amplitudes and calculated structure factors in Table OM11M100##fnt The computer programs used in this analysis are listed in ref 23.

Acknowledgment. We thank NSERC (Canada) for financial support (R.J.P.), NATO for a travel grant (R.J.P. and M.P.B.), and the University of Glasgow for a studentship (A.A.F.).

Registry No. Ia, 63911-00-2; Ib, 82864-97-9; IIa, 74587-82-9; IIb, 82864-99-1; III, 78064-41-2; IV, 69215-82-3; V, 68851-46-7; VI, 64387-54-8; VII, 81533-22-4; $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]Cl$, 63910-98-5; Pt, 7440-06-4; carbon monoxide, 630-08-0; hydrogen, 1333-74-0; dimethylphenylphosphine, 1486-28-8; methanethiol, 74-93-1.

Supplementary Material Available: Listings of observed and calculated structure factors (Table VI) and H atom fractional coordinates (Table V; 32 pages). Ordering information is given on any current masthead page.

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(22) Supplementary material.

(23) The Enraf-Nonius Software Package for the CAD-4F diffractometer: CAD4 Data Processing Program (M. B. Hursthouse), a local version of G. M. Sheldrick's SHELX system, GEOM molecular functions program (P. R. Mallinson), and ORTEP (C. K. Johnson), adapted for the local ICL 2976 computer by P. R. Mallinson and K. W. Muir.

Comparative Reactivities of the Cyclopolyarsines $(C_6H_5As)_6$ and $(CH_3As)_5$. The Crystal and Molecular Structure of *trans*-1,2-(1,2-Diphenyldiarsino)bis[(η^5-cyclopentadienyl)dicarbonyliron], $[CpFe(CO)_2]_2(C_6H_5As)_2$

Arnold L. Rheingold,* Michael J. Foley, and Patrick J. Sullivan

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received July 1, 1982

The bis metal-substituted diarsine species $[CpFe(CO)_2]_2(C_6H_5As)_2$ (3), synthesized from $[CpFe(CO)_2]_2$ and c-$(C_6H_5As)_6$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C^5_{2h}, No. 14] with a = 6.534 (2) Å, b = 11.191 (2) Å, c = 17.529 (5) Å, β = 99.60 (2) Å, V = 1263.9 (6) Å^3, and ρ = 1.73 g cm^{-3} for Z = 2 (mol wt 657.98). Diffraction data were collected with a Nicolet R3 diffractometer, and the structure was refined to R_F = 6.60% for 1579 reflections with $3° < 2\theta < 45°$ (Mo Kα radiation). The molecule is the tetrasubstituted diarsine *trans*-1,2-(1,2-diphenyldiarsino)bis[(η^5-cyclopentadienyl)dicarbonyliron]; as such it represents the first example of a new class of bridged dinuclear metal complexes. The As–Fe bond distance, 2.450 (2) Å, is long in keeping with the formal one-electron As donation to Fe. The As–As′ bond distance, 2.456 (2) Å, is within the range of "normal" As–As single bonds. In comparison, replacement of $(C_6H_5As)_6$ for $(CH_3As)_5$ in reactions with $[CpFe(CO)_2]_2$ produces as the primary Fe–As-containing product a four-membered, diiron-bridging chain $[Fe(CO)Cp]_2[\mu\text{-}catena\text{-}(CH_3As)_4]$ (4), identified by its spectroscopic properties. Accompanying the formation of 4 under open system conditions in refluxing hexane with UV irradiation is a substantial yield of $[CpFe(CO)]_4$ (~55%).

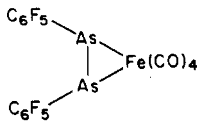
Introduction

Understanding how main-group elements bridge transition-metal centers is a major goal in inorganic chemistry. Such bridges often possess desirable structural characteristics for the design of binuclear and cluster catalysts. The extraordinary structural diversity of transition-metal carbonyl derivatives of catenated organophosphinidene and arsinidene groups (RP or RAs) makes them particularly rewarding subjects for study. Our studies of the products of the reactions of cyclopentadienylmetal carbonyls with polyorganocyclopolyarsines have shown that a characteristic feature of these reactions is ring cleavage and reformation of the resulting chain into a variety of lengths (from two to nine atoms) and configurations.[1-3]

We have also been interested in determining what effects the organic substitution on the cycloarsine precursor has in controlling the course of these reactions. West has studied the reactions of $Fe(CO)_5$ with three cyclopolyarsines: $(CH_3As)_5$, $(C_6H_5As)_6$, and $(C_6F_5As)_4$.[3-5] In the first two cases, the rings were cleaved and shortened to form $[Fe(CO)_3]_2[\mu\text{-}(RAs)_4]$ (1); with $(C_6F_5As)_4$, $[Fe(CO)_4][\eta^2\text{-}(AsC_6F_5)_2]$ (2) was obtained.

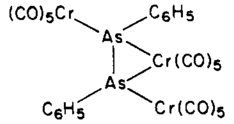
In the study we now report, we compare the reactions of $(C_6H_5As)_6$ and $(CH_3As)_5$ with $[CpFe(CO)_2]_2$. In the former case we obtain a diarsine derivative, *trans*-1,2-(1,2-diphenyldiarsino)bis(cyclopentadienyldicarbonyliron), $[CpFe(CO)_2]_2(AsC_6H_5)_2$ (3), which is the first example of a new class of arsenic-bridged dinuclear complexes. An X-ray crystallographic structure is included. In the latter case, an analogue of 1 containing a four-membered, RAs chain bridged complex is obtained: $[CpFe(CO)][\mu\text{-}(CH_3As_4)]$ (4) along with up to 55% yield of $[CpFe(CO)]_4$.

Structurally confirmed examples of complexes containing two linked RAs units are surprisingly few and are limited to three-membered heterocycles, e.g., the As_2Fe ring in 2[4] and an As_2Cr ring in $\{[Cr(CO)_5]_2(AsC_6H_5)_2\}[\mu\text{-}Cr(CO)_5]$ (5).[6]



2

As–As = 2.388 (7) Å



5

As–As = 2.371 Å

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0276-7333/82/2301-1429$01.25/0

Table I. Crystal and Refinement Data

formula	$C_{26}H_{20}As_2Fe_2O_4$
cryst system	monoclinic
space group	$P2_1/c$ [C^5_{2h}, No. 14]
a, Å	6.534 (2)[a]
b, Å	11.191 (2)
c, Å	17.529 (5)
β, deg	99.60 (2)
V, Å^3	1263.9 (6)
Z	2
mol wt	657.98
ρ(calcd), g cm^{-3}	1.729
temp, °C	25
crystal dimens, mm; color	0.20 × 0.25 × 0.32; dark red
radiation	graphite-monochromated Mo Kα (λ = 0.710 73 Å)
diffractometer	Nicolet R3
abs coeff, cm^{-1}	37.70
scan speed, deg/min	variable, 3.0–15.0
2θ scan range, deg	$3.0 \leqslant 2\theta \leqslant 45.0$
scan technique	2θ/θ
data collected	±*h*, ±*k*, +*l*
scan width, deg	$2.0 + \Delta(\alpha_1 - \alpha_2)$
weighting factor (*g*)[b]	0.0001
unique data	1880 reflctns (3923 collected)
unique data with $(F_o)^2 > 3\sigma(F_o)^2$	1579
std reflctns	3/97
R_F	6.60%
R_{wF}	5.75%

[a] Unit-cell parameters were obtained from the angular settings of 25 reflections with 2θ = 25–30°. [b] $W^{-1} = \sigma^2(F_o) + g(F_o)^2$.

Table II. Atomic Fractional Coordinates for $[CpFe(CO)_2]_2(C_6H_5As)_2$

atom	*x*	*y*	*z*
As	0.8249 (1)	−0.0178 (1)	0.4639 (1)
Fe	0.8814 (2)	−0.1465 (1)	0.3563 (1)
O(1)	0.6592 (10)	0.0229 (7)	0.2481 (4)
O(2)	1.2782 (10)	−0.0392 (8)	0.3451 (4)
C(1)	0.7452 (16)	−0.0424 (9)	0.2941 (6)
C(2)	1.1176 (17)	−0.0813 (9)	0.3532 (6)
Cb(1)	0.7883 (14)	0.1449 (8)	0.4228 (5)
Cb(2)	0.9329 (16)	0.2096 (9)	0.3914 (6)
Cb(3)	0.9027 (18)	0.3253 (10)	0.3649 (7)
Cb(4)	0.7205 (18)	0.3814 (10)	0.3735 (7)
Cb(5)	0.5718 (20)	0.3184 (11)	0.4028 (8)
Cb(6)	0.6056 (15)	0.2036 (9)	0.4281 (6)
Cp(1)	0.9873 (23)	−0.3133 (11)	0.4008 (8)
Cp(2)	0.9562 (21)	−0.3164 (10)	0.3201 (8)
Cp(3)	0.7555 (24)	−0.2949 (10)	0.2959 (8)
Cp(4)	0.6547 (20)	−0.2749 (10)	0.3572 (9)
Cp(5)	0.8025 (31)	−0.2913 (10)	0.4239 (9)
Hb(2)	1.0631	0.1719	0.3881
Hb(3)	1.0067	0.3669	0.3425
Hb(4)	0.6943	0.4622	0.3562
Hb(5)	0.4416	0.3561	0.4061
Hb(6)	0.5016	0.1633	0.4512
HCp(1)	1.1141	−0.3265	0.4361
HCp(2)	1.0626	−0.3279	0.2890
HCp(3)	0.6917	−0.2946	0.2424
HCp(4)	0.5100	−0.2564	0.3539
HCp(5)	0.7739	−0.2854	0.4758

Experimental Section

A. Preparation of $[CpFe(CO)_2As(C_6H_5)]_2$ (3). $[CpFe(CO)_2]_2$[7] (0.50 g, 1.41 mmol) and c-$(C_6H_5As)_6$[8] (0.50 g, 0.55 mmol) were combined in a heavy-wall Pyrex tube with 25.0 mL of dried toluene. The contents were thoroughly degassed, and the tube was sealed under vacuum and heated at 90 °C for 24 h in a dark oven. The oven was then switched off and the reaction tube left in the oven undisturbed for 24 h while being cooled to room temperature. Examination of the tube revealed the presence of crystallographic grade crystals that were removed by filtration and washed with cold hexane. Compound 3 was obtained as a dark red, air-stable solid (mp 195 °C) that is only slightly soluble in common organic solvents: ^1H NMR Cp 4.50 (5), C_6H_5, 7.23 ppm (5); IR (KBr) carbonyl 2020 (s), 1945 cm^{-1} (s). Column chromatography on deactivated alumina failed to reveal any other products present in significant quantities.

B. Reactions of $[CpFe(CO)_2]_2$ and c-$(AsCH_3)_5$. 1. Thermal Reaction. Equimolar quantities (2.0 mmol) of $[CpFe(CO)_2]_2$ and $(CH_3As)_5$[9] were combined with 20 mL of toluene in a heavy-wall Pyrex tube, the contents were degassed, and the tube was flame sealed under vacuum and heated to 90 °C for 36 h. (Below 95° no apparent reaction occurred; above 95° extensive decomposition occurred.) The progress of the reaction was monitored by ^1H NMR by observing changes in an identically prepared and manipulated sample in a medium wall, 5-mm NMR tube. After the reaction tube was cooled and opened, the contents were chromatographed by using a low-pressure column on alumina (highly deactivated) and eluted with a 90/10 (v/v) C_6H_6–$CHCl_3$ mixture. In addition to starting material (<10%), a dark red band (∼70%; $[CpFe(CO)]_2(CH_3As)_4$ (4) and a dark green band (∼1%; $[CpFe(CO)]_4$) were identified. Additional bands were observed but decomposed on the column. Evaporation of the eluting solvent from 4 produced a moderately viscous dark red oil, mp 10 °C. $[CpFe(CO)]_4$ was identified by its characteristic NMR and IR spectra and melting point.[10] $[CpFe(CO)]_2(CH_3As)_4$: ^1H NMR CH_3 1.60 (3), 1.68 (3), Cp 4.46 ppm (5); IR carbonyl 1904 (vs), 1870 (vs), 1843 (w) cm^{-1}. Anal. Calcd: C, 29.21; H, 3.37; Fe, 16.98; As, 45.59. Found: C, 29.99, H, 3.01; Fe, 16.11; As, 46.32.

2. Photolytic Reaction. Using otherwise identical reaction conditions to those used in the previous thermal reactions, we irradiated samples with a high-intensity source (336 nm). At 90 °C, very nearly identical product ratios were obtained as observed in the thermal reactions. If, however, photolysis occurred in an open system in refluxing hexane (4 mmol of each reactant, 50 mL of hexane), the yield of 4 dropped to ∼10% while that for the iron tetramer increased to ∼55% after 72 h. Products were separated and identified as given in the previous section.

C. Data Collection. The crystal parameters and collection data are provided in Table I. An irregular crystalline fragment cleaved from a larger crystal was cemented to the end of a glass fiber. Two forms of the data (±*h*,*k*,*l*; ±*h*,−*k*,*l*) were collected and averaged due to low diffraction intensities. The intensities were corrected for *Lp* effects as well as for absorption by using empirical ψ scan data; I_{max}/I_{min} values were in the range 1.15–1.19. Data averaging, as well as all subsequent calculations, utilized the Nicolet SHELXTL program package (version 3.0).

D. Solution and Refinement of the Structure. An *E* map produced from the direct methods routine SOLV with the highest combined figures of merit provided the As and Fe positions. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. The asymmetric unit contains one As, one Fe, one Cp ring, one phenyl ring, and two carbonyl groups. The molecule, which is composed of two asymmetric units, is situated on an inversion center midway along the As–As′ bond. The final cycles of refinement were performed with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in idealized positions (C–H = 0.96 Å and *U* = 1.2 times the isotropic equivalent for the atom to which it was attached). A final difference map revealed a peak, 1.05 e Å^{-3}, 1.17 Å from the As atom; otherwise only a featureless background (≤0.5 e Å^{-3}) remained. Final positional parameters are provided in Table II. Selected bond distances and angles are given in Table III. Thermal parameters and a listing of observed and calculated structure factor amplitudes are available as Tables IV and V.

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(7) King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. 1.

(8) Reesor, J. W. B.; Wright, G. F. *J. Org. Chem.* **1957**, *22*, 382.

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Table III. Selected Bond Distances (Å) and Angles (Deg) with Esd's for $[CpFe(CO)_2]_2(AsC_6H_5)_2$

(a) Bond Distances

As-As′	2.456 (2)	Fe-C(2)	1.716 (11)
As-Fe	2.450 (2)	C(1)-O(1)	1.163 (12)
Fe-CENT[a]	1.732 (9)	C(2)-O(2)	1.180 (13)
Fe-C(1)	1.735 (10)		

(b) Bond Angles

Fe-As-As′	104.2 (1)	C(2)-Fe-As	91.5 (4)
Fe-As-Cb(1)	106.8 (3)	C(1)-Fe-C(2)	93.7 (5)
Fe-C(1)-O(1)	175.0 (10)	CENT-Fe-As	119.8 (5)
Fe-C(2)-O(2)	174.8 (9)	CENT-Fe-C(1)	126.8 (5)
Cb(1)-As-As′	94.9 (3)	CENT-Fe-C(2)	126.4 (5)
C(1)-Fe-As′	87.8 (4)		

[a] Center of gravity of the Cp ring.

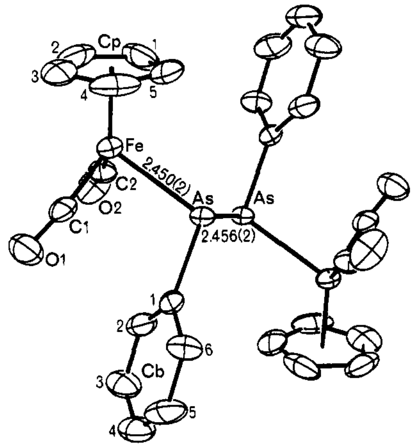
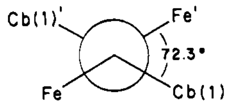


Figure 1. Thermal elipsoid diagram and numbering scheme for $[CpFe(CO)_2]_2(C_6H_5As)_2$ (**3**). Primed atom designations are symmetry related to the equivalent unprimed atom.

Crystal and Molecular Structure of $[CpFe(CO)_2]_2(AsC_6H_5)_2$ (3)

The crystal structure of **3** consists of discrete well-separated molecules of $[CpFe(CO)_2]_2(AsC_6H_5)_2$. The structure and numbering scheme are shown in Figure 1. The complex may best be described as a tetrasubstituted diarsine: *trans*-1,2-(1,2-diphenyldiarsino)bis[(η^5-cyclopentadienyl)dicarbonyliron]. This product is conveniently viewed as the addition of $[CpFe(CO)_2]_2$ to the hypothetical molecule, $C_6H_5As{=}AsC_6H_5$. The Fe–As distance, 2.450 (2) Å, is considerably longer than that found in complexes in which As functions as a two-electron donor, e.g., $(CO)_4FeAs(CH_3)_3$, 2.30 Å,[11] $C_6H_4[As(CH_3)_2]_2Fe(CO)_3$, 2.31 and 2.36 Å.[12] The Fe–As distance supports the view that each As atom functions as a one-electron donor fulfilling the one-electron deficiency of the $CpFe(CO)_2$ group.[13]

We have been unable to locate any previous structures of diarsines for comparison. The bond angles about As in **3** (Fe–As–As′ = 104.2 (1)°, Fe–As–Cb(1) = 106.8 (3)°, and Cb(1)–As–As′ = 94.9 (3)°; average 102.0°) are predictably larger than the corresponding angles in tetraphenyldistibine (average 94.9°)[14] in keeping with the increased s character of bonding orbitals as the pnictogen family is ascended. The crystallography imposed symmetry constrains the torsion angles Fe–As–As′–Fe′ and Cb(1)–As–As′–Cb(1)′ to 180°; the Fe–As–As′–Cb(1) torsion angle is 72.3 (2)°. A projection along the As–As′ is shown in A.



A

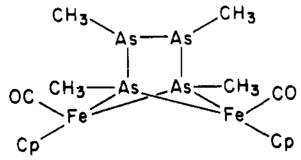
The As–As′ bond distance, 2.456 (2) Å, is within the range accepted as normal for As–As single bonds,[15] and the parameters of the $CpFe(CO)_2$ group all conform to expectations on the basis of structural studies of a large variety of $CpFe(CO)_2$ complexes.[16]

Comparative Reactivities of $(CH_3As)_5$ and $(C_6H_5As)_6$

A primary goal of this study was to compare the reactivities of differently substituted cyclopolyarsines in reactions with $[CpFe(CO)_2]_2$. Both of the cyclopolyarsines, $(C_6H_5As)_6$ and $(CH_3As)_5$, undergo ring-opening and chain-shortening reactions, presumably the result of attack of $CpFe(CO)_2$ radicals. Curiously, UV irradiation did not, in the case of $(CH_3As)_5$, accelerate product formation under closed-system conditions. In both cases, twofold changes in initial molar ratios of reactants failed to produce different Fe–As bonded products. The ratios given in the Experimental Section represent the ratios found to maximize product formation. The approximately 3:1 $[CpFe(CO)_2]_2$:$(C_6H_5As)_6$ molar ratio of starting materials would ultimately lead to the observed product as the end result of stepwise shortening of the initially formed As_6 chain.

$$3[CpFe(CO)_2] + (C_6H_5As)_6 \rightarrow \underset{\mathbf{3}}{[CpFe(CO)_2]_2(AsC_6H_5)_2}$$

On the basis of the spectroscopic evidence and by comparison to known structures,[1,4,17] we assign the structure



4

to the major product derived from $(CH_3As)_5$. (The subambient-temperature melting point for **5** prevented obtaining a crystal structure for this complex.) The proposed structure is similar to the product obtained from reactions of $[CpMo(CO)_2]_2$ and $(CH_3As)_5$.[1]

$$[CpFe(CO)_2]_2 + (4/5)\ (CH_3As)_5 \rightarrow \underset{\mathbf{4}}{[CpFe(CO)]_2(AsCH_3)_4}$$

An essential difference between the two new Fe–As complexes obtained in this study is the donor properties of phenyl- vs. methyl-substituted polyarsinidene chains. In **4**, the CH_3As chain termini act as three-electron donors, whereas in **3**, the C_6H_5As groups act as one-electron donors. In effect, the "nonbonding" electron pair on As is in competition with CO; CH_3As displaces CO, and C_6H_5As does not. This result is in keeping with the expected trend in donor properties of alkyl- vs. arylarsines.[18]

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That substantial quantities of the tetrameric iron cluster $[CpFe(CO)]_4$ 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 $[CpFe(CO)_2]_2$ 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 $[CpFe(CO)]_4$ 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; $[CpFe(CO)_2]_2$, 12154-95-9; c-$(C_6H_5As)_6$, 20738-31-2; c-$(CH_3As)_5$, 20550-47-4; $[CpFe(CO)]_4$, 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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Metal Vapor Synthesis of Iron η^6-Arene Complexes[†]

Steven D. Ittel* and Chadwick A. Tolman

Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received May 27, 1982

New Fe(η^6-arene)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. Fe(η^6-arene)(η^4-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 Fe(η^6-arene)(η^4-diene) complex[1] preceded reports[2,3] of Fe(η^6-arene)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 $[Fe(arene)_2]^{2+}$ in the presence of phosphorus ligands to obtain Fe(η^6-arene)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 $^{31}P\{^1H\}$ 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}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.

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