

Iridium Chemistry of 1,6-Bis((*tert*-butylphosphino)methyl)-1,3,5-cycloheptatriene

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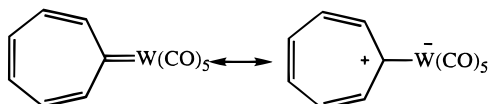
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The new pincer ligand 1,6-bis((*tert*-butylphosphino)methyl)-1,3,5-cycloheptatriene is metallated by Ir(CO)_xCl at the 7-position to give a pincer complex. This complex when treated with LiBEt₃H gives a mixture of products which result from the unusual migration of both an ethyl group and the replacement of the chlorine atom with a hydride. Individual components of the mixture can be prepared separately by treatment of the pincer complex with NaH to give dehydrochlorination followed by a protopic rearrangement and NaBEt₄, which generates the corresponding ethyl derivative.

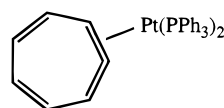
1. Introduction

The chemistry of cycloheptatriene metal compounds is of current interest because various modes of bonding can be exhibited in closely related compounds. For example, there are η^1 -C₇H₆Re(CO)₅,¹ η^1 -carbene,² η^2 -allene, and cycloheptatrienyliene complexes.³ In the area of chemical dynamics, gas-phase cycloheptatriene intermediates have been helpful in predicting the course of carbene metathesis reactions.^{4,5}

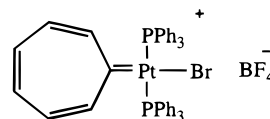
Jones et al. has elegantly shown that different transition-metal complexes can elicit different bonding modes for the C₇H₆ system and, thereby, stabilize different structural features.² For instance, early transition metals promote the carbene



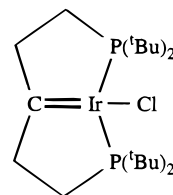
(cycloheptatrienyliene) structure where aromaticity of the tropylium resonance form and low-lying vacant orbitals on the metal atom⁶ are important features. Late transition metals on the other hand favor 1,2,4,6-cycloheptatetraene or the allene structure, i.e.,⁷



with d¹⁰ Pt⁰. An exception to this is d⁸ Pt(II) which prefers the carbene structure.⁸



Isoelectronic Ir(I) also stabilizes the carbene structure. This was shown earlier by Shaw⁹ who used pincer¹⁰ ligands to form internalized carbenes.



The compounds which exhibit these different bonding modes to the cycloheptatriene moiety are prepared by treating tropylium salts with transition-metal anions. Another method is the treatment of a mixture of 1,2,3-cycloheptatrienyllithiums with suitable transition-metal halides¹¹ at low temperature. An example of a third reaction is the treatment of (PPh₃)₃Pt with halogenated cycloheptatrienes and base. The resultant cycloheptatetraene is trapped as the platinum complex.⁸

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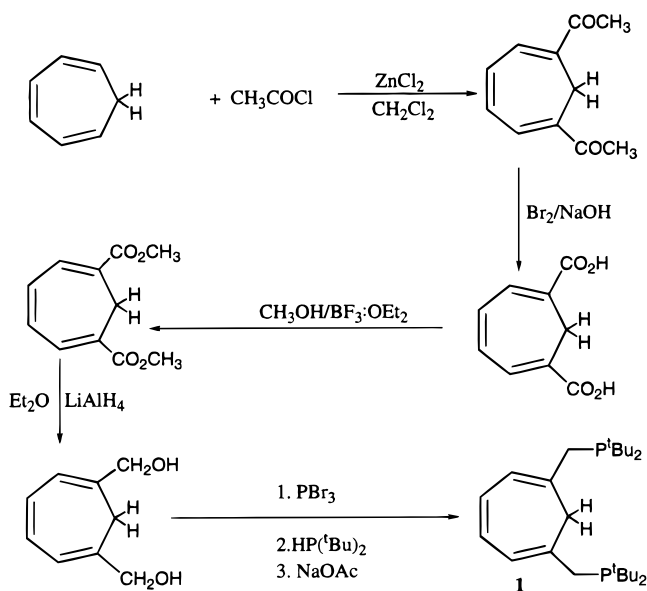
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Scheme 1



We have expanded the use of pincer ligands by incorporating cycloheptatriene in the framework. The synthesis of **1** is shown in Scheme 1. The pincer ligand effect uses a direct metalation of a hydrocarbon to introduce a transition metal in the complex.

In this paper, we describe the first direct C–H metalation of the cycloheptatriene CH₂ system by d⁸ Ir(CO)_xCl (isoelectronic with Pt(II)) with the assistance of **1** as a pincer ligand. Evidence is also presented for unusual dual reactivity of ethyl and hydride groups in the super nucleophile LiBEt₃H.

2. Results and Discussion

2.1. Synthesis of 1,6-Bis((tert-butylphosphino)methyl)-1,3,5-cycloheptatriene. The pincer ligand can be prepared in a series of alkylation and reduction steps that have been described in the literature, cf. Experimental Section. An overall yield of 88% is obtained from cycloheptatriene.

The ligand **1** was characterized by NMR spectroscopy. The most salient features are a singlet at δ 17.5 in the ³¹P{¹H} NMR spectrum and a singlet at δ 2.9 in the ¹H NMR spectrum for the methylene group in the cycloheptatriene ring at room temperature, which indicates a fast flip of the CH₂ group between two possible conformers.¹² The ¹³C{¹H} NMR spectrum is consistent with the structure displayed in Scheme 1, although the methylene carbon atom is split by long-range phosphorus coupling, cf. Experimental Section.

2.2. Synthesis and Reactions of the Iridium Complex. Treatment of **1** with low-valent iridium complexes [COIrCl]₂ and [CODIrCl]₂ gave complex mixtures and no metalation of the aliphatic CH₂ carbon. Only with Ir(CO)_xCl does intramolecular metalation of the cycloheptatriene C–H bonds occur to give [IrClH-

(CO)(^tBu₂)PCH₂C₇H₅CH₂P(^tBu₂)] **2**, shown in Scheme 2.

The metalated product **2** can be identified by its IR and NMR spectra. The ³¹P{¹H} NMR spectrum displays a single resonance at δ 50.3, which is consistent with a mirror plane perpendicular to the metalated ring systems. Thus, two sets of virtual triplets at δ 1.4 and 2.5 in the ¹H NMR spectrum are indicative of *tert*-butyl groups in different chemical environments, which are generated by the substitution pattern at the metal center and the bending of the cycloheptatriene ring (vide infra). A triplet at δ –18.6 confirms the presence of an iridium hydride with coupling to the mutually trans phosphorus atoms. Its chemical shift is characteristic of a hydride trans to chlorine, and the size of the ²J(PH) coupling constant (14.5 Hz) supports the *cis* position compared to the phosphine groups.¹³ Since the ν (CO) absorption in the infrared spectrum (2000 cm⁻¹) is typical for CO located trans to a strong trans influencing ligand, the structure of **2** is unambiguous as shown in Scheme 2. This is supported by the ¹³C{¹H} NMR spectrum of **2**, which shows two sets of resonances for the *tert*-butyl groups and only one set of signals for the olefinic cycloheptatriene carbon atoms and the methylene groups. Further characteristic features are the singlet at δ 46.1 for the metalated carbon atom and the triplet at δ 178.2 due to the carbonyl group.

The stereochemical configuration about the iridium atom and the nature of the cycloheptatriene ring configuration was determined with an X-ray molecular structure of the complex. Single crystals of the complex were obtained from THF as needles which crystallized in a *Cc* space group. A Schakal drawing is shown in Figure 1, and crystal data is included in Table 1. Selected bond distances and angles are provided in Table 2.

The structure shows an equatorial carbon monoxide ligand trans to the cycloheptatriene-metalated carbon atom (C9). This arrangement fixes the chlorine atom as trans to the iridium-bonded hydrogen atom, which could not be located. The metalated carbon atom C(9) is 0.446 Å above a plane which contains Ir–C(2)–C(7). This means that there is a hydrogen atom on C(9) which is *cis* to the Ir–Cl bond. Moreover, the angles around the cycloheptatriene carbon also confirm that the *ipso* hydrogen atom is *cis* to the chlorine atom on the iridium. The backbone of the seven-membered ring with its olefinic bonds is bent upward at an angle of 147.11° to the Ir–C(2)–C(7) plane as a normal triene-based system.

To prepare [IrH₂(^tBu₂)PCH₂C₇H₅CH₂P(^tBu₂)] from the corresponding iridium hydrochloride by treatment with LiBEt₃H, we attempted to remove the iridium-coordinated carbon monoxide from **2** with trimethylamine oxide, photolysis, and thermal methods. Since these methods failed, **2** was treated independently with LiBEt₃H to access the carbonyl dihydride. The products detected in the reaction were unexpected and are shown in Scheme 2. Product **3** is a prototopically rearranged dihydride; the result of dehydrohalogenation and **4** is the ethyl-alkylated product.

We unwittingly used impure LiBEt₃H, a mixture of LiBEt₂H₂ and LiBEt₄, in the reaction with **2**. This is

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Scheme 2

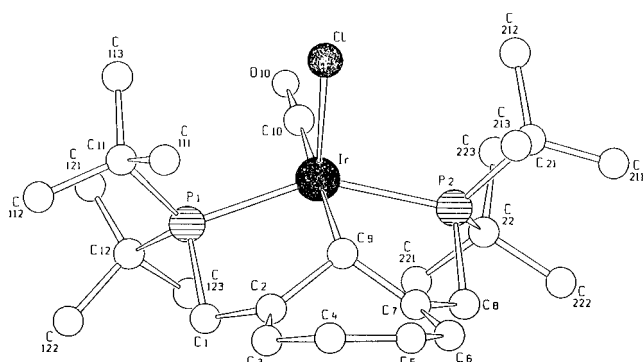
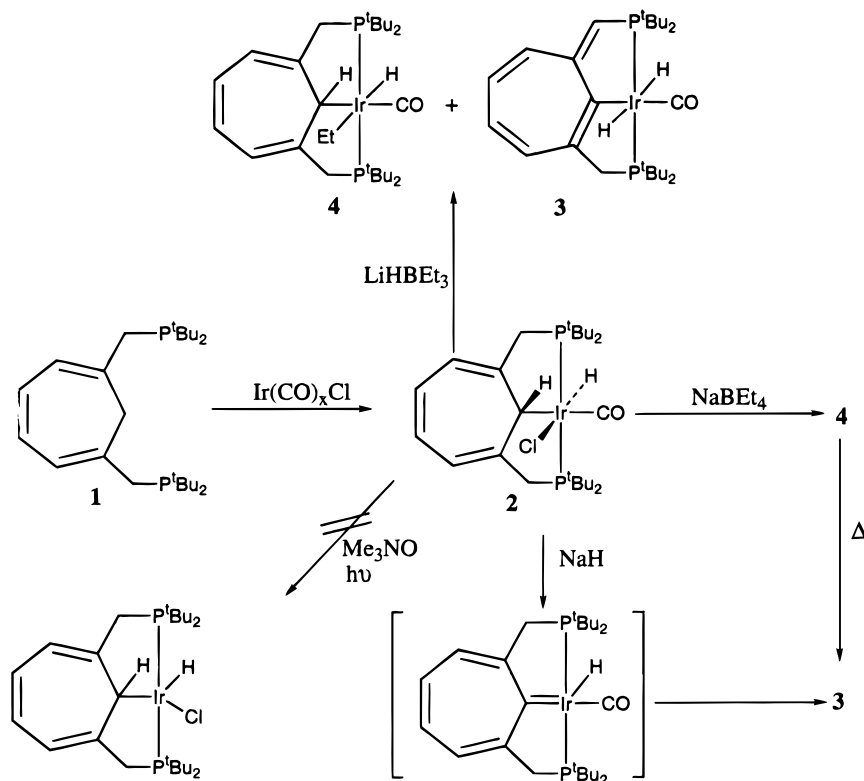


Figure 1. SCHAKAL view of **2**. Hydrogen atoms are omitted for clarity.

evident from the ^{11}B NMR spectrum of impure LiBEt_3H , which showed a triplet from the presence of LiBEt_2H_2 and singlets for LiBEt_4 and BEt_3 . Fresh solutions of LiBEt_3H show only two ^{11}B NMR resonances, a doublet for LiBEt_3H and a singlet for the small amount of BEt_3 .¹⁴ Treatment of **2** with fresh LiBEt_3H still gives mixtures of **3** and **4**, although the major product is **4**. Both complexes were synthesized independently from **2** by reaction with NaBEt_4 and NaH , respectively. No reaction of **2** occurs with $\text{NaB(OMe)}_3\text{H}$.

Complex **3** was independently prepared by treatment of **2** with NaH in THF. As shown in Scheme 2, this most probably arises from dehydrohalogenation and an interesting prototropic rearrangement. There was no NMR evidence for the proposed prototropic intermediate described in Scheme 2.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the dihydride **3** shows an AB pattern of two nonequivalent phosphorus nuclei

Table 1. Crystal and Structure Solution Data for Compound **2**

formula	$\text{C}_{26}\text{H}_{46}\text{ClOP}_2\text{Ir}$
color	pale yellow
M_r	664.28
a [Å]	11.730(3)
b [Å]	16.910(4)
c [Å]	14.922(4)
β [deg]	108.58(2)
V [Å ³]	2805.8
ρ_{calc} [g/cm ³]	1.568
Z	4
cryst syst	monoclinic
space group	Cc
radiation	0.710 73 Å (Mo K α)
diffractometer	CAD4
cryst size [mm]	$0.4 \times 0.2 \times <0.01$
temperature [°C]	-76
scan range (deg, 2θ)	6–72
measd reflns	7052
obsd reflns	6863
indep obsd reflns, $I > 4\sigma(I)$	5545
data collected (h, k, l)	0–19, 0–28, -24–24
R (F)	0.043
R_w	0.059
GOF	5.348
$\Delta/\sigma(\text{max})$	0.73
$\Delta(\rho)$ (eÅ ⁻³)	2.54

$$^a R = \sum ||F_o(hkl)| - |F_c(hkl)|| / \sum |F_o(hkl)|; R_w = \sum w_{hk}(|F_o(hkl)| - |F_c(hkl)|)^2 / \sum w_{hk}(|F_o(hkl)| + |F_c(hkl)|)^2; w = 1/\sigma^2.$$

with a large $^2 J(\text{PP})$ coupling constant of 269.6 Hz. This is strong evidence that the phosphine groups remain in mutually trans positions after the reaction. The splitting of the phosphorus resonances into triplets in an off-resonance decoupled ^{31}P NMR experiment proves that two hydrides are bound to the iridium atom. The chemical shift at $\delta -9.3$ in the ^1H NMR spectrum and the $\nu(\text{IrH})$ stretching frequency at 1804 cm^{-1} ¹⁵ support the mutually trans hydride positions. The $\nu(\text{CO})$ at 1972 cm^{-1} is not greatly affected by the trans sp^2 carbon

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

Ir–Cl	2.468(3)	P(1)–Ir–P(2)	149.44(9)
Ir–P(1)	2.357(2)	P(1)–Ir–C(9)	81.6(2)
Ir–P(2)	2.374(3)	P(2)–Ir–C(9)	79.0(3)
Ir–C(9)	2.25(2)	P(2)–Ir–C(10)	99.9(4)
Ir–C(10)	1.78(1)	Cl–Ir–P(1)	101.6(1)
P(1)–C(1)	1.86(1)	Cl–Ir–P(2)	101.0(1)
P(2)–C(8)	1.84(1)	Cl–Ir–C(9)	87.7(2)
C(2)–C(9)	1.57(1)	Cl–Ir–C(10)	92.1(4)
C(7)–C(9)	1.51(2)	P(1)–Ir–C(10)	99.6(4)
C(2)–C(3)	1.35(2)	P(2)–Ir–C(9)	79.0(3)
C(6)–C(7)	1.35(2)	C(2)–C(9)–C(7)	107.5(8)
C(5)–C(6)	1.47(3)	C(9)–Ir–C(10)	178.8(4)
C(4)–C(5)	1.38(2)	Ir–P(1)–C(1)	101.6(4)
O(10)–C(10)	1.16(2)	Ir–P(2)–C(8)	102.8(4)

atom of the cycloheptatriene ring. Selective heteronuclear decoupling experiments ($^1\text{H}\{^{31}\text{P}\}$) demonstrate that the four *tert*-butyl groups which are bound to two different phosphorus nuclei give rise to two doublets in the alkane region of the ^1H NMR spectrum. This indicates that the cycloheptatriene and the two internal five-membered rings are flat. This is also confirmed by the doublet at δ 3.2 which stems from the methylene group bound to the phosphorus at δ 68.5. This CH_2 group is only observed as a doublet ($^2J(\text{PH}) = 9.2$ Hz) if both hydrogen nuclei are magnetically equivalent, which is only the case if the condensed ring system is planar. In the olefin region between 5.3 and 6.8 there are four multiplets which integrate to five hydrogen atoms. The doublet of doublets at δ 5.6 is the only one which responds to the decoupling experiments with the phosphorus nuclei. The observation of a large and a small coupling ($^2J(\text{PH}) = 6.9$ Hz, $^4J(\text{PH}) = 4.0$ Hz) as well as its chemical shift are in agreement with an olefinic CH group bound to a phosphorus nucleus. The number of carbon resonances and their interaction with the phosphorus nuclei is consistent with the asymmetric structure displayed in Scheme 1. It is noteworthy that the metalated carbon atom is shifted to δ 132.0, which is consistent with vinylic carbon atoms bound to iridium.^{16,17} Structure **3** might be considered an isomeric form of the 1,2,4,6-cycloheptatetraene $\text{Pt}(\text{PPh}_3)_2$ complex, cf. vide infra. On the other hand, it is interesting that **3** is preferred rather than the d^8 carbene form which predominates for Pt(II). Complex **3** is a novel example of an octahedral pincer *trans*-dihydride complex. Such octahedral complexes are reportedly unstable compared to the corresponding *cis* complexes because the two *trans* hydrogen atoms have a mutually strong *trans* influence on each other. Milstein¹⁵ has reported that $[\text{trans-}[\text{IrH}_2(\text{CO})(^i\text{Pr}_2)\text{PCH}_2\text{C}_6\text{H}_5\text{CH}_2\text{P}(^i\text{Pr}_2)]]$ is both kinetically and thermodynamically more stable than the corresponding *cis* isomer because of a combination of steric and electronic factors. Similar arguments can also characterize the stability of **3**.

Identification and synthesis of pure compound **4** was accomplished by treating **2** with NaBET_4 in THF followed by chromatography. This was after we learned that LiBET_3H always gave mixtures of both **3** and **4**.

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Tetraethylborate has been used previously as an ethyl transfer reagent.¹⁸ The singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 49.0 and two virtual triplets observed for the *tert*-butyl groups in the ^1H NMR spectrum indicate that the structure of complex **4** is comparable with that of compound **2**. The hydride triplet in the ^1H NMR spectrum, however, is shifted downfield to δ –10.5, which is typical for a strong *trans* influencing ligand. While the triplet at δ 2.3 can be unambiguously assigned to the methyl group of the ethyl ligand, the methylene protons of the ethyl group are obscured by the *tert*-butyl group, which resonates at δ 1.4. This has been confirmed by 2D HH COSY and CH correlation spectroscopy as well as DEPT experiments. The change of the electronegative chlorine in **2** by the more electropositive ethyl group in **4** is expressed in an upfield shift of the metalated carbon atom and a downfield shift of the carbonyl group in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4**.¹⁹ This is consistent with a shift of $\nu(\text{CO})$ to lower frequencies by 10 cm^{-1} in the IR spectrum of **4**.

The behavior of LiBET_3H as a powerful nucleophile²⁰ and alkyl transfer agent is unusual. Normally, one would expect that hydride transfer would occur much faster than alkyl transfer in these compounds.²¹ This anomaly can be explained by referring to the recent work of Fryzuk^{14,22} who has elegantly described this as the result of ion–dipole complex formation between the transition-metal hydrogen atom and the alkali-metal atom of the soluble alkali-metal organoborate. Even though the alkali-metal organoborate coordinates more strongly with a transition-metal hydride with two or more hydrogen atoms, the interaction with a transition-metal complex with one hydrogen atom is thermodynamically strong. It is even possible that the polarized carbonyl group can assist in this process. If such a complex is formed, it places the alkyl borate group close to the removable chlorine and alkyl group substitution can occur just as readily as hydride transfer.

Compound **4** can be cleanly thermalized to compound **3** by careful sublimation. The exact process of alkane and/or hydrogen elimination to produce **3** is not known at this time.

3. Experimental Section

Materials and Procedures. Compound **1** was synthesized from 1,6-dibromomethylcycloheptatriene,²³ which was prepared from the corresponding diol and PBr_3 .²⁴ The diol was synthesized according to procedures described by Vogel and Darms.^{25–27}

Chlorocarbonyliridium was purchased from Strem Chemicals as a brown solid and used as received. Use of the blue

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Ir(CO)_xCl^{28,29} did not give consistent results. Di-*tert*-butylphosphine was prepared according to the literature.³⁰ Silica gel for chromatography was heated at 160 °C for 24 h and stored under argon. Solvents and general procedures were performed as described previously.³¹ Dioxane-*d*₆ was obtained from Aldrich Chemical Co. and distilled from sodium before use; acetone was distilled from anhydrous boron oxide. Analyses were done at Desert Analytics, Tuscon, AZ. ¹H NMR spectra were obtained on Bruker DRX 250 (250.13 MHz), General Electric GN-500 (500.12 MHz), and Nicolet NT 300 (300.16 MHz) instruments. ¹³C NMR spectra were obtained on the same instruments at 63.9, 125.76, and 75.4 MHz, respectively; ³¹P NMR spectra were obtained at 101.26, 202.47, and 121.4 MHz, respectively. The ³¹P NMR chemical shifts are reported in ppm referenced to a capillary of 85% H₃PO₄ set at 0 ppm in a 5 mm tube that contained benzene-*d*₆. Downfield resonances are positive. The ¹H and ¹³C chemical shifts are reported relative to Me₄Si. The number of hydrides bound to the metal centers were also confirmed on the basis of multiplicities of the off-resonance proton-decoupled ³¹P NMR spectra. 2D HH COSY and CH correlation spectroscopy as well as the DEPT experiments were performed on a Bruker DRX250 with standard pulse techniques and software packages. X-ray structure determination: Enraf-Nonius CAD4 diffractometer.

Synthesis of 1,6-Bis((*tert*-butylphosphino)methyl)-1,3,5-cycloheptatriene. To a 100 mL flask with 50 mL of dry acetone and 5.8 g (0.0179 mol) of 1,6-bis(bromomethyl)-1,3,5-cycloheptatriene was added 5.3 g (0.036 mL) of di-*tert*-butylphosphine by syringe. The brown-orange solution became slightly cloudy. After 1 h of stirring at room temperature, copious amounts of white solid formed. The reaction mixture was filtered after stirring overnight, and the off-white precipitate was washed once with acetone, 9.5 g yield (93%). This dried material was treated on the fritted disk with a solution of 10.3 g of sodium acetate in 26 mL of degassed water. The water solution was extracted with ether. The ether extract was dried over degassed magnesium sulfate and filtered, and the ether was removed to give a clear oil which solidified after 7 h. Yield: 4.8 g (70%). Mp: 68–70 °C. ¹H NMR (300.06 MHz, C₆D₆): δ 1.1 (d, ³J(PH) = 10.5 Hz, 36H, C(CH₃)), 2.7 (d, ²J(PH) = 4.2 Hz, 4H, CH₂P), 3.0 (s, 2H, CH₂), 6.1, 6.4 (m, 4H, CH). ³¹P{¹H} NMR (202.47 MHz, C₆D₆): δ 17.5 (s). ¹³C{¹H} NMR (75.4 MHz, C₆D₆): δ 30.0 (d, ²J(PC) = 13.7 Hz, C(CH₃)), 32.0 (d, ¹J(PC) = 24.2 Hz, C(CH₃)), 32.8 (m, CH₂P), 38.1 (t, ³J(PC) = 8.5 Hz, CH₂), 124.0 (d, ³J(PC) = 7.1 Hz, =CH–CH=), 129.0 (s, HC=CH), 136.8 (d, ²J(PC) = 11 Hz, CH₂CCH–). Anal. Calcd for C₂₅H₄₆P₂: C, 73.49; H, 11.35. Found: C, 73.20; H, 11.16.

Reaction of Ir(CO)_xCl and 1,6-Bis((*tert*-butylphosphino)methyl)-1,3,5-cycloheptatriene. Dry THF, 15 mL, was added to a mixture of Ir(CO)_xCl 0.088 g (0.282 mmol) and **1** (0.115 g, 0.282 mmol) at room temperature. The initially brown mixture became yellow as the carbonyl dissolved over a 24 h period. The pale cloudy solution was filtered, and the filtrate was concentrated under vacuum to give an off-white solid, which can be purified by using THF/ether. Yield: 0.175 g, 93.4%. Mp: 192–194 °C. ¹H NMR (500 MHz, C₆D₆): δ –18.6 (t, ²J(PH) = 14.5 Hz, 1H, IrH), 1.0, 1.5 (A₉XX'A₉ pattern, N = ³J(PH) + ⁵J(PH) = 12.4, 13.5 Hz, 36H, C(CH₃)), 2.5 (m, 2H, CH₂P), 3.1 (d, ²J(HH) = 15 Hz, 2H CH₂P), 4.0 (s, 1H, CH), 6.2, 6.4 (s, 2H, HC=CH, =CH–CH=). ³¹P{¹H} NMR (121.4 MHz, C₆D₆): δ 50.3 (s). ¹³C{¹H} NMR (125.76 MHz, dioxane-*d*₆): δ 29.3, 31.0 (br s, C(CH₃)), 35.7, 39.4 (AXX'A' pattern, N = ¹J(PC) + ³J(PC) = 26.1, 15.3 Hz, C(CH₃)), 45.4 (AXX'A'

pattern, N = ¹J(PC) + ³J(PC) = 31.9 Hz, CH₂P), 46.1 (s, CHIr), 120.2, (AXX'A' pattern, N = ³J(PC) + ⁵J(PC) = 13.3 Hz, =HC–CH=), 129.3 (s, –HC=CH–), 149.4 (AXX'A' pattern, N = ²J(PC) + ⁴J(PC) = 15.0 Hz CH₂CCH), 178.2 (t, ²J(PC) = 7.2 Hz, CO). MS (FAB) for C₂₆H₄₆ClOP₂Ir: calcd *m/e* 664, found *m/e* 664 – HCl = 628. IR (cm^{–1}, pellet on AgCl): 2000 ν(C=O); ν(IrH) 2270. Anal. Calcd for C₂₆H₄₆ClOP₂Ir: C, 47.01; H, 6.98. Found: C, 46.97; H, 6.83.

Reaction of 1,6-Bis((*tert*-butylphosphino)methyl)-1,3,5-cycloheptatriene, **2 with Sodium Hydride.** The cycloheptatriene iridium complex (0.025 g, 0.038 mmol) was treated in THF with a 100% excess of NaH. The almost colorless mixture was stirred at room temperature for 1 h and then stirred in a sonication bath for 12 h with intermittent cooling whereupon it became yellow and then finally deep red-orange. This material was filtered onto fresh NaH and sonicated again at room temperature for two additional hours. The THF was removed, and benzene was added. This was filtered, and the benzene was sublimed away at 0 °C to give a red solid. Yield: 0.019 g, 76%. Mp: 119–123 °C. ¹H NMR (400 MHz, C₆D₆): δ –9.3 (dd, ²J(PH) = 13.4, 13.4 Hz, 2H, IrH), 1.3, 1.5 (d, ³J(PH) = 14.3, 13.4 Hz, 36H, C(CH₃)), 3.2 (d, ²J(PH) = 9.2 Hz, 2H CH₂P), 5.6 (dd, ²J(PH) = 7.0 Hz, ⁴J(PH) = 4.1 Hz, 1H, CHP), 5.8, 6.1, 6.5 (m, 4H, HC=CH, =HC–CH=). ³¹P{¹H} NMR (121.4 MHz, C₆D₆): δ 62.2 (AB, ²J(PP) = 269.6 Hz, CH₂P), 68.5 (AB, ²J(PP) = 269.6 Hz, CHP). ¹³C{¹H} NMR (125.76 MHz, C₆D₆): δ 29.4, 30.3 (d, ²J(PC) = 2.4, 2.5 Hz, C(CH₃)), 34.3 (dd, ¹J(PC) = 21.3 Hz, ³J(PC) = 4.3 Hz, CP), 35.3 (dd, ¹J(PC) = 25.9 Hz, ³J(PC) = 3.8 Hz, CP), 47.6 (d, ¹J(PC) = 29.8 Hz, CH₂P), 116.1 (d, ¹J(PC) = 50.4 Hz, CHP), 124.6 (d, ⁴J(PC) = 1.5 Hz, CH), 127.7 (s, CH), 130.3 (d, ³J(PC) = 22.1 Hz, CH), 131.0 (d, ³J(PC) = 15.3 Hz, CH), 132.0 (m, IrC), 144.8, 176.4 (dd, ²J(PC) = 12.8, 21.6 Hz, ⁴J(PC) = 3.0, 3.3 Hz, CH₂CCH), 180.1 (t, ²J(PC) = 7.6 Hz, CO). MS (APCI/hexane) for C₂₆H₄₅OP₂Ir: calcd *m/e* 627.82, found 628.3. IR (cm^{–1}, pellet on AgCl): 2195, 1972 ν(C=O); 1927, 1804 ν(IrH). Anal. Calcd for C₂₆H₄₅OP₂Ir: C, 49.74; H, 7.22. Found: C, 51.37; H, 7.57. These were repeat analyses. The material was sublimed because it decomposed during chromatography, and it was too soluble in all solvents for any recrystallization.

Reaction of 1,6-Bis((*tert*-butylphosphino)methyl)-1,3,5-cycloheptatriene with Pure Sodium Tetraethylboron. The iridium complex **2** (0.015 g, 0.023 mmol) in THF was treated with 0.003 g (0.023 mmol) of sodium tetraethylboron in THF by dropwise addition over a 0.5 h period. The mixture was allowed to stir for 24 h, and the THF was removed under vacuum. The crude sample was chromatographed on silica gel with benzene as the eluant to give a pale yellow solid. Yield: 10 mg, 66%. Mp: 142–146 °C. ¹H NMR (250.13 MHz, C₆D₆): δ –10.5 (t, ²J(PH) = 20.9 Hz, 1H, IrH), 1.3, 1.4 (A₉XX'A₉ pattern, N = ³J(PH) + ⁵J(PH) = 12.7, 18.5 Hz, 36H, C(CH₃)), 1.4 (q, ³J(HH) = 7.7 Hz, 2H, CH₃CH₂), 2.3 (t, ³J(HH) = 7.7 Hz, 3H CH₃CH₂), 2.8 (AFMXX'M' pattern, ²J(HH) = 15.4 Hz, ⁴J(HH) < 2 Hz, N = |²J(HH) + ⁴J(HH)| < 6 Hz, 2H, CH₂H_bP), 3.4 (br s, 1H, CH), 3.5 (AFMXX'X' pattern, ²J(HH) 15.4 Hz, ⁴J(HH) 2.9 Hz, N = |²J(HH) + ⁴J(HH)| < 2 Hz, 2H, CH₂H_bP), 6.4–6.6 (m, 4H, =CH). ³¹P{¹H} NMR (202.46 MHz, C₆D₆): δ 49.0 (s). ¹³C{¹H} NMR (125.76 MHz, C₆D₆): δ 25.4 (s, CH₃CH₂), 26.2 (s, CHIr), 29.3 (A₃XX'A₃ pattern, N = ²J(PC) + ⁴J(PC) = 5.0 Hz, C(CH₃)), 31.1 (br s, C(CH₃)), 35.4, 37.0 (AXX'A' pattern, N = ¹J(PC) + ³J(PC) = 26.5, 14.5 Hz, C(CH₃)), 47.5 (s, CH₃CH₂), 49.0 (AXX'A' pattern, N = ¹J(PC) + ³J(PC) = 35.2 Hz, CH₂P), 120.2 (AXX'A' pattern, N = ³J(PC) + ⁵J(PC) = 12.6 Hz, =HC–CH=), 129.3 (s, HC=CH), 149.5 (AXX'A' pattern, N = ²J(PC) + ⁴J(PC) = 6.3 Hz, CH₂CCH), 187.7 (t, ²J(PC) = 7.2 Hz, CO). MS (APCI) for C₂₈H₅₁OP₂Ir: calcd *m/e* 657.886, found 658.4. IR (cm^{–1}, pellet on AgCl): 1937 ν(C=O); ν(IrH) 2125; Anal. Calcd for C₂₈H₅₁OP₂Ir: C, 51.11; H, 7.81%. Found: C, 49.22; H, 7.53. These were repeat analyses.

X-ray Structure Determination. Crystal, data collection, and refinement parameters are given in Table 1. The crystals

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were grown from THF–pentane. A suitable crystal was selected and mounted on a glass fiber. The unit cell parameters were obtained by least-squares refinement of the angular settings of 25 reflections.

The systematic absences of diffraction data show two possible space groups (*Cc* and *C2/c*). Structure calculations confirm that the noncentrosymmetric space group *Cc* is correct. The structure was solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. Semiempirical ellipsoid absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients.

All software and sources of scattering factors are contained in the SDP program library.³²

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Supporting Information Available: Tables with full crystallographic details, bond distances, bond angles, atomic positional parameters, general displacement parameter expressions, root-mean square amplitude of thermal vibrations, for **3** (8 pages). Ordering information is given on any current masthead page.

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