

# Reactions of bis[dichloro( $\eta^5$ -pentamethylcyclopentadienyl)iridium(III)] with bulky and highly basic aromatic phosphines containing *ortho*-methoxy groups

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## Abstract

Reaction of  $[\text{Cp}^*\text{IrCl}_2]_2$  **1** ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) with (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) at room temperature gave a monohapto-complex  $[\text{Cp}^*\text{IrCl}_2(\text{MDMPP-}P)]$  **2a**, whereas the reaction with bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) led to loss of one molecule of  $\text{CH}_3\text{Cl}$  to give  $\text{Cp}^*\text{IrCl}[\text{P}(\text{C}_6\text{H}_3-2-O-6-\text{OMe})\{\text{C}_6\text{H}_3-2,6-(\text{MeO})_2\} \text{Ph}]$  ( $= \text{Cp}^*\text{IrCl}(\text{BDMPP-}\kappa^2P,O)$ ) **3b** with a chelated *P,O* coordination, in which the structure was confirmed by an X-ray analysis:  $a = 15.994(3) \text{ \AA}$ ,  $b = 10.471(2) \text{ \AA}$ ,  $c = 17.727(3) \text{ \AA}$ ,  $\beta = 94.12(1)^\circ$ , monoclinic,  $P2_1/n$ ,  $Z = 4$ ,  $R = 0.032$ . Tris(2,6-dimethoxyphenyl)phosphine (TDMPP) reacted with **1** to afford  $\text{Cp}^*\text{Ir}[\text{P}(\text{C}_6\text{H}_3-2-O-6-\text{OMe})_2\{\text{C}_6\text{H}_3-2,6-(\text{MeO})_2\}]$  ( $= \text{Cp}^*\text{IrCl}(\text{TDMPP-}\kappa^3P,O,O')$ ) **4c**. It was confirmed by an X-ray analysis that the molecule has a trihapto coordination (*P,O,O'*) derived from demethylation of two molecules of  $\text{CH}_3\text{Cl}$ :  $a = 17.55(1) \text{ \AA}$ ,  $b = 21.22(3) \text{ \AA}$ ,  $c = 15.92(2) \text{ \AA}$ , orthorhombic,  $Pbcn$ ,  $Z = 8$ ,  $R = 0.044$ . Complex **1** was treated with MDMPP, BDMPP or TDMPP in acetone in the presence of a  $\text{PF}_6^-$  anion to give salt-like complexes  $[\text{Cp}^*\text{IrCl}(\text{XDMPP-}\kappa^2P,O\text{Me})][\text{PF}_6]$  **5** ( $X = \text{M, B, T}$ ) with a *P,O* coordination. The structures of **5b** and **5c**· $\text{CHCl}_3$  were confirmed by X-ray analyses: for **5b** ( $X = \text{B}$ ),  $a = 11.679(2) \text{ \AA}$ ,  $b = 15.389(4) \text{ \AA}$ ,  $c = 10.251(3) \text{ \AA}$ ,  $\alpha = 103.92(2)^\circ$ ,  $\beta = 91.76(2)^\circ$ ,  $\gamma = 105.15(2)^\circ$ , triclinic,  $P\bar{1}$ ,  $Z = 2$ ,  $R = 0.046$ ; for **5c**· $\text{CHCl}_3$  ( $X = \text{T}$ ),  $a = 14.730(7) \text{ \AA}$ ,  $b = 18.55(2) \text{ \AA}$ ,  $c = 15.753(9) \text{ \AA}$ ,  $\beta = 91.76(2)^\circ$ ,  $\gamma = 105.45(5)^\circ$ , monoclinic,  $P2_1/n$ ,  $Z = 4$ ,  $R = 0.048$ . In complexes **5a** and **5b** the exchange between free and coordinated OMe groups was observed, whereas in **5c** such exchange was not observed. Complex **2a** readily reacted with Lewis bases (L) such as isocyanide and CO in the presence of a  $\text{PF}_6^-$  anion to produce  $[\text{Cp}^*\text{IrCl}(\text{L})(\text{MDMPP-}P)][\text{PF}_6]$  **6**. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** (2,6-Dimethoxyphenyl)diphenylphosphine; Bis(2,6-dimethoxyphenyl)phenylphosphine; Tris(2,6-dimethoxyphenyl)phosphine; Bis[dichloro(pentamethylcyclopentadienyl)iridium(II)]; P-O and P,O,O' chelating ligands; Demethylation from phosphines

## 1. Introduction

The chemistry of tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) bearing the methoxy groups at the 2, 4 and 6-positions of the phenyl groups has been performed by Dunbar's groups [1]. This phosphine undergoes demethylation from methoxy groups to form various coordination modes. Tris(2,6-dimethoxyphenyl)phosphine (TDMPP), being less basic than TMPP exhibits similar reaction behaviors. We have been interested in interactions of this and related phosphines with

the complexes containing pentamethylcyclopentadienyl or arene groups. Bis[dichloro( $\eta^6$ -arene) ruthenium(II)] readily reacted with (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP), bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP), or TDMPP to give various type of complexes bearing  $\kappa^1$ -*P*,  $\kappa^2$ (*P,O*) or  $\kappa^3$ (*P,O,O'*) coordinations, depending on hydrocarbon ligands, phosphines and reaction conditions [2]. We reported that the reaction of bis[dichloro( $\eta^5$ -pentamethylcyclopentadienyl)rhodium(III)] with MDMPP afforded  $\text{Cp}^*\text{RhCl}_2(\text{MDMPP-}P)$  or  $\text{Cp}^*\text{RhCl}(\text{MDMPP-}\kappa^2P,O)$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{MDMPP-}\kappa^2P,O = \text{PPh}_2(\text{C}_6\text{H}_3-2-O-6-\text{MeO})$ ) [3]. We report the reactions of bis[dichloro( $\eta^5$ -pentamethylcyclopentadienyl)iridium(III)], isoelectronic

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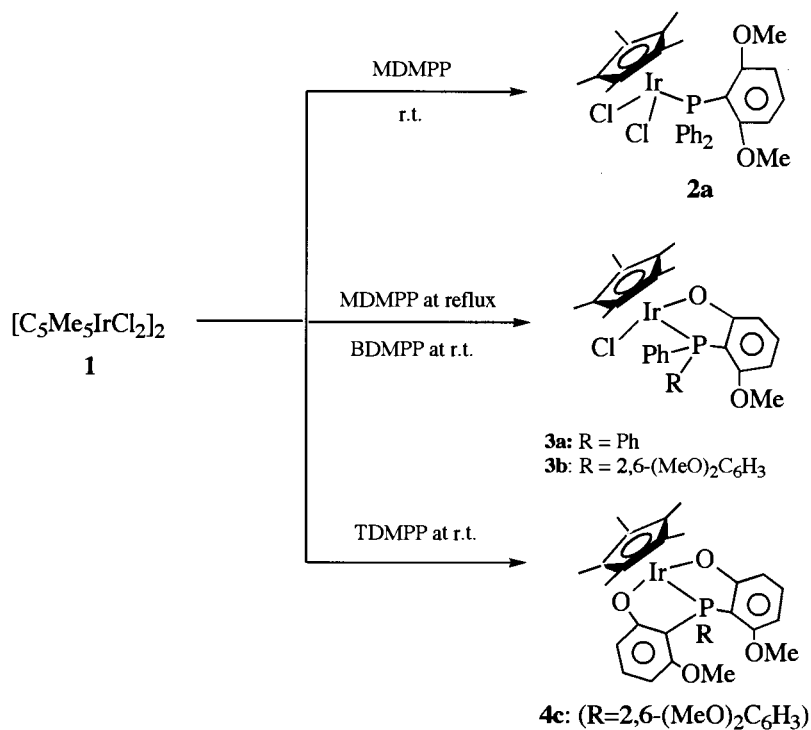
E-mail address: yamamoto@chem.sci.toho-u.ac.jp (Y. Yamamoto)

Table 1  
 Crystal data of [Cp\*IrCl(BDMPP-*P,O'*)] **3b**, [Cp\*IrCl(TDMPP-*P,O,O''*)] **4c**, [Cp\*IrCl(BDMPP-*P,OMe*)]PF<sub>6</sub> **5b** and [Cp\*IrCl(BDMPP-*P,OMe*)]PF<sub>6</sub> **5c**·CHCl<sub>3</sub>

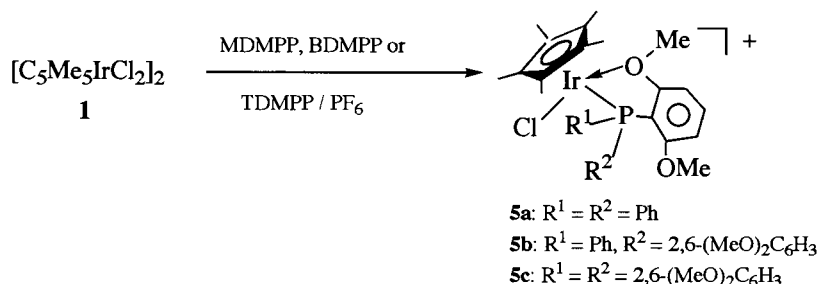
Compound	<b>3b</b>	<b>4c</b>	<b>5b</b>	<b>5c</b> ·CHCl <sub>3</sub>
Formula	C <sub>31</sub> H <sub>35</sub> ClO <sub>4</sub> PIr	C <sub>32</sub> H <sub>36</sub> O <sub>6</sub> PIr	C <sub>33</sub> H <sub>38</sub> ClO <sub>4</sub> P <sub>2</sub> F <sub>6</sub> Ir	C <sub>35</sub> H <sub>43</sub> P <sub>2</sub> O <sub>6</sub> Cl <sub>4</sub> F <sub>6</sub> Ir
Molecular weight	730.26	739.83	890.26	1069.69
Color	Yellow	Yellow	Orange	Orange
Crystal dimensions (mm)	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.10	0.40 × 0.20 × 0.20
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>Pbcn</i> (No. 60)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
<i>Lattice parameters</i>				
<i>a</i> (Å)	15.994(3)	17.55(1)	11.679(2)	14.730(7)
<i>b</i> (Å)	10.471(2)	21.22(3)	15.389(4)	18.753(2)
<i>c</i> (Å)	17.727(3)	15.92(2)	10.251(3)	15.753(9)
$\alpha$ (°)	90.0	90.0	103.92(2)	90.0
$\beta$ (°)	94.12(1)	90.0	91.76(2)	105.45(5)
$\gamma$ (°)	90.0	90.0	105.15(2)	90.0
<i>V</i> (Å <sup>3</sup> )	2961.3(8)	5930(11)	1717.4(7)	4149(6)
<i>Z</i>	4	8	2	4
Scan rate (° min <sup>-1</sup> )	8	8	16	8
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.638	1.657	1.721	1.712
$\mu$ (cm <sup>-1</sup> )	46.99	46.12	41.36	36.30
<i>F</i> (000)	1448	2944	880	2120
No. of reflections	5524	5785	6050	7562
No. of data ( <i>I</i> > 3.0 $\sigma$ ( <i>I</i> ))	4041	2307	3776	3039
No. of variables	343	361	415	487
<i>R</i> ; <i>R</i> <sub>w</sub> <sup>a</sup>	0.032; 0.078	0.044; 0.045	0.046; 0.057	0.048; 0.048
GOF <sup>b</sup>	1.98	1.25	1.62	1.16

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  ( $w = 1/\sigma^2(F_o)$ ).

<sup>b</sup>  $GOF = [\sum w(|F_o| - |F_c|)^2 / \sum (No - Nv)]^{1/2}$ , where *No* = number of data, *Nv* = number of variables.



Scheme 1.



Scheme 2.

to ruthenium(II) and rhodium(III) complexes with TDMPP, BDMPP or MDMPP and of the resulting products with Lewis bases.

## 2. Experimental

All reactions were carried out under nitrogen atmosphere. Bis[dichloro( $\eta^5$ -pentamethyl cyclopentadienyl)iridium(III)] ( $[\text{Cp}^*\text{IrCl}_2]_2$ ) **1** was prepared by refluxing a mixture of  $\text{IrCl}_4 \cdot 3\text{H}_2\text{O}$  and pentamethylcyclopentadiene in MeOH. Phosphines [4] (MDMPP, BDMPP and TDMPP) and isocyanides [5] (xylyl isocyanide (XylNC) and mesityl isocyanide (MesNC)) were prepared according to the literature. *p*-TosCH<sub>2</sub>NC was available commercially. Benzene, CH<sub>2</sub>Cl<sub>2</sub> and other solvents were distilled over CaH<sub>2</sub>. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 spectrometers, respectively. NMR spectroscopy was carried out on a Bruker AC250. <sup>1</sup>H-NMR spectra were measured at 250 MHz and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra were measured using 85% H<sub>3</sub>PO<sub>4</sub> as an external reference. The FAB mass spectra were measured on a JMS-DX300 spectrometer.

### 2.1. Reaction of **1** with MDMPP

#### 2.1.1. At room temperature

A mixture of **1** (70 mg, 0.088 mmol) and MDMPP (57 mg, 0.174 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at room temperature (r.t.). After 80 min, the solvent was removed to ca. 3 ml and diethyl ether was added to give orange crystals of  $[\text{Cp}^*\text{IrCl}_2(\text{MDMPP-P})]$  **2a** (43.8 mg, 34.9%). IR (Nujol): 1580 cm<sup>-1</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  324, 295 nm. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  1.24 (s, Cp\*, 15H), 3.28 (s, MeO, 6H), 7.1–7.5 (m, Ph, 13H) ppm. <sup>31</sup>P{<sup>1</sup>H}-NMR(CDCl<sub>3</sub>):  $\delta$  -4.67 (s, 1P) ppm. Anal. Calc. for C<sub>30</sub>H<sub>34</sub>O<sub>2</sub>Cl<sub>2</sub>PIr: C, 50.00; H, 4.76. Found: C, 50.63; H, 4.84.

#### 2.1.2. At reflux

A solution of **1** (81.0 mg, 0.102 mmol) and MDMPP (74 mg, 0.23 mmol) in methanol (15 ml) was refluxed for 3 h. The solvent was removed to dryness under

reduced pressure and the residue was chromatographed on alumina. Yellow eluate with CH<sub>2</sub>Cl<sub>2</sub> was concentrated to ca. 3 ml and hexane was added to give yellow crystals of  $[\text{Cp}^*\text{IrCl}(\text{MDMPP-}\kappa^2\text{P,O})]$  **3a** (57 mg, 41.7%). IR (Nujol): 1588, 1541 (P,O chelate) cm<sup>-1</sup>. <sup>1</sup>H-NMR(CDCl<sub>3</sub>):  $\delta$  1.51 (d,  $J_{\text{PH}} = 2.0$  Hz, Cp\*, 15H), 3.37 (s, MeO, 3H), 5.8–7.9 (m, Ph, 13H) ppm. <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>):  $\delta$  28.3 (s, 1P) ppm. Anal. Calc. for C<sub>29</sub>H<sub>31</sub>O<sub>2</sub>ClPIr: C, 51.96; H, 4.66. Found: C, 51.65; H, 4.51.

### 2.2. Reaction of **1** with BDMPP

#### 2.2.1. At room temperature in MeOH

A mixture of **1** (50 mg, 0.063 mmol) and BDMPP (50.4 mg, 0.132 mmol) was stirred in MeOH (10 ml) at r.t. After 80 min, the solvent was removed to dryness and the residue was crystallized from CH<sub>2</sub>Cl<sub>2</sub> and benzene to yield colorless crystals (10 mg), identified as phosphonium salt BDMPP·MeCl. The mother liquor is

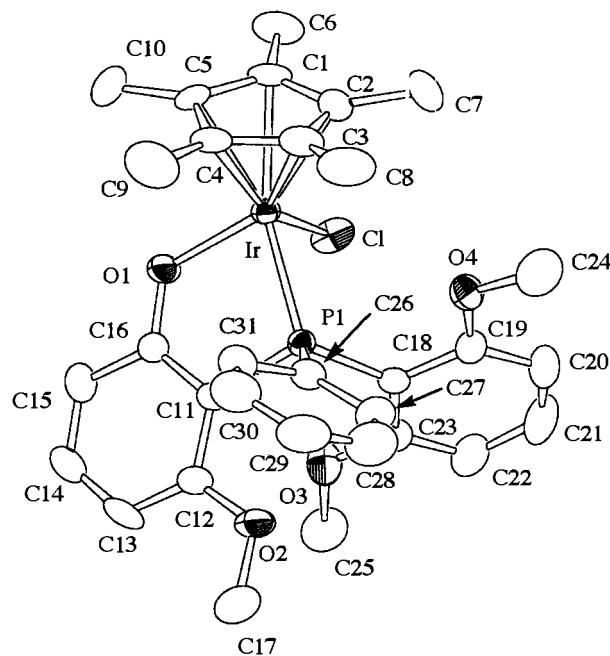


Fig. 1. The molecular structure of **3b** (hydrogen atoms omitted for clarity).

Table 2  
Selected bond lengths (Å) and angles (°) of [Cp\*IrCl(BDMPP-*P,O'*)] **3b**

Complex					
Ir–P(1)	2.311(3)	Ir–Cl(1)	2.399(3)	Ir–O(1)	2.084(8)
P(1)–C(11)	1.80(1)	C(11)–C(16)	1.41(2)	O(1)–C(16)	1.32(1)
O(2)–C(12)	1.38(1)	O(3)–C(23)	1.34(1)	O(4)–C(19)	1.38(2)
P(1)–Ir–Cl(1)	86.9(1)	Cl(1)–Ir–O(1)	86.5(3)	P(1)–Ir–O(1)	82.8(2)
Ir–P(1)–C(11)	99.9(4)	P(1)–C(11)–C(16)	115.2(8)	C(11)–C(16)–O(1)	121(1)
Ir–O(1)–C(16)	120.2(7)	Ir–P(1)–C(18)	114.6(4)	Ir–P(1)–C(26)	120.6(4)
C(11)–P(1)–C(18)	111.3(5)	C(11)–P–C(26)	103.4(5)	C(18)–P(1)–C(26)	106.1(5)

chromatographed on alumina. Yellow eluate with CH<sub>2</sub>Cl<sub>2</sub> (containing a trace amount of acetone) was concentrated to dryness and the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–hexane to give orange crystals of [Cp\*IrCl(BDMPP-κ<sup>2</sup>P,*O*)] **3b** (44.4 mg, 43.2%). FAB mass: *m/z* 730 (M<sup>+</sup>), 695 (M–Cl<sup>+</sup>). IR (Nujol): 1588, 1555 (P,*O* chelate) cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.54 (d, *J*<sub>PH</sub> = 1.8 Hz, Cp\*, 15H), 3.09 (s, MeO, 3H), 3.25 (s, MeO, 3H), 3.72 (s, MeO, 3H), 5.23 (s, CH<sub>2</sub>Cl<sub>2</sub>, 1H), 5.6–7.5 (m, Ph, 11H) ppm. <sup>31</sup>P{<sup>1</sup>H}-NMR(CDCl<sub>3</sub>): δ 12.1 (s, 1P). Anal. Calc. for C<sub>32</sub>H<sub>35</sub>O<sub>4</sub>ClIr·1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 49.74; H, 4.62. Found: C, 49.65; H, 5.19.

A similar reaction was carried out at reflux in MeOH to give **3b** (67.3%).

### 2.3. Reaction of **1** with TDMPP

#### 2.3.1. At room temperature

A mixture of **1** (50 mg, 0.063 mmol) and TDMPP (66.5 mg, 0.132 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at r.t. After 80 min, the solvent was dried and the residue was crystallized from benzene–hexane to give pale yellow TDMPP·MeCl (12.8 mg). The mother liquor was concentrated to dryness and recrystallization of the residue from CH<sub>2</sub>CH<sub>2</sub>–benzene–hexane gave yellow crystals of **4c** (49 mg, 44.2%).

#### 2.3.2. At reflux in MeOH

A mixture of **1** (118 mg, 0.148 mmol) and TDMPP (269 mg, 0.607 mmol) was refluxed in MeOH (10 ml) for 3 h. The solvent was removed to dryness and the residue was crystallized from CH<sub>2</sub>Cl<sub>2</sub>–benzene to yield very pale yellow crystals (133 mg), identified as a phosphonium salt TDMPP·MeCl. The mother liquor is chromatographed on alumina. Yellow eluate with CH<sub>2</sub>Cl<sub>2</sub> (containing a trace amount of acetone) was concentrated to dryness and the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–benzene–hexane to give yellow crystals of [Cp\*IrCl(TDMPP-κ<sup>3</sup>P,*O,O'*)] **4c** (77 mg, 35.2%). FAB mass: *m/z* 740 (M<sup>+</sup>). IR (Nujol): 1584, 1553 (P,*O* chelate) cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.51 (d, *J*<sub>PH</sub> = 1.8 Hz, Cp\*, 15H), 3.45 (s, MeO, 6H), 3.50 (s, MeO, 6H), 3.25 (s, CH<sub>2</sub>Cl<sub>2</sub>, 1H), 5.6–7.5 (m, Ph, 9H)

ppm. <sup>31</sup>P{<sup>1</sup>H}-NMR(CDCl<sub>3</sub>): δ 18.6 (s, 1P). Anal. Calc. for C<sub>32</sub>H<sub>36</sub>O<sub>6</sub>PIr·1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 51.49; H, 4.91. Found: C, 51.42; H, 4.61.

### 2.4. Reaction of **1** with phosphines in the presence of a PF<sub>6</sub> anion

#### 2.4.1. With MDMPP

A mixture of **1** (50 mg, 0.063 mmol) and NaPF<sub>6</sub> (22 mg, 0.132 mmol) in acetone–CH<sub>2</sub>Cl<sub>2</sub> (10:5 ml) was stirred at r.t. After 0.5 h, MDMPP (43 mg, 0.132 mmol) was added and the solution was stirred for 2 h. The solvent was removed to dryness and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Orange crystals of [Cp\*IrCl(MDMPP-κ<sup>2</sup>P,*O*Me)][PF<sub>6</sub>] **5a** (38.8 mg, 44%) were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–diethyl ether. IR (Nujol): 835 (PF<sub>6</sub>) cm<sup>-1</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 295 nm. <sup>1</sup>H-NMR(CDCl<sub>3</sub>): δ 1.50 (d, *J*<sub>PH</sub> = 2.5

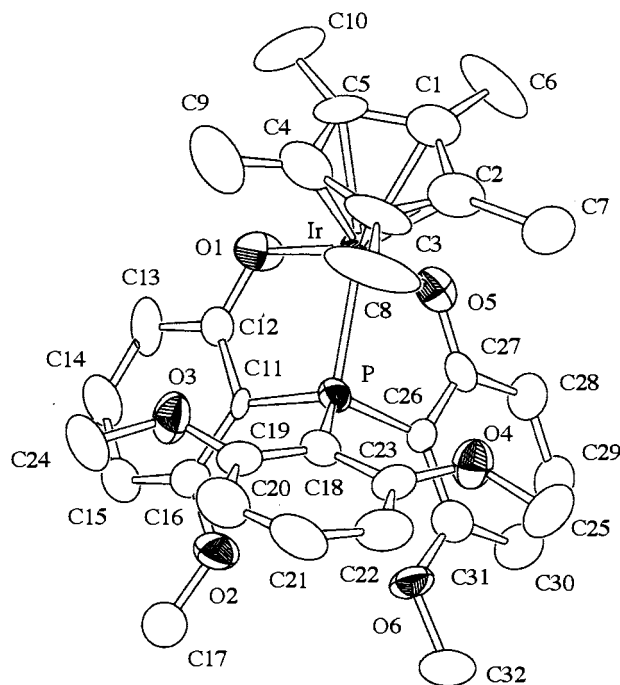


Fig. 2. The molecular structure of **4c** (hydrogen atoms omitted for clarity).

Table 3  
Selected bond lengths (Å) and angles (°) of [Cp\*Ir(TDMPP-*P,O,O'*)] **4c**

Ir–P(1)	2.281(3)	Ir–O(1)	2.080(7)	Ir–O(5)	2.063(7)
P(1)–C(11)	1.784(10)	C(11)–C(12)	1.41(1)	O(1)–C(12)	1.32(1)
P(1)–C(26)	1.79(1)	C(26)–C27	1.41(2)	O(5)–C(27)	1.33(1)
O(2)–C(16)	1.34(1)	O3–C19	1.38(1)	O(4)–C(23)	1.35(1)
O6–C31	1.39(1)				
O1...O5					
P(1)–Ir–O(1)	83.1(2)	P(1)–Ir–O(5)	80.8(2)	O(1)–Ir–O(5)	85.1(3)
Ir–P(1)–C(11)	101.2(3)	P(1)–C(11)–C(12)	113.4(7)	C(11)–C(12)–O(1)	123.2(9)
Ir–O(1)–C(12)	118.5(6)	Ir–P(1)–C(26)	101.3(4)	P(1)–C(26)–C(27)	112.1(9)
C(26)–C(27)–O(5)	121(1)	Ir–O(5)–C(27)	120.1(7)	C(11)–P(1)–C(26)	105.5(5)
C(11)–P(1)–C(18)	112.0(5)	C(18)–P(1)–C(26)	114.2(5)	Ir–P(1)–C(18)	120.6(4)

Hz, Cp\*, 15H), ca 3.90 (b, MeO, 6H), 7.2–7.4 (m, Ph, 13H) ppm.  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  24.7 (s, 1P), –143.9 (sep.  $J_{\text{PF}} = 713$  Hz) ppm. Anal. Calc. for  $\text{C}_{30}\text{H}_{34}\text{O}_2\text{ClF}_6\text{P}_2\text{Ir}$ : C, 43.40; H, 4.13. Found: C, 42.82; H, 4.34.

#### 2.4.2. With BDMPP

According to a procedure similar to that described above, orange crystals of [Cp\*IrCl(BDMPP- $\kappa^2\text{P,O,Me}$ )][PF<sub>6</sub>] **5b** (59.8 mg, 50.9%) were prepared by the reaction of **1** (50 mg, 0.063 mmol) and BDMPP (52 mg, 0.132 mmol) in the presence of NaPF<sub>6</sub> (22 mg, 0.132 mmol). IR (Nujol): 840 (PF<sub>6</sub>) cm<sup>-1</sup>. UV–vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  288 nm.  $^1\text{H}$ -NMR( $\text{CDCl}_3$ ):  $\delta$  1.44 (d,  $J_{\text{PH}} = 2.0$  Hz, Cp\*, 15H), ca. 3.55 (b, MeO, 12H), 6.6–7.6 (m, Ph, 11H) ppm.  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  21.1 (s, 1P), –144 (sep.  $J_{\text{PF}} = 713$  Hz) ppm. Anal. Calc. for  $\text{C}_{33}\text{H}_{37}\text{O}_4\text{ClF}_6\text{P}_2\text{Ir}$ : C, 43.17; H, 4.30. Found: C, 42.61; H, 4.27.

#### 2.4.3. With TDMPP

Orange complex **5c** (68%) was obtained by using KPF<sub>6</sub>. FAB mass:  $m/z$  805 ( $\text{M}^+$ ). IR (Nujol): 835 (PF<sub>6</sub>) cm<sup>-1</sup>.  $^1\text{H}$ -NMR( $\text{CDCl}_3$ ):  $\delta$  1.44 (d,  $J_{\text{PH}} = 2.5$  Hz, Cp\*, 15H), 3.10 (s, MeO, 3H), 3.21 (s, MeO, 3H), 3.34 (s, MeO, 3H), 3.50 (s, MeO, 3H), 3.72 (s, MeO, 3H), 4.56 (s, MeO, 3H), 6.3–7.5 (m, Ph, 9H) ppm.  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  –7.08 (s, 1P), –144 (sep.  $J_{\text{PF}} = 713$  Hz) ppm. Anal. Calc. for  $\text{C}_{34}\text{H}_{42}\text{O}_6\text{ClF}_6\text{P}_2\text{Ir}$ : C, 43.08; H, 4.46. Found: C, 43.12; H, 4.41.

Complex **5c** was refluxed in MeOH for 2 h, and the work-up of the reaction mixture recovered the starting material.

#### 2.5. Reaction of **2a** with Lewis base in the presence of NaPF<sub>6</sub>

The representative reaction is described. A mixture of **2a** (30 mg, 0.045 mmol) and NaPF<sub>6</sub> (7.6 mg, 0.045 mmol) in acetone– $\text{CH}_2\text{Cl}_2$  (4:4 ml) was stirred for 0.5 h at r.t. and xylyl isocyanide (5.9 mg, 0.045 mmol) was added. After 1.5 h, the solvent was removed to dryness

and the extraction of the residue with  $\text{CH}_2\text{Cl}_2$  and addition of diethyl ether yielded yellow crystals of [Cp\*IrCl(MDMPP-*P*)(XylNC)][PF<sub>6</sub>] **6a** (13.8 mg, 32.1%). IR (Nujol): 2160 (N≡C), 839 (PF<sub>6</sub>) cm<sup>-1</sup>.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  1.71 (d,  $J_{\text{PH}} = 2.0$  Hz, Cp\*, 15H), 2.06 (s, *o*-Me, 3H), 3.36 (s, MeO, 6H), 6.6–7.7 (m, Ph, 16H) ppm.  $^{31}\text{P}\{^1\text{H}\}$ -NMR( $\text{CDCl}_3$ ):  $\delta$  –11.4 (s, 1P), –144 (sep.  $J_{\text{PF}} = 712$  Hz, PF<sub>6</sub>, 1P). Anal. Calc. for  $\text{C}_{39}\text{H}_{43}\text{NO}_2\text{P}_2\text{F}_6\text{ClIr}$ : C, 48.72; H, 4.51; N, 1.46. Found: C, 48.45; H, 4.61; N, 1.56. Analogously, yellow crystals of [Cp\*IrCl(MDMPP-*P*)(L)][PF<sub>6</sub>] (**6b**: L = MesNC, 68.1%; **6c**: L = TosCH<sub>2</sub>NC, 22.3%; **6d**: L = CO, 48.5%) were obtained by using a corresponding Lewis base (L). **6b**: IR (Nujol): 2160 (N≡C), 839 (PF<sub>6</sub>) cm<sup>-1</sup>.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  1.70 (d,  $J_{\text{PH}} = 2.0$  Hz, Cp\*, 15H), 2.01 (s, *o*-Me, 6H), 2.28 (s, *p*-Me, 3H), 3.28 (s, MeO, 6H), 6.6–7.7 (m, Ph, 15H) ppm.  $^{31}\text{P}\{^1\text{H}\}$ -NMR( $\text{CDCl}_3$ ):  $\delta$  –11.4 (s, 1P), –144 (sep.  $J_{\text{PF}} = 712$  Hz, PF<sub>6</sub>, 1P).

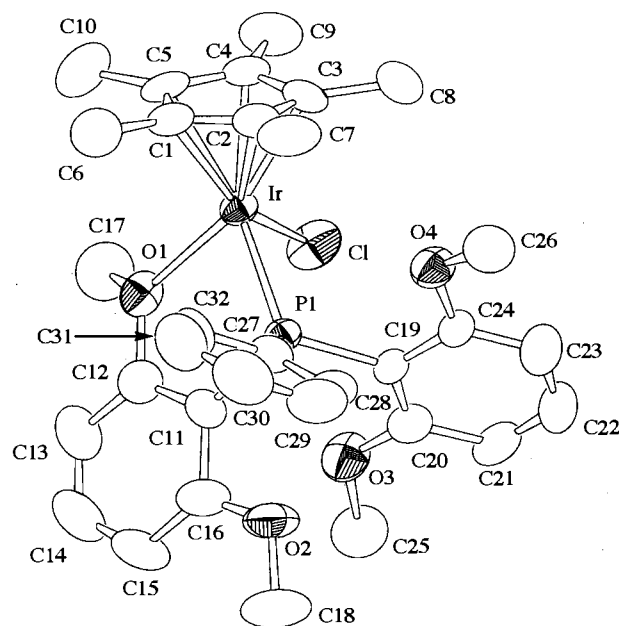


Fig. 3. The molecular structure of **5b** (a PF<sub>6</sub> anion and hydrogen atoms omitted for clarity).

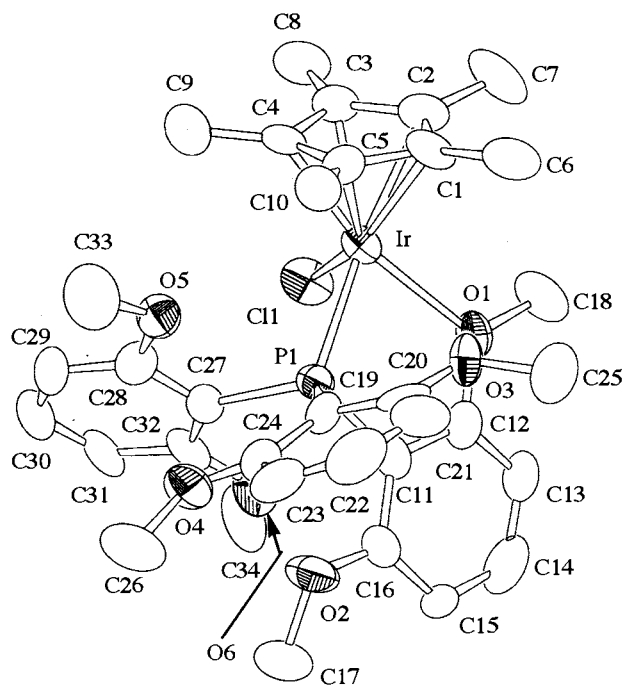


Fig. 4. The molecular structure of **5c** (a  $\text{PF}_6^-$  anion and hydrogen atoms omitted for clarity).

Anal. Calc. for  $\text{C}_{40}\text{H}_{45}\text{NO}_2\text{P}_2\text{F}_6\text{ClIr}$ : C, 49.25; H, 4.65; N, 1.44. Found: C, 49.45; H, 4.77; N, 1.49. **6c**: IR (Nujol): 2207 ( $\text{N}\equiv\text{C}$ ), 841 ( $\text{PF}_6^-$ )  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.61 (d,  $J_{\text{PH}} = 2.5$  Hz,  $\text{Cp}^*$ , 15H), 2.47 (s, *p*-Me, 3H), 3.28 (s, MeO, 6H), 4.71 (center of an AB type quartet,  $J = 15.4$  Hz, 2H), 6.6–7.6 (m, Ph, 17H) ppm.  $^{31}\text{P}\{^1\text{H}\}$ -NMR( $\text{CDCl}_3$ ):  $\delta$  -11.4 (s, 1P), -144 (sep.  $J_{\text{PF}} = 712$  Hz,  $\text{PF}_6^-$ , 1P). Anal. Calc. for

$\text{C}_{39}\text{H}_{43}\text{NO}_4\text{P}_2\text{F}_6\text{ClIr}$ : C, 45.68; H, 4.23; N, 1.37. Found: C, 45.99; H, 4.07; N, 1.44. **6d**: IR (Nujol): 2047 ( $\text{N}\equiv\text{C}$ ), 835 ( $\text{PF}_6^-$ )  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.79 (d,  $J_{\text{PH}} = 2.5$  Hz,  $\text{Cp}^*$ , 15H), 3.35 (bs, MeO, 6H), 6.7–7.8 (m, Ph, 13H) ppm.  $^{31}\text{P}\{^1\text{H}\}$ -NMR( $\text{CDCl}_3$ ):  $\delta$  -12.9 (s, 1P), -144 (sep.  $J_{\text{PF}} = 712$  Hz,  $\text{PF}_6^-$ , 1P). Anal. Calc. for  $\text{C}_{31}\text{H}_{34}\text{O}_3\text{P}_2\text{F}_6\text{ClIr}$ : C, 47.42; H, 4.36. Found: C, 47.78; H, 4.55.

Complex **6a** (41.3 mg, 85.8%) was prepared from **5a** (42 mg, 0.050 mmol) and XylNC (10 mg, 0.076 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml).

## 2.6. Crystal structure determination

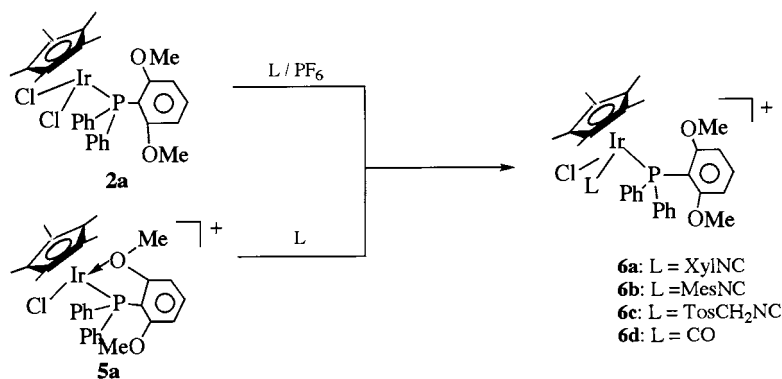
Complexes (**3b**, **4c** and **5b**) were recrystallized from  $\text{CH}_2\text{Cl}_2$ -ether. Complex **5c**- $\text{CHCl}_3$  was recrystallized from  $\text{CHCl}_3$ -ether. Data collection was carried out by an AFC5S-Rigaku automatic diffractometer (26°C,  $\text{Mo-K}\alpha$  radiation, graphite monochromator,  $\lambda = 0.71069$  Å). Cell constants were determined from 20 high-angle reflections. The crystal parameters along with data collection are summarized in Table 1. Intensities were measured by the  $2\theta - \omega$  scan method and corrected for Lorentz and polarization effects. Throughout the data collection the intensities of the three standard reflections were measured every 200 reflections as a check of the stability of the crystals and any decay was not observed. Semiempirical absorption correction ( $\psi$ -scan method) was made. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber [6]. Anomalous dispersion effects were included in  $F_{\text{calc}}$  [7]; the values of  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley [8]. All calculations

Table 4  
Selected bond lengths (Å) and angles (°) of  $[\text{Cp}^*\text{IrCl}(\text{BDMPP-}P, \text{OMe})][\text{PF}_6^-]$  **5b**

Ir–P(1)	2.319(3)	Ir–Cl(1)	2.364(3)	Ir–O(1)	2.242(8)
P(1)–C(11)	1.81(1)	C(11)–C(12)	1.40(2)	O(1)–C(12)	1.42(1)
O(2)–C(16)	1.38(1)	O(3)–C(20)	1.35(1)	O(4)–C(26)	1.41(1)
P(1)–Ir–Cl(1)	86.9(1)	Cl(1)–Ir–O(1)	82.4(2)	P(1)–Ir–O(1)	79.8(2)
Ir–P(1)–C(11)	102.8(4)	P(1)–C(11)–C(12)	121.3(8)	C(11)–C(12)–O(1)	113(1)
Ir–O(1)–C(12)	122.3(6)	Ir–P(1)–C(19)	115.5(3)	Ir–P(1)–C(27)	119.1(3)
C(11)–P(1)–C(19)	111.9(5)	C(11)–P(1)–C(27)	100.7(5)	C(19)–P(1)–C(27)	105.9(5)

Table 5  
Selected bond lengths (Å) and angles (°) of  $[\text{Cp}^*\text{IrCl}(\text{TDMPP-}P, \text{OMe})][\text{PF}_6^-]\text{CHCl}_3$  **5c**

Ir–P(1)	2.353(3)	Ir–Cl(1)	2.386(3)	Ir–O(1)	2.320(8)
P(1)–C(11)	1.81(1)	C(11)–C(12)	1.38(2)	O(1)–C(12)	1.40(1)
O(2)–C(16)	1.35(1)	O(3)–C(20)	1.39(1)	O(4)–C(24)	1.34(1)
O(5)–C(28)	1.36(1)	O(6)–C(32)	1.33(1)		
P(1)–Ir–Cl(1)	88.1(1)	Cl(1)–Ir–O(1)	81.0(2)	P(1)–Ir–O(1)	77.3(2)
Ir–P(1)–C(11)	104.1(4)	P(1)–C(11)–C(12)	120.2(10)	C(11)–C(12)–O(1)	116(1)
Ir–O(1)–C(12)	120.6(6)	Ir–P(1)–C(19)	121.2(4)	Ir–P(1)–C(27)	109.5(4)
C(11)–P(1)–C(19)	100.7(5)	C(11)–P(1)–C(27)	110.3(6)	C(19)–P(1)–C(27)	110.2(5)



Scheme 3.

were performed using the teXsan crystallographic software package of Molecular Structure Corporation [9].

The structures were solved by Patterson methods (DIRDIF92). The positions of iridium and other non-hydrogen atoms were anisotropically refined by full-matrix least-squares methods. Hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å. Maximum and minimum peaks in the final difference Fourier maps were +0.74 and –0.86 e Å<sup>-3</sup> for **3b**, +1.16 and –0.90 e Å<sup>-3</sup> for **4c**, and +0.91 and –0.84 e Å<sup>-3</sup> for **5b**, and +0.85 and –0.77 e Å<sup>-3</sup> for **5c**·CHCl<sub>3</sub>, respectively.

### 3. Results and discussion

#### 3.1. Reactions with phosphines

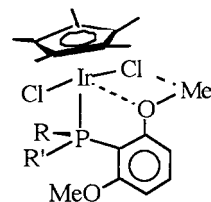
The overall reactions are depicted in Schemes 1 and 2. Complex **1** reacted with MDMPP at r.t. to give an orange complex **2a** formulated as [Cp\*IrCl<sub>2</sub>(MDMPP-P)]. In the <sup>1</sup>H-NMR spectrum the Cp\* protons showed a doublet at δ 1.43 ppm due to a coupling with <sup>31</sup>P atom. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum appeared at δ –4.67 ppm, shifting upfield in comparison with that found in the rhodium analog [3]. The IR spectrum showed only one band (1580 cm<sup>-1</sup>) in the range from 1500 to 1600 cm<sup>-1</sup>, suggesting the presence of the η<sup>1</sup>-P coordination [2]. When the reaction was refluxed in MeOH, one of the *ortho*-methoxy groups in MDMPP was demethylated to give [Cp\*IrCl(MDMPP-κ<sup>2</sup>P,O)] **3a** with a P,O-chelating phosphine. In the IR spectrum two peaks (1586 and 1555 cm<sup>-1</sup>) were found in the range of 1600–1500 cm<sup>-1</sup>, suggesting the presence of a P,O(σ-) bidentate ligand [2].

Reaction of **1** with BDMPP in MeOH at r.t. underwent demethylation from BDMPP to afford an orange complex [Cp\*IrCl(BDMPP-κ<sup>2</sup>P,O)] **3b**. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum showed the only one resonance at δ 12.1 ppm, suggesting the absence of isomers. The <sup>1</sup>H-NMR spectrum showed three singlets at δ 3.09, 3.25,

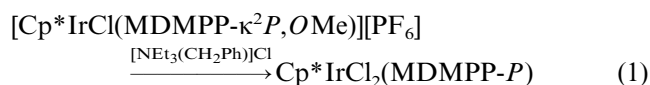
and 3.72 ppm consisting of a 1:1:1 ratio for the MeO groups, suggesting that all methoxy groups are inequivalent, probably resulted in steric demand. The X-ray analysis indicated that the molecule has two chiral centers (Ir and P atoms) (Fig. 1) (vide infra). A priority order of the ligands is Cp\* ring > Cl > P > O for a metal center and Ir > 2-O-6-MeOC<sub>6</sub>H<sub>3</sub> > 2,6-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> > Ph for a P center [2,10]. Fig. 1 showed that the molecule is an Ir<sub>R</sub>P<sub>R</sub>/Ir<sub>S</sub>P<sub>S</sub> pair. Complex **3b** has a similar stereochemistry in solution and in the solid state, whereas the ruthenium analog [(η<sup>6</sup>-arene)RuCl(BDMPP-κ<sup>2</sup>P,O)] is consistent of a Ru<sub>R</sub>P<sub>R</sub>/Ru<sub>S</sub>P<sub>S</sub> pair in the solid state and of two pairs of diastereomers in solution [2] (Table 2).

When **1** was treated with much bulky TDMPP at r.t. or at reflux in MeOH, the reaction underwent demethylation of two methyl groups from the *ortho*-methoxy groups to form yellow complex [Cp\*Ir(TDMPP-κ<sup>3</sup>P,O,O')] **4c**, in addition to TDMPP·MeCl. Monodemethylated complex such as **3** was not obtained even at r.t., due to sterically crowded TDMPP. It was confirmed by an X-ray analysis that TDMPP acted as a P,O,O' tridentate ligand (Fig. 2). The <sup>1</sup>H-NMR spectrum showed two singlets at δ 3.43 and 3.50 ppm consisting of a 1:1 intensity ratio and was in agreement with the structure of solid state. Two absorption bands appeared in the range from 1500 to 1600 cm<sup>-1</sup> in the infrared spectrum, again suggesting the presence of a (P,σ-O) coordination (Table 3).

Demethylation is assumed to proceed through a four-centered intermediate which was suggested in the reactions of [(η<sup>6</sup>-arene)RuCl<sub>2</sub>]<sub>2</sub> with TDMPP [2].



Reaction of **1** with MDMPP, BDMPP or TDMPP in the presence of a PF<sub>6</sub> anion readily gave a salt-like complex [Cp\*IrCl(L-κ<sup>2</sup>P,O Me)][PF<sub>6</sub>] **5** (**a**: L = MDMPP; **b**: L = BDMPP; **c** = TDMPP). The FAB mass spectroscopy of **5c** showed the *m/z* value of 803 which is in agreement with a molecular peak of a cationic moiety. The PF<sub>6</sub> group was found by a strong band at ca. 840 cm<sup>-1</sup>. X-ray crystal analyses of **5b** and **5c** showed that phosphine acted as a P,O bidentate ligand (Figs. 3 and 4). In the <sup>1</sup>H-NMR spectra of complexes **5a** and **5b** the methoxy protons showed only one broad signal at δ ca. 3.8 ppm, suggesting a rapid exchange between free and coordinated MeO groups. The weak Ir–O(Me) interaction was revealed by the fact that addition of [NEt<sub>3</sub>(CH<sub>2</sub>Ph)]Cl to a solution of **5a** regenerated **2a** (Eq. (1)). A similar behavior has been observed in the rhodium analog [Cp\*RhCl(MDMPP-κ<sup>2</sup>P,O Me)][PF<sub>6</sub>] [**3**] (Tables 4 and 5).



The <sup>1</sup>H-NMR spectrum of **5c** showed six sharp singlets at δ 3.10, 3.21, 3.34, 3.50, 3.72 and 4.56 ppm for six methoxy groups, showing the absence of an exchange between free and coordinated methoxy groups. The last one is probably assigned for a coordinated methoxy group. The inequivalence for six methoxy groups showed a characteristic feature of bulky phosphine. When **5** was refluxed in methanol, the starting compound was recovered quantitatively. The elongation of an Ir←O coordination length by ca. 0.25 Å in comparison with the P–O σ-bond length prevented approach between Cl and Me groups to undergo a second demethylation.

### 3.2. Reactions with Lewis bases

Complex **2a** readily reacted with Lewis bases (L) such as isocyanides or CO in the presence of a PF<sub>6</sub> anion to afford yellow complex formulated as [Cp\*Ir(MDMPP-P)(L)][PF<sub>6</sub>] **6** (Scheme 3). Complex **6** showed a sharp band at ca. 2100 cm<sup>-1</sup> due to ν(N≡C) or ν(C≡O) in the infrared spectra. The molecule is assumed to have a piano-stool structure surrounded by Cp\*, Cl, phosphine and isocyanide (or CO). The <sup>1</sup>H-NMR spectra supported the proposed structure. In the <sup>31</sup>P{<sup>1</sup>H}-NMR spectra the signal appeared at δ ca. -12 ppm, again indicating η<sup>1</sup>-P coordination. Complex **6** was also prepared by direct treatment of a salt-like complex **5a** with Lewis base. Similar reactions have been noted in rhodium analogs [**3**].

### 3.3. X-ray structural analyses

The Ir–P length of 2.281(3) Å in **4c** is shorter than those for **3b** (2.311(3) Å), **5b** (2.319(3) Å) and **5c**

(2.353(3) Å), due to difference between a κ<sup>3</sup>(P,O,O') tridentate ligand and a κ<sup>2</sup>(P,O) bidentate one. The Ir–O σ-bond lengths in **3b** (2.084(8) Å for Ir–O(1)) and **4c** (2.080(7) Å for Ir–O(1) and 2.063(7) Å for Ir–O(5)) are shorter than the Ir←O(1) coordination lengths of 2.242(8) for **5b** and 2.320(8) Å for **5c** depending on bonding modes. Especially, these differences were traced back the Ir–Cl lengths for **3b**, **5b** and **5c**; Ir–Cl length (2.399(3) Å) for **3b** is slightly longer than those (2.364(3) Å and 2.386(3) Å) for **5b** and **5c**. The O(1)–C(12) bond lengths of 1.42(1) Å for **5b** and of 1.40(1) for **5c** were longer than those found in the corresponding O–C(aromatic) lengths in **3b** (O(1)–C(16) = 1.32 Å) and **4c** (O(1)–C(12) = 1.32 Å and O(5)–C(27) = 1.33 Å); this elongation being arisen from coordination of lone pair electrons to the metal atom. The P–Ir–O(σ-bond) bite angles are in the range 83–80°, being narrower than P–Ir–Cl (~87°), O–Ir–Cl (87–82°) and O–Ir–O (~85°) angles. The P–Ir–O bite angle-range (~82°) in five-membered rings appears to be common to compounds with P,O chelating ligands derived by demethylation from MDMPP, BDMPP or TDMPP [2,3]; 82.50(9)° for [(η<sup>6</sup>-1,2,3,4-Me<sub>4</sub>C<sub>6</sub>H<sub>2</sub>)-RuCl(MDMPP-κ<sup>2</sup>P,O)], 82.2(2)° for [(η<sup>6</sup>-*p*-cymene)-RuCl(BDMPP-κ<sup>2</sup>P,O)], [(η<sup>6</sup>-arene)RuCl(TDMPP-κ<sup>3</sup>P,-O,O')] (80.1–82.9°) ca. 82° for [Cp\*RhCl(MDMPP-κ<sup>2</sup>P,O)] and [Cp\*Rh(MDMPP-κ<sup>2</sup>P,O)(L)][PF<sub>6</sub>] (L = *p*-TosCH<sub>2</sub>NC).

In complexes of bis(diphenylphosphino)ethane constructing the five-membered chelating ring the P–M–P bite angles are approximately 85° [11] and are wider than the average P–M–O bite angle of 82° in P,O-chelating complexes, depending on the atomic radii; 0.74 Å for an O atom and 1.10 Å for a P atom. The P–Ir←O bite angles were narrower than those found in P–Ir–O (σ-bond).

Remarkable difference in complexes **5b** and **5c** was observed around the iridium metals; the bond distances Ir–A (A = P, Cl, O) of **5c** are longer than those of **5b**, due to the steric demand of TDMPP ligand

## 4. Conclusions

MDMPP acted as a monohapto ligand in the reaction with [Cp\*IrCl<sub>2</sub>]**1** at r.t., whereas a demethylation of one methyl group for BDMPP occurred to give the complex with a κ<sup>2</sup>(P,O) chelating ligand. For much bulky TDMPP two methyl groups were easily eliminated to form the complex with a κ<sup>3</sup>(P,O,O') tridentate ligand. These reactions depend on steric demand of phosphines rather than basicity. For MDMPP, BDMPP and TDMPP cationic complexes with a P,O Me coordination mode were obtained in the presence of a PF<sub>6</sub> anion, independent of phosphines.



## 5. Supplementary material

Listings of data collection, positional coordinates, anisotropic thermal parameters, bond lengths and angles (49 pages) are available from Y. Yamamoto on request.

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