Synthetic Approaches to Macromolecules Containing the Bis(η^6-naphthalene)metal Moiety

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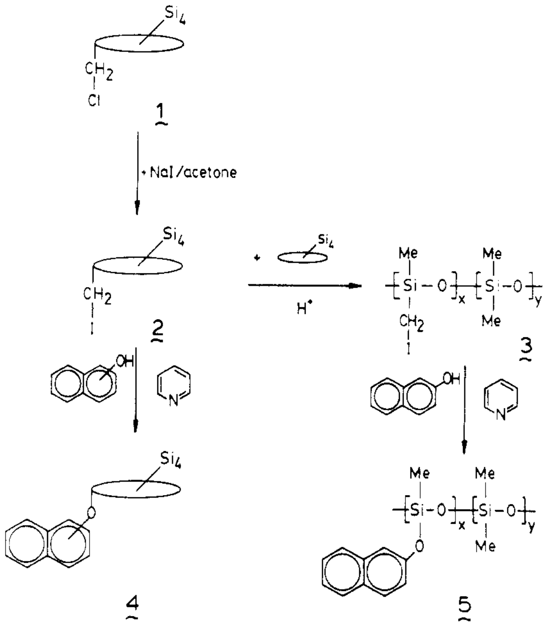
A poly[(dimethylsiloxane)-*co*-(2-naphthoxymethylsiloxane)], **5**, has been synthesized from either (chloromethyl)heptamethylcyclotetrasiloxane (**1**) or poly(dimethylsiloxane). The synthetic procedures also permit the preparation of the corresponding 1- or 2-naphthoxyheptamethylcyclotetrasiloxane, **4** (**a** and **b**), starting from 1. These siloxanes react with Cr or V vapors to afford poly- or cyclosiloxane bound bis(η^6-naphthalene)metal complexes. In contrast, reaction with Ti leads to attack on the siloxane and no bis(arene) complex is observed. Using cyclosiloxane **4b** as a model for the polymer **5** in macroscale metal vapor reactions, it is found that chromium coordinates exclusively to the nonsubstituted ring. The chromium complexes of **4b** and **5** exhibit very similar ligand displacement chemistry although some differences from that of (η^6-$C_{10}H_8$)$_2$Cr are noted. Thus reaction with CO leads to the analogous (arene)Cr(CO)$_3$ complexes while RNC (R = *tert*-butyl or cyclohexyl) affords the corresponding Cr(CNR)$_6$ species.

Introduction

The inclusion of transition metals into polymers is a well-recognized way of introducing specific physicochemical properties within a macromolecular environment.[1] Interest in such metallopolymers as new electroconducting materials,[2] in the chemical modification of electrode surfaces[3] for photocatalytic and electrocatalytic purposes,[4,5] or as hybrid forms of catalyst[6] has resulted in the development of a number of routes for inclusion of the metal species.

One such approach, the metal vapor technique, has broadened appreciably the range of organometallic polymers amenable to synthesis,[7] particularly those in which the metal is in a low or (formally) zerovalent oxidation state. This unique synthetic entry has prompted us to turn our attention to the area of polymer-bound catalysts.[6] These materials often termed hybrid catalysts[8] are prepared normally via ligand exchange with a preformed complex,[9] although an attractive alternative is to construct a reactive organometallic center using organic groups within the polymer.[10] Combining the metal vapor method and the high reactivity of complexes containing polycyclic aromatic ligands, attributable to their ability to undergo facile haptotropic rearrangements,[11-13] we have designed and synthesized a new type of organometallic moiety within a polymer environment which exhibits an extensive reaction chemistry under mild conditions.

Scheme I



The polymer used in this study, a poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)], incorporates two important features—(i) naphthalene is known to react with metal vapors to form *highly reactive* bisarene complexes,[13-15] and (ii) polysiloxanes with $M_n \leq 100\,000$ are normally liquids, thereby facilitating the metal atom reaction *and*, of greatest ultimate significance, allowing soluble macromolecular metal complexes to be obtained. These

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[5] Grätzel, M., Ed. "Energy Resources through Photochemistry and Catalysis"; Academic Press: New York, 1983.

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[8] Grubbs, R. H. *CHEMTECH* **1977**, 512.

[9] See, for example: Allum, K. G.; Hancock, R. D.; Howell, I. V.; Pitkethly, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1975**, *87*, 189.

[10] See, for example: Bonds, W. D.; Brubaker, C. H.; Chandrasekaran, E. S.; Gibbons, C.; Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* **1975**, *97*, 2128. Verdet, L.; Stille, J. K. *Organometallics* **1982**, *1*, 380.

[11] Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396. Eden, Y.; Fraenkel, D.; Cais, M.; Halevi, E. A. *Isr. J. Chem.* **1976/1977**, *15*, 223. Cais, M.; Kaftory, M.; Kohn, D. H.; Tatarsky, D. *J. Organomet. Chem.* **1979**, *184*, 103. Landis, C. R.; Halpern, J. *Organometallics* **1983**, *2*, 840.

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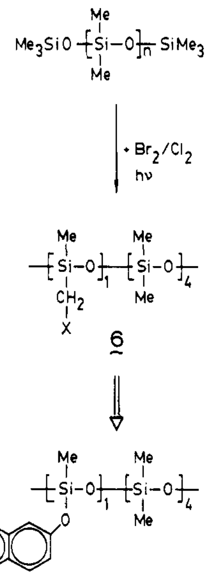
Scheme II



are of interest as homogeneous polymer-based catalysts.[16]

In this paper we describe the preparation of the organofunctional polysiloxane and show that the synthetic procedure is applicable as well to a small-molecule cyclosiloxane which may be considered as a model for the polymer. We present then the results of metal vapor fluid-matrix studies[17] with the polysiloxane and cyclosiloxane as a preliminary probe of the metal atom reaction. On the basis of these matrix studies, larger scale metal vapor rotary reactor experiments have been performed in order to characterize further the products and investigate their reactivity. A preliminary account of this research has been published.[18]

Results

Preparation of Poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)] and Naphthoxyheptamethylcyclotetrasiloxane. While a number of methods exist for the preparation of substituted polysiloxanes,[19] only two reports[20] describe the incorporation of a naphthalene functionality and these concern end-capping of polysiloxane chains. Our desire to form a polysiloxane with pendent naphthalene groups prompted us to develop a new synthetic path (Scheme I). The approach involves the preparation of a poly[(dimethylsiloxane)-*co*-((halomethyl)methylsiloxane)] as a precursor to the naphthalene-functionalized polysiloxane. Two routes to this polymer are described in Schemes I and II.

Synthesis of the poly[(dimethylsiloxane)-*co*-((iodomethyl)methylsiloxane)], **3**, from (chloromethyl)heptamethylcyclotetrasiloxane (Cl-D$_4$), **1** (Scheme I), was based on a procedure described previously.[21] Our observation that halogen exchange occurred much more rapidly for Cl-D$_4$ than for a chloromethyl-substituted polysiloxane however led us to reverse the literature steps. Thus, **1** was converted to the I-D$_4$ (**2**) via a Finkelstein procedure. Elution from a silica column yielded pure **2**, as determined by ^{1}H NMR spectroscopy, the resonance of Si–CH$_2$X arising at δ 2.65 for X = Cl but at δ 1.90 for X = I. Acid-catalyzed ring opening of **2** in the presence of octamethylcyclotetrasiloxane afforded **3**, the percentage of halomethyl substituent being controlled by the ratio of I-D$_4$ and D$_4$ used. For a 1:1 mole ratio, a linear polymer containing a Me:CH$_2$I ratio of 15:1, corresponding to x:y = 1:7, was obtained with M_w = 138 000.

Although reaction of **3** with LiPPh$_2$ has been reported to give the (diphenylphosphino)polysiloxane,[21] our attempts to perform a similar reaction with naphthyllithium proved unsuccessful, yielding only fine dispersions of naphthalene in the polysiloxane fluid. However, the naphthalene group could be introduced through a Williamson ether synthesis[22] (Scheme I). This approach was found to be suitable for synthesis of polymer **5**, starting from **3**, as well as a naphthalene-substituted cyclosiloxane **4**, beginning with the I-D$_4$ (**2**). Focussing initially on the cyclosiloxane, **2** was dissolved in toluene and an excess of freshly recrystallized 1- or 2-naphthol and a corresponding amount of pyridine were added. Refluxing for 24 h, followed by workup and purification on deactivated silica afforded the naphthoxyheptamethylcyclotetrasiloxane (C$_{10}$H$_7$O-D$_4$*), **4**, in about 75% yield. ^{1}H and ^{13}C NMR, IR, UV–visible, and mass spectra and elemental analysis were all consistent with the indicated formulation.

Reaction of polysiloxane **3** under similar conditions also yielded the required poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)], **5**, although longer reaction times were necessary. However, while 2-naphthol reacted with **2** and the analogous polymer **3** quantitatively, 1-naphthol reacted to 100% conversion only with **2**. In the polymer preparation, about 50% of the iodomethyl groups on the polymer remain intact even after extended reflux (as determined by ^{1}H NMR). After workup, **5** was obtained as a pale yellow, viscous oil characterized by its ^{1}H and ^{13}C NMR and UV–visible spectra.

Two features of this final step are noteworthy. First, in products **4** and **5** the methylene group attached to the silicon has been removed with the halogen. Under these reaction conditions, the presence of an electronegative halogen bound to the α-carbon appears to render the silicon sufficiently electron deficient that it becomes susceptible to direct nucleophilic attack, leading to the formation of a silyl ether. Evidence for this unusual reaction was provided by the disappearance of the resonances for the methylene group in the ^{1}H and ^{13}C NMR spectra of **4** and **5** as well as the mass of the parent ion in the mass spectra of **4a** and **4b**. Also, extraction of the toluene-insoluble material at the end of the reaction yielded a white deliquescent solid whose ^{1}H NMR spectrum was consistent with that expected for *N*-methylpyridinium iodide. While this appears at first an extremely unusual reaction, precedents do exist in the literature.[23]

Second, the formation of a Si–O–R link renders the final product, **4** or **5**, acid sensitive. As a result, acid-catalyzed ring opening and polymerization of **4** occur only with cleavage of the naphthalene function, precluding this as an alternative route to **5**.

While the synthesis starting from Cl-D$_4$ (Scheme I) is highly suitable for small-scale polymer preparations, limitations associated with Cl-D$_4$ make the route less attractive for large-scale syntheses such as are necessary for

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[16] Bayer, E.; Schurig, V. *CHEMTECH* **1976**, 212; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 493.

[17] Ozin, G. A.; Francis, C. G. *J. Mol. Struct.* **1980**, *59*, 55.

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[20] Murray, J. G.; Holub, F. F. U.S. Patent 3 125 634, 1964. Cappo, G. R. U.S. Patent 4 147 646, 1979.

[21] Farrell, M. O.; VanDyke, C. H.; Boucher, L. J.; Metlin, S. J. *J. Organomet. Chem.* **1979**, *172*, 367.

[22] A similar procedure has been reported as a route for end capping of polysiloxane chains with groups other than naphthalene—Simmler, W.; Kauczor, H.-W. U.S. Patent 3 174 987, 1966.

[23] See ref 19, pp 129–133 and references therein. However, compare ref 22, in which retention of the CH$_2$ moiety was claimed.

macroscale metal vapor preparations. An alternative route to the halomethyl-substituted polysiloxane was found in the method of Speier[24] which involves free radical halogenation of a poly(dimethylsiloxane).[25]

Two poly(dimethylsiloxanes), with viscosities of 0.10 and 0.50 P and listed molecular weights of 1500 and 4000, respectively, were chosen for study (Scheme II). Bromine was added slowly to the *neat* polysiloxane and chlorine allowed to bubble through the liquid under an external light source. The chlorine is required due to the extremely slow reaction for bromine alone. The resulting polymer **6** contains both CH_2Cl and CH_2Br groups as shown by the ^1H NMR spectrum. Optimum conditions for the free radical halogenation yielded a polymer containing CH_2X groups with 60% bromine and 40% chlorine substitution. A slight disadvantage of this route is that the ease of displacement of the CH_2X group in the Williamson ether synthesis is reduced for X = Cl. This can be circumvented by carrying out a halogen exchange prior to the ether synthesis to give the analogue of **3**.

A small amount of very viscous, presumably cross-linked polymer was formed during the reaction. It was, however, insoluble in ether and could be removed accordingly. The final polymer **6** showed no evidence of cross-linking based on ^1H NMR spectroscopy and molecular weight determinations.

This method of inclusion of the halogen is completely lacking in selectivity however, so that there is a greater possibility of halomethyl groups being on adjacent siloxane units or even on the same silicon atom. This latter situation is prohibited by the first reaction sequence (Scheme I). That a variety of methylene environments does exist is evidenced by the ^1H NMR spectrum of **6**, in which the single resonance due to a particular CH_2X group is replaced by multiplets centered at δ 2.65 for X = Cl and δ 2.35 for X = Br. The random nature of incorporation of the halogen also prevented its use as a route for the preparation of X-D_4 (X = Cl and Br) from D_4. A large number of isomers were obtained with varying amounts of halogen substitution as evidenced by NMR and GC studies.[26]

Metal Vapor Modeling Studies Utilizing Matrix-Isolation Spectroscopic Techniques. The metal vapor matrix optical spectroscopic technique has been used successfully for the study of metal incorporation into functionalized organic polymers and has proven to be a valuable tool for investigating both the site and extent of metal attachment to the polymer.[17,27] In the present study we have used the method as an initial probe of the reaction of the new naphthalene–siloxane species **4** and **5** with metal vapors, prior to larger scale preparations.

The optical spectra arising from deposition of Cr atoms into a thin film of either the poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane] (**5**) or $C_{10}H_7O$-D_4* (**4b**) held on an optical window cooled to 270 K are shown in parts a and b of Figure 1, respectively.[28] The similarity of the two spectra and their resemblance to that of an authentic $Cr(\eta^6$-$C_{10}H_8)_2$ sample (Figure 1c) suggest an assignment for the former species to the siloxane-attached bis(η^6-naphthalene)chromium moieties. In addition to the $\pi \rightarrow \pi^*$ transitions of the parent ligand, in all cases three bands are observed, which may be assigned to MLCT transitions by reference to our previous study[15] of bis(naphthalene)metal complexes.

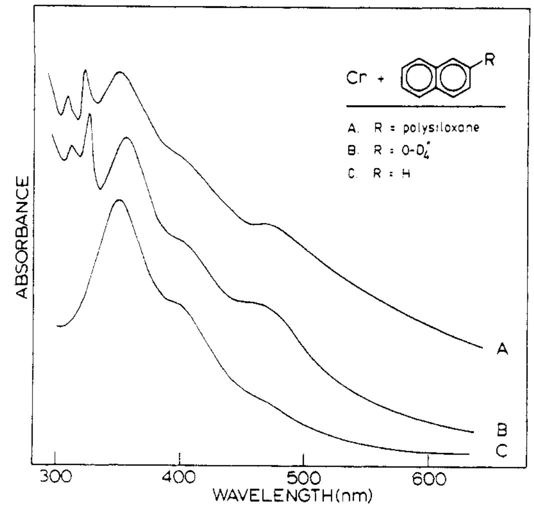


Figure 1. UV–visible spectra of products arising from reaction of Cr vapor with (a) poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)], (b) 2-$C_{10}H_7O$-D_4* at 270 K. (c) $(\eta^6$-$C_{10}H_8)_2Cr$.

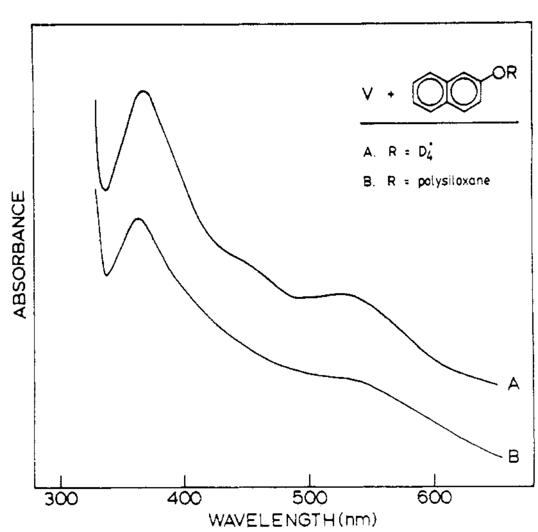
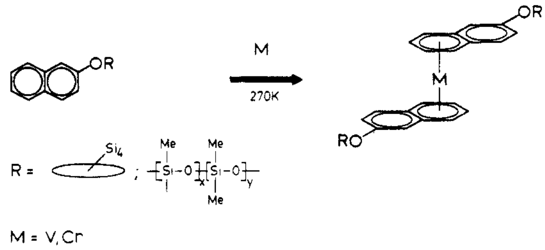


Figure 2. UV–visible spectra of products arising from reaction of V vapor with (a) 2-$C_{10}H_7O$-D_4* and (b) poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)] at 270 K.

Similar results are obtained for deposition of V vapor into **4b** and **5**, as shown in parts a and b of Figure 2, respectively, with three bands appearing shifted slightly to the red with respect to the chromium case. Comparison of these results with those obtained for $(\eta^6$-$C_{10}H_8)_2V$ again clearly points to a corresponding assignment to a supported bis(arene)vanadium (eq 1).



(1)

A very different situation pertains for reaction with titanium vapor for which no evidence of an arene complex

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[24] Speier, J. L. *J. Am. Chem. Soc.* **1951**, *73*, 826.

[25] Other routes for introducing CH_2X groups into polysiloxanes do exist. See, for example: Reyx, D.; Guillaume, P. *Makromol. Chem.* **1983**, *184*, 263, 1179.

[26] For a discussion of the halogenation of D_4 see ref 25.

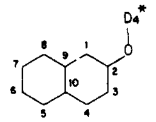
[27] Ozin, G. A.; Andrews, M. P.; Nazar, L. F.; Huber, H. X.; Francis, C. G. *Coord. Chem. Rev.* **1983**, *48*, 203.

[28] The reaction of metal vapors with **4a** afforded spectra similar to those of the **4b** analogues. Preparation of **5** from **3** or **6** resulted in materials which underwent reaction with Cr or V. However, the apparently greater viscosity of the polymer derived from **3** appeared to result in enhanced formation of colloidal metal as evidenced by a steeply rising base line underneath the absorption bands of the complexes.

Table I. NMR Data[a,b] of Chromium Complexes of $C_{10}H_7O\text{-}D_4{}^*$ (4b) in the Coordinated Arene Region

$^1H^c$		$^{13}C^d$	
	$(C_{10}H_7O\text{-}D_4{}^*)_2Cr$		
5.06, 5.41 (d, 5.4)	H_5, H_8		
4.00, 4.48 (t, 4.9)	H_6, H_7	73.9, 74.7, 75.5, 76.2, 76.8, 78.4, 79.3	C_{5-8}
5.16, 5.29 (d, 5.4)	H_5, H_8	85.5, 86.0, 93.6, 94.0	C_9, C_{10}
4.17, 4.28 (t, 4.9)	H_6, H_7		
	$(C_{10}H_7O\text{-}D_4{}^*)Cr(CO)_3$		
5.23, 5.27 (d, 6.5)[e]	H_5, H_8	88.9, 90.4, 91.1, 92.7	C_{5-8}
4.51, 4.69 (t, 6.5)[e]	H_6, H_7	100.3, 102.1	C_9, C_{10}

[a] Numbering scheme



[b] Positions of peaks due to $H_{1,3,4}$ and C_{1-4} were obscured by uncomplexed **4b**. [c] Chemical shifts (ppm) relative to C_6H_6 (in C_6D_6) solvent) with multiplicity and coupling constants (Hz). [d] Chemical shifts (ppm) relative to C_6D_6. [e] In $CDCl_3$ solvent, a downfield shift occurs for both sets of resonances: δ 5.98, 6.10 (d), 5.36, 5.54 (t). Compare also ref 13 and 14.

could be discerned in the optical spectrum. In this case, it appears that reaction of titanium with the oxygen atom linking the naphthalene moiety to the backbone precludes the formation of the polymer-anchored $(\eta^6\text{-}C_{10}H_8)_2Ti$.

Metal Vapor Synthesis with 4b and 5 and Studies of Complex Reactivity. On the basis of the results from the matrix scale experiments, macroscale metal vapor studies have been performed. Reaction of chromium vapor with the neat liquid poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)], **5**, at ~270 K resulted in the formation of a deep red-brown fluid.[29] The electronic spectrum of the extremely air-sensitive product was in good agreement with that obtained in the matrix study (Figure 1a) indicating the formation of the polysiloxane-bound bis(η^6-naphthalene)chromium species. However, all attempts to obtain good quality NMR spectra were unsuccessful due to the low concentration of complex attainable. A surprising feature of this particular reaction is the inefficiency of the interaction between the metal vapor and the polysiloxane **5**. Typically conversion of the evaporated metal to complex was only ~20%, an observation which is in strong contrast with the extremely high reaction efficiency noted previously[7] for reactions of poly(methylphenylsiloxanes) under comparable conditions. The uncomplexed metal appears to be present in the polymer **5** as small metal particles of colloidal dimensions as evidenced by their reaction with carbon monoxide (to be described later). The reason for the low efficiency of this reaction of Cr with the naphthalene-substituted polysiloxane is not understood at present.

The similarity of the products obtained in the matrix-scale reactions of chromium with **5** and **4b** points to the great importance of the bis(arene) complex of **4b** as a model for the metal site in the polymeric system. Deposition of Cr into a solution of **4b** in tetrahydrofuran at ~150 K yielded a clear red-black oil. The UV-visible spectrum of this material was in agreement with that of the product from the matrix study (Figure 1b) and indicated that about 40% of the $C_{10}H_7O\text{-}D_4{}^*$ was complexed, corresponding to a 25–30% yield of product based on metal evaporated. The majority of the unreacted ligand could be removed by high vacuum sublimation, although a small amount always remained.

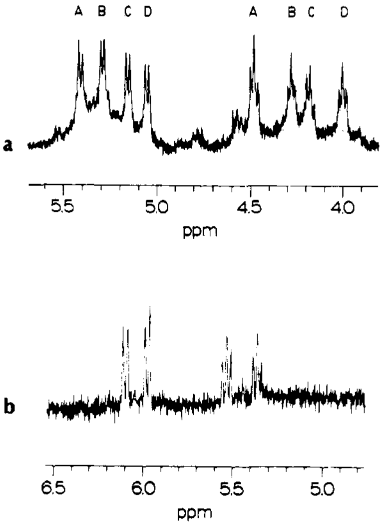
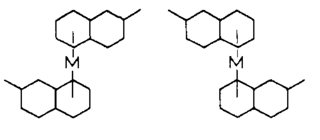


Figure 3. ^1H NMR spectra for the coordinated naphthalene ring in (a) $(\eta^6\text{-}C_{10}H_7O\text{-}D_4{}^*)_2Cr$ (solvent = C_6D_6) and (b) $(\eta^6\text{-}C_{10}H_7O\text{-}D_4{}^*)Cr(CO)_3$ (solvent = $CDCl_3$).

The ^1H and ^{13}C NMR data of the product (Table I) are consistent with the formulation $Cr(\eta^6\text{-}C_{10}H_7O\text{-}D_4)_2$ as well as elucidating the point of attachment. The coordinated arene region of the ^1H NMR spectrum (Figure 3a) contains two groups of signals occurring in a 1:1 ratio, consisting of four triplets in the region δ 4.6–5.3 and four doublets in the region δ 5.5–6.2. A number of isomers exist in principle for the complex depending on—(a) whether coordination takes place to the substituted or unsubstituted ring and (b) whether the substituent on one ring takes up a syn or an anti conformation with respect to that on the other ring in the (arene)$_2$Cr species. One can deduce that complexation occurs only to the unsubstituted ring since attachment of Cr to the 2-substituted ring should give rise to a singlet and two doublets. We expect therefore two doublets, due to H_5 and H_8, and two triplets,[30] due to H_6 and H_7, provided that the presence of the substituent on the adjacent ring produces a significant perturbation of the local symmetry in the complexed ring. It follows that the observed spectrum suggests *two* distinct sets of resonances due to complexed naphthalene rings, a conclusion that is confirmed by spin decoupling studies. Referring to Figure 3a, doublets A and D are coupled to triplets A and D as follows: $d_A\text{-}t_D\text{-}t_A\text{-}d_D$. Doublets B and C are in turn coupled to triplets B and C according to $d_B\text{-}t_B\text{-}t_C\text{-}d_C$.

Final elucidation of the ^1H NMR spectrum is provided by the structures below. If the complex exists in the syn conformation, a pair of enantiomers are formed (I) whereas a meso structure results for the anti conformation (II). We propose therefore that the observed ^1H NMR spectrum of $Cr(C_{10}H_7O\text{-}D_4{}^*)_2$ arises from a 1:1 mixture of diastereomers I and II.



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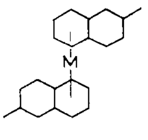

II

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[29] The polymer used for this reaction was derived from the 0.50 P poly(dimethylsiloxane) via the method outlined in Scheme II.

[30] An X-ray structure determination of $(\eta^6\text{-}C_{10}H_8)_2Cr^{14}$ shows that the metal is slightly shifted from the "formally" sixfold axis toward the edge of the naphthalene ring.

This proposal also explains satisfactorily the ^{13}C NMR spectrum (Table I). In the coordinated arene region, seven peaks are observed due to C_{5-8} in the two diastereomers, but with a single coincidental peak overlap at 78.4 ppm. Two pairs of very weak signals are also observed at 85.8 and 93.8 ppm corresponding to the fused carbon atoms C_9 and C_{10} for each diastereomer. The downfield shift of these carbon resonances relative to C_{5-8} is in agreement with the reported spectral data for the parent $(\eta^6\text{-}C_{10}H_8)_2Cr$.[13,14] It has been suggested[12] recently that an intermediate shift of the fused carbon resonances in $Ir(NpEt)L_2^+$ may reflect the occurrence of a η^4-mode of coordination rather than the normal η^6-case. However, we anticipate that any deviation from the idealized D_{6h} local symmetry in the $(C_{10}H_7O\text{-}D_4^*)_2Cr$ complex will be very small.[31]

A final comment regarding the NMR data relates to the existence of two small bands at δ 4.6 and 4.8 in the ^1H spectrum which appear to correspond to several weak resonances in the ^{13}C spectra. This may indicate the presence of a very small amount of the species in which Cr is bound to the substituted ring.

Further evidence in support of our analysis of the NMR spectra of $Cr(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)_2$ was obtained from studies of the reaction chemistry of these bis(arene)chromium species. As was noted earlier, the vastly increased ligand lability of (arene)metal complexes for polycyclic aromatics such as naphthalene, when compared with benzene, has been recognized recently.[11-13] This reactivity may be rationalized in terms of an induced haptotropic rearrangement of the complex under the influence of the incoming ligand molecule. A sideways displacement of the metal from an η^6-interaction to η^4 is favored by the lower localization energy for naphthalene relative to benzene.[32]

An important aspect of this study was to establish the effect, if any, of the siloxane moiety on the reactivity of the (naphthalene)$_2$Cr center. Reaction of a hexane solution of $Cr(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)_2$ with 1 atm of CO at room temperature in a sealed ampule for 16 h resulted in a change in color of the solution from deep red to orange. The IR spectrum of the resulting solution was consistent with two products—$Cr(CO)_6$[33] and $(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)Cr(CO)_3$, the latter with bands in the ν(CO) region occurring at 1976 cm^{-1} (A_1) and 1913/1898 cm^{-1} (E) assuming C_{3v} local symmetry. The identity of the tricarbonyl was confirmed by its ^1H and ^{13}C NMR spectra. The ^1H spectrum contains two doublets and two triplets centered at δ 6.04 and 5.45, respectively (see Figure 3b and Table I), while four resonances due to C_{5-8} are observed in the ^{13}C spectrum with two weak resonances at 100.3 and 102.1 ppm attributed to C_9 and C_{10} (Table I). Thus the NMR spectra show only a single set of resonances due to the complexed $C_{10}H_7O\text{-}D_4^*$ in the tricarbonyl species, with chromium bound to the unsubstituted ring. Moreover this is what would be predicted based on our analysis of the bis(arene) complex as a mixture of diastereomers, since on replacement of one ring by a tricarbonyl group the diastereomeric property is destroyed, leaving $(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)Cr(CO)_3$ as an enantiomeric pair of complexes. While the products are similar in nature to those obtained from reaction of CO with $(\eta^6\text{-}C_{10}H_8)_2Cr$, the extent to which reaction has occurred is rather different.[13] After prolonged exposure of $(\eta^6\text{-}C_{10}H_8)_2Cr$ to CO the only product obtained was $Cr(CO)_6$, although the formation of $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ was observed on exposure for shorter time periods. In our case, although $Cr(CO)_6$ was formed, the major product after 16 h was still the $(\eta^6\text{-arene})Cr(CO)_3$.

On passing to the bis(η^6-naphthalene)chromium product for polysiloxane **5**, reaction with CO afforded the polymer-attached (η^6-naphthalene)$Cr(CO)_3$ as the major product, even after extended reaction with CO. This is in good agreement with the observed behavior of $Cr(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)_2$. However, when CO was bubbled through a hexane solution of the polymer-attached bis(η^6-naphthalene)chromium with frequent IR spectroscopic monitoring, it was found that $Cr(CO)_6$ was formed *initially* and rapidly reached a maximum value while the tricarbonyl continued to be produced. This reactivity differs to that for $Cr(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)_2$ or even for $(\eta^6\text{-}C_{10}H_8)_2Cr$ for which $Cr(CO)_6$ is postulated to be formed via the tricarbonyl.[13] A possible explanation of this behavior was provided by monitoring the reaction of a chromium slurry, produced by deposition of chromium atoms into a poly(dimethylsiloxane),[7] with CO. After the mixture was stirred overnight under 1 atm of CO in a sealed ampule, the IR spectrum of the product revealed the presence of $Cr(CO)_6$. Thus, we believe that the low efficiency of the Cr reaction with **5** leads to the formation of chromium particles of colloidal dimensions which are reactive toward CO resulting in the enhanced initial formation of $Cr(CO)_6$.

Clearly, for reactions with CO, both $Cr(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)_2$ and the polysiloxane-supported bis(η^6-naphthalene)chromium complexes exhibit similar reactivity in terms of chemistry occurring at the metal site. The major difference in their behavior appears best explained in terms of the existence of colloidal metal in the polymer case. The different behavior, compared to $(\eta^6\text{-}C_{10}H_8)_2Cr$ itself, is of interest and may reflect either the steric bulk of the siloxane attached to naphthalene or the potential coordinating ability of the oxygen atoms in the backbone. Alternatively one may postulate an electronic effect of the Me–Si–(O)$_3$ group on the complexed ring. Further studies are necessary to elucidate this point. It is interesting to note that, in contrast, reactions of the polymer-supported bis(η^6-naphthalene)chromium with organic isocyanides, such as *t*-BuNC or CN-c-Hex, yielded only the analogous CrL_6 complexes, in keeping with the results of similar reactions with the parent $(\eta^6\text{-}C_{10}H_8)_2Cr$.[13]

In summary, we have shown that the preparation of the macromolecular ligand **5** affords an important synthetic entry to organometallic polymers containing the bis(η^6-naphthalene)metal moiety via reaction with the metal vapors of chromium or vanadium. The synthesis of $Cr(\eta^6\text{-}C_{10}H_7O\text{-}D_4^*)_2$ from **4b** provides a complex which may be expected to model the metal site in the polymer analogue and indicates that binding of chromium to **5** occurs only to the unsubstituted ring of the naphthalene group. In addition, further studies have revealed the similarity between the reaction chemistry for the model complex and the polymer species but suggest that the presence of the siloxane group on the complexed naphthalene does affect the reactivity when compared with $(\eta^6\text{-}C_{10}H_8)_2Cr$. Further experiments are being attempted to try to establish the role of the polysiloxane backbone—an important aspect of any catalytic chemistry which may be anticipated for these systems.

Experimental Section

Octamethylcyclotetrasiloxane and two poly(dimethylsiloxanes) with listed viscosities of 0.10 and 0.50 P were purchased from Petrarch Systems. (Chloromethyl)heptamethylcyclotetrasiloxane was purchased from Petrarch Systems or Columbia Organic

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[31] Substituents have only small effects on the magnitudes of aromatic coupling constants. If one anticipates that $J_{5-6} \simeq J_{6-7} \simeq J_{7-8}$, then the signals due to H_6 and H_7 should approximate more closely to triplets rather than doublets of doublets.

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Chemical Co. All siloxanes were used as received. NMR spectra were recorded on a JEOL FX90Q (90 MHz) or IBM WP270 SY (270 MHz) spectrometer. ^{1}H chemical shifts are reported relative to an internal standard of $CHCl_3$ in $CDCl_3$ or C_6H_6 in C_6D_6. ^{13}C chemical shifts are reported relative to the $CDCl_3$ or C_6D_6 used as solvent. Mass spectra were obtained on a Hewlett-Packard 5985 GC–MS at an ionizing voltage of 70 eV. Molecular weights for polymer samples were determined via gel permeation chromatography techniques. We wish to thank Dr. Robin Wright of the 3-M Co. for obtaining these molecular weight measurements. All macroscale manipulations of $(\eta^6\text{-naphthalene})_2Cr$ complexes were performed under an atmosphere of prepurified argon using standard Schlenk techniques.

(Iodomethyl)heptamethylcyclotetrasiloxane (I-D$_4$), 2. Sodium iodide (47 g, 315 mmol) was added to a solution of (chloromethyl)heptamethylcyclotetrasiloxane (Cl-D$_4$), 1 (10 mL, 31.5 mmol), in acetone (500 mL) and the mixture heated under reflux for 16 h. The solvent was removed from the resulting yellow solution yielding a yellow solid. This was dissolved in water (500 mL) and extracted with hexane (3 × 150 mL). The hexane extracts were combined, dried over magnesium sulfate, and evaporated to dryness to give **2** as a slightly pink oil in 90–95% yield.

NMR ($CDCl_3$): ^{1}H, δ 1.90 (s, 2 H, CH_2I), 0.26 (s, 3 H, CH_3SiCH_2I), 0.05–0.15 (m, 18 H, $Si(CH_3)_2$); ^{13}C, −16.2 (CH_2I), −2.6 (CH_3SiCH_2I), 0.52 ppm ($Si(CH_3)_2$).

Poly[(dimethylsiloxane)-*co*-((iodomethyl)methylsiloxane)] (I-D$_n$)$_x$, 3. I-D$_4$ (**2**) and octamethylcyclotetrasiloxane (D$_4$) were mixed in varying proportions depending on the degree of substitution required in the final polymer, for example 1:1 for (I-D$_8$)$_x$ and 1:5 for (I-D$_{20}$)$_x$. Typically 90 mL of the mixture was stirred at room temperature for 16 h with about 10 drops of concentrated sulfuric acid. The resulting viscous liquid was dissolved in ether and the solution washed with sodium bicarbonate solution. After the solution was dried over magnesium sulfate, the solvent was removed in vacuo to give a 90% yield of the desired polymer.

^{1}H NMR ($CDCl_3$): δ 2.0 (s, 2 H, CH_2I), 0.3 (s, 3 H, CH_3SiCH_2I), 0.1 (m, 6*n*H, $n(Si(CH_3)_2)$, *n* depending on the original ratios of I-D$_4$ and D$_4$ used). Molecular weight (GPC): $M_w = 1.38 \times 10^5$; $M_w/M_n = 2.36$.

1- and 2-Naphthoxyheptamethylcyclotetrasiloxane ($C_{10}H_7O$-D$_4$*), 4a and 4b. To a solution of **2** (5 mL, 12 mmol) in toluene (200 mL) was added freshly recrystallized 1- or 2-naphthol (3 g, 23 mmol) and pyridine (5 mL). The resulting mixture was heated under reflux for 24 h in the case of 1-naphthol and 16 h in the case of 2-naphthol. The product mixture was washed with 10% sodium hydroxide solution (2 × 50 mL), 5% hydrochloric acid (2 × 50 mL), and finally water (2 × 50 mL) and the volume of the organic layer reduced under vacuum. The product in each case was chromatographed on silica, which had been pretreated with hexamethyldisilazane, using hexane as the eluent. This afforded 1-$C_{10}H_7O$-D$_4$* (**4a**) or 2-$C_{10}H_7O$-D$_4$* (**4b**) in 70–75% yield as the pure products.

1-$C_{10}H_7O$-D$_4$* (**4a**): ^{1}H NMR ($CDCl_3$) δ 8.43 (m, 1 H), 7.96 (m, 1 H), 7.64 (m, 3 H), 7.51 (t, 1 H), 7.26 (d, 1 H, $C_{10}H_7O$-D$_4$*), 0.45 (s, 3 H, $C_{10}H_7OSiCH_3$), 0.21 (m, 18 H, $Si(CH_3)_2$); ^{13}C NMR ($(CD_3)_2CO$) 149.9, 135.1, 127.7, 127.5, 126.2, 125.8, 125.1, 122.5, 121.8, 113.3 ($C_{10}H_7O$-D$_4$*), 0.7 ($Si(CH_3)_2$), −3.2 ppm ($C_{10}H_7OSiCH_3$); UV–visible (hexane) λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}), 224 (35 000), 275 (5100), 285 (4600), 310 (312); mass spectrum, *m/e* (relative intensity) 424 ($C_{17}H_{28}O_5Si_4^+$, 61), 409 ($C_{16}H_{25}O_5Si_4^+$, 34), 281 ($C_7H_{21}O_4Si_4^+$, 100), 251 ($C_5H_{15}O_4Si_4^+$, 20), 193 ($C_3H_9O_4Si_3^+$, 25), 141 ($C_{11}H_9^+$, 23), 127 ($C_{10}H_7^+$, 23), 73 ($C_3H_9Si^+$, 15). Anal. Calcd for $C_{17}H_{28}O_5Si_4$ (**4a**): C, 48.11; H, 6.60. Found: C, 47.97; H, 6.81.

2-$C_{10}H_7O$-D$_4$* (**4b**): ^{1}H NMR ($CDCl_3$) δ 7.87 (m, 3 H), 7.49 (m, 3 H), 7.31 (m, 1 H, $C_{10}H_7O$-D$_4$*), 0.4 (s, 3 H, $C_{10}H_7OSiCH_3$), 0.22 (m, 18 H, $Si(CH_3)_2$); ^{13}C NMR ($(CD_3)_2CO$) 153.9, 134.9, 130.0, 129.9, 127.5, 126.5, 126.2, 123.7, 121.6, 115.0 ($C_{10}H_7O$-D$_4$*), 0.3 ($Si(CH_3)_2$), −5.2 ppm ($C_{10}H_7OSiCH_3$); UV–visible (hexane) λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}), 225 (80 000), 262 (4150), 272 (4700), 282 (3500), 310 (1150), 324 (1140); mass spectrum, *m/e* (relative intensity) 424 ($C_{17}H_{28}O_5Si_4^+$, 89), 409 ($C_{16}H_{25}O_5Si_4^+$, 100), 281 ($C_7H_{21}O_4Si_4^+$, 55), 267 ($C_6H_{19}O_4Si_4^+$, 32), 251 ($C_5H_{15}O_4Si_4^+$, 49), 205 ($C_3H_9O_3Si_4^+$, 26), 193 ($C_3H_9O_4Si_3^+$, 40), 141 ($C_{11}H_9^+$, 53), 127 ($C_{10}H_7^+$, 64), 115 ($C_9H_7^+$, 19), 73 ($C_3H_9Si^+$, 39). Anal. Calcd for $C_{17}H_{28}O_5Si_4$ (**4b**): C, 48.11; H, 6.60. Found C, 47.83; H, 6.80.

Poly[(dimethylsiloxane)-*co*-(2-naphthoxymethylsiloxane)], 5. To a solution of (I-D$_8$)$_x$, **3** (10 mL, 15 mmol of CH_2I), or poly[(dimethylsiloxane)-*co*-((halomethyl)methylsiloxane)], **6** (15 mmol of CH_2X), in toluene (300 mL) was added freshly recrystallized 2-naphthol (4.4 g, 30 mmol) and pyridine (5 mL). The resulting mixture was heated under reflux for 72 h and then washed with 10% sodium hydroxide solution (3 × 100 mL), 5% hydrochloric acid (3 × 100 mL), and finally water (2 × 100 mL). The organic layer was dried over magnesium sulfate and the solvent removed in vacuo to give a pale yellow oil (8 mL, 80% yield) of the desired product. In larger scale preparations the final product was a much darker brown color. In these cases the oil was decolorized simply with activated charcoal.

NMR ($CDCl_3$): ^{1}H, δ 7.0–7.9 (m, 7 H, $C_{10}H_7OSiCH_3$), 0.28 (s, 3 H, $C_{10}H_7OSiCH_3$), 0.10 (m, 6*n*H, $n(Si(CH_3)_2)$); ^{13}C, 152.5, 134.6, 129.5, 129.3, 127.6, 126.8, 126.0, 124.0, 121.8, 114.7 ($C_{10}H_7OSiCH_3$), 3.0, 1.8 ($Si(CH_3)_2$), −2.8 ppm ($C_{10}H_7OSiCH_3$). Molecular weight (GPC): $M_w = 7.86 \times 10^3$, $M_w/M_n = 2.39$ for polymer prepared from **6**. UV–visible (hexane): λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}), 222 (72 000), 260 (4090), 272 (4350), 282 (3200), 310 (900), 322 (1150).

Poly[(dimethylsiloxane)-*co*-((halomethyl)methylsiloxane)], 6. Polydimethylsiloxane (0.50 or 0.10 P viscosity) (20 mL) was placed in a three-necked flask equipped with an addition funnel, a chlorine gas inlet, a condenser, magnetic stirrer, and an external light source (a powerful desk lamp suffices). Under an atmosphere of nitrogen, a few drops of bromine were added to the polymer. The lamp was turned on and chlorine bubbled into the mxiture. Once the red color had dissipated, more bromine was added. This process was repeated until a total of 0.9 mL (0.125 equiv based on silicon) of bromine had been added. (Significant heating and copious hydrogen chloride evolution was noted during the reaction.) The polymer was then allowed to cool, dissolved in ether, and washed with 5% sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo to give a 90–95% yield of a mixed bromomethyl/chloromethyl-substituted polymer **6**. ^{1}H NMR shows an approximately 3:2 ratio of CH_2Br:CH_2Cl group with between 12 and 20% of the siloxane units substituted. (These ratios can be changed by altering the conditions; e.g., a fast chlorine flow gives a higher chlorine content.)

NMR ($CDCl_3$): ^{1}H, δ 2.67 (m, $ClCH_2$), 2.35 (m, $BrCH_2$), 0.23 (s, CH_3SiCH_2Br), 0.20 (s, CH_3SiCH_2Cl), 0.05 (m, $SiCH_3$); ^{13}C, 30.8, 28.7 (CH_2Cl), 17.0, 15.5 (CH_2Br), 2.8 (CH_3SiCH_2Br), 2.2 (CH_3SiCH_2Cl), 1.8, 0.3, −0.8, −2.1 ppm ($SiCH_3$). Molecular weight (GPC): $M_w = 5.23 \times 10^3$, $M_w/M_n = 1.94$ starting from a poly(dimethylsiloxane) with $M_w = 5.04 \times 10^3$ and $M_w/M_n = 2.05$.

This halo polymer can then be conveniently converted to an iodo-substituted polymer similar to **3** by refluxing for 72 h with sodium iodide in acetone. (NB: ^{1}H NMR shows a CH_2I multiplet at δ 1.92 as opposed to the singlet in **3**). Alternatively **6** affords directly the naphthoxy polymer **5** by refluxing for 72 h in toluene with 2-naphthol and pyridine. This process yields a polymer containing 8–10% naphthoxyl substitution based on available silicon.

Matrix-Isolation Studies. Metal vapors were generated by resistive heating of a metal filament (V, 99.5%; Ti, 99.96%, Alfa Ventron) or from a tantalum Knudsen cell containing the metal powder (Cr, 99%, Alfa Ventron). They were deposited into a thin film of the ligand adhering to the surface of a quartz optical plate held at 270 K by means of an Air Products Displex closed-cycle helium refrigeration system within a standard matrix apparatus. Metal deposition rates were calibrated by means of a quartz crystal microbalance (AT-cut quartz wafer, C.R. Snellgrove Ltd, Ontario, Canada) and were typically on the order of 0.2 μmol h^{-1}. The ensuing reactions were monitored by UV–visible spectroscopy, using a Varian DMS 90 UV–vis spectrophotometer.

UV–visible: see Figures 1 and 2. For comparison $(\eta^6\text{-}C_{10}H_8)_2Cr$: λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) 352 (10 400), 405 (6400), 476 (2500).

Macroscale Metal Vapor Studies. Cr + 2-$C_{10}H_7O$-D$_4$*, 4b. Chromium (890 mg, 17 mmol) was evaporated and deposited into a solution of 2-$C_{10}H_7O$-D$_4$*, **4b** (10 mL), in tetrahydrofuran (120 mL) over 2 h. The rotating flask was cooled to 150 K by means of a pentane/liquid-nitrogen slush bath so as to maintain a pressure of less than 10^{-3} torr during the evaporation. The resulting air-sensitive deep red solution was extracted and filtered under argon and the tetrahydrofuran removed in vacuo to leave a black tar. This was then redissolved in degassed hexane and refiltered to give a clear, deep red solution. The hexane solution was transferred to a sublimation vessel, where the solvent was first removed in vacuo and then the excess **4b** removed by sublimation at 10^{-6} torr. UV-visible (THF): 353, 408, and 475 nm.

Cr + Poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)], 5. Chromium (1.5 g, 28.5 mmol) was evaporated over a period of 90 min into 120 mL of **5** [$C_{10}H_7OSiMe:Si(Me)_2$ ratio = 1:13] within a rotary solution reactor.[29] The flask was cooled to ~270 K so as to maintain a pressure of less than 10^{-3} torr during the metal evaporation. After the crucible was allowed to cool at the end of the reaction, the flask was backfilled with argon and the resulting deep red liquid extracted into a Schlenk tube. The extremely air-sensitive liquid was then filtered through a glass frit to remove excess metal particles. From the UV-visible spectrum of the product it was possible to determine that 10-12% of the naphthalene groups present were complexed, corresponding to a 20% yield of product based on metal evaporated. UV-visible (C_6H_{12}): 354, 408, and 470 nm.

Ligand Substitution Reactions. In the reaction of the bis(naphthalene)chromium complexes of **4b** and **5** with carbon monoxide two methods were employed: (i) A saturated solution of the complex was prepared in degassed hexane (30 mL) in a Schlenk tube fitted with a rubber septum and magnetic stir bar. Carbon monoxide was bubbled through the stirred solution, and aliquots of the reaction mixture were taken for infrared spectroscopic examination. (ii) A saturated solution was placed in an ampule with a magnetic stir bar. One atmosphere of carbon monoxide was added and the mixture stirred overnight. The solvent was removed in vacuo leaving an orange oil.

In all cases two products were formed. $Cr(CO)_6$ was identified by its ν_{CO} stretching frequency at 1990 cm^{-1} and could be sublimed from the product oil. The (naphthalene)$Cr(CO)_3$ complexes for **4b** and **5** were identified by ^1H and ^{13}C NMR and IR spectroscopy for the former and IR spectroscopy for the latter. IR spectra (hexane) of the (naphthalene)$Cr(CO)_3$ complexes: for **4b**, ν(CO) = 1976, 1913, 1898 cm^{-1}; for **5**, ν(CO) = 1978, 1910, 1895 cm^{-1}. Reaction of the $(naphthalene)_2Cr$ complexes with RNC (R = *t*-Bu, c-Hex) was performed by adding the isocyanide to a hexane solution of the complex under an argon atmosphere and stirring for approximately 3 h. The IR spectra of the products in all cases contained an extremely broad band due to ν(CN) with maximum absorption in the 1900 cm^{-1} region. The products were identified as the corresponding $Cr(CNR)_6$ complexes from their IR data.[13]

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Registry No. 1, 17882-66-5; **2**, 17882-88-1; **4a**, 98194-75-3; **4b**, 98216-99-0; I (M = Cr), 98194-72-0; I (M = V), 98194-73-1; II (M = Cr), 98300-87-9; II (M = V), 98300-88-0; D_4, 556-67-2; $Cr(CO)_6$, 13007-92-6; (η^6-$C_{10}H_7O$-D_4*)$Cr(CO)_3$, 98194-74-2; $Cr(CN$-*t*-$Bu)_6$, 61817-78-5; $Cr(CN$-c-$Hc)_6$, 68829-55-0; Cr, 7440-47-3; V, 7440-62-2; Ti, 7440-32-6; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3; *tert*-butyl isocyanide, 7188-38-7; cyclohexyl isocyanide, 931-53-3.

MNDO Calculations for Compounds Containing Mercury[1]

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MNDO has been parametrized for mercury. Calculations are reported for a number of compounds of mercury. The results are comparable with those for other metals.

Introduction

Table I. MNDO Parameters for Mercury

optimized parameters	value	derived parameters	value
U_{ss}	−19.809 574[a]	E_{heat}	14.69[b]
U_{pp}	−13.102 530[a]	E_{el}	−28.819 148[a]
ζ_s	2.218 184[c]	D_1	1.737 804 8[d]
ζ_p	2.065 038[c]	D_2	1.460 806 4[d]
β_s	−0.404 525[a]	A_M	0.396 912 9[d]
β_p	−6.206 683[a]	A_D	0.304 769 4[d]
A_{1p}	1.335 641[e]	A_Q	0.348 310 2[d]
G_{ss}	10.800 000[a]		
G_{pp}	14.300 000[a]		
G_{sp}	9.300 000[a]		
G_{p2}	13.500 000[a]		
H_{sp}	1.300 000[a]		

[a] In eV. [b] In kcal/mol at 298 K (heat of atomization). [c] Atomic units (Bohrs). [d] In atomic units. [e] In $Å^{-1}$.

The MNDO method[4,5] is now established[6] as a practical procedure for studying chemical behavior, giving results comparable[7] with those from quite good ab initio models (e.g., 4-31G) while requiring only one-thousandth as much computer time. Parameters have been reported for hydrogen,[4] for the second-period elements beryllium,[8] boron,[9] carbon,[4] nitrogen,[4] oxygen,[4] and fluorine,[10] for the third-period elements aluminum,[11] silicon,[12] phosphorus,[12] sulfur,[13] and chlorine,[14] and for bromine,[15] iodine,[16] and tin.[17] Since d AOs are not currently included[17] in MNDO, calculations are confined to compounds involving only normal group valencies. Schleyer et al.[18] have reported extensive

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(1) Part 74 of the series "Ground States of Molecules". For part 73 see Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P., to be submitted for publication.

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