Synthesis and Structure of Novel Iridium(I) Complexes Containing η^4-1,6-Diene and Diphosphine Ligands: Remarkable Effect of Ligand Bite Angle upon Ligand Dissociation

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Received November 6, 2003

The treatment of $[IrCl(cod)]_2$ with a bidentate diphosphine ligand, bis(diphenylphosphino)-methane (dppm), and 1,6-dienes such as dimethyl 2,2-diallylmalonate (**1**) and diallyl ether (**2**) produces a ligand replacement reaction to afford novel iridium(I) complexes bearing η^4-1,6-diene ligands, IrCl(dppm)[η^4-CH_2=$CHCH_2C(CO_2Me)_2CH_2CH$=CH_2] (**3**) and IrCl(dppm)-(η^4-CH_2=$CHCH_2OCH_2CH$=CH_2) (**4**), respectively, in excellent yields. The molecular structure of the diallyl ether complex **4**, which has been unequivocally determined by a single-crystal X-ray diffraction study, discloses that **2** coordinates to the iridium metal in an η^4 fashion with a distorted-trigonal-bipyramidal geometry. In a similar manner, 1,2-bis(diphenylphosphino)ethane (dppe) is also a tolerant diphosphine ligand, and the corresponding η^4-1,6-diene complexes IrCl(dppe)[η^4-CH_2=$CHCH_2C(CO_2Me)_2CH_2CH$=CH_2] (**5**) and IrCl(dppe)(η^4-CH_2=$CHCH_2OCH_2CH$=CH_2) (**6**) have been isolated in high yields. On the other hand, diphosphine ligands with a carbon linkage longer than that in dppe, such as 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb), never activate the cod ligand, resulting in no exchange with the 1,6-dienes. Instead of the expected η^4-1,6-diene complexes, IrCl(cod)(dppp) (**7**) and IrCl(cod)(dppb) (**8**) are exclusively formed. The molecular structure of **8** is also confirmed by an X-ray crystallographic analysis. The coordination geometry of **8** is consistent with a distorted square pyramid. The reactivity toward the ligand displacement depends on the natural bite angle of the bidentate phosphine ligands.

Introduction

The chemistry of transition-metal complexes bearing nonconjugated *cyclic* diene ligands such as 1,5-cyclooctadiene (cod) and 2,5-norbornadiene (nbd) has been extensively investigated, because such complexes could be readily prepared and handled without special care. The facile replacement of these ligands to with others such as phosphines and amines makes them versatile materials for the preparation of a wide range of transition-metal complexes.[1] In this regard, these complexes are also known as extremely useful catalyst precursors and have been employed in a number of transition-metal-catalyzed reactions.[2] On the other hand, nonconjugated *acyclic* dienes, such as 1,6-heptadiene and diallyl ether, have received less attention as a supporting ligand of transition metals. There have been only a limited number of complexes of the group 10 elements, and all of them are claimed to have planar structures.[3−6] Among them, the most important one is the Karstedt complex [Pt(η^4-dvds)]$_2$(μ-η^2-η^2-dvds) (dvds = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane), which is recognized as

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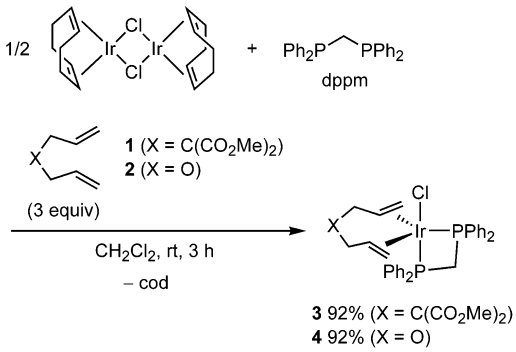
10.1021/om034282y CCC: $27.50
Publication on Web 03/16/2004

an efficient catalyst for the hydrosilylation of alkenes, including industrial processes.[7]

In sharp contrast to the formation of the η^4-1,6-diene complexes, the reaction of low-valent early transition metals such as titanium,[8] zirconium,[9] and tantalum species[10] with 1,*n*-dienes furnishes the corresponding metallabicyclic complexes through an oxidative cyclization process. In particular, bicyclic zirconacycloalkanes have been ingeniously applied to the efficient construction of ring systems.[11] Several nickel complexes also brought about oxidative cyclization to afford nickelacycloalkanes.[12]

Moreover, the reaction of transition-metal complexes with nonconjugated acyclic dienes has already become a very important process not only in organometallic chemistry but also in synthetic organic chemistry, as a result of the significant development of the transition-metal-catalyzed carbocyclization reactions of 1,*n*-dienes over the past decade.[13] For example, the catalytic cycloisomerizations of 1,*n*-dienes, which have been recognized as atom-economical and environmentally benign synthetic processes, have been eagerly investigated with a variety of transition-metal complexes (Sc,[14] Ti,[8c,15] Zr,[16] Ta,[10a,b] Ru,[17] Rh,[5d,18] Ni,[19] and Pd[20]). In several cases of such catalyses, the η^4-1,*n*-diene complexes and bicyclic metallacycloalkanes may behave as key intermediates.[21] Therefore, further elucidation of the interaction of transition-metal complexes with nonconjugated *acyclic* dienes should be undertaken in more detail.

Scheme 1



Herein, we now report that the reaction of the iridium(I) complex $[IrCl(cod)]_2$ with bidentate diphosphine ligands and 1,6-dienes such as dimethyl 2,2-diallylmalonate and diallyl ether smoothly provided the displacement of the cod ligand to furnish the novel iridium(I) η^4-1,6-diene diphosphine complexes. It is noteworthy that diphosphines with a longer linkage inhibit the exchange of the cod ligand. In such cases, the corresponding iridium(I) cod diphosphine complexes are exclusively formed. The structural aspects of the two representatives are also discussed.

Results and Discussion

To a dichloromethane solution of $[IrCl(cod)]_2$ and bis(diphenylphosphino)methane (dppm) was added 3 equiv of dimethyl 2,2-diallylmalonate (**1**), and the resultant yellow mixture was stirred for 3 h at room temperature to afford the novel 1,6-diene complex **3** after recrystallization from dichloromethane/*n*-hexane as pale yellow-green solids in 92% yield (Scheme 1). Remarkably, this product is air-stable even in solution for several days. The IR spectrum of complex **3**, which exhibited a very strong absorption at 1739 cm^{-1}, apparently indicates that the ester moiety remained intact. The ^1H NMR spectrum of **3** showed two characteristic peaks corre-

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sponding to methoxy groups in **1** at δ 3.65 (s) and 3.89 (s) ppm in chloroform-*d*. Signals for the coordinated olefinic protons were observed at higher field, δ 2.24 (dd, J_{HH} = 7.5 Hz, J_{PH} = 7.5 Hz), 2.45−2.49 (m), and 3.52−3.61 (m) ppm, relative to the uncoordinated ones. The appearance of only three peaks corresponding to olefinic protons implies that this complex has a highly symmetrical structure. The signal for the methylene protons of dppm appeared at δ 4.65 (dd, J_{PH} = 9.0, 11.0 Hz) ppm, which shifted to a lower field than that of the free dppm at δ 2.80 (s) ppm. Similarly, the $^{13}C\{^1H\}$ NMR spectrum also indicated the structural symmetry of **1**, except for the two ester moieties. The $^{31}P\{^1H\}$ NMR spectrum showed two signals at higher field, δ −69.9 (d, J_{PP} = 45.7 Hz) and −56.8 (d, J_{PP} = 45.7 Hz) ppm, suggesting that the two phosphorus atoms were not equivalent to each other. These spectral features of complex **3** support that the geometry of **3** is a trigonal bipyramid rather than a square pyramid. The axial positions are occupied by one of the phosphorus atoms of dppm and the chlorine atom, whereas the two olefinic π-bonds of **1** and the other phosphorus atom are present at equatorial positions. Any attempts to obtain crystals of **3** suitable for X-ray structural analysis were unsuccessful. Obviously, the formation of **3** stems from the displacement of the cod ligand in the mononuclear IrCl(cod)(dppm) intermediate initially formed in situ. In contrast, the analogous dinuclear iridium(I) complex $[IrCl(coe)_2]_2$ (coe = cyclooctene) did not lead to any expected complex **4** but an uncharacterized dark brown solid, presumably by way of $[IrCl(diphosphine)]_2$, under identical conditions. This result proved that only a mononuclear complex such as IrCl(cod)(dppm) plays a key role in this substitution of the cod ligand (vide infra).

Diallyl ether (**2**) also induces the ligand displacement reaction to produce **4** from the reaction of $[IrCl(cod)]_2$ with dppm and **2** in 92% yield (Scheme 1). The spectral features of **4** were analogous to those of **3** described above; i.e., the $^{31}P\{^1H\}$ NMR spectrum showed that the two phosphorus atoms were placed under different circumstances at δ −70.4 (d, J_{PP} = 48.2 Hz) and −59.7 (d, J_{PP} = 48.2 Hz) ppm. Fortunately, recrystallization of **4** afforded yellow prismatic crystals from dichloromethane/methanol suitable for single-crystal X-ray diffraction. The structure of the diallyl ether complex **4** has been unambiguously determined by X-ray crystallographic analysis. Figure 1 gives an ORTEP drawing of the molecular structure for **4**. The selected bond distances and angles are listed in Table 1, and a summary of the crystallographic data and structure refinement details of **4** is given in Table 3. The molecular structure of **4** shows that diallyl ether (**2**) coordinates to the iridium metal in an η^4 fashion (Figure 1). As expected from the NMR spectral data, the geometry of **4** is quite consistent with a distorted trigonal bipyramid, in which the P2 and Cl1 atoms lie in the axial positions and the P1 atom, C1−C2, and C5−C6 bonds lie in the equatorial positions.[22] The distances for both C1−C2 (1.427(9) Å) and C5−C6 (1.428(9) Å) are slightly longer than that of the olefinic C−C in the rhodium(I) analogue Rh(acac)[η^4-$CH_3CH{=}CHCH_2OCH(CH_3)CH{=}CH_2$] (1.368 and 1.400 Å) (Table 1).[6] The Ir1−Cl1 bond is almost perpendicular to the basal plane consisting of the P1 atom and C1−C2 and C5−C6 bonds, and not the Ir1−P2 bond. The bite angle β_n of coordinated dppm, i.e., P1−Ir1−P2, is 72.7(5)°, which is consistent with the natural values reported by van Leeuwen and co-workers (β_n = 72°).[23]

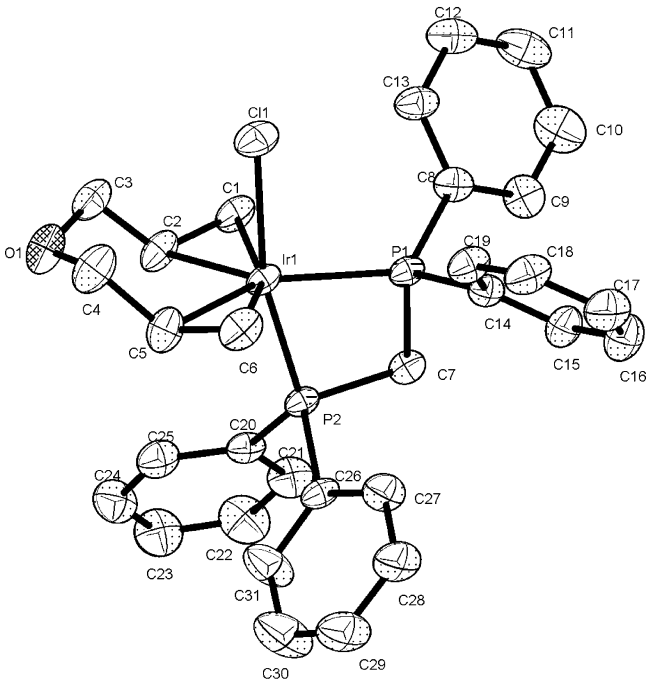

Figure 1. ORTEP drawing of the structure of IrCl(dppm)-(η^4-$CH_2{=}CHCH_2OCH_2CH{=}CH_2$) (**4**). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles for 4

Bond Distances (Å)			
Ir(1)−C(1)	2.191(6)	C(1)−C(2)	1.427(9)
Ir(1)−C(2)	2.182(6)	C(2)−C(3)	1.493(8)
Ir(1)−C(5)	2.153(6)	C(4)−C(5)	1.501(9)
Ir(1)−C(6)	2.162(6)	C(5)−C(6)	1.428(9)
Ir(1)−P(1)	2.317(6)	O(1)−C(3)	1.447(9)
Ir(1)−P(2)	2.233(13)	O(1)−C(4)	1.450(8)
Ir(1)−Cl(1)	2.478(14)		

Bond Angles (deg)			
P(1)−Ir(1)−P(2)	72.7(5)	P(2)−Ir(1)−C(6)	97.0(18)
P(1)−Ir(1)−Cl(1)	94.1(5)	Cl(1)−Ir(1)−C(1)	86.5(16)
P(2)−Ir(1)−Cl(1)	166.6(5)	Cl(1)−Ir(1)−C(2)	93.0(16)
P(1)−Ir(1)−C(1)	91.1(17)	Cl(1)−Ir(1)−C(5)	92.8(18)
P(1)−Ir(1)−C(2)	128.0(17)	Cl(1)−Ir(1)−C(6)	85.3(19)
P(1)−Ir(1)−C(5)	147.4(17)	Ir(1)−P(1)−C(7)	93.5(17)
P(1)−Ir(1)−C(6)	110.4(17)	Ir(1)−P(2)−C(7)	96.7(17)
P(2)−Ir(1)−C(1)	95.8(15)	P(1)−C(7)−P(2)	93.8(2)
P(2)−Ir(1)−C(2)	97.0(16)	C(1)−C(2)−C(3)	122.8(6)
P(2)−Ir(1)−C(5)	97.2(18)	C(4)−C(5)−C(6)	122.8(6)

1,2-Bis(diphenylphosphino)ethane (dppe) was also available as the ancillary ligand to furnish the corresponding η^4-1,6-diene complexes **5** and **6** from **1** and **2** in 89% and 94% yields under identical conditions, respectively (Scheme 2). The simplicity of the ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** and **6** suggested that these have symmetrical structures. The $^{31}P\{^1H\}$ NMR spectra

(22) Quite recently, Oro, Astruc et al. have confirmed by an X-ray crystallographic analysis that an analogous Fe−Ir heterodinuclear triene complex had a similar trigonal-bipyramidal structure; see: Marcén, S.; Jiménez, M. V.; Dobrinovich, I. T.; Lahoz, F. J.; Oro, L. A.; Ruiz, J.; Astruc, D. *Organometallics* **2002**, *21*, 326−330.

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Table 2. Selected Bond Distances and Angles for 8

Bond Distances (Å)			
Ir(1)−C(29)	2.144(3)	C(30)−C(31)	1.528(4)
Ir(1)−C(30)	2.152(3)	C(31)−C(32)	1.521(4)
Ir(1)−C(33)	2.189(3)	C(32)−C(33)	1.512(4)
Ir(1)−C(34)	2.221(3)	C(33)−C(34)	1.391(5)
Ir(1)−P(1)	2.335(7)	C(34)−C(35)	1.532(4)
Ir(1)−P(2)	2.337(7)	C(35)−C(36)	1.530(5)
Ir(1)−Cl(1)	2.581(7)	C(36)−C(29)	1.510(4)
C(29)−C(30)	1.428(5)		

Bond Angles (deg)			
P(1)−Ir(1)−P(2)	93.1(5)	P(2)−Ir(1)−Cl(1)	86.1(2)
C(29)−Ir(1)−C(34)	78.9(12)	Cl(1)−Ir(1)−C(29)	133.5(9)
C(30)−Ir(1)-C(33)	79.7(11)	Cl(1)−Ir(1)−C(30)	96.3(9)
P(1)−Ir(1)−C(33)	95.8(8)	Cl(1)−Ir(1)-C(33)	84.3(9)
P(1)−Ir(1)−C(34)	84.4(8)	Cl(1)−Ir(1)-C(6)	119.3(9)
P(2)−Ir(1)-C(29)	85.3(9)	Ir(1)−P(1)−C(')	117.7(10)
P(2)−Ir(1)−C(30)	92.7(8)	Ir(1)−P(2)−C(4)	117.7(10)
P(1)−Ir(1)−Cl(1)	91.0(3)		

Table 3. Selected Crystallographic Data and Structure Refinement Details for 4 and 8·CHCl$_3$

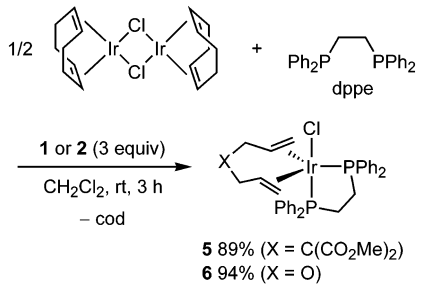
	4	**8**·$CHCl_3$
empirical formula	$C_{31}H_{32}ClIrOP_2$	$C_{37}H_{41}Cl_4IrP_2$
fw	710.16	881.64
cryst color	yellow	yellow
cryst habit	prismatic	prismatic
temp (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	14.6479(13)	11.2689(10)
b (Å)	11.6123(11)	20.7628(18)
c (Å)	18.0017(16)	14.9551(13)
β (deg)	101.389(2)	91.205(2)
V (Å^3)	3001.75(5)	3498.3(5)
Z	4	4
D_{calcd} (Mg m^{-3})	1.571	1.674
abs coeff (mm^{-1})	4.665	4.240
F(000)	1400	1752
cryst size (mm^3)	0.3 × 0.3 × 0.8	0.6 × 0.6 × 0.8
scan range θ (deg)	1.64−29.30	1.68−29.14
GOF on F^2	1.016	0.972
R1 ($I > 2\sigma(I)$)	0.0447	0.0278
wR2 ($I > 2\sigma(I)$)	0.1363	0.0709

showed pairs of signals at δ 20.8 (d, J_{PP} = 3.3 Hz) and 24.3 (d, J_{PP} = 3.3 Hz) ppm for **5** and δ 22.3 (d, J_{PP} = 3.4 Hz) and 25.6 (d, J_{PP} = 3.4 Hz) ppm for **6**. These observations apparently indicate that the dppe complexes **5** and **6** also have trigonal-bipyramidal geometries similar to those of the dppm complexes **3** and **4**.

Subsequently, the reaction of [IrCl(cod)]$_2$ with 1,3-bis(diphenylphosphino)propane (dppp, n = 3) and the 1,6-diene **1** (3 equiv) was examined in order to prepare another η^4-1,6-diene complex bearing a bidentate diphosphine ligand with a carbon linkage longer than that of dppe. This reaction, however, did not provide the expected η^4-1,6-diene complex at all but the known mononuclear cod complex IrCl(cod)(dppp) (**7**) in 98% yield (Scheme 3).[24] The obtained cod complex **7** totally agreed with the authentic sample prepared according to a literature procedure.[24] The $^{31}P\{^1H\}$ spectrum **7** showed a feature different from that of the η^4-1,6-diene complexes **3**−**6**; only one signal appeared at δ −13.87 (s) ppm. Notably, the cod complex **7** was so stable that

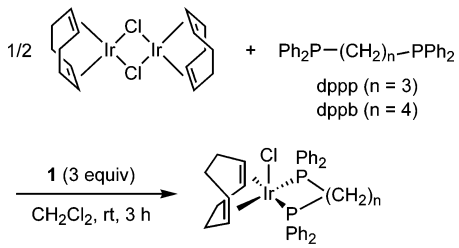
(24) Recently, Shibata and co-workers reported the preparation of **7** by the reaction of [IrCl(cod)]$_2$ with dppp in hot toluene. They also determined the molecular structure of **7**·$CHCl_3$ as square pyramidal by single-crystal X-ray diffraction; see: Shibata, T.; Yamashita, K.; Ishida, H.; Takagi, K. *Org. Lett.* **2001**, *3*, 1217−1219.

Scheme 2



5 89% (X = C(CO$_2$Me)$_2$)
6 94% (X = O)

Scheme 3



7 98% (n = 3)
8 98% (n = 4)

the expected ligand displacement did not occur even in refluxing dichloromethane or 1,2-dichloroethane.

In a similar manner, the employment of 1,4-bis(diphenylphosphino)butane (dppb, n = 4) never displaced the cod ligand with **1** to form the cod complex IrCl(cod)(dppb) (**8**) in 98% yield (Scheme 3). The $^{31}P\{^1H\}$ spectrum of **8** exhibited a peak at δ 0.0 (s) ppm, which is assigned to a pair of equivalent phosphorus atoms, the same as for the dppp complex **7**. Recrystallization of **8** from chloroform/*n*-hexane afforded yellow prismatic single crystals suitable for X-ray analysis, and its structure was unequivocally determined. Figure 2 shows an ORTEP drawing of the molecular structure of **8**. The selected bond distances and angles and a summary of the crystallographic data and structure refinement details are given in Tables 2 and 3, respectively. As depicted in Figure 2, the geometry of **8** takes a distorted-square-pyramidal structure, in which cod and dppb exist in the same plane and the Cl1 atom occupies the apical position, which accounts for the characteristic difference between **8** and **4** in the NMR spectra. The bite angle β_n of dppb in **8** (β_n = 93.1(3)° for P1−Ir1−P2) is somewhat smaller than the natural values in the literature (β_n = 98°).[23] A similar observation was reported in the case of the dppp complex **7** (β_n = 86.4(4)° for **7** versus 91° for the natural values).[23,24]

To uncover whether the η^4-1,6-diene complexes **4**−**7** are indeed generated via the mononuclear complexes IrCl(cod)(diphosphine), the reaction of IrCl(cod)(dppe) (**9**) with the 1,6-diene **1** was examined as depicted in Scheme 4. Complex **9** was readily prepared from [IrCl(cod)]$_2$ and dppe in 90% yield. In its $^{31}P\{^1H\}$ NMR spectrum, only a signal at δ 35.3 (s) ppm was observed to indicate that **9** had a square-pyramidal structure similar to **7** and **8**. To a chloroform-*d* solution of **9** was added 3 equiv of **1**, and the resulting yellow solution was periodically monitored by ^1H and $^{31}P\{^1H\}$ NMR at ambient temperature. After 1 h, a pair of new peaks appeared at 21.0 (d, J_{PP} = 3.3 Hz) and 24.5 (d, J_{PP} = 3.3 Hz) ppm. They are assigned as two nonequivalent

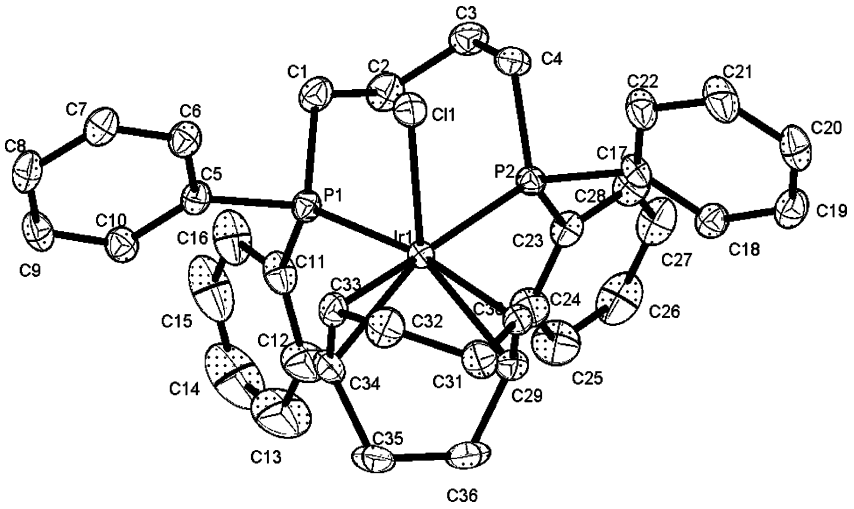
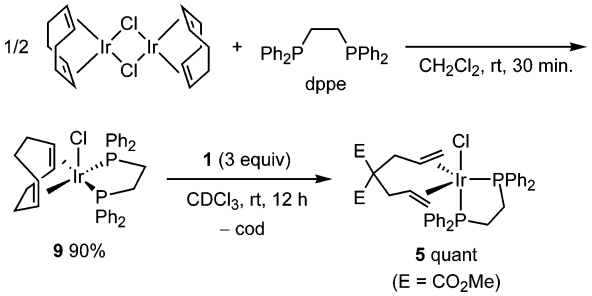


Figure 2. ORTEP drawing of the structure of IrCl(cod)(dppb) (**8**). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

Scheme 4



phosphorus atoms in the η^4-1,6-diene complex **5**, whereas the singlet at δ 35.3 ppm in **9** still remained in the $^{31}P\{^1H\}$ NMR spectrum. Ultimately, the complete conversion of **9** into **5** was accomplished within 12 h and no signals for other species were observed, except for the liberated cod. It was once again verified that the η^4-1,6-diene complexes **3**−**6** were generated through the replacement of the cod ligand in IrCl(cod)(diphosphine) with the corresponding 1,6-diene **1** or **2**.

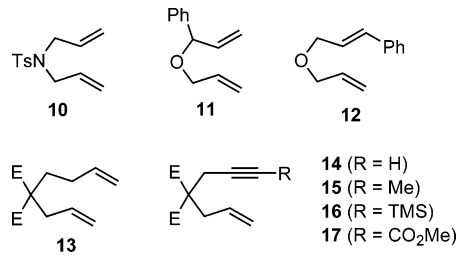
The results shown in Schemes 1−4 suggest that the value of the bite angle β_n for each diphosphine (the natural values reported in the literatures are the following: 72° for dppm, 85° for dppe, 91° for dppp, and 98° for dppb)[23] played a key role in the liberation of the coordinated cod ligand. We assumed that the narrow bite angle β_n in dppm and dppe provided distortion toward the square-bipyramidal structure of the corresponding cod complexes IrCl(cod)(diphosphine) to decrease the orbital overlap between the iridium(I) metal and the cod ligand. As a consequence, the cod ligand was readily dissociated, and then a more flexible acyclic 1,6-diene ligand occupied the resultant vacant sites to afford the more stable η^4-1,6-diene complexes **3**−**6**. On the other hand, the cod complexes **7** and **8** with the wider bite angle β_n were too stable to release the coordinated cod ligand because those received only negligible distortion. This strongly supports the suggestion that a monodentate ligand such as PPh_3 cannot trigger such ligand replacement. The structural difference between the η^4-1,6-diene complexes **3**−**6** and cod complexes **7**−**9** might be attributed to the following: the greater flexibility of the acyclic 1,6-diene ligands relative to a cod ligand permitted these structures to change into a trigonal-bipyramidal geometry, in which a smaller steric repulsion is present between the η^4-1,6-diene ligand and phenyl groups bound to phosphorus atoms, as well as a chlorine atom, than in the square-pyramidal geometry. Therefore, the structural alteration occurred at the dissociation step of the cod ligand upon the transformation from a cod complex into an η^4-1,6-diene complex.

It is noteworthy that the reaction of $[IrCl(cod)]_2$ with **1** without phosphine ligands provided pale yellow solids. Although its ^1H NMR spectrum was quite complicated in benzene-d_6, the characteristic signals corresponding to the methoxy groups were observed at δ 3.23 (s) and 3.42 (s) ppm concomitant with that of the uncoordinated **1** at δ 3.29 (s) ppm. It was disappointing that this solid was unstable in solution and decomposed into **1** and unidentified iridium species. Consequently, further characterization hardly provided any more detailed information on the molecular structure. It is known that the reaction of $[IrCl(cod)]_2$ with **2** afforded the dinuclear complex $[IrCl(cod)(\eta^4\text{-}CH_2{=}CHCH_2OCH_2CH{=}CH_2)]_2$, even though the structure was ambiguous.[25] We anticipate that the analogous dinuclear complex $[IrCl(cod)(\eta^4\text{-}CH_2{=}CHCH_2C(CO_2Me)_2CH_2CH{=}CH_2)]_2$ was generated in the reaction of $[IrCl(cod)]_2$ with **1**.

Since the η^4-1,6-diene complexes **3**−**6** could be regarded as model intermediates of the transition-metal-catalyzed cycloisomerization reactions of 1,6-dienes as described above,[21] we inspected the behavior of $IrCl(dppe)[\eta^4\text{-}CH_2{=}CHCH_2C(CO_2Me)_2CH_2CH{=}CH_2]$ (**5**). Though a chloroform-*d* solution of **5** was heated at 60 °C and monitored by ^1H NMR, no cycloisomerized product was observed, resulting in the partial decomposition of **5** into undefined iridium complexes and **1** even after 24 h (**5**/**1** = 64/36 after 24 h). The addition of a silver salt such as $AgPF_6$, which brought about an unoccupied coordinating site by abstraction of a chlorine atom, had no effect. In addition, the reaction in the presence of a trialkylsilane such as dimethylethylsilane did not promote the cycloisomerization,[13c,20c−f] cyclization/hydrosilylation,[13c,26,27] or even hydrosilylation reaction with or without $AgPF_6$.[28]

(25) Pannetier, G.; Bonnaire, R.; Fougeroux, P. *J. Organomet. Chem.* **1971**, *30*, 411−419.

Chart 1



Unsuitable substrates for the reported ligand exchange reactions are depicted in Chart 1. *N*,*N*-Diallyltosylamide (**10**) gave an intractable reaction mixture, as was also true for the phenyl-substituted 1,6-dienes **11** and **12** and the 1,7-diene **13**. Similarly, the enynes **14**−**17** produced unidentified viscous oils. We also examined auxiliary ligands other than the diphosphines as potential substrates, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) and 2,2′-bipyridine (bipy), albeit without success.

Conclusion

We have found that the reaction of $[IrCl(cod)]_2$ with bidentate diphosphines in the presence of 1,6-dienes furnished the novel iridium(I) complexes IrCl(η^4-1,6-diene)(diphosphine) in excellent yields. The X-ray crystallographic analysis unambiguously revealed that the η^4-1,6-diene complexes assume a distorted-trigonal-bipyramidal geometry. On the other hand, the homologation of the carbon linkage in diphosphines resulted in the exclusive formation of IrCl(cod)(diphosphine) with a distorted-square-pyramidal structure, even in the presence of 1,6-dienes.

Experimental Section

General Remarks. Air- and moisture-sensitive reactions were carried out under an atmosphere of argon or nitrogen by employing standard Schlenk techniques. NMR spectra were measured on a Varian INOVA 500 (^{1}H at 500 MHz, ^{13}C{^{1}H} at 125 MHz) or a Varian MERCURY 300 (^{1}H at 300 MHz, ^{13}C{^{1}H} at 75 MHz, ^{31}P{^{1}H} at 121 MHz) magnetic resonance spectrometer. ^{1}H NMR spectra are reported in terms of chemical shifts (δ, ppm) relative to the residual solvent peak (7.26 ppm for chloroform-*d*). The multiplicities were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. ^{13}C{^{1}H} NMR spectra were fully decoupled by broad-band decoupling and are reported in terms of chemical shifts (δ, ppm) relative to the solvent peak (77.0 ppm, the center line of a triplet for chloroform-*d*). ^{31}P{^{1}H} NMR spectra were fully decoupled by broad-band decoupling and are reported in terms of chemical shifts (δ, ppm) relative to H_3PO_4 (85% in H_2O) as external standard. IR data were recorded on a JASCO IR-810 spectrometer. Absorbance frequencies are reported in cm^{-1}. Fast atom bombardment mass spectra (FABMS) were measured on a JEOL JMS-AX505HA spectrometer employing *m*-nitrobenzyl alcohol (NBA) as a matrix. Melting points were measured in sealed capillary tubes and are uncorrected. Elemental analyses were performed by the Microanalytical Center of Kyoto University.

Materials. Chloroform, dichloromethane, *n*-hexane, and *n*-pentane were distilled from CaH_2. Methanol was distilled from magnesium alkoxide. All solvents utilized in the reactions were degassed prior to use. $[IrCl(cod)]_2$[29] and $[IrCl(coe)_2]_2$[30] were prepared according to literature procedures. Dimethyl 2,2-diallylmalonate (**1**) was prepared from dimethyl malonate and allyl bromide with sodium methoxide in methanol. Other reagents were obtained from commercial sources and used without further purification.

Preparation of IrCl(dppm)[η^4-CH$_2$=CHCH$_2$C(CO$_2$Me)$_2$CH$_2$CH=CH$_2$] (3). To a dichloromethane solution (4 mL) of $[IrCl(cod)]_2$ (33.7 mg, 0.050 mmol) was added dppm (39.3 mg, 0.10 mmol). Subsequently, a solution of dimethyl 2,2-diallylmalonate (**1**; 64.5 mg, 0.30 mmol) in dichloromethane (1 mL) was added to the mixture, and the resultant yellow solution was stirred at room temperature. After 3 h, the volatile materials were removed in vacuo. Then, the residue was recrystallized from dichloromethane/*n*-hexane to afford **3** (76.1 mg, 92%) as pale yellow-green crystals (needle). Mp: 191−193 °C dec. IR (KBr): ν 1096 (s), 1150 (s), 1254 (vs), 1312 (m), 1436 (s), 1739 (vs), 2955 (m), 3046 (m) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.07 (dd, J_{HH} = 11.5, 14.5 Hz, 2H), 2.24 (dd, J_{HH} = 7.5 Hz, J_{PH} = 7.5 Hz, 2H), 2.43−2.49 (m, 4H), 3.52−3.61 (m, 2H), 3.65 (s, 3H), 3.89 (s, 3H), 4.65 (dd, J_{PH} = 9.0, 11.0 Hz), 6.97−7.01 (m, 4H), 7.24−7.28 (m, 4H), 7.33−7.36 (m, 2H), 7.43−7.50 (m, 6H), 8.08−8.12 (m, 4H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 30.9 (d, J_{CP} = 3.8 Hz), 40.0 (d, J_{CP} = 6.5 Hz), 44.2 (d, J_{PC} = 15.2 Hz), 47.2 (dd, J_{PC} = 24.9, 36.8 Hz), 52.2 (s), 52.2 (s), 62.7 (d, J_{PC} = 9.8 Hz), 126.0 (dd, J_{PC} = 4.6, 48.5 Hz), 128.4 (d, J_{PC} = 10.6 Hz), 128.6 (d, J_{PC} = 10.7 Hz), 130.3 (d, J_{PC} = 2.3 Hz), 130.6 (d, J_{PC} = 2.6 Hz), 130.8 (d, J_{PC} = 9.5 Hz), 132.5 (d, J_{PC} = 12.2 Hz), 136.6 (dd, J_{PC} = 4.1, 32.3 Hz), 173.1 (s), 173.2 (s) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ −69.9 (d, J_{PP} = 45.7 Hz), −56.8 (d, J_{PP} = 45.7 Hz) ppm. MS (FAB; *m*/*z* (relative intensity, %)): 419 ([Cl(dppe)]$^+$, 19), 612 ([IrCl(dppm)]$^+$, 100), 1224 ([Ir$_2$Cl$_2$(dppm)$_2$]$^+$, 3). Anal. Calcd for $C_{36}H_{38}ClIrO_4P_2$: C, 52.45; H, 4.65. Found: C, 52.33; H, 4.75.

Preparation of IrCl(dppm)(η^4-CH$_2$=CHCH$_2$OCH$_2$CH=CH$_2$) (4). To a dichloromethane solution (20 mL) of $[IrCl(cod)]_2$ (171.3 mg, 0.26 mmol) was added dppm (196.0 mg, 0.51 mmol). Subsequently, a solution of diallyl ether (**2**; 152.5 mg, 1.55 mmol) in dichloromethane (5 mL) was added to the mixture, and the resultant yellow solution was stirred at room temperature. After 3 h, the volatile materials were removed in vacuo. Then, the residue was recrystallized from dichloromethane/*n*-pentane to afford **4** (331.9 mg, 92%) as yellow crystals (prismatic). Mp: 151−153 °C dec. IR (KBr): ν 925 (m), 1053 (m), 1098 (vs), 1184 (m), 1332 (m), 1435 (s), 1479 (m), 2850 (m), 2907 (s), 2965 (m), 3050 (m) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.27 (dd, J_{HH} = 7.5 Hz, J_{PH} = 7.5 Hz, 2H), 2.42 (d, J_{HH} = 11.0 Hz, 2H), 3.34 (dd, J_{HH} = 11.8, 11.8 Hz, 2H), 3.58−3.66 (m, 2H), 3.95 (ddd, J_{HH} = 4.0, 11.8 Hz, J_{PH} =

(26) Y: (a) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415−4416. (b) Molander, G. A.; Nichols, P. J.; Noll, B. C. *J. Org. Chem.* **1998**, *63*, 2292−2306. Nd: (c) Onozawa, S.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, *35*, 8177−8180. Pd: (d) Widenhoefer, R. A.; DeCarli, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 3805−3806. (e) Widenhoefer, R. A.; Vadehra, A. *Tetrahedron Lett.* **1999**, *40*, 8499−8502. (f) Widenhoefer, R. A.; Stengone, C. N. *J. Org. Chem.* **1999**, *64*, 8681−8692. (g) Pei, T.; Widenhoefer, R. A. *Org. Lett.* **2000**, *2*, 1469−1471. (h) Perch, N. S.; Pei, T.; Widenhoefer, R. A. *J. Org. Chem.* **2000**, *65*, 3836−3845. (i) Wang, X.; Chakrapani, H.; Stengone, C. N.; Widenhoefer, R. A. *J. Org. Chem.* **2001**, *66*, 1755−1760. For application of the yttrium-catalyzed cyclization/hydrosilylation of 1,*n*-dienes to the total synthesis of (±)-epilupinine, see: (j) Molander, G. A.; Nichols, P. J. *J. Org. Chem.* **1996**, *61*, 6040−6043.

(27) Recently, Widenhoefer and co-workers have prepared a cationic palladium(II) cyclopentyl chelate complex from the reaction of the cationic palladium(II) phenanthroline complex with **1** and determined the molecular structure by X-ray crystallographic analysis.[20f]

(28) Widenhoefer et al. have also reported that the cationic palladium(II) phenanthroline complex rapidly reacted with **1** in the presence of triethylsilane to form a palladium(II) 5-hexenyl chelate complex. This unprecedented complex facilely converted the palladium(II) cyclopentyl chelate via β-migratory insertion; see: Perch, N. S.; Widenhoefer, R. A. *Organometallics* **2001**, *20*, 5251−5253.

(29) Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395−403.

(30) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Chem.* **1974**, *15*, 18−20.

8.0 Hz, 2H), 4.70 (dd, J_{PH} = 9.0, 11.0 Hz, 2H), 7.03−7.07 (m, 4H), 7.27−7.31 (m, 4H), 7.35−7.39 (m, 2H), 7.45−7.51 (m, 6H), 8.07−8.12 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 36.4 (d, J_{PC} = 5.3 Hz), 47.5 (d, J_{PC} = 14.0 Hz), 48.0 (dd, J_{PC} = 25.8, 37.1 Hz), 64.5 (d, J_{PC} = 4.6 Hz), 126.4 (dd, J_{PC} = 4.4, 48.9 Hz), 128.5 (d, J_{PC} = 10.2 Hz), 128.6 (d, J_{PC} = 10.2 Hz), 130.4 (d, J_{PC} = 2.3 Hz), 130.7 (d, J_{PC} = 2.7 Hz), 130.9 (d, J_{PC} = 9.1 Hz), 132.4 (d, J_{PC} = 11.7 Hz), 136.4 (dd, J_{PC} = 3.8, 34.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): d −70.4 (d, J_{PP} = 48.2 Hz), −59.7 (d, J_{PP} = 48.2 Hz) ppm. MS (FAB; *m*/*z* (relative intensity, %)): 612 ([IrCl(dppm)]$^+$, 100), 675 ([Ir($C_6H_{10}O$)(dppm)]$^+$, 7), 710 (M^+, 4). Anal. Calcd for $C_{31}H_{32}ClIrOP_2$: C, 52.43; H, 4.54. Found: C, 52.63; H, 4.72.

Preparation of IrCl(dppe)[η^4-CH_2=$CHCH_2C(CO_2Me)_2CH_2CH$=CH_2] (5). To a dichloromethane solution (25 mL) of $[IrCl(cod)]_2$ (206.6 mg, 0.31 mmol) was added dppe (244.8 mg, 0.61 mmol). Subsequently, a solution of **1** (394.9 mg, 1.86 mmol) in dichloromethane (5 mL) was added to the mixture, and the resultant red-orange solution was stirred at room temperature. After 3 h, the volatile materials were removed in vacuo. Then, the residue was recrystallized from dichloromethane/*n*-pentane to afford **5** (459.9 mg, 89%) as white crystals (needle). Mp: 153−155 °C dec. IR (KBr): ν 1065 (s), 1098 (s), 1142 (s), 1191 (s), 1229 (vs), 1310 (m), 1432 (s), 1736 (vs), 2949 (m), 3047 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.97 (dd, J_{HH} = 11.3 Hz, J_{PH} = 2.8 Hz, 2H), 2.12 (dd, J_{HH} = 11.8, 14.3 Hz, 2H), 2.26−2.43 (m, 8H), 3.10−3.18 (m, 2H), 3.57 (s, 3H), 3.70 (s, 3H), 7.18−7.22 (m, 4H), 7.30−7.34 (m, 4H), 7.38−7.46 (m, 8H), 7.82−7.86 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 26.5 (dd, J_{PC} = 6.7, 40.0 Hz), 30.2 (d, J_{PC} = 3.1 Hz), 34.2 (dd, J_{PC} = 17.0, 44.3 Hz), 39.7 (d, J_{PC} = 6.7 Hz), 47.2 (d, J_{PC} = 14.0 Hz), 52.1 (s), 52.3 (s), 62.3 (d, J_{PC} = 8.5 Hz), 126.5 (d, J_{PC} = 51.5 Hz), 127.9 (d, J_{PC} = 9.7 Hz), 128.4 (d, J_{PC} = 9.7 Hz), 129.8 (d, J_{PC} = 2.5 Hz), 130.6 (d, J_{PC} = 2.4 Hz), 132.2 (d, J_{PC} = 7.9 Hz), 132.8 (d, J_{CP} = 9.7 Hz), 137.4 (d, J_{PC} = 43.7 Hz), 172.4 (s), 173.3 (s) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 20.8 (d, J_{PP} = 3.3 Hz), 24.3 (d, J_{PP} = 3.3 Hz) ppm. MS (FAB; *m*/*z* (relative intensity, %)): 626 ([IrCl(dppe)]$^+$, 100), 803 ([Ir($C_{11}H_{16}O_4$)(dppe)]$^+$, 27). Anal. Calcd for $C_{37}H_{40}ClIrO_4P_2$: C, 53.01; H, 4.81. Found: C, 52.89; H, 4.75.

Preparation of IrCl(dppe)(η^4-CH_2=$CHCH_2OCH_2CH$=CH_2) (6). To a dichloromethane solution (3 mL) of $[IrCl(cod)]_2$ (34.4 mg, 0.051 mmol) was added dppe (41.7 mg, 0.11 mmol). Subsequently, a solution of **2** (31.4 mg, 0.32 mmol) in dichloromethane (2 mL) was added to the mixture, and the resultant yellow solution was stirred at room temperature. After 3 h, the volatile materials were removed in vacuo. Then, the residue was recrystallized from dichloromethane/*n*-hexane to afford **6** (70.0 mg, 94%) as yellow crystals (needle). Mp: 138−140 °C dec. IR (KBr): ν 817 (m), 926 (m), 1062 (s), 1099 (vs), 1184 (s), 1252 (m), 1333 (m), 1433 (vs), 1480 (vs), 2853 (s), 2907 (vs), 2978 (s), 3055 (vs) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.92 (dd, J_{HH} = 11.3 Hz, J_{PH} = 2.3 Hz, 2H), 2.20 (dd, J_{HH} = 6.8 Hz, J_{PH} = 6.8 Hz, 2H), 2.30−2.46 (m, 4H), 3.13−3.21 (m, 2H), 3.41 (dd, J_{HH} = 11.5, 12.0 Hz, 2H), 3.86 (ddd, J_{HH} = 3.5, 11.5 Hz, J_{HP} = 7.0 Hz, 2H), 7.25−7.29 (m, 4H), 7.33−7.36 (m, 4H), 7.41−7.47 (m, 8H), 7.83−7.87 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 26.9 (dd, J_{PC} = 6.5, 31.1 Hz), 34.3 (dd, J_{PC} = 17.1, 43.6 Hz), 36.1 (d, J_{PC} = 6.1 Hz), 49.9 (d, J_{PC} = 13.7 Hz), 63.9 (d, J_{PC} = 3.8 Hz), 126.4 (d, J_{PC} = 51.5 Hz), 127.9 (d, J_{PC} = 9.9 Hz), 128.5 (d, J_{PC} = 9.9 Hz), 129.7 (d, J_{PC} = 2.0 Hz), 130.8 (d, J_{PC} = 2.6 Hz), 132.2 (d, J_{PC} = 8.3 Hz), 132.8 (d, J_{PC} = 9.8 Hz), 137.3 (d, J_{PC} = 44.8 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 22.3 (d, J_{PP} = 3.4 Hz), 25.5 (d, J_{PP} = 3.4 Hz) ppm. MS (FAB; *m*/*z* (relative intensity, %)): 626 ([IrCl(dppe)]$^+$, 100). Anal. Calcd for $C_{32}H_{34}ClIrOP_2$: C, 53.07; H, 4.73. Found: C, 52.89; H, 4.88.

Preparation of IrCl(cod)(dppp) (7). To a dichloromethane solution (3 mL) of $[IrCl(cod)]_2$ (37.4 mg, 0.056 mmol) was added dppp (45.4 mg, 0.11 mmol). Subsequently, a solution of **1** (72.6 mg, 0.34 mmol) in dichloromethane (2 mL) was added to the mixture, and the resultant light brown solution was stirred at room temperature. After 3 h, the volatile materials were removed in vacuo. Then, the residue was recrystallized from dichloromethane/*n*-hexane to afford **7** (81.0 mg, 98%) as yellow crystals (prismatic). Mp: 181−183 °C dec. IR (KBr): ν 833 (w), 916 (w), 973 (s), 1094 (vs), 1150 (m), 1191 (w), 1268 (m), 1328 (m), 1433 (vs), 1483 (s), 1586 (w), 2824 (s), 2867 (s), 2917 (s), 3052 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.91 (bd, J_{PH} = 8.7 Hz, 6H), 2.43 (bs, 6H), 3.23 (bs, 6H), 7.28 (bs, 12H), 7.57 (bs, 8H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −13.9 (s) ppm. MS (FAB; *m*/*z* (relative intensity, %)): 640 ([IrCl(dppp)]$^+$, 77), 713 ([Ir(cod)(dppp)]$^+$, 100). Anal. Calcd for $C_{35}H_{38}ClIrP_2$: C, 56.18; H, 5.12. Found: C, 56.02; H, 5.30.

Preparation of IrCl(cod)(dppb) (8). To a dichloromethane solution (3 mL) of $[IrCl(cod)]_2$ (35.2 mg, 0.052 mmol) was added dppb (44.0 mg, 0.10 mmol). Subsequently, a solution of **1** (68.2 mg, 0.32 mmol) in dichloromethane (2 mL) was added to the mixture, and the resultant yellow-brown solution was stirred at room temperature. After 3 h, the volatile materials were removed in vacuo. Then, the residue was recrystallized from dichloromethane/*n*-hexane to afford **8** (76.7 mg, 98%) as yellow crystals (prismatic). Mp: 160−163 °C dec. IR (KBr): ν 899 (m), 1010 (w), 1094 (s), 1134 (w), 1158 (m), 1269 (w), 1326 (w), 1434 (vs), 1481 (m), 1542 (w), 1586 (w), 2823 (m), 2873 (m), 2926 (m), 3049 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.23 (bs, 4H), 1.83 (bd, J_{PH} = 8.7 Hz, 4H), 2.32−2.42 (m, 4H), 3.00 (bs, 4H), 3.18 (bs, 4H), 7.31−7.34 (m, 12H), 7.61−7.68 (m, 8H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 0.0 (s) ppm. MS (FAB; *m*/*z* (relative intensity, %)): 725 (Ir(cod)(dppb) − $2H^+$, 100). Anal. Calcd for $C_{36}H_{40}ClIrP_2$: C, 56.72; H, 5.29. Found: C, 56.51; H, 5.42.

Preparation of IrCl(cod)(dppe) (9). To a dichloromethane solution (6 mL) of $[IrCl(cod)]_2$ (40.7 mg, 0.061 mmol) was added dppe (48.9 mg, 0.12 mmol), and the resultant yellow solution was stirred at room temperature for 30 min. After the volatile materials were removed in vacuo, the residue was recrystallized from dichloromethane/*n*-hexane to afford **9** (80.4 mg, 90%) as yellow crystals (prismatic). Mp: 177−180 °C dec. IR (KBr): ν 814 (w), 886 (w), 999 (w), 1099 (vs), 1185 (m), 1244 (w), 1326 (m), 1435 (vs), 1483 (m), 1573 (m), 1998 (w), 2817 (m), 2868 (m), 2904 (m), 3046 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.01 (bd, J_{PH} = 8.4 Hz, 4H), 2.37−2.54 (m, 8H), 3.72 (bs, 4H), 7.31−7.37 (m, 12H), 7.52−7.59 (m, 8H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 35.3 (s) ppm. MS (FAB; *m*/*z* (relative intensity, %)): 697 ([Ir(cod)(dppe)]$^+$ − 2H, 100). Anal. Calcd for $C_{34}H_{36}ClIrP_2$: C, 55.62; H, 4.94. Found: C, 55.38; H, 5.02.

X-ray Crystallographic Structural Determinations of 4 and 8·$CHCl_3$. The single crystals of **4** and **8**·$CHCl_3$ suitable for X-ray diffraction analysis were obtained by recrystallization from dichloromethane/methanol for **4** or from chloroform/*n*-hexane for **8**·$CHCl_3$. A crystal of dimensions 0.3 × 0.3 × 0.8 mm (**4**) or 0.6 × 0.6 × 0.8 mm (**8**·$CHCl_3$) was mounted on a quartz fiber, and diffraction data were collected in the θ range of 1.64−29.30° for **4** and 1.68−29.14° for **8**·$CHCl_3$, respectively, at 173 K on a Brucker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The absorption correction was made using SADABS. The structure was solved by direct methods and refined by full-matrix least squares on F^2 by using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. Final refinement details are compiled in Tables S1-1 and S2-1 (Supporting Information).

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research and the 21st Century COE Program "Nature-Guided Materials Processing" of the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We also gratefully

acknowledge Dr. Kozo Matsumoto, Mr. Haruhisa Choushi, and Mr. Shin-ichi Komai for the mass spectral measurements.

Supporting Information Available: Tables of crystallographic data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **4** and **8**·$CHCl_3$ and figures giving ORTEP drawings of the full structures of **4** and **8**·$CHCl_3$; alternatively, these data can be acquired as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data for **4** and **8**·$CHCl_3$ are also available free of charge from the Cambridge Crystallographic Data Centre via the Internet at http://www.ccdc.cam.ac.uk. The CCDC file numbers of **4** and **8**·$CHCl_3$ are as follows: **4**, CCDC 223428; **8**·$CHCl_3$, CCDC 223429.

OM034282Y