That substantial quantities of the tetrameric iron cluster $[\mathrm{CpFe(CO)}]_4$ can only be obtained in reactions of the methyl-substituted cyclopolyarsine also supports the apparent large differences in donor properties. Previous studies indicate that the mechanism for the catalyzed formation of the tetrameric cluster most likely involves an initial displacement of CO from $[\mathrm{CpFe(CO)_2}]_2$ by a group 5 donor molecule.[19] In an open system in which CO is irreversibly removed following dissociation, the primary iron-containing product is the tetrameric cluster. In closed systems, formation of $[\mathrm{CpFe(CO)}]_4$ is inhibited allowing, instead, for eventual formation of 4. The conditions under which the iron tetramer is prepared in this study are considerably milder than those previously reported (refluxing hexane vs. toluene).[10,19,20]

Acknowledgment. We are grateful for financial support from NSF.

Registry No. 3, 82871-00-9; **4**, 82864-96-8; $[\mathrm{CpFe(CO)_2}]_2$, 12154-95-9; c-$(\mathrm{C_6H_5As})_6$, 20738-31-2; c-$(\mathrm{CH_3As})_5$, 20550-47-4; $[\mathrm{CpFe(CO)}]_4$, 12203-87-1.

Supplementary Material Available: Listing of anisotropic thermal paraments (Table IV) and observed and calculated structure factor amplitudes (Table V) (11 pages). Ordering information is given on any current masthead page.

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(18) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine and Stibine Complexes of Transition Metals"; Elsevier: Amsterdam, 1978.

(19) Landon, S. J.; Rheingold, A. L. *Inorg. Chim. Acta* **1981,** *47,* 187.

(20) White, A. J. *J. Organomet. Chem.* **1977,** *168,* 197.

Metal Vapor Synthesis of Iron η^6-Arene Complexes[†]

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New $\mathrm{Fe}(\eta^6\text{-arene})\mathrm{L}_2$ complexes (where L = phosphorus ligands) have been prepared by cocondensing iron atoms simultaneously with arene and L or by cocondensing iron atoms with the arene followed by low-temperature reaction of the cocondensate with L. $\mathrm{Fe}(\eta^6\text{-arene})(\eta^4\text{-diene})$ complexes have been prepared similarly, but in some cases, alternative techniques must be used to avoid hydrogen-transfer reactions.

Introduction

The chemistry of zerovalent iron arene complexes was slow to develop but has recently begun to blossom. The first report of an $\mathrm{Fe}(\eta^6\text{-arene})(\eta^4\text{-diene})$ complex[1] preceded reports[2,3] of $\mathrm{Fe}(\eta^6\text{-arene})\mathrm{L}_2$ complexes (where L = phosphorus ligand) by over 10 years. There were few reports of new compounds in either of these classes until a recent renaissance of interest in these[4] and related[5] compounds.

Our continuing interest in the chemistry of zerovalent iron complexes and the activation of aromatic C–H bonds[6] prompted us to investigate the reactions of iron atoms with aromatic substrates. While we expected η^6-coordination to be the most commonly observed mode of coordination, we were also eager to discover η^4 and η^2 species as well as divalent aryl complexes. Reductive techniques allow the synthesis of certain special classes of zerovalent species such as η^6-hexamethylbenzene complexes,[7] but they are not generally applicable. Reductions of $[\mathrm{Fe(arene)_2}]^{2+}$ in the presence of phosphorus ligands to obtain $\mathrm{Fe}(\eta^6\text{-arene})\mathrm{L}_2$ complexes are complicated by nucleophilic addition of the phosphorus ligands to the arene rings.[8] The results of a systematic study of iron atom–arene cocondensation reactions are reported here.[9] In a subsequent paper we will detail the stepwise stoichiometric hydrogenation of these η^6-arenes through η^4-dienes to cyclohexene.

Experimental Section

All manipulations other than the cocondensation reactions were carried out in the dry nitrogen atmosphere of a Vacuum Atmospheres drybox or on a standard vacuum line. Melting points were measured under nitrogen and are uncorrected. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra were recorded on a Bruker HFX-90 spectrometer at 36.43 MHz. Proton spectra were recorded by using Varian HR-220 and XL-100 spectrometers. $^{13}\mathrm{C}$ NMR spectra were recorded on a Bruker WH-90 spectrometer. See Table I for NMR results, all of which were recorded in toluene-d_8. High-resolution mass spectra were recorded on a CEC-110B spectrometer. Analyses were carried out at our analytical facilities (see Table II for results).

The arenes and olefins are commercially available and were used after filtration through neutral-grade alumina and degassing. The phosphorus ligands are commercially available and were used after purification and degassing. Solvents were dried by standard techniques.

Most of the metal vapor syntheses were carried out in an apparatus of a modified Skell design[10] described previously,[6] using

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[†] Contribution No. 2798.

(1) Fischer, E. O.; Muller, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962,** *17B,* 776.

(2) William-Smith, D. L.; Wolf, L. R.; Skell, P. S. *J. Am. Chem. Soc.* **1972,** *94,* 4042.

(3) Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973,** 120.

(4) (a) von Gustorf, E. A. K.; Fischler, I.; Leitich, J.; Dreeskamp, H. *Angew. Chem., Int. Ed., Engl.* **1972,** *11,* 1088. (b) Fischler, I.; von Gustorf, E. A. K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975,** *30B,* 291.

(5) (a) Muetterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* **1979,** *178,* 197. (b) Bennett, M. A.; Huang, T.-N.; Smith, A. K.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1978,** 582. (c) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972,** *50,* 3063. (d) Werner, H.; Werner, R. *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 683. (e) Werner, H.; Kletzin, H. *J. Organomet. Chem.* **1982,** *228,* 289. (f) Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976,** *109,* 132.

(6) (a) Ittel, S. D.; van Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979,** *101,* 3874. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *Ibid.* **1979,** *101,* 1742.

(7) Weber, S. R.; Brintzinger, H. H. *J. Organomet. Chem.* **1977,** *127,* 45.

(8) Domaille, P. J.; Ittel, S. D.; Jesson, J. P.; Sweigart, D. A. *J. Organomet. Chem.* **1980,** *202,* 191.

(9) Ittel, S. D.; Tolman, C. A. *J. Organomet. Chem.* **1979,** *172,* C47.

(10) Skell, P. S.; Wescott, L. D. *J. Am. Chem. Soc.* **1963,** *85,* 1023.

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Table I. NMR Parameters[a] of (η^6-Arene)iron Complexes

Fe(toluene)(P(OMe)$_3$)$_2$	^{1}H	5.34, ortho (2, m), 4.80 meta, para (3, m), 3.55 OMe (18, s), 2.25 Me (3, s)
	^{31}P{^{1}H}	179.7
Fe(toluene)(P(OEt)$_3$)$_2$	^{1}H	5.35 para (1, m), 4.83 meta (2, m, $J = 3$), 4.73 ortho (2, d, $J = 3$), 3.93 CH$_2$ (12, tq, $J = 7$, $J_{PH} = 3.5$), 2.30 Me (3, s), 1.17 CCH$_3$ (18, t, $J = 7$)
	^{13}C{^{1}H}	93.7 α, 81.2 ortho, 79.9 para, 77.8 meta, 58.7 OCH$_2$, 22.0 Me, 16.6 CCH$_3$
	^{31}P{^{1}H}	173.9
Fe(toluene)(1,5-COD)	^{1}H	5.06 para (1, t, $J = 6$), 4.37 meta (2, t, $J = 6$), 4.27 ortho (2, d, $J = 6$), 2.81 CH (4, m), 2.46 endo-CH$_2$ (4, m), 1.93 Me (3, s), 1.89 exo-CH$_2$ (4, d, $J = 8$)
	^{13}C{^{1}H}	99.4 α, 88.1 para, 87.1 meta, 85.4 ortho, 65.1 CH, 33.1 CH$_2$, 19.3 Me
Fe(benzene)(1,5-COD)	^{1}H	4.56 C$_6$H$_6$ (6, s), 2.93 CH (4, m); 2.45 endo-CH$_2$ (4, m), 1.86 exo-CH$_3$ (4, m)
Fe(toluene)(1,3-COD)	^{1}H	4.92 para (1, t), 4.86 meta (2, m), 4.72 ortho (2, m), 4.60 2,3-CH (2, b), 2.68 1,4-CH (2, b), 2.17 5,8-CH$_2$ (4, M), 1.95 Me (3, s), 1.60 6,7-CH$_2$ (4, m)
	^{13}C{^{1}H}	94.7 α, 84.4 meta, 83.7 2,3-CH, 82.6 ortho, 82.1 para, 52.7 1,4-CH, 28.5 5,8-CH$_2$, 25.3 6,7-CH$_2$, 20.0 Me
Fe(toluene)(CHT)	^{1}H	5.87 6-CH (1, ddd, $J = 10, 3, 1$), 5.09 5-CH (1, dd, $J = 10, 7$), 4.90 para (1, t, $J = 6$), 4.84 meta (2, t, $J = 6$), 4.76 ortho (2, d, $J = 6$), 4.63 2-CH (1, m), 4.36 3-CH (1, dd, $J = 7, 4$), 2.57 1-CH (1, m), 2.33 4-CH (1, t, $J = 7$), 2.09 endo-CH$_2$ (1, ddd, $J = 4, 5, 2$), 1.95 Me (3, 5), 1.20 exo-CH$_2$ (1, ddd, $J = 21, 3, 1$)
	^{13}C{^{1}H}	130.8 t-CH, 121.3 6-CH, 95.2 α, 84.8 2-CH, 84.5 meta, 83.0 ortho, 81.6 3-CH, 78.0 para, 51.7 4-CH, 48.0 1-CH, 32.3 CH$_2$, 20.3 Me
Fe(toluene)(COT)	^{1}H	5.2 COT (8, s), 5.0 para (1, t), 4.9 meta (2, m), 4.7 ortho (2, m), 1.9 Me (3, s)
Fe(benzene)(CHT)	^{1}H	5.88 6-CH (1, t, $J = 8$), 5.10 5-CH (1, d, $J = 10$), 4.85 C$_6$H$_6$ (6, s), 4.70 2-CH (1, m), 4.42 3-CH (1, m), 2.75 1-CH (1, m), 2.45 4-CH (1, t, $J = 7$), 2.08 endo-CH$_2$ (1, dm, $J = 22$), 1.25 exo-CH$_2$ (1, dm, $J = 22$)
Fe(benzene)(1,3-CHD)	^{1}H	4.82 C$_6$H$_6$ (6, s), 4.50 2,3-CH (2, dd, $J = 2, 4$), 2.45 1,4-CH (2, dtd, $J = 4, 2, 1$), 1.15 endo-CH$_2$ (2, dd, $J = 8, 2$), 1.20 exo-CH$_2$ (2, dd, $J = 8, 1$)
	^{13}C	82.0 C$_6$H$_6$ (d, $J_{CH} = 168$), 75.1 2,3-CH (d, $J_{CH} = 158$), 54.1 1,4-CH (d, $J_{CH} = 152$), 27.1 5,6-CH$_2$ (t, $J_{CH} = 127$)
Fe(toluene)(butadiene)	^{1}H	4.87 para (1, t), 4.81 meta (2, m), 4.66 ortho (2, m), 4.58 2,3-CH (2, b), 2.05 *syn*-1,4-CH (2, m), 1.45, anti-1,4-CH (2, m)
Fe(benzene)(COT)	^{1}H	5.2 COT (8, s), 4.8 C$_6$H$_6$ (6, s)
Fe(*p*-xylene)(P(OMe)$_3$)$_2$	^{1}H	4.67 CH (4, t, $J_{PH} = 3$) 3.41 OMe (18, t, $J_{PH} = 5.5$), 2.30 Me (6, s)
	^{31}P{^{1}H}	179.9
Fe(toluene)(PMe$_3$)$_2$	^{1}H	5.02, ortho (2, m), 4.68 meta, para (3, m), 2.21 Me (3, s), 1.33 PMe$_3$ (18, dm)
	^{31}P{^{1}H}	22.8
Fe(mesitylene)(P(OMe)$_3$)$_2$	^{1}H	4.61 CH (3, t, $J = 2$), 3.34 OMe (18, t, $J_{PH} = 6$), 2.14 Me (9, s)
	^{31}P{^{1}H}	180.8
Fe(benzene)(P(OMe)$_3$)$_2$	^{1}H	4.94 C$_6$H$_6$ (6, t, $J_{PH} = 2.5$), 3.36 OMe (18, t, $J_{PH} = 6$)
	^{13}C	80.0 C$_6$H$_6$ (d, $J_{CH} = 171$), 50.2 OMe (d, $J_{CH} = 144$)
	^{31}P{^{1}H}	178.9
Fe(cumene)(P(OMe)$_3$)$_2$	^{1}H	5.74 para (1, m), 4.60 meta and ortho (4, m), 3.41 OMe (18, t, $J = 6$), 2.84 CH (1, septet, $J = 7$), 1.39 CMe$_2$ (6, d, $J = 7$)
	^{31}P{^{1}H}	180.3

[a] Given in parentheses are (in order): the relative intensity, the multiplicity (abbreviated s, singlet; d, doublet; t, triplet; m, multiplet; b, broad, dd, double doublet, etc.), and if measured, the coupling constant in hertz. Chemical shifts are positive downfield for internal Me$_4$Si for ^{1}H and ^{13}C and from external H$_3$PO$_4$ for ^{31}P.

the general conditions described. Reactions done in a rotating flask evaporator were carried out in a Planer VSP-302 vapor synthesis plant using a single crucible in the resistance heated mode of operation or in an apparatus of a modified Timms design.[11,12]

Design of the Rotary Metal Atom Evaporator. The small rotary, metal atom evaporator described by Timms[11,12] is of a convenient size for many applications. Two of its most serious limitations are low pumping capacity and poor dissipation of radiant heat. Both of these problems can be overcome, to some degree, by a minor change in design. Pumping capacity is limited by the narrow vapor duct of the Büchi evaporator used, so pumping efficiency is improved by using smaller diameter water-cooled electrodes to the heater. This can be done by using one electrode for water in and the other for water out. To keep the electrodes from short circuiting, the water circulation is completed through a small block of heat resistant Vespel engineering plastic. The same cooling water is used to cool a metal heat shield under and around the crucible so that much of the radiant heat is carried away by the cooling water and not absorbed by the cocondensate on the walls of the flask where it contributes greatly to the increased vapor pressures in the system. For more detail on the radiant energy problem, see ref 11.

A Caution on Cooling Baths. One solvent commonly used as a slush bath for cooling rotary metal atom evaporators is pentane. We feel such a bath presents an unacceptable hazard. While the pentane is cooled well below its flash point, it is separated from a crucible heated to >1500 °C by a very short distance. If the flask breaks, this high heat will contact the pentane with serious potential for explosion and fire. As a much safer alternative, we have used a cooling bath of Freon-114B2 fluorocarbon. Rapidly heated solvent may still cause an explosion if the flask breaks, but the danger of an ensuing fire is greatly diminished.

Preparation of Fe(η^6-toluene)(P(OMe)$_3$)$_2$. Iron (11 g) was cocondensed with toluene (150 mL) on a liquid-nitrogen-cooled surface. The resultant mixture was reacted with P(OMe)$_3$ (50 mL) in methylcyclohexane (100 mL) at −120 °C. The stirred mixture was slowly warmed to room temperature and then filtered through Celite. Volatile components were removed under vacuum to give a dark oil. The oil was taken up in pentane and chromatographed on alumina (neutral grade, P(OMe)$_3$ deactivated). The complex was eluted with pentane, leaving a dark band on

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(11) Timms, P. L. "Cryochemistry"; Moskovitz, M., Ozin, G. A., Eds.; Wiley-Interscience: New York, 1976.

(12) Timms, P. L. *J. Chem. Educ.* **1972**, *49*, 782.

Table II. Analytical Results for the (η^6-Arene)iron Complexes

	anal.[a]			mass spectra[a]				
	C	H	P	parent	loss	ion	loss	ion
Fe(toluene)(P(OMe)$_3$)$_2$	39.4	6.6						
	39.1	6.7						
Fe(toluene)(P(OEt)$_3$)$_2$	47.5	8.0	12.9	480.1493	toluene	388.0867	P(OEt)$_3$	314.0709
	48.0	7.7	11.8	480.1522		388.0805		314.0749
Fe(toluene)(1,5-COD)	*b*			*c*				
Fe(benzene)(1,5-COD)	*b*			*c*				
Fe(toluene)(1,3-COD)	*b*			*c*				
Fe(toluene)(CHT)	70.0	6.7		240.0600	C_7H_8	147.9973		
	69.6	6.4		240.0617		147.9975		
Fe(toluene)(COT)	71.5	6.4		252.0600	toluene	159.9975	COT	147.9975
	71.4	6.4		252.0621		159.9992		147.9987
Fe(toluene)(NBD)	*e*			240.0600[e]				
				240.0664				
Fe(benzene)(CHT)	69.1	6.2						
	68.8	6.0						
Fe(benzene)(1,3-CHD)	67.3	6.6		214.0444	CHD	133.9819		
	67.4	6.6		214.0463		133.9833		
Fe(benzene)(COT)	70.6	5.9						
	70.3	6.0						
Fe(*p*-xylene)(P(OMe)$_3$)$_2$	41.0	6.9	15.1	410.0709	P(OMe)$_3$	285.0342		
	40.8	6.7	14.6	410.0670		285.0366		
Fe(toluene)(PMe$_3$)$_2$	52.0	8.7	20.7					
	52.1	8.6	19.9					
Fe(mesitylene)(P(OMe)$_3$)$_2$	42.5	7.1	14.6	424.0865	P(OMe)$_3$	304.0889		
	42.2	7.2	14.0	424.0848		304.0894		
Fe(benzene)(P(OMe)$_3$)$_2$	37.7	6.3	16.2	*d*	P(OMe)$_3$	258.0148		
	37.6	6.3	16.1			258.0127		
Fe(toluene)(butadiene)	65.4	7.0		202.0445	BD	147.9975		
	56.9	7.1		202.0410		147.9967		

[a] Calculated values are above found values. [b] Not analyzed due to instability. [c] Decomposing at inlet temperature; parent ion observed at low resolution. [d] Not observed. [e] Not isolated. Mass spectrum from crude mixture.

the column. Pentane was removed, leaving the desired product as a dark red liquid; yield 7.5 g.

Preparation of Fe(η^6-benzene)(P(OMe)$_3$)$_2$. Iron (14 g) was cocondensed simultaneously with benzene (100 mL) and P(OMe)$_3$ (150 mL) onto a liquid-nitrogen-cooled surface that had been previously coated with a layer of methylcyclohexane. After the cocondensation was complete, the flask was allowed to warm to −120 °C. Additional methylcyclohexane was then condensed into the flask, washing the contents to the bottom. The mixture was stirred as it warmed to room temperature. The workup of the mixture was similar to that for Fe(η^6-toluene)(P(OMe)$_3$)$_2$. The final product is a low melting, dark red, crystalline solid; yield 6.8 g.

Preparation of Fe(η^6-toluene)(η^4-cycloheptatriene). Iron atoms (18 g) were cocondensed with toluene (180 mL) onto a liquid-nitrogen-cooled surface over a period of 3.5 h. The resultant mixture was reacted with cycloheptatriene in ether at −120 °C and warmed slowly to 0 °C. The mixture was filtered at 0 °C and the volatile components were removed under vacuum. The residue was chromatographed on an alumina column (neutral grade, activity 1) using pentane. A brown band remained on the column. The red band, which eluted with pentane, was collected. Removal of pentane under vacuum at −20 °C gave deep red crystals that were collected and dried under vacuum. These crystals were of analytical purity. A second crop of product could be obtained by taking the filtrate to dryness; total yield 9 g. Both samples melted to red liquids as they warmed to room temperature; the melting point was not determined. The compound is not stable at room temperature for prolonged periods and should be stored at −40 °C.

Preparation of Fe(η^6-toluene)(η^4-1,5-cyclooctadiene). Iron atoms (14 g) were cocondensed with toluene (210 mL) onto a liquid-nitrogen-cooled surface over 3.5 h. The resultant mixture was reacted with 1,5-cyclooctadiene in ether at −120 °C. The mixture was stirred as it slowly warmed to 0 °C. The mixture was then filtered through Celite, and the volatile component was removed under vacuum. The dark solids were taken up in pentane and chromatographed on alumina (neutral grade, activity 1). The column was eluted with pentane and then pentane–ether (4/1). The eluents were combined, and solvent was removed under vacuum, giving bright orange crystals that were collected by vacuum filtration and dried under vacuum; yield 7 g. The compound is thermodynamically unstable, decomposing to metal and ligands, and must be stored at −40 °C. The compound is rapidly catalytically decomposed to free ligands and iron metal by pentane containing several parts per million of chlorinated solvent. (The stability of this complex and others in hexane and ether but not in pentane led us to do a careful chromatographic analysis of this particular solvent. The discovery of several parts per million of chlorinated species prompted our switch to pesticide grade pentane. Since that switch, we have had no further problems.)

Reaction of Iron, Toluene, and Norbornadiene. Norbornadiene (30 mL) was condensed onto the walls of the flask. On top of this layer, iron (14 g) and toluene (180 mL) were cocondensed over 3 h. Then a second (30 mL) layer of norbornadiene and a layer (50 mL) of pentane were condensed into the flask. Still under vacuum the reaction flask was warmed slowly to 0 °C with stirring. At this temperature, an exothermic reaction began. Though the flask was immersed in ice water, the temperature of the contents quickly rose to greater than the atmospheric boiling point of pentane, as evidenced by the refluxing pentane and ultimate separation of the 6 in. glass-to-metal flange at the top of the reactor to vent pentane vapors. This venting (viewed from outside the laboratory) lasted only a few seconds and then the pressure inside the flask dropped back below atmospheric as the rate of cooling became sufficient. The mixture was taken into the drybox and filtered. After filtration, flocculent solids continued to precipitate for 1 h. The mixture was refiltered, and the readily volatile components were removed under vacuum, giving a dark viscous oil. Chromatography on alumina gave a yellow-orange solution that was reduced to an orange oil under vacuum. The major components of the mixture were norbornadiene oligimers (dimers, trimers, and higher)[13] though the parent ion of the desired product, Fe(η^6-toluene)(η^4-norbornadiene), was observed by high-resolution mass spectrum: calcd for $FeC_{14}H_{16}$, 240.0600; obsd, 240.0664. No attempt was made to isolate the organometallic product or to further characterize the oligimers.

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(13) Skell, P. S.; Havel, J. J.; Williams-Smith, D. L.; McGlinchey, M. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1098. Ballivet, D.; Billard, C.; Tkatchenko, I. B.; Young, D. *Proc. Int. Conf. Coord. Chem., 19th* **1978**.

Preparation of Fe(η^6-benzene)(η^4-1,5-cyclooctadiene). The liquid nitrogen cooled walls of the metal atom reactor were precoated with methylcyclohexane (60 mL). Then iron (12 g) was cocondensed with 1,5-cyclooctadiene (160 mL) and benzene (100 mL). An additional 60 mL of methylcyclohexane was added as the flask was allowed to warm to −120 °C. The contents of the flask slid to the bottom where they were stirred as they warmed to 0 °C. The mixture was filtered through Celite to remove suspended solids. Then volatile components were removed under vacuum to give a dark orange crystalline residue. The residue was dissolved in pentane at −10 °C and refiltered through Celite, removing additional iron metal. Removal of pentane under vacuum gave an orange, crystalline product. One final recrystallization from ether gave bright orange crystals, yield 3.5 g. This complex is thermodynamically unstable and must be stored at −40 °C.

Cocondensation of Iron, Benzene, and Cycloheptatriene. The concondensation and workup was carried out as in the preceding synthesis. Proton NMR indicated the final product was a mixture of at least two compounds. The first was Fe(η^5-cycloheptadienyl)(η^5-cycloheptatrienyl), a known compound formed[14] in the cocondensation of iron and cycloheptatriene. The second was the desired Fe(η^6-benzene)(η^4-cycloheptatriene), identified by comparison with the pure material synthesized in the following procedure. These two compounds could not be separated by crystallization or chromatography except with great loss in yield.

Preparation of Fe(η^6-benzene)(η^4-cycloheptatriene). Iron (10 g) was cocondensed with benzene (120 mL) and methylcyclohexane (120 mL) onto a liquid-nitrogen-cooled surface over 2.5 h. Cycloheptatriene (50 mL) was condensed into the reactor followed by more methylcyclohexane (50 mL). The mixture was allowed to melt and run to the bottom of the reactor where it was stirred as it warmed to 0 °C. The mixture was filtered through Celite, and volatile components were removed under vacuum. The red, solid residue was extracted with ether, and the solution was filtered to remove suspended iron metal. Cooling by removal of ether under vacuum precipitated red crystals that were collected by vacuum filtration and dried under vacuum; yield 3.3 g.

Preparation of Fe(cumene)(P(OMe)$_3$)$_2$. A solution of P(OMe)$_3$ (50 mL) and cumene (25 mL) in methylcyclohexane (150 mL) was cooled with a dry-ice bath in the rotary metal atom evaporator. Iron (~5 g) was condensed into the mixture over 1.5 h. The resultant suspension was filtered through Celite and stripped to a thick brown oil under high vacuum. The oil was taken up in pentane and filtered through a plug of alumina (neutral grade, activity 1). Removal of the pentane under vacuum gave a red oil. Further drying under vacuum removed residual cumene. A final chromatographic separation using pentane through a plug of alumina gave a product that crystallized at low temperature but melted on warming to room temperature; yield 6.5 g.

Results and Discussion

The cocondensation of iron atoms with aromatic molecules gives an unstable mixture of "solvated" iron atoms which can be reacted at low temperature to give a wide variety of Fe(η^6-arene)L$_2$ complexes (where L = phosphorus ligands or L$_2$ = η^4-diene). The solvated iron atoms have been described both as Fe(arene)$_2$[15] and as Fe(arene)[16] species. Previous studies have indicated that the stability of the metastable solvated iron species increases with increasing methylation of the arene ring to the point that the permethylated species Fe(η^6-C$_6$Me$_6$)(η^4-C$_6$Me$_6$) is an isolable complex.[7]

When iron atoms are cocondensed with toluene on a liquid-nitrogen-cooled surface, an unstable red-brown mixture results. If the mixture warms to room temperature, the color darkens as bulk iron metal separates. If kept in suspension, these iron particles oxidize quickly upon exposure to air. If they are filtered and dried, they are pyrophoric, so care must be exercised when removing any fritted filters from the drybox or otherwise exposing material to the atmosphere.

If the iron–toluene cocondensate is reacted with phosphorus ligands at its melting point before decomposition to metal occurs, Fe(η^6-toluene)L$_2$ complexes are formed. These complexes are readily isolated dark red liquids which are stable at room temperature. Spectroscopic properties are listed in Table I and are discussed later in this paper.

If the iron–toluene cocondensate is treated with dienes, thermally unstable Fe(η^6-toluene)(η^4-diene) complexes can be isolated at reduced temperatures. In most cases, isomerization of the reacting olefin does not occur. Thus, 1,5-cyclooctadiene (COD) gives Fe(η^6-toluene)(η^4-1,5-COD). When given the choice of 1,3- or 1,5-coordination, the arene iron complexes assume the normally preferred 1,3 geometry; thus, Fe(η^6-toluene)(η^4-1,3,5-cycloheptatriene) is coordinated through C$_1$–C$_4$ with no exchange of the coordinated and uncoordinated olefinic groups. We assume that Fe(η^6-toluene)(1,3,5,7-cyclooctatetraene) is also C$_1$–C$_4$ coordinated but the olefin undergoes an exchange process like that of its ruthenium analogue,[17] and we have not obtained NMR spectra at the slow-exchange limit to define the mode of coordination.

In two other recent papers, we have noted facile hydrogen transfer by iron atoms under metal atom reactor conditions. Reaction of iron–benzene cocondensate with cyclopentadiene gives Fe(η^5-cyclopentadienyl)(η^5-cyclohexadienyl).[15,18] Cocondensation of iron atoms with either 1,3- or 1,4-cyclohexadiene gives complexes with both 1,3- and 1,4-cyclohexadienes as well as benzene.[6] Thus, it is not surprising that Fe(η^6-toluene)(η^4-1,3-cyclohexadiene) is obtained upon starting from 1,4-cyclohexadiene as well as from 1,3-cyclohexadiene. This complex is unusual in that it is much more stable than any of the other arene diene complexes, not decomposing when stored at room temperature for several years.

The cocondensation of iron atoms with aromatic molecules other than toluene is more complicated because in most cases, these reactants/solvents melt above the decomposition points of their respective solvates. Several alternate techniques are available, so the desired compounds can normally be prepared. The first and most obvious technique is to cocondensate the iron atoms with the arene and the desired ligand simultaneously. For example, Fe(η^6-benzene)(P(OMe)$_3$)$_2$ and Fe(η^6-mesitylene)(η^4-1,3-cyclooctadiene) can be prepared by this technique.

On the other hand, pure Fe(η^6-benzene)(η^4-cycloheptatriene) cannot be prepared by the simultaneous condensation of benzene and cycloheptatriene. Such a technique gives a difficulty separated mixture of the desired product and Fe(η^5-cycloheptadienyl)(η^5-cycloheptatrienyl).[14] This second compound is the product obtained by the cocondensation of iron atoms with cycloheptatriene alone, and in the matrix the probability of an iron atom reacting with two cycloheptatriene molecules would be about the same as reacting with one cycloheptatriene and one benzene. As an alternative technique,

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[14] Blackborow, J. R.; Grubbs, R. H.; Hildenbrand, K.; von Gustorf, E. A. K.; Miyashita, A.; Scrivanti, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2205.

[15] Beard, L. K.; Silvon, M. P.; Skell, P. S. *J. Organomet. Chem.* **1981**, *209*, 245.

[16] Efner, H. F.; Tevault, D. E.; Fox, W. B.; Smardzewski, R. R. *J. Organomet. Chem.* **1978**, *146*, 132.

[17] Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *J. Organomet. Chem.* **1976**, *121*, C18; *Inorg. Chem.* **1980**, *19*, 1014.

[18] Ittel, S. D. *J. Organomet. Chem.* **1980**, *195*, 331.

a solution of the cycloheptatriene in a low melting diluent such as methylcyclohexane is frozen in the bottom of the reactor flask. The walls of the reactor flask are then coated with a layer of the diluent. Finally, iron atoms are cocondensed with benzene and the diluent, giving the (benzene)iron complex. After the cocondensation is complete, the walls of the flask are allowed to warm slowly to the melting point of the diluent and the cocondensate slides to the bottom of the flask. The iron benzene complex then reacts with cycloheptatriene giving the desired product with little contamination. The technique is applicable to the preparation of Fe(arene)(cycloheptatriene) complexes. More importantly, it generally applies to the preparation of Fe(arene)L_2 complexes when the ligands, L, are nonvolatile or not readily cocondensed simultaneously with the desired arene.

A final technique used for nonvolatile or solid arene ligands involves the use of a rotary-type metal vaporization apparatus such as those described by Green[19] or Timms.[11,12] The desired ligands are dissolved in an inert, low-melting diluent such as methyl- or ethylcyclohexane, which has low vapor pressure under normal reactor conditions. The solution can be sprayed onto a liquid-nitrogen-cooled surface during the cocondensation, or a solution can be placed in the rotary flask and cooled in a slush bath to maintain fluidity while the vapor pressure is kept low. The advantages of our modifications of the standard apparatus are discussed in the Experimental Section. We have also included a warning on the hazards of a pentane cooling bath for this technique.

An example of a compound prepared by this technique is $Fe(\eta^6\text{-cumene})(P(OMe)_3)_2$. Evaporation of iron atoms into a rotating solution of the reactants in methylcyclohexane gave a good yield of the desired product. The fluidity of the matrix may improve the relative yields by allowing the initial metal-stable products to find additional ligands and achieve coordinative saturation.

Spectroscopic Results

The ^1H NMR spectra of these zerovalent complexes (listed in Table I) display large upfield shifts of the coordinated arene resonances in keeping with their electron-rich nature. As typical examples, the benzene proton resonances in $Fe(benzene)(P(OMe)_3)_2$ and Fe(benzene)(1,3-cyclohexadiene) are observed at 4.94 and 4.82 ppm. For comparison, the benzene resonance for the Fe(II) species $[Fe(benzene)_2]^{2+}$ is observed at 7.00 ppm[8] while free benzene is found at 7.14 ppm.

Upfield shifts of the π-arene resonances are also noted in the $^{13}C\{^1H\}$ NMR spectra of these zerovalent complexes. Thus the $^{13}C\{^1H\}$ resonances of $Fe(benzene)(P(OMe)_3)_2$ and Fe(benzene)(1,3-cyclohexadiene) are observed at 80.0 and 82.0 ppm, respectively, compared to free benzene at 128.7 ppm.[20] The ^1H-coupled spectra of the same benzene complexes show $^1J_{CH}$ of 171 and 168 Hz, respectively, for the coordinated benzene. This value is increased from that of free benzene (157.5 Hz,[21] indicating some increase in the s character of the C–H bonds as π bonding to the metal center occurs.

The long-range coupling constants of 2–4 Hz between the protons of the π-bonded arene molecules and the phosphorus atoms of ligands attached to the iron center are similar in magnitude to those observed in other carbocyclic systems. For example, in $Co(\eta^5\text{-}C_5H_5)(S_2C_2(CN)_2(P(OMe)_3)$, $J_{PH} = 5.4$ Hz,[22] and in $Mo(\eta^7\text{-}C_7H_7)(CO)I(P(OMe)_3)$, $J_{P\text{-}H} = 3.0$ Hz.[23]

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Registry No. $Fe(toluene)(P(OMe)_3)_2$, 71465-08-2; $Fe(toluene)(P(OEt)_3)_2$, 82798-49-0; Fe(toluene)(1,5-COD), 71465-10-6; Fe(benzene)(1,5-COD), 82798-50-3; Fe(toluene)(1,3-COD), 71465-09-3; Fe(toluene)(CHT), 71465-11-7; Fe(toluene)(COT), 71465-12-8; Fe(benzene)(CHT), 82798-51-4; Fe(benzene)(1,3-CHD), 71265-76-4; Fe(toluene)(butadiene), 38720-20-6; Fe(benzene)(COT), 72765-35-6; $Fe(p\text{-xylene})(P(OMe)_3)_2$, 82798-52-5; $Fe(toluene)(PMe_3)_2$, 82798-53-6; $Fe(mesitylene)(P(OMe)_3)_2$, 71633-33-5; $Fe(Benzene)(P(OMe)_3)_2$, 68643-83-4; $Fe(cumene)(P(OMe)_3)_2$, 82798-54-7; Fe(toluene)(NBD), 82798-55-8; Fe, 7439-89-6.

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(19) Young, D.; Green, M. L. H. *J. Appl. Chem. Biotechnol.* **1975**, *25*, 641.

(20) Stothers, J. B. "Carbon-^{13}NMR Spectroscopy"; Academic Press: New York, 1972.

(21) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 2967.

(22) Henderson, S. D.; Stephenson, T. A.; Wharton, E. J. *J. Organomet. Chem.* **1979**, *179*, 43.

(23) Beall, T. W.; Houk, L. W. *Inorg. Chem.* **1972**, *11*, 915.