never any evidence for additional absorption(s) to the red of the 418-nm transition analogous to that observed under high Mo loadings in reactions of Mo with the α,ω-diphenyloligo(ethylene oxides) or to those observed in reactions with the DC 510 polymer. An interpretation of this observation is presented later in the paper.

EPR Experiments. A series of microscale EPR experiments on the V/DC 510 system indicated only the eight-line hyperfine spectrum due to the polymer-supported DC 510/(arene)$_2$V;[20] careful examination under various conditions of vanadium loading and temperature (293–12 K) disclosed only that the bis(arene)vanadium complex was EPR active under our conditions. The same behavior was found in this study when V was deposited into 1,10-diphenylhexaethylene glycol or cocondensed with benzene at 77 K at high V atom concentrations. Moreover, when Cr atoms were deposited into bis(toluene)chromium (EPR silent) dissolved in DC 200 (250 K microscale) no EPR signal developed. In the reverse reaction, Cr atoms were deposited into bis(toluene)vanadium dissolved in DC 200. The eight-line spectrum decreased in intensity with the amount of deposited chromium, showing that reaction had occurred, but there was no evidence of a new EPR signal either at 250 or 12 K.

IR and Raman Experiments. The room-temperature infrared spectrum of DC 510-bound bis(arene)chromium is reported to show absorptions at 488 (ν(MR)) and 458 cm^{-1} (asymmetric ring tilt).[3] This spectrum is characteristic of a neat thin film of the polymer prepared by the rotary-resistive metal vapor method. The UV–visible absorption spectrum of the same polymer is free of bands to low energy beyond 395 nm. Bis(benzene)chromium exhibits absorptions at 492 (A_{2u} ν(MR)) and 459 cm^{-1} (E_{1u} asymmetric ring tilt) in KBr. In our own experiments we were unable to detect the IR absorptions at 488 and 458 cm^{-1} in DC 510/Cr because the low-energy region is congested with polymer absorptions that obscure the 400–500-cm^{-1} window. A band has however, been detected at 432 cm^{-1} in Santovac 5/Cr (a liquid pentaphenyl ether) prepared in situ in a microscale IR experiment. Similarly the metal–ring modes of DC 510/V expected in this region are obliterated by the polymer absorptions. In contrast the low-frequency Raman bands of the metal atom free polymer, although rather broad, are few in number and occur at 490 cm^{-1} (polarized) and 180 cm^{-1} (depolarized). Since the Raman experiment can provide evidence of a symmetric M–M stretching mode[21] in a dimeric species of the type we have postulated, a series of matrix isolation and microsolution Raman experiments was initiated.

Depicted in Figure 9 is the Raman spectrum resulting from depositing Cr atoms into DC 510 at 240 K. The spectrum was recorded of the sample cooled to 100 K, under conditions of low Cr loading such that only the bis(arene)chromium complex is presumably present. The upper and lower traces respectively show the perpendicular and parallel polarizations. The symmetric metal ring stretching mode can be assigned with some certainty to the band at 290 cm^{-1} on the basis of the A_{1g} (polarized) vibration observed at 277 cm^{-1} in $(C_6H_6)_2Cr$.[22] The remaining bands arising at 350, 424, and 452 cm^{-1} for this polymer-supported complex are assigned on the basis of analogous modes that occur at 335 cm^{-1} (E_{1g} (symmetric tilt)) and 459 cm^{-1} (E_{1u} (asymmetric tilt), IR active), in the more symmetric bis(benzene)chromium complex. The ν(MR) that occurs at 490 cm^{-1} in the infrared spectra of both the polymer-bound sandwich complex and the (A_{2u}) bis(η^6-benzene)chromium complex is quite possibly obscured by the intense 490-cm^{-1} polymer band. The $\nu(MR_2)$ assignment at

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(20) Andrews, M. P.; Mattar, S. M.; Ozin, G. A. *J. Phys. Chem.* **1986**, *90*, 1037.

(21) Shriver, D. F.; Cooper C. V., III. *Adv. Infrared Raman Spectrosc.* **1980**, *6*, 127.

(22) Fritz, H. P. *Adv. Organomet. Chem.* **1964**, *1*, 239.

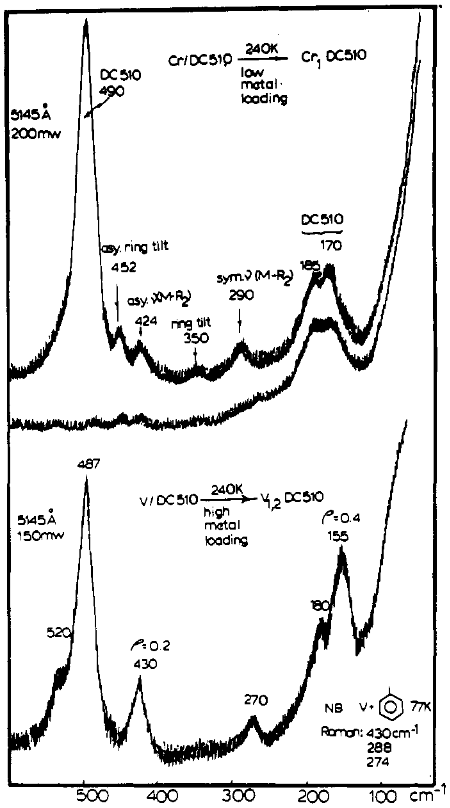
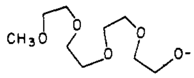
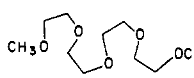
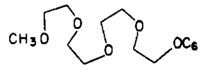


Figure 9. Raman spectra representing the outcome of metal atom titrations into the DC 510 polymer and matrix-isolation reactions with toluene/vanadium. The upper trace (recorded at 100 K, products prepared from reaction with Cr atoms at 240 K) shows Raman-active modes (polarized) of polymer-supported (arene)$_2$Cr. The bottom trace shows the outcome of depositing 3 × 10^{-3} mmol of vanadium at 1.6 × 10^{-3} mmol h^{-1} into 240 K DC 510. Recorded at 100 K, the spectrum shows a band at 155 cm^{-1} (strongly polarized), which is assigned to the vanadium dimer and is not found in the Raman spectrum of bis(toluene)vanadium (details inserted).

424 cm^{-1} in the Cr/DC 510 spectrum is tentative.

When vanadium is deposited at 1.6 × 10^{-3} mmol h^{-1} into DC 510 at 240 K to a total loading of 3 × 10^{-3} mmol of vanadium, a transparent deep yellow-gold product develops. Under these deposition conditions the vanadium dimer species is expected to form readily. New Raman bands at 520, 430, 270, and 155 cm^{-1} appear, all of which are polarized by comparison with the depolarized 180-cm^{-1} polymer reference line (Figure 9). The bands at 520, 430, and 270 cm^{-1}, by analogy with the vibrational spectrum of $(C_6H_6)_2V$ and other discrete bis(arene)metal sandwich complexes,[22] are assigned to M–arene ring deformation and stretching modes. The band at 155 cm^{-1} has no counterpart in bis(arene)vanadium generated in situ in a V/toluene 77 K matrix or in reactions of V with DC 510 under mononuclear metal atom conditions and therefore may be characteristic of the polymer-supported divanadium species. Low-frequency Raman spectra of other M–M-bonded dimer and cluster complexes range typically from 100 to 425 cm^{-1}, depending on the multiplicity of the bonding and the nature of the bonding interactions with associated ligands.[21] Within a given class of dimers the stretching frequencies can be spread over a broad range. Thus the formally quadruply bonded Mo–Mo dimers exhibit vibrational frequencies from 339 to 413 cm^{-1}, although the range of Mo–Mo internuclear distances is rather small (2.05–2.13 Å). These observations should be contrasted with those of analogous dirhenium complexes. These compounds show a very narrow range of stretching frequencies, 272–293 cm^{-1}. It is still largely a matter of conjecture whether the stretching frequencies reflect trends in metal–metal bonding or the influence of coupling of the symmetric metal–metal stretching mode to M–ligand displacement coordinates. Thus the Raman band we have observed at 155 cm^{-1} (polarized) in the high-loading V/DC 510 system may be associated with the symmetric V–V stretching mode coupled with the arene ligands of DC 510.

Table II. Reactivity of Transition Metal Atomic Vapors toward Liquid Polymeric and Oligomeric Materials[a]

1. DC 510 + M(g) ^1H NMR—only a multiplet for the bis(arene)metal complex at δ 5.39 (Ti), 4.85 (Mo), 4.59 (Cr); infrared shows no Si–O–M for M = Ti, V, Cr, Mo
2. DC 510 + Ti(g) (DC 510)[(arene)$_2$Ti] $\xrightarrow{O_2}$ TiO_2 + DC 510 GPC=> shows molecular weight unchanged[27]
3. DC 200 (poly(dimethylsiloxane)) or paraffin oil + M(g) → colloidal metal
4.  + Cr(g) → Cr(III) alkoxide
+ V(g) → no reaction (microscale only)
5.  + M(g) → colloidal metal
6.  + M(g) → (arene)2M complex see 1 above, NMR data
7. $C_{10}H_{21}OCH_3 + Cr(g) \xrightarrow[(2)\ \Delta]{(1)\ 77\ K\ \text{cocondense}} C_{10}H_{21}OCH_3 + Cr(colloid)$ ref 24

[a] For a list of solvents that are "inert" toward metal atoms under normal synthetic conditions see: Blackborrow, J.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer-Verlag: New York, 1979.

Reactions of Organic and Inorganic Molecules with Metal Vapors. Relevance to Metal Atom Multimerization in Arene-Containing Media. There have been a number of applications of metal vapors to effect functional group transformations of molecules. These applications include (i) the radical reduction of cyclohexanone to [1,1′-bicyclohexyl]-1,1′-diol by early-transition-metal atoms and clusters[23] and (ii) deoxygenation and desulfurization[24] of a host of organic compounds. With the observation that the deposition of nickel[25] or zirconium[26] vapor into various organic matrices can result in cleavage of the organic species, an explanation of the red-shifted bands seen in absorption for the M/DC 510 and M/arene reactions must include reference to the possibility that metal atom induced fragmentation reactions leading to organometallic species might be responsible for the additional absorptions.

We have examined this latter possibility by performing a series of control experiments on the same and related compounds, the results of which are summarized in Table II. Except for the NMR experiments, the conversion of Ti/DC 510 to TiO_2 and analysis of the liberated DC 510 by gel permeation chromatography (GPC),[27] all reactions could be carried out as both microsolution or gram-scale rotary reactor preparations. In general, we found that silyl ethers and alkyl ethers are unreactive toward the metal atoms examined. A similar conclusion regarding alkyl ethers was reached by Gladysz.[24] Titanium atoms, which are particularly oxophilic,[23,24] showed no tendency to cleave the backbone SiO linkages of the DC 510 chain (GPC) under the usual rotary reactor metal vapor conditions (reaction 2). Depositions of Ti, Cr, and Mo into DC 510 gave room-temperature ^1H NMR multiplets only of the respective bis(arene)M products at δ 5.39 (Ti), 4.59 (Cr), and 4.85 (Mo) in agreement with previous observations.[3] There was no evidence of a band in the infrared region 910–930 cm^{-1}, diagnostic of an Si–O–Ti linkage,[28] in agreement with the GPC analysis. Negative IR evidence regarding Si–O–M resulted also

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(23) Miller, J. T.; DeKock, C. W. *J. Org. Chem.* **1981**, *46*, 516.
(24) Togashi, S.; Fulcher, J. G.; Cho, B. R.; Hasegawa, M.; Gladysz, J. A. *J. Org. Chem.* **1980**, *45*, 3044 and references therein.
(25) Matsuo, K.; Klabunde, K. J. *J. Org. Chem.* **1982**, *47*, 843. Klabunde, K. J.; Tanaka, Y. *J. Mol. Catal.* **1983**, *21*, 57.
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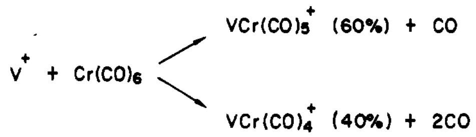
(28) Borisov, S. N.; Voronokov, M. G.; Lukevits, E. Ya. *Organosilicon Heteropolymers and Heterocompounds*; Plenum: New York, 1970.

for M = V, Cr, and Mo reactions with DC 510. As remarked upon earlier and described in ref 4–8, vaporization into poly(dimethylsiloxane) or paraffin oil resulted only in dispersions of colloidal metal (V,Cr,Mo). In the microsolution experiments involving vaporization into DC 200 there was no evidence of UV-visible absorptions of the type observed when the metals were deposited into the DC 510 polymer. The same results were obtained for reactions of the dimethyl ether of tetraethylene glycol with vanadium or chromium. By contrast, Cr atoms reacted with the acidic hydroxyl proton of the monomethyl ether of the aforementioned molecule to give a green product, which is probably the chromium alkoxide.[29] Unlike the $Cr^{III}(OMe)_3$ compound,[29a] this complex is soluble in THF. The infrared spectrum measured in mulls and KBr disks shows a strong band at 1053 cm^{-1} due to ν(C–O)M, and a band at 600 cm^{-1} (ν(M–O)).[29b] The electronic spectrum was measured in situ (microsolution) for depositions of Cr into the monomethyl ether at 260–290 K; however, no transitions due to the expected alkoxide product were observed under the experimental conditions (8×10^{-4} mmol of Cr; 7×10^{-4} mmol h^{-1}). A gray-green product was isolated from the reaction of Cr with the monomethyl ether in a rotary metal vapor reaction and gave an absorption spectrum that showed three transitions: an intense absorption at 43 500 cm^{-1}, and two much weaker bands at 24 000 and 17 240 cm^{-1}. This absorption pattern is similar to that of known chromium(III) alkoxides,[29a] for example $Cr(OCH_3)_3$ (E_1 = 47 200 cm^{-1} (charge transfer); E_2 = 24 200 cm^{-1}; E_3 = 17 000 cm^{-1}). Depositions of vanadium atoms into the monomethyl ether at room temperature (2.8×10^{-3} mmol of V at 2×10^{-3} mmol h^{-1}), or poly(ethylene oxide diol) (average mol wt 400) (1.7 mmol of V; 2×10^{-3} mmol h^{-1}) gave no EPR signal, although a resonance may be expected.[29b]

Gladysz has demonstrated[24] that decyl methyl ether does not react with chromium atoms on warming the 77 K cocondensate to room temperature. In fact, it is the relative inertness of ether and alkane compounds under most metal vapor synthetic conditions that makes them desirable solvents for metal atom reactions. Insertion products of the type described in Klabunde[25] and Webb et al.[30] appear most likely to occur on the surface of small metal aggregates, and the production and reactivity of these too are sensitive to the conditions of sample preparation. Our own experience has shown that *very rapid* electron-beam vaporization of vanadium in a 77 K cocondensation experiment involving toluene in hexane produces a highly reactive dispersion of colloidal metal in the frozen matrix, in addition to the bis(arene)vanadium complex, whose presence was inferred from the color of the codeposit. On meltdown in vacuo, rapid bubbling was observed and the bis(toluene)vanadium that had probably formed on deposition was completely destroyed. Bibenzyl was separated as one of the products of this reaction. The remaining products appeared to be a complex series of aryl-substituted alkanes and olefins from the proton NMR.

In conclusion we regard it as unlikely that organometallic fragments resulting from cleavage of alkyl or ether bonds are responsible for the trends in the optical spectra observed in reactions of transition-metal atoms with the arene containing systems presented in this paper and earlier reports.

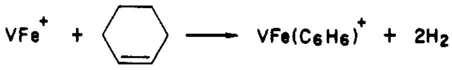
Mass Spectral Detection of Organometallic Metal Dimers and Heterodimers and Higher Multimers. Support for the existence of compounds formulated as $(C_6H_6)_2M_2$ comes from the gas-phase ion–molecule reactions involving $C_6H_6Cr(CO)_3$ reported by Gilbert et al.[17] In Gilbert's MS experiments the existence of $[(C_6H_6)_2Cr_2]^+$ was established. This dimer species is isoelectronic with our proposed $(C_6H_6)_2VCr$ heterodimer. The same heterodimer, ligated with CO, has been synthesized in the gas phase by pulsed-laser volatilization and source ionization of vanadium in the reaction[31]



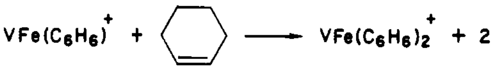
$$V^+ + Cr(CO)_6 \rightarrow VCr(CO)_5^+ \ (60\%) + CO$$
$$V^+ + Cr(CO)_6 \rightarrow VCr(CO)_4^+ \ (40\%) + 2CO$$

We note in addition that the heterodimer, $MnCr(CO)_6^+$ (80% yield), is isoelectronic with our proposed $(arene)_2Cr_2$ compound. The above ion–molecule reaction between V^+ and $Cr(CO)_6$ is particularly significant because the observed products are the result of a first-step direct addition of the metal cation to a metal center in $Cr(CO)_6$, a process in line with our proposed view of direct addition of a metal atom to a preformed bis(arene)metal site.[19]

In this context, two other very recent gas-phase studies are worthy of mention. First, Hettich and Freiser[32] have shown that gaseous VFe^+ (isoelectronic with Cr_2) rapidly dehydrogenates cyclohexene according to



forming $VFe(C_6H_6)^+$ containing a metal–metal bond. In a secondary reaction this species dehydrogenates another molecule of cyclohexene to give a 45% yield of $VFe(C_6H_6)_2^+$ through the reaction



A bis(benzene)dimetal structure similar to that of our proposed $M_2(arene)_2$ clusters was suggested for $VFe(C_6H_6)_2^+$. Second, recent gas-phase studies of Whetten et al.[33] have revealed that a beam of Pt_n clusters react with benzene to form dibenzene adducts of the form $Pt_n(C_6H_6)_2$, where n = 2–6. No structural information was reported in these studies although the stoichiometric resemblance to our proposed $M_n(arene)_m$ clusters is striking.

Summary

In earlier studies from this laboratory, single metal atoms have been found to react with one or two benzene rings in rare-gas matrices to form the respective half-sandwich $(\eta^6\text{-}C_6H_6)M$ or bis(benzene)metal complex $(\eta^6\text{-}C_6H_6)_2M$, depending on the relative concentrations of the various components.[34] At higher metal atom concentrations, matrix kinetic studies have revealed the existence of $(C_6H_6)_nM_2$ for M = V, Cr, and Mo where n may be 2.[4–7,18] With the use of a poly(dimethylsiloxane-*co*-methylphenylsiloxane) liquid, the metal concentration dependence of the changes in the absorption spectrum of the products has been followed near room temperature. These studies were made possible by the development of an in situ microscale metal vapor spectroscopic technique, which provided controlled conditions under which we probed the outcome of metal vapor liquid and solution phase reactions.[9] The technique was shown to form a natural bridge between matrix isolation and macroscale spectroscopic and synthetic methods.[4] For example, at sufficiently high loadings of vanadium atoms in DC 510, a new band appeared at 455 nm, which showed a concentration dependence independent of that shown by the polymer-supported bis(arene)vanadium complex.[4,5] Similar results were obtained for Ti, Cr, and Mo.[4–8] A synthetic strategy was worked out in which it was shown that the only condition necessary for the occurrence of the new species was the presence of arene ligands. Thus, the outcome of metal atom deposition into low-temperature, methylcyclohexane solutions of $(arene)_2M$, (M = Cr, V), suggested that a metal dimer species forms by direct addition of the atom to a preformed parent $(arene)_2M$ complex. The arene stoichiometry suggested was two.[19]

In the present study, some further insight into the mode of stabilization of metal clusters in the DC 510 system is obtained from similar studies involving different phenyl-substituted mo-

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(30) Reid, A. H., Jr.; Shevlin, P. B.; Yun, S. S.; Webb, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 709.

(31) Kappes, M. M.; Staley, R. H. *J. Chem. Phys.* **1982**, *86*, 1332.

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nomers and oligomers in metal vapor reactions surveying a thermal gradient varying from 12 to 300 K. In the context of the M_n/DC 510 work, a series of control experiments were performed which demonstrated that metal atoms are unreactive toward substituents (ether linkages, Si–O, C–H, etc.) other than the arene. In addition an experiment was designed which demonstrated that molybdenum atoms can be used to quantitatively titrate (arene)$_2$Mo dissolved in an unreactive liquid polymer, exemplified by poly(dimethylsiloxane), DC 200. The product in DC 200 absorbed at 418 nm, identical in position with the Mo/DC 510 concentration-dependent absorption, thereby providing further credence for the binuclear formulation (arene)$_n$Mo$_2$.

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Registry No. $HO(CH_2CH_2O)_6H$, 2615-15-8; $HO(CH_2CH_2O)_2H$, 111-46-6; $BrCH_2CH_2OCH_2CH_2Br$, 5414-19-7; $TsO(CH_2CH_2O)_6Ts$, 42749-27-9; TsCl, 98-59-9; $C_6H_5O(CH_2CH_2O)_6C_6H_5$, 20740-88-9; C_6H_5OH, 108-95-2; $C_6H_5O(CH_2CH_2O)_4C_6H_5$, 20768-77-8; $C_6H_5O(CH_2CH_2O)_5C_6H_5$, 20612-83-3; $CH_3C_6H_4O(CH_2CH_2O)_7C_6H_4CH_3$, 102073-92-7; $C_6H_5O(CH_2CH_2O)_7C_6H_5$, 20740-89-0; CH_3-*p*-$C_6H_4(CH_2)_{10}C_6H_4$-*p*-CH_3, 102073-91-6; *p*-$BrC_6H_4CH_3$, 106-38-7; $Br(CH_2)_{10}Br$, 4101-68-2; $CH_3O(CH_2CH_2O)_4Ts$, 62921-76-0; $CH_3O(CH_2CH_2O)_4C_6H_5$, 80392-31-0; V, 7440-62-2; Cr, 7440-47-3; Mo, 7439-98-7; $CH_3O(CH_2CH_2O)_4H$, 23783-42-8; $CH_3O(CH_2CH_2O)_4CH_3$, 143-24-8; $C_{10}H_{21}OCH_3$, 7289-52-3; Santovac-5, 2455-71-2; 1,3-diphenylbutane, 1083-56-3; phenyldecane, 104-72-3; benzene, 71-43-2; toluene, 108-88-3.

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Bis(nitroxyl) Adducts of Bis(hexafluoroacetylacetonato)manganese(II). Preparation, Structures, and Magnetic Properties

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Adducts of bis(hexafluoroacetylacetonato)manganese(II) with the cyclic nitroxyl radicals 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) and 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (proxyl) have been prepared. Both products are bis adducts, $Mn(F_6acac)_2L_2$ (L = tempo, proxyl), and have been shown by crystal structure analyses to have centrosymmetric trans octahedral structures. In each case, the metal ion is bound to two chelating F_6acac ligands and two monodentate nitroxyls, with Mn–O distances ranging from 2.12 to 2.16 Å. The configurations of the metal-bound nitroxyls closely resemble those of analogous uncoordinated radicals. Magnetic susceptibility measurements (6–300 K) are consistent with an $S = {}^3/_2$ ground state for both complexes, with a significant population at higher temperatures of one or more states of greater multiplicity. The susceptibility data are well-represented by a spin-only (${}^1/_2$–${}^5/_2$–${}^1/_2$) interaction model, with J(Mn–nitroxyl) values of −79 (tempo adduct) and −105 cm^{-1} (proxyl adduct). Both adducts crystallize in the monoclinic space group $P2_1/c$ with $Z = 2$. For the tempo adduct $[Mn(C_5HF_6O_2)_2(C_9H_{18}NO)_2]$, $a = 10.698$ (5) Å, $b = 14.715$ (6) Å, $c = 12.378$ (5) Å, and $\beta = 113.48$ (3)°. For the proxyl adduct $[Mn(C_5HF_6O_2)_2(C_8H_{16}NO)_2]$, $a = 10.472$ (2) Å, $b = 14.488$ (4) Å, $c = 12.090$ (2) Å, and $\beta = 111.08$ (2)°.

Introduction

Complexes in which a transition metal center is coordinated to a nitroxyl radical function have been the subjects of considerable recent interest in our laboratory and elsewhere.[1-14] One of the motivations for the study of these compounds is the potential they give for the investigation of interactions between the free spins on the nitroxyl radical and on a paramagnetic metal center. Compounds prepared and characterized to date have shown interactions spanning a wide range of magnitudes. Strong interactions, characterized by room-temperature diamagnetism, have been found in a series of five-coordinate copper(II) complexes with short metal–nitroxyl distances.[4,8,12,15] Very weak couplings, with no measurable effect on magnetic behavior at ordinary temperatures, have also been observed.[3,5,10,13,14] The intermediate coupling regime, in which room-temperature magnetic susceptibility is determined by a distribution over more than one spin state, has had the fewest well-characterized examples. A series of cobalt(II) halide complexes of di-*tert*-butyl nitroxide appear to fall into this category, but quantitative interpretation of their magnetic properties has been hampered by instability.[7,11]

We now wish to report the preparation, crystal structures, and magnetic properties of a pair of bis(nitroxyl) adducts of Mn(II), which, in addition to providing the best characterized cases of metal–nitroxyl coupling in the intermediate range, are the first reported systems in which two nitroxyl radicals are coordinated to a single metal ion.

Experimental Section

Synthesis. $Mn(F_6acac)_2$ was prepared from the metal acetate by a standard procedure.[16] The 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) ligand was used as purchased from Aldrich Chemicals. The ligand 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (proxyl) was synthesized from the corresponding crude hydroxylamine[17-19] by air oxidation in aqueous

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