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The Metal Vapor–Fluid Matrix Technique for the Formation of Polymer-Supported Molybdenum and Molybdenum/Titanium Cluster Species

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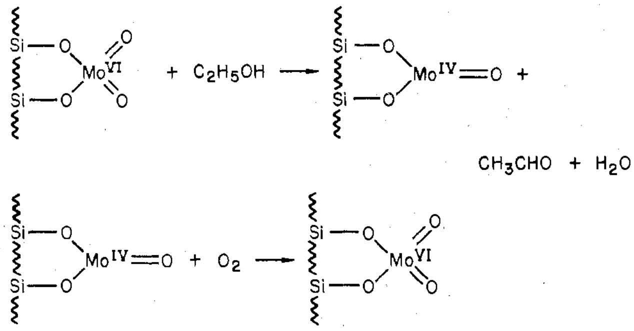
Problems in the fields of chemisorption and heterogeneous catalysis have acted as an incentive for experimental research in the field of small, well-defined metal clusters. We have set out to devise a method for the generation and spectroscopic investigation of such clusters close to room temperature, the final goal being the stabilization of these species on a support. This report demonstrates that very low-nuclearity unimetallic and bimetallic clusters can be efficiently anchored to a liquid poly(methylphenylsiloxane) (DC510) by designed manipulation of metal atom diffusion/aggregation/immobilization processes within a thin viscous film of the polymer, held on a cooled spectroscopic window. The experimental parameters which appear to control cluster size, optimize reaction efficiency, and help maintain homogeneous conditions are investigated. By use of these experimental data, a macrosynthetic metal vapor reaction was undertaken to obtain the unimetallic clusters in quantities suitable for further catalytic investigation. Ultraviolet–visible spectroscopic methods for quantitatively monitoring these metal vapor–liquid polymer reactions and for characterizing reaction intermediates and products are also described.

Introduction

The use of molybdenum compounds as active catalysts in olefin metathesis reactions[1] and the role of molybdenum in the reduction of nitrogen[2] have both been widely studied. In a recent report,[3] a molybdenum-fixed catalyst was shown to possess a high degree of activity and selectivity in the oxidation of ethanol, the reaction proceeding via a two-stage redox mechanism:



Similarly, high-surface-area materials consisting of molybdenum metal and MoO_2 have been found to possess high catalytic activity and selectivity for the isomerization of *n*-hexane to 2- and 3-methylpentane.[4] However, as far as we are aware, very little is known about the catalytic properties of finely divided molybdenum metal.

By their very nature, highly dispersed metal catalysts are difficult to understand at an atomic level, but it has become evident that a detailed knowledge of both the molecular and electronic properties, as well as chemical reactivity, of very small naked metal clusters, as a function of nuclearity and geometry, can provide useful information relating to chemisorption and surface chemical reactions occurring on supported or unsupported metal particle catalysts.

Two techniques have mainly been used to form small, well-defined, matrix-isolated ligand-free metal clusters, both of which involve initially the cocondensation of metal vapor with a weakly interacting support such as argon, at 10–12 K. The methods basically involve (i) use of a low M:Ar concentration ratio (typically $1{:}10^4$) to ensure efficient trapping of metal atoms, followed by either controlled annealing of the matrix[5] or cryophotoclustering[6] to give oligonuclear clusters, and (ii) use of a higher M:Ar ratio (typically $1{:}(10^2{-}10^3)$), which leads to the formation of dimers and trimers in the surface regions during deposition before the matrix becomes quenched.[7] Typical results of the deposition and photoaggregation routes to obtain small molybdenum clusters such as Mo_2 and Mo_3 in Ar are depicted in Figure 1.

Although such clusters trapped at 10–12 K provide spectroscopic information which is of interest in conjunction with various molecular orbital computational techniques,[8] the ultimate aim must be to find ways of stabilizing these species at higher temperatures and to devise a method for investigating their catalytic properties either by transferring them to a support such as alumina or silica or by investigating them in the trapping medium itself. With this in mind we have previously investigated low-molecular-weight acyclic and cyclic alkanes (C_1 to C_{10}),[27] high-molecular-weight paraffin waxes (C_{22} to C_{32}), and polar matrices such as ice[28] with little success. Cocondensation on a macroscale of metal vapor and a matrix material (e.g., toluene, pentane, or tetrahydrofuran) at low temperatures (typically 77 K) followed by warming to room temperature has been used recently[9] to produce metal particles of Ni, Pd, Pt, or Ag, consisting of crystallites of diameter <100 Å. Alternatively, by allowing the cocondensate to melt and permeate a support material such as Al_2O_3 or SiO_2, one obtains supported nickel particles with crystallite size in the range 30–80 Å.[10] In the case of the Ni particles, the supported and unsupported samples were found to possess catalytic activity for various hydrogenation, disproportionation, or isomerization reactions.

We are interested, however, in attempting the preparation of much lower nuclearity metal clusters using a different trapping method and growth medium in an effort to control the rapid oligomerization process occurring immediately succeeding metal vapor deposition.

In a continuing quest to secure supported, few-atom aggregates we have now conducted a study of polysiloxanes and polyethers as possible high-temperature fluid matrices in which to generate and stabilize both unimetallic and bimetallic clusters.

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(1) W. B. Hughes, *Adv. Chem. Ser.*, **No. 132**, 192 (1974).
(2) J. Chatt, J. R. Dilworth, and R. Richards, *Chem. Rev.*, **78**, 589 (1978).
(3) Y. Iwasawa, Y. Nakamo, and S. Ogasawara, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2968 (1978).
(4) R. Burch, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2991 (1978).
(5) D. W. Green and D. M. Gruen, *J. Chem. Phys.*, **60**, 1797 (1974).
(6) G. A. Ozin and W. Klotzbücher, *J. Mol. Catal.*, **3**, 195 (1977/78); H. Huber and G. A. Ozin, *Inorg. Chem.*, **17**, 155 (1978).
(7) W. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, **16**, 984 (1977).
(8) W. Klotzbücher, G. A. Ozin, J. G. Norman, Jr., and H. J. Kolari, *Inorg. Chem.*, **16**, 2871 (1977), and references therein.
(9) K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, **98**, 1021 (1976); B. A. Scott, personal communication.
(10) K. J. Klabunde, D. Ralston, R. Zoellner, H. Hattori, and Y. Tanaka, *J. Catal.*, **55**, 213 (1978).

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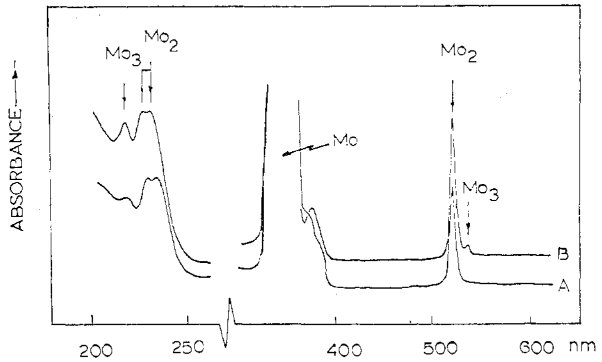


Figure 1. Ultraviolet–visible spectra of a Mo:Ar $\simeq$ 1:10^3 mixture (A) upon deposition at 10 – 12 K and (B) after photoexcitation into the 366-nm Mo atomic resonance absorption.[6-8]

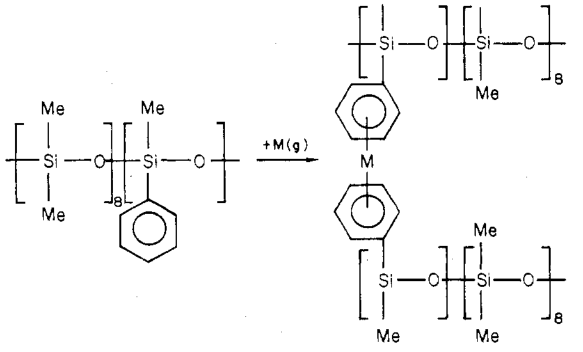
Experimental Section

Matrix-Scale Reactions. The metal vapor–fluid matrix technique has been described previously.[11] In a typical experiment, a thin film ($\sim 10^{-6}$ m) of a liquid is painted on an optical window (area $\sim 3 \times 10^{-4}$ m^2) of quartz or sodium chloride in a standard matrix isolation apparatus and the reaction chamber evacuated to a pressure suitable for the generation of metal vapors ($\lesssim 10^{-6}$ torr). The window is cooled by means of an Air Products Displex refrigeration system to a temperature at which the fluid possesses mobility and volatility suitable for carrying out a metal vapor reaction. For involatile liquids such as the poly(methylphenylsiloxane), Dow Corning 510 [viscosity 0.5 cm^2 s^{-1}, vapor pressure less than 10^{-3} torr at 290 K], this temperature is in the range 240–270 K. Molybdenum is evaporated from a filament and is deposited into the liquid film, typically at a rate of approximately 0.2 μmol h^{-1}, as measured by a quartz crystal microbalance in a calibrated furnace assembly. The formation of products is then followed by means of ultraviolet–visible spectroscopy.

Macroscale Reaction. Molybdenum (1 g, 10 mmol) is evaporated from a wire filament and condensed into 100 cm^3 of DC510 contained in a rotary solution reactor[12] at 250 K over a period of 2 h. The method differs from that of Francis and Timms[13] in the lowering of the temperature of the fluid during reaction from 270 to 250 K and the deposition of more metal into the fluid. The products are worked up by using standard Schlenk-type inert-atmosphere techniques, with the fluid maintained at 250 K during workup. A sample of the product is transferred under nitrogen to a cooled optical window (200 K) and the ultraviolet–visible spectrum measured.

Results and Discussion

It has been reported[13] that metal vapors of Ti, V, Cr, Mo, and W react with DC510, a poly(methylphenylsiloxane) with a Me:Ph ratio of 17:1 and a viscosity of 0.5 cm^{-2} s^{-1}, at 270 K in a metal vapor rotary reactor to give an organometallic polymer:



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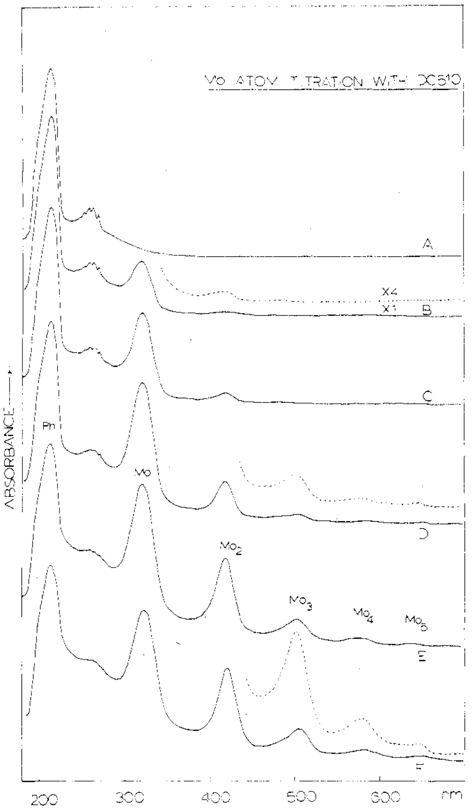

Figure 2. Ultraviolet–visible spectra of a thin film of DC510: (A) initial spectrum; (B–F) spectra with increasing loading of Mo vapor.

In the case of M = Mo, the product was a gold-brown liquid characterized by means of its ^{1}H NMR spectrum which showed a multiplet at δ 4.85 indicative of a bis(π-arene)molybdenum species.

When this system is investigated by using the fluid matrix technique at 250 K, the ultraviolet–visible spectrum consists of bands in the region 200–300 nm due to free phenyl groups in the DC510 plus a band at 318 nm (Figure 2B). By comparison with the reported optical spectrum of the bis(π-arene)molybdenum[13] and (π-C_6H_6)$_2$Mo,[14] the formation of this absorption is assigned to a metal-to-ligand charge-transfer transition of the polymer-anchored bis(arene)molybdenum species I where M = Mo.

On increase of the metal loading to roughly 10^{-8} mol, a new band at 418 nm begins to emerge (Figure 2C), and, as the concentration of molybdenum is progressively increased, further bands at 502, 578, and 640 nm become apparent, as shown in Figure 2D–F. 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.

Referring back to Figure 1, we see that the excitation energies of the species Mo_2 and Mo_3 in solid argon exhibit a red shift with increasing nuclearity. In the analogous Cr/DC510 reaction,[11] two bands were also observed at 402 and 479 nm in addition to that attributable to polymer-supported bis(arene)chromium. The energies for these transitions are close to the two higher energy bands in the Mo/DC510 spectrum (see Figure 4), a reasonable observation if the transitions are of similar origin, considering that the two metals have comparable valence orbital ionization potentials. The two bands described above in the Cr/DC510 system were assigned to metal-localized electronic excitations in polymer-stabilized (solvated) Cr_2 and Cr_3 species, respectively, by comparison

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(11) C. G. Francis, H. Huber and G. A. Ozin, *J. Am. Chem. Soc.*, **101**, 6250 (1979).

(12) R. Mackenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 650 (1974).

(13) C. G. Francis and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 466 (1977); *J. Chem. Soc., Dalton Trans.*, in press.

(14) L. F. Nazar and G. A. Ozin, unpublished results.

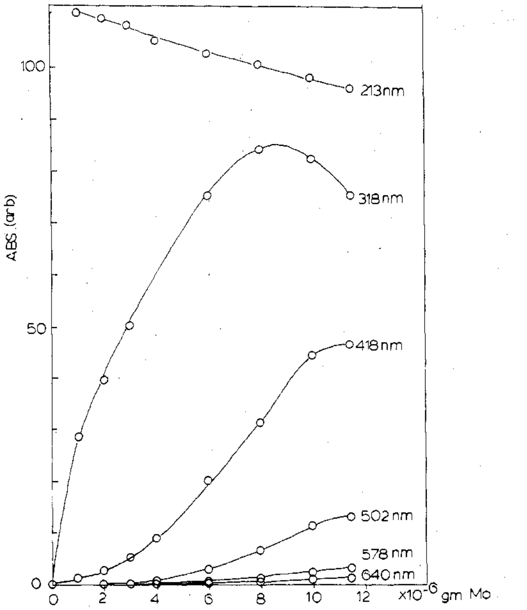


Figure 3. Graphical representation of a Mo/DC510 reaction at 250 K of the type shown in Figure 2.

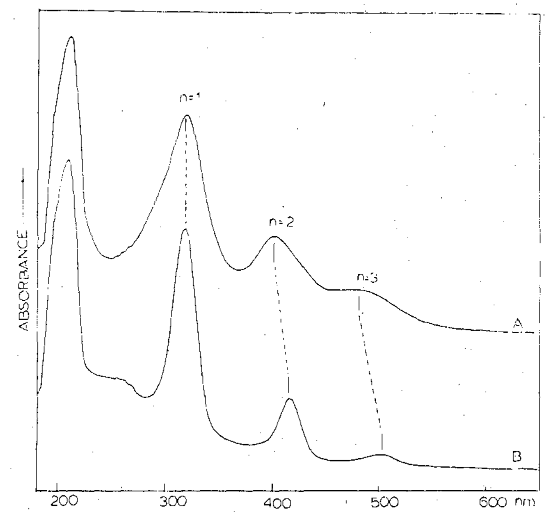


Figure 4. Ultraviolet–visible spectra of the products of (A) Cr/DC510 and (B) Mo/DC510 deposited at 250 K with metal loading up to the $n = 3$ stage (see text).

with the spectrum obtained from the cocondensation of chromium vapor with a mixture of C_6H_6/Ar at 14 K,[14] which showed bands to the low-energy side of the $(\pi\text{-}C_6H_6)_2Cr$ charge-transfer band, possessing a metal concentration dependence consistent with that expected for binuclear species.[15]

The most probable explanation of the bands in the visible region of the Mo/DC510 spectrum is that they are also associated with metal-localized excitations in small molybdenum clusters, with nuclearity in the range $n = 2$–5. A graph of the energies of these transitions as a function of the reciprocal of the suggested metal nuclearity (Figure 5) displays a monotonic correlation. The metal-to-ligand charge-transfer transition for anchored bis(arene)molybdenum lies off the line, indicating that it is of different origin. A recent ground-state SCF–Xα–SW molecular orbital calculation[16] for an assumed octahedral Mo_6 cluster enabled us to approximately predict the

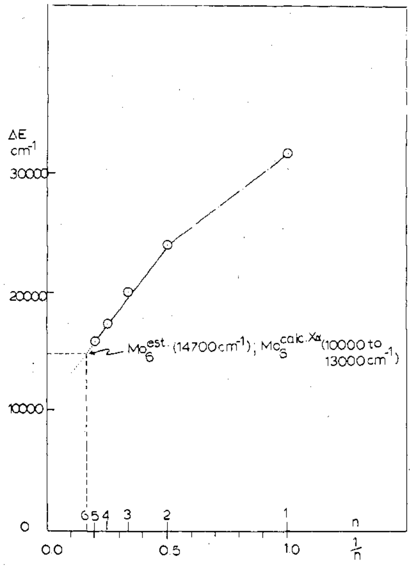
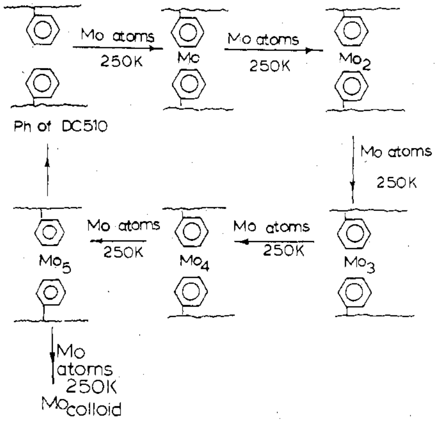


Figure 5. Graphical representation of the transition energies observed for the DC510-stabilized Mo_n species as a function of n^{-1} (see text for details).

Scheme I



HOMO–LUMO transition energy for Mo_6. This procedure gave a value of 10 000–13 000 cm^{-1}, whereas we estimated an extrapolated value of roughly 14 700 cm^{-1} from the graph depicted in Figure 5. The closeness of the two values provides support for our Mo_n ($n = 2$–5) assignments.[17]

With the observation that the deposition of nickel[9] or zirconium[18] vapor into various organic matrices results in cleavage of the organic species, another explanation could be that fragmentation of the polymer is leading to the formation of organometallic species which are giving rise to the additional absorptions. We do not think that this is occurring as a result of the observation that no such bands are formed by the deposition of metal vapors into a poly(methylsiloxane) or high-molecular-weight alkane.[19]

An interesting observation is that Cr/DC510 condensations are only able to stabilize a maximum nuclearity for a well-

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(15) J. Hulse and M. Moskovits, *J. Chem. Phys.*, **66**, 3988 (1977); *J. Chem. Soc., Faraday Trans. 2*, 471 (1977).

(16) G. Seifert, E. Mrosan, and H. Müller, *Phys. Status Solidi B*, **89**, 553 (1978).

(17) Using the metal vapor–polymer titration curves of the type illustrated in Figure 3, we have been able to estimate molar extinction coefficients for the mononuclear, binuclear, and trinuclear molybdenum-containing sites on the polymer: $\epsilon_{Mo_1} \approx 2.7 \times 10^5$, $\epsilon_{Mo_2} \approx 7.4 \times 10^4$, $\epsilon_{Mo_3} \approx 2.2 \times 10^4$ L mol^{-1} cm^{-1}. Note that the value for the polymer-supported bis(arene)molybdenum site is within a factor of 10 of the values reported for the metal-to-arene charge-transfer absorption (310–320 nm) of a series of (arene)chromium and (arene)molybdenum complexes.[22,29]

(18) R. J. Remick, T. A. Asunta, and P. S. Skell, *J. Am. Chem. Soc.*, **101**, 1320 (1979).

(19) C. G. Francis and G. A. Ozin, unpublished results.

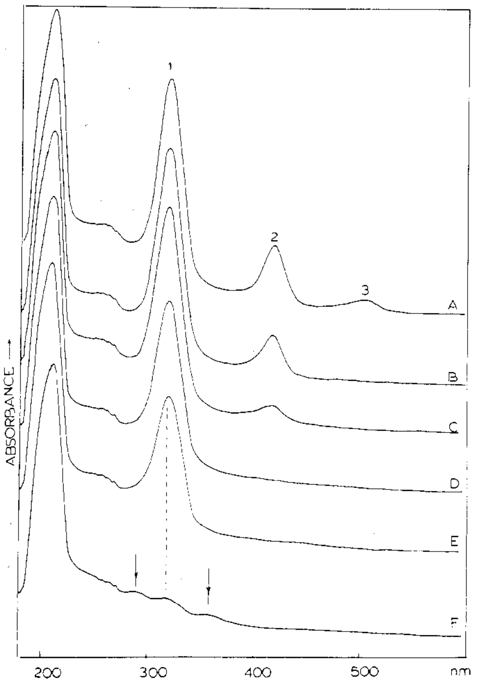


Figure 6. Ultraviolet–visible spectra of the Mo/DC510 reaction (A) loaded up to the $n = 3$ stage, (B) warmed to room temperature, and (C–F) controlled oxidation by 1 torr of O_2 at 290 K (arrows indicate polymer anchored bis(arene)molybdenum(I) cation species—see text).

defined cluster of $n = 3$, whereas with molybdenum an $n = 5$ cluster is formed. Two possible explanations can be put forward: first, that the rate of diffusion of the metal atom shows an inverse mass dependence so that the rate of nucleation to give colloidal metal is disfavored in the molybdenum reaction; second, that the strength of Mo–Mo bonds is expected to be much higher than for Cr–Cr bonds, as indicated by the gas-phase bond dissociation energies of Mo_2 and Cr_2, which are approximately 400 and 150 kJ mol^{-1}, respectively,[20] thereby permitting more extensive molybdenum cluster growth and entrapment.

We feel reasonably confident that our assignment of the new visible absorptions to small molybdenum clusters, in the range $n = 2$–5, is correct but the nature of the stabilization by the polysiloxane is not clear. A preliminary kinetic analysis of the reaction[21] confirms that the rates of formation of the species are consistent with a number of sequential processes (see Scheme I), but whether the clusters are stabilized by phenyl groups or solvated by lone pairs of electrons on the oxygen atoms in the polysiloxane backbone, or both, is not known at present. It is important to note that the poly(phenyl ether) Santovac 5, which has been used previously in metal vapor reactions,[13] also gives metal cluster formation with molybdenum vapor,[21] and the absorptions assigned to these clusters are unshifted compared with the polysiloxane case, so that it can be deduced that the environments for the cluster species are similar in both liquid polymeric media.

The polymer-stabilized molybdenum cluster species are thermally stable only below 290 K, and they decay rapidly on allowing a small amount of oxygen (1 torr) to diffuse into the fluid matrix at 290 K (Figure 6). In contrast, the polymer-anchored bis(arene)molybdenum species is oxidized only slowly, as is shown by the decrease in the band at 318 nm and the appearance of two new bands at 292 and 360 nm (Figure 6). By analogy with the spectrum of $[(\pi\text{-}C_6H_6)_2Cr^+][I^-]$[22] and

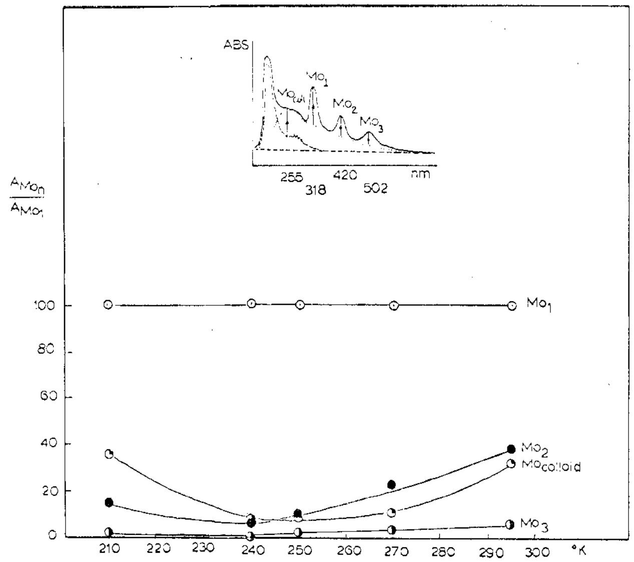
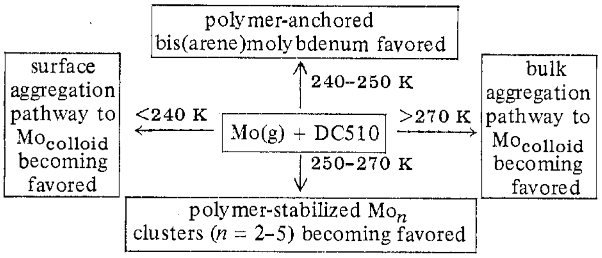


Figure 7. Graphical representation of reaction efficiency and product distribution as a function of the temperature of deposition of Mo vapor into DC510, recorded immediately after deposition.

Scheme II



$(arene)_2Cr^+$,[13] where arene ≡ phenyl group on DC510, this must be assigned to $(arene)_2Mo^+$, although $(\pi\text{-}C_6H_6)_2M$, where M = Mo or W, is usually considered as being converted to the cation only by strong oxidizing agents such as iodine.

Also, the polymer-anchored bis(arene)molybdenum is stable, and the molybdenum clusters show reasonable stability, when irradiated at all wavelengths in the range 230–700 nm at 240 K, behavior somewhat unlike that observed for molybdenum clusters in argon at 10–12 K, although irradiation at 290 K does lead to decay of the cluster species while the bis(arene)molybdenum remains unaffected.

Figure 7 shows a plot of product distribution in the Mo/DC510 reaction as a function of the temperature of deposition for identical metal vapor loadings. The graph represents the absorbance behavior of the three cluster products Mo_2, Mo_3, and $Mo_{colloid}$ normalized with respect to the bis(arene)molybdenum complex (Mo_1). It can be seen that formation of the bis (arene)molybdenum species is favored in the range 240–250 K, while formation of higher nuclearity species becomes more important at both higher and lower temperatures in the region 210–300 K. The origin of the $Mo_{colloid}$ absorption, however, appears to be different in the 210 and 300 K extremes, namely, rapid metal aggregation in the surface layers of the film at the lower temperature and colloidal metal formation within the film at the higher temperature (illustrated in Scheme II).

Considering the conditions for product formation, outlined in Scheme II, it is possible to carry out a metal vapor macroscale reaction in which molybdenum vapor is deposited into DC510 in a rotary solution reactor at 250 K to give a red-

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(20) S. K. Gupta, R. M. Atkins, and K. A. Gingerich, *Inorg. Chem.*, **17**, 3211 (1978).
(21) M. P. Andrews, C. G. Francis, and G. A. Ozin, unpublished results.
(22) R. D. Feltham, *J. Inorg. Nucl. Chem.*, **16**, 197 (1961).
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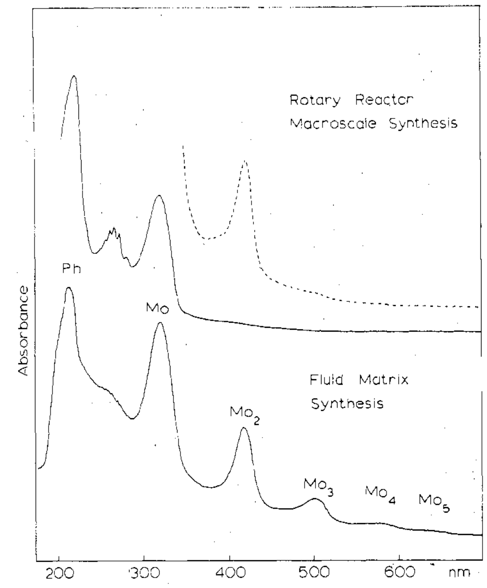

Figure 8. Ultraviolet-visible spectra of the Mo/DC510 reaction. Comparison of the products from the macrosynthetic and matrix-scale routes.

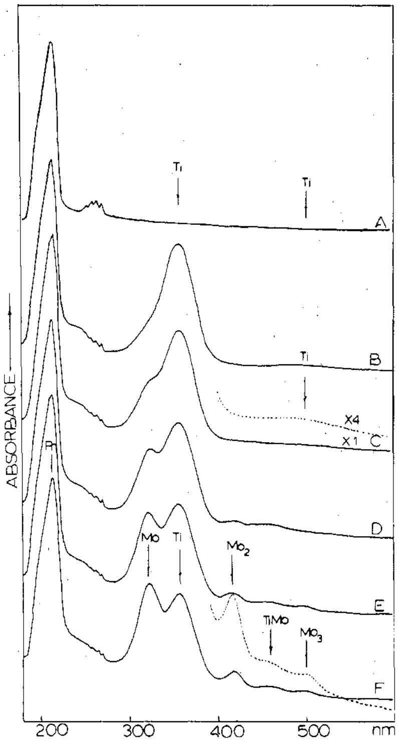

Figure 9. Ultraviolet-visible spectra of a thin film of DC510: (A) initial spectrum; (B) spectrum upon deposition of Ti vapor up to the saturation value; (C-F) spectra showing progressive Mo vapor deposition into the Ti/DC510 film (dotted lines indicate 4× scale expansion).

brown liquid. Manipulation of the fluid at 250 K under a nitrogen atmosphere allowed the ultraviolet-visible spectrum of the product to be obtained. This is shown in Figure 8 and indicates the presence of bis(arene)molybdenum as well as the Mo_2 and Mo_3 species.

With the increasing interest in high-dispersion, multicomponent metal catalysts,[24] we have also attempted to produce

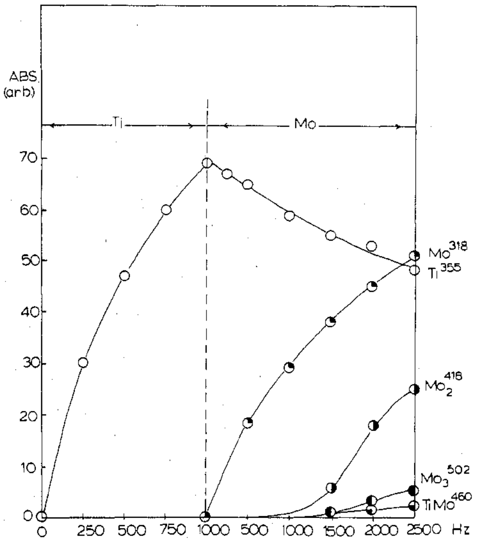

Figure 10. Graphical representation of a sequential Ti/Mo vapor deposition into DC510 of the type shown in Figure 9.

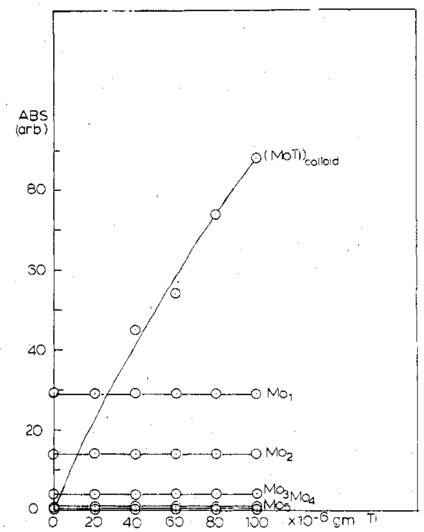

Figure 11. Graphical representation of the absorbance of the polymer-supported molybdenum species ($n = 1-5$) in a molybdenum-saturated DC510 film at 250 K as a function of Ti vapor loading.

bimetallic sites within the polysiloxane matrix. We have investigated both the Ti/Cr[11] and the Ti/Mo systems in DC510 so far. The spectra for the sequential deposition of Ti followed by Mo into DC510 are shown in Figure 9, the growth of the bands being plotted as a function of metal evaporated in Figure 10. Initially, as titanium vapor is deposited into the liquid polymer matrix at a rate of approximately 0.25 μmol h^{-1}, formation of supported bis(arene)titanium is observed, as shown by the appearance of an absorption at 355 nm.[13] As deposition progresses, the concentration of supported $(arene)_2Ti$ increases until all of the phenyl groups suitable for coordination to metal to give bis(arene)titanium are complexed. Molybdenum vapor is then deposited at a similar rate, and the 318-nm band due to supported bis(arene)molybdenum appears (Figure 9C). On an increase in the molybdenum loading to approximately 10^{-4} mmol, three bands begin to grow in at 418 nm (Mo_2), 502 nm (Mo_3), and 460 nm. The last band is not present in either of the individual spectra and so must be associated with a polymer-stabilized TiMo cluster species. The fact that it appears between the bands due to Mo_2 (418 nm) and Ti_2 (590 nm (br)) supports the assignment and metal-localized nature of the transition, since one would expect to see an average environment effect for the visible

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(24) J. H. Sinfelt, Y. L. Lam, J. A. Cusumano, and A. E. Barnett, *J. Catal.*, **42**, 227 (1976), and references therein.

transition energies of the heteronuclear cluster, as is observed in Ti/Cr/DC510,[11] in Cr/Mo/Ar,[8] and also in a wide range of heterobinuclear metal carbonyl cluster complexes.[25]

While these species are growing, the bis(arene)titanium is decaying, as is indicated by the decrease of the 355-nm band (Figure 10). Although the decrease may be rationalized in terms of the reaction Mo + $(arene)_2Ti \rightarrow (arene)_2TiMo$, it is possible that the presence of excess molybdenum brings about the autocatalytic decomposition of $(arene)_2Ti$, by analogy with the effect of excess titanium on $(\pi\text{-}C_6H_6)_2Ti$.[26] That the reverse process does not occur can be seen from the invariance of the absorptions of the polymer-supported molybdenum species (n = 1–5) when titanium vapor is allowed to react at 250 K with a molybdenum-saturated DC510 polymer film (Figure 11) generated also at 250 K. The only observable effect is the monotonic growth of an absorption around 240 nm attributed to a bulklike optical resonance of a Ti_x or Ti_xMo_y cluster of colloidal dimensions.

Therefore it is possible to stabilize small unimetallic and bimetallic clusters at close to room temperature by means of a fluid polymer matrix. Furthermore, it is possible to modify the macroscale reactions of DC510 to allow the isolation of a polymer containing both the bis(arene)metal complex and cluster species. It is now our task to find a way to investigate the catalytic activity of these unique cluster species.

Acknowledgment. We wish to acknowledge the financial assistance of the Natural Sciences and Engineering Council of Canada, Imperial Oil, Erindale College, and Lash Miller Chemical Laboratories.

Registry No. Mo, 7439-98-7; Ti, 7440-32-6; DC510, 63148-53-8.

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[28] H. Huber, P. Mackenzie, and G. A. Ozin, *J. Am. Chem. Soc.*, in press.

[29] R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

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High-Pressure Mass Spectra and Gaseous Ion Chemistry of Metal β-Diketonates with Bulky Substituents

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Mass spectra at normal and elevated pressures are reported and interpreted for chelates of 2,2,6,6-tetramethyl-3,5-heptanedione anion with Cr(III), Fe(III), Co(II), Co(III), Ni(II), Cu(II), Zn(II), and Al(III). At the higher pressures in each case primary positive fragment ions undergo gaseous bimolecular reaction with the neutral mononuclear complexes to form heavier polynuclear positive ions usually with unfragmented ligands. These are analogous to those previously observed for chelates of sterically less hindered β-diketone ligands. Competing with the association reaction in most cases is charge transfer between fragment ions and the neutral complex. Although they are known to prevent intermolecular association in condensed phases, the *tert*-butyl groups on the present complexes are found to hinder, but not prevent, gaseous ion/neutral association in the tetrahedral and octahedral complexes. There is no significant hindrance for the planar complexes. The *tert*-butyl substituents tend also to enhance charge transfer. In the absence of steric hindrance and charge transfer, the tendency to undergo ion/neutral association follows the polarizability or basicity of the ligand. The tendency of the metal to maintain its preferred oxidation state determines which of the possible polynuclear ions will form. These heavy ions are considered to be Lewis acid/base complexes rather than van der Waals complexes.

Introduction

Previous studies of gaseous positive ion/neutral reactions of organometallic complexes have involved mainly metallocenes and their derivatives and have used the techniques of chemical ionization,[1] high-pressure mass spectrometry,[2,3] and ion cyclotron resonance spectrometry.[4–6]

Another class of complexes amenable to such studies consists of the metal acetylacetonates, which have been investigated in this laboratory by using high-pressure mass spectrometry. Reaction of the neutral monomeric vapor with its positive molecular and fragment ions was found to give high abundances of a variety of heavy, polynuclear ions at ion-source pressures up to 10^{-2} torr.[7] The observation of these product ions raises the need to elucidate their structure and to rationalize the preferential formation of certain such ions from certain precursors.

Neutral metal complexes of the conjugate base of 2,2,6,6-tetramethyl-3,5-heptanedione (thd^-)[8] are similar in molecular structure to those of acetylacetone and, because of their high volatility and thermal stability,[9,10] have been used in gas chromatography and chemical ionization[11] for analysis of metals. The low-pressure positive[12,13] and negative ion[14] mass

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