its derivatives are potentially useful starting materials for organometallic chemistry and catalysis on a diiridium center.

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Supplementary Material Available: Tables of bond distances and angles and a listing of anisotropic displacement parameters for compound 4 and a table of fractional atomic coordinates and isotropic displacement parameters for compound 3 (11 pages); a table of observed and calculated structure factors for compound 4 (23 pages). Ordering information is given on any current masthead page.

Preparation, Properties, and Reactivity of Dihydridosilyl(η^4-cycloocta-1,5-diene)iridium(III) Complexes. X-ray Crystal Structures of the Dihydrido Silyl Complex $IrH_2(SiEt_3)(\eta^4\text{-}C_8H_{12})(AsPh_3)$ and the Cyclooctenyl Derivative $Ir(1\text{-}\sigma,4,5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$

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The synthesis, properties, and reactivity of the dihydridosilyl(η^4-cycloocta-1,5-diene)iridium(III) complexes $IrH_2(SiR_3)(cod)L$ (SiR_3 = $SiEt_3$ or $SiMe_2Ph$; cod = cycloocta-1,5-diene; L = PPh_3 or $AsPh_3$) are described. They are prepared by reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with L and $HSiR_3$. The $IrH_2(SiR_3)(cod)L$ complexes undergo silyl exchange on reaction with $HSiR'_3$ and reductive elimination of $HSiR_3$ on treatment with PPh_3. Reaction of $IrH_2(SiEt_3)(cod)(AsPh_3)$ with CO affords white crystals of $Ir(1\text{-}\sigma,4,5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$. Two representative (triphenylarsine)iridium complexes have been characterized by X-ray diffraction. $IrH_2(SiEt_3)(\eta^4\text{-}C_8H_{12})(AsPh_3)$: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 14.8007$ (6) Å, $b = 19.3871$ (9) Å, $c = 11.1029$ (3) Å, $\beta = 110.445$ (2)°. $Ir(1\text{-}\sigma,4,5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 16.2962$ (11) Å, $b = 16.5549$ (10) Å, $c = 9.3819$ (3) Å, $\beta = 97.761$ (5)°. The structures were solved by Patterson and difference direct methods and refined to conventional agreement factors equal to 0.043 and 0.055, respectively. The coordination around iridium is distorted octahedral for the first compound with a As–Ir–Si angle of 133.40 (4)°, and, for the second one it is slightly distorted trigonal-bipyramidal, with a σ(Ir–C,cyclooctenyl) distance of 2.150 (11) Å.

Introduction

Hydrido(diolefin)iridium complexes have proved to be useful models for understanding catalytic processes related to the hydrogenation of unsaturated organic compounds.[1–4] This paper reports the formation, properties, and reactivity of $IrH_2(SiR_3)(cod)L$ compounds (SiR_3 = $SiEt_3$ or $SiMe_2Ph$; cod = cycloocta-1,5-diene (C_8H_{12}); L = PPh_3 or $AsPh_3$) that we believe are of interest not only because they are the first isolated examples of hydridosilyl(diolefin)metal complexes but also because they appear to be intermediates in the hydrosilylation of olefins by $[Ir(\mu\text{-}OMe)(cod)]_2$/L systems. These systems catalyze the normal hydrosilylation of olefins, along with the unusual dehydrogenative silylation.[5] Several rhodium,[6] ruthenium,[6b,7] cobalt,[8] and iron[9] complexes have been described as catalysts for the dehydrogenative silylation of olefins, but, to the best of our knowledge, no iridium catalysts were reported before. Part of this work has been the subject of a preliminary communication.[10]

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Table I. NMR Data of the $IrH_2(SiR_3)(cod)L$ Complexes[a]

compound	$\delta_{CH_2,CH_3}(SiR_3)$	$\delta_{CH_2,CH}(cod)$	$\delta_{C_6H_5}(L,SiPh)$	δ_{IrH} (J(HP))	δ(P)
$IrH_2(SiEt_3)$-(cod)($AsPh_3$)	0.79 (br, 15 H)	1.4–2 (m, 6 H), 2.32 (br, 2 H), 3.44 (br, 2 H), 3.98 (br, 2 H)	7.34 (br, 9 H), 7.48 (br, 6 H)	−12.60 (2 H)	
$IrH_2(SiMe_2Ph)$-(cod)($AsPh_3$)	0.76 (s, 6 H)	1.4–2 (m, 6 H), 2.30 (br, 2 H), 3.34 (br, 2 H), 3.83 (br, 2 H)	7.34 (br, 12 H), 7.48 (br, 6 H), −12.45 (2 H), 7.62 (br, 2 H)	−12.45 (2 H)	
$IrH_2(SiEt_3)$-(cod)(PPh_3)	0.83 (br, 15 H)	1.3–2 (m, 6 H), 2.38 (br, 2 H), 3.11 (br, 2 H), 3.89 (br, 2 H)	7.33 (br, 9 H), 7.55 (6 H)	−12.85 (d, 2 H, 21.4 Hz)	7.22
$IrH_2(SiMe_2Ph)$-(cod)(PPh_3)	0.75 (s, 6 H)	1.3–2 (m, 6 H), 2.24 (br, 2 H), 3.05 (br, 2 H), 3.76 (br, 2 H)	7.33 (br, 12 H), 7.55 (br, 6 H), 7.69 (br, 2 H)	−12.73 (d, 2 H, 19.6 Hz)	8.43

[a] ^1H NMR spectra (200 MHz, $CDCl_3$); $^{31}P\{^1H\}$NMR spectra (80 MHz, $CDCl_3$).

Results and Discussion

The synthesis of the dihydrido silyl(diolefin)iridium complexes $IrH_2(SiR_3)(cod)L$ (SiR_3 = $SiEt_3$ or $SiMe_2Ph$; L = PPh_3 or $AsPh_3$) involves a straightforward reaction in acetone between $[Ir(\mu\text{-}OMe)(cod)]_2$, L, and $HSiR_3$ according to eq 1. The complexes were isolated as white,

$$^1/_2[Ir(\mu\text{-}OMe)(cod)]_2 + L + 2\,HSiR_3 \rightarrow IrH_2(SiR_3)(cod)L + MeOSiR_3 \quad (1)$$

air-stable powders in good yield (68–96%), and their purity was ascertained by microanalysis. This reaction (eq 1) also leads to the formation of the corresponding $MeOSiR_3$, detected by GC. The ^1H NMR spectra (Table I) of the complexes show only one high-field signal for the equivalent hydrides. In particular, the $IrH_2(SiR_3)(cod)(PPh_3)$ compounds show the hydride resonance as a doublet due to coupling with the cis phosphorus nucleus; the coupling ^2J(HP) constant in the range 19–22 Hz is typical of the cis H–Ir–P grouping.[11] The IR spectra show strong absorptions above 2000 cm^{-1}, attributable to ν(Ir–H), in concordance with a cis arrangement of these ligands.[12] All the spectroscopic data suggest an octahedral structure with the hydrogen atoms in positions trans to the chelating diolefin. This proposal has been confirmed by a single-crystal X-ray diffraction study of $IrH_2(SiEt_3)(cod)(AsPh_3)$ (see below, Figure 1). Most probably the cis configuration of the dihydrides, which are trans to the cycloocta-1,5-diene, could explain the unusual stability of the complexes, at room temperature, toward hydrogen migration to the diolefin, similar to that found by Crabtree et al. with related cationic dihydrido diolefin complexes.[11]

We have recently reported that the $[Ir(\mu\text{-}OMe)(cod)]_2$/L systems are catalyst precursors for the dehydrogenative silylation of hex-1-ene as well as for normal hydrosilylation.[5] As expected, the $IrH_2(SiEt_3)(cod)L$ (L = PPh_3 or $AsPh_3$) complexes are also active catalyst precursors for the reaction of hex-1-ene with $HSiEt_3$; under catalytic conditions (60 °C) the coordinated cycloocta-1,5-diene is probably removed from $IrH_2(SiR_3)(cod)L$ by initial isomerization to cycloocta-1,3-diene, giving rise to the active catalytic species (see ref 10). Many transition-metal complexes act as hydrosilylation catalysts, and although mechanistic schemes involving $M(H)(SiR_3)$(olefin) species have been proposed,[13] only very recently have complexes of formula $Rh(C_5R_5)(H)(SiEt_3)(CH_2{=}CH_2)$ (R = Me[14a] or H[14b]) been detected in solution, and $Rh(C_5Me_5)H(Si(OEt)_3)(CH_2{=}CH_2)$ has been isolated.[14c]

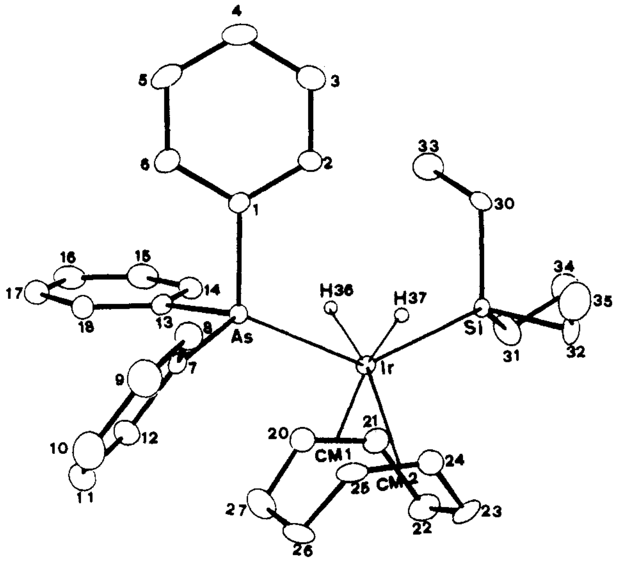

Figure 1. A general view of $IrH_2(SiEt_3)(cod)(AsPh_3)$. Key bond lengths and angles are listed in Table II.

Comments on the Formation of the $IrH_2(SiR_3)$(cod)L Complexes. In order to obtain information about this process, we initially studied by ^1H NMR the reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with 1 mol of PPh_3/iridium in $CDCl_3$. The ^1H NMR spectrum of the resulting orange solution shows a singlet at 3.22 ppm due to the methoxy protons of the starting material $[Ir(\mu\text{-}OMe)(cod)]_2$ and two additional singlets at 3.38 and 3.47 ppm. Upon addition of a second mole of PPh_3 to the solution, only the resonances at 3.38 and 3.47 ppm are observed. These results could be explained in terms of an equilibrium between species containing 1 and 2 mol of PPh_3/iridium, according to eq 2. It is worth mentioning that the reaction of the analogous chloro dimer $[Ir(\mu\text{-}Cl)(cod)]_2$ with 1 mol of PPh_3/iridium gives $IrCl(cod(PPh_3)$, and only on addition of an excess of PPh_3 has an equilibrium similar to that shown in eq 2 been proposed.[15]

$$[Ir(\mu\text{-}OMe)(cod)]_2 \xrightarrow{PPh_3} Ir(OMe)(cod)(PPh_3) \overset{PPh_3}{\rightleftharpoons} Ir(OMe)(cod)(PPh_3)_2 \quad (2)$$

As shown in Scheme I, we believe that the formation of the $IrH_2(SiR_3)(cod)(PPh_3)$ complexes involves an oxidative addition of $HSiR_3$ to $Ir(OMe)(cod)(PPh_3)$ followed by a reductive elimination of $MeOSiR_3$ (detected by GC) and subsequent oxidative addition of the $HSiR_3$ to the hy-

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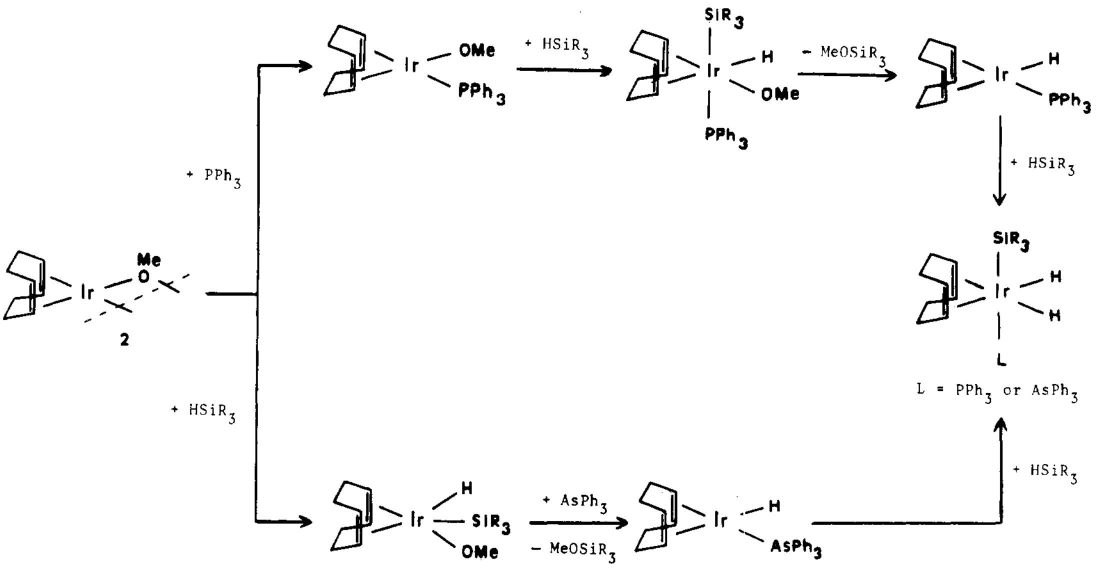
Scheme I. Formation of the $IrH_2(SiR_3)(cod)L$ Complexes from $[Ir(\mu\text{-}OMe)(cod)]_2$



phothetical intermediate $IrH(cod)(PPh_3)$. We have tried to detect this proposed hydrido intermediate by treating the mixture $[Ir(\mu\text{-}OMe)(cod)]_2 + 2PPh_3$ with 1 mol of $HSiR_3$/iridium, but under these conditions only a mixture of the starting materials and the final product was observed by ^1H NMR. The formation of the $IrH_2(SiR_3)(cod)(AsPh_3)$ complexes most likely involves a similar hydrido intermediate, $IrH(cod)(AsPh_3)$, but this species probably is formed by a different pathway, since, according to ^1H NMR measurements, the dimer $[Ir(\mu\text{-}OMe)(cod)]_2$ remains unchanged on treatment with $AsPh_3$. We believe that the first step in this process could be the reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with $HSiR_3$ to give an intermediate which reacts rapidly with $AsPh_3$, as is tentatively shown in Scheme I. However, $[Ir(\mu\text{-}OMe)(cod)]_2$ reacts instantaneously with $HSiR_3$, giving a mixture of products as shown by the ^1H NMR spectra; further reaction of this mixture with $AsPh_3$ does not lead to $IrH_2(SiR_3)(cod)(AsPh_3)$, probably due to the formation of side products in the absence of $AsPh_3$. In both routes the complexes are formed by successive oxidative additions of $HSiR_3$. In fact, most of the silyliridium(III) complexes previously reported have been obtained by oxidative addition of silanes to iridium(I) complexes.[16]

Reactivity. The $IrH_2(SiR_3)(cod)L$ complexes undergo silane exchange at room temperature in the yields shown in eq 3, according to ^1H NMR measurements. The yield

$$\mathrm{IrH_2(SiR_3)(cod)L + HSiR'_3 \rightarrow IrH_2(SiR'_3)(cod)L + HSiR_3} \quad (3)$$

SiR_3	L	SiR'_3	conv after 15 min, %
$SiEt_3$	PPh_3	$SiMe_2Ph$	100
$SiEt_3$	$AsPh_3$	$SiMe_2Ph$	64
$SiMe_2Ph$	PPh_3	$SiEt_3$	50
$SiMe_2Ph$	$AsPh_3$	$SiEt_3$	0[17]

of the exchange reaction is dependent on the silane and is favored by PPh_3 relative to $AsPh_3$. It is worth noting that by ^1H NMR only the hydride signals corresponding to the complexes described in this paper are detected in the silane exchange process (eq 3) as well as in the formation of these compounds (eq 1). The silane exchange could proceed via reductive elimination of $HSiR_3$, followed by oxidative addition of $HSiR'_3$.[18] This mechanism would also account for the reaction of $IrH_2(SiR_3)(cod)L$ with PPh_3 to give the well-known $IrH(cod)(PPh_3)_2$[19] complex and $HSiR_3$ (eq 4) although other mechanisms cannot be ruled out.

$$\mathrm{IrH_2(SiR_3)(cod)L \xrightarrow{PPh_3} IrH(cod)(PPh_3)_2 + HSiR_3} \quad (4)$$

According to ^1H NMR measurements, the reductive elimination of $HSiR_3$ by reaction with PPh_3 at room temperature is very rapid for the compounds with $SiR_3 = SiEt_3$, but when $SiR_3 = SiMe_2Ph$, two hours are required for a conversion of 70–90%.

Reaction of $IrH_2(SiEt_3)(cod)(AsPh_3)$ with carbon monoxide (room tempeature, 1 atm) causes reductive elimination of $HSiEt_3$ and the formation of $Ir(C_8H_{13})(CO)_2(AsPh_3)$ (eq 5). The X-ray structure analysis of this

$$\mathrm{IrH_2(SiEt_3)(C_8H_{12})(AsPh_3) \xrightarrow{CO} Ir(C_8H_{13})(CO)_2(AsPh_3) + HSiEt_3} \quad (5)$$

carbonyl iridium complex (see below, Figure 2) shows the cyclooctenyl ligand coordinated as $1\text{-}\sigma, 4,5\text{-}\eta^2\text{-}C_8H_{13}$. Most probably, transformation of $\eta^4\text{-}C_8H_{12}$ to $1\text{-}\sigma, 4,5\text{-}\eta^2\text{-}C_8H_{13}$ results via hydride migration to the cod ligand in an iridium(I) intermediate; precedents for such a process have been reported for several transition-metal diolefin hydrides.[20]

A remarkable feature of the $IrH_2(SiR_3)(cod)L$ complexes is their tendency to reductive eliminate $HSiR_3$. This elimination is favored relative to H_2 loss probably because the chelating cyclocta-1,5-diene *trans* to both hydrides should disfavor the concerted process of H_2 elimination;[16c] however, the observation may also be correlated with the stability towards H_2 loss of dihydridosilyl-iridium(III) complexes.[16b]

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[17] Although no conversion was detected after 15 min, measurements taken after 16 h gave a conversion of 30%.

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Table II. Selected Geometrical Parameters[a] with Esd's in Parentheses for $IrH_2(SiEt_3)(\eta^4\text{-}C_8H_{12})(AsPh_3)$

(a) Interatomic Distances (Å)

Ir–As	2.4675 (7)	As–C1	1.947 (6)	C30–C33	1.504 (10)
Ir–Si	2.414 (2)	As–C7	1.950 (5)	C31–C34	1.518 (15)
Ir–H36	1.65 (···)	As–C13	1.951 (5)	C32–C35	1.498 (17)
Ir–H37	1.57 (···)	Si–C30	1.899 (7)	C20–C21	1.391 (11)
Ir–CM1	2.122 (7)	Si–C31	1.902 (10)	C24–C25	1.396 (11)
Ir–CM2	2.093 (6)	Si–C32	1.897 (7)		

(b) Bond Angles (deg)

As–Ir–Si	133.40 (4)	C30–Si–C31	103.2 (4)
H36–Ir–H37	109 (···)	C30–Si–C32	102.1 (3)
H36–Ir–CM1	86 (···)	C31–Si–C32	105.9 (4)
H37–Ir–CM2	80 (···)	Si–C30–C33	117.0 (5)
CM1–Ir–CM2	84.5 (3)	Si–C31–C34	116.2 (7)
Ir–As–C1	114.9 (2)	Si–C32–C35	117.0 (7)
Ir–As–C7	119.9 (2)	C27–C20–C21	124.1 (7)
Ir–As–C13	117.5 (2)	C20–C21–C22	122.5 (6)
Ir–Si–C30	114.3 (2)	C23–C24–C25	122.9 (7)
Ir–Si–C31	113.9 (3)	C24–C25–C26	122.9 (8)
Ir–Si–C32	116.0 (3)		

(c) Torsion Angles (deg)

Ir–As–C1–C2	0.3 (4)	As–Ir–C25–C24	−161.7 (4)
Ir–As–C7–C8	88.9 (5)	C30–Si–As–C21	146.2 (2)
Ir–As–C13–C14	−33.2 (5)	C30–Si–As–C25	−156.9 (2)
Si–Ir–As–C1	−14.6 (1)	Si–Ir–C20–C21	25.0 (4)
Si–Ir–As–C7	−133.4 (2)	Si–Ir–C25–C24	−14.0 (5)
Si–Ir–As–C13	99.9 (2)	C20–C21–C22–C23	−88 (1)
Ir–Si–C30–C33	−64.2 (8)	C21–C22–C23–C24	21 (1)
Ir–Si–C31–C34	173.2 (8)	C22–C23–C24–C25	57 (1)
Ir–Si–C32–C35	−63.7 (7)	C23–C24–C25–C26	−1 (1)
As–Ir–Si–C30	−4.4 (2)	C24–C25–C26–C27	−86 (1)
As–Ir–Si–C31	−122.7 (3)	C25–C26–C27–C20	23 (1)
As–Ir–Si–C32	113.9 (3)	C26–C27–C20–C21	53 (1)
As–Ir–C20–C21	168.5 (3)	C27–C20–C21–C22	3 (1)

(d) Least-Squares Planes (Deviations (Å) of the As Atoms in Brackets)

1: Ir,CM1, CM2	4: C1,C2,C3,C4,C5,C6	[As: 0.0702 (6)]
2: Ir,H36,H37	5: C7,C8,C9,C10,C11,C12	[As: −0.1290 (5)]
3: Ir,As,Si	6: C13,C14,C15,C16,C17,C18	[As: 0.1709 (6)]

planes	angles, deg	planes	angles, deg
1–2	17.8 (2)	3–4	13.5 (2)
1–3	90.6 (2)	3–5	70.2 (2)
2–3	76 (···)	3–6	99.0 (2)

[a] CM1 and CM2 are the midpoints on the C20–C21 and C24–C25 bonds, respectively.

X-ray Crystal Structures $IrH_2(SiEt_3)(\eta^4\text{-}C_8H_{12})(AsPh_3)$. The coordination around the iridium atom is distorted octahedral (see Figure 1) involving the positions given for the hydrides. The small As–Ir–Si angle, 133.40 (4)°, is notable. Significant distortions of this type have been observed for the P–Ir–P angle in hydrido(phosphine)metal complexes, ranging from 169.3 to 149.9°.[21] The value observed in the present complex may be due to the different steric requirements, relatively small for the hydrides and comparatively large for the cod ligand. Thus, considering the mentioned values of 169.3 and 149.9° for the As–Ir–Si angle, the calculated positions of the As and Si atoms gave As···H(20) and Si···H(24) contacts shorter than those found in the present situation (2.59 and 2.49 Å with 169.3° and 2.74 and 2.62 Å with 149.9° vs. 2.87 and 2.76 Å).

The mean values for the three different types of C–C bond distances in the cod ligand (1.394 (8), 1.512 (6), and 1.530 (8) Å) are in agreement with those found in the literature.[22] The pseudo-twofold symmetry presented by the ring is described by the values of the torsion angles (see Table II).

Table III. Selected Geometrical Parameters[a] with Esd's in Parentheses for $Ir(1\text{-}\sigma,4\text{-}5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$

(a) Interatomic Distances (Å)

Ir–As	2.472 (1)	C10–CM	3.584 (18)
Ir–C5	2.150 (11)	C9–C10	3.005 (13)
Ir–C9	1.918 (10)	As–C20	1.925 (10)
Ir–C10	1.900 (10)	As–C30	1.938 (9)
Ir–CM	2.032 (15)	As–C40	1.954 (10)
C9–CM	3.493 (18)		

(b) Bond Angles (deg)

C5–Ir–CM	82.6 (5)	C9–Ir–As	92.5 (3)
C5–Ir–As	173.5 (3)	C10–Ir–As	93.4 (3)
C5–Ir–C9	92.4 (5)	CM–Ir–As	91.2 (4)
C5–Ir–C10	89.5 (5)	Ir–As–C20	115.4 (3)
C9–Ir–C10	103.8 (4)	Ir–As–C30	115.0 (3)
CM–Ir–C9	124.3 (5)	Ir–As–C40	115.9 (3)
CM–Ir–C10	131.4 (5)		

(c) Torsion Angles (deg)

Ir–As–C20–C21	64.6 (10)	C1–C2–C3–C4	72 (2)
Ir–As–C30–C31	−142.2 (8)	C2–C3–C4–C5	−21 (2)
Ir–As–C40–C41	−168.6 (8)	C3–C4–C5–C6	−84 (1)
C9–Ir–As–C20	−89.0 (5)	C4–C5–C6–C7	54 (2)
C9–Ir–As–C30	30.8 (4)	C5–C6–C7–C8	61 (2)
C9–Ir–As–C40	150.5 (4)	C6–C7–C8–C1	−45 (3)
C10–Ir–As–C20	167.0 (5)	C7–C8–C1–C2	−48 (3)
C10–Ir–As–C30	−73.2 (4)	C8–C1–C2–C3	11 (3)
C10–Ir–As–C40	46.5 (4)		

(d) Deviations (Å) of Some Atoms from the Least-Squares Plane through CM,C9,C10

Ir, 0.0784 (4); As, 2.550 (1); C1, 0.109 (16); C2, −0.110 (15); C5, −2.061 (11)

[a] CM is the midpoint on the C1–C2 bond.

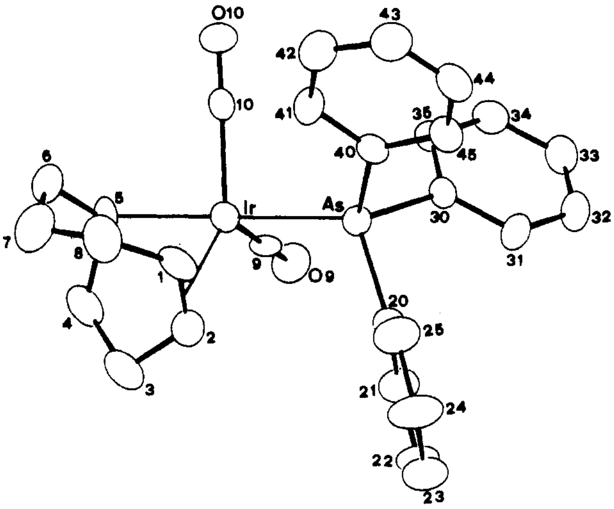

Figure 2. A general view of $Ir(C_8H_{13})(CO)_2(AsPh_3)$. Key bond lengths and angles are listed in Table III.

$Ir(1\text{-}\sigma,4,5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$. This complex has the metal atom in a slightly distorted trigonal-bipyramidal coordination (see Figure 2), with the C(5) and As atoms situated at the axial positions. Table III reflects this distortion in terms of the different angular values around the Ir atom. The Ir–C(5) distance of 2.150 (11) Å and that between the Ir and the midpoint (CM in tables) of the double bond, in the eight-membered ring system, of 2.032 (15) Å compare well with analogous values found in the literature.[20a,23] The observed Ir–As distance (2.472 (1) Å)

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Table IV. Crystal Data and Data Collection Parameters for $IrH_2(SiEt_3)(C_8H_{12})(AsPh_3)$ and $Ir(C_8H_{13})(CO)_2(AsPh_3)$

	$IrH_2(SiEt_3)(C_8H_{12})(AsPh_3)$	$Ir(C_8H_{13})(CO)_2(AsPh_3)$
	Crystal Data	
formula	$C_{32}H_{44}SiAsIr$	$C_{28}H_{28}O_2AsIr$
cryst habit	prismatic, rectangular base	prismatic, hexagonal base
cryst size, mm	0.30 × 0.23 × 0.17 × 0.17	0.30 × 0.30 × 0.30 × 0.50
symmetry	monoclinic, $P2_1/n$	monoclinic $P2_1/n$
unit-cell determinatn	least-squares fit from 97 reflections ($\theta < 45°$)	least-squares fit from 96 reflections ($\theta < 45$)
unit-cell dimens	a = 14.8007 (6), b = 19.3871 (9), c = 11.1029 (3) Å β = 110.445 (2)°	a = 16.2962 (11), b = 16.5549 (10), c = 9.3819 (3) Å β = 97.761 (5)°
packing: V, Å^3, Z	2985.2 (2), 4	2507.9 (2), 4
D_{calcd}, g·cm^{-3}, M_r, $F(000)$	1.611, 723.93, 1440	1.758, 663.67, 1288
μ, cm^{-1}	102.5	117.6
	Experimental Data	
technique	four-circle diffractometer bisecting geometry graphite-oriented monochromator, Cu Kα	
	$\omega/2\theta$ scans, scan width 1.40°	$\omega/2\theta$ scans, scan width 1.5°
total measurements	up to 65°	
no. of reflections		
measd	5041	4263
independent	5041	4263
obsd	4855 [$3\sigma(I)$ criterion]	4054 [$3\sigma(I)$ criterion]
extinction correctn	affected 11 higher F_o were considered as unobserved	no
max-min transmissn factors	1.245–0.604	1.258–0.521
	Solution and Refinement	
solution	Patterson function and DIRDIF	
refinement	L.S. on F_o with 1 block	
H atoms	differences synthesis	
final ΔF peaks	1.30 e/Å^3 near As atom	1.34 e/Å^3 near the Ir atom
final R and R_w	0.043–0.046	0.055–0.067
computer and programs	VAX 11/750 XRAY 76 System[25] and DIRDIF[26]	
scattering factors	International Tables for X-Ray Crystallography[27]	

is comparable with that found in the preceding dihydrido complex (2.468 (1) Å).

The overall conformation of the 1-σ,4,5-η^2-C_8H_{13} ring (see Table III) is similar to that found in a related complex,[23] but in the present case the torsion angle around the double bond has a higher value (11 (3)° vs. 1°) and the C(1) and C(2) atoms do not lie in the equatorial plane of coordination (0.11 (2) and −0.11 (2) Å away from the mentioned plane). The bond lengths range from 1.426 (19) to 1.770 (27) Å, with the atoms involved in the longest distance affected by the highest thermal values, the ellipsoids being elongated in the bond direction (Figure 2).

Experimental Section

General Data. All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Triethylsilane and dimethylphenylsilane (Fluka, 99%) were used without further purification. $[Ir(\mu\text{-}OMe)(cod)]_2$ was prepared as previously reported.[24] ^1H and ^{31}P NMR spectra were carried out in $CDCl_3$ solution at room temperature on a Varian XL 200 spectrometer. IR spectra were recorded on a Perkin-Elmer 783 spectrometer. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer.

Synthesis of the Complexes. $IrH_2(SiEt_3)(cod)(PPh_3)$. $[Ir(\mu\text{-}OMe)(cod)]_2$ (232 mg, 0.35 mmol) was added to a solution of PPh_3 (183 mg, 0.7 mmol) in 20 mL of acetone. The mixture was allowed to react for 30 min at room temperature, during which time an orange solution was formed. $HSiEt_3$ (1 mL) was added to this solution, and the color of the solution changed immediately to yellow. The solution was stirred for 1 h, after which time GC analysis showed the formation of $MeOSiEt_3$. The solution was concentrated under reduced pressure, and methanol was added to give a white precipitate which was filtered, washed with methanol, and dried under vacuum: yield 338 mg (71%). Anal. Calcd: C, 56.53; H, 6.52. Found: C, 56.38; H, 6.49. IR (Nujol, ν(Ir–H)): 2106, 2091 cm^{-1}.

$IrH_2(SiMe_2Ph)(cod)(PPh_3)$. The complex was prepared by using the procedure described for $IrH_2(SiEt_3)(cod)(PPh_3)$, with $[Ir(\mu\text{-}OMe)(cod)]_2$ (350 mg, 0.53 mmol), PPh_3 (277 mg, 1.06 mmol), and $HSiMe_2Ph$ (1.5 mL). $IrH_2(SiMe_2Ph)(cod)(PPh_3)$ was obtained in a 507-mg (68%) yield. Anal. Calcd: C, 58.24; H, 5.71. Found: C, 58.30; H, 5.60. IR (Nujol, ν(Ir–H)): 2106, 2070 cm^{-1}.

$IrH_2(SiEt_3)(cod)(AsPh_3)$. $[Ir(\mu\text{-}OMe)(cod)]_2$ (232 mg, 0.35 mmol), $AsPh_3$ (642 mg, 2.1 mmol), and $HSiEt_3$ (1 mL) were stirred in acetone (20 mL), at room temperature, for 3 h. GC analyses of the resulting pale yellow solution showed the presence of $MeOSiEt_3$. The solution was concentrated under reduced pressure, and methanol was added to give a white precipitate that was filtered, washed with methanol, and dried under vacuum: yield 408 mg (80%). Anal. Calcd: C, 53.11; H, 6.08. Found: C, 53.18; H, 6.03. IR (Nujol, ν(Ir–H)): 2081 cm^{-1}.

$IrH_2(SiMe_2Ph)(cod)(AsPh_3)$. The complex was prepared by using the procedure described for $IrH_2(SiEt_3)(cod)(AsPh_3)$, with $[Ir(\mu\text{-}OMe)(cod)]_2$ (100 mg, 0.3 mmol), $AsPh_3$ (277 mg, 0.9 mmol), and $HSiMe_2Ph$ (0.5 mL). $IrH_2(SiMe_2Ph)(cod)(AsPh_3)$ was obtained in 217-mg (96%) yield. Anal. Calcd: C, 54.80; H, 5.37. Found: C, 54.88; H, 5.38. IR (Nujol, ν(Ir–H)): 2096, 2059 cm^{-1}.

$Ir(1\text{-}\sigma,4,5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$. $IrH_2(SiEt_3)(cod)(AsPh_3)$ (100 mg, 0.14 mmol) was dissolved in 30 mL of dichloromethane, and CO was bubbled through the solution for 24 h at room temperature. Methanol was added to the solution, and after 2 days white crystals were formed. The crystals were filtered off to give 55 mg (60%) of $Ir(C_8H_{13})(CO)_2(AsPh_3)$. Anal. Calcd: C, 50.67; H, 4.25. Found: C, 50.20; H, 4.05. IR (Nujol, ν(C≡O)): 2000, 1951 cm^{-1}.

Reaction of $IrH_2(SiR_3)(cod)L$ with $HSiR'_3$. The reactions were carried out at room temperature by using 0.06 mmol of the

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Table V. Final Atomic Coordinates for $IrH_2(SiEt_3)(\eta^4\text{-}C_8H_{12})(AsPh_3)$

atom	x/a	y/b	z/c
Ir	0.43244 (1)	0.25970 (1)	0.67118 (2)
As	0.49204 (4)	0.29658 (3)	0.49968 (5)
Si	0.37317 (11)	0.15145 (7)	0.72142 (14)
C1	0.5230 (4)	0.2216 (3)	0.4040 (5)
C2	0.5107 (4)	0.1538 (3)	0.4335 (6)
C3	0.5296 (5)	0.1002 (3)	0.3629 (7)
C4	0.5590 (5)	0.1145 (4)	0.2608 (7)
C5	0.5708 (5)	0.1814 (4)	0.2294 (6)
C6	0.5524 (4)	0.2347 (3)	0.3000 (6)
C7	0.6106 (4)	0.3502 (3)	0.5429 (5)
C8	0.6979 (4)	0.3157 (3)	0.5731 (6)
C9	0.7836 (5)	0.3521 (4)	0.6126 (7)
C10	0.7836 (5)	0.4227 (4)	0.6233 (7)
C11	0.6977 (5)	0.4579 (4)	0.5959 (6)
C12	0.6105 (4)	0.4217 (3)	0.5555 (6)
C13	0.4028 (4)	0.3467 (3)	0.3542 (5)
C14	0.3051 (5)	0.3289 (3)	0.3166 (6)
C15	0.2388 (5)	0.3589 (4)	0.2075 (7)
C16	0.2684 (6)	0.4043 (4)	0.1355 (7)
C17	0.3639 (6)	0.4219 (3)	0.1699 (6)
C18	0.4319 (5)	0.3932 (3)	0.2814 (6)
C20	0.3507 (5)	0.3589 (3)	0.6430 (7)
C21	0.3188 (5)	0.3163 (4)	0.7208 (7)
C22	0.3447 (7)	0.3288 (5)	0.8631 (8)
C23	0.4386 (7)	0.2951 (5)	0.9474 (7)
C24	0.5070 (5)	0.2775 (4)	0.8768 (6)
C25	0.5411 (5)	0.3267 (4)	0.8114 (6)
C26	0.5116 (8)	0.4019 (4)	0.8022 (9)
C27	0.4177 (7)	0.4191 (4)	0.6918 (10)
C30	0.3623 (5)	0.0805 (3)	0.5992 (6)
C31	0.2467 (6)	0.1567 (4)	0.7282 (10)
C32	0.4503 (6)	0.1088 (4)	0.8771 (7)
C33	0.2911 (8)	0.0917 (5)	0.4658 (8)
C34	0.2012 (8)	0.0887 (6)	0.7442 (14)
C35	0.5493 (9)	0.0863 (6)	0.8864 (12)
CM1	0.3348 (5)	0.3376 (3)	0.6819 (7)
CM2	0.5241 (5)	0.3021 (4)	0.8441 (6)

Table VI. Final Atomic Coordinates for $Ir(1\text{-}\sigma,4,5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$

atom	x/a	y/b	z/c
Ir	0.06664 (2)	0.11228 (2)	0.33507 (4)
C1	0.1791 (8)	0.1381 (10)	0.2503 (15)
C2	0.1229 (8)	0.1017 (9)	0.1390 (14)
C3	0.1291 (12)	0.0190 (14)	0.0842 (21)
C4	0.1043 (9)	−0.0495 (10)	0.2168 (18)
C5	0.1146 (7)	−0.0085 (7)	0.3632 (17)
C6	0.2037 (9)	−0.0110 (10)	0.4349 (16)
C7	0.2671 (9)	0.0208 (13)	0.3507 (22)
C8	0.2591 (11)	0.1039 (13)	0.3093 (25)
C9	−0.0448 (6)	0.0744 (6)	0.2854 (9)
O9	−0.1108 (5)	0.0529 (6)	0.2554 (10)
C10	0.0780 (5)	0.1244 (6)	0.5381 (11)
O10	0.0829 (5)	0.1287 (6)	0.6604 (9)
As	0.02556 (6)	0.25470 (6)	0.28967 (10)
C20	0.0266 (7)	0.2917 (6)	0.0954 (11)
C21	−0.0291 (9)	0.2560 (9)	−0.0140 (14)
C22	−0.0270 (10)	0.2781 (10)	−0.1552 (13)
C23	0.0305 (13)	0.3338 (12)	−0.1926 (16)
C24	0.0847 (13)	0.3695 (13)	−0.0847 (16)
C25	0.0832 (10)	0.3478 (11)	0.0615 (17)
C30	−0.0855 (6)	0.2811 (5)	0.3267 (10)
C31	−0.1364 (7)	0.3349 (7)	0.2392 (13)
C32	−0.2168 (7)	0.3500 (7)	0.2674 (14)
C33	−0.2461 (8)	0.3119 (8)	0.3785 (15)
C34	−0.1972 (8)	0.2590 (9)	0.4640 (14)
C35	−0.1167 (7)	0.2432 (7)	0.4378 (12)
C40	0.0932 (6)	0.3352 (6)	0.4036 (11)
C41	0.0697 (8)	0.4160 (7)	0.4087 (14)
C42	0.1175 (9)	0.4689 (8)	0.4939 (15)
C43	0.1870 (8)	0.4442 (9)	0.5801 (16)
C44	0.2097 (9)	0.3643 (9)	0.5847 (17)
C45	0.1624 (7)	0.3100 (7)	0.4937 (13)

complex and 1.28 mmol of $HSiR'_3$ in 1 mL of $CDCl_3$. Conversions were calculated by the integration of the high-field ^1H NMR signals. In a typical procedure, $IrH_2(SiEt_3)(cod)(AsPh_3)$ (46 mg, 0.06 mmol) was dissolved in 1 mL of $CDCl_3$ and $HSiMe_2Ph$ (0.2 mL, 1.28 mmol) was added. The solution was placed in a nitrogen-purged NMR tube. After the compounds were mixed 15 min, the ^1H NMR spectrum showed the presence of 36% of $IrH_2(SiEt_3)(cod)(AsPh_3)$ and 64% of $IrH_2(SiMe_2Ph)(cod)(AsPh_3)$.

Reaction of $IrH_2(SiR_3)(cod)L$ with PPh_3. The reactions were carried out at room temperature by using 0.06 mmol of the complex and 0.12 mmol of PPh_3 in 1 mL of $CDCl_3$. The resulting products were identified by the ^1H NMR spectra. In a typical procedure, $IrH_2(SiEt_3)(cod)(AsPh_3)$ (46 mg, 0.06 mmol) and PPh_3 (34 mg, 0.12 mmol) were dissolved in 1 mL of $CDCl_3$, and the solution was placed in a nitrogen-purged NMR tube, after which time the ^1H NMR spectrum showed only the presence of $IrH(cod)(PPh_3)_2$ and $HSiEt_3$.

Determination and Refinement of the Structures. Crystal data are listed in Table IV. The stability and orientation of both crystals were checked by measuring two standard reflections every 90 min. No significant variations were detected. An empirical absorption correction was applied.[28]

In the final cycles of the refinement weighting schemes were applied as to give no trends in $\langle w^2F \rangle$ vs. $\langle F_o \rangle$ and $\langle (\sin \theta)/\lambda \rangle$. The final positional parameters are displayed in Tables V and VI.

In the $IrH_2(SiEt_3)(\eta^4\text{-}C_8H_{12})(AsPh_3)$ complex, it was not possible to locate unambigously the hydride atoms H(36) and H(37), but the ^1H NMR data and the coordination suggested the selection of the given positions as the most likely, among the maxima surrounding the metal atom in a difference Fourier synthesis. The rest of the hydrogen atoms in this complex, as well as in the second one, were sought from a difference synthesis and were included isotropically in the final cycles of the refinement. Some of them (those with no estimated standard deviations given in Tables VII and VIII (supplementary material)) had to be kept fixed to preserve the geometry.

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Registry No. $IrH_2(SiEt_3)(cod)(PPh_3)$, 102735-77-3; $[Ir(\mu\text{-}OMe)(cod)]_2$, 12148-71-9; $HSiEt_3$, 617-86-7; $IrH_2(SiMe_2Ph)(cod)(PPh_3)$, 108366-60-5; $HSiMe_2Ph$, 766-77-8; $IrH_2(SiEt_3)(cod)(AsPh_3)$, 102735-78-4; $IrH_2(SiMe_2Ph)(cod)(AsPh_3)$, 108366-61-6; $Ir(1\text{-}\sigma,4,5\text{-}\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)$, 108366-62-7; $IrH(cod)(PPh_3)_2$, 31781-78-9.

Supplementary Material Available: Hydrogen parameters (Tables VII and VIII) and thermal factors (Tables IX and X) (4 pages); structure factors (Tables XI and XII) (63 pages). Ordering information is given on any current masthead page.

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