DALTON
FULL PAPER

Catalytic transfer hydrogenation of ketones by the use of ruthenium complexes incorporating the new tridentate ligand, bis(2-oxazolin-2-ylmethyl)phenylphosphine

Pierre Braunstein,*[a] Michael D. Fryzuk,*[b] Frédéric Naud[a] and Steven J. Rettig[b]

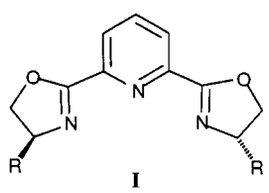
[a] *Université Louis Pasteur, Laboratoire de Chimie de Coordination (UMR 7513 CNRS), 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France. E-mail: braunst@chimie.u.-strasbg.fr*
[b] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, V6T 1Z1, Canada*

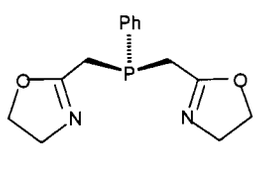
Received 21st October 1998, Accepted 15th December 1998

The new heterofunctional phosphine ligand bis(2-oxazolin-2-ylmethyl)phenylphosphine (*N*,*P*,*N*) has been prepared and has allowed the synthesis of the ruthenium complexes *fac*-[$RuCl_2(DMSO)(N,P,N)$] **1**, *fac*-[$RuCl_2(PPh_3)(N,P,N)$] **2**, [$RuCl(\eta^6\text{-}C_6H_6)(N,P,N)][O_3SCF_3$] **3** and [$Ru(\eta^6\text{-}C_6H_6)(N,P,N)][O_3SCF_3]_2$ **4**. When tridentate, as in **1**, **2**, and **4**, this ligand co-ordinates in a facial-type mode. In complex **3**, it acts as a *P*,*N*-chelate with a dangling oxazoline ring. The structures of the ligand, **2**·CH_2Cl_2·$0.25C_6H_{14}$ and **3** have been determined by X-ray diffraction. Complexes **1**–**4** catalyse the transfer hydrogenation reaction between propan-2-ol and ketones. Only small differences in reactivity were observed between **3** and **4**, despite the different ligand bonding mode in these complexes. For the best catalyst, **2**, yields up to 97% were obtained and turnover frequencies may be as high as 112 000 h^{-1}.

Improved or novel stoichiometric or catalytic reactivities are continuously achieved with co-ordination and organometallic compounds. One major way to control and orient the reactivity of a metal containing species is by modifying the structure or the nature of the surrounding ligands. Among the most common donor atoms, C, N and P play a central role.[1,2] In homogeneous and asymmetric catalysis homotopic or heterotopic polydentate ligands have attracted much attention. Thus ligands bearing different donor atoms can induce increased selectivity owing to different electronic properties of these atoms which is relayed to the reactive metal site.[3] In the fast growing field of asymmetric catalysis high enantioselectivity is usually obtained by using enantiomerically pure ligands designed with a rigid platform supporting chiral information. Since the late eighties advances in this field have been achieved by the use of the nitrogen based chiral oxazoline heterocycle as the chiral fragment.[4] The fact that the synthesis involves the use of readily available aminoalcohols allows for a variety of substitution patterns and most importantly the preparation of enantiomerically pure oxazolines. Several chiral bidentate or tridentate oxazoline-containing ligands have been prepared and successfully used for asymmetric catalysis. The C_2-symmetric tridentate ligands of the type 2,6-bis(2-oxazolin-2-yl)pyridine (Pybox) **I** have shown interesting activity and enantioselectivity in the Rh-catalysed hydrosilylation of ketones and the Ru-catalysed cyclopropanation of olefins with diazoacetates.[5] As part of a general program to examine the co-ordination properties of multidentate ligands that contain mixed donors, the preparation of new ligands that contain both phosphines and oxazolines in a chelating array has been initiated.

In this paper we detail the synthesis of the achiral, tridentate system **II** which is similar to the Pybox ligand **I** with the pyridine moiety replaced by a phosphine donor. Thus changing both electronic and steric properties of the ligand should modify the reactivity of the resulting complexes. We first investigated the co-ordination chemistry of the achiral ligand **II** and evidenced two different co-ordination modes. We report the synthesis of four ruthenium(II) complexes and describe some preliminary results on the catalytic transfer hydrogenation of ketones by propan-2-ol.

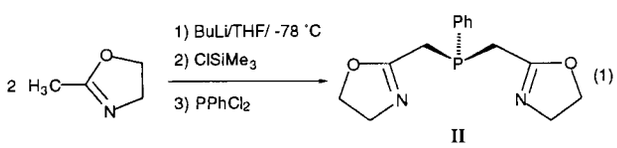




Results and discussion

Synthesis and characterization of the ligand

The synthesis of bis(2-oxazolin-2-ylmethyl)phenylphosphine (**II** or *N*,*P*,*N*) was performed in THF at −78 °C *via* a one-pot reaction by first deprotonation of the commercially available 2-methyl-2-oxazoline and then addition of Me_3SiCl to form the *N*-silyl derivative, which was followed by reaction with $PPhCl_2$ [eqn. (1)]. The use of Me_3SiCl was found to be crucial as some



(1)

uncharacterized side products were formed in its absence. This is consistent with previous findings on the synthesis of related, chelating *P*,*N* ligands.[6]

The ^1H NMR spectrum of compound **II** in $CDCl_3$ at room temperature reveals a set of 3 complex multiplets for the aliphatic protons. The PCH_2 protons were assigned by $^1H\text{-}\{^{31}P\}$ NMR experiments. Considering that there is no symmetry operation that can interchange these protons and only a mirror plane in the molecule, the two methylene sets of protons form an enantiotopic pair of diastereotopic protons. Thus, the pattern for this spin system was expected to be of the ABX type. However, selective ^1H homonuclear decoupling experiments evidenced the existence of a $^5J_{HH}$ coupling of 1.2 Hz between the PCH_2 protons and a methylene set of the oxazoline. This

Table 1 Selected bond distances (Å) and angles (°) for compound *N*,*P*,*N* **II**

P(1)–C(9)	1.827(4)	C(2)–O(1)	1.301(4)
P(1)–C(1)	1.860(4)	C(1)–C(2)	1.472(5)
P(1)–C(5)	1.849(4)	C(2)–N(1)	1.252(5)
C(9)–P(1)–C(1)	102.5(2)	C(1)–C(2)–N(1)	123.3(4)
C(1)–P(1)–C(5)	98.7(2)	P(1)–C(1)–C(2)	112.8(3)
C(5)–P(1)–C(9)	98.2(2)	O(1)–C(2)–N(1)	117.4(4)
		O(1)–C(2)–C(1)	119.2(4)

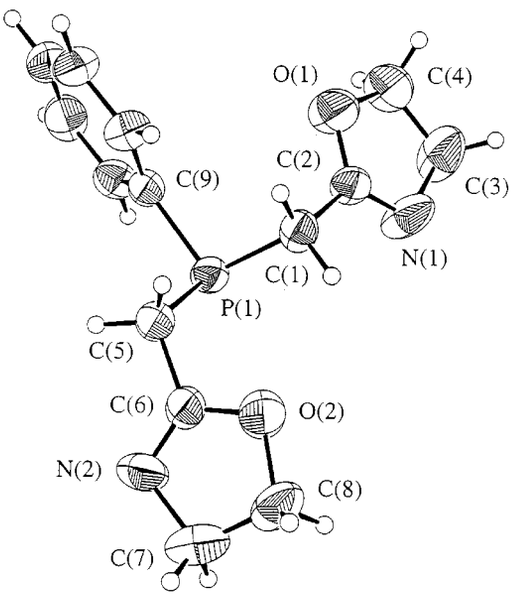
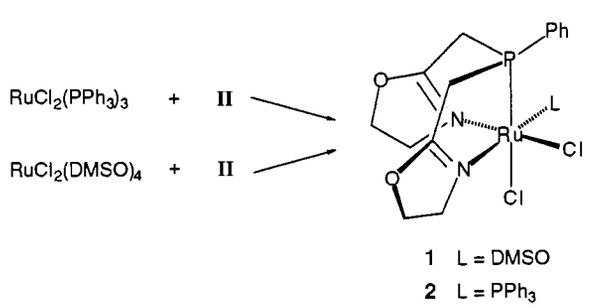


Fig. 1 An ORTEP[7] view of the structure of compound *N*,*P*,*N* **II**.

long range coupling is responsible for the ABMX spin system observed. Knowing that long range coupling is likely to occur where the conjugation is best, we assign the multiplet at δ 3.75 to the NCH_2 protons. This $^5J_{HH}$ coupling is observed also for the precursor 2-methyl-2-oxazoline. A single-crystal X-ray diffraction study (Fig. 1) confirmed the structure of **II**. Selected bond distances and angles are given in Table 1 and will be used for comparison with values found for this ligand in ruthenium complexes (see below).

Synthesis and characterization of the [$RuCl_2$(L)(*N*,*P*,*N*)] (L = DMSO 1 or PPh_3 2)

The incorporation of the *N*,*P*,*N* ligand **II** onto ruthenium was achieved *via* ligand substitution processes. Reaction of **II** with *cis*-[$RuCl_2(DMSO)_4$] in refluxing toluene resulted in the formation of complex [$RuCl_2$(DMSO)(*N*,*P*,*N*)] **1** (90% yield) (Scheme 1). The ^{1}H NMR resonances of the PCH_2 protons



Scheme 1

were assigned by ^{1}H-{^{31}P} experiments and they exhibit two ABX spin systems corresponding to two protons each. Thus all

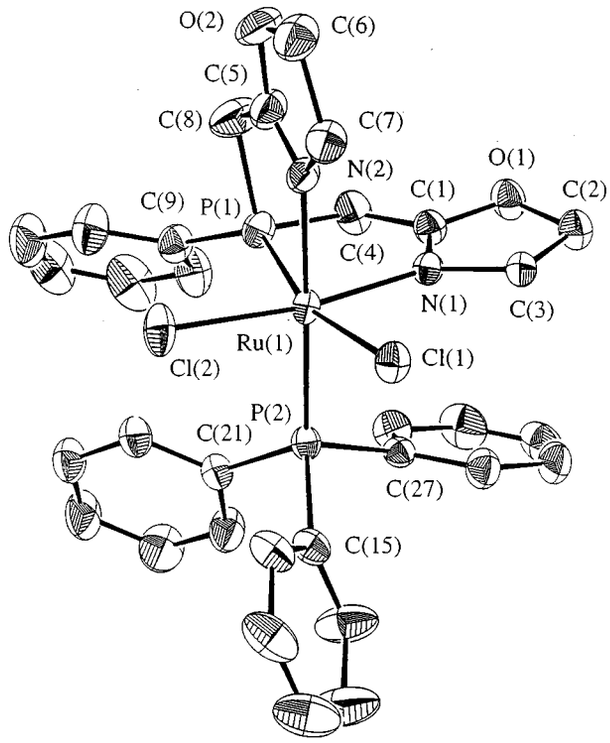


Fig. 2 An ORTEP view of the structure of *fac*-[$RuCl_2(PPh_3)$(*N*,*P*,*N*)] in complex **2**·CH_2Cl_2·0.25C_6H_{14}.

four protons are chemically and magnetically inequivalent which indicates there is no symmetry element in the molecule. Furthermore, the far infrared (FIR) spectrum of complex **1** shows absorptions at 297 and 222 cm^{-1} which strongly supports a *cis* arrangement of the two chloride ligands. From these data one can conclude that the *N*,*P*,*N* ligand is co-ordinated in a *fac* mode with the phosphorus atom *cis* to one chloride and one DMSO ligand.

Reaction of compound **II** with [$RuCl_2(PPh_3)_3$] in refluxing THF yielded complex **2** (85% yield) (Scheme 1). The ^{1}H NMR resonances of the PCH_2 protons were located by ^{1}H-{^{31}P} experiments and they exhibit two ABX spin systems. Thus the protons are chemically and magnetically inequivalent which indicates that there is again no symmetry element in the molecule. The ^{31}P-{^{1}H} NMR spectrum shows the two phosphines to be in a *cis* arrangement ($^2J_{PP}$ = 31.2 Hz). Furthermore, the far infrared spectrum shows absorptions at 305 and 243 cm^{-1} which are consistent with a *cis* arrangement of the two chloride ligands. From these data one can conclude that the ligand co-ordinates in a *fac* mode with its phosphorus atom *cis* to the triphenylphosphine and *cis* to one chloride. Single crystals of **2**·CH_2Cl_2·0.25C_6H_{14} were obtained and an X-ray diffraction study confirmed the stereochemistry of the molecule (Fig. 2). There are two independent, almost identical molecules and three solvent regions in the asymmetric unit (see details in the Experimental section). Selected bond distances and angles are given in Table 2.

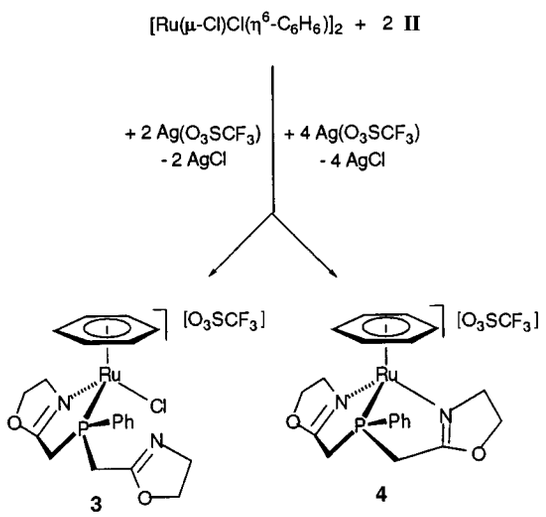
There are two independent but very similar molecules in the unit cell. The Ru–P [2.2227(8) and 2.2993(8) Å] and Ru–N distances [2.085(2) and 2.129(2) Å] in one molecule are comparable to literature values.[2b] The lengthening of the Ru(1)–Cl(1) distance compared with Ru(1)–Cl(2) may be related to the larger *trans* influence of phosphorus compared to nitrogen. The N–Ru–N [86.72(9)°] and P–Ru–P [98.59(3)°] angles indicate slight distortions from ideal octahedral angles. The chelation of the ligand is characterised by a pinch of the P–C–C angle going from 112.8(3)° in the 'free' ligand to 106.0(2)° once co-ordinated. The C–O and C=N bond distances are not significantly elongated by co-ordination of the oxazoline.

Table 2 Selected bond distances (Å) and angles (°) for *fac*-[$RuCl_2$-(PPh_3)(*N*,*P*,*N*)]·CH_2Cl_2·0.25C_6H_{14} **4**·CH_2Cl_2·0.25C_6H_{14}

Molecule 1		Molecule 2	
Ru(1)–Cl(1)	2.4678(7)	Ru(2)–Cl(3)	2.4674(7)
Ru(1)–Cl(2)	2.4255(7)	Ru(2)–Cl(4)	2.4398(7)
Ru(1)–P(1)	2.2227(8)	Ru(2)–P(3)	2.2219(7)
Ru(1)–P(2)	2.2993(8)	Ru(2)–P(4)	2.2900(7)
Ru(1)–N(1)	2.085(2)	Ru(2)–N(3)	2.077(2)
Ru(1)–N(2)	2.129(2)	Ru(2)–N(4)	2.141(2)
C(1)–N(1)	1.274(4)	N(3)–C(33)	1.269(3)
C(1)–C(4)	1.469(4)	C(33)–C(36)	1.488(4)
P(1)–C(4)	1.848(4)	P(3)–C(36)	1.844(3)
P(1)–C(8)	1.852(4)	P(3)–C(40)	1.858(3)
C(8)–C(5)	1.487(5)	C(40)–C(37)	1.469(5)
C(5)–N(2)	1.255(4)	C(37)–N(4)	1.272(4)
O(1)–C(1)	1.344(3)	O(3)–C(33)	1.342(3)
N(1)–Ru(1)–N(2)	86.72(9)	N(3)–Ru(2)–N(4)	84.23(9)
P(1)–Ru(1)–P(2)	98.59(3)	P(3)–Ru(2)–P(4)	99.39(3)
Cl(1)–Ru(1)–Cl(2)	91.92(3)	Cl(3)–Ru(2)–Cl(4)	93.07(3)
Cl(1)–Ru(1)–P(1)	164.41(3)	Cl(3)–Ru(2)–P(3)	167.06(3)
Cl(1)–Ru(1)–N(1)	88.14(6)	Cl(3)–Ru(2)–N(3)	89.24(7)
N(1)–C(1)–C(4)	123.2(3)	N(3)–C(33)–C(36)	123.0(3)
P(1)–C(4)–C(1)	106.0(2)	P(3)–C(36)–C(33)	104.4(2)
N(1)–C(1)–O(1)	117.8(3)	N(3)–C(33)–O(3)	117.3(3)
O(1)–C(1)–C(4)	119.0(3)	O(3)–C(33)–C(36)	119.7(2)

Synthesis and characterization of cationic ruthenium(II) benzene complexes

Complex [$RuCl(\eta^6$-$C_6H_6)$(*N*,*P*,*N*)][O_3SCF_3] **3** was obtained in two steps from the reaction of two equivalents of **2** with one equivalent of [{$Ru(\mu$-Cl)$Cl(\eta^6$-$C_6H_6)$}$_2$] followed by addition of two equivalents of AgO_3SCF_3 (Scheme 2).



Scheme 2

The ^{1}H resonances for the two PCH_2 protons were located by ^{1}H-{^{31}P} NMR experiments and they exhibit two ABX spin systems corresponding to two protons each. Both signals are shifted downfield when compared to those of the 'free' ligand, one by 0.7 ppm the other by 0.35 ppm. The most deshielded methylenic protons are assigned to the chelate ring. It is noteworthy that PCH_2 protons of the unco-ordinated arm of the ligand are diastereotopic, thus indicating restricted flexibility owing to steric hindrance around the phosphorus atom. The IR spectrum in a KBr pellet shows two bands at 1666 and 1645 cm^{-1} assigned to the C=N vibrations of the unco-ordinated and co-ordinated oxazoline, respectively. This is in agreement with the data found for the 'free' ligand and for **II** as a chelating ligand in complex **1** or **2**. The structure is static on the NMR timescale and there is no exchange between the co-ordinated and unco-ordinated arms of the ligand. The *P*,*N* chelate is strongly bound to the metal since one equivalent of 4-methylpyridine does not displace the oxazoline. This structure of **3** was confirmed by a single crystal X-ray diffraction study (Fig. 3, Table 3). The complex adopts a piano-stool type of geometry with a P–Ru–N bite angle of 79.53(10)°. For the chelated arm of the ligand the P–C–C angle of 107.4(3)° is much smaller than the related P–C–C of the dangling oxazoline 116.6(3)°. In a smaller range the O–C–N angle from the oxazoline increases from co-ordinated [117.4(4)] to unco-ordinated [119.6(4)°].

Table 3 Selected bond distances (Å) and angles (°) for [$RuCl(\eta^6$-$C_6H_6)$-(*N*,*P*,*N*)][O_3SCF_3] **3**

Ru(1)–Cl(1)	2.403(1)		
Ru(1)–N(1)	2.076(3)		
Ru(1)–P(1)	2.318(1)		
P(1)–C(5)	1.818(4)	P(1)–C(1)	1.842(4)
C(5)–C(6)	1.492(6)	C(1)–C(2)	1.477(6)
C(6)–N(2)	1.276(5)	C(2)–N(1)	1.263(5)
C(6)–O(2)	1.318(5)	C(2)–O(1)	1.339(5)
Cl(1)–Ru(1)–P(1)	85.74(4)	N(1)–C(2)–C(1)	123.5(4)
P(1)–Ru(1)–N(1)	79.53(10)	P(1)–C(1)–C(2)	107.4(3)
P(1)–C(1)–C(2)	107.4(3)	C(1)–C(2)–O(1)	119.2(4)
Ru(1)–P(1)–C(1)	103.9(1)	O(1)–C(2)–N(1)	117.3(4)
Cl(1)–Ru(1)–N(1)	84.4(1)	N(2)–C(6)–C(5)	122.4(4)
Ru(1)–N(1)–C(2)	124.4(3)	P(1)–C(5)–C(6)	116.6(3)
		C(5)–C(6)–O(2)	117.9(4)
		O(2)–C(6)–N(2)	119.6(4)

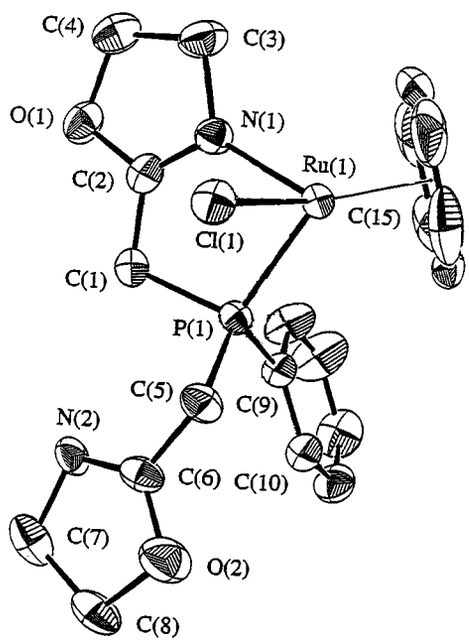


Fig. 3 An ORTEP view of the structure of [$RuCl(\eta^6$-$C_6H_6)$(*N*,*P*,*N*)]-[O_3SCF_3] **3**.

Complex **4** was isolated in 60% yield in two steps from the reaction of two equivalents of **II** with one equivalent of [{$RuCl_2(\eta^6$-$C_6H_6)$}$_2$] followed by the addition of four equivalents of $Ag(O_3SCF_3)$. The ^{1}H NMR spectrum shows a ABX spin system for the four PCH_2 protons of the tridentate ligand since a mirror plane makes the two pairs of diastereotopic methylene protons enantiotopic. The IR spectrum in KBr shows only one band at 1648 cm^{-1}.

Catalytic transfer hydrogenation of ketones

Preliminary catalytic studies with the complexes **1** and **2** have been performed for the transfer hydrogenation of ketones by propan-2-ol, a reaction of current interest.[8] For comparative purposes, the experiments were performed using the reaction conditions described by Chowdhury and Bäckvall[8c] with [$RuCl_2$-

Table 4 Transfer hydrogenation of ketones catalysed by the ruthenium(II) complexes **1–4**[a]

Substrate	Catalyst	Ketone : Ru : base	Yield (%)	*t*/min	Turnover h^{-1}
Cyclohexanone	**1**	1000 : 1 : 24[a]	7	0.5	8400
			99 (89)[b]	60	990
	2	1000 : 1 : 24[a]	94 (99)[c]	0.5	112800 (118800)[c]
			99.5	15	3980
Acetophenone	**1**	1000 : 1 : 24[a]	4	0.5	4800
			58 (48)[b]	60	580
	2	1000 : 1 : 24[a]	58.5 (50)[c]	0.5	70200 (60000)[c]
			88 (88)[c]	15	3520
	2	200 : 1 : 24[d]	61	0.5	14600
			97	15	776
	3	200 : 1 : 24[d]	13.5	15	108
			54	60	108
	4	200 : 1 : 24[d]	11	15	88
			45	60	90

[a] Reactions were carried out in refluxing propan-2-ol using 1 M substrate concentration and NaOH as a base, unless otherwise specified. [b] Values in parentheses refer to results from ref. 8(*c*) under similar conditions. [c] Values in parentheses refer to results from ref. 8(*d*) under similar conditions. [d] Using a 0.1 M substrate concentration and KOH as a base.

$(PPh_3)_3$] as a catalyst precursor. The use of the DMSO complex **1** as catalyst precursor indicates that it has a reactivity only slightly higher than that of $[RuCl_2(PPh_3)_3]$ in terms of conversion and turnover frequency (TOF) for cyclohexanone and acetophenone. However, the use of precursor **2** leads to higher yields than for **1** for the same substrates and to a TOF more than 10 times larger. The activity of catalyst **2** is comparable to that of $[RuCl_2(PPh_3)(P,N,O)]$ [*P*,*N*,*O* = 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane] which appears to show the highest activity reported for the ruthenium-catalysed transfer hydrogenation of ketones by propan-2-ol.[8c,d] No activity was observed in the absence of NaOH. The difference in activity between complexes **1** and **2** is therefore related to the change in the ancillary ligand. We have noticed that one equivalent of PPh_3 does not displace the ligand DMSO from complex **1** in chloroform at room temperature. This would tend to support the idea that dissociation of a neutral ligand is necessary during the catalytic cycle; given that PPh_3 is bulkier than DMSO, its ease of dissociation is perhaps not surprising.[9] Further work to confirm this is in progress. Since the conversion rate is dependent on substrate concentration,[8] *e.g.*,[10] we performed the transfer hydrogenation reaction of acetophenone with our most active catalyst **2** using a 0.1 M substrate concentration and obtained a yield of 97%.

Following the optimized procedure for complex **2** we tested the catalytic activity of **3** and **4** (Table 4). Both complexes were less efficient than **2** under similar conditions. Their similar activity suggests that replacing a terminal chloride (in **3**) with a chelating oxazoline (in **5**) does not significantly affect the rate-determining step in the catalysis. Compared with the *mono*-cationic **3**, the expected increased efficiency of the *di*cationic complex **4** appears to be counterbalanced by the formation of a bis-chelating system.[8f]

During the course of our work, Zhang and co-workers[11] reported another *N*,*P*,*N*-type ligand with a C_2H_4 spacer between the oxazoline rings and the phosphorus atom. Although a benzene ruthenium complex was used as catalyst for transfer hydrogenation of ketones, the precursor complex was prepared *in situ* and not isolated. Their best result with acetophenone (0.2 M) as a substrate was 72% with ratio ketone : Ru : base = 200 : 1 : 30 at 80 °C.

Further work from our laboratories will expand the results here to chiral systems since the chiral versions of compound **II** are readily available. Of particular interest is the comparison of tridentate ligands such as **II** that prefer a facial co-ordination mode to Pybox systems that are known to bind in a meridional fashion.

Experimental

All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^1H and ^{31}P-{^1H} NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a FT Bruker AC300 instrument, ^{13}C NMR spectra at 50.32 MHz on a FT Bruker AC200 instrument, ^1H-{^{31}P} NMR at 500.13 MHz on a FT Bruker AMX500 instrument, IR spectra in the 4000–400 cm^{-1} range on a Bruker IFS66 FT spectrometer and FIR spectra in the 500–90 cm^{-1} range on a Bruker ATS 83 spectrometer.

Syntheses

The compounds $[RuCl_2(PPh_3)_3]$,[12] *cis*-$[RuCl_2(DMSO)_4]$,[13] and $[\{Ru(\mu\text{-}Cl)Cl(\eta^6\text{-}C_6H_6)\}_2]$[14] were prepared according to literature procedures. The 2-methyl-2-oxazoline was purchased from Aldrich.

Bis(2-oxazolin-2-ylmethyl)phenylphosphine II. A THF solution of degassed 2-methyl-2-oxazoline (5.00 g, 58.7 mmol) was added dropwise over a 10 min period to a LiBu solution (58.7 mmol, 1.6 M hexane) cooled at −78 °C in 100 mL of THF. After the pale yellow mixture was stirred for 1 h at −78 °C, 7.45 mL (58.7 mmol) of degassed chlorotrimethylsilane in 5 mL of THF were injected into the solution, and stirring was continued for 2 h. The compound $PPhCl_2$ (5.250 g, 29.3 mmol) was rapidly added to the cloudy solution at −78 °C. A white powder precipitated and the mixture was allowed to reach room temperature overnight. The solvents were evaporated under reduced pressure until a beige solid was obtained. The powder was then treated with 50 mL of degassed water containing 0.80 g of NaOH. The product was extracted with 4 × 50 mL of Et_2O and the extract dried over $MgSO_4$. The pale yellow oil thus obtained was dissolved in the minimum of Et_2O and 80 mL of hexane were added, the solution was then heated for a few minutes under stirring and then placed overnight at −28 °C. This afforded the pure ligand as a pale yellow powder (3.630 g, 45%), mp 56 °C (Found: C, 60.43; H, 6.00; N, 9.84. $C_{14}H_{17}N_2O_2P$ requires C, 60.86; H, 6.20; N, 10.14%). IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ (C=N) 1661. δ_H ($CDCl_3$, 300 MHz): ABMX spin system (A, B, M = H, X = P) 2.82 (m with appearance of dq, 2 H, J_{AB} = 14.4, $^2J_{XB}$ = 3.3, $^5J_{MB}$ = 1.2), 2.95 (m with appearance of dt, 2 H, J_{AB} = 14.4, $^2J_{XA}$ = 1.2, $^5J_{MA}$ = 1.2 Hz), 3.75 (m, 4 H, NCH_2), 4.10 (m, 4 H, OCH_2), 7.30–7.40 (m, 3 H, aromatic H) and 7.50–7.60 (m, 2 H, aromatic H). ^{31}P-{^1H} NMR ($CDCl_3$, 121.5 MHz): δ −27 (s). ^{13}C-{^1H} NMR ($CDCl_3$, 50 MHz): δ 26.7 (d, J_{PC} = 21.3, PCH_2), 54.6 (s, NCH_2), 67.4 (s, OCH_2), 128.4

(d, J_{PC} = 6.7, *o*-C of aryl), 129.4 (s, *p*-C of aryl), 132.0 (d, J_{PC} = 20.7, *m*-C of aryl), 135.70 (d, J_{PC} = 17.2, *o*-C of aryl) and 164.9 (d, J_{PC} = 5.7 Hz, C=N).

Ruthenium complexes. All the complexes are air-stable for a short period of time but should be better kept under an inert atmosphere.

[RuCl$_2$(DMSO)(N,P,N)] ***1***. In a 150 mL Schlenk tube fitted with a reflux condenser were placed together 0.430 g (1.56 mmol) of compound **II** and 0.756 g (1.56 mmol) of *cis*-[RuCl$_2$(DMSO)$_4$] in 50 mL of toluene. The suspension was heated under reflux for 4 h. The volume of toluene was reduced to about 10 mL and the yellow precipitate obtained filtered off and washed with 2 × 30 mL portions of Et$_2$O. Drying *in vacuo* yielded complex **1** as a yellow solid (0.740 g, 90%) (Found: C, 36.62; H, 4.20; N, 5.10. $C_{16}H_{23}Cl_2N_2O_3PRuS$ requires C, 36.51; H, 4.40; N, 5.32%). IR: $\tilde{\nu}_{max}$/cm^{-1} (C=N) 1650 (KBr), (Ru–Cl) 297, 222 (polyethylene). ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 2.85 [s, 3 H, S(O)(CH$_3$)$_2$], 3.08 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 18.5, $^2J_{PH}$ = 8, PCH$_2$], 3.12 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 18.5, $^2J_{PH}$ = 8, PCH$_2$], 3.17 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 19, $^2J_{PH}$ = 8, PCH$_2$], 3.30 [s, 3 H, S(O)(CH$_3$)$_2$], 3.50 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 19, $^2J_{PH}$ = 8 Hz, PCH$_2$], 2.85 [s, 3 H, CH$_3$S(O)CH$_3$], 3.85 (m, 1 H), 3.95 (m, 1 H), 4.15 (m, 1 H), 4.30 (m, 1 H), 4.50–4.70 (m, 4 H), 7.35–7.55 (m, 3 H) and 8.05 (m, 2 H). ^{31}P-{^{1}H} NMR (CDCl$_3$, 121.5 MHz): δ 56.8 (s).

[RuCl$_2$(PPh$_3$)(N,P,N)] ***2***. In a 150 mL Schlenk tube fitted with a reflux condenser were placed together (0.420 g, 1.52 mmol) of compound **II** and 1.460 g (1.52 mmol) of [RuCl$_2$(PPh$_3$)$_3$] in 50 mL of THF. After the THF was added a cloudy yellow solution was rapidly obtained and after a few minutes upon reflux a yellow precipitate formed. The suspension was heated under reflux for 2.5 h. The solvent was then evaporated to about 10 mL. The yellow precipitate was filtered off and washed with 2 × 10 mL of Et$_2$O. The solid was then dissolved in the minimum of CH$_2$Cl$_2$ and precipitated by addition of hexane. This procedure repeated twice afforded 0.915 g (85% yield) of the pure complex (Found: C, 53.61; H, 4.75; N, 3.83. $C_{32}H_{32}Cl_2N_2O_2P_2Ru$ requires C, 54.09; H, 4.54; N, 3.94%); IR: $\tilde{\nu}_{max}$/cm^{-1} (C=N) 1649 (KBr), (Ru–Cl) 305, 243 (polyethylene). ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 2.35 (m, 1 H), 2.83 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 18.5, $^2J_{PH}$ = 11.5, PCH$_2$], 2.85 [AB part of ABX spin system (X = P), overlapping dd, 1 H, $^2J_{HH}$ = 19, $^2J_{PH}$ = 6.5, PCH$_2$], 2.91 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 18.5, $^2J_{PH}$ = 11.5, PCH$_2$], 3.22 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 19, $^2J_{PH}$ = 6.5, PCH$_2$], 3.15 (m, 1 H), 3.62 (m, 1 H), 4.16 (m, 1 H), 4.22 (m, 1 H), 4.45 (m, 1 H), 4.55 (m, 1 H) and 4.70 (m, 1 H). ^{31}P-{^{1}H} NMR (CDCl$_3$, 121.5 MHz): δ 46.2 (AB spin system d, 1 P, $^2J_{PP}$ = 31.2) and 52.3 (AB spin system d, 1 P, $^2J_{PP}$ = 31.2 Hz).

[RuCl(η^6-C$_6$H$_6$)(N,P,N)][O$_3$SCF$_3$] ***3***. In a Schlenk tube were placed together the ligand **II** (0.147 g, 0.53 mmol) and [{Ru(μ-Cl)Cl(η^6-C$_6$H$_6$)}$_2$] (0.133 g, 0.265 mmol) in CH$_2$Cl$_2$ (10 mL). The dark orange solution obtained was stirred for 1 h at room temperature and then filtered through a cannula fitted with glass fiber paper. The resulting orange solution was evaporated to about 1 mL and an orange precipitate obtained by addition of hexane. The orange solid was further washed with 2 × 10 mL of hexane. After drying under vacuum for 2 h, solid Ag(O$_3$SCF$_3$) (0.121 g, 0.47 mmol) and 20 mL of CH$_2$Cl$_2$ were added. After a few minutes a pale yellow suspension appeared and the reaction mixture was stirred for 1 h. The suspension was filtered over Celite and the orange solution obtained reduced under vacuum to about 2 mL. Addition of Et$_2$O afforded a yellow solid which was further washed with 10 mL of hexane and Et$_2$O. Pure complex **3** was obtained by crystallization from 1 : 3 CH$_2$Cl$_2$–hexane (0.203 g, 60%) (Found: C, 39.87; H, 3.80. $C_{21}H_{23}ClF_3N_2O_5PRuS$ requires C, 39.41; H, 3.62%); IR (KBr): $\tilde{\nu}_{max}$/cm^{-1} (C=N non co-ordinated) 1666 and 1645. ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 3.25 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 18.7, $^2J_{PH}$ = 9.5, PCH$_2$], 3.31 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 18.7, $^2J_{PH}$ = 9.5, PCH$_2$], 3.60 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 16.5, $^2J_{PH}$ = 7.6, PCH$_2$], 3.68 [AB part of ABX spin system (X = P), dd, 1 H, $^2J_{HH}$ = 18.7, $^2J_{PH}$ = 9.5 Hz, PCH$_2$], 3.75 (m, 2 H, CH$_2$ from unco-ordinated oxazoline), 4.10 (m, 1 H, CH$_2$ co-ordinated oxazoline), 4.15 (m, 2 H, CH$_2$ unco-ordinated oxazoline), 4.70 (m, 2 H, CH$_2$ co-ordinated oxazoline) and 5.05 (m, 1 H, CH$_2$ co-ordinated oxazoline). ^{31}P-{^{1}H} NMR (CDCl$_3$, 121.5 MHz): δ 40.7.

[Ru(η^6-C$_6$H$_6$)(N,P,N)][O$_3$SCF$_3$]$_2$ ***4***. In a Schlenk tube were placed together the ligand **II** (0.260 g, 0.944 mmol) and [{Ru(μ-Cl)Cl(η^6-C$_6$H$_6$)}$_2$] (0.236 g, 0.472 mmol) in CH$_2$Cl$_2$ (10 mL). The dark orange solution obtained was stirred for 1 h at room temperature and then filtered through a cannula fitted with glass fiber paper. The resulting orange solution was evaporated to about 1 mL and an orange precipitate was obtained by addition of hexane. The orange solid was further washed with 2 × 10 mL of hexane. After drying under vacuum for 2 h, solid Ag(O$_3$SCF$_3$) (0.485 g, 1.888 mmol) and 30 mL of CH$_2$Cl$_2$ were added. After a few minutes a pale yellow suspension appeared and the reaction mixture was stirred for 2 h. The solvent was evaporated and 20 mL of acetone were added. The suspension was filtered twice over Celite and the orange solution obtained reduced under vacuum to about 2 mL. Addition of Et$_2$O afforded a yellow-brown solid which was further washed with 10 mL of hexane and Et$_2$O (0.416 g, 60%) (Found: C, 34.50; H, 2.97. $C_{22}H_{23}F_6N_2O_8PRuS_2$ requires C, 35.06; H, 3.08%). IR (KBr): $\tilde{\nu}_{max}$/cm^{-1} (C=N) 1648. δ_H (acetone-d$_6$, 300 MHz): 3.93 [AB part of ABX spin system (X = P), dd, 2 H, J_{AB} = 18.6, $^2J_{AX}$ = 13.6, PCH$_2$], 3.98 [AB part of ABX spin system (X = P), dd, 2 H, J_{AB} = 18.6, $^2J_{BX}$ = 10.2 Hz, PCH$_2$], 4.40 (m, 4H, NCH$_2$), 4.85 (m, 4 H, OCH$_2$), 6.20 (s, 6 H, benzene), 7.70–7.80 (m, 3 H, aromatic H) and 8.20–8.30 (m, 2 H, aromatic H).

Catalytic experiments

Typical procedure for catalytic transfer hydrogenation of ketones: in a Schlenk round bottom flask were added together the ruthenium complex (0.01 mmol) and 5 mL of degassed propan-2-ol and the solution was heated at 82 °C for 5–10 min under N$_2$. Acetophenone (1.201 g, 10.0 mmol) dissolved in degassed propan-2-ol (3 mL) was added dropwise to the refluxing mixture. The resulting yellow solution was stirred for 10 min and then a solution of NaOH (0.0095 g, 0.237 mmol) in propan-2-ol (2 mL) was added dropwise. The yellow solution turned slightly orange after the addition of base. The extent of conversion was determined by gas chromatography using a CPWAX58CB column (50 m × 0.25 mm).

X-Ray crystallographic analyses

Bis(2-oxazolin-2-ylmethyl)phenylphosphine II. *Crystal data.* $C_{14}H_{17}N_2O_2P$, M = 276.27, monoclinic, space group $P2_1/a$ (no. 14), a = 7.0634(6), b = 17.961(1), c = 11.688(1) Å, β = 103.89(1)°, U = 1439.4(2) Å^3 (by least-squares refinement on the setting angles for 25 reflections with 55 < 2θ < 72°, λ = 1.541 78 Å, T = 21 °C), Z = 4, D_c = 1.275 g cm^{-3}, F(000) = 584. Colorless prisms. Crystal dimensions 0.20 × 0.25 × 0.40 mm, μ(Cu-Kα) = 16.98 cm^{-1}.

Data collection and processing.[15] Rigaku AFC6S diffractometer, graphite–monochromated Cu-Kα radiation; 3074 unique reflections measured (1 < θ < 77.5°, h,k,±l), 1674 having $I \geq 3\sigma(I)$. Absorption correction: azimuthal scans for three reflections (relative transmission factors 0.933–1.000). The intensities of three standard reflections, measured each 200 reflections, decayed linearly by 2.3% (correction applied).

Structure analysis and refinement. Direct methods followed

by Fourier synthesis. Full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions [C–H 0.98 Å, $B_{iso} = 1.2B$(parent atom)]. Unit weights = 1.[15] Final $R = 0.053$, $R' = 0.048$ for 1674 reflections with $I \geqslant 3\sigma(I)$. Computer programs and source of scattering factors are given in ref. 15.

***fac*-[RuCl$_2$(PPh$_3$)(*N*,*P*,*N*)]·CH$_2$Cl$_2$·0.25C$_6$H$_{14}$ 2·CH$_2$Cl$_2$·0.25C$_6$H$_{14}$.** *Crystal Data.* $C_{34.5}H_{37.5}Cl_4N_2O_2P_2Ru$, space group *C*2/*c* (no. 15), $M = 817.01$, monoclinic, $a = 38.3173(3)$, $b = 18.2006(2)$, $c = 20.5863(1)$ Å, $\beta = 106.818(1)°$, $U = 13742.8(2)$ Å^3 (by least-squares refinement on setting angles for 19556 reflections with $2 < \theta < 31°$, $\lambda = 0.710\ 69$ Å, $T = 25$ °C), $Z = 16$, $D_c = 1.577$ g cm^{-3}, $F(000) = 6648$. Pale yellow prism. Crystal dimensions 0.20 × 0.25 × 0.30 mm, μ(Mo-Kα) = 0.896 mm^{-1}.

Data collection and processing.[16] Rigaku/ADSC CCD diffractometer, graphite-monochromated Mo-Kα radiation; 56084 reflections, 18843 unique ($1 < \theta < 30.9°$, $\pm h$, $\pm k$, $\pm l$), 10897 having $I \geqslant 3\sigma(I)$. Absorption correction: analysis of symmetry-equivalent data (decay/absorption correction factors: 0.890–1.000).

Structure analysis and refinement. Direct methods followed by Fourier synthesis. There are two independent molecules and three solvent regions in the asymmetric unit. The first solvent region was modeled as a dichloromethane molecule 1:1 disordered about a twofold axis. The second region is complex and was modeled by anisotropic carbon atoms of varying occupancy [C(66–74)]. This region is probably overlapping CH_2Cl_2 and hexane molecules. The third solvent region consists of a single peak on a twofold axis [C(75)]. Full-matrix least squares with all non-hydrogen atoms except C(75) anisotropic and hydrogen atoms in calculated positions [C–H 0.97–0.98 Å, $B_{iso} = 1.2B$(parent atom)]. Refinement on F^2. Final $R = 0.045$ [for 10897 reflections with $I \geqslant 3\sigma(I)$], $R' = 0.105$ for all 18003 reflections with $\theta < 30°$. Computer programs and source of scattering factors are given in ref. 16.

[RuCl(η^6-C$_6$H$_6$)(*N*,*P*,*N*)][O$_3$SCF$_3$] 3. *Crystal Data.* $C_{21}H_{23}ClF_3N_2O_5PRuS$, $M = 639.98$, monoclinic, space group $P2_1/a$ (no. 14), $a = 10.526(2)$, $b = 20.611(2)$, $c = 11.592(1)$ Å, $\beta = 90.36(1)°$, $U = 2514.9(6)$ Å^3 (by least-squares refinement on setting angles for 25 reflections with $17 < 2\theta < 28°$, $\lambda = 0.710\ 69$ Å, $T = 21$ °C), $Z = 4$, $D_c = 1.690$ g cm^{-3}, $F(000) = 1288$. Orange prism. Crystal dimension: 0.20 × 0.25 × 0.55 mm, μ(Mo-Kα) = 9.34 cm^{-1}.

Data collection and processing.[15] Rigaku AFC6S diffractometer, graphite-monochromated Mo-Kα radiation; 5954 unique reflections measured ($1 < \theta < 27.5°$, $h,k,\pm l$), 3088 having $I \geqslant 3\sigma(I)$. Absorption correction: azimuthal scans for three reflections (relative transmission factors 0.918–1.000). The intensities of three standard reflections, measured each hour of X-ray exposure time, showed only small random fluctuations.

Structure analysis and refinement. Patterson method followed by Fourier synthesis. There is a possibility of O/N disorder in the unco-ordinated ring of the ligand. Full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions [C–H 0.98 Å, $B_{iso} = 1.2B$(parent atom)]. Final $R = 0.035$, $R' = 0.032$ for 3088 reflections with $I \geqslant 3\sigma(I)$. Computer programs and source of scattering factors are given in ref. 15.

CCDC reference number 186/1286.

See http://www.rsc.org/suppdata/dt/1999/589/ for crystallographic files in cif. format.

Acknowledgements

We are grateful to Mrs Libs for the GC measurements, Dr Graff for NMR experiments, the Centre National de la Recherche Scientifique (Paris) and the Natural Sciences and Engineering Council of Canada for support, the Université Louis Pasteur for a Visiting-Professor position for M. D. F. and the Ministère de l'Enseignement Supérieur et de la Recherche (Paris) for a PhD grant to F. N.

References

1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Book, CA, 1987; A. Yamamoto, *Organotransition Metal Chemistry*, Wiley, New York, 1986.
2 (*a*) A. Togni and L. M. Venanzi, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 497; (*b*) H. A. Mayer and W. C. Kaska, *Chem. Rev.*, 1994, **94**, 1239.
3 J. M. J. Williams, *Synlett*, 1996, 705.
4 H. Brunner, U. Obermann and P. Wimmer, *Organometallics*, 1989, **8**, 821; C. Bolm, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 542; A. Pfaltz, *Acta Chem. Scand.*, 1996, **50**, 189.
5 H. Nishiyama, M. Kondo, T. Nakamura and K. Itoh, *Organometallics*, 1991, **10**, 500; H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki and K. Itoh, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1247.
6 J. Sprinz and G. Helmchen, *Tetrahedron Lett.*, 1993, **34**, 1769.
7 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
8 (*a*) G. Zassinovich, G. Mestroni and S. Gladiali, *Chem. Rev.* 1992, **92**, 1051; (*b*) P. A. Chaloner, M. A. Esteruelas, F. Joo and L. A. Oro, *Homogeneous Hydrogenation*, Kluwer Academic Publishers, Dordrecht, 1994, pp. 87–118; (*c*) R. Chowdhury and J.-E. Bäckvall *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1063; (*d*) H. Yang, M. Alvarez, N. Lugan and R. Mathieu, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1721; (*e*) H. Yang, M. Alvarez, N. Lugan and R. Mathieu, *Organometallics*, 1997, **16**, 1401; (*f*) P. Barbaro, C. Bianchini and A. Togni, *Organometallics*, 1997, **16**, 3004; (*g*) J.-X. Gao, T. Ikaria and R. Noyori, *Organometallics*, 1996, **15**, 1087; (*h*) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikaria and R. Noyori, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 285.
9 M. D. Fryzuk, M. J. Jonker and S. J. Rettig, *Chem. Commun.*, 1997, 377.
10 C. F. de Graauw, J. A. Peters, H. van Bekkum and J. Huskens, *Synthesis*, 1994, 1007.
11 Y. Jiang, Q. Jiang, G. Zhu and X. Zhang, *Tetrahedron Lett.*, 1997, **38**, 215.
12 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.
13 B. R. James, E. Ochiai and G. I. Rempel, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 781.
14 R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, 1972, **50**, 3063.
15 M. D. Fryzuk, J. B. Love and S. J. Rettig, *Organometallics*, 1998, **17**, 846.
16 T. Y. Fu, Z. Liu, S. J. Rettig, J. R. Scheffer and J. Trotter, *Acta Crystallogr.*, *Sect. C*, 1997, **53**, 1577.

Paper 8/08170K