Alkoxylation and Amination of Ring-Methyl Group in Pentamethylcyclopentadienyliridium Complexes

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Reactions of a unidentate bis(diphenylphosphino)methane (dppm) complex Cp*$IrCl_2$(η^1-dppm) (**1**) with 2 equiv of NaOR (R = Et, Me, or ^{i}Pr) give ring-methyl-alkoxylated complexes ($C_5Me_4CH_2OR$)Ir(η^2-dppm) [R = Et (**5a**); R = Me (**5b**); R = ^{i}Pr (**5c**)], respectively. Cationic complexes [Cp*IrCl(η^2-dppm)]OTf (**2**), [Cp*IrCl{$P(OPh)_3$}$_2$]OTf (**3**), and [Cp*IrCl(PPh_3)$_2$]OTf (**4**) react with 2 equiv of NaOEt to give ($C_5Me_4CH_2OEt$)IrL_2 [L_2 = dppm (**5a**); L = $P(OPh)_3$ (**6a**); L = PPh_3 (**7a**)], respectively. The complex **3** reacts with 2 equiv of NaO^{t}Bu in ethanol, methanol, 2-propanol, allyl alcohol, or propargyl alcohol to give ($C_5Me_4CH_2OR$)Ir{$P(OPh)_3$}$_2$ [R = Et (**6a**); R = Me (**6b**); R = ^{i}Pr (**6c**); R = allyl (**6d**); R = propargyl (**6e**)], respectively. Furthermore, treatment of **3** with 2 equiv of ^{n}BuLi and excess diethylamine, propylamine, *N*-methylaniline, or aniline in triethylamine as solvent gives ring-methyl aminated complexes ($C_5Me_4CH_2NR^1R^2$)Ir{$P(OPh)_3$}$_2$ [$R^1 = R^2$ = Et (**8a**); $R^1 = {}^n$Pr, R^2 = H (**8b**); R^1 = Ph, R^2 = Me (**8c**); R^1 = Ph, R^2 = H (**8d**)], respectively. The structure of **8a** has been confirmed by X-ray analysis.

Introduction

The cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) groups are widely used as ligands in organometallic chemistry,[1] since they form inert bonds to metals and stabilize metal complexes in both high and low oxidation states. Recently, much attention has been paid to functionalized cyclopentadienyl or permethylcyclopentadienyl ligands C_5H_4R[2] or $C_5Me_4CH_2R$[3−6] because the chemical properties of the organometallic complex with those ligands often change dramatically due to electronic and steric effects. There have been variety of methods of synthesizing metal complexes with functionalized cyclopentadienyl ligands C_5H_4R.[2] On the contrary, relatively few methods of preparing metal complexes with the permethylcyclopentadienyl analogue $C_5Me_4CH_2R$ have been known. The reaction of permethylcyclopentadiene bearing the functional group with appropriate metal salt is one of the ways to synthesize a metal complex with a functionalized cyclopentadienyl ligand.[3] However, such reactions suffer the severe limitation of the functional groups to be introduced. On the other hand, functionalization of a metal permethylcyclopentadienyl complex is another way.[4,5] Maitlis and co-workers have reported ring-methyl activations and functionalizations of Cp* complexes of iridium,[4a−c] rhodium,[4c] and ruthenium.[4d−h] They have revealed that the functionalizations of the ring-methyl group of iridium and rhodium complexes proceed in an electrophilic manner. In this paper we wish to report the first example of the direct alkoxylation and amination of the ring-methyl group in Cp*Ir complexes, which proceed in a nucleophilic manner.[6]

Results and Discussion

Alkoxylation of the Ring-Methyl Group in Cp*Ir Complexes. Formation of ($C_5Me_4CH_2OR$)IrL_2 [R = Et, L_2 = dppm (5a); R = Me, L_2 = dppm (5b); R = ^{i}Pr, L_2 = dppm (5c); R = Et, L = $P(OPh)_3$ (6a); R = Me, L = $P(OPh)_3$ (6b); R = ^{i}Pr, L = $P(OPh)_3$ (6c); R = allyl, L = $P(OPh)_3$ (6d); R = propargyl, L = $P(OPh)_3$ (6e); R = Et, L = PPh_3 (7a)]. Treatment of Cp*$IrCl_2$(η^1-dppm) (**1**) with 2 equiv of sodium ethoxide at room temperature in ethanol afforded a ring-methyl-alkoxylated complex ($C_5Me_4CH_2OEt$)Ir(η^2-dppm) (**5a**) as a yellow powder in 82% yield (eq 1). The ^{1}H and ^{13}C-

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Table 1. ^{1}H NMR Data for Complexes 5−8[a]

complex	C_5Me_4	CH_2E	E	Ph	other signal
5a	2.15 (6H), 2.29 (6H)[b]	4.60	OEt, 1.20 (t, J = 6, 3H), 3.50 (q, J = 6, 2H)	7.09−7.23, 7.73−7.77 (20H)	4.32 (t, J = 11, 2H, PCH_2P)
5b	2.06 (6H), 2.21 (6H)[b]	4.49	OMe, 3.21 (s, 3H)	7.02−7.15, 7.65−7.69 (20H)	4.24 (t, J = 11, 2H, PCH_2P)
5c	2.07 (6H), 2.22 (6H)[b]	4.45	O^{i}Pr, 1.12 (d, J = 6, 6H), 3.56 (m, 1H)	7.01−7.13, 7.66−7.70 (20H)	4.25 (t, J = 11, 2H, PCH_2P)
6a	1.61 (6H), 1.88 (6H)[c]	3.61	OEt, 1.10 (t, J = 7, 3H), 3.30 (q, J = 7, 2H)	6.86−7.28 (30H)	
6b	1.60 (6H), 1.87 (6H)	3.53	OMe, 3.09 (s, 3H)	6.86−7.25 (30H)	
6c	1.61 (6H), 1.86 (6H)	3.55	O^{i}Pr, 1.09 (d, J = 6, 6H), 3.41 (m, 1H)	6.86−7.26 (30H)	
6d	1.60 (6H), 1.87 (6H)	3.62	OAllyl, 3.82 (dt, J = 5, 2, 2H), 5.04 (ddt, J = 10, 2, 2, 1H), 5.24 (ddt, J = 17, 2, 2, 1H), 5.85 (ddt, J = 17, 10, 5, 1H)	6.86−7.25 (30H)	
6e	1.58 (6H), 1.88 (6H)	3.67	OPropargyl, 2.06 (t, J = 2, 1H), 3.83 (d, J = 2, 2H)	6.86−7.25 (30H)	
7a	1.58 (6H), 1.61 (6H)	3.98	OEt, 1.09 (t, J = 7, 3H), 3.35 (q, J = 7, 2H)	6.91−7.03, 7.69−7.76 (30H)	
8a	1.67 (6H), 1.93 (6H)	2.81	NEt_2, 0.92 (t, J = 7, 6H), 2.34 (q, J = 7, 4H)	6.86−7.28 (30H)	
8b	1.66 (6H), 1.83 (6H)	3.01	NH^{n}Pr, 0.82 (t, J = 7, 3H), 1.36 (m, 2H), 2.40 (t, J = 7, 2H)	6.85−7.28 (30H)	
8c	1.66 (6H), 1.78 (6H)	3.72	NMePh, 2.39 (s, 3H, N*Me*)	6.76−7.32 (35H)	
8d	1.70 (6H), 1.78 (6H)	3.42[d]	NHPh, 3.14 (t, J = 5, 1H, N*H*)	6.46−7.27 (35H)	

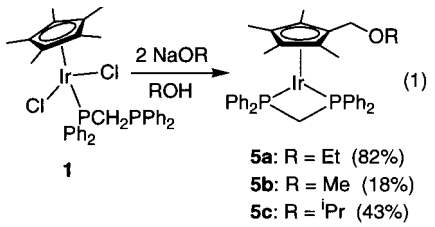
[a] Measured in C_6D_6; coupling constants in hertz. [b] Triplet, J = 2 Hz. [c] Triplet, J = 3 Hz. [d] Doublet, J = 5 Hz.

Table 2. ^{13}C{^{1}H} NMR Data for Complexes 5−8[a]

complex	C_5Me_4	CH_2E	E	dppm, $P(OPh)_3$ or PPh_3	other signal
5a	11.46, 11.49, 90.0, 90.4, 91.3	65.2	OEt, 15.7, 64.9	127.8 (t, J = 4), 128.8, 131.9 (t, J = 6), 139.1 (t, J = 23)	56.7 (t, J = 31, PCH_2P)
5b	11.45, 11.48, 90.06, 90.07, 91.4	67.0	OMe, 57.1	127.8 (t, J = 5), 128.8, 131.9 (t, J = 6), 139.1 (t, J = 22)	56.7 (t, J = 30, PCH_2P)
5c	11.4, 11.5, 90.1 (t, J = 4), 90.4, 91.2	62.8	O^{i}Pr, 70.1, 22.5	127.8 (t, J = 5), 128.8, 131.9 (t, J = 5), 139.2 (t, J = 22)	56.7 (t, J = 30, PCH_2P)
6a	10.0, 10.1, 94.7, 95.3, 97.1	63.6	OEt, 15.6, 65.4	121.8, 123.5, 129.5, 153.2	
6b	10.0, 10.1, 94.4, 95.3 (t, J = 6), 97.2	65.6	OMe, 57.6	121.7, 123.5, 129.5, 153.2	
6c	10.0, 94.8, 95.1 (t, J = 6), 97.0	61.3	O^{i}Pr, 22.5, 70.7	121.8, 123.5, 129.4, 153.2	
6d	10.0, 10.1, 94.3, 95.3 (t, J = 5), 97.2	63.4	OAllyl, 71.1, 116.0, 135.9	121.7, 123.5, 129.7, 153.2	
6e	10.0, 93.6, 95.4 (t, J = 6), 97.4	62.9	OPropargyl, 57.0, 74.1, 81.1	121.7, 123.6, 129.5, 153.2	
7a	10.2, 10.6, 92.3, 93.8 (t, J = 3), 95.3	64.6	OEt, 15.7, 65.5	126.7 (t, J = 4), 128.2, 135.3 (t, J = 6), 139.5 (t, J = 24)	
8a	10.2, 10.8, 95.5 (t, J = 5), 96.3, 96.9	48.5	NEt_2, 12.1, 46.3	121.8, 123.5, 129.4, 153.3	
8b	10.2, 94.5, 96.2, 97.3	44.4	NH^{n}Pr, 11.9, 23.5, 51.9	121.7, 123.5, 129.5, 153.3	
8c	10.2, 10.7, 95.2, 95.3 (t, J = 6), 96.9	46.7	NMePh, 35.0, 114.6, 117.7, 129.3, 151.2	121.7, 123.6, 129.5, 153.2	
8d	10.0, 10.1, 94.8 (t, J = 6), 96.1, 96.6	39.1	NHPh, 113.1, 117.4, 129.4, 148.9	121.7, 123.7. 129.5, 153.2	

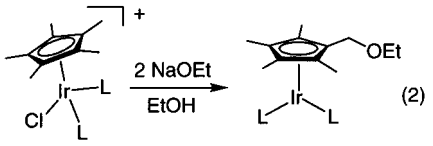
[a] Measured in C_6D_6; coupling constants in hertz.

{^{1}H} NMR data of **5a** are summarized in Tables 1 and 2. The ^{1}H NMR spectrum of **5a** showed two signals for the different types of ring-methyl groups (δ 2.29 and 2.15) and one signal for the substituted methylene (δ 4.60). Signals for the methylene protons of dppm were observed at δ 4.32 as a triplet, indicating that these protons are equivalent. The ^{13}C{^{1}H} NMR spectrum of **5a** showed three signals for C_5Me_4 (δ 91.3, 90.4, and 90.0), two signals for C_5Me_4 (δ 11.49 and 11.46), and a signal for $C_5Me_4CH_2$ (δ 65.2). In the ^{31}P{^{1}H} NMR spectrum, one singlet at δ −50.6 was observed, indicating that two phosphorus are equivalent and the dppm is η^2 bonded. Considering these NMR data, it was revealed that alkoxylation of one of the ring-methyl groups in **1** occurred. Similar reactions of **1** with 2 equiv of sodium methoxide or sodium isopropoxide also gave ring-methyl alkoxylated complexes **5b** and **5c**, respectively (eq 1). NMR signal patterns of **5b** and **5c** were similar to that of **5a** except for the alkoxy group.



We next tried the reactions of cationic complexes $[Cp^*IrCl(\eta^2\text{-dppm})]^+$ (**2**), $[Cp^*IrCl\{P(OPh)_3\}_2]^+$ (**3**), and $[Cp^*IrCl(PPh_3)_2]^+$ (**4**) with sodium ethoxide. Treatment of **2**−**4** with 2 equiv of sodium ethoxide at room temperature in ethanol gave ring-methyl-alkoxylated

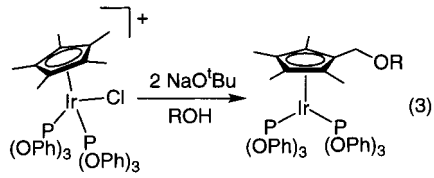
complexes (C_5Me_4OEt)IrL_2 [L_2 = dppm (**5a**), L = $P(OPh)_3$ (**6a**), L = PPh_3 (**7a**)] (eq 2). The ^1H and $^{13}C\{^1H\}$ NMR data of the products are summarized in Tables 1 and 2.



2: L,L = dppm
3: L = $P(OPh)_3$
4: L = PPh_3

5a: L,L = dppm (78%)
6a: L = $P(OPh)_3$ (57%)
7a: L = PPh_3 (78%)

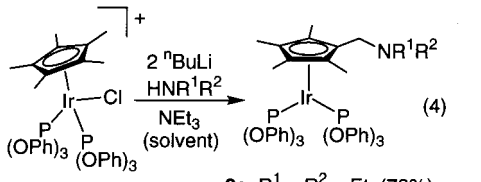
We have also found that present ring-methyl alkoxylations can be generally achieved when the reactions are carried out using sodium *tert*-butoxide in appropriate alcohol as solvent. Thus, the cationic complex **3** reacted with 2 equiv of sodium *tert*-butoxide at room temperature in ethanol, methanol, 2-propanol, allyl alcohol, or propargyl alcohol to give the corresponding alkoxy complexes, ($C_5Me_4CH_2OR$)$Ir\{P(OPh)_3\}_2$ [R = Et (**6a**); R = Me (**6b**); R = ^{i}Pr (**6c**); R = allyl (**6d**); R = propargyl (**6e**)] in good yield, respectively (eq 3). The ^1H and $^{13}C\{^1H\}$ NMR data of the products are summarized in Tables 1 and 2. In the ^1H NMR spectrum of **6d** olefinic protons were observed at δ 5.85, 5.24, and 5.04, indicating no coordination of the allyl moiety to the iridium center.



3

6a: R = Et (88%)
6b: R = Me (84%)
6c: R = ^{i}Pr (71%)
6d: R = allyl (93%)
6e: R = propargyl (87%)

Amination of the Ring-Methyl Group in the Cp*Ir Complex. Formation of ($C_5Me_4CH_2NR^1R^2$)-$Ir\{P(OPh)_3\}_2$ [R^1 = R^2 = Et (8a); R^1 = ^{n}Pr, R^2 = H (8b); R^1 = Ph, R^2 = Me (8c); R^1 = Ph, R^2 = H (8d)]. The complex **3** reacted with 2 equiv of ^{n}BuLi in the presence of excess diethylamine in triethylamine as solvent to give the ring-methyl-aminated complex ($C_5Me_4CH_2NEt_2$)$Ir\{P(OPh)_3\}_2$ (**8a**) as a yellow powder in 78% yield (eq 4). The complex **8a** was also obtained in a reasonable yield when the reaction was carried out using diethylamine as solvent. However, no ring-methylaminated complex was afforded when tetrahydrofuran was used as solvent. Reactions of **3** with ^{n}BuLi in the presence of propylamine, *N*-methylaniline, or aniline in triethylamine also gave aminated complexes ($C_5Me_4CH_2NR^1R^2$)$Ir\{P(OPh)_3\}_2$ [R^1 = ^{n}Pr, R^2 = H (**8b**); R^1 = Ph, R^2 = Me (**8c**); R^1 = Ph, R^2 = H (**8d**)], respectively (eq 4). These reactions are, to the best of our knowledge, the first example of direct amination of a ring-methyl group in pentamethylcyclopentadienylmetal complexes.[7] ^1H and $^{13}C\{^1H\}$ NMR data of **8a**−**d** are summarized in Tables 1 and 2. NMR signal patterns for the C_5Me_4 moiety in **8a**−**d** were similar to those of alkoxylated complexes.



3

8a: R^1 = R^2 = Et (78%)
8b: R^1 = ^{n}Pr, R^2 = H (95%)
8c: R^1 = Ph, R^2 = Me (81%)
8d: R^1 = Ph, R^2 = H (68%)

X-ray Crystal Structure of 8a. The structure of **8a** was confirmed by an X-ray diffractional study. The molecular geometry and atom-numbering system of **8a** are shown in Figure 1, and Tables 3 and 4 summarize the results obtained. The iridium atom is five site coordinated if the η^5-$C_5Me_4CH_2NEt_2$ group is considered as filling three coordination sites. The iridium atom would be formally in the oxidation state +I. Two triphenyl phosphite ligands coordinate to the iridium center with a P(1)−Ir(1)−P(2) angle of 90.9(1)°. The diethylamino moiety is located above the C_5 ring and opposite the iridium center, indicating that there are no interaction between iridium and nitrogen. The C_5 ring is nonsymmetrically η^5-bonded, with C(1) slightly closer to the iridium center [2.233(9) Å] than C(2)−C(5) [2.27(1)−2.30(1) Å].

Mechanism for the Alkoxylation and Amination of the Ring-Methyl Group in the Cp*Ir Complex. A possible mechanism for the alkoxylation and amination reaction is shown in Scheme 1. In the reaction of neutral complex **1**, coordination of the dangling phosphine moiety to the iridium center would occur at first. Base-promoted deprotonation from the ring-methyl in the cationic Cp* complex could take place to afford a η^4-tetramethylfulvene intermediate **A**.[8] It has been reported that η^4-tetramethylfulvene complexes react with electrophiles to afford substituted permethylcyclopentadienyl complexes.[4c] On the other hand, it has also been reported that η^6-tetramethylfulvene complexes react with nucleophiles.[4d,5a,c] Considering these facts, in the present reactions the intermediate **A** would transform into a cationic η^6-tetramethylfulvene intermediate **A′**, which could be subjected to nucleophilic addition of alkoxide or amide anion to the methylidene moiety. However, we cannot rule out the other route via a chloride-migrated intermediate **B**, from which the product could be afforded by nucleophilic substitution. To isolate the plausible intermediate **A**, **A′**, or **B**, the reaction of **3** with 1 equiv of NaO^{t}Bu in ethanol was attempted, which resulted in formation of **5a** in low yield in addition to the recovery of starting complex **3**.

Summary

In this paper we have reported the direct alkoxylation and amination of the ring-methyl group in Cp*Ir complexes. The present results indicate that a wide variety of alkoxylation of Cp*Ir complexes could be achieved in a facile manner by use of NaO^{t}Bu in various alcohols as solvent. The amination reactions reported here are, to the best of our knowledge, the first examples

(7) Maitlis, P. M. et al. have reported the synthesis of amino-substituted permethylcyclopentadienylruthenium complexes derived from chloro-substituted complexes.[4d]

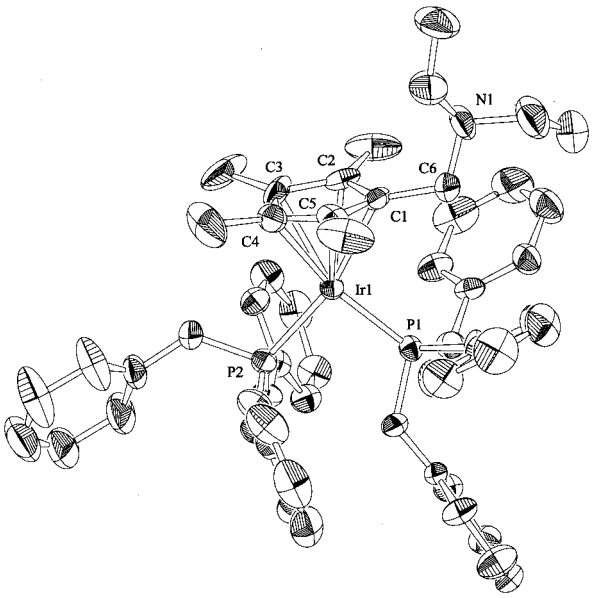


Figure 1. ORTEP view of **8a**.

Table 3. Crystal Data and Structure Refinement Parameters for $(C_5Me_4CH_2NEt_2)Ir\{P(OPh)_3\}_2$ (8a)

Description of Crystal	
color	yellow
habit	plate
max cryst dimens (mm)	0.50 × 0.30 × 0.10
cryst syst	trigonal
space group	$R\bar{3}$
a (Å)	43.11(3)
c (Å)	13.14(1)
V (Å^3)	21145(17)
Z	18
formula	$C_{50}H_{54}NO_6P_2Ir$
fw	1019.15
D_{calc} (g cm^{-3})	1.440
Data Collection	
radiation (λ, Å)	Mo Kα (0.71069)
scan technique	$\omega-2\theta$
scan width (deg)	(1.00 + 0.30 tan θ)
$2\theta_{max}$ (deg)	50.0
no. of rflns measd	6403
Structure Determination	
no. of rflns used	4593 ($I > 1.00\sigma(I)$)
no. of params varied	541
data/param ratio	8.49
transmn factors	0.63−1.00
goodness of fit	1.73
R^a	0.051
$R_w{}^a$	0.050
p factor	0.030

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$.

of direct aminations of the ring-methyl group in Cp* metal complexes. Investigation of the reactivities of functionalized permethylcyclopentadienyl complexes is now in progress.

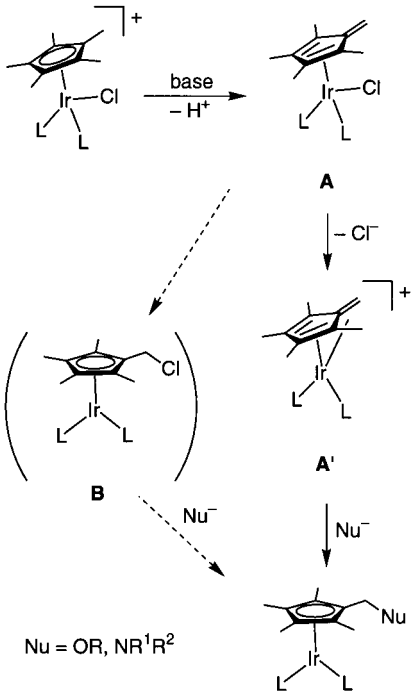
Experimental Section

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. Melting points were determined on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Infrared spectra were taken on a HORIBA FT-300 spectrometer. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} spectra were measured with JEOL EX-270 and JEOL A-500 spectrometers. Solvents were dried by using

Table 4. Selected Bond Lengths and Angles for $(C_5Me_4CH_2NEt_2)Ir\{P(OPh)_3\}_2$ (8a)

Bond Lengths (Å)			
Ir(1)−P(1)	2.141(3)	Ir(1)−P(2)	2.156(3)
Ir(1)−C(1)	2.233(9)	Ir(1)−C(2)	2.29(1)
Ir(1)−C(3)	2.30(1)	Ir(1)−C(4)	2.27(1)
Ir(1)−C(5)	2.30(1)	C(1)−C(2)	1.45(1)
C(1)−C(5)	1.39(1)	C(1)−C(6)	1.50(1)
C(2)−C(3)	1.38(2)	C(3)−C(4)	1.48(2)
C(4)−C(5)	1.37(2)	C(6)−N(1)	1.42(1)
Bond Angles (deg)			
P(1)−Ir(1)−P(2)	90.9(1)	C(1)−C(6)−N(1)	113.3(9)

Scheme 1



standard procedures and distilled prior to use. The complexes $[Cp^*IrCl_2]_2$[9a,b] and $Cp^*IrCl_2(\eta^1$-dppm) (**1**)[9c] were prepared by literature methods. Other reagents were used as obtained from commercial sources.

Synthesis of [Cp*IrCl(η^2-dppm)]OTf (2). To a mixture of $Cp^*IrCl_2(\eta^1$-dppm) (**1**) (0.277 g, 0.354 mmol) and silver trifluoromethanesulfonate (0.102 g, 0.399 mmol) was added tetrahydrofuran (10 mL), and the mixture was stirred for 4.5 h. The color of the solution changed to pale yellow accompanied by precipitation of white powder (AgCl). After filtration, evaporation of the solvent, followed by washing with hexane (25 mL) gave **1** as a pale yellow powder (0.139 g, 0.155 mmol, 44%). Mp: 262.1 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.79 (t, J = 2 Hz, 15H, C_5Me_5), 4.63 (td, J_{HP} = 13 Hz, J_{HH} = 16 Hz, 1H, PC*H*HP), 6.30 (td, J_{HP} = 10 Hz, J_{HH} = 16 Hz, 1H, PCH*H*P), 7.23−7.58 (m, 20H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.3 (s, C_5Me_5), 45.3 (t, J = 33 Hz, PCH_2P), 98.2 (s, C_5Me_5), 126.8 (t, J = 33 Hz, Ph), 127.2 (t, J = 27 Hz, Ph), 128.9 (t, J = 6 Hz, Ph), 129.2 (t, J = 5 Hz, Ph), 131.9 (s, Ph), 132.3 (t, J = 5 Hz, Ph), 132.4 (t, J = 5 Hz, Ph), 132.6 (s, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −37.8. Anal. Calcd for $C_{36}H_{37}ClF_3O_3P_2SIr$: C, 48.24; H, 4.16; Cl, 3.96. Found: C, 48.23; H, 4.03; Cl, 3.93.

(8) Formation of a tetramethylfulvene iridium complex by the reaction of a Cp* complex with base has been reported. Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862, and ref 4c.

(9) (a) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) Ball, R. G.; Graham, W. A. G.; Heinekey, D. M.; Hoyano, J. K.; McMaster, A. D.; Mattson B. M.; Michel S. T. *Inorg. Chem.* **1990**, *29*, 2023. (c) Valderrama, M.; Contreras, R. *J. Organomet. Chem.* **1996**, *513*, 7.

Synthesis of [Cp*IrCl{P(OPh)$_3$}$_2$]OTf (3). To a solution of [Cp*IrCl$_2$]$_2$ (0.930 g, 1.17 mmol) in chloroform (23 mL) was added triphenyl phosphite (1.35 mL, 1.60 g, 5.16 mmol), and the mixture was stirred for 1 h. Then silver trifluoromethanesulfonate (0.641 g, 2.50 mmol) was added. The mixture was stirred for 16 h. The color of the solution changed from orange to yellow accompanied by precipitation of a white powder (AgCl). After filteration, evaporation of the solvent followed by washing with hexane (70 mL) gave **3** as a pale yellow powder (2.44 g, 2.15 mmol, 92%). Mp: 129.5 °C (dec). ^{1}H NMR (CDCl$_3$): δ 1.70 (t, J = 4 Hz, 15H, C$_5$Me$_5$), 7.05−7.23 (m, 30H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.2 (C$_5$*Me*$_5$), 104.3 (*C*$_5$Me$_5$), 120.5 (Ph), 125.9 (Ph), 129.9 (Ph), 150.9 (t, J = 7 Hz, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 59.6. Anal. Calcd for C$_{47}$H$_{45}$ClF$_3$O$_9$P$_2$SIr: C, 49.84; H, 4.00; Cl, 3.13. Found: C, 49.87; H, 3.89; Cl, 3.00.

Synthesis of [Cp*IrCl(PPh$_3$)$_2$]OTf (4). To a mixture of [Cp*IrCl$_2$]$_2$ (0.468 g, 0.588 mmol) and PPh$_3$ (0.620 g, 2.36 mmol) was added chloroform (18 mL), and the mixture was stirred for 4 h. Then silver trifluoromethanesulfonate (0.307 g, 1.20 mmol) was added. The mixture was stirred for 15 h. The color of the solution changed from orange to yellow accompanied by precipitation of a white powder (AgCl). After filtration, evaporation of the solvent followed by washing with hexane (35 mL) gave **4** as a yellow powder (1.12 g, 1.08 mmol, 92%). Mp: 235.7−237.2 °C. ^{1}H NMR (CDCl$_3$): δ 1.14 (s, C$_5$Me$_5$), 7.10−7.48 (br, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 8.8 (C$_5$Me$_5$), 101.6 (C$_5$Me$_5$), 128.0 (Ph), 131.1 (Ph), 134.7 (Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −11.2. Anal. Calcd for C$_{47}$H$_{45}$ClF$_3$O$_3$P$_2$SIr: C, 54.46; H, 4.38; Cl, 3.42. Found: C, 53.68; H, 4.58; Cl, 3.33.

Synthesis of (C$_5$Me$_4$CH$_2$OR)Ir(η^2-dppm) [R = Et (5a); R = Me (5b); R = ^{i}Pr (5c)]. To a mixture of **1** (0.195 g, 0.250 mmol) and NaOEt (0.0372 g, 0.547 mmol) was added ethanol (10 mL) at room temperature, and the mixture was stirred for 2.3 h. After removal of volatiles, the residue was extracted with hexane (8 mL). Evaporation of solvent gave **5a** as a yellow powder (0.155 g, 0.205 mmol, 82%). Mp: 98.3 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −50.6. Anal. Calcd for C$_{37}$H$_{41}$OP$_2$Ir: C, 58.79; H, 5.47. Found: C, 58.53; H, 5.54.

Similar reaction of **1** (0.0963 g, 0.123 mmol) and NaOMe (0.0133 g, 0.246 mmol) in methanol gave a pale yellow powder, **5b** (0.0160 g, 0.0216 mmol, 18%). The yield of **5b** was low (18%) because of its instability. Mp: 87.3 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −50.6. Anal. Calcd for C$_{36}$H$_{39}$OP$_2$Ir: C, 58.28; H, 5.30. Found: C, 57.78; H, 5.33.

Similar reaction of **1** (0.0617 g, 0.0788 mmol) and NaO^{i}Pr (0.0118 g, 0.144 mmol) in 2-propanol gave a pale yellow powder, **5c** (0.0263 g, 0.0342 mmol, 43%). Mp: 103.0 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −50.7. Anal. Calcd for C$_{36}$H$_{39}$OP$_2$Ir: C, 59.28; H, 5.63. Found: C, 59.36; H, 5.45.

Synthesis of (C$_5$Me$_4$CH$_2$OEt)IrL$_2$ [L$_2$ = dppm (5a); L = P(OPh)$_3$ (6a); L = PPh$_3$ (7a)]. To a mixture of **2** (0.050 g, 0.056 mmol) and NaOEt (0.0095 g, 0.14 mmol) was added ethanol (4 mL) at room temperature, and the mixture was stirred for 10 min. After removal of volatiles, the residue was extracted with hexane (7 mL). Evaporation of solvent gave a yellow powder, **5a** (0.033 g, 0.044 mmol, 78%).

Similar reaction of **3** (0.0863 g, 0.0762 mmol) and NaOEt (0.0173 g, 0.254 mmol) in ethanol gave a pale yellow powder, **6a** (0.0428 g, 0.0431 mmol, 57%). Mp: 106.2 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.5. Anal. Calcd for C$_{48}$H$_{49}$O$_7$P$_2$Ir: C, 58.11; H, 4.98. Found: C, 58.28; H, 4.77.

Similar reaction of **4** (0.0419 g, 0.0404 mmol) and NaOEt (0.0150 g, 0.220 mmol) in ethanol gave a red powder, **7a** (0.0284 g, 0.0317 mmol, 78%). Mp: 60.2 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 19.4. Elemental analysis for **7a** was unsatisfactory because of a small amount of contaminant.

Synthesis of (C$_5$Me$_4$CH$_2$OR)Ir{P(OPh)$_3$}$_2$ [R = Et (6a); R = Me (6b); R = ^{i}Pr (6c); R = allyl (6d); R = propargyl (6e)]. To a mixture of **3** (0.115 g, 0.102 mmol) and NaO^{t}Bu (0.0197 g, 0.205 mmol) was added ethanol (6 mL) at room temperature, and the mixture was stirred for 1 h. After removal of volatiles, the residue was extracted with diethyl ether (7 mL). Evaporation of solvent gave **6a** as a pale yellow powder (0.0883 g, 0.0890 mmol, 88%).

Similar reaction of **3** (0.114 g, 0.101 mmol) and NaO^{t}Bu (0.0196 g, 0.204 mmol) in methanol gave **6b** as a pale yellow powder (0.0829 g, 0.0848 mmol, 84%). Mp: 86.4 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.4. Anal. Calcd for C$_{47}$H$_{47}$O$_7$P$_2$Ir: C, 57.72; H, 4.84. Found: C, 57.71; H, 4.87.

Similar reaction of **3** (0.108 g, 0.0951 mmol) and NaO^{t}Bu (0.0183 g, 0.190 mmol) in 2-propanol gave **6c** as a pale yellow powder (0.0681 g, 0.0677 mmol, 71%). Mp: 87.9 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.6. Anal. Calcd for C$_{49}$H$_{51}$O$_7$P$_2$Ir: C, 58.50; H, 5.11. Found: C, 58.23; H, 4.92.

Similar reaction of **3** (0.0746 g, 0.0659 mmol) and NaO^{t}Bu (0.0128 g, 0.133 mmol) in allyl alcohol gave **6d** as a pale yellow powder (0.0618 g, 0.0615 mmol, 93%). Mp: 126.5 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.4. Anal. Calcd for C$_{49}$H$_{49}$O$_7$P$_2$Ir: C, 58.61; H, 4.92. Found: C, 58.79; H, 4.88.

Similar reaction of **3** (0.0665 g, 0.0587 mmol) and NaO^{t}Bu (0.0105 g, 0.109 mmol) in propargyl alcohol gave **6e** as a pale yellow powder (0.0511 g, 0.0510 mmol, 87%). Mp: 139.2 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.4. Anal. Calcd for C$_{49}$H$_{47}$O$_7$P$_2$Ir: C, 58.73; H, 4.73. Found: C, 58.66; H, 4.78.

Synthesis of (C$_5$Me$_4$CH$_2$NR^{1}R^2)Ir{P(OPh)$_3$}$_2$ [R^1 = R^2 = Et (8a); R^1 = ^{n}Pr, R^2 = H (8b); R^1 = Ph, R^2 = Me (8c); R^1 = Ph, R^2 = H (8d)]. To a suspension of **3** (0.072 g, 0.064 mmol) in triethylamine (2 mL) was added diethylamine (17 μL, 0.16 mmol). ^{n}BuLi (1.7 M hexane solution, 0.080 mL, 0.14 mmol) was added at −50 °C. The mixture was slowly warmed to room temperature and stirred for 2 h. After removal of volatiles, the residue was extracted with hexane (5 mL). Evaporation of solvent gave **8a** as a yellow powder (0.051 g, 0.050 mmol, 78%). Mp: 127.2 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 77.7. Anal. Calcd for C$_{50}$H$_{54}$NO$_6$P$_2$Ir: C, 58.93; H, 5.34; N, 1.37. Found: C, 58.95; H, 5.39; N, 1.25.

Similar reaction of **3** (0.142 g, 0.126 mmol) with ^{n}BuLi (0.26 mmol) in the presence of propylamine (45 μL, 0.55 mmol) gave **8b** as a pale yellow powder (0.120 g, 0.119 mmol, 95%). Mp: 93.1 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.0. Anal. Calcd for C$_{49}$H$_{52}$NO$_6$P$_2$Ir: C, 58.55; H, 5.21; N, 1.39. Found: C, 58.82; H, 5.21; N, 1.24.

Similar reaction of **3** (0.102 g, 0.0904 mmol) with ^{n}BuLi (0.18 mmol) in the presence of *N*-methylaniline (0.37 mmol) gave **8c** as a yellow powder (0.0770 g, 0.0731 mmol, 81%). Mp: 68.1 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 77.2. Elemental analysis for **8c** was unsatisfactory because of a small amount of contaminant.

Similar reaction of **3** (0.50 g, 0.44 mmol) with ^{n}BuLi (0.90 mmol) in the presence of aniline (0.89 mmol) gave **8d** as a yellow powder (0.31 g, 0.30 mmol, 68%). Mp: 121.4 °C (dec). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 77.2. Anal. Calcd for C$_{52}$H$_{50}$NO$_6$P$_2$Ir: C, 60.10; H, 4.85; N, 1.35. Found: C, 59.37; H, 4.84; N, 1.25.

X-ray Structure Analysis of 8a. The crystal data and experimental details for **8a** are summarized in Table 3. Diffraction data were obtained with a Rigaku AFC-5S. The reflection intensities were monitored by three standard reflections at every 150 measurements. Decay correction was applied. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections were empirically applied. The structure was solved by the heavy-atom Patterson methods[10,11] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering fac-

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tors and anomalous dispersion terms were taken from literature.[12] All hydrogen atoms were not refined; hydrogen atoms were located on idealized positions. The calculations were performed using the program system teXsan.[13] Selected bond lengths and angles are summarized in Table 4.

Supporting Information Available: X-ray structural data for **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000718N

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