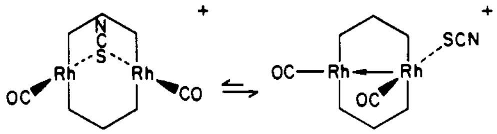
equilibrium being responsible:



There is ample precedent for the nonbridged structure depicted above. For example, the $[Pt_2(CH_3)_3(\mu\text{-dppm})_2]^+$ cation[16] has been shown to possess a similar structure (albeit with a cis arrangement of phosphine ligands on one metal center), and a similar complex has been proposed as an intermediate in the A-frame inversion of $[Pd_2(CH_3)I(\mu\text{-I})(\mu\text{-dppm})_2]BF_4$.[17] The discomfort associated with identifying the expected S-bridged structure for **15** as the minor component of this equilibrium was somewhat alleviated for us by the observation that, to the best of our knowledge at least, no example of a stable, symmetrically S-bridged thiocyanate complex has been reported. It is also obvious, however, that the numerous different species identified in spectra of **15** and the observed tendency of this complex to decompose readily at room temperature admit interpretations other than that above. We have been attempting to grow single crystals of this complex for some time but without success. It appears that decomposition outpaces good crystal growth under all the conditions we have so far tried, and hence it may be some time before the true nature of **15** is verified.

Unlike the reactions with KOCN and $NH_4NCS$, the reaction of **7** or **2** with $NaN_3$ does not require the stoichiometry to be carefully controlled. Thus, solutions of **7** and acidified **2** react with excess $NaN_3$ to yield $[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**16**), in excellent yield. The infrared spectrum of **16** is closely comparable to those of the A-frame complexes described above with the exception of $\nu(N_3)$ at 2077 (s) cm$^{-1}$, and the $^{31}P\{^1H\}$ NMR spectrum is also consistent with the A-frame assignment. The absence of a neutral species in this reaction is somewhat surprising, but similar behavior has been observed in the reaction of $[RhCl(COD)]_2$ with $NaN_3$, dppm, and carbon monoxide.[5]

**Acknowledgment.** The authors thank the Natural Sciences and Engineering Research Council of Canada and Dalhousie University for financial support. Our thanks are also extended to Johnson Matthey Ltd. for a generous loan of rhodium trichloride and to Drs. J. Walters and D. Hooper for their assistance in obtaining the $^{31}P$ and $^1H$ NMR spectra.

**Registry No.** **1**, 91581-08-7; **2**, 91581-10-1; **3**, 91581-06-5; **4**, 91580-98-2; **5**, 93646-74-3; **6**, 93646-75-4; **7**, 93646-77-6; **8**, 93646-79-8; **9**, 93683-47-7; **10**, 93646-81-2; **11** (X = I), 93646-83-4; **11** (X = Cl), 93646-86-7; **11** (X = Br), 93646-87-8; **12** (X = NCO), 77010-18-5; **12** (X = NCS), 93646-88-9; **13**, 91581-01-0; **14**, 91581-03-2; **15** (isomer I), 91581-12-3; **15** (isomer II), 93646-85-6; **16**, 91581-00-9; *trans*-$[RhCl(CO)(dppm)]_2$, 22427-58-3.

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# Modeling Macroscale Metal Vapor Reactions: Synthesis of Bis($\eta^6$-naphthalene)titanium

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The interaction of metal vapors of Cr, V, and Ti with naphthalene, and selected naphthalene derivatives, has been studied by means of matrix-isolation UV-visible spectroscopy. The electronic spectra of the Cr and V products are analyzed in terms of their known bis($\eta^6$-arene)metal conformations via a simple molecular orbital ordering scheme. On the basis of the data for Cr and V, the spectra of the Ti species appear to be best assigned to an analogous bis($\eta^6$-naphthalene)titanium complex. Preliminary studies on the reactivity of this complex reveal that it is apparently thermally stable at 290 K under matrix conditions, although it exhibits high reactivity toward ether solvents even at 190 K.

## Introduction

Metal vapor synthesis is now recognized as providing a valuable route to a wide range of organometallic complexes.[1] Indeed, a number of metal species have been generated from metal vapors for which no conventional synthesis exists. Molecules such as $(\eta^6\text{-}C_6H_{6-n}Me_n)_2M$ (M = Ti, Nb, Ta),[2,3] $(\eta^4\text{-}C_8H_{12})_2Fe$,[4] and $(\eta^6\text{-}C_6H_{6-n}Me_n)_2MPMe_3$ (M = Zr, Hf)[3,5] were unknown prior to their metal vapor preparations and still can be accessed only in this way.

Recently, it has been reported that naphthalene interacts with chromium, molybdenum, or vanadium vapors under macroscale synthetic conditions, by either cocondensation of reagents at 77 K or deposition of metals into solutions containing the aromatic molecule at 150 K, to give the corresponding bis($\eta^6$-naphthalene)metal complexes.[6,7] This represents an important new area for study in metal vapor chemistry; no conventional route exists for the preparation of homoleptic (naphthalene)metal complexes (the well-known Fischer–Hafner synthetic scheme

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**Table I.** UV–Visible Absorption Data[a] for Metal–Naphthalene Complexes and Their Derivatives

| M | naphthalene | 1-methyl-naphthalene | 2-isopropyl-naphthalene | 2,6-diisopropyl-naphthalene | 1-eicosyl-naphthalene | 1,2,3,4-tetrahydro-naphthalene |
|---|---|---|---|---|---|---|
| Ti | 392, 440, 540[b] | | | | | |
| | (310) | | | | | (320) |
| | 382, 466[c] | 394, 450, 538 | 394, 450, 530 | 395, 450, 530 | 392, 442, 530 | 378, 460, 560 (w) |
| V | 370, 455, 545[b] | | | | | |
| | 362, 415, 468, 530[c] | 370, 455, 540 | 372, 445, 550 | 375, 440, 550 | 374, 450, 555 | 353, 472 |
| Cr | 350, 412, 480[b] | | | | | |
| | 350, 412, 490[c] | 354, 414, 480 | 356, 410, 485 | 358, 416, 482 | 354, 410, 482 | 340, 395, 440 (w) |

[a] λ in nm. [b] 150 K. [c] ≥220 K.

leading to hydrogenation of the ring),[8] and in addition, the apparent property of naphthalene complexes to undergo an $\eta^6 \rightarrow \eta^4$ haptotropic rearrangement results in, for example, the chromium complex exhibiting an extensive ligand-displacement chemistry under very mild conditions.[6]

There has been a suggestion that titanium vapor and 1-methylnaphthalene yield a complex, possibly bis(arene)titanium.[6] When viewed in context of the elegant studies by Green and co-workers on the reaction of Ti, Zr, and Hf with $C_6H_{6-n}Me_n$,[2,3,5] the coupling of a 16-electron $(\eta^6\text{-}C_{10}H_8)_2Ti$ complex with an $\eta^6 \rightarrow \eta^4$ haptotropic rearrangement should provide an important precursor for a wide range of new complexes, but also a catalytically active species by virtue of its ability to readily become highly coordinatively unsaturated. Such catalytic behavior is now well-known for mono(naphthalene)metal species.[9]

The modeling of macroscale metal vapor cocondensation or solution procedures by matrix-isolation spectroscopic techniques has proven invaluable for the study of a small number of pivotal metal vapor reactions.[10,11] Fundamental information about the products formed in the metal vapor reaction itself, as well as the fate of the low-temperature species on warming the matrix, have contributed toward elucidation of previously investigated macroscale reactions in which the products were too unstable to be precisely defined.

Furthermore, this microscale technique is ideally suited for a preliminary exploration of the synthesis and structure of novel systems. We have now begun to use this technique to investigate new binary (naphthalene)metal complexes, in particular those of group 4a. In this paper we initially present our results for the reaction of chromium and vanadium vapor with naphthalene derivatives, thereby demonstrating the feasibility of the microscale method for modeling the macroscale metal vapor–naphthalene syntheses. In addition, we present for the first time the electronic spectral data for the bis($\eta^6$-naphthalene)chromium and -vanadium species and provide a rationale of these spectra in terms of a simple molecular orbital ordering scheme. Using this information, we then probe the corresponding reactions of titanium vapor and show that the best assignment of the observed data is to a novel, highly reactive bis($\eta^6$-naphthalene)titanium complex.

## Experimental Section

**Fluid Matrix Technique.** This method has been described in detail previously.[10] In this set of experiments, the ligand (a liquid naphthalene derivative) was applied to the surface of a quartz optical window, within a metal vapor matrix-isolation spectroscopic apparatus. The furnace and shroud were evacuated, and the window was cooled to the desired temperature (250–270 K) by means of an Air-Products Displex closed-cycle helium refrigeration system.

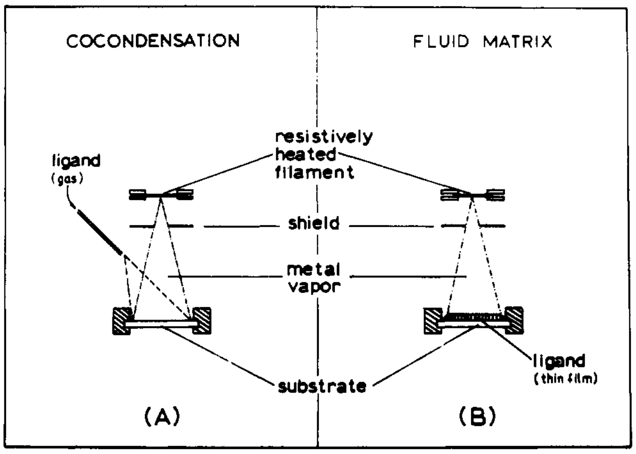

**Figure 1.** Schematic of (A) cocondensation and (B) fluid matrix metal vapor matrix-isolation experiments.

The transition-metal vapors originating from a resistively heated filament (titanium, 99.96%; vanadium, 99.7%; Alfa Ventron), Vacuum), from a tantalum Knudsen cell containing the desired metal powder (chromium, 99%; Alfa Ventron), were deposited into a thin film of the ligand at $10^{-7}$ torr (Figure 1). The ensuing reactions were monitored by means of UV–visible spectroscopy, using a Varian DMS 90 spectrometer.

The fluid matrix technique was found to be suitable for studies with 1-eicosylnaphthalene (Edwards High Vacuum), 2-isopropylnaphthalene (American Cyanamid Co., 99% purity), and 2,6-diisopropylnaphthalene (American Cyanamid Co., 96% purity[12]).

**Condensation Experiments.** Naphthalene (Mallinckrodt, purified) or 1-methylnaphthalene (Aldrich, 97%[13]) was placed in a flask connected to the matrix shroud via the gas inlet line. The ligand and metal vapors were then cocondensed on the quartz specimen holder cooled to 150 K (Figure 1). Heating of the matrix to above 220 K after codeposition allowed the uncomplexed naphthalene to be sublimed from the window. However, 1-methylnaphthalene could not be easily removed without disturbing the optical quality of the matrix, due to its tendency to flow at the temperature necessary for evaporation of the excess ligand. Cocondensations of 1,2,3,4-tetrahydronaphthalene (Tetralin) (Alfa Ventron, 99%, redistilled under vacuum) were carried out in a similar manner, but with the quartz window cooled to 120 K.

In a separate series of experiments, a 20% solution of naphthalene in tetraethylene glycol dimethyl ether (Tetraglyme) (Aldrich, 99%) was cocondensed with the metal vapors. The experimental conditions were similar to those described above. The choice of tetraglyme as diluent was dictated by the known solubility of bis(naphthalene)metal complexes in ethers,[6] but also by the similar vapor pressures of naphthalene and tetraglyme, which result in the condensed matrix having approximately the same composition as the starting solution. After completion of the reaction, tetraglyme and excess naphthalene were removed as before.

Calibration of the rate of metal deposition was performed by means of a quartz crystal microbalance[1] (AT-cut quartz wafer, C.R. Snellgrove

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(12) The impurity in the 2,6-diisopropylnaphthalene is listed by the supplier as 2-isopropylnaphthalene.

(13) The impurity in the 1-methylnaphthalene is the 2-isomer.

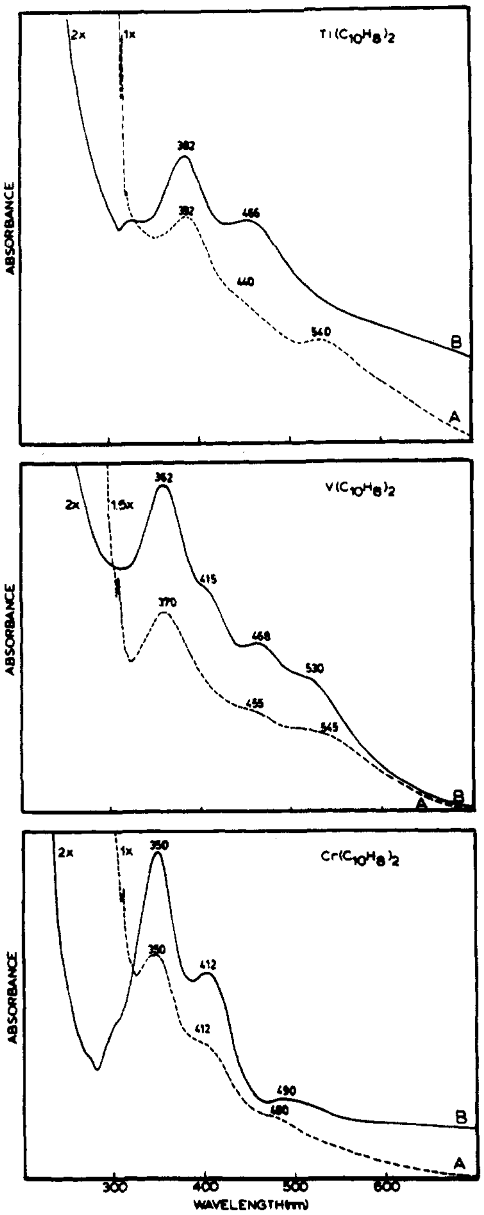


**Figure 2.** Ultraviolet–visible spectra obtained after the cocondensation of metal vapors with naphthalene at 150 K: (A) spectrum obtained at 150 K; (B) spectrum obtained after removal of excess naphthalene at ~220 K.

Ltd., Ontario, Canada) positioned directly behind the metal filament. Due to geometric factors, there is a discrepancy between the metal flow at the sample and that at the microbalance. This ratio was evaluated for a given metal filament by mounting a second microbalance in place of the specimen holder. The metal flow at the sample position was found to be about 37% of that at the mass monitor. The relative proportions of metal to ligand in the cocondensation reactions were established for naphthalene by measuring the absorbance of the ligand deposited on the sample holder as a function of gas flow, assuming a constant concentration approximately equal to the density of solid naphthalene. For the naphthalene–metal systems, the metal-to-ligand ratio was typically on the order of 1:400.

## Results

In the case of naphthalene itself, or when the naphthalene ring is substituted (1-; 2-; or 2,6-), product formation initially results in the appearance of three bands in the UV–visible spectrum (Figures 2A and 3; Table I). A first band occurs between 350 and 394 nm, depending on the nature of the metal, while the second band appears in the region 400–450 nm, moving to lower energy and decreasing in intensity on going from chromium to vanadium but then moving to the blue by ~10 nm on passing from vanadium to titanium. The third band, which occurs in the region 480–550 nm, also behaves in a seemingly irregular way. Not only do its shape and intensity change dramatically along the series, but it shifts to lower energy from Cr → V and then to higher energy for V → Ti. These observations suggest either that the orgin of the latter two transitions is not constant for the three metals or that the titanium complex possesses a structure different from that of chromium or vanadium.

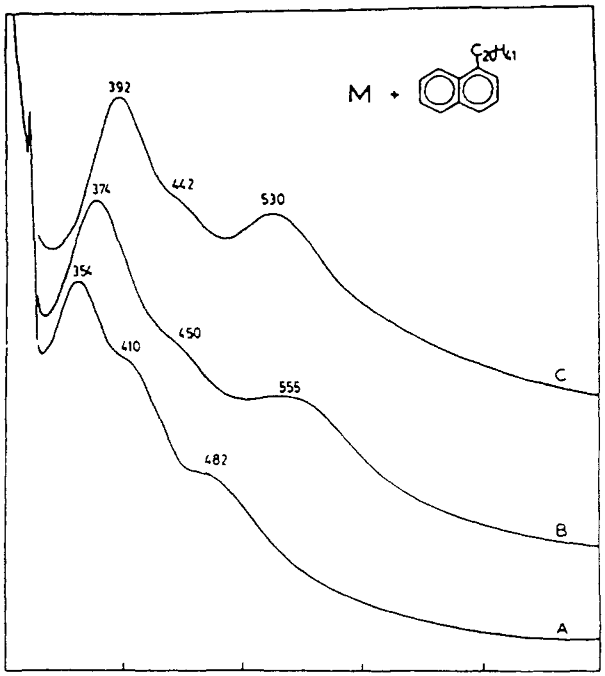


**Figure 3.** Ultraviolet–visible spectra arising from the deposition of metal vapors into a thin film of 1-eicosylnaphthalene at 270 K: (A) Cr vapor; (B) V vapor; (C) Ti vapor.

A unique feature of the cocondensations of metal vapors with naphthalene at 150 K is that it is possible to sublime away the excess ligand, leaving only a metal species trapped on the matrix window. For chromium, removal of free naphthalene leads to sharpening of the two high-energy bands while the third band decreases in intensity and shifts slightly to lower energy (Figure 2; Cr, A → B). This final spectrum remains unchanged upon raising the temperature to 280 K, although on prolonged standing under dynamic vacuum at room temperature the complex is sufficiently volatile to be removed from the window. Similar behavior is also found for the naphthalene/tetraglyme system.

When the matrix resulting from the vanadium/naphthalene codepositon is warmed, removal of excess ligand is accompanied by a major change in the spectrum, yielding four new absorption maxima at 362, 415, 468, and 530 nm (Figure 2; V, A → B). Similarly, evaporation of the naphthalene host in the titanium case results in loss of the third band at 540 nm while the major band blue shifts and the 440-nm maximum moves to 466 nm (Figure 2; Ti, A → B). The latter remains intact on warming the matrix window to 290 K. However, when titanium is deposited with naphthalene and tetraglyme, warming of the matrix to 190 K results in the progressive decrease in intensity of the initially formed three bands, while two bands begin to appear at 610 and 695 nm. Further warming to 200 K yields a multiple-band spectrum, with maxima at 392, 410, 440, 480, 530, 610, and 695 nm. Finally, when the matrix is warmed to 210 K, all bands disappear, indicating decomposition of the matrix species.

The cocondensation of Tetralin with chromium, vanadium, or titanium at 120 K leads to electronic spectra (Table I) that are very similar to the literature spectra for the corresponding ($\eta^6$-$C_6H_6)_2M$ species,[14] apart from a 20–30-nm shift to the red for

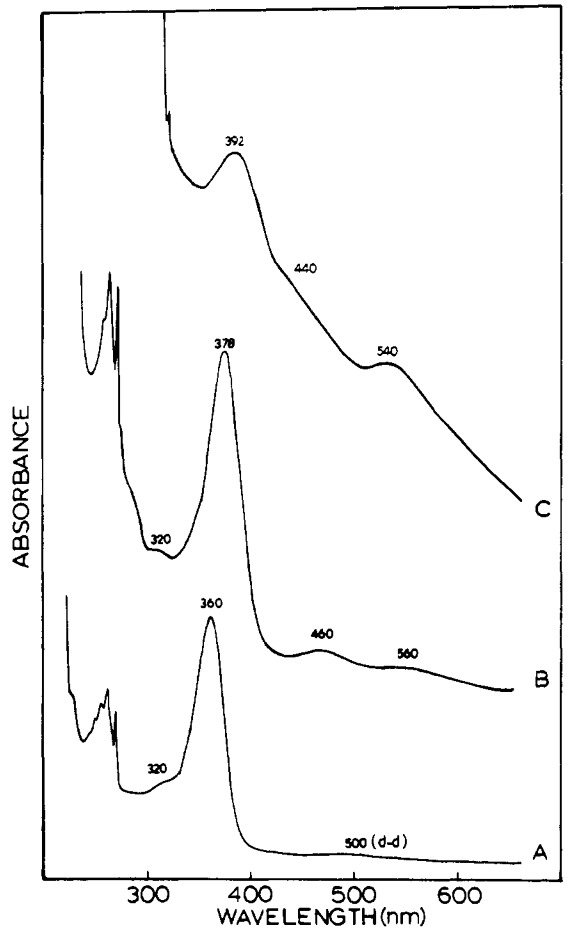


**Figure 4.** Comparison of the ultraviolet–visible spectra of (A) $(C_6H_5CH_3)_2Ti$, (B) $(C_{10}H_{12})_2Ti$, and (C) $(C_{10}H_8)_2Ti$. [$(C_6H_5CH_3)_2Ti$ was obtained by depositing Ti vapor into a thin film of toluene dissolved in methylcyclohexane cooled to 140 K; $(C_{10}H_{12})_2Ti$ was obtained by cocondensation of Tetralin with Ti vapor at 120K.]

the entire spectrum. [This is consistent with the general lack of sensitivity of these MLCT bands to the lowering of symmetry when substituents are placed on the ring (see for example Figure 4)].

## Discussion

It is now well established that the reaction of chromium vapor with naphthalene or 1-methylnaphthalene leads to the corresponding bis($\eta^6$-arene)chromium.[6,7,15] Although the vanadium complexes are not so well characterized, the available data point to their being the analogous bis($\eta^6$-arene)vanadium species.[6]

In the absence of electronic spectral data for these complexes, authentic samples of $(\eta^6\text{-}C_{10}H_8)_2Cr$ and $(\eta^6\text{-}C_{10}H_7Me)_2Cr$ were prepared by the method of Kündig and Timms.[6] Comparison of the spectra arising from the corresponding matrix syntheses (Figure 2; Table I) with those of macroscale samples[16] not only demonstrates that the matrix studies do mimic the macroscale metal vapor reactions but confirms that our matrix-isolation spectra can reasonably be assigned to bis($\eta^6$-arene)metal complexes.

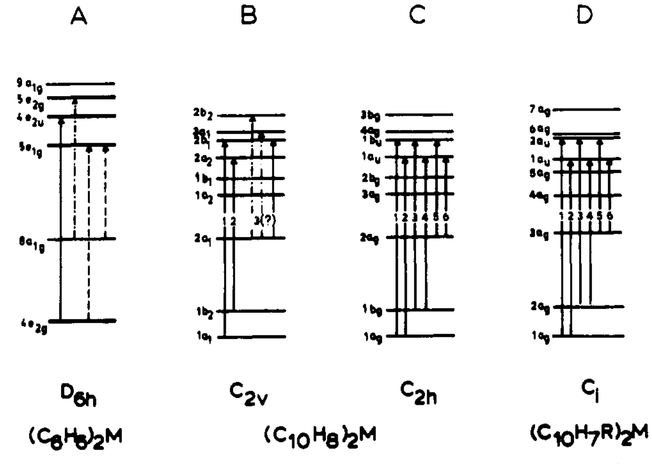
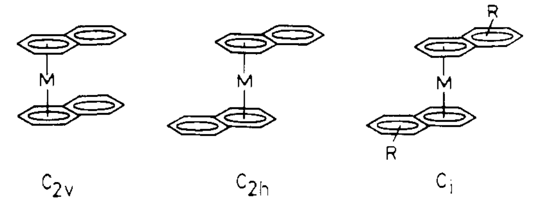


**Figure 5.** Qualitative molecular orbital ordering for (A) $(C_6H_6)_2M$,[18] (B and C) $(C_{10}H_8)_2M$, and (D) $(C_{10}H_7R)_2M$.

**Chart I**



A number of features of the spectra of the chromium and vanadium complexes are worthy of note. First, the electronic spectra of the (naphthalene)metal complexes are not sensitive to the presence of substituents on the naphthalene ring (Figures 2 and 3) and are only slightly affected by the substitution pattern (Table I). While one might expect the symmetry of the complex to be reduced on passing from naphthalene to the substituted naphthalene case, nevertheless this does not seem to induce dramatic changes in the spectra, an observation that can be made also for the benzene systems. This is most clearly revealed through a comparison of the bis(arene)metal complexes, for arene = naphthalene and 2,6-diisopropylnaphthalene, which are characterized by the same UV–visible spectra (Table I), apart from a 5–10-nm shift in the absorption maxima, when present in the host matrix. It is therefore not possible to distinguish interaction of the metal with a substituted vs. an unsubstituted ring in a ligand such as 1-methylnaphthalene. Note that it has been reported that chromium binds to the unsubstituted ring to the extent of 70% in 1-methylnaphthalene.[7]

Second, the UV–visible spectra of the $(\eta^6\text{-}C_{10}H_8)_2M$ (M = Cr, V) complexes are appreciably different from those of the analogous $(\eta^6\text{-}C_6H_6)_2M$ species (compare for example Figure 2 with ref 14). This point is highlighted by reference to the spectra for the Tetralin derivatives (Table I). While we have commented previously on the lack of sensitivity of the spectra of the bis(benzene)metal complexes to the lowering of symmetry when substituents are placed on the ring (as evidenced by Tetralin), our studies clearly reveal that naphthalene cannot be merely considered as an *ortho-disubstituted benzene ligand.*

These results represent the first report of the electronic spectra for the chromium- and vanadium–naphthalene sandwich complexes. It is also possible to probe the electronic structures of the complexes in a qualitative manner, through consideration of the nature of the observed transitions, and hence to assign a structure for the product of the titanium/naphthalene reaction.

As far as we are aware, no molecular orbital calculations have been carried out for a bis($\eta^6$-naphthalene)metal complex. On the basis of the ESR spectra of $[(\eta^6\text{-}C_{10}H_8)_2M]$ (M = V(0), Cr(I)), it has been suggested[17] that the ordering may resemble that for $(\eta^6\text{-}C_6H_6)_2Cr$. Our electronic spectroscopic studies indicate,

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(16) The UV–visible data for authentic samples of (naphthalene)chromium complexes are as follows [λ, nm (ε, L mol$^{-1}$ cm$^{-1}$)]: $[(C_{10}H_7CH_3)_2Cr]$ (in $C_6H_{12}$) 354 (10000), 405 (7500), 470 (3200); $[(C_{10}H_8)_2Cr]$ (in THF) 352 (10400), 405 (6400), 476 (2500).

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however, that this may not be appropriate. In the absence of suitable MO calculations, we have taken as our model the results of an SCF-X$\alpha$ calculation for $(\eta^6\text{-}C_6H_6)_2Cr$,[18] with an assumed $D_{6h}$ symmetry, *but* we have considered further the lowering of symmetry on passing from a coordinated benzene to naphthalene ring.[19] Although only approximate, this approach provides an overall picture that is more consistent with an actual $(\eta^6\text{-}C_{10}H_8)_2M$ MO scheme.

The effect on the MO ordering of changing the symmetry from $D_{6h}$ to $C_{2v}$ or $C_{2h}$ (see Chart I) is shown qualitatively in Figure 5A–C, respectively, with the transitions allowed (by dipole selection rules) for $C_{2v}$ and (by Laporte and dipole selection rules) for $C_{2h}$ symmetry. d–d transitions may occur, although they will not be discussed here. In Figure 5D is also shown a MO ordering for $(\eta^6\text{-}C_{10}H_7R)_2M$, with assumed $C_i$ symmetry.[20]

While $(\eta^6\text{-}C_{10}H_8)_2Cr$ has been shown[15] to crystallize with $C_{2v}$ symmetry, the $C_{2h}$ (trans) form may coexist within a frozen or fluid matrix. In addition, reorientation of the naphthalene rings may occur in a similar manner to that observed for various $(\eta^6\text{-}C_6H_6)_2M$ species by NMR,[21] ESR,[22] and ENDOR[23] techniques.

Focusing on the electronic spectra, a consistent interpretation can be obtained if we reason in terms of a $C_{2h}$ or pseudo-$C_{2h}$ ($C_i$) symmetry for all complexes. The regular shift of the three bands to lower energy on passing from Cr → V follows the same trend as that for the major absorption band in the benzene[14] and Tetralin[24] analogues and similarly may be assigned to MLCT transitions.[10] This assignment is further supported by the magnitude of the molar extinction coefficients for the macroscale chromium complexes,[16] which are in the range 5000–10000 L mol$^{-1}$ cm$^{-1}$. In Figure 5C we favor therefore the most intense, highest energy band as arising from transition 1/2 (?), with the second and third lower energy bands due to transitions 3/4 and 5/6, respectively.

**Titanium + Naphthalene and Alkylnaphthalene.** It is now possible to investigate the reactions of titanium vapor with various naphthalene ligands in light of the results for the chromium and vanadium complexes.

As in the case of Cr and V, the UV–visible spectrum obtained after codeposition of naphthalene and titanium vapor at 150 K (Figure 2A, top) is identical with those of the corresponding alkylnaphthalene derivatives (Figure 3C; Table I). The smooth shift to lower energy for the three absorption bands on passing from Cr → V, however, is interrupted when one moves to Ti (Figures 2 and 3). While it may be inferred that the Ti/naphthalene product is different, the band pattern is consistent with a $(\eta^6\text{-}C_{10}H_8)_2Ti$ complex with $C_{2h}$ symmetry. In view of the fact that a bis(arene) complex for a d$^4$ metal is a 16-electron species, the formally metal $d_{z^2}$ orbital ($2a_1$ in $C_{2v}$ symmetry; $2a_g$ in $C_{2h}$ symmetry) is vacant. With the qualitative nature of our MO scheme in mind, the three-band spectrum for the titanium complex eliminates a $C_{2v}$ form from our arguments since only two transitions are predicted to occur (Figure 5B).

**Table II.** Esimated Molar Extinction Coefficients and Tentative Assignments for the Electronic Spectra of the Bis(naphthalene)metal Complexes

| M | $\lambda_{max}$, nm | $\epsilon$, L mol$^{-1}$ cm$^{-1}$ | assgnt |
|---|---|---|---|
| Cr | 350 | 10200$^b$ | |
| V | 370 | 11200 | $1a_g \rightarrow 1b_u$ (1) |
| Ti | 392 | 10200 | |
| Cr | | | |
| V | | | |
| Ti | 440 | 6800 | $1a_g \rightarrow 1a_u$ (2) |
| Cr | 412 | 7700$^b$ | |
| V | 455 | 7400 | $1b_g \rightarrow 1b_u/1a_u$ (3/4) |
| Ti | 540 | 8500 | |
| Cr | 480 | 4100$^b$ | |
| V | 545 | 4100 | $2a_g \rightarrow 1b_u/1a_u$ (5/6) |
| Ti | *a* | | |

[a] Not allowed for bis($\eta^6$-naphthalene)metal. [b] See ref 16.

Reference to Figure 2 (dotted-line spectra) and Figure 3 reveals that the highest energy band for Ti, occurring at 392nm, is in line with the corresponding bands for Cr and V and may similarly be assigned to transition 1 in Figure 5C. Since transitions 5/6 will not exist for a d$^4$ system, the lowest energy band of Cr and V should not occur on passing to Ti. Extrapolation of the observed series would place the band in the range 600–700 nm, a region that is totally clear for Ti. We now see that, rather than an irregular sequence of bands, in fact a smooth trend is observed in which the lowest energy band for Ti, occurring at 530–540 nm, arises from transitions 3/4 and is the counterpart to the second transition in the Cr and V systems. The second band in Ti may then be assigned to transition 2, a transition that is obscured for Cr and V, although it appears on warm-up for the latter.

An estimate has been made for the molar extinction coefficients[25] for the three bands observed in the spectra of the $(\eta^6\text{-}C_{10}H_8)_2M$ complexes on deposition (Table II). Apart from the fairly good agreement between the $\epsilon$ values for chromium and those measured in solution for authentic samples,[16] they also corroborate our assignments by exhibiting a constant value for any given band along the metal series. The existence of bent-back arene complexes for group 4 metals must be taken into consideration at this stage. Zr and Hf are known[3,5] to form complexes of the type $(arene)_2MPR_3$. For a bent-back (naphthalene)metal species to be formed in these studies, one may envisage a third arene acting as a $\eta^2$ ligand, a species similar to that postulated in previous Zr–toluene microsolution studies.[11] Alternatively, one may conceive formation of an ($\eta^6$-naphthalene)($\eta^4$-naphthalene)$_2$metal (18-electron) species. Naphthalene has been shown to bind in an $\eta^4$ fashion in $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$[26] and in $(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}OMN)$ (OMN = octamethylnaphthalene).[27] We believe however that the evidence mitigates against such possibilities, the electronic spectrum of the titanium complex being entirely consistent with a $(\eta^6\text{-}C_{10}H_8)_2Ti$ assignment. The results arising from the Ti codeposition with naphthalene/tetraglyme at 150 K tend to support this argument, as well as provide an indication of the high reactivity of the titanium complex. On deposition, three bands are observed that may be superimposed on those arising from the neat naphthalene or alkylnaphthalene reactions. If a bent $(arene)_2ML$ species is indeed being formed in this reaction, the

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(19) A unique feature of naphthalene relative to benzene is that the ligand represents formally a 10-electron $\pi$ system. The additional "butadiene-like" orbitals, while they do not take part in the bonding, present high-lying levels that may become occupied in the excited state. While this may offer an alternative explanation for the differences in the spectra of $(C_6H_6)_2M$ and $(C_{10}H_8)_2M$, nothing further can be deduced in the absence of a detailed molecular orbital calculation.

(20) On passing to lower symmetry forms for $(C_{10}H_7R)_2M$, the number of allowed transitions renders a qualitative analysis not at all meaningful. The preferred conformation may be expected to be the trans ($C_i$) form since it minimizes interaction between the alkyl groups, particularly for bulkier groups such as isopropyl or eicosyl.

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(25) Molar extinction coefficients for the matrix-isolated $(C_{10}H_8)_2M$ were determined by measuring the amount of metal depositing onto the window during the metal evaporation and assuming that, under the experimental conditions, the metal is quantitatively converted into the complex. The volume of the matrix and the path length were estimated from the absorbance of the band in free naphthalene at 312 nm ($\epsilon$ 289).

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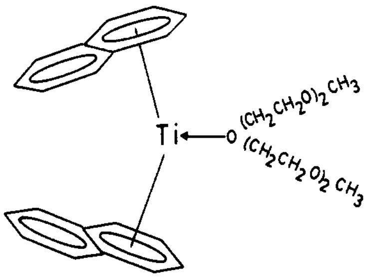
(27) Hull, J. W.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605.

UV–visible spectrum should be sensitive to the nature of L.[11] In a strongly coordinating solvent such as tetraglyme, it is anticipated that the ether molecule should preferentially provide the extra ligand. The insensitivity of the initial spectrum to the presence of the tetraglyme suggests therefore that the low-temperature species in each case is merely an ($\eta^6$-naphthalene)$_2$titanium complex. However, the decay of the original spectrum on warming above 150 K accompanied by the growth of new bands appears more consistent with an increasing participation of the ether in the coordination sphere around titanium. One may postulate that a species such as I may be responsible for the new spectrum, representing the first step on the path to decomposition of the complex at 190 K.



I

This extremely high reactivity of the ($\eta^6$-$C_{10}H_8$)$_2$Ti complex may be compared with that of ($\eta^6$-$C_6H_6$)$_2$Ti, which is reported not to react with tetrahydrofuran even at elevated temperatures (<100 °C) although it does bring about deoxygenation of some alcohols and ketones.[28] While the greater reactivity may be attributable to the anticipated lower Ti–arene bond energy for arene ≡ naphthalene vs. benzene,[29] it also is plausible that an $\eta^6 \rightarrow \eta^4$ rearrangement may facilitate the initial interaction of ether molecules.

In Figure 4 is illustrated the variation of the electronic spectra of the bis($\eta^6$-arene)titanium complexes, for the series toluene (A), tetrahydronaphthalene (B), and naphthalene (C), demonstrating the similarity between the toluene and tetrahydronaphthalene cases and clearly showing the difference when the ligand is a fused aromatic ring system. It is interesting to note the band at 320 nm in the (toluene)$_2$titanium and (Tetralin)$_2$titanium spectra, which has not previously been reported for the bis(arene)titanium system[14] but may arise from a LMCT transition to the vacant metal $a_{1g}$ orbital.

Finally, thus far we have focused our discussion on the spectra of the bis(arene)metal complexes in the presence of excess ligand. A number of interesting changes are observed (Figure 2) upon removal of the host matrix. Several factors may be reflected: (i) At 150 K, the matrix can be regarded as rigid so that no rearrangement or diffusion of the trapped species can occur. When the temperature is raised, annealing of the matrix may result in reorganization toward the most stable structure. Note that the high-temperature forms of the Cr and Ti species (Figure 2B) may be explained in terms of the $C_{2v}$ symmetry[30] (Figure 5B). (ii) Alternatively, the spectra may reflect a solid-state effect, which is known to induce changes in the band intensities and bandwidths. (iii) In the case of the vanadium complex, a 17-electron species, the existence of an interaction of the type $(C_{10}H_8)_2V\text{---}V(C_{10}H_8)_2$ appears possible after evaporation of the free naphthalene. Such an interaction would cause slight energy perturbations in the metal-centered orbitals, resulting in small shifts in the band positions. This seems to be the best rationale for the observed four-band pattern (Figure 2B), where a blue shift of the first MLCT reveals a previously obscured shoulder at 415 nm (see Table II).

## Conclusions

The major observation from this study is that a highly reactive titanium–naphthalene complex does exist, which is stable to room temperature. On the basis of available spectroscopic data, we believe that this is best explained in terms of a bis($\eta^6$-naphthalene)titanium complex. While the macroscale interaction of titanium vapor with naphthalene has been reported previously to yield a red solution,[6] it is this observed reactivity that has presumably precluded its identification to date. This aspect reflects an important feature of the microscale modeling reaction, namely that one can preview a macroscale metal vapor reaction by providing an initial characterization of the products as well as information regarding their oxidative and thermal stability.

In this study we have also sought to provide some rationalization of the electronic transitions in the bis(naphthalene)metal complexes. However it must be stressed that this approach is at best qualitative. Obviously, detailed molecular orbital calculations and further spectroscopic and magnetic studies are required before the ($\eta^6$-$C_{10}H_8$)$_2$M complexes are understood in as much detail as their benzene analogues.

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**Registry No.** ($\eta^6$-$C_{10}H_8$)$_2$Ti, 93646-09-4; ($\eta^6$-$C_{10}H_7$Me)$_2$Ti, 93646-10-7; ($\eta^6$-$C_{10}H_7$-*i*-Pr)$_2$Ti, 93646-11-8; ($\eta^6$-$C_{10}H_6$(*i*-Pr)$_2$)$_2$Ti, 93646-12-9; ($\eta^6$-$C_{10}H_7(C_{20}H_{41})$)$_2$Ti, 93646-13-0; ($\eta^6$-$C_{10}H_{12}$)$_2$Ti, 93646-22-1; ($\eta^6$-$C_{10}H_8$)$_2$V, 31833-27-9; ($\eta^6$-$C_{10}H_7$Me)$_2$V, 93646-14-1; ($\eta^6$-$C_{10}H_7$-*i*-Pr)$_2$V, 93646-15-2; ($\eta^6$-$C_{10}H_6$(*i*-Pr)$_2$)$_2$V, 93683-44-4; ($\eta^6$-$C_{10}H_7(C_{20}H_{41})$)$_2$V, 93646-16-3; ($\eta^6$-$C_{10}H_{12}$)$_2$V, 93646-17-4; ($\eta^6$-$C_{10}H_8$)$_2$Cr, 33085-81-3; ($\eta^6$-$C_{10}H_7$Me)$_2$Cr, 74453-92-2; ($\eta^6$-$C_{10}H_7$-*i*-Pr)$_2$Cr, 93646-18-5; ($\eta^6$-$C_{10}H_6$(*i*-Pr)$_2$)$_2$Cr, 93646-19-6; ($\eta^6$-$C_{10}H_7(C_{20}H_{41})$)$_2$Cr, 93646-20-9; ($\eta^6$-$C_{10}H_{12}$)$_2$Cr, 93646-21-0; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; ($C_6H_5CH_3$)$_2$Ti, 55527-82-7; naphthalene, 91-20-3; 1-methylnaphthalene, 90-12-0; 2-isopropylnaphthalene, 2027-17-0; 2,6-diisopropylnaphthalene, 24157-81-1; 1-eicosylnaphthalene, 93646-23-2; 1,2,3,4-tetrahydronaphthalene, 119-64-2; toluene, 108-88-3.

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(30) UV–visible studies performed in our laboratories on the bis(naphthalene)chromium complex indicate that the intensity of the 476-nm band is solvent dependent. This suggests that this transition shows some d–d character.