DOI: 10.1002/ejic.201100647

Coordination and Catalytic Activity of Ruthenium Complexes Containing Tridentate P,N,O Ligands

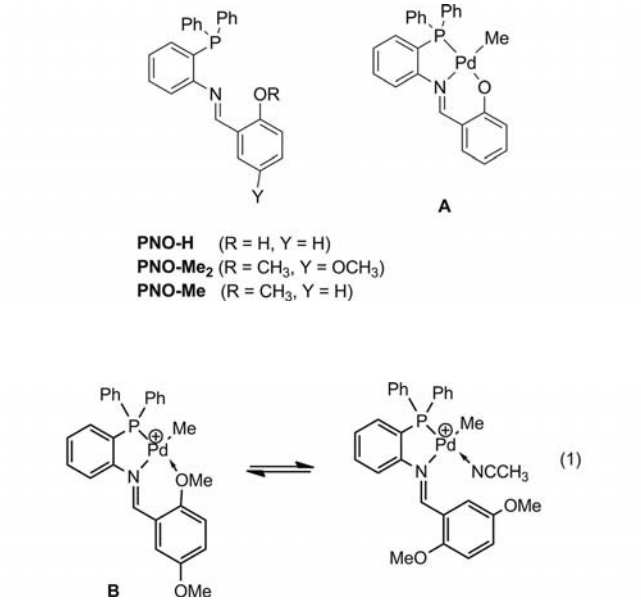
Chun-Chin Lee,[a] Wan-Yi Chu,[a] Yi-Hong Liu,[a] Shie-Ming Peng,[a] and Shiuh-Tzung Liu*[a]

Keywords: Ruthenium / Tridentate ligands / Amination / Hydrogen transfer / N,P ligands

The coordination chemistry of Ru^{II} ions with [2-(diphenylphosphanyl)-*N*-(*o*-hydroxybenzylidene)]aniline (**PNO-H**) and the methylated analogue **PNO-Me** have been studied. Thus, [(**PNO**)RuCl(dmso)$_2$] (**1**), [(**PNO**)$_2$Ru] (**2**), [(**PNO**)RuCl(PPh$_3$)] (**3**) and [(**PNO**)RuCl(CO)$_2$] (**4**) were synthesized by reactions of various Ru^{II} precursors with **PNO-H**. Treatment of **PNO-Me** with [RuCl$_2$(dmso)$_4$] resulted in in the formation of [*P,N*-(**PNO-Me**)Ru(dmso)$_2$Cl$_2$] (**5**). However, complexation of **PNO-Me** with [RuCl$_2$(CO)$_3$(THF)] (THF = tetrahydrofuran) provided a mixture of [*P,N*-(**PNO-Me**)Ru(CO)$_2$Cl$_2$] (**6**) and **4** because *O*-demethylation took place during the reaction. All of the Ru^{II} complexes have been characterized by elemental analysis and spectroscopic techniques, as well as X-ray crystal structural analysis for **2**, **4** and **6**. The ruthenium complexes investigated in this work, except **2**, are good precatalysts for the reductive amination of amine with alcohols, and **4** appears to be the best. Moreover, **4** can catalyze the direct amination of nitrobenzene with benzyl alcohol to the corresponding secondary amine.

Introduction

As part of our ongoing research on the coordinating capability of tridentate ligands containing phosphorus, nitrogen and oxygen donors towards transition metal ions, we have described the coordination chemistry of **PNO-H** and **PNO-Me$_2$** towards [(COD)PdMeCl].[1] The substituent on the oxygen atom influences its coordination nature. The oxygen donor in **PNO-Me$_2$** appears to be quite labile as demonstrated in Equation (1), whereas **PNO-H** can lose the phenolic proton and act as a stable chelator in **A**. Such a difference in coordination makes **B** catalytically active in the oligomerization of ethylene, whereas **A** is inactive.



Ruthenium is known to be catalytically active for various organic transformations. Thus, the modification of ligands to fine tune the activity of ruthenium ions has received much attention. In this context, several Ru^{II} complexes containing P,N,O tridentate ligands have been reported.[2–4] The aim of this paper is to describe the complexation of **PNO-H** and **PNO-Me** towards Ru^{II} ions and the catalytic activity of the resulting complexes in hydrogen transfer reduction for the preparation of amines.

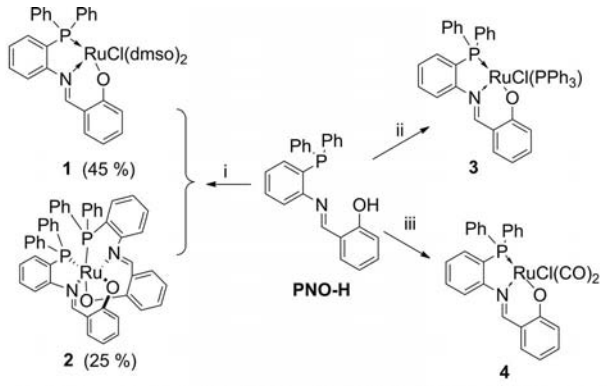
Results and Discussion

Synthesis and Characterization of Ruthenium(II) Complexes

PNO-H and **PNO-Me** were prepared according to reported methods.[1] A series of ruthenium(II) complexes containing **PNO-H** were synthesized as depicted in Scheme 1. In the presence of excess of triethylamine, reaction of **PNO-H** with [RuCl$_2$(dmso)$_4$] (dmso = CH_3SOCH_3), in a 1:1 ratio, afforded a mixture of **1** and **2**. Complex **1** was characterized spectroscopically, and the data were found to be identical to those reported.[3] Complex **2** was purified by column chromatography and obtained as a purple-red crystalline solid. The ^{31}P NMR spectra of **1** and **2** in $CDCl_3$ show only

[a] Department of Chemistry, National Taiwan University 1, Sec. 4, Roosevelt Road, Taipei, Taiwan
Fax: +886-2-23636359
E-mail: stliu@ntu.edu.tw

one resonance signal, which appears at 55.9 and 64.1 ppm, respectively. The ^{31}P resonance signals for **1** and **2** are shifted downfield compared to the free ligand, which is typical for the coordination of phosphane ligands.



i: $[RuCl_2(dmso)_4]$, Et_3N; ii:$[RuCl_2(PPh_3)_3]$, Et_3N; iii: $[(THF)RuCl_2(CO)_3]$, Et_3N

Scheme 1. Preparation of **1**–**4**.

The structure of **2** was confirmed by single-crystal X-ray diffraction analysis, and the ORTEP plot is shown in Figure 1. The two **PNO** ligands around the metal centre in **2** are arranged in a *mer–mer* configuration with the two nitrogen atoms *trans* to one another and the two phosphorus and two oxygen atoms in a *cis* configuration. This coordination mode is similar to that of other ruthenium(II)–PNO complexes with similar ligands.[3,4a,4b] The average Ru–P, Ru–O and Ru–N bond lengths in **2** are 2.23, 2.10 and 2.07 Å, respectively, which compare well to those observed in related Ru^{II} complexes.

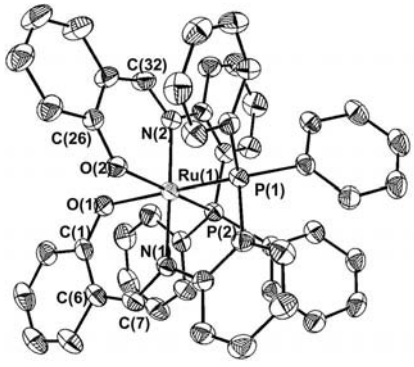


Figure 1. ORTEP plot of **2** (drawn with 30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ru(1)–N(1) 2.081(3), Ru(1)–N(2) 2.067(3), Ru(1)–O(1) 2.102(2), Ru(1)–O(2) 2.101(3), Ru(1)–P(1) 2.2323(9), Ru(1)–P(2) 2.238(1), N(2)–Ru(1)–N(1) 177.5(1), P(1)–Ru(1)–P(2) 96.97(4), O(2)–Ru(1)–O(1) 83.7(1).

Treatment of **PNO-H** with equimolar amounts of $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(CO)_3(THF)]$ yielded the substitution products **3** and **4**, respectively (Scheme 1). Complex **3** was characterized by mass spectrometry and elemental analysis. The ESI-MS confirms the formation of **3** with a peak at m/z = 785.1432 $[M - Cl + CH_3CN]^+$. The fluxional nature of **3** is similar to that of complexes with the chemical formula $[(R_3P)_3RuCl_2]$.[5]

Characterization of carbonyl-substituted **4** was achieved by spectroscopic and elemental analyses. Carbonyl stretching frequencies appear at 2053 and 2000 cm^{-1} in the IR spectrum of **4**, which are characteristic for a $[L_3RuCl(CO)_2]$ species. Carbon–phosphorus coupling constants obtained from the NMR spectra (J_{PC} = 12 Hz), suggest that the carbonyl ligands are *cis* to the phosphane donor of the complexes. The *cis* arrangement of the two carbonyl donors in **4** is evidenced by two sets of carbonyl resonances (193.9 and 191.3 ppm) in the ^{13}C NMR spectrum. The formulation is further confirmed by single-crystal X-ray crystallographic analysis. Crystals were grown by slow evaporation of a CH_2Cl_2/THF solution of **4** at room temperature. The ORTEP plot of **4** is shown in Figure 2, and selected bond lengths and angles are collected in Table 1. The ruthenium atom is hexacoordinate in an octahedral geometry, analogous to **2**. The coordination geometry is completed by the **PNO** chelate ligand, two carbonyl groups and a chloride ion, and the stereochemistry around the metal centre is consistent with the spectroscopic analysis. The P(1)–Ru(1)–N(1) angle [83.36(11)°] is not 90°, showing a small bite angle attributable to the *o*-phenylene linkage of the phosphane and imine donors. The Ru–N and Ru–O bond lengths are slightly shorter in **4** than **2**, which may be associated with the change of coordinating ligands around the metal centre.

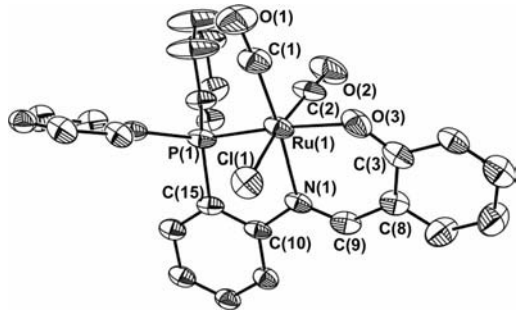


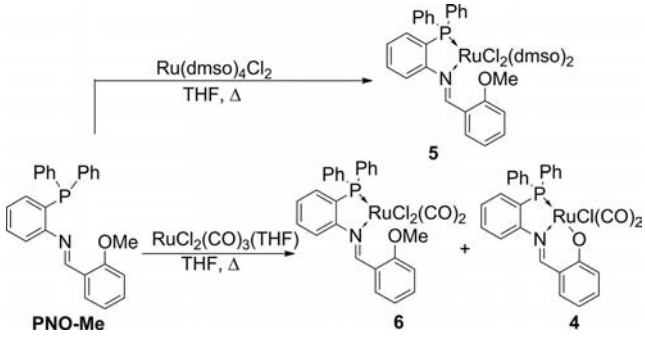
Figure 2. ORTEP plot of **4** (drawn with 30% probability ellipsoids).

Table 1. Selected bond lengths [Å] and angles [°] for **4**.

Bond lengths		Bond angles	
Ru(1)–C(1)	1.886(4)	N(1)–Ru(1)–P(1)	83.36(11)
Ru(1)–C(2)	1.880(4)	C(1)–Ru(1)–C(2)	91.31(17)
Ru(1)–N(1)	2.109(3)	C(1)–Ru(1)–N(1)	175.12(15)
Ru(1)–P(1)	2.297 (1)	C(2)–Ru(1)–N(1)	92.57(13)
Ru(1)–Cl(1)	2.4175(9)	C(2)–Ru(1)–P(1)	91.28(15)
Ru(1)–O(3)	2.091(3)	P(1)–Ru(1)–Cl(1)	94.72(3)
O(1)–C(1)	1.137(5)	C(2)–Ru(1)–Cl(1)	173.36(16)
O(2)–C(2)	1.121(4)	O(3)–Ru(1)–P(1)	174.17(8)
O(3)–C(3)	1.289(5)	Ru(1)–N(1)–C(9)	122.1(2)

Similarly, **PNO-Me** reacted with $[RuCl_2(dmso)_4]$ in THF with heating, affording the substitution product **5** (Scheme 2). Based on NMR and MS data (Table 2), the coordination environment around ruthenium centre in **5** is proposed to be similar to that of the previously reported complex $[(bidentate)Ru(dmso)_2Cl_2]$, i.e. **PNO-Me** acts as a bidentate ligand. The dmso methyl resonances appear as four singlets between 2.85 and 3.69 ppm, a pattern typical

for dmso coordinated to ruthenium in a *cis* fashion.[6] HRMS (ESI) of **5** shows a peak at m/z = 729.0730, which corresponds to $[M - Cl + CH_3CN]^+$.

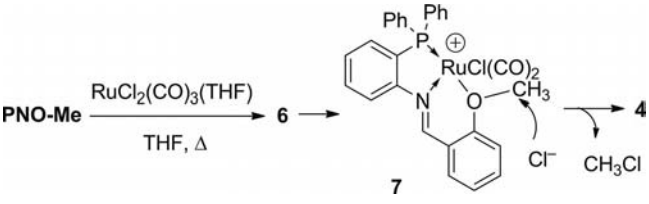


Scheme 2. Complexation of Ru^{II} ions with **PNO-Me**.

Table 2. Selected bond lengths [Å] and angles [°] for **6**.

Bond lengths		Bond angles	
Ru(1)–C(1)	1.88(2)	N(1)–Ru(1)–P(1)	79.2(5)
Ru(1)–C(2)	1.79(17)	C(1)–Ru(1)–C(2)	90(4)
Ru(1)–N(1)	2.164(18)	C(1)–Ru(1)–N(1)	175.9(8)
Ru(1)–P(1)	2.308(5)	C(2)–Ru(1)–N(1)	90(4)
Ru(1)–Cl(1)	2.425(5)	P(1)–Ru(1)–Cl(1)	171.0(2)
Ru(1)–Cl(2)	2.41(4)	Cl(2)–Ru(1)–Cl(1)	86.4(7)

The reaction of **PNO-Me** with an equimolar amount of $[RuCl_2(CO)_3(THF)]$ in THF with heating, led to the precipitation of **4** and **6** (Scheme 2). Apparently, the formation of **4** occurs through the cleavage of the ligand C–O bond. Scheme 3 illustrates the possible pathway of this demethylation. It is believed that **6** undergoes chloride substitution by the ether donor around the metal centre, which yields **7**. The free chloride acts as a nucleophile and undergoes nucleophilic attack at the methyl carbon atom, providing the C–O cleavage product. However, carrying out the same reaction in the presence of triethylamine yielded **6** exclusively.



Scheme 3. Pathway for the demethylation of **6**.

The structure of **6** is supported by elemental analysis and IR and NMR spectroscopic data. The ^{31}P NMR spectrum of **6** shows a single resonance at 50.7 ppm, which is shifted by ca. 10 ppm compared to that of **5**. The crystal structure of **6**·1/2(Et_2O) confirms its formulation. The ORTEP plot of **6** is shown in Figure 3, and the relevant geometric parameters are collected in Table 2. The structure has a slightly distorted octahedral geometry at the metal centre with *P*,*N*-coordination of **PNO-Me**. The Ru(1)–N(1) and Ru(1)–P(1) distances are 2.16(2) and 2.308(5) Å, respectively, which lie in the expected ranges.[3–4]

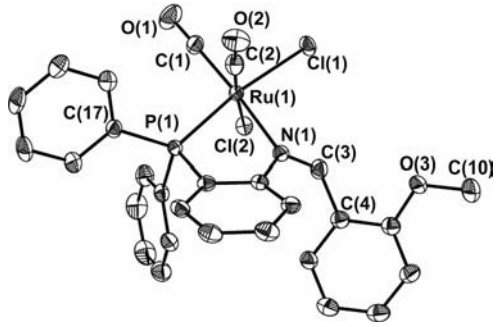
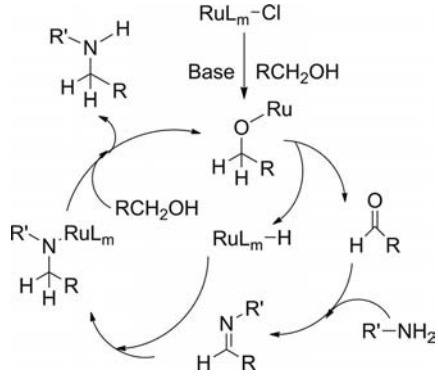


Figure 3. ORTEP plot of **6** (drawn with 30% probability ellipsoids).

Catalysis

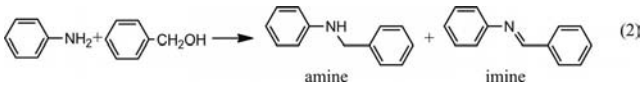
It was of interest to test the catalytic activity of **1**–**6**. We have recently shown that phosphane–amine complexes of ruthenium(II) are excellent precatalysts for *N*-alkylation of amines with alcohols, which involves a series of tandem reactions: oxidation of alcohols, condensation of amines with carbonyl compounds and reduction of imines (Scheme 4).[7] Such a synthetic methodology is of interest for its relevance to atom-economical synthesis.[8–10] We investigated the activity of **1**–**6** as catalysts for the *N*-alkylation of amines with alcohols.



Scheme 4. Reaction pathway of *N*-alkylation with alcohols.

We initially explored the reaction of aniline with benzyl alcohol as a model system [Equation (2)]. In a typical experiment, a mixture of aniline, benzyl alcohol, KO*t*Bu and Ru^{II} complex (1:3:0.4:0.01) was placed in a flask. Excess benzyl alcohol was used as the solvent, and the mixture was heated to 110 °C. The desired amine and/or imine products were extracted from the reaction mixture and analyzed by GC and ^1H NMR spectroscopy. The results are summarized in Table 3. Catalyst screening in the model reaction revealed that all the ruthenium(II) complexes triggered the reaction, except **2**. Owing to the bischelation of the **PNO** ligands around the metal centre in **2**, the lack of a vacant coordination site hinders its catalytic activity. All the other complexes show good catalytic activities in this reaction, although significant differences in the ratio of amine vs. imine products are observed. Taking into account the short reaction times needed and the high percentage of amine yielded, complex **4** lies among the most efficient catalysts

for this type of reaction (Table 3, Entry 4). In terms of turnover frequency (TOF) for this reaction, these results are comparable to or better than previously reported ruthenium(II) systems such as $[RuCl_2(PPh_3)_3]$[11] and $[Ru(p\text{-cymene})Cl_2]_2$.[12]



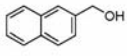
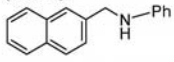
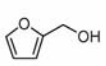
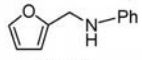
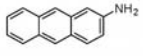
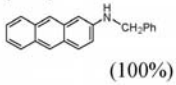
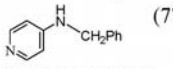
(2)

Table 3. Reductive amination catalyzed by **1**–**6**.[a]

Entry	Catalyst	Time [h]	Amine[b]	Imine[b]	TOF[c]
1	**1**	24	92%	3%	4
2	**2**	24	trace	14%	< 1
3	**3**	4	72%	6%	18
4	**4**	3	> 99%	–	33
5	**5**	4	87%	trace	22
6	**6**	4	93%	trace	23

[a] Reaction conditions: benzylamine (0.3 mmol), Ru^{II} complex (3×10^{-3} mmol) and *t*BuOK (0.12 mmol) in benzyl alcohol (0.9 mmol). [b] Yields based on integrations from ^1H NMR spectroscopy. [c] TOF = mol(substrate)/mol(Ru complex)/h (based on conversion to the amine).

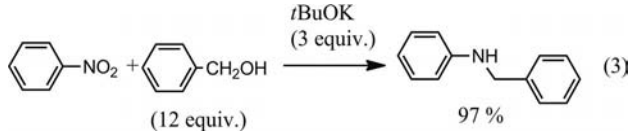
Table 4. Results of reductive amination catalyzed by **4**.

Entry	Amine	Alcohol	Amine product (yield)[b]
1	$C_6H_5NH_2$	4-$ClC_6H_4CH_2OH$	4-$ClC_6H_4CH_2NHPh$ (88%)
2	$C_6H_5NH_2$	4-$MeC_6H_4CH_2OH$	4-$MeC_6H_4CH_2NHPh$ (100%)
3	$C_6H_5NH_2$	4-$MeOC_6H_4CH_2OH$	4-$MeOC_6H_4CH_2NHPh$ (100%)
4	$C_6H_5NH_2$		 (87%)
5	$C_6H_5NH_2$		 (68%)[c]
6	*p*-$MeC_6H_4NH_2$	$C_6H_5CH_2OH$	*p*-$MeC_6H_4NHCH_2Ph$ (95%)
7	*p*-$ClC_6H_4NH_2$	$C_6H_5CH_2OH$	*p*-$ClC_6H_4NHCH_2Ph$ (100%)
8	*p*-$MeOC_6H_4NH_2$	$C_6H_5CH_2OH$	4-$MeOC_6H_4NHCH_2Ph$ (92%)
9		$C_6H_5CH_2OH$	 (100%)
10		$C_6H_5CH_2OH$	 (77%)
11[d]	$C_6H_{11}NH_2$	$C_6H_5CH_2OH$	$C_6H_5CH_2NHC_6H_{11}$ (86%)
12	piperidine	$C_6H_5CH_2OH$	$C_5H_{10}NCH_2Ph$ (60%)
13	$C_6H_{11}NH_2$	$C_6H_{11}OH$	$(C_6H_{11})_2NH$ (9%)[e]

[a] Reaction conditions: amine (0.3 mmol), *t*BuOK (0.12 mmol), **4** (3×10^{-3} mmol) in alcohol (0.9 mmol) at 110–130 °C for 4 h. [b] Yield based on NMR integration. [c] 10% of imine product. [d] At 150 °C. [e] 38% of imine product.

Using our protocol, we were able to produce a variety of amines from the corresponding alcohols (Table 4). Under the optimized reaction conditions, various substituted benzyl alcohols reacted with anilines to yield the corresponding amines in excellent yields (Entries 1–4 and 6–10). Other amines such as cyclohexylamine or piperidine reacted smoothly with benzyl alcohol to give the corresponding amine in good yields (Entries 11 and 12). However, the reaction of a secondary alcohol with cyclohexylamine was not quite as successful (Entry 13).

It is worth mentioning that **4** can also catalyze the direct amination of nitrobenzene with an alcohol, which is more sustainable for the synthesis of amines.[7,10] Typically, a mixture of nitrobenzene, potassium *tert*-butoxide, **4** and benzyl alcohol was heated under a nitrogen atmosphere for 24 h, and *N*-benzylaniline was obtained in 97% yield [Equation (3)]. Apparently, the reduction of a nitro group can be achieved by a hydrogen transfer reduction with **4**.



(3)

Conclusions

We have reported the synthesis and characterization of a series of ruthenium complexes bearing **PNO** ligands. Typically, [(**PNO**)RuCl(dmso)$_2$], [(**PNO**)$_2$Ru], [(**PNO**)RuCl(PPh$_3$)] and [(**PNO**)RuCl(CO)$_2$] were synthesized by reactions of various Ru^{II} precursors with deprotonated **PNO-H**. Complexation of $[RuCl_2(CO)_3(THF)]$ with **PNO-Me** in THF with heating causes demethylation of the ligand to yield [(**PNO**)RuCl(CO)$_2$]. The structures of these complexes were unambiguously determined by spectroscopic methods and X-ray single crystal analysis (**2**, **4** and **6**). Complex **4** is catalytically active for the reductive amination of amines with alcohols. Furthermore, the direct amination of nitrobenzene with benzyl alcohol leading to the secondary amine can be achieved with **4** as the catalyst. This study provides an insight into ligand effects on Ru^{II} complexes. Studies on the catalytic reactivity of these complexes are ongoing in our laboratory.

Experimental Section

General: All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. THF was distilled under nitrogen with sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried with CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after being degassed. **PNO-H** and **PNO-Me** were prepared according to the reported method.[1a]

NMR spectra were recorded in $CDCl_3$ or [D$_6$]acetone with a Bruker AVANCE 400 spectrometer. Chemical shifts are given in ppm relative to Me_4Si for ^1H and ^{13}C and to 85% H_3PO_4 for ^{31}P

NMR spectroscopy. IR spectra were measured with a Nicolet Magna-IR 550 spectrometer (Series-II).

[(PNO)RuCl(dmso)$_2$] (1) and [(PNO)$_2$Ru] (2): A mixture of **PNO-H** (104 mg, 0.27 mmol), [RuCl$_2$(dmso)$_4$] (131 mg, 0.27 mmol) and triethylamine (0.5 mL) in anhydrous THF (3 mL) was heated to reflux for 6 h. Filtration of the reaction mixture gave a dark red solid, which was washed with water to remove ammonium salts. Crystallization from ether yielded **1** as an orange solid (81 mg, 45%). The residue was then chromatographed on alumina oxide with THF/CH_3OH. A dark-red band was collected and concentrated to give **2** as a purple-red solid (58 mg, 25%). **1**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (s, 1 H, *H*C=N), 7.90–6.85 (m, 16 H, Ar-*H*), 6.87 (d, J = 8 Hz, 1 H, Ar-*H*), 6.51 (t, J = 8 Hz, 1 H, Ar-*H*), 3.29 (s, 3 H, dmso), 3.07 (s, 3 H, dmso), 2.53 (s, 3 H, dmso), 2.48 (s, 3 H, dmso) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 55.9 ppm (identical to reported data).[3] **2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 2 H, *H*C=N), 7.98 (d, J = 8.0 Hz, 2 H, Ar-*H*), 7.53 (t, J = 8.0 Hz, 2 H, Ar-*H*), 7.45 (d, J = 8.0 Hz, 2 H, Ar-*H*), 7.17–6.65 (m, 13 H, Ar-*H*), 6.02 (br., 2 H, Ar-*H*) ppm. ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ = 64.1 ppm. $C_{50}H_{38}N_2O_2P_2Ru\cdot CH_3OH$ (825.9): calcd. C 68.52, H 4.74, N 3.13; found 68.75, H 4.46, N 2.99.

[(PNO)RuCl(PPh$_3$)] (3): A mixture of **PNO-H** (104 mg, 0.27 mmol), [RuCl$_2$(PPh$_3$)$_3$] (259 mg, 0.27 mmol) and triethylamine (0.5 mL) in THF (5 mL) was heated to reflux for 6 h. Upon removal of THF, the residue was washed with diethyl ether/CH_2Cl_2 and reprecipitated by acetone to yield **2** as a brown solid (111 mg, 53%). HRMS (ESI): calcd. for $C_{45}H_{37}N_2OP_2Ru$ [M – Cl + MeCN]$^+$ 785.1425; found 785.1432. $C_{43}H_{34}ClNOP_2Ru$ (779.22): calcd. C 66.28, H 4.40, N 1.80; found C 66.75, H 4.60, N 1.99.

[(PNO)RuCl(CO)$_2$] (4): A mixture of **PNO-H** (97 mg, 0.25 mmol), [RuCl$_2$(CO)$_3$(THF)] (82 mg, 0.25 mmol) and triethylamine (0.5 mL) in THF (3 mL) was heated to reflux for 5 h. Upon cooling, the reaction mixture was filtered to give **4** as an orange solid (97 mg, 67%). IR (THF): $\tilde{\nu}$ = 2053, 2000 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, *H*C=N), 8.04 (dd, J = 8.0, J = 12.0 Hz, 2 H, Ar-*H*), 7.82 (dd, J = 4.0, J = 8.0 Hz, 1 H, Ar-*H*), 7.60 (t, J = 8.0 Hz, 1 H, Ar-*H*), 7.56–7.27 (m, 11 H, Ar-*H*), 7.20 (d, J = 8.0 Hz, 1 H, Ar-*H*), 7.00 (d, J = 8.0 Hz, 1 H, Ar-*H*), 6.51 (t, J = 8.0 Hz, 1 H, Ar-*H*) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 51.0 ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9 (d, J_{CP} = 12.0 Hz, *C*=O), 191.3 (d, J_{CP} = 12.0 Hz, *C*=O), 170.2, 161.0, 156.4 (d, J_{CP} = 19.0 Hz), 137.2, 137.2, 134.9 (d, J_{CP} = 11.0 Hz), 134.1 (d, J_{CP} = 51.0 Hz), 133.8, 133.6, 131.9, 131.3 (d, J_{CP} = 10.0 Hz), 131.2, 129.2 (d, J_{CP} = 11.0 Hz), 128.8 (d, J_{CP} = 11.0 Hz), 127.7 (d, J_{CP} = 56.0 Hz), 127.4 (d, J_{CP} = 7.0 Hz), 125.8 (d, J_{CP} = 56.0 Hz), 124.2 (d, J_{CP} = 6.0 Hz), 120.3, 118.1 (d, J_{CP} = 10.0 Hz), 115.2 ppm. $C_{27}H_{19}ClNO_3PRu$ (572.95): calcd. C 56.60, H 3.34, N 2.44; found C 56.93, H 3.64, N 2.16.

[*P*,*N*-(PNO-Me)Ru(dmso)$_2$Cl$_2$] (5): A mixture of **PNO-Me** (198 mg, 0.5 mmol) and [RuCl$_2$(dmso)$_4$] (164 mg, 0.48 mmol) in THF (5 mL) was heated to reflux for 6 h under a nitrogen atmosphere. During the reaction, an orange solid formed. The solid was collected by filtration to give **5** (64 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.60 (s, 1 H, *H*C=N), 8.23 (dd, J_{HH} = 8.0, J_{HH} = 12.0 Hz, 2 H, Ar-*H*), 7.57–7.14 (m, 14 H, Ar-*H*), 6.97 (d, J_{HP} = 8 Hz, 1 H, Ar-*H*), 6.93 (d, J_{HP} = 8 Hz, 1 H, Ar-*H*), 3.80 (s, 3 H, OMe), 3.69 (s, 3 H, dmso), 3.52 (s, 3 H, dmso), 3.29 (s, 3 H, dmso), 2.82 (s, 3 H, dmso) ppm. ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ = 60.8 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 173.9, 158.5, 154.3 (d, J_{CP} = 16.0 Hz), 137.8 (d, J_{CP} = 11.0 Hz), 136.7 (d, J_{CP} = 45.0 Hz), 134.7 (d, J_{CP} = 50.5 Hz), 134.0 (d, J_{CP} = 14.9 Hz), 133.2, 131.7, 131.0, 129.7, 129.6 (d, J_{CP} = 2.3 Hz), 129.2, 128.4 (d, J_{CP} = 6.3 Hz), 128.0 (d, J_{CP} = 10.5 Hz), 127.5 (d, J_{CP} = 10.0 Hz), 127.0 (d, J_{CP} = 50.0 Hz), 122.8, 122.3 (d, J_{CP} = 8.9 Hz), 120.4, 111.8, 55.8 (OMe), 51.2 (dmso), 47.9 (dmso), 45.9 (dmso), 45.2 (dmso) ppm. HRMS (ESI): calcd. for $C_{32}H_{37}ClN_2O_3PRuS_2$ [M – Cl + MeCN]$^+$ 729.0715; found 729.0730. $C_{30}H_{34}Cl_2NO_3PRuS_2\cdot H_2O$ (759.69): calcd. C 48.58, H 4.89, N 1.89; found C 48.90, H 4.60, N 1.91.

[*P*,*N*-(PNO-Me)Ru(CO)$_2$Cl$_2$] (6): A mixture of **PNO-Me** (105 mg, 0.26 mmol), [RuCl$_2$(CO)$_3$(THF)] (86 mg, 0.26 mmol) and triethylamine (1 mL) in THF (3 mL) was stirred at room temperature for 10 min. During the reaction, a yellow precipitate formed, which was collected by filtration and washed with small amount of THF to give **6** (62 mg, 40%). IR (THF): $\tilde{\nu}$ = 2061, 1999 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.4 (s, 1 H, N=C*H*), 7.91 (m, 2 H, Ar-*H*), 7.53–7.15 (m, 14 H, Ar-*H*), 6.88 (t, J_{HH} = 7.6 Hz, 1 H Ar-*H*), 6.86 (d, J_{HH} = 7.6 Hz, 1 H Ar-*H*), 3.61 (s, 3 H, O*CH*$_3$) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 50.7 ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6 (d, J_{CP} = 12.2 Hz, *C*O), 193.6 (d, J_{CP} = 10.7 Hz, *C*O), 172.9, 157.6, 154.9 (d, J_{CP} = 16.7 Hz), 134.5 (d, J_{CP} = 10.7 Hz), 134.0, 132.7 (d, J_{CP} = 57.7 Hz), 132.6, 131.92 (d, J_{CP} = 3.0 Hz), 131.68 (d, J_{CP} = 10.6 Hz), 131.5, 131.3, 130.0, 129.2 (d, J_{CP} = 10.7 Hz), 129.1 (d, J_{CP} = 73.7 Hz), 128.7 (d, J_{CP} = 11.4 Hz), 128.1 (d, J_{CP} = 6.9 Hz), 126.8 (d, J_{CP} = 55.5 Hz), 123.34 (d, J_{CP} = 9.9 Hz), 121.9, 120.6, 111.8, 55.6 ppm. ESI-MS: m/z = 552.07 [M – Cl]$^+$. $C_{28}H_{22}Cl_2NO_3PRu$ (623.44): calcd. C 53.94, H 3.56, N 2.25; found C 53.59, H 3.61, N 2.01.

Catalysis: Typical procedure for *N*-alkylation of amine with an alcohol. A mixture of amine (0.3 mmol), Ru^{II} complex (3×10^{-3} mmol), *t*BuOK (0.12 mmol) in an alcohol (0.9 mmol) was placed in a flask under atmospheric pressure of nitrogen and heated by an oil bath at 110–150 °C. On completion of the reaction, brine (3 mL) and CH_2Cl_2 (5 mL) were added. The organic layer was separated and the aqueous layer was extracted into CH_2Cl_2. The combined organic extracts were dried with magnesium sulfate and concentrated. Products were characterized by NMR spectroscopy and the data were consistent with those reported. Product yields were obtained by the ^{1}H NMR integration compared to the internal standard. Some compounds were purified by chromatography and characterized by NMR spectroscopy. ^{1}H NMR spectroscopic data of these compounds are essentially similar to those reported.

***N*-Benzylaniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.35 (m, 5 H), 7.14 (m, 2 H), 6.71 (t, 1 H, J_{HH} = 7 Hz), 6.59 (d, 2 H, J = 7 Hz), 4.27 (s, 2 H), 3.93 (br., 1 H) ppm.

***N*-(*p*-Chlorobenzyl)aniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.28 (m, 6 H), 6.71 (t, J_{HH} = 7.7 Hz, 1 H), 6.57 (d, J_{HH} = 7.7 Hz, 2 H), 4.28 (s, 2 H), 4.02 (br., 1 H) ppm.

***N*-(*p*-Methylbenzyl)aniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (m, 7 H), 6.68 (m, 3 H), 4.23 (s, 2 H), 3.81 (br., 1 H), 2.32 (s, 3 H) ppm.

***N*-(*p*-Methoxybenzyl)aniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.39 (m, 4 H), 6.91 (d, J_{HH} = 7.7 Hz, 2 H), 6.72 (t, J_{HH} = 7.7 Hz, 1 H), 6.21 (d, J_{HH} = 7.7 Hz, 2 H), 4.24 (s, 2 H), 3.95 (br., 1 H), 3.81 (s, 3 H) ppm.

***N*-(Naphthalen-2-ylmethyl)aniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (m, 4 H), 7.37 (m, 3 H), 7.09 (m, 2 H), 6.62 (d, J_{HH} = 9.2 Hz, 1 H), 6.57 (d, J_{HH} = 10.2 Hz, 2 H), 4.40 (d, 2 H), 4.22 (br., 1 H) ppm.

***N*-(2-Furfurylmethyl)aniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J_{HH} = 1.0 Hz, 1 H), 7.19 (t, J_{HH} = 7.2 Hz, 2 H), 6.72 (t, J_{HH} = 7.2 Hz, 1 H), 6.67 (d, J_{HH} = 7.2 Hz, 2 H), 6.32 (m, 1 H), 6.23 (m, 1 H), 4.30 (s, 2 H), 3.99 (br., 1 H) ppm.

***N*-Benzyl-*p*-methylaniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.32 (m, 5 H), 6.94–6.97 (d, J_{HH} = 8.0 Hz, 2 H), 6.51–6.54 (d, J_{HH} = 8.0 Hz, 2 H), 4.29 (s, 2 H), 2.21 (s, 3 H) ppm.

***N*-Benzyl-*p*-chlorolaniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, J = 7.2 Hz, 2 H), 7.03–7.08 (m, 5 H), 6.36 (d, J = 7.2 Hz, 2 H), 4.32 (s, 2 H), 4.03 (br., 1 H) ppm.

***N*-Benzyl-*p*-methoxyaniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 5 H), 7.25 (d, J = 6.9 Hz, 2 H), 6.75 (d, J = 6.9 Hz, 2 H), 4.25 (s, 2 H), 3.72 (s, 3 H) ppm.

***N*-(Anthracen-2-yl)benzylamine:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1 H), 8.09 (s, 1 H), 7.89 (d, J = 8.3 Hz, 1 H), 7.80 (d, J = 6.7 Hz, 1 H), 7.78 (d, J = 9.0 Hz, 1 H), 7.23–7.44 (m, 7 H), 6.93 (d, J = 9.0 Hz, 1 H), 6.88 (s, 1 H), 4.45 (s, 2 H) ppm.

4-(Benzylamino)pyridine: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.21 (m, 2 H), 7.26–7.40 (m 5 H), 6.47 (m, 2 H), 4.55 (br., 1 H), 4.38 (s, 2 H) ppm.

***N*-Benzylcyclohexylamine:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (m, 5 H), 3.74 (s, 2 H), 2.41 (m, 1 H), 1.90–1.86 (m, 2 H), 1.68–1.40 (m, 4 H), 1.11 (m, 5 H) ppm.

***N*-Benzylpiperidine:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43–1.45 (m, 2 H), 1.52–1.62 (m, 4 H), 2.35 (t, J = 5.2 Hz, 4 H), 3.46 (s, 2 H), 7.23–7.32 (m, 5 H) ppm.

Dicyclohexylamine: ^{1}H NMR: δ = 2.52 (t, J = 10.8 Hz, 2 H), 1.94–1.50 (m, 8 H), 1.32–0.89 (m, 12 H), 0.77 (br., 1 H) ppm.

***N*-Benzylaniline by Direct Amination of Nitrobenzene with Benzyl Alcohol:** A mixture of nitrobenzene (0.3 mmol), **4** (0.003 mmol) and *t*BuOK (0.9 mmol) in benzyl alcohol (3.6 mmol) was placed in a flask under atmospheric pressure of nitrogen and heated by an oil bath at 150 °C for 24 h. On completion of the reaction, brine (3 mL) and CH_2Cl_2 (5 mL) were added. The organic layer was separated and the aqueous layer was extracted into diethyl ether. The combined organic extracts were dried with magnesium sulfate and concentrated. Products were characterized by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.35 (m, 5 H), 7.14 (dd, J_{HH} = 7, 7 Hz, 2 H), 6.71 (t, J_{HH} = 7 Hz, 1 H), 6.59 (d, J = 7 Hz, 2 H), 4.27 (s, 2 H), 3.93 (br., 1 H) ppm, which are identical to the authentic sample of *N*-benzylaniline.

Crystallography: Crystals suitable for X-ray determination were obtained for **2**·$(CH_2Cl_2)_{0.5}(H_2O)_{0.5}$, **4** and **6**·$(C_2H_5OC_2H_5)_{0.5}$ by recrystallization at room temperature. Cell parameters were determined with a Siemens SMART CCD diffractometer. The structure was solved using the SHELXS-97 program[13] and refined using the SHELXL-97 program[14] by full-matrix least-squares on $F2$ values.

CCDC-830870 (for **2**), -830871 (for **4**) and -830872 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex 2·[$(CH_2Cl_2)_{0.5}(H_2O)_{0.5}$]: Monoclinic; space group $P2_1/n$; a = 16.3229(2), b = 12.4424(2), c = 22.0748(3) Å; α = 90, β = 93.118(1), γ = 90°; V = 4476.7(1) Å^3; Z = 4; $\rho_{calcd.}$ = 1.355 mg m^{-3}; F(000) 1872; crystal size = 0.30 × 0.25 × 0.20 mm^3; reflections collected: 29935; independent reflections: 10239 [R(int) = 0.0522]; θ range 1.51 to 27.50°; goodness-of-fit on $F2$ = 1.054; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0493, $wR2$ = 0.1573; R indices (all data): $R1$ = 0.0722, $wR2$ = 0.1749.

Complex 4: Monoclinic; space group $P2_1/c$; a = 15.754(1), b = 14.784(3), c = 11.0385(6) Å; α = 90, β = 103.701(7), γ = 90°; V = 2497.9(5) Å^3; Z = 1; $\rho_{calcd.}$ = 1.523 mg m^{-3}; F(000) 1152; crystal size = 0.15 × 0.10 × 0.05 mm^3; reflections collected: 13714; independent reflections: 5717 [R(int) = 0.0350]; θ range 2.35 to 27.50°; goodness-of-fit on $F2$ = 0.817; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0384, $wR2$ = 0.0759; R indices (all data): $R1$ = 0.1163, $wR2$ = 0.0898.

Complex 6·$(C_2H_5OC_2H_5)_{0.5}$: Triclinic; space group $P\bar{1}$; a = 9.3298(2), b = 10.6879(3), c = 16.2407(4) Å; α = 97.142(2), β = 98.051(2), γ = 114.524(2)°; V = 1428.60(6) Å^3; Z = 2; $\rho_{calcd.}$ = 1.535 mg m^{-3}; F(000) 670; crystal size = 0.20 × 0.15 × 0.10 mm^3; reflections collected: 32338; independent reflections: 6543 [R(int) = 0.0484]; θ range 2.81 to 27.50°; goodness-of-fit on $F2$ = 0.909; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0330, $wR2$ = 0.1076; R indices (all data): $R1$ = 0.0383, $wR2$ = 0.1140.

Acknowledgments

We thank the National Science Council for financial support (NSC97-2113-M-002-013-MY3).

[1] a) P.-Y. Shi, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *Organometallics* **2002**, *21*, 3203–3207; b) P.-Y. Shi, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *J. Chin. Chem. Soc.* **2003**, *50*, 89–94.
[2] a) M. Alvarez, N. Lugan, R. Mathieu, *J. Chem. Soc., Dalton Trans.* **1994**, 2755–2760; b) H. Yang, M. Alvarez, N. Lugan, R. Mathieu, *J. Chem. Soc., Chem. Commun.* **1995**, 1721–1722; c) H. Yang, M. Alvarez, N. Lugan, R. Mathieu, *Organometallics* **1997**, *16*, 1401–1409.
[3] P. Bhattacharyya, M. L. Loza, J. Parr, A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.* **1999**, 2917–2921.
[4] a) K. Nakajima, S. Ishibashi, M. Kojima, *Chem. Lett.* **1998**, *27*, 997–998; b) S. R. Bayly, A. R. Cowley, J. R. Dilworth, C. V. Ward, *Dalton Trans.* **2008**, *16*, 2190–2198; c) P. Pelagatti, A. Bacchi, M. Balordi, S. Bolaño, F. Calbiani, L. Elviri, L. Gonsalvi, C. Pelizzi, M. Peruzzini, D. Rogolino, *Eur. J. Inorg. Chem.* **2006**, *12*, 2422–2436; d) H.-L. Kwong, W.-S. Lee, T.-S. Lai, W.-T. Wong, *Inorg. Chem. Commun.* **1999**, *2*, 66–69.
[5] K. G. Caulton, *J. Am. Chem. Soc*. **1974**, *96*, 3005–3006.
[6] I. P. Evans, A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1973**, 204–209.
[7] C.-C. Lee, S.-T. Liu, *Chem. Commun.* **2011**, *47*, 6981–6983.
[8] G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703.
[9] Recent examples: a) M. Zhu, K. Fujita, R. Yamaguchi, *Org. Lett.* **2010**, *12*, 1336–1339; b) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell, M. Beller, *Chem. Asian J.* **2007**, *2*, 403; c) O. Saidi, A. Blacker, M. Farah, S. Marsden, J. M. J. Williams, *Chem. Commun.* **2010**, *46*, 1541–1543; d) H. Tuerkmen, T. Pape, F. E. Hahn, B. Cetinkaya, *Organometallics* **2008**, *27*, 571–575; e) C.-Y. Wang, C.-F. Fu, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *Inorg. Chem.* **2007**, *46*, 5779–5786; f) D. Gnanamgari, A. Moores, E. Rajaseelan, R. H. Crabtree, *Organometallics* **2007**, *26*, 1226–1230, and references therein.
[10] a) C. Feng, Y. Liu, S. Peng, Q. Shuai, G. Deng, C.-J. Li, *Org. Lett.* **2010**, *12*, 4888–4891; b) Y. Liu, W. Chen, C. Feng, G. Deng, *Chem. Asian J.* **2011**, *6*, 1142–1146.
[11] Y. Watanabe, Y. Tsuji, H. Ige, Y. Ohsugi, T. Ohta, *J. Org. Chem.* **1984**, *49*, 3359–3363.
[12] M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson, J. M. J. Williams, *J. Am. Chem. Soc.* **2009**, *131*, 1766–1774.
[13] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 467–473.
[14] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**.

Received: June 25, 2011
Published Online: September 7, 2011

