(0.0048 mol), and the mixture was stirred at room temperature for 2 h (GLC on column B was used as control). After standard workup, there was obtained 19, which was identical with that prepared from *N*,*N*-dichlorourethane and methyl acrylate:[26] yield 57% (GLC data).

Registry No. 1a, 754-05-2; 1c, 1112-54-5; 1d, 13683-41-5; 1e, 18276-17-0; 1f, 97042-85-8; 2a, 16487-46-0; 2b, 13698-16-3; 3a, 91935-98-7; 3b, 97042-67-6; 3c, 97042-68-7; 3d, 97042-69-8; 3e, 97042-70-1; 3f, 97042-71-2; 4a, 91935-99-8; 4b, 97042-72-3; 4c,

97042-73-4; 4d, 97042-74-5; 4e, 97059-47-7; 4f, 97042-75-6; 5, 473-34-7; 7a, 97042-76-7; 7c, 97042-84-7; 7d, 97042-77-8; 9, 762-72-1; 10, 91936-03-7; 11, 91936-04-8; 12, 97042-78-9; 13a, 91936-00-4; 13b, 97042-79-0; 13c, 97042-80-3; 14, 97042-81-4; 15, 91936-05-9; 16, 97042-82-5; 18, 97042-83-6; 19, 13698-14-1; CH_2=CHBr, 593-60-2.

Supplementary Material Available: Tables IV and VII, mass spectra (3 pages). Ordering information is given on any current masthead page.

Modeling Macroscale Metal Vapor Reactions. 2.[†] Bis(arene)iron Revisited

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The reaction of iron vapor with naphthalene and 1-methylnaphthalene was studied by metal atom matrix optical spectroscopy in the temperature range 30–290 K. Two different products were obtained, which have been assigned to a highly unstable, 16-electron bis(η^4-naphthalene)iron(0) and a room-temperature-stable, 20-electron bis(η^6-naphthalene)iron(0) species. The former is observed in the range 30–77 K, while the latter forms at $T \geq 150$ K. Assignments for these complexes were based on an extensive study involving iron atoms and selected arene ligands, also including cyclohexadiene as a model for η^4-binding.

Introduction

The versatility of arene ligands in their mode of coordination to transition metals represents a fundamental concept in the current understanding of homogeneous[1] and heterogeneous[2] catalytic processes involving aromatic molecules. Interest in such systems has resulted in an extensive research effort directed toward the structural, electronic, and catalytic properties of (arene)metal complexes.[3] Our studies have recently focused on the interaction of iron atoms with aromatic molecules, the primary motivation being our interest in the ligand properties of fused rings such as naphthalene.[4] In addition, we[5] and others[6] have shown that thermally unstable complexes, specifically bis(toluene)iron, provide valuable precursors for the preparation of supported metal particles. The need to obtain precisely defined materials by reproducible doping procedures has prompted us to pose several questions regarding the nature and behavior of the products formed when iron atoms are allowed to react with aromatic ligands at low temperature.

It is perhaps surprising that, in spite of the considerable attention the Fe/arene system has received, the identity of the initially formed species remains unresolved. Although the product can be intercepted at low temperature by stabilizing ligands, such as phosphine, phosphite, or selected dienes,[7] resulting in the isolation of complexes of the form (η^6-arene)FeL$_n$, its poor thermal stability has prevented its definitive characterization in macroscale metal vapor reactions.

Attempts to elucidate the nature of the product by matrix-isolation spectroscopic studies have led so far to differing conclusions. It has been reported,[8] on the basis of infrared spectroscopy, that iron reacts with benzene in

C_6H_6/Ar matrices at 10–12 K *and* in pure C_6H_6 matrices at 77 K to yield a monoarene species, (η^6-C_6H_6)Fe. However, other workers have expressed their preference for a bis(arene)iron formulation.[9,10] Indeed, it could be argued that one would not anticipate a monoarene complex to be favored in neat C_6H_6 matrices. The reaction of iron with toluene in solution-phase experiments at 150 K,[11] as observed by UV–visible spectroscopy, reveals the formation of a single species, suggested to be (η^6-$C_6H_5CH_3$)Fe(η^4-$C_6H_5CH_3$), *but* two species on cocondensation at 77 K, viz., the η^6:η^4 complex and another species of uncertain composition. Keeping in mind the existence of (η^6-C_6Me_6)$_2$Fe,[12]

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(5) Radford, P. P.; Francis, C. G. *J. Chem. Soc., Chem. Commun.* 1983, 1520.

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[†]For part 1 of this series, see: Morand, P. D.; Francis, C. G. *Inorg. Chem.* 1985, *24*, 56.

one possible conformation for the second species may be a 20-electron $\eta^6{:}\eta^6$ bis(arene)iron. However, another possibility may be a 16-electron[13] $\eta^4{:}\eta^4$ complex similar to that postulated as an intermediate in the ring exchange process observed for $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_6Me_6)$.[3c]

In this paper, we present the results from a matrix-isolation spectroscopic study (UV–visible, infrared) designed to provide an overall rationalization of the reaction of iron atoms with arenes. An initial reinvestigation of the arene = benzene and toluene cases has revealed a number of new features about these systems. The importance of η^6- and η^4-bonding of arenes, when viewed in the context of our previous studies of naphthalene with early transition metals,[4] indicated that naphthalene would constitute an excellent ligand for study because of its demonstrated ability to stabilize an η^4-binding mode[14] in addition to the "normal" η^6-mode, as well as the apparent readiness of η^6-naphthalene complexes to undergo a haptotropic rearrangement involving an $\eta^6 \rightarrow \eta^4$ ring slippage.[15] Finally, results from the reaction of iron atoms with cyclohexa-1,3-diene have been included as representative of binding of iron to a conjugated diene ligand.

The nature and behavior of these species are demonstrated to shed some doubt on the presupposed identity of the low-temperature form of the bis(arene)iron(0) moieties.

Experimental Section

Iron vapor was generated by resistive heating of an iron filament (Johnson Matthey, 99.998%, 0.25 mm thick). 1-Methylnaphthalene (Aldrich, 97%) and 1,2,3,4-tetrahydronaphthalene (Alfa Ventron, 99%) were redistilled under vacuum prior to use. Naphthalene (Mallinckrodt, purified), hexamethylbenzene (Aldrich, 99+%), and benzene (Matheson, Collman and Bell, spectro grade) were used without further purification. The reagents were codeposited with iron vapor onto an optical window [quartz (UV–visible), KBr (infrared)] cooled to the desired temperature by means of an Air Products Displex closed-cycle helium refrigerator within a standard matrix apparatus. Cocondensation and microsolution experiments using a 10% solution of toluene (reagent grade, dried over Na and distilled under N_2) in methylcyclohexane (Eastman Kodak, spectro grade) have been described elsewhere.[11] 1,3-Cyclohexadiene (Alfa Ventron, 98%) was used as a 10% solution in methylcyclohexane for cocondensation experiments monitored by UV–visible and infrared spectroscopies. In addition, infrared experiments were performed by using neat 1,3-cyclohexadiene.

The rates of metal and ligand depositions were calibrated as previously described.[4] Deposition rates were typically 0.2 $\mu mol/h$ for the metal and $\sim$40 $\mu mol/h$ for the ligand, which gave a final metal-to-ligand ratio of $\sim$1:200. UV–visible spectra were recorded on a Varian DMS 90 spectrophotometer and infrared spectra on a Perkin-Elmer 1330 IR spectrophotometer.

Results

Fe/C_6Me_6. Due to its low vapor pressure at room temperature, solid hexamethylbenzene was heated slightly for

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(13) Although all bis(arene)iron complexes are formally 20-electron species (as a whole), we will use the 16- or 18-electron designation throughout this paper when referring to an $\eta^4{:}\eta^4$ or $\eta^6{:}\eta^6$ complex, respectively, thereby only considering, in addition to the metal electrons, those on the ligand directly involved in the bonding.

(14) (a) Albright, J. O.; Brown, L. D.; Datta, S.; Kouba, J. K.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 5518. Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611. (b) Gladfelter, W. L.; Hull, J. W. *Organometallics* **1984**, *3*, 605.

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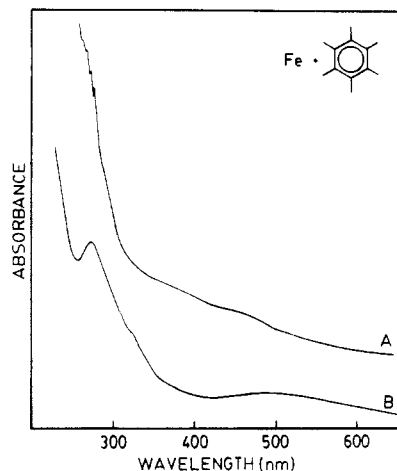

Figure 1. Optical spectrum obtained (A) on depositing Fe atoms with C_6Me_6 at 77 K and (B) after removal of the excess ligand at 280 K.
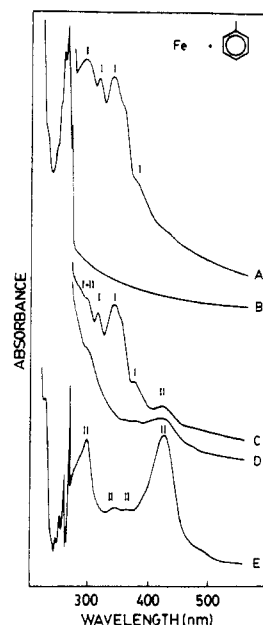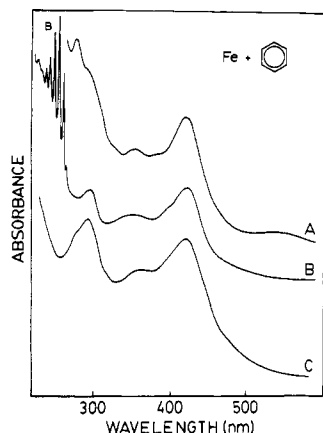

Figure 2. Results of cocondensation and microsolution studies for Fe + $C_6H_5CH_3/C_6H_{11}CH_3$ (1:10): (A) spectrum obtained after cocondensation at 50 K followed by (B) warming to 100 K; (C) spectrum obtained after cocondensation at 77 K followed by (D) warming to 150 K; (E) spectrum obtained on depositing Fe atoms into toluene/methylcyclohexane solution at 150 K (see Table I and text for I and II notation).

the cocondensation experiments. Codeposition with iron vapor at 77 and 150 K produced a complex with the electronic spectrum shown in Figure 1A. A weak, broad band is discernible in the visible ($\lambda_{max} \simeq$ 470 nm), the ultraviolet region being masked by the strong π–π^* transitions of the excess ligand. After completion of the cocondensation, it was possible to remove the excess ligand from the matrix by warming to 280 K under dynamic vacuum, leaving only the complex on the optical support (in this particular study, KBr). The electronic spectrum (Figure 1B) of this room-temperature-stable complex consists of a strong absorption at 278 nm, accompanied by a shoulder at 322 nm. A weak band covering the entire visible region is also seen with a maximum at 480–500 nm.

Fe/$C_6H_5CH_3/C_6H_{11}CH_3$ (1:10). On cocondensation at 50 K, a yellow complex is obtained with absorptions at 298, 315, 336, 358, and 380 nm (Figure 2A). This species decomposes at 100 K, apparently to metal and ligand. No

Figure 3. Optical spectra obtained after cocondensation of Fe vapor and C_6H_6 (A) at 15 K, 1:20 matrix, and (B) 15 K, 1:50 matrix, and (C) spectrum of the complex after removal of unreacted C_6H_6 at 170 K (B = benzene).

other species is observed to form on warming this matrix to 150 K (Figure 2B).

The spectra of the products obtained by cocondensation of metal and ligand at 77 K (Figure 2C) and by deposition of Fe vapor into a $C_6H_5CH_3/C_6H_{11}CH_3$ microsolution at 150 K (Figure 2E) are in good agreement with those obtained previously.[11] The 77 K spectrum reveals bands at 298, 314, 336, 358, 380, and 427 nm, while that at 150 K contains bands at 298 (with components at 285 and 278 nm), 350, 365,[16] 390, 427, and 470 nm.[17]

In the temperature range 160–180 K, the solvent mixture evaporates, and subsequent warming of the complex left on the optical support results in its decomposition at ~240 K.

Fe/C_6H_6. Cocondensation of Fe vapor with benzene was carried out at 15 and 50 K. At 15 K, in dilute matrices (1:50 and above), an orange complex forms with an electronic spectrum showing absorptions at 298, 350, 390, 424, and 470 nm (Figure 3B). In more concentrated matrices (1:20), new bands appear at 278, 320, and 540 nm (Figure 3A) on top of the spectrum described above. These bands remain unperturbed on warming to at least 50 K, the opacity of the benzene matrix at and above 77 K preventing further observation.

The spectrum obtained following cocondensation at 50 K (Figure 4A) is identical with that obtained at 15 K (1:50 matrix), independent of the matrix concentration. Rapidly warming this matrix to 170 K, followed by recooling to 140 K, allows removal of the unreacted benzene (Figure 3C), revealing a shoulder at 278 nm on the side of the 298-nm band. Decomposition of the complex is observed around 200–210 K.

The infrared spectrum taken after reaction at 50 K reveals bands at 1450, 1440, 968, 775, 475, and 440 cm^{-1}. However, on warming, we were unable to retain the complex on the optical window in sufficient quantity for spectroscopic study.

Fe/C_6H_8. When Fe vapor is codeposited with a 1,3-$C_6H_8/C_6H_{11}CH_3$ (1:10) solution at 80 K, an electronic spectrum with maxima at 315, 338, 356, and 378 nm is observed (Figure 5A). Warming the matrix to 100 K results in the loss of the spectral features, indicating decomposition of the complex. The same reaction at $T \le$

Figure 4. Comparison between the matrix spectra following (A) Fe/C_6H_6 cocondensation at 50 K, (B) deposition of iron atoms into $C_6H_5CH_3/C_6H_{11}CH_3$ (1:10) at 150 K (see also Figure 2E), and (C) Fe/$C_{10}H_{12}$ cocondensation at 77 or 150 K (B = benzene, T = toluene, TNp = tetrahydronaphthalene).
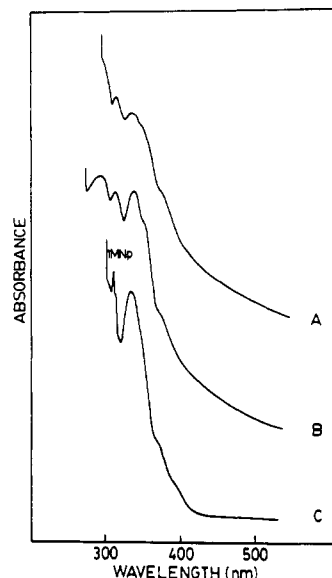
Figure 5. Comparison between the matrix spectra obtained following (A) codeposition of Fe atoms with 1,3-$C_6H_8/C_6H_{11}CH_3$ (1:10) solution at 80 K, (B) Fe/$C_6H_5CH_3/C_6H_{11}CH_3$ cocondensation at 50 K (see also Figure 2A), and (C) Fe/1-methylnaphthalene cocondensation at 77 K (see also Figure 6A) (1MNp = 1-methylnaphthalene).

77 K *does not* result in product formation, however, yielding only a dark gray matrix indicative of the presence of metal aggregates. The infrared spectrum taken after cocondensation of iron and 1,3-C_6H_8 (neat or 10% in $C_6H_{11}CH_3$) in the range 20–80 K shows new peaks at 1485 (s), 1036 (s), 875 (w), and 720 cm^{-1} (w).

Fe/$C_{10}H_7CH_3$. From the Fe/$C_{10}H_7CH_3$ cocondensation at 77 K, one obtains a spectrum with maxima at 336, 372, and 394 nm (Figure 6A), which begins to decay on warming the matrix to 120 K (Figure 6B). Decomposition is complete at 150 K (Figure 6C) apparently giving only metal and ligand.

Fe/$C_{10}H_8$. The cocondensation of Fe vapor and naphthalene did not give any product at 77 K. However, when

(16) This band is not always resolved.
(17) The color of the complex is yellow-green, in agreement with observations from macroscale preparations. While red-brown matrices have been reported previously,[7e] in our hands, such colors were only observed under conditions favoring metal aggregation.
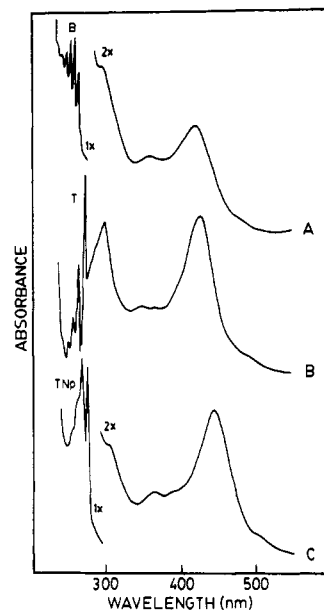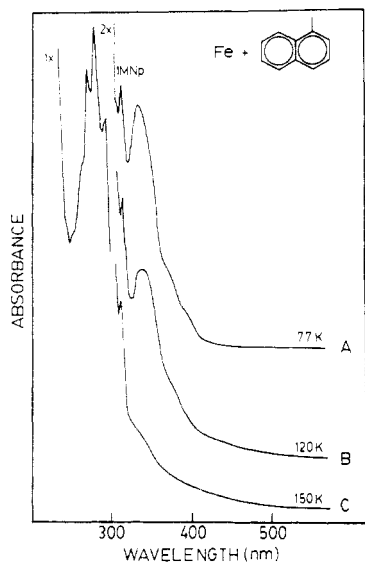
Figure 6. Optical spectra obtained (A) on deposition of Fe atoms and $C_{10}H_7CH_3$ at 77 K followed by (B) warming to 120 K and (C) warming to 150 K.
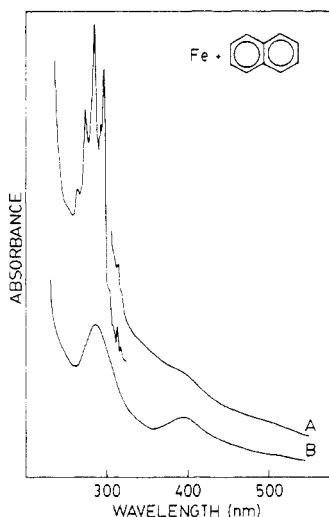

Figure 7. Optical spectra resulting from (A) codeposition of Fe atoms and naphthalene at 150 K followed by (B) warmup to 230 K.

carried out at $T < 50$ K, the reaction yielded a yellow complex with a spectrum similar to that of the 1-methylnaphthalene derivative, showing bands at 338, 380, and 400 nm. These bands decay to zero on raising the temperature to 80–90 K. After codeposition at 150 K, a different spectrum is obtained, with bands discernible at ~400 and 520 nm in addition to the absorptions due to the excess naphthalene (Figure 7A). Warming the matrix to 230 K allows the excess ligand to sublime from the matrix, leaving the complex on the optical support. A new band is thus revealed at 296 nm followed by a weak shoulder at 340 nm (Figure 7B). This spectrum remains unperturbed on further warming to 290 K.

Fe/$C_{10}H_{12}$. A green complex is formed after cocondensation of iron and Tetralin both at 77 and at 150 K, with a spectrum consisting of bands at 305, 360, 390, 446, and 500 nm (Figure 4C). This species decomposes at ~200 K. Infrared studies were also attempted on this system but failed to provide satisfactory results.

Discussion

Among the still ambiguous points regarding the iron/arene systems are the following: (i) the nature of the low

temperature ($T \leq 77$ K) species observed in the case of iron toluene ($\eta^6:\eta^6$, $\eta^4:\eta^4$, or monoarene);[8,10,11] (ii) whether this species is formed in all iron/arene reactions, and (iii) is this species the precursor to the high temperature ($T > 77$ K) species, i.e. do the low- and high-temperature forms interconvert?

Consider first the results obtained when iron is reacted with hexamethylbenzene. On warming the matrix to room temperature to remove excess C_6Me_6, the spectrum (Figure 1B) consists of a strong band at 278 nm with a weaker shoulder at 322 nm and a weak broad band in the visible ($\lambda_{max} \simeq 480–500$ nm). These features differ slightly from those reported[12] for (η^6-C_6Me_6)$_2$Fe [$\lambda_{max} = 298$ (ϵ 3450), 465 nm (470)], although the ratio of the absorbances of the bands observed at 278 and 480 nm are in agreement with the results of Fischer.[12] However, it is important to note that the literature spectrum is that of the complex in benzene, while Figure 1B represents that of a pure species in the solid state. We, therefore, believe that this matrix spectrum is consistent with an assignment to the known (η^6-C_6Me_6)$_2$Fe^0. In addition, it appears that this is the species formed initially (either at 77 or 150 K, Figure 1A) although the major absorptions are obscured by those of C_6Me_6.

Interestingly, when the spectrum of (η^6-C_6Me_6)$_2$Fe is considered with those for other (η^6-arene)$_2$M species (M = Ti, V, Cr),[18] a monotonic blue-shift in the main MLCT bands is observed as one progresses across the first-row elements, suggesting that the 278- and 322-nm bands in the spectrum of (η^6-C_6Me_6)$_2$Fe may be assigned to the transitions $e_{2g} \rightarrow e_{2u}$ and $a_{1g} \rightarrow e_{2u}$ respectively based on a previous analysis for the chromium analogue.[19] In addition, the intensity and the temperature and/or solvent dependence of the 480–500-nm band point to its arising from a d–d transition absorbing essentially throughout the visible spectrum, consistent with the reported black color of the complex.[12,20]

Focusing next on the iron/toluene reaction, although this system has been discussed elsewhere,[11] some aspects need further comment in light of our present results. Reaction of Fe atoms with a 1:10 solution of toluene in methylcyclohexane at 77 K yields a mixture of two products, previously designated as a "low"- and a "high"-temperature form[11] (hereafter referred to as I and II, respectively), which coexist at this temperature (Figure 2C). We observe that I is formed predominantly at 77 K, while II is the major product at 90 K.

I begins to decay upon warming the matrix to 90 K, leaving II as the only species on the optical support after subsequent heating to 100 K (Figure 2D). The relative intensities of the bands show conclusively that I does not undergo a transformation to yield II, an argument which is further supported by the observation that, under conditions where only I is formed, i.e., at 50 K (Figure 2A), warming of the matrix to 100 K results in the total disappearance of the matrix species (Figure 2B). Metal depositions into a $C_6H_5CH_3/C_6H_{11}CH_3$ 1:10 microsolution at 150 K produced only II (Figure 2E), in agreement with the results obtained by Ozin et al.[11] II can be observed to remain on the matrix support above the evaporation temperature of the excess ligand and is stable to 240 K, in

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(19) Weber, J.; Geoffroy, M.; Goursot, A.; Pénigault, E. *J. Am. Chem. Soc.* **1978**, *100*, 3995.
(20) Michaud, P.; Mariot, J.-P.; Varret, F.; Astruc., D. *J. Chem. Soc., Chem. Commun.* **1982**, 1383.

Table I. Domains of Existence and Optical Data for
Iron Vapor Reaction Products with Selected Benzene and
Naphthalene Derivatives and Cyclohexadiene[a]

LIGAND	TEMPERATURE RANGE (KELVIN) 50 — 100 — 150 — 200 — 250
(benzene)	c) η^6,η^6 278,322,500[d]
(toluene)[b]	I η^6,η^4 298,314,336,358,380 / II η^6,η^4 298,350,390,427,470
(arene)	η^6,η^4 298,350,390,424,470
(cyclohexadiene)[b]	η^6,η^4 315,338,356,378
(naphthalene)	η^6,η^4 338,380,400 / c) η^6,η^6 296,340,400,520[d]
(tetralin)	η^6,η^4 336,372,392
(dihydronaphthalene)	η^6,η^4 305,360,390,446

[a] All values in nm.   [b] 10% in methylcyclohexane.
[c] Spectrum as revealed after removal of unreacted ligand.
[d] d-d transitions

keeping with observations from macroscale preparations.[7f] Cooling the matrix to 20 K after completion of the reaction at 150 K leaves the spectrum unperturbed, indicating that conversion of II to I also does not occur.

In contrast, the cocondensation of iron with benzene in the temperature range 50–150 K appears to yield only a single species. The spectrum resulting from a Fe/C_6H_6 cocondensation at 50 K is shown in Figure 4A and is seen to be very similar to that of species II in the toluene case (Figure 4B). After removal of excess benzene at 170 K, the spectrum (Figure 3C) is stable to 200–210 K. The matrix infrared spectrum obtained following cocondensation of Fe and C_6H_6 at 50 K essentially agrees with that reported by Efner[8] and Skell[10] for the same reaction at 77 K. Deviations from these results are (i) we observe two peaks of equal intensity at 1450 and 1440 cm^{-1}, indicative of perturbed $\nu(C\cdots C)$, and (ii) the bands at 1175, 855, and 810 cm^{-1}, originally reported[8] as part of the complex spectrum, are observed in the spectrum of the *pure ligand* at 50 or 77 K.

Notably, although a mono(arene)iron moiety is extremely unlikely to exist in a pure arene matrix, the analysis of Efner et al.[8] would appear to be correct in that the matrix-isolated species is not bis(η^6-benzene)iron, based on our electronic spectra for (η^6-C_6Me_6)$_2$Fe (Figure 1B; Table I) and the iron/benzene complex (Figures 3C and 4A; Table I). For comparison, the behavior of the Fe/ $C_{10}H_{12}$ system in the range 77–150 K follows a trend similar to that observed for Fe/C_6H_6. If the results for the iron/benzene, iron/toluene (II), and iron/tetralin systems (Figure 4A–C; Table I) are considered together, one observes the following: (i) their comparable optical data are indicative of a similar structural formulation, (ii) the shift to the red for the band at 424 nm in benzene to 446 nm in tetrahydronaphthalene is consistent with at least one η^6-bound arene [we have shown previously[4] that the $(C_{10}H_{12})_2$M, M = Ti, V, and Cr, spectra are identical with those of their C_6H_6 counterparts, but a 20-nm red-shift is observed for the former], (iii) the two bands observed in the infrared at 1450–1440 cm^{-1} for the iron/benzene system suggests two distinguishable arene-to-iron binding modes. The most reasonable assignment would seem to be to an 18-electron[13] (η^6-arene)Fe(η^4-arene) species for all three complexes. Comparison of the electronic spectra shown in Figure 4 with that for the known (η^6-arene)Fe(η^4-C_6H_8)[21]

reveals a major difference in the absence of the intense band at ~420 nm in the latter complexes. While this may be construed as evidence for a different structural formulation for II, i.e., not $\eta^6:\eta^4$, it should be noted that it may reflect an origin for the transition in the a' orbital[22] in the bis(arene) species. No corresponding transition would be anticipated in the rigorously 18-electron (η^6-arene)Fe-(η^4-diene).

Turning to the reaction of Fe with C_6H_6 at 15 K, several observations can be made. First, iron/benzene appears to differ from iron/toluene in that (i) no evidence for a complex similar to I is found for the former and (ii) whereas II does not form below 77 K, the benzene analogue exists at very low temperatures. Secondly, a strong ligand concentration dependence is observed at 15 K, revealing formation of a single species (similar to II) in 1:50 matrices but two species in 1:20 matrices, the concentration of the second species increasing with decreasing amount of ligand. Surprisingly, although the latter seems to be stable up to 50 K, its actual formation was not observed at this temperature, even in very concentrated matrices.

The assignment of this second product is complicated by the fact that it could not be isolated as a single species. It would be tempting, in view of the similarity of this spectrum to that for $(C_6Me_6)_2$Fe (Figure 1B), to formulate an $\eta^6:\eta^6$ structure for the Fe/C_6H_6 complex. However, it is difficult to rationalize why bis(η^6-arene)iron would preferentially form in concentrated matrices. Recent Mössbauer studies[23] seem to suggest the formation, inter alia, of $\eta^6:\eta^6$ and $\eta^6:\eta^4$ complexes in both dilute and concentrated benzene matrices (based on metal concentration) at 7 (in a 1:1 ratio) and 77 K (1:3 ratio), but in the absence of detailed experimental conditions, it is difficult to compare these results with our observations.

Alternatively, if low matrix dilution can be argued to favor cluster formation, an assignment to a multinuclear species such as $Fe_2(C_6H_6)_3$ may be more appropriate. It is interesting to note that this complex might be expected to exhibit reasonable stability[24] since it is formally isoelectronic with the known $[Ni_2(C_5H_5)_3]^+$.[25] Further studies are in progress to ascertain the identity of this second Fe/C_6H_6 species.

Particularly significant results are obtained, which have bearing on the identity of species I, when iron atoms are reacted with 1,3-cyclohexadiene. When Fe atoms are codeposited with a 1,3-C_6H_8/$C_6H_{11}CH_3$ (1:10) solution at 80 K,[26] a spectrum similar to that of I is observed (Figure 5A, to be compared with Figure 5B). This species is stable over a narrow temperature range and decomposes to give $Fe_{colloid}$ at 100 K, well below the melting point of the matrix. Infrared studies failed to elucidate the nature of the complex but revealed that disproportionation of the diene to yield benzene (1485 and 1036 cm^{-1}) and cyclohexene (875 and 720 cm^{-1}) occurs on deposition at temperatures even as low as 20 K, both in neat 1,3-cyclohexadiene and 1,3-cyclohexadiene/methylcyclohexane (1:10) matrices.[27] However,

(21) (η^6-$C_6H_5CH_3$)Fe(η^4-C_6H_8) was prepared by us under macroscale metal vapor conditions[7e] and found to exhibit a UV–visible spectrum with bands at 261, 324 (sh), and 420 nm (sh). (η^6-C_6H_6)Fe(η^4-C_6H_8) has been reported recently to show a similar electronic spectrum.[23]

(22) For a discussion of orbital symmetry on passing from (η^6-arene)$_2$M to (η^6-arene)Fe(η^4-arene) see ref 3b.

(23) Parker, S. F.; Peden, C. H. F. *J. Organomet. Chem.* **1984**, *272*, 411.

(24) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

(25) Salzer, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930. Dubler, E.; Textor, M.; Oswald, H.-R.; Salzer, H. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 135.

(26) The observation that no complex forms below 80 K is similar to that for bis(cyclooctadiene)iron (see: Atkins, R. M. Ph.D. Thesis, University of Bristol, 1977).

it is not clear at this stage whether more benzene/cyclohexene is produced on warming the matrix. While this disproportionation has been previously observed[7a,d,e] in macroscale preparations involving iron atoms and 1,3-cyclohexadiene, it is surprising to find that formation of benzene and cyclohexene occurs during the short time between deposition and quenching of the matrix. The observation of this process occurring both when the complex is known to form *and* when only metal aggregation is favored tends to suggest that such a reaction is due to the presence of iron clusters in the matrix rather than catalyzed by the bis(1,3-cyclohexadiene)iron.

With the presence of nonnegligible amounts of benzene in the low-temperature matrix one might anticipate the formation of a species such as $(\eta^6\text{-}C_6H_6)Fe(\eta^4\text{-}C_6H_8)$. Although this complex is observed in varying amounts as a product in the macroscale preparations, that it is not the complex initially formed in our matrix studies may be deduced from its different electronic spectrum[21] and the fact that $(\eta^6\text{-}C_6H_6)Fe(\eta^4\text{-}C_6H_8)$ exhibits excellent thermal stability[7a,d,28] whereas the matrix species decomposes at 100 K. We therefore infer that the product in the Fe/1,3-cyclohexadiene reaction is the bis(η^4-cyclohexadiene)iron(0) complex. On the basis of the iron/1,3-cyclohexadiene result, combined with the difference between the spectrum of I (Figure 5B) and that for a (η^6-arene)$_2$Fe (Figure 1B), we feel reasonably confident in assigning I to a 16-electron, bis(arene)iron complex in which both rings are bound in a η^4 manner.

Turning now to the iron/naphthalene or iron/1-methylnaphthalene reactions, we find that a low-temperature species is produced in both cases, with an electronic spectrum consisting of one major absorption at 336–338 nm with two weak shoulders in the region 370–400 nm (Figure 5C; Table I). The 1-methylnaphthalene derivative is observed to form at 77 K and is stable to 150 K, while the parent naphthalene complex is obtained at 30 K and decomposes in the range 80–90K. The optical data for iron/toluene (I), iron/1-methylnaphthalene, and iron/naphthalene (low temperature) (Figure 5B,C; Table I) suggest an isostructural formulation for all three complexes, viz., bis(η^4-arene)iron.

For naphthalene as a ligand, such a mode of coordination allows retention of aromaticity in the uncomplexed ring, thereby providing some stabilization to the complex. This is evidenced for example by the 1-methylnaphthalene derivative being more stable than its toluene analogue (T_{decomp} = 150 K vs. 100 K). It is interesting to note that only two examples of η^4-bonding have been reported to date for naphthalene, namely, (η^4-OMN)Ru(η^6-benzene) [OMN = octamethylnaphthalene][14b] and TaCl(η^4-C$_{10}$H$_8$)(dmpe)$_2$[14a] although no such evidence yet exists for first-row transition metals.

Focusing on the reaction at 150 K, one observes a different behavior for 1-methylnaphthalene compared with naphthalene. While no reaction appears to occur in the first case, a product is obtained in the second case. From the spectrum taken at 150 K, two absorptions at 390–400 and 510 nm (weak) are discernible aside from the bands associated with the uncomplexed naphthalene in the matrix (Figure 7A). Within the range 230–240 K, the excess ligand sublimes and new bands emerge at 296 and 340 nm, remaining unchanged up to room temperature (Figure 7B). We have shown[4] recently that the electronic spectral features of the (η^6-C$_{10}$H$_8$)$_2$M complexes (M = Ti, V, Cr) are

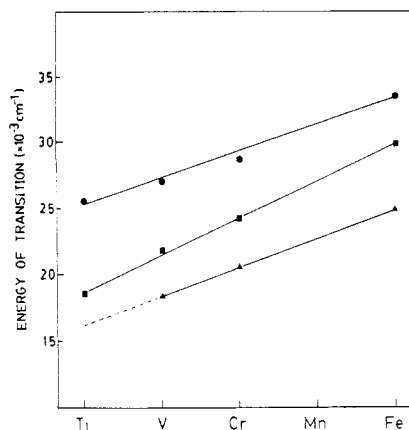**Figure 8.** Trend observed in the energies for the MLCT transitions of (C$_{10}$H$_8$)$_2$M complexes. The values for Ti, V, and Cr are taken from ref 4: ●, first MLCT; ■, second MLCT; ▲, third MLCT (this band is absent in (Np)$_2$Ti) (for assignments, see ref 4).

noticeably different from those of their benzene analogues with the main absorption red-shifted by 30–35 nm relative to the latter. Characteristic of these spectra are three MLCT bands in the region 350–550 nm, smoothly blue-shifting on passing from Ti → V → Cr. A similar behavior is found for the Fe/C$_{10}$H$_8$ (high-temperature) spectrum (Figure 7); namely, a three-band pattern with a 20-nm shift of the main absorption relative to that of bis(η^6-hexamethylbenzene)iron (Figure 1B). In addition, the regular blue-shift for all transitions along the series Ti → Fe (see Figure 8) is consistent with an assignment to a bis(η^6-naphthalene)iron species.

As it may seem rather puzzling that no such complex could be obtained from the iron/1-methylnaphthalene cocondensation at 150 K, some aspects concerning this particular experiment should be stressed. First, this temperature corresponds to the decomposition temperature of the first complex. A parallelism can be drawn with the naphthalene system which would indicate that there is a temperature "gap" between the decay of the η^4:η^4 and the formation of the η^6:η^6 species where no product is observed to be stable. Unfortunately, the naphthalene and 1-methylnaphthalene systems are different in the respect that, while naphthalene can be removed readily from the matrix on warming, the 1-methylnaphthalene matrix has a tendency to flow within the range 200–220 K, preventing observation at higher temperatures. A spectrum indicative of an η^6:η^6 species was observed at $T > 150$ K for this system, but insufficient information could be gained from such a spectrum to clearly identify the product.[29]

In summary, our metal vapor matrix isolation studies have revealed that the nature of the iron/arene complex is highly sensitive to both the identity of the arene *and* the temperature at which the reaction occurs (Table I). It is important at this point to comment briefly on the suggested[3b] role of the Jahn–Teller distortion process in the stability of 20-electron bis(arene)iron complexes. The molecule in its electronic ground state (^{3}A$_{2g}$) is Jahn–Teller "inactive", because of the symmetrical occupation of the e$_{1g}$* orbital. A degenerate electronic state (^{1}E$_{2g}$) can be achieved only on pairing of the two e$_{1g}$* electrons, in which case the Jahn–Teller "active" coordinate is of symmetry e$_{2g}$.[30] The latter point also requires that the distortion

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(29) A similar spectrum was obtained again when iron atoms were deposited into a thin film of 2,6-diisopropylnaphthalene at 250 K.

(30) For discussion of the Jahn–Teller effect, see for example: Burdett, J. K. "Molecular Shapes"; Wiley-Interscience: New York, 1980.

conserve the center of symmetry of the molecule. As a consequence, a molecule approximating to an $\eta^4{:}\eta^4$ bis-(arene)iron(0) configuration would result. We may suggest therefore that the observation of a "$\eta^4{:}\eta^{4\prime\prime}$" species for toluene I probably arises from formation of a $\eta^6{:}\eta^6$ species which then distorts to the $\eta^4{:}\eta^4$. As a result of this argument, the most stable $\eta^6{:}\eta^4$ species (benzene, tetralin, toluene II) must be produced via a different reaction path possibly involving a concerted bending of one arene on coordination of the second ring.

Passing to the naphthalene case, the existence of a bis(η^6-naphthalene)iron(0) constitutes a rare example of a room-temperature-stable, 20-electron (arene)$_2$M species [others being $(\eta^6\text{-}C_6Me_6)_2M$ for M = Fe and Co$^+$].[12,31] However while one may assume that the absence of a Jahn–Teller distortion for arene = C$_6$Me$_6$ must result from the excited singlet states being sufficiently destabilized relative to the $^3A_{2g}$ state, the picture is simpler for naphthalene. We have recently suggested that the electronic spectra of $(\eta^6\text{-}C_{10}H_8)_2M$ (M = Ti, V, Cr) complexes may best be understood based on an assumed C_{2h} or C_{2v} symmetry.[4] For M = Fe, the highest occupied molecular orbital is therefore a nondegenerate level, thereby eliminating the possibility of a distortion as well as implying diamagnetism for the complex. Hence, we must invoke that

the observation of a highly unstable $\eta^4{:}\eta^4$ species for naphthalene and 1-methylnaphthalene arises *not* from a Jahn–Teller distortion but through the ability of naphthalene to bind η^4 to a metal.

Finally, it is interesting to note that the prior macroscale metal vapor reactions between iron atoms and arenes[7] may be understood reasonably in the light of these matrix studies. Under the reaction conditions employed, addition of stabilizing ligands to the low-temperature species was carried out in a temperature range (>77 K)[32] in which the $\eta^6{:}\eta^4$ species is the major (or sole) product. Hence the isolated products reflect displacement of the η^4-arene, resulting in a $(\eta^6\text{-arene})FeL_n$ complex.

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ESR Spectra for Anion Radicals of Alkylcyclotetrasilanes and -cyclopentasilanes

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ESR spectra are reported for anion radicals formed by reduction of the cyclosilanes (Me$_2$Si)$_4$, (Et$_2$Si)$_4$, (Et$_2$Si)$_5$, [(CH$_2$)$_4$Si]$_5$, [(CH$_2$)$_5$Si]$_4$, [(CH$_2$)$_5$Si]$_5$, (*i*-Pr$_2$Si)$_4$, (*i*-Bu$_2$Si)$_4$, (*s*-Bu$_2$Si)$_4$, two isomers of (*t*-BuMeSi)$_4$, (*n*-Pr$_2$Si)$_5$, (*n*-Bu$_2$Si)$_5$, (*n*-PrMeSi)$_5$, and (*i*-BuMeSi)$_5$. All produce anion radicals in which the unpaired electron is delocalized over the cyclosilane ring. Most give single line spectra, but proton hyperfine splittings are resolved for (Me$_2$Si)$_4^{-\cdot}$, [(CH$_2$)$_4$Si]$_5^{-\cdot}$, and [(CH$_2$)$_5$Si]$_5^{-\cdot}$. Splitting constants for α-^{13}C decrease with increasing bulk of the alkyl substituents. For (*i*-Pr$_2$Si)$_4^{-\cdot}$ and (*s*-Bu$_2$Si)$_4^{-\cdot}$ two equally intense α-^{13}C hyperfine splitting constants (hfsc) are observed, consistent with a bent structure for these anion radicals.

Cyclopolysilanes, especially those containing four- and five-membered rings of silicon atoms, undergo reduction to anion radicals in which the unpaired electron is delocalized over the ring.[1] Systems studied earlier by electron spin resonance (ESR) spectroscopy include permethyl-[2] and perphenylcyclosilanes,[3] *tert*-butylmethylcyclotetrasilane,[4] and a number of substituted methylcyclosilanes

Si$_5$Me$_9$X$^{-\cdot}$ and Si$_6$Me$_{11}$X$^{-\cdot}$.[5] In this paper, we report the ESR spectra of anion radicals of (Me$_2$Si)$_4$,[6] the perethylcyclosilanes (Et$_2$Si)$_n$,[7] organosilicon rotanes containing cyclotetramethylenesilane or cyclopentamethylenesilane groups,[8] and several peralkylcyclotetrasilanes and -pen-

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