Preparation of carbonyltungsten(0) complexes of 2-pyridylphosphines showing a stepwise coordination pattern by way of monodentate to chelate mode

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Abstract

2-Pyridylphosphines, R_2PyP (R = Ph, NMe_2; Py = 2-pyridyl), were allowed to react with $W(CO)_5(thf)$ to afford the monocoordinated tungsten(0) complexes on the phosphorus $[R_2PyP][W(CO)_5]$ and their structures were confirmed by X-ray crystallography. No ligation of the 2-pyridyl groups was found but a considerable p-donating effect of the dimethylamino groups in $(Me_2N)_2PyP$ was observed. The monocoordinated complexes were irradiated with light to afford the chelate complexes $[R_2PyP][W(CO)_4]$ by loss of one CO from the pentacarbonyls. X-ray structural analysis and spectroscopic data of $[R_2PyP][W(CO)_4]$ indicated that the electron-donating effect of the nitrogen atom in the 2-pyridyl group upon the carbonyls is slightly larger than that of the phosphorus atom in spite of the reluctant coordination at the early stage of ligation.
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Keywords: 2-Pyridylphosphines; Tungsten; Coordination; X-ray crystallography

1. Introduction

Diphenyl(2-pyridyl)phosphine (**1**) has been used for ligands of metal complexes analogously to triphenylphosphine [1]. Basically **1** behaves as a phosphorus-monodentate ligand for transition metal complexes and indeed more than one equivalent of **1** coordinate on one metal even if **1** possesses competitive coordinating sites at P and N [1,2]. Compound **1**, however, may act as a chelating ligand to afford the four-membered ring structure [3], but the studies on conversion of the coordination mode from monodentate to chelate have been limited so far [4]. In addition to triarylphosphines, such phosphines as bis(dimethylamino)phenylphosphine bearing amino group(s) are expected to display some unique properties due to the effect of additional nitrogen-containing moieties [5] and may be utilized for
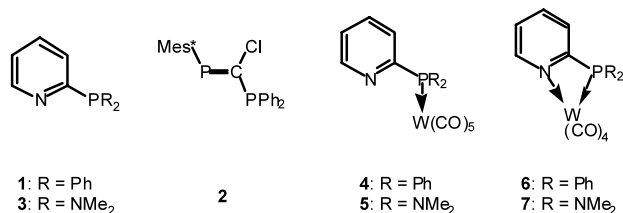
preparation of synthetic catalysts [6]. Thus, diamino(pyridyl)phosphines are attractive, but the derivatives have not been reported so far.

We have previously reported coordination properties of 2-chloro-3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphapropene (**2**) which possesses low-coordinated sp^2 phosphorus atom and a normal sp^3-phosphino phosphorus atom within a molecule and is considered to be a congener of **1** [7]. Both of the monodentate and chelate coordinations of **2** on the tungsten metal were found indicating the stepwise coordinating nature due to the difference of basicity of the two different phosphorus atoms. Moreover, we have recently reported a 3,3-diamino-1,3-diphosphapropene to utilize it for novel low-coordinated phosphorus compounds.[8]

Here we report structural elucidation of a monodentate tungsten(0) complex of **1** and conversion to the corresponding chelate derivative. Moreover, we report a complex formation reaction of bis(dimethylamino)(2-pyridyl)phosphine (**3**) with a carbonyltungsten(0) reagent.

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Table 1
Bond lengths (Å) and bond angles (°) around the tungsten metal for compounds **4**–**7**

	4	**5**	**6**	**7**
W–P	2.529(2)	2.540(1)	2.543(2)	2.507(2)
W–N	–	–	2.256(5)	2.273(7)
W–C1	2.053(8)	2.057(5)	1.947(7)	1.94(1)
W–C2	2.034(8)	2.049(6)	1.985(8)	1.99(1)
W–C3	2.061(9)	2.059(6)	2.049(8)	2.03(1)
W–C4	2.071(8)	2.049(6)	2.049(8)	2.05(1)
W–C5	2.016(8)	1.997(5)	–	–
C1–O	1.11(1)	1.121(6)	1.160(8)	1.17(2)
C2–O	1.15(1)	1.131(7)	1.137(10)	1.13(1)
C3–O	1.12(1)	1.119(6)	1.126(9)	1.11(1)
C4–O	1.09(1)	1.134(6)	1.126(9)	1.10(2)
C5–O	1.129(9)	1.145(6)	–	–
P–Py	1.840(7)	1.837(5)	1.831(6)	1.840(9)
P–R	1.838(6)	1.671(4)	1.823(5)	1.636(9)
	1.821(6)	1.682(4)	1.823(5)	1.689(7)
C–N(Py)	1.408(9)	1.339(6)	1.338(10)	1.35(1)
W–P–C	111.5(2)	107.6(1)	83.7(3)	84.8(3)
P–W–N	–	–	63.2(1)	63.6(2)
W–N–C	–	–	108.6(4)	107.7(5)
P–C–N	114.0(5)	114.8(3)	104.6(5)	103.8(6)
R–P–Py	103.2(3)	102.0(2)	108.1(2)	109.7(4)
	102.6(3)	100.7(2)	108.1(2)	102.0(4)
R–P–R	102.5(3)	113.0(2)	104.8(3)	102.0(5)

2. Results and discussion

2.1. Preparation and characterization of monodentate tungsten(0) complexes

Complex **4** was prepared from **1** and W(CO)$_5$(thf) as a pale yellow solid almost quantitatively. The most spectroscopic data of **4** were identical with the reported data by Zhang et al. [9].[1] The molecular structure was unambiguously characterized by X-ray crystallography and an ORTEP drawing is displayed in Fig. 1 [10]. As displayed in Table 1, the P–W distance is shorter compared with the corresponding values in [Ph$_3$P][W(CO)$_5$] (2.545(1) Å) [11] or [Mes*P = C(Cl)PPh$_2$][W(CO)$_5$] (2.540(1) Å) [7], probably due to the greater π-accepting ability of **3** rather than that of triphenylphosphine as well as **2**. On the other hand, the W–C$_{ax}$ (W–C5) distance in **4** is slightly longer than that in [Ph$_3$P][W(CO)$_5$] (2.006(5) Å) [11] as well as [2][W(CO)$_5$] (1.996(4) Å) [7], which corresponds to the C–O$_{ax}$ (C5–O) distances: [Ph$_3$P][W(CO)$_5$]: 1.125(6) Å [2]; [W(CO)$_5$]: 1.156(5) Å. The average W–C$_{eq}$ and the C–O$_{eq}$ distances in **4** are 2.06(1) Å and 1.1(1) Å,

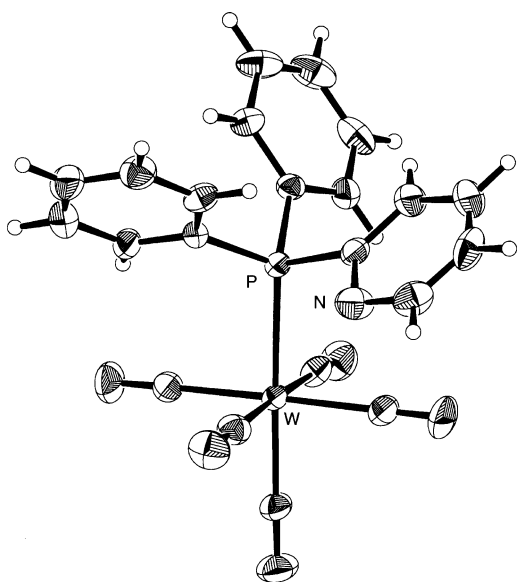Fig. 1. Molecular structure of **4** with 30% probability ellipsoids.

respectively, which are comparable to the corresponding data of [Ph$_3$P][W(CO)$_5$] (2.033(5), 1.135(6) Å) [11]. The distance between the nitrogen atom and the tungsten metal in **4** is 3.86 Å, indicating that there is no bonding nature, and moreover the torsion angle of N–C1–P–W was 54.8(6)°.

Similarly diamino(pyridyl)phosphine (**3**), prepared from the reaction of 2-bromopyridine with butyllithium and then with chlorobis(dimethylamino)phosphine [12],[2] was allowed to react with W(CO)$_5$(thf) to afford the corresponding complex **5**. Complex **5** was stable in the air and purified by column chromatography on silica gel. Molecular structure of **5** is described in Fig. 2. The phosphorus atom solely coordinates on the tungsten metal and is less pyramidalized judging from the sum of the angles of 316°, compared with that of **4** (308°), probably due to the p-donating effect of the nitrogen atoms.

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[1] The J_{PW} value in this article was described as the half value.

[2] Compound **3** was allowed to react with four equivalents of HCl to afford 2-pyridylphosphonous dichloride (PyPCl$_2$: δ_P 139) and was converted to 2-pyridylphosphine (PyPH$_2$) by reduction with LiAlH$_4$.
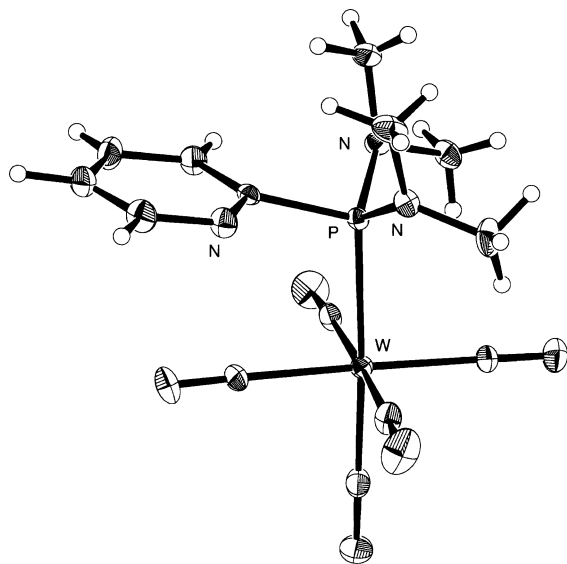
Fig. 2. Molecular structure of **5** with 30% probability ellipsoids.

Some selected ^{13}C-NMR data for **4** and **5** are listed in Table 2. There are observed almost the same chemical shifts as well as the coupling constants J_{PC} found in the CO ligands and the 2-pyridyl groups. The typical σ coordination on the metal was indicated from the ^{31}P-NMR data including the $^{1}J_{PW}$ satellite peaks and the IR data also supported this ligating mode in **4** and **5** (Table 3).

2.2. Chelate carbonyltungsten(0) complexes

The monodentate complex **4** in THF was irradiated with a mercury lamp (100 W) at 0 °C and the color of the solution turned red from pale yellow. After the solvent having been removed in vacuo, the residue was purified by silica-gel column chromatography to afford the chelate complex **6** almost quantitatively. The structure of **6** was confirmed by X-ray crystallography and Fig. 3 displays its molecular structure. The four-membered chelate ring is planar. The W–C1 bond is shorter than the W–C2 distance, indicating that the electron-donating effect of the nitrogen atom in the pyridyl group upon the CO group is larger than that of the phosphino group. On the other hand, in the reaction of **1** with $W(CO)_5$(thf), the nitrogen atom in the 2-pyridyl group might first permit the phosphorus atom to ligate the metal. The angle P–C–N is 104.6(5)° indicating a large deformation due to the formation of the four-membered ring. Similarly chelate complex **7** was obtained from **5** and its molecular structure is shown in Fig. 4.

In the ^{13}C-NMR spectoroscopy of **6** and **7**, the large $^{2}J_{PC}$ values were observed for the CO_{eq} carbon atom at the trans position to the phosphorus atom, respectively (Table 2). Almost the same ^{13}C-NMR spectroscopic properties were clarified for both **6** and **7** as well as $[Ph_3P][Py][W(CO)_4]$ [2]. The ^{31}P-NMR signals of **6** and **7** were observed at a higher field compared to **4** and **5**, respectively (Table 3). The IR spectroscopic patterns of

Table 2
Selected ^{13}C-NMR data (δ_C and J_{PC}) [a] for compounds **4**–**7**

	4		**5**		**6**		**7**	
	δ_C	J_{PC}/HZ	δ_C	J_{PC}/HZ	δ_C	J_{PC}/HZ	δ_C	J_{PC}/HZ
CO_{ax}	200.3	22.7	200.5	26.5	206.5	6.5	207.2	7.9
CO_{eq}	197.8	7.1	197.7	8.0	212.8	6.6	213.6	7.3
CO_{eq}	–	–	–	–	212.3 [b]	30.1	212.7 [b]	35.2
C2	160.3	65.9	162.1	85.0	169.2	46.2	173.0	52.1
C3	127.3	18.2	125.9	19.0	128.3	0 [c]	124.8	2.8
C4	136.5	5.9	136.1	6.6	137.0	0 [c]	136.1	0 [c]
C5	124.0	0 [c]	125.0	0 [c]	127.7	0 [c]	127.2	0 [c]
C6	150.5	17.5	150.4	16.9	153.0	21.5	152.9	25.1

[a] Measured at 101 MHz, in CD_2Cl_2.
[b] CO trans to the atom.
[c] Appeared as a singlet.

Table 3
^{31}P-NMR data (δ_P and $^1J_{PW}$) [a] and IR data (v_{CO}) [b] for compounds **4**–**7**

4			5			6			7		
δ_P	$^1J_{PW}$ (Hz)	v_{CO} (cm^{-1})	δ_P	$^1J_{PW}$ (Hz)	v_{CO} (cm^{-1})	δ_P	$^1J_{PW}$ (Hz)	v_{CO} (cm^{-1})	δ_P	$^1J_{PW}$ (Hz)	v_{CO} (cm^{-1})
25	245	2050 [c]	111	289	2071	−11	196	2017	85	245	2002
		1980 [c]			1936			1890			1890
		1920 [c]			1920			1870			1871
								1826			1840

[a] Measured at 162 MHz in CD$_2$Cl$_2$.
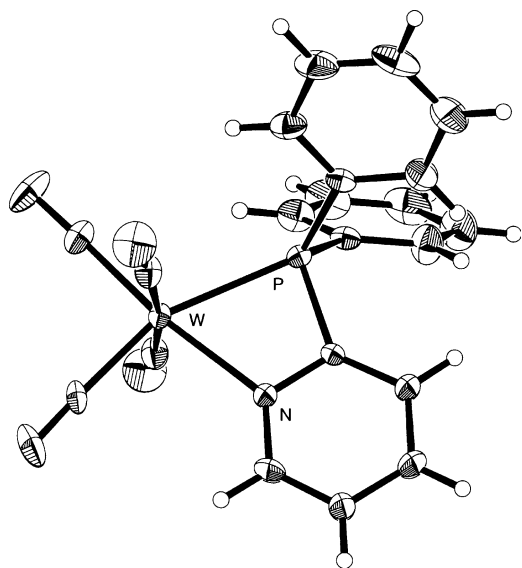[b] Measured as a KBr pellet.
[c] Data taken from Ref. [9].

Fig. 3. Molecular structure of **6** with 30% probability ellipsoids.
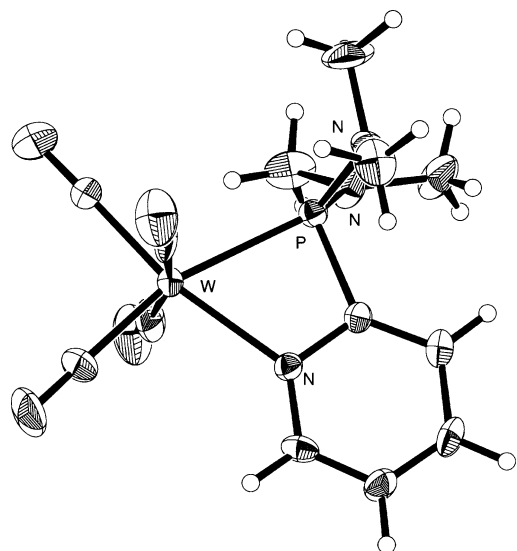

Fig. 4. Molecular structure of **7** with 30% probability ellipsoids.

the chelate complexes, **6** and **7**, changed from those of the monodentate derivatives.

3. Conclusion

We described preparation and characterization of monodentate carbonyltungsten(0) complexes of 2-pyridylphosphines revealing that the phosphorus atom solely coordinated on the metal. These monodentate complexes were converted to the chelate derivatives by irradiation of light. Electronic properties of substituents, 2-pyridyl and dimethylamino groups, were characterized. This study will prompt further investigation concerning coordination chemistry as well as development of synthetic catalysts. Attempts to replace the carbonyl groups in **4**–**7** with other ligand such as isocyanides to afford novel transition metal complexes are in progress.

4. Experimental

4.1. General

All manipulations were carried out under an argon atmosphere by means of the standard Schlenk techniques or in a glove box. All solvents employed were dried by appropriate methods. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker AVANCE400 spectrometer in CDCl$_3$ with Me$_4$Si (^{1}H, ^{13}C) and H$_3$PO$_4$ (^{31}P), respectively, as internal or external standard. IR spectra were measured on a Horiba FT-300 spectrometer as KBr pellets. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Elemental analyses were performed in the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. MARDI-TOF Mass spectra were recorded on a Bruker autoflex spectrometer. Compound **1** was prepared by the procedures described in the literature [13].

4.2. Preparation of 3

Butyllithium (1.0 mmol, 1.6 M solution in hexane, 1 M = 1 mol dm^{-3}) was added to a solution of 2-bromopyridine (0.16 g, 1.0 mmol) in THF (20 ml) at -78 °C and was followed by the addition of chlorobis(dimethylamino)phosphine (1.0 mmol). The reaction mixture was warmed to room temperature (r.t.) and stirred for 2 h. The solvent was removed in vacuo and the residue was purified by silica-gel column chromatography (hexane) to afford PyP(NMe$_2$)$_2$ as a colorless oil containing a small amount of the starting 2-bromopyridine; ^{31}P{^{1}H}-NMR (162 MHz, CD$_2$Cl$_2$) δ 99. The crude material **3** was employed for the preparation of **5**.

4.3. Preparation of 5

A THF solution of the crude PyP(NMe$_2$)$_2$, prepared by the procedure described in Section 4.2, was stirred for 24 h with an excess amount of W(CO)$_5$(thf) (prepared from W(CO)$_6$ in THF by irradiation for 12 h with a medium-pressure 100 W Hg lamp at 0 °C). Purification by column chromatography (hexane–AcOEt, 19:1) gave [PyP(NMe$_2$)$_2$][W(CO)$_5$] (94 mg, 18% yield based on 2-bromopyridine). Compound **5**: yellow crystals, m.p. 87–89 °C; ^{13}C{^{1}H}-NMR (101 MHz, CD$_2$Cl$_2$) δ 41.0 (d, $^{2}J_{PC}$ 4.2 Hz, NMe$_2$). ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 2.84 (d, $^{3}J_{PH}$ 10.8 Hz, NMe$_2$). Anal. Found: C, 31.84; H, 3.81; N, 6.23. Calc. for C$_{14}$H$_{16}$N$_3$O$_5$PW: C, 32.27; H, 3.09; N, 8.06%. HRMS (MARDI-TOF-MS) Found: 493.105. Calc. for C$_{14}$H$_{16}$N$_3$O$_5$PW–CO: 493.039.

4.4. Preparation of 6 and 7

A THF (0.4 ml) solution of **4** (25 mg, 0.043 mmol) was irradiated with a medium-pressure 100 W Hg lamp at 0 °C for 30 h. The solvent was removed in vacuo and the residue was purified by silica-gel column chromatography (hexane–AcOEt, 4:1) to afford 17 mg of **6** (70% yield). Compound **6**: yellow crystals, m.p. 183–185 °C; ^{13}C{^{1}H}-NMR (101 MHz, CD$_2$Cl$_2$) δ 133.6 (d, $^{2}J_{PC}$ 14.2 Hz, *o*-Ph), 131.7 (s, *p*-Ph), 130.3 (d, $^{2}J_{PC}$ 37.7 Hz, *ipso*-Ph), 129.5 (d, $^{3}J_{PC}$ 10.4 Hz, *m*-Ph), 128.0). Anal. Found: C, 46.57; H, 3.79; N, 2.28. Calc. for C$_{21}$H$_{14}$NO$_4$PW: C, 45.11; H, 2.52; N, 2.50%. HRMS (MARDI-TOF-MS) Found: 559.031. Calc. for C$_{14}$H$_{16}$N$_3$O$_5$PW: 559.017. Similarly **5** (25 mg, 0.048 mmol) was irradiated in THF (0.4 ml) for 24 h at 0 °C to afford 16 mg of **7** (68% yield). Compound **7**: yellow crystals, m.p. 164–166 °C; ^{13}C{^{1}H}-NMR (101 MHz, CD$_2$Cl$_2$) δ 39.3 (d, $^{2}J_{PC}$ 9.6 Hz, NMe$_2$); ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 2.75 (d, $^{3}J_{PH}$ 10.9 Hz, NMe$_2$). Anal. Found: C, 31.57; H, 3.39; N, 8.14. Calc. for C$_{13}$H$_{16}$N$_3$O$_4$PW: C, 31.66; H, 3.27; N, 8.52%.

4.5. X-ray crystallography

X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer. The structure was solved by direct methods (SIR-92) [14], expanded using Fourier techniques (DIRDIF-94) [15]. A symmetry-related absorption correction using the program AB-SCOR [16] was applied. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found by the difference Fourier synthesis for **4**–**6** but for **7** the hydrogen atoms were generated at the calculated positions. They were refined isotropically for **5** but not refined for **4**, **6** and **7**. Structure solution, refinement, and graphical representation were carried out using the TEXSAN package [17].

Compound **4**: C$_{22}$H$_{14}$NO$_5$PW, $M = 587.18$, triclinic, $P\bar{1}$ (no. 2), $a = 9.6201(8)$, $b = 12.196(1)$, $c = 9.455(1)$ Å, $\alpha = 90.625(3)$, $\beta = 95.370(5)$, $\gamma = 74.655(2)$°, $V = 1064.9(2)$ Å^3, $Z = 2$, $2\theta_{max} = 55.0$°, $T = 296$ K, $\rho = 1.831$ g cm^{-1}, $\mu = 5.538$ mm^{-1}, $F(000) = 564.00$, 8535 collected reflections, 4455 unique reflections ($R_{int} = 0.095$), $R_1 = 0.041$ ($I > 2\sigma(I)$), $R_w = 0.063$ (all data), $S = 1.42$ (271 parameters).

Compound **5**: C$_{14}$H$_{16}$N$_3$O$_5$PW, $M = 521.12$, monoclinic, $P2_1/n$ (no. 14), $a = 7.2042(5)$, $b = 16.6954(7)$, $c = 15.3474(6)$ Å, $\beta = 96.874(2)$°, $V = 1832.7(2)$ Å^3, $Z = 4$, $2\theta_{max} = 55.0$°, $T = 223$ K, $\rho = 1.889$ g cm^{-1}, $\mu = 6.425$ mm^{-1}, $F(000) = 1000.00$, 8457 collected reflections, 4163 unique reflections ($R_{int} = 0.088$), $R_1 = 0.031$ ($I > 2\sigma(I)$), $R_w = 0.044$ (all data), $S = 0.94$ (281 parameters).

Compound **6**: C$_{21}$H$_{14}$NO$_4$PW, $M = 559.17$, orthorhombic, *Pnma* (no. 62), $a = 16.7705(4)$, $b = 12.6363(5)$, $c = 9.4942(4)$ Å, $V = 2012.0(1)$ Å^3, $Z = 4$, $2\theta_{max} = 55.0$°, $T = 296$ K, $\rho = 1.846$ g cm^{-1}, $\mu = 5.854$ mm^{-1}, $F(000) = 1072.00$, 16 369 collected reflections, 2384 unique reflections ($R_{int} = 0.084$), $R_1 = 0.030$ ($I > 2\sigma(I)$), $R_w = 0.044$ (all data), $S = 0.91$ (145 parameters).

Compound **7**: C$_{13}$H$_{16}$N$_3$O$_4$PW, $M = 493.11$, triclinic, $P\bar{1}$ (no. 2), $a = 8.576(1)$, $b = 15.399(2)$, $c = 7.0926(6)$ Å, $\alpha = 97.282(9)$, $\beta = 108.758(9)$, $\gamma = 101.364(3)$°, $V = 851.1(2)$ Å^3, $Z = 2$, $2\theta_{max} = 55.0$°, $T = 296$ K, $\rho = 1.924$ g cm^{-1}, $\mu = 6.907$ mm^{-1}, $F(000) = 472.00$, 6523 collected reflections, 3478 unique reflections ($R_{int} = 0.150$), $R_1 = 0.055$ ($I > 2\sigma(I)$), $R_w = 0.088$ (all data), $S = 1.31$ (199 parameters).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 210859, 210860, 210858 and 210857 for compounds **4**, **5**, **6** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336066; e-mail:

deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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