1776 Bull. Chem. Soc. Jpn. Vol. 80, No. 9, 1776–1779 (2007)

Solid-State Structures of *trans*-[$RuCl_2\{Cl_2PN(Me)N(Me)PCl_2\}_2$] and *cis*-[$MCl_2\{Cl_2PN(Me)N(Me)PCl_2\}$] (M = Pt^{II} and Pd^{II}) Studied by X-ray Crystallography and ^{13}C CPMAS NMR Spectroscopy

Satoshi Takara,[*1,†] **Andrei S. Batsanov,**[2] **Douglas J. Schaffer,**[1] **Michael Takase,**[1] **Janice A. Kunishige,**[1] **and Susan J. Lee**[1]

[1]Department of Chemistry, University of Hawai‘i at Mānoa, Honolulu, HI 96822, U.S.A.

[2]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

Received January 23, 2007; E-mail: stakara@sci.u-ryukyu.ac.jp

Solid-state structures of *trans*-[$RuCl_2\{Cl_2PN(Me)N(Me)PCl_2\}_2$] (**1**), *cis*-[$PdCl_2\{Cl_2PN(Me)N(Me)PCl_2\}$] (**2**), and *cis*-[$PtCl_2\{Cl_2PN(Me)N(Me)PCl_2\}$] (**3**) were studied by using ^{13}C CPMAS NMR spectroscopy and X-ray crystallography. The ruthenium atom in **1** was on a crystallographic inversion center and had a slightly distorted octahedral coordination. **2** and **3** contained palladium and platinum atoms in a square-planar geometry, respectively. In **2**, axial sites of the Pd atom were filled by intermolecular Pd···Cl contacts to form an infinite chain. Molecules of **3** pack in an edge-to-face manner and no obvious "axial" contacts at the Pt atom were observed. Different geometries of hydrazide nitrogens in **1**, **2**, and **3** were observed: in **1** and **2**, one of the nitrogen atoms was trigonal planar and the other one was pyramidal; the two hydrazine nitrogen atoms in **3** had trigonal planar geometry. ^{13}C CPMAS NMR spectra are consistent with X-ray data. The P–N distances are shorter than normally accepted P–N single bond lengths, suggesting a degree of P–N π bonding.

The development of a new class of chelating bis(phosphines) is fundamentally interesting. Compared to the vast studies using diphosphinoamines and bisphosphines containing carbon backbones such as dppe, only a few works have exploited the dinitrogen-bridged diphosphine ligands ($X_2PN(R)N(R)PX_2$) in transition-metal chemistry,[1–9] despite the fact that these ligands have been readily available since Katti and Reddy discovered 1,2-bis(dichlorophosphino)-1,2-dimethylhydrazine, $Cl_2PN(Me)N(Me)PCl_2$ (=ClPNNP) (Fig. 1), which have weak σ-donor and strong π-acceptor characteristics.[1–4] It has been reported that such characteristics improve selectivity in some catalysis. It is of particular significance to develop the chemistry of bis(phosphanyl)hydrazines in catalytic systems due to their structural similarity with 1,2-diphosphinoethane ($R_2PCH_2CH_2PR_2$) ligands. A search of the Cambridge Structural Database has yielded 14 transition-metal complexes containing $X_2PN(R)N(R)PX_2$ ligands (all with X = aryl or aryloxy)[1–9] and no uncoordinated molecules of this type. No bis(dihalophosphine)hydrazine derivatives of any kind have been found.

Herein, we report solid-state structures of *trans*-[$RuCl_2(ClPNNP)_2$] (**1**), *cis*-[$PdCl_2(ClPNNP)$] (**2**), and *cis*-[$PtCl_2(ClPNNP)$] (**3**) characterized by X-ray and ^{13}C CPMAS NMR studies. These are, to the best of our knowledge, the first X-ray structures of the transition-metal complexes of the ClPNNP ligand.

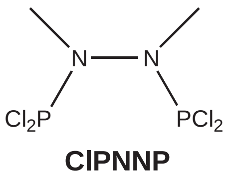

Fig. 1. Molecular structure of $Cl_2PN(Me)N(Me)PCl_2$.

Results and Discussion

The synthesis of **1** proceeds by mixing the ligand, ClPNNP, and [$RuCl_2(PPh_3)_3$] in toluene in high yield at room temperature. $^{31}P\{^1H\}$ NMR showed that the Cl atoms *trans* to each other, because only one singlet was observed at δ 172.5, consistent with four equivalent phosphorus nuclei. The chemical shift appeared at a much lower chemical shift than that of analogous compound *trans*-[$RuCl_2\{Ph_2PN(Me)N(Me)PPh_2\}_2$] ($\delta$ 123.3) due to the electron-withdrawing Cl substituents on the phosphorus atoms. In molecule **1** (Fig. 2), the Ru atom was on a crystallographic inversion center and had a slightly distorted octahedral coordination geometry (Table 1). The Ru–P bond distances are similar to those in the isoelectronic octahedral complex *trans*-[$RuHCl\{Ph_2PN(Me)N(Me)PPh_2\}_2$] (2.294–2.314 Å),[7] shorter than in the *trans*-[$RuCl(CO)\{Ph_2PN(Me)N(Me)PPh_2\}_2$]$^+$ cation (2.380–2.396 Å)[8] and longer than in [$LRuCl\{(PhO)_2PN(Me)N(Me)P(OPh)_2\}$] (where L = Cp or Cp*) (2.191–2.221 Å).[6] Both the Ru–P and Ru–Cl distances in **1** are shorter than in *trans*-[$RuCl_2(dppe)_2$] (Ru–P 2.35–2.40 Å, Ru–Cl 2.41–2.44 Å) in various pseudo-polymorphs,[10–12] indicating stronger back-donation. Intermolecular distances agree

---

[†] Present address: Department of Chemistry, Biology and Marine Science, Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213

Published on the web September 13, 2007; doi:10.1246/bcsj.80.1776

with van der Waals radii, except for a relatively short contact Cl(1)···Cl(2) ($-x$, $1-y$, $1-z$) of 3.28 Å.

Katti and Reddy have reported the syntheses and characterization by using elemental analysis, ^{1}H and ^{31}P NMR of complexes **2** and **3**. However, their molecular structures were yet to be confirmed by X-ray crystallography. We found that molecules **2** and **3** (Fig. 3) had no crystallographic symmetry. The bond distances agree well with those in previously reported complexes of the form $[MCl_2\{(RO)_2N(R')N(R')P(OR)_2\}]$ (where M = Pd, Pt; R = Ph, *o*-C_6H_4OMe, *o*-$C_6H_4CH_2CH{=}CH_2$; R′ = Me, Et).[2,3,9] The square-planar coordination of the metal atom is distorted due to the narrow bite of the chelate ligand (P–M–P $< 90°$) and by deviation from planarity, which was slight in **3** but substantial in **2** (see Table 1). The dihedral angle between the MP_2 and MCl_2 planes was 11° in **2** and 2° in **3**. The difference is possibly due to crystal-packing arrangements. In **2**, axial sites of the Pd atom were filled by intermolecular Pd···Cl contacts of ca. 3.68 and 3.44 Å (Fig. 4), which connect molecules into an infinite chain (parallel to the *z* axis). Within the chain, the Pd···Pd distances alternated between 4.53 and 5.50 Å, whereas the coordination planes of all Pd atoms were parallel. Molecules of **3** packed in an edge-to-face (herringbone) manner (Fig. 5) with the PtP_2Cl_2 planes of adjacent molecules forming an angle of 83°. There were no obvious "axial" contacts at the Pt atom, and both the intermolecular Cl···Cl contacts (the shortest being 3.40 Å, all others being >3.5 Å) and Pt···Cl distances (the shortest being 4.08 Å) are much longer than the corresponding distances in **2**. Interestingly, this does not result in a lower packing density of **3** (Fig. 5). In fact, the latter has a smaller (by 1%) volume per molecule at 200 K than that of **2** at 120 K, although the intramolecular dimensions of **2** and **3** are practically identical. On cooling, crystalline **3** underwent a phase transition between 200 and 190 K, accompanied by twinning and usually by

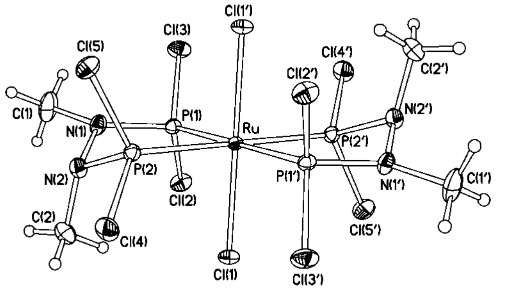

Fig. 2. Molecular structure of **1**. Primed atoms are generated by the inversion centre. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Angles (°)

	1	2	3
M–P(1)	2.2905(4)	2.1839(4)	2.175(2)
M–P(2)	2.2872(4)	2.2170(5)	2.173(2)
M–Cl(1)	2.3933(3)	2.3311(5)	2.324(3)
M–Cl(2)	—	2.3459(4)	2.325(2)
P(1)–N(1)	1.675(1)	1.686(1)	1.661(8)
P(2)–N(2)	1.706(1)	1.660(1)	1.655(11)
N(1)–N(2)	1.438(2)	1.430(2)	1.465(14)
P–Cl, av.	2.023[13]	1.996[11]	1.996[11]
P(1)–M–P(2)	80.17(1)	82.45(2)	84.16(9)
Cl(1)–M–P(1)	90.71(1)	89.65(2)	92.23(9)
Cl(1)–M–P(2)	93.89(2)	166.85(2)	176.12(9)
Cl(2)–M–P(1)	—	173.71(1)	175.32(10)
Cl(2)–M–P(1)	—	92.27(2)	91.38(9)
Cl(1)–M–Cl(2)	—	96.16(2)	92.26(10)
Σ of X–N(1)–Y	355.5(2)	342.3(2)	344(1)
Σ of X–N(2)–Y	341.1(2)	359.9(2)	346(1)
Deviations of atoms from MP_2 plane/Å			
N(1), N(2)	0.13, −0.55	−0.55, −0.01	−0.33, 0.23
Cl(1), Cl(2)	—	0.43, −0.14	0.06, −0.06

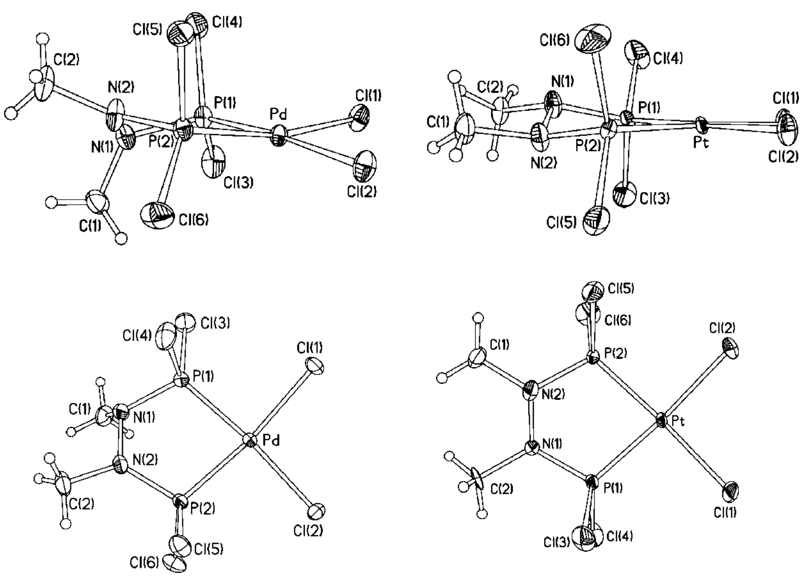

Fig. 3. Molecular structures of **2** (left, top and bottom) and **3** (right, top and bottom). Thermal ellipsoids are drawn at the 50% probability level.

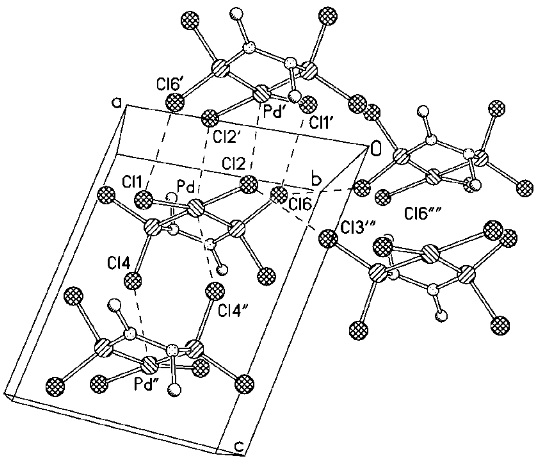

Fig. 4. Crystal packing of **2**. Symmetry operations: (i) $1-x$, $1-y$, $-z$; (ii) $1-x$, $1-y$, $1-z$; (iii) $x-1$, y, z; (iv) $-x$, $2-y$, $-z$. Short intermolecular contacts (Å): Pd···Cl(2^{i}) 3.68, Pd···Cl(4^{ii}) 3.44, Cl(1)···Cl(6^{i}) 3.35, Cl(2)···Cl(3^{iii}) 3.16, Cl(6)···Cl(6^{iv}) 2.34.

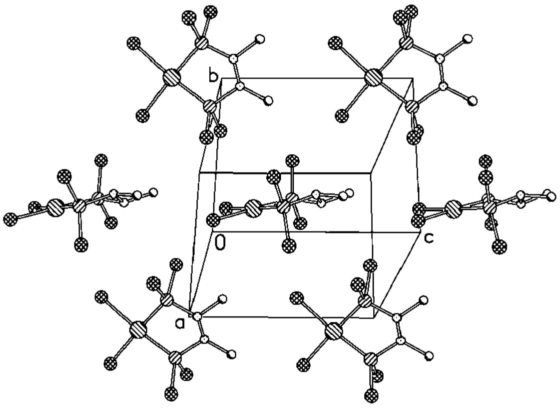

Fig. 5. Crystal packing of **3**.

cracking of the crystals. We did not manage to deconvolute the diffraction pattern of the low-temperature phase.

The chelate ring in **2** adopted an envelope conformation with the N(2) tilting out of the plane of the other four atoms (see Table 1). Compound **1** had an intermediate geometry between the envelope and the twisted conformation; the nitrogen atoms were tilted to opposite sides of the MP$_2$ plane by unequal distances, whereas the geometry of **3** was closer to the symmetrical twisted conformation. In each case, the more out-of-plane nitrogen atom had a more pyramidal geometry (see the sums of bond angles in Table 1, cf. 360° for planar trigonal and 328.5° for tetrahedral geometry) and formed a longer P–N bond. In the ^{13}C CPMAS NMR spectra (Fig. 6), two singlets at δ 39.0 and 35.0 for **1**; two singlets at δ 41.7 and 35.5 for **2** were observed, whereas one singlet at δ 36.6, attributed to the methyl carbon, was observed for **3**, which is consistent with X-ray structures.

In any case, the P–N bonds in **1**–**3**, as in previously studied analogues with aryl or aryloxy substituents at the phosphorus atoms, are shorter than typical single bonds (1.75 to 1.80 Å).[9] These observations indicate a degree of pπ–dπ interaction between nitrogen and phosphorus atoms (Fig. 7).

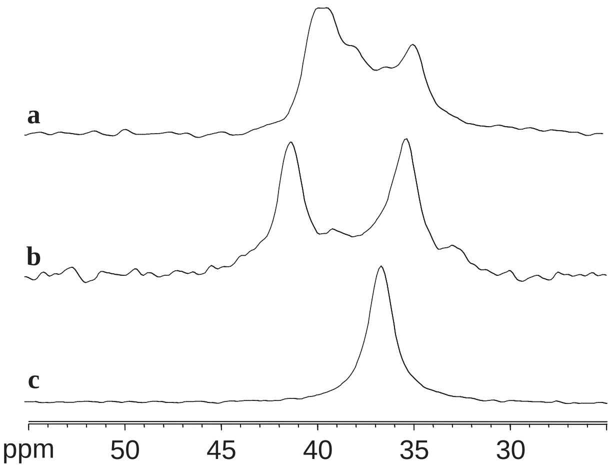

Fig. 6. ^{13}C CPMAS NMR spectra at rt of (a) **1**, (a) **2**, and (b) **3**.

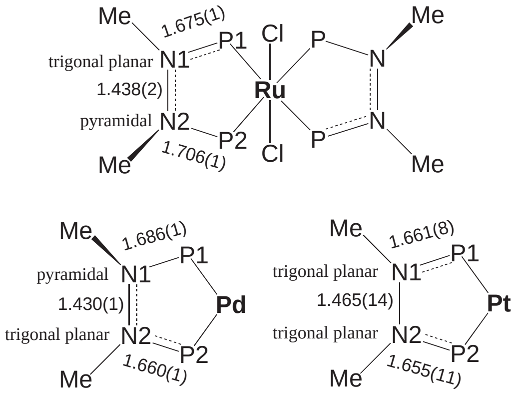

Fig. 7. The bonding in **1**, **2**, and **3**.

Experimental

Materials and Methods. The manipulations described below were performed under argon with rigorous exclusion of air and moisture in a glovebox (Innovative Technology, Inc.). The ligand, Cl$_2$PN(Me)N(Me)PCl$_2$, and [RuCl$_2$(PPh$_3$)$_3$] were purchased from Strem and used without further purification. All other chemicals used were purchased from Aldrich and purified accordingly. CDCl$_3$ was purchased from Cambridge Isotope Laboratories and degassed by using a freeze–pump–thaw method and dried over 4A molecular sieves. Toluene, dichloromethane, diethyl ether, and hexane were purchased from Fisher Scientific and were degassed and dried over columns containing copper catalysts and alumina. **2** and **3** were prepared according to the literature.[1]

Synthesis of *trans*-[RuCl$_2${Cl$_2$PN(Me)N(Me)PCl$_2$}$_2$] (1). A mixture of [RuCl$_2$(PPh$_3$)$_3$] (500 mg, 0.52 mmol) and Cl$_2$PN(Me)N(Me)PCl$_2$ (270 mg, 1.04 mmol) dissolved in toluene (10 mL) was stirred for 8 h under an inert atmosphere, during which time a yellow precipitate formed. The yellow powder was collected on a frit, washed with toluene and ether, and dried in vacuo. Yield: 295 mg (80%) The single crystals (yellow hexagonal plate, $0.51 \times 0.45 \times 0.26$ mm^3) were obtained from CH$_2$Cl$_2$/hexane at room temperature. ^{1}H NMR (CDCl$_3$): δ 3.34 (q, 12H, NCH_3). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 172.5 (s). Anal. Calcd for **1** (C$_4$H$_{12}$Cl$_{10}$N$_4$P$_4$Ru): C, 6.91; H, 1.74; N, 8.05%. Found: C, 7.12; H, 1.85; N, 7.22%.

NMR Spectroscopy. ^{1}H and ^{31}P NMR spectra for **1**, **2**, and **3** were recorded as saturated $CDCl_3$ solutions at room temperature on a Bruker 300 MHz spectrometer. ^{1}H and ^{31}P NMR were performed at 299.8 and 121.4 MHz, respectively. ^{1}H NMR spectra were referenced to the residual $CHCl_3$ proton signal (δ 7.26). ^{31}P NMR spectra were measured using 85% H_3PO_4 as an external standard. Chemical shifts are reported in parts per million. ^{13}C CPMAS NMR data were acquired on a Varian Unity Inova WB 400 spectrometer, equipped with a 4-mm double resonance MAS probe (Chemagnetics, Fort Collins, CO). 4-mm rotors (Varian Instruments, Palo Alto, CA) were packed with 100–150 mg of sample and restricted to the center part of the rotor with Kel-F spacers (sample volume 80 µL). CPMAS was preformed at 8 kHz spinning speed using a CP contact time of 2 ms with ^{1}H and ^{13}C power levels (B1 field strength) at 50 kHz. ^{1}H decoupling was done at a power level of 75 kHz. Spectral widths were 45 kHz acquired in 2 K data points. Spectra were processed using FT and a line broadening factor of 50 Hz.

Crystallographic Studies. X-ray diffraction experiments were carried out on Bruker 3-circle diffractometers equipped with CCD area detectors (SMART 6 K for **1** and **3** and APEX ProteumM for **2**), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from a sealed-tube X-ray source (**1** and **3**) or a 60 W microfocus Bede Microsource® with glass polycapillary optics (**2**). The crystals were sealed in thin-walled Lindemann capillary tubes and cooled using a Cryostream (Oxford Cryosystems) open-flow N_2 cryostat. A full sphere of reciprocal space was covered by three (**1**) or four (**2** and **3**) runs of narrow frame (0.3°) ω scans, and each run had a different φ angle. Reflection intensities of **1** were corrected for absorption by applying numerical integration based on crystal face indexing, and of **2** and **3** by using a semi-empirical method based on multiple scans and Laue equivalents.[13] The structures were solved by a combination of Patterson and direct methods and refined by full-matrix least squares against F^2 of all data using SHELXTL software.[14] The polarity of structure **3** was determined from anomalous scattering, and the Flack parameter[15] converged at 0.010(9). Crystal data and other experimental details are listed in Table 2. Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data, CCDC-252666 for **1**, -633442 for **2** and -633443 for **3**. Copies of data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crsytallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

The authors extend their Mahalo to Prof. Todd B. Marder (Department of Chemistry, University of Durham), Mr. Wesley Yoshida and Dr. Walter Niemczura (NMR facility, Department of Chemistry, University of Hawai‘i at Mānoa) for their Kōkua. University of Hawai‘i is gratefully acknowledged for financial support.

Table 2. Details of X-ray Data Collection and Refinement

	1	**2**	**3**
Formula	$C_4H_{12}Cl_{10}N_4P_4Ru$	$C_2H_6Cl_6N_2P_2Pd$	$C_2H_6Cl_6N_2P_2Pt$
Formula weight	695.63	439.13	542.66
T/K	120	120	200
Symmetry	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)	Pn (# 7[a])
a/Å	8.250(1)	8.3560(8)	8.1170(8)
b/Å	8.385(1)	8.8310(8)	8.7525(8)
c/Å	8.913(1)	9.9587(9)	9.1599(8)
α/°	74.01(1)	88.48(1)	90
β/°	78.85(1)	83.24(1)	102.42(1)
γ/°	66.32(1)	61.85(1)	90
V/Å^3	540.4(1)	643.1(2)	635.5(1)
Z and D_{calcd}/g cm^{-3}	1, 2.138	2, 2.268	2, 2.758
μ/mm^{-1}	2.26	2.90	12.51
Refls collected	9749	10068	11077
Unique refls	4725	3727	3700
Transmission	0.43–0.60	0.32–0.57	0.045–0.113
R_{int}/%[b]	9.3, 2.6	8.5, 2.0	19.2, 6.6
Refls $I > 2\sigma(I)$	4247	3634	3531
$R(F)$[c], $wR(F^2)$[d]	0.021, 0.054	0.017, 0.043	0.045, 0.112

a) Non-standard setting of *Pc*. b) Before and after absorption correction. c) Against reflections with $I > 2\sigma(I)$. d) Against all data.

References

1 V. S. Reddy, K. V. Katti, *Inorg. Chem.* **1994**, *33*, 2695.

2 V. S. Reddy, K. V. Katii, C. L. Barnes, *Chem. Ber.* **1994**, *127*, 1355.

3 V. S. Reddy, K. V. Katii, C. L. Barnes, *Inorg. Chem.* **1995**, *34*, 5483.

4 K. V. Katii, V. S. Reddy, P. R. Singh, *Chem. Soc. Rev.* **1995**, *24*, 97.

5 T. Appleby, J. D. Woolins, *Coord. Chem. Rev.* **2002**, *235*, 121.

6 J. Shen, E. D. Stevens, S. Nolan, *Organometallics* **1998**, *17*, 3000.

7 J. Shen, E. D. Stevens, S. P. Nolan, *Organometallics* **1998**, *17*, 3875.

8 J. Shen, C. M. Haar, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **1998**, *571*, 205.

9 A. M. Z. Slawin, M. Wainwright, J. D. Woolins, *J. Chem. Soc., Dalton Trans.* **2002**, 513.

10 T. S. Lobana, R. Singh, E. R. T. Tiekink, *J. Coord. Chem.* **1990**, *21*, 225.

11 J. R. Polam, L. C. Porter, *J. Coord. Chem.* **1993**, *29*, 109.

12 C.-W. Chang, P.-C. Ting, Y.-C. Lin, G.-H. Lee, Y. Wang, *J. Organomet. Chem.* **1998**, *553*, 417.

13 *SADABS, Version 2.10*, Bruker AXS, Madison WI, U.S.A., **2003**.

14 *SHELXTL, Version 5.10*, Bruker AXS, Madison, Wisconsin, U.S.A., **1997**.

15 H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876.