Synthesis, Molecular Structure, and Reactivity of the Octahedral Iridium(III) Compound [IrH(η^1,η^3-C_8H_{12})(dppm)] (dppm = Bis(diphenylphosphino)methane)

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The complex [Ir(μ-OCH_3)(η^4-1,5-COD)]$_2$ (1) reacts in methanol with dppm (bis(diphenylphosphino)-methane) to give [IrH(η^1,η^3-C_8H_{12})(dppm)] (2). The molecular structure of this compound has been determined by X-ray investigation. 2 crystallizes in the space group $P2_1/n$ with a = 10.406 (1) Å, b = 17.703 (3) Å, c = 15.894 (2) Å, and β = 102.15 (1)°. The coordination geometry about the iridium center can be rationalized as a distorted octahedron with the phosphorus atoms of the dppm ligand, one terminal allyl carbon atom, and the C–Ir carbon atom forming the equatorial plane. The apical positions are occupied by the other terminal allyl carbon atom, and the hydride ligand. The reaction of [Ir(μ-OCD_3)(η^4-1,5-COD)]$_2$ (1-d_6) with dppm in methanol-d_4 leads to 2-d_3. Two of the three deuterium atoms of 2-d_3 are located on the methylene group of the diphosphine ligand, and the other on one of the two carbon atoms bonded to the C–Ir carbon atom of the carbocyclic ligand. On the basis of this result and other considerations, a mechanism for the formation of 2 is proposed. 2 is formed via the intermediate [IrH(η^4-1,5-COD)(dppm)] which evolves to [Ir(η^3-C_8H_{13})(dppm)] by hydride transfer from the metal to an olefin group of the coordinated diolefin, and subsequent double-bond migration. The last step is the intramolecular C–H (sp^3) activation of one of the two C–H bonds on the carbon atom that is equidistant from the terminal allyl atoms of the carbocyclic ligand of [Ir(η^3-C_8H_{13})(dppm). 2 reacts with electrophiles and nucleophiles; the reaction with HBF_4 leads to *cis*-[IrH_2(η^4-1,5-COD)(dppm)]BF_4 (13), while in the presence of CO and $P(OMe)_3$ the compounds [Ir(η^1,η^2-C_8H_{13})(dppm)L] (L = CO (14), $P(OMe)_3$ (15)) are obtained.

Introduction

We have previously reported that in the presence of potassium hydroxide the cationic complexes [Rh(η^4-NBD)$(PPh_3)_2$]$^+$, [Rh(η^4-NBD)L_2]$^+$, [Ir(η^4-TFB)$(PPh_3)_2$]$^+$, and [Ir(η^4-TFB)L_2]$^+$ (NBD = 2,5-norbornadiene, TFB = tetrafluorobenzobarrelene; L_2 = 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)-ethane (dppe), and bis(diphenylphosphino)methane (dppm)) catalyze the hydrogen-transfer reactions from 2-propanol to ketones and olefins.[1,2] Subsequently, we observed that the hydridoiridium compounds [IrH(η^4-diene)$(PPh_3)_2$] (diene = 1,5-COD (1,5-cyclooctadiene), TFB), obtained by addition of potassium hydroxide to 2-propanol solutions of [Ir(η^4-diene)$(PPh_3)_2$]$^+$, also catalyze the hydrogen-transfer reactions from alcohols to cyclohexanone. In this case, the presence of the cocatalyst was not necessary, suggesting that the potassium hydroxide was needed for the formation of coordinated isopropoxide groups which can lead to the formation of hydride intermediates by a β-elimination reaction. In agreement with this, reactions of [Ir(μ-$OCHR_2$)(η^4-diene)]$_2$ with PPh_3 gave [IrH(η^4-diene)$(PPh_3)_2$] and R_2CO.[3]

These results prompted us to study the reactivity of [Ir(μ-OCH_3)(η^4-1,5-COD)]$_2$ toward dppp, dppe, and PCy_3. Thus, the complexes [IrH(η^4-diene)L_2] (L_2 = dppp, dppe) were obtained in the presence of dppp or dppe,[3] while the reaction with PCy_3 leads to [Ir(OMe)(η^4-1,5-COD)(PCy_3)] which is a useful starting material for the synthesis of σ-alkynyl, dihydride silyl, and new alkoxy compounds.[4,5] We have now observed that the reaction of [Ir(μ-OCH_3)(η^4-1,5-COD)]$_2$ with dppm leads to an unusual iridium(III) compound of formula [IrH(η^1,η^3-C_8H_{12})-(dppm)].

Three years ago, Bönnemann et al.[6] described a family of compounds containng the Co(η^1,η^3-C_8H_{12}) fragment. The reaction of [Co(η^3-C_8H_{13})(η^4-1,5-COD)] with HBF_4·Et_2O and arene ligands results in the formation of [Co-(η^1,η^3-C_8H_{12})(η^6-arene)]$^+$ complexes. The arene ligands in these compounds are easily displaced by acetonitrile to give [Co(η^1,η^3-C_8H_{12})$(CH_3CN)_3$]$^+$, which is a versatile starting material for the synthesis of neutral cobalt compounds with the η^1,η^3-C_8H_{12} ligand. Complexes containing such a C_8 ring linked by a σ-bond and a η^3-enyl group to a central atom have also been reported for some derivatives of iron, ruthenium, and osmium.[7] Most recently, the synthesis and X-ray crystal structure of the anion [Ir-(η^1,η^3-$C_8H_{11}OH$)(P_3O_9)]$^{2-}$, which is an intermediate in the oxidation of [Ir(P_3O_9)(η^4-1,5-COD)]$^{2-}$ with O_2 to give [Ir-(P_3O_9)(η^3-$C_8H_{12}O$)]$^{2-}$, have been described.[8]

The present paper describes the preparation and X-ray structure of [IrH(η^1,η^3-C_8H_{12})(dppm)] and illustrates its reactivity toward HBF_4, CO, and $P(OMe)_3$.

Results and Discussion

Synthesis and Characterization. Treatment of [Ir-(μ-OMe)(η^4-1,5-COD)]$_2$ (1) with dppm in a 1:2 ratio, in methanol, gives a red solution from which the compound [IrH(η^1,η^3-C_8H_{12})(dppm)] (2) is separated as a white solid

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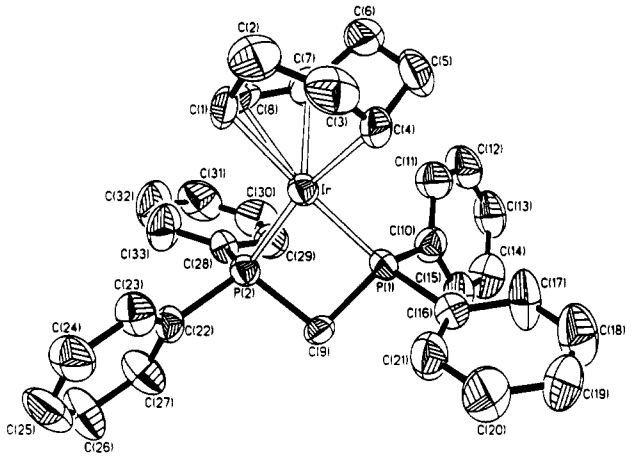

Figure 1. ORTEP diagram of $[IrH(\eta^1,\eta^3\text{-}C_8H_{12})(dppm)]$.

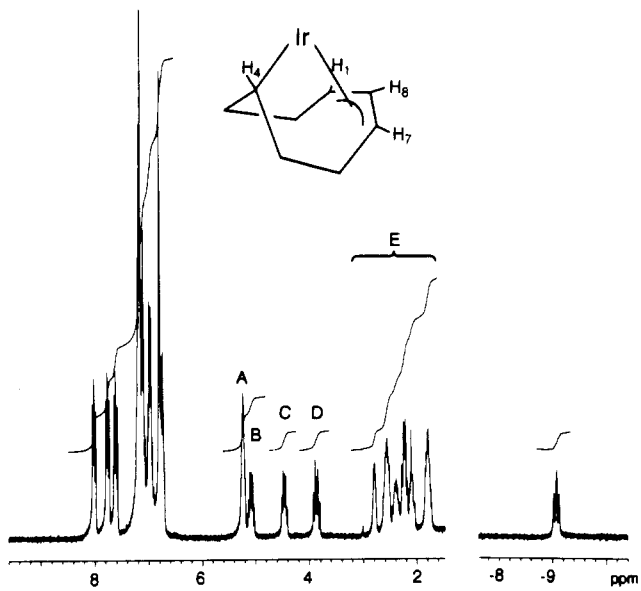

Figure 2. ^1H NMR (benzene-d_6) spectrum of $[IrH(\eta^1,\eta^3\text{-}C_8H_{12})(dppm)]$.

in 70% yield. **2** was fully characterized by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction.

A single-crystal X-ray diffraction analysis of **2** demonstrates the unusual η^1,η^3-binding mode of the carbocyclic ligand. The coordination geometry about the iridium center can be rationalized as a distorted octahedron, with the two phosphorus atoms of the dppm ligand and the carbon atoms C1 and C4 forming the equatorial plane. The apical positions are occupied by the atom C7 and the hydride ligand (Figure 1), which could not be located. The presence of the hydride ligand in the complex is inferred from the IR and ^1H NMR spectra. The IR spectrum of **2** in Nujol shows a strong ν(Ir–H) absorption at 2042 cm^{-1}, while the ^1H NMR spectrum in benzene-d_6 contains a virtual triplet at −9.0 ppm with a P–H coupling constant of 15.5 Hz. Furthermore, the ^1H NMR spectrum shows a broad signal in the region of the aromatic protons, assigned to the phenyl groups of the diphosphine ligand, and a more complicated group of signals between 5.5 and 1.0 ppm (Figure 2). In order to assign the signals of this region to the carbocyclic protons, a COSY experiment was carried out. As a result, we have observed that the A signal is coupled to the signals C and E, B to D, and C to A. On the other hand, the integration of A, B, C, D, and E gives an intensity ratio of 2:1:1:1:9. On the basis of these data, we have assigned H_1 and H_7 to A, H_8 to C, and H_4 together with the eight CH_2 protons of the carbocyclic ligand to the signals group E. The signals B and D which appear as a doublet of triplets ($J_{H\text{-}H}$ = 14.7, $J_{P\text{-}H}$ = $J_{P'\text{-}H}$ = 10.5 Hz (B); $J_{H\text{-}H}$ = 14.7, $J_{P\text{-}H}$ = $J_{P'\text{-}H}$ = 8.7 Hz (D)) were assigned to the CH_2 protons of the dppm ligand.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations

Bond Distances			
Ir–P1	2.259 (1)	P2–C22	1.821 (6)
Ir–P2	2.316 (2)	P2–C28	1.833 (6)
Ir–C1	2.189 (6)	C1–C2	1.52 (1)
Ir–C4	2.115 (6)	C1–C8	1.40 (1)
Ir–C7	2.256 (7)	C2–C3	1.53 (1)
Ir–C8	2.147 (6)	C3–C4	1.55 (1)
P1–C9	1.867 (6)	C4–C5	1.49 (1)
P1–C10	1.822 (6)	C5–C6	1.52 (1)
P1–C16	1.828 (6)	C6–C7	1.50 (1)
P2–C9	1.838 (6)	C7–C8	1.45 (1)
Bond Angles			
P1–Ir–P2	72.55 (6)	Ir–C1–C8	69.5 (4)
P1–Ir–C1	177.1 (2)	C2–C1–C8	127.5 (7)
P1–Ir–C4	97.2 (2)	C1–C2–C3	111.9 (6)
P1–Ir–C7	110.1 (2)	C2–C3–C4	110.7 (6)
P1–Ir–C8	142.1 (2)	Ir–C4–C3	109.7 (5)
P2–Ir–C1	110.2 (2)	Ir–C4–C5	110.3 (5)
P2–Ir–C4	168.1 (2)	C3–C4–C5	114.7 (6)
P2–Ir–C7	109.5 (2)	C4–C5–C6	110.5 (6)
P2–Ir–C8	96.5 (2)	C5–C6–C7	113.4 (6)
C1–Ir–C4	80.2 (3)	Ir–C7–C6	109.3 (5)
C1–Ir–C7	68.3 (3)	Ir–C7–C8	66.8 (4)
C1–Ir–C8	37.6 (3)	C6–C7–C8	124.6 (7)
C4–Ir–C7	79.5 (3)	Ir–C8–C1	72.8 (4)
C4–Ir–C8	95.3 (3)	Ir–C8–C7	74.9 (4)
C7–Ir–C8	38.3 (5)	C1–C8–C7	122.6 (7)
Ir–C1–C2	112.7 (5)	P1–C9–P2	93.9 (3)

Table I lists selected bond distances and angles for the structure of **2**. The Ir–C4 distance (2.115 (6) Å) is in the expected range for an iridium to carbon single bond (sum of covalent radii 2.07 Å) and is quite similar to that found for the Ir–C σ-bond in the compounds $[Ir(\eta^1,\eta^2\text{-}C_8H_{13})(PNP)]$ (PNP = $Pr^nN(CH_2CH_2PPh_2)_2$) (2.109 (5) Å),[9] $[Ir(\eta^1,\eta^2\text{-}C_8H_{13})(CO)_2(AsPh_3)]$ (2.150 (11) Å),[10] and $[(\eta^4\text{-}1,5\text{-}COD)Ir(\mu\text{-}pz)(\mu\text{-}PPh_2)_2Ir(\eta^1,\eta^2\text{-}C_8H_{13})]$ (2.159 (13) Å).[11] The allylic unit of the carbocyclic ligand is coordinated to the metal in the typical π-allyl manner, which means that the center carbon atom C8 is significantly closer to the metal (Ir–C8, 2.147 (6) Å) than the two terminal allyl carbon atoms (Ir–C1, 2.189 (6) Å; Ir–C7, 2.256 (7) Å). The Ir–C(allyl) and C(allyl)–C(allyl) distances are in the typical range reported for π-allyliridium complexes.[12]

The Ir–P2 distance (P trans to C4) is 0.057 Å longer than the Ir–P1 distance (P trans to C1–C8), which can be assigned to the different trans influence of the alkyl and π-allyl groups. In keeping with the crystal structure, the $^{31}P\{^1H\}$ NMR spectrum of **2** in benzene-d_6 exhibits two doublets at 73.5 and −35.8 ppm with a P–P coupling constant of 24 Hz.

The $^{13}C\{^1H\}$ NMR spectrum of **2** in benzene-d_6 contains the signals assigned to the phenyl carbons of the dppm ligand, together with nine signals between 90 and 20 ppm. Figure 3 shows the DEPT $^{13}C\{^1H\}$ NMR spectrum of **2** in the 90–20 ppm region. Signal F (δ = 56.4, dd, $J_{P\text{-}C}$ = 23.6 and 29.2 Hz) was assigned to the CH_2 carbon of the di-

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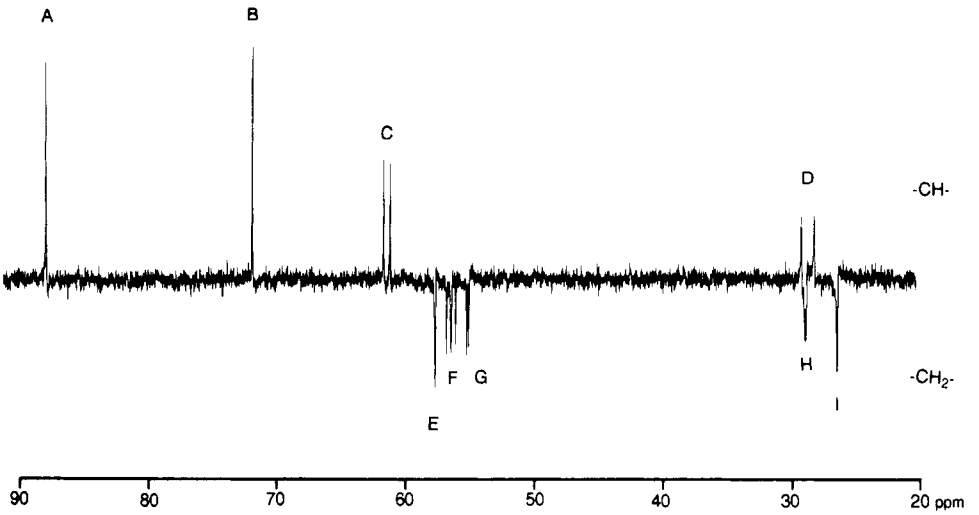
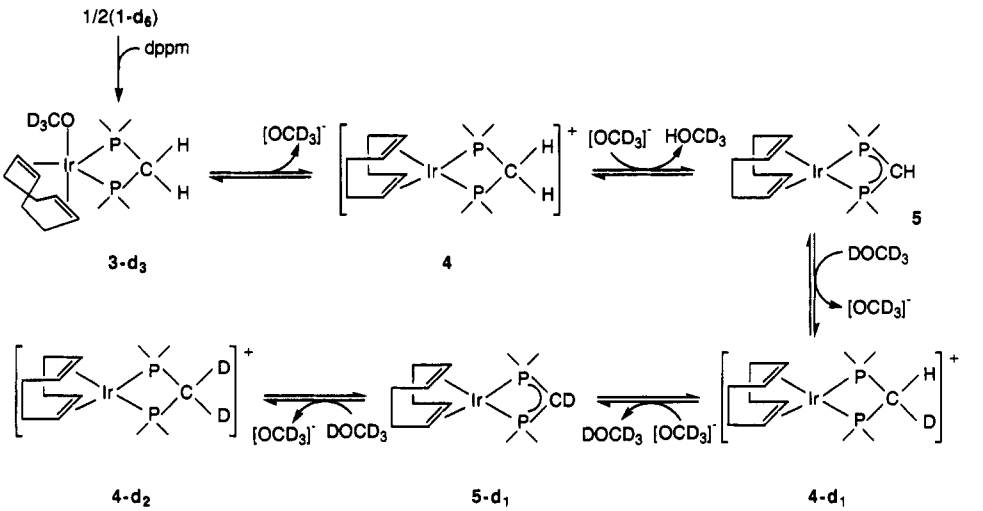


Figure 3. DEPT $^{13}C\{^1H\}$ NMR (benzene-d_6) spectrum of [IrH(η^1,η^3-C_8H_{12})(dppm)] in 90–20 ppm region.

Scheme I



phosphine ligand. The other eight signals were assigned to the carbon atoms of the carbocyclic ligand. Signal D (δ = 28.9, dd, J_{P-C} = 74.5 and 4.5 Hz) shows the largest P–C coupling constant and is undoubtedly due to C4. So, A, B, and C correspond to the allyl carbons of the C_8H_{12} ligand. Signals H and I were assigned to the carbons linked to the terminal allyl carbon atoms (C2 and C6 (Figure 1)), while E and G were assigned to the carbons bonded to C4 (C3, C5 (Figure 1)). It is known, from previous studies,[6] that, for the η^1,η^3-C_8H_{12} ligand, the signals of the carbon atoms bonded to the extremes of the allyl group appear at higher field than those observed for carbon atoms linked to the carbon which is σ-bonded to the metallic center.

Mechanism. In order to determine the mechanism of the formation of **2**, we have studied the reaction of the dimer [(Ir(μ-OCD_3)(η^4-1,5-COD)]$_2$ (**1**-d_6) with dppm in methanol-d_4. Under the experimental conditions described for **2**, a white solid was obtained, assigned according to its elemental analysis to **2**-d_x. The IR spectrum of the solid in Nujol contains a band at 2042 cm^{-1}, assigned to a ν(Ir–H) absorption, and is essentially identical to the IR spectrum of **2**. This suggests that the source of the hydride ligand of **2** is the carbocyclic ligand. In agreement with this, the ^1H NMR spectrum of **2**-d_x in benzene-d_6 shows a doublet of doublets at –9.0 ppm with a P–H coupling constant of 15.5 Hz. The intensity of this signal corresponds to one proton, while the intensity ratio of the signals due to the allylic and aliphatic protons is 3:8. Furthermore, the ^1H NMR spectrum indicates that the two protons of the CH_2 group of the diphosphine ligand have been substituted by two deuterium atoms. On the basis of these observations, **2**-d_x can be formulated as **2**-d_3.

The $^{13}C\{^1H\}$ NMR spectrum of **2**-d_x in benzene-d_6 is also in agreement with this formulation. Thus, the comparison of the $^{13}C\{^1H\}$ NMR spectra of **2** and **2**-d_x reveals that the carbocyclic ligand of **2**-d_x contains only one deuterium atom, located at the carbon atom corresponding to the G signal of the spectrum shown in Figure 3. G appears now as a broad doublet of triplets.

With regard to these spectroscopic data, there is no doubt that two deuterium atoms of **2**-d_3 are located on the methylene group of the diphosphine ligand, and the other in the carbon atoms C3 or C5 of the carbocyclic ligand. The deuteration of the methylene group of dppm can be rationalized in terms of the reaction in Scheme I, suggesting the formation of a [Ir(Ph_4P_2CH)(η^4-1,5-COD)] intermediate. It is known that the CH_2 group of dppm can be deprotonated by bases to give the anion bis(diphenylphosphino)methanide ([Ph_4P_2CH]$^-$), which is itself a good ligand.[13] The presence of the cationic intermediates **4**, **4**-d_1, and **4**-d_2 is consistent with the red color of the solutions formed by addition of dppm to **1** or **1**-d_6.

On the other hand, the total deuteration of the CH_2 group of the diphosphine ligand in **2**-d_3 suggests that this

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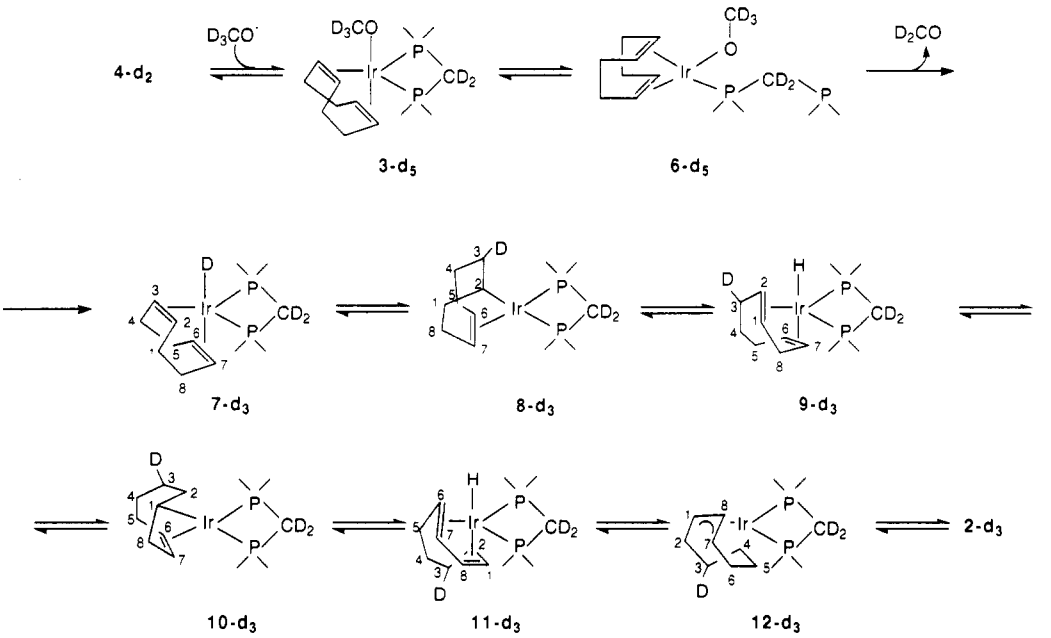
Scheme II

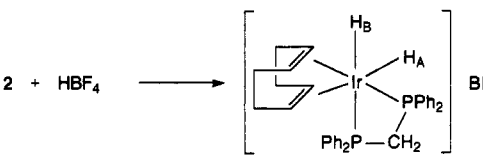


process occurs previously to the deuteration of the carbocyclic group. In accordance with this, it was found that the treatment of **2** with methanol-d_4 for 5 h does not produce the deuteration of the complex. Following this idea, Scheme II illustrates a plausible reaction pathway that allows the formation of **2**-d_3 to be rationalized. The first steps of this sequence lead to **7**-d_3. Cationic iridium complexes have been suggested to act as Lewis acids.[14] Thus, the cationic species **4**-d_2 probably undergoes nucleophilic attack by the methoxide-d_3 group at the metal, and this is followed by a β-hydrogen elimination. Evidence in support of the initial formation of **7**-d_3 came from the isolation of the complex $[IrH(\eta^4\text{-}1,5\text{-}COD)(PPh_3)_2]$ from reaction of $[Ir(\eta^4\text{-}1,5\text{-}COD)(PPh_3)_2]^+$ with sodium methoxide.[5]

The subsequent step is most likely a hydride transfer from the metal to an olefin group to form the coordinatively unsaturated species **8**-d_3 of Scheme II. Following the hydride-transfer step, the resultant $\eta^1,\eta^2\text{-}C_8H_{12}D$ ligand can undergo a successive addition elimination reaction of β-hydrogen atoms (i.e., double-bond migration) until the η^3-cyclooctenyl species **12**-d_3 is formed. Similar equilibria involving species related to **7**-d_3 for **12**-d_3 have been identified previously for several organometallic complexes including $[RuH(\eta^4\text{-}1,5\text{-}COD)(PR_3)_3]PF_6$, $[RuH(\eta^6\text{-}C_6H_3Me_3)(\eta^4\text{-}1,5\text{-}COD)]PF_6$,[15] $[CoH(\eta^4\text{-}1,5\text{-}COD)_2]$,[16] $[Rh(\eta^5\text{-}C_5H_5)(\eta^1,\eta^2\text{-}C_8H_{13})]^+$,[17] $[Pt(\eta^1,\eta^2\text{-}C_8H_{13})L_2]$ (L_2 = acac, F_6-acac, F_3-acac) and $[Pt(\eta^1,\eta^2\text{-}C_8H_{13})(\eta^4\text{-}1,5\text{-}COD)]^+$.[18] Finally, the intramolecular C–H activation of one of the two C–H bonds of C4 in **12**-d_3 gives **2**-d_3.

The regioselective deuteration of C3 or C5 in **2**-d_3 deserves further comment. In pentacoordinate complexes of d^8 electronic configuration, the ground-state geometry is almost exclusively trigonal bipyramidal (TBP) or square pyramidal (SP). For $[IrH(\eta^4\text{-diene})L_2]$ (L_2 = phosphine or diphosphine), a TBP ground-state geometry with the hydride ligand in one axial position, the phosphine or diphosphine occupying two equatorial sites, and the diene spanning the remaining axial and equatorial sites (C_s symmetry) is more favored than any SP ground-state geometry.[19] For **9**-d_3 and **11**-d_3, a TBP ground state like that described above allows only one carbon–carbon double bond of the diene to be coplanar with the Ir–H bond, an arrangement that is necessary for the hydride transfer from the metal to the diene. Thus, the structures shown for **9**-d_3 and **11**-d_3 in Scheme II may explain why the deuteration of the carbocyclic ligand occurs just at one specific carbon atom.

Reactivity. The hydride complex **2** reacts with HBF_4 in diethyl ether to give the cis cation **13** (eq 1). **13** was isolated as a white solid in 85% yield. The IR spectrum



(1)

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of this complex in Nujol shows two Ir–H bands at 2100 and 2075 cm^{-1}, as expected for cis hydride ligands, along with the absorption due to the $[BF_4]^-$ anion with T_d symmetry. In the ^1H NMR spectrum of **13** in acetone-d_6, two sets of metal hydride resonances can be distinguished: one, due to H_A, is coupled to two inequivalent cis phosphorus nuclei ($J_{P\text{-}H} = J_{P'\text{-}H} = 16$ Hz); another, due to H_B, appears as a broad doublet and is coupled to one trans phosphorus nucleus ($J_{P\text{-}H} = 107$ Hz). In addition, four peaks due to the four magnetically inequivalent 1,5-cyclooctadiene vinyl protons at 5.12, 4.94, 4.40, and 4.06 ppm are observed.

The preparation of the cation *cis*-$[IrH_2(\eta^4\text{-}1,5\text{-}COD)(dppe)]^+$ comparable in structure to **13** has been reported previously. This compound decomposes in solution by hydrogenation of the coordinated diene (ca. 30% at 20 °C).[20] In contrast, **13** is stable at this temperature, neither

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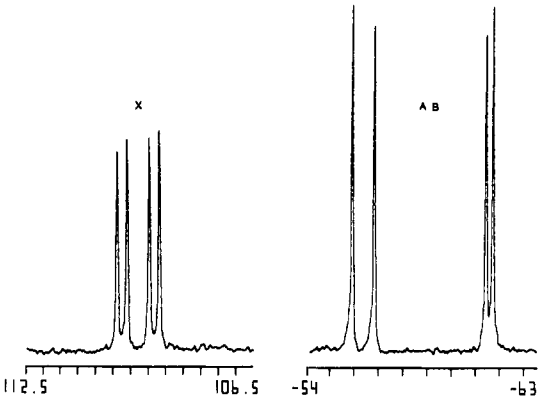
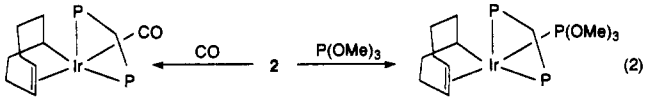


Figure 4. $^{31}P\{^1H\}$ NMR (benzene-d_6) spectrum of [Ir(η^1,η^2-C_8H_{13})(dppm)(P(OMe)$_3$)].

losing molecular H_2 nor transferring it to the coordinated 1,5-cyclooctadiene.

2 reacts also with Lewis bases; the reaction with CO and P(OMe)$_3$ leads to new iridium(I) compounds containing the η^1,η^2-C_8H_{13} ligand (eq 2). The proposed structures for **14** and **15**, in solution, are strongly supported by the



(2)

14 **15**

spectroscopic data (see Experimental Section), mainly by the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. Thus, the $^{31}P\{^1H\}$ NMR spectrum of **14** contains two doublets, as expected for two inequivalent phosphorus nuclei. The $^{31}P\{^1H\}$ NMR spectrum of **15** (Figure 4) shows a characteristic ABX splitting pattern. In addition, the values of the P–C coupling constants for the signals assigned to the vinyl resonances of the coordinated C_8H_{13} group, in the $^{13}C\{^1H\}$ NMR spectra of **14** and **15**, are characteristic for a disposition of the carbon–carbon double bond cis to the two inequivalent phosphorus atoms of the diphosphine ligand (between 0 and 9 Hz), and trans to P(OMe)$_3$ in **15**. Furthermore, the position, multiplicity, and value of the coupling constant of the signal at higher field (13.6 ppm for **14**, 12.57 ppm for **15**) are indicative of the presence of a M–C σ-bond between the carbocyclic ligand (C_8H_{13}) and the iridium atom.

Concluding Remarks

The results reported by us, in this paper and previously, show that the products obtained by reaction of [Ir(μ-OMe)(η^4-1,5-COD)]$_2$ with phosphines and diphosphines depend on the nature of the phosphorus donor ligand. The reaction with PCy_3 leads to [Ir(OMe)(η^4-1,5-COD)(PCy_3)]. In the presence of PPh_3, dppe, and dppp, the hydride complexes [IrH(η^4-1,5-COD)L_2] (L_2 = 2 PPh_3, dppe, and dppp) are obtained, while the reaction with dppm gives the hydridoiridium(III) complex [IrH(η^1,η^3-C_8H_{12})(dppm)].

The formation of this latter compound occurs via the intermediate [IrH(η^4-1,5-COD)(dppm)] which isomerizes to the η^3-cyclooctenyl species [Ir(η^3-C_8H_{13})(dppm)] by hydride transfer from the metal to an olefin group, and subsequent double-bond migration. The last step is the intramolecular C–H (sp^3) activation of one of the two C–H bonds on the carbon atom that is equidistant to the terminal allyl C atoms of the carbocyclic ligand of [Ir(η^3-C_8H_{13})(dppm)].

[IrH(η^1,η^3-C_8H_{12})(dppm)] reacts with HBF_4, CO, and P(OMe)$_3$. The reaction with HBF_4 leads to *cis*-[IrH_2(η^4-1,5-COD)(dppm)]BF_4, while the compounds [Ir(η^1,η^2-C_8H_{13})(dppm)L] (L = CO, P(OMe)$_3$) are obtained on addition of CO and P(OMe)$_3$. The conclusion is that the complex [IrH(η^1,η^3-C_8H_{12})(dppm)] reacts with electrophiles and nucleophiles. The reaction with electrophiles effects the isomerization of η^1,η^3-C_8H_{12} to η^4-1,5-COD, while the reaction with nucleophiles leads to the transformation of the unit IrH(η^1,η^3-C_8H_{12}) to Ir(η^1,η^2-C_8H_{13}), involving the formal reduction for Ir(III) to Ir(I).

Experimental Section

General Data. All reactions were carried out with the use of standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled prior to use. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Unity 300 spectrometer at room temperature. Chemical shifts are expressed in parts per million upfield from $Si(CH_3)_4$. $^{31}P\{^1H\}$ spectra were recorded on a Varian XL 200 spectrometer. Chemical shifts are expressed in parts per million upfield from H_3PO_4 (85%). Infrared spectra were run on a Perkin-Elmer 783 spectrophotometer, as either solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). The starting materials dppm[21] and [Ir(μ-OMe)(η^4-1,5-COD)]$_2$[22] were prepared by published methods.

Preparation of [IrH(η^1,η^3-C_8H_{12})(dppm)] (2). A stoichiometric amount of bis(diphenylphosphino)methane (dppm) (115.9 mg, 0.29 mmol) was added to a suspension of [Ir(μ-OMe)(η^4-1,5-COD)]$_2$ (100 mg, 0.147 mmol) in methanol (10 mL), and the mixture was stirred for 3 h at room temperature. The white solid formed was filtered off, washed with methanol, and dried in vacuo. Yield: 143.7 mg (70%). ^1H NMR (C_6D_6, 20 °C): δ −9.0 (dd, J_{P-H} = $J_{P'-H}$ = 15.5 Hz, 1 H, IrH), 1.80–2.40 (m, 9 H, H_4 and $-CH_2-$), 3.85 (dt, J_{H-H} = 14.7, J_{P-H} = $J_{P'-H}$ = 10.5 Hz, 1 H, PCH_2P), 4.45 (dt, 1 H, H_8), 5.06 (dt, J_{H-H} = 14.7, J_{P-H} = $J_{P'-H}$ = 8.7 Hz, 1 H, PCH_2P), 5.60 (br, 2 H, H_1 and H_7), 6.6–8.0 (m, 20 H, ((C_6H_5)$_2$P)$_2$$CH_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ −35.8 (d, J_{P-P} = 24 Hz), 73.5 (d, J_{P-P} = 24 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 26.7 (d, J_{P-C} = 6 Hz, C2 or C6), 28.9 (dd, J_{P-C} = 74.5, J_{P-C} = 4.5 Hz, C4), 29.1 (dd, J_{P-C} = 8.5, J_{P-C} = 3,5 Hz, C2 or C6), 55.2 (d, J_{P-C} = 12, C3 or C5), 56.4 (dd, J_{P-C} = 29.2, J_{P-C} = 23.6 Hz, PCH_2P), 57.6 (d, J_{P-C} = 4 Hz, C3 or C5), 61.40 (d, J_{P-C} = 37.3 Hz, C1), 71.82 (s, C7), 87.78 (s, C8). IR (Nujol): ν(Ir–H) 2042 (s) cm^{-1}. Anal. Calcd for $C_{33}H_{35}IrP_2$: C, 57.79; H, 5.14. Found: C, 57.96; H, 5.51.

Preparation of [IrH(η^1,η^3-$C_8H_{11}D$)(Ph_2P-CD_2-PPh_2)] (2-d_3). The procedure is the same as that described for **2**, starting from [Ir(μ-OCD_3)(η^4-1,5-COD)]$_2$ (100 mg, 0.15 mmol) and dppm (111.6 mg, 0.30 mmol) in methanol-d_4. Yield: 136 mg (68%). ^1H NMR (C_6D_6, 20 °C): δ −9.0 (dd, J_{P-H} = $J_{P'-H}$ = 15.5 Hz, 1 H, IrH), 1.80–2.40 (m, 8 H, H_4 and $-CH_2-$), 4.45 (dt, 1 H, H_8), 5.60 (br, 2 H, H_1 and H_7), 6.6–8.0 (m, 20 H, ((C_6H_5)$_2$P)$_2$$CH_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ −35.7 (d, J_{P-P} = 24 Hz), 73.3 (d, J_{P-P} = 24 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 24.99 (d, J_{P-C} = 6 Hz, C2 or C6), 27.2 (dd, J_{P-C} = 80, J_{P-C} = 4.8 Hz, C4), 27.37 (dd, J_{P-C} = 8.5, J_{P-C} = 3.5 Hz, C2 or C6), 53.4 (dt, C3 or C5), 55.97 (d, J_{P-C} = 3.5 Hz, C3 or C5), 59.71 (d, J_{P-C} = 37 Hz, C1), 70.15 (s, C7), 86.07 (s, C8). IR (Nujol): ν(Ir–H) 2042 (s) cm^{-1}. Anal. Calcd for $C_{33}D_3H_{32}IrP_2$: C, 57.54; H, 4.68. Found: C, 57.26; H, 5.12.

Preparation of *cis*-[IrH_2(η^4-1,5-COD)(dppm)]BF_4 (13). A stoichiometric amount of HBF_4·Et_2O (20 μL, 0.146 mmol) was added to a suspension of [IrH(η^1,η^3-C_8H_{12})(dppm)] (100 mg, 0.146 mmol) in diethyl ether (10 mL), and the resulting suspension was stirred for 2 h at room temperature. The white solid formed was filtered off, washed with diethyl ether, and vacuum dried. Yield: 96 mg (85%). ^1H NMR (acetone-d_6, 20 °C): δ − 11.56 (dd, J_{P-H} = $J_{P'-H}$ = 16 Hz, 1 H, IrH), −11.1 (d, J_{P-H} = 107 Hz, 1 H, IrH), 1.25–2.8 (m, 8 H, $-CH_2-$), 4.06 (br, 1 H, =CH), 4.40 (br, 1 H, =CH), 4.94 (br, 1 H, =CH), 5.12 (br, 1 H, =CH), 5.45 (dt, J_{P-H} = $J_{P'-H}$ = 11 Hz, J_{H-H} = 15.6 Hz, 1 H, PCH_2P), 5.95 (dt, J_{P-H} =

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Table II. Crystallographic Data for 2

formula	$C_{33}H_{35}IrP_2$
formula wt	685.81
crystal size, mm	0.2 × 0.2 × 0.3
crystal system	monoclinic
space group	$P2_1/n$ (14)
cell dimen determn	23 reflcns, 10° < θ < 14°
a, Å	10.406 (1)
b, Å	17.703 (3)
c, Å	15.894 (2)
β, deg	102.15 (1)
V, Å^3	2862.3
Z	4
d_{calcd}, g cm^{-3}	1.59
diffractometer	Enraf-Nonius CAD4
radiation (graphite monochromated)	Mo Kα (0.709 30 Å)
temp, °C	20 ± 1
μ, cm^{-1}	47.8
scan method	ω/θ
2θ(max), deg	46
total no. of reflcns scanned	4394
no. of unique reflcns	3725
no. of obsd reflcns ($I > 3\sigma(I)$)	2423
no. of params refined	325
R	0.035
R_w	0.039
reflcn/param ratio	7.46
residual electron density, e Å^{-3}	+0.84/−0.56

$J_{P'-H}$ = 11 Hz, J_{H-H} = 15.6 Hz, 1 H, PCH_2P), 7.25–8 (m, 20 H, $((C_6H_5)_2P)_2CH_2$). $^{31}P\{^1H\}$ NMR (acetone-d_6, 20 °C): δ −60 (br), 40.20 (d, J_{P-P} = 43 Hz). IR (Nujol): ν(Ir–H) 2100 (s), 2075 (s) cm^{-1}; ν(BF_4^-) 1100–1000 (s) cm^{-1}. Anal. Calcd for $BC_{33}F_4H_{36}IrP_2$: C, 51.24; H, 4.69. Found: C, 51.48; H, 4.95.

Preparation of [Ir(η^1,η^2-C_8H_{13})(dppm)(CO)] (14). A solution of [IrH(η^1,η^3-C_8H_{12})(dppm)] in dichloromethane (10 mL) was stirred under CO for 3 h and the resulting solution concentrated under reduced pressure to 0.5 mL. Addition of hexane caused the precipitation of a white solid, which was filtered off, washed with hexane, and dried in vacuo. Yield: 85 mg (82%). ^1H NMR (C_6D_6, 20 °C): δ 1.65–2.2 (m, 7 H, –CH–, –CH_2–), 2.38 (m, 1 H, –CH_2–), 2.6–2.9 (m, 2 H, –CH_2–), 3.2 (br, 1 H, –CH_2–), 3.4 (br, 1 H, =CH), 3.8 (br, 1 H, =CH), 4.2 (dt, $J_{P-H} = J_{P'-H}$ = 9.3 Hz, J_{H-H} = 15 Hz, 1 H, PCH_2P), 4.8 (dt, $J_{P-H} = J_{P'-H}$ = 9 Hz, J_{H-H} = 15 Hz, 1 H, PCH_2P), 6.80–7.80 (m, 20 H, $(C_6H_5)_2P)_2CH_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ −58.9 (d, J_{P-P} = 5 Hz), −56.5 (d, J_{P-P} = 5 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 13.6 (dd, J_{P-C} = 2, J_{P-C} = 68.5 Hz, C_σ), 27.16 (dd, J_{P-C} = 5, J_{P-C} = 10.5 Hz, —CH_2CH=) 27.26 (s, —CH_2CH=), 27.29 (s, –CH_2–), 35.95 (dd, J_{P-C} = 1, J_{P-C} = 26 Hz, –CHCH_2–), 37.12 (dd, $J_{P-C} = J_{P'-C}$ = 2 Hz, –CHCH_2–), 46.75 (dd, J_{P-C} = 6, J_{P-C} = 1.5 Hz, =CH), 48.48 (dd, J_{P-C} = 1.7, J_{P-C} = 8.2, =CH), 52.04 (dd, J_{P-C} = 26, J_{P-C} = 24.7 Hz, PCH_2P), 184.4 (dd, J_{P-C} = 5, J_{P-C} = 18.6 Hz, CO). IR: ν(CO) (Nujol) 1929 (s), (CH_2Cl_2) 1935 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{35}IrOP_2$: C, 57.21; H, 4.94. Found: C, 57.51; H, 5.31.

Preparation of [Ir(η^1,η^2-C_8H_{13})(dppm)(P(OMe)$_3$)] (15). A solution of [IrH(η^1,η^3-C_8H_{12})(dppm)] (100 mg, 0.146 mmol) in toluene (8 mL) was treated with $P(OMe)_3$ (21 μL, 0.175 mmol). The reaction mixture was stirred for 100 min at 75 °C and filtered through Kieselguhr. The filtrate was concentrated to 0.5 mL, and then methanol was added to give a pale yellow solid, which was filtered off, washed with methanol, and dried in vacuo. Yield: 92 mg (78%). ^1H NMR (C_6D_6, 20 °C): δ 1.9–3.0 (m, 10 H, –CH–, –CH_2–), 3.10 (br, 1 H, –CH_2–), 3.14 (d, J_{P-H} = 11.1 Hz, 9 H, P(OMe)$_3$), 3.25 (br, 1 H, =CH), 3.93 (br, 1 H, =CH), 4.30 (m, 1 H, PCH_2P), 5.07 (dt, $J_{P-H} = J_{P'-H}$ = 8 Hz, J_{H-H} = 13.7 Hz, 1 H, PCH_2P), 6.9–7.9 (m, 20 H, $(C_6H_5)_2P)_2CH_2$)). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): see Figure 4. $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 12.57 (ddd, J_{P-C} = 3, J_{P-C} = 7, J_{P-C} = 73 Hz, C_σ), 25.89 (dd, J_{P-C} = 10, J_{P-C} = 31 Hz, –CH_2CH=), 26.17 (s, –CH_2–), 26.37 (dd, $J_{P-C} = J_{P'-C}$ = 3.5 Hz, —CH_2CH=), 28.73 (m, –CHCH_2–), 36.3 (m, –CHCH_2–), 45.83 (dd, J_{P-C} = 8, J_{P-C} = 48.5 Hz, =CH), 47.59 (dd, J_{P-C} = 24, J_{P-C} = 24, PCH_2P), 48.9 (d, J_{P-C} = 3.5 Hz, P(OCH_3)$_3$), 49.15 (dd, J_{P-C} = 4.5, J_{P-C} = 51 Hz, =CH). IR (Nujol): ν($P(OMe)_3$) 1100–1100 (s) cm^{-1}. Anal. Calcd for $C_{36}H_{44}IrO_3P_3$: C, 53.39; H, 5.48. Found: C, 53.41; H, 5.58.

X-ray Data Collection. Crystals of compound 2 suitable for X-ray diffraction studies were obtained by the slow diffusion of methanol into a saturated benzene solution of the compound. Crystal data collection parameters are summarized in Table II. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied (Ψ-scan method, minimum transmission 69.7%). The structure was solved by direct methods (SHELXS-86).[23] Atomic coordinates (see Table III) and anisotropic thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares analysis. The positions of all hydrogen atoms were calculated according to ideal geometry and refined using the riding method. For the carbon atoms C1, C7, and C8, sp^2 geometry was assumed, whereas atom C4 and the other ring carbon atoms were considered to have sp^3 geometry. All calculations were performed on a Micro-VAX computer using the program package SDP[24] from Enraf-Nonius.

Table III. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{eq}, Å^2
Ir	0.192 08 (4)	0.246 14 (3)	0.495 83 (3)	2.861 (7)
P1	0.4078 (3)	0.2510 (2)	0.4924 (2)	3.16 (5)
P2	0.2833 (3)	0.1304 (2)	0.5431 (2)	2.93 (6)
C1	−0.019 (1)	0.2463 (8)	0.4946 (8)	4.3 (2)
C2	−0.076 (1)	0.3256 (8)	0.490 (1)	6.1 (4)
C3	0.031 (1)	0.3862 (7)	0.504 (1)	5.9 (4)
C4	0.148 (1)	0.3607 (7)	0.4645 (9)	4.4 (3)
C5	0.129 (1)	0.3723 (7)	0.3701 (9)	5.4 (4)
C6	0.043 (1)	0.3109 (9)	0.3216 (9)	5.7 (4)
C7	0.070 (1)	0.2340 (8)	0.3612 (8)	4.8 (3)
C8	0.007 (1)	0.2030 (7)	0.4264 (9)	4.6 (3)
C9	0.454 (1)	0.1638 (6)	0.5578 (7)	3.0 (2)
C10	0.473 (1)	0.2348 (7)	0.3963 (7)	3.9 (3)
C11	0.390 (1)	0.2373 (9)	0.3164 (7)	5.0 (3)
C12	0.435 (2)	0.2224 (8)	0.2409 (8)	5.5 (4)
C13	0.564 (1)	0.2055 (8)	0.2458 (9)	5.6 (3)
C14	0.647 (1)	0.2010 (8)	0.3261 (9)	5.3 (3)
C15	0.603 (1)	0.2168 (7)	0.4011 (8)	4.5 (3)
C16	0.508 (1)	0.3297 (6)	0.5440 (7)	2.9 (2)
C17	0.570 (1)	0.3795 (7)	0.4989 (9)	5.9 (3)
C18	0.636 (2)	0.4398 (8)	0.541 (1)	7.0 (5)
C19	0.643 (2)	0.4544 (8)	0.624 (1)	6.6 (4)
C20	0.578 (2)	0.4083 (9)	0.670 (1)	8.1 (5)
C21	0.509 (1)	0.3448 (8)	0.6300 (9)	5.9 (4)
C22	0.268 (1)	0.0872 (6)	0.6444 (8)	3.4 (3)
C23	0.188 (1)	0.1222 (8)	0.6915 (7)	4.4 (3)
C24	0.176 (1)	0.0899 (9)	0.7693 (9)	5.7 (4)
C25	0.241 (2)	0.0264 (9)	0.8014 (9)	6.9 (5)
C26	0.317 (2)	−0.0082 (8)	0.7525 (9)	6.3 (4)
C27	0.332 (2)	0.0215 (8)	0.6738 (9)	5.4 (4)
C28	0.266 (1)	0.0490 (6)	0.4702 (7)	3.2 (3)
C29	0.335 (1)	0.0455 (7)	0.4054 (8)	4.4 (3)
C30	0.311 (2)	−0.0116 (8)	0.3441 (9)	5.5 (4)
C31	0.217 (2)	−0.0640 (9)	0.346 (1)	6.8 (5)
C32	0.149 (2)	−0.0605 (9)	0.410 (1)	6.9 (4)
C33	0.173 (1)	−0.0037 (8)	0.472 (1)	5.8 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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Supplementary Material Available: Tables of positional parameters, general displacement parameter expressions, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

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