A new class of anionic phosphinooxazoline ligands in palladium and ruthenium complexes: catalytic properties for the transfer hydrogenation of acetophenone†

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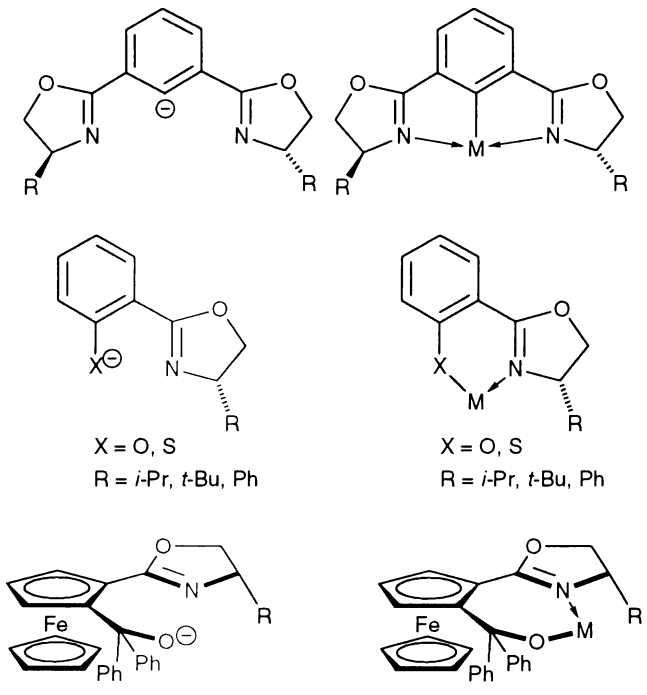
The synthesis of the cationic Pd complex [Pd(dmba)(PCH_2-oxazoline)]Cl [PCH_2-oxazoline = 2-oxazoline-2-ylmethyl)diphenylphosphine] (**2**) has allowed for the first time the observation of hemilabile behaviour for a phosphinooxazoline ligand. This molecular dynamics is stopped upon removal of the chloride anion, by reaction with either NH_4PF_6, which retains the cationic nature of the complex, or Bu^{t}OK. The latter reaction leads to the formation of the first example of a Pd complex bearing an anionic phosphinooxazoline ligand, [Pd(dmba){$Ph_2PCH{=}C(=N)CH_2CH_2O$}], abreviated [Pd(dmba)(PCH-oxazoline)] (**7**), the anionic charge resulting from the monodeprotonation of the PCH_2 group. Following this methodology, the Ru complex [RuCl(*p*-cymene){$Ph_2PCH{=}C(=N)CH_2CH_2O$}], abreviated [RuCl(η^6-*p*-cymene)(PCH-oxazoline)] (**8**) and containing this four-electron chelating anionic ligand, was prepared and shown to be more reactive for the catalytic transfer hydrogenation of acetophenone in propan-2-ol than the analogous complex bearing the neutral phosphinooxazoline ligand PCH_2-oxazoline. The crystal structure of *cis*-[Pd{$Ph_2PCH{=}C(=N)CH_2CH_2O$}$_2$], abbreviated *cis*-[Pd(PCH-oxazoline)$_2$] (**6**), was determined by X-ray diffraction.

Oxazolines are versatile synthons for ligand design[1,2] and readily available in enantiomerically pure forms, which accounts for their increasing use in asymmetric reactions catalysed by transition metal complexes.[2–5] Nevertheless, reports on *anionic* ligands incorporating an oxazoline ring are not legion compared to their neutral analogs and such ligands may be classified according to two main families. In class A compounds, the anionic charge is carried by an external heteroatom (C^-, O^-, S^-) and the nitrogen atom of the oxazoline remains a neutral donor. This includes ligands such as bis(oxazolinyl)phenyl,[6–8] (hydroxyphenyl)oxazoline,[9–15] (hydroxyferrocenyl)oxazoline[16,17] and (mercaptoaryl)oxazoline,[17] which upon deprotonation allowed the preparation of complexes with metals such as Ti, Zr, Hf, V, Mn, Ni, Pd, Pt or Cu. An oxazoline moiety was recently combined to a pyrrole for use in copper-catalysed enantioselective cyclopropanation reactions; the NH group is expected to be deprotonated upon *in situ* reaction with Cu(I) triflate.[18] Some of the isolated complexes were found to be catalysts for reactions such as ethylene polymerisation,[9] epoxydation,[11b] alkyl- and phenylzincation of aldehydes,[16] and conjugate addition to ketones.[17]

In the second class of ligands, B, the anionic charge is largely delocalised onto the nitrogen atom of the oxazoline but only one such ligand type has been reported, as illustrated in eqn. (1). The corresponding complexes were obtained by first deprotonation of the acidic CH_2 of the bis(oxazoline) ligand at low temperature and subsequent quenching with a metal salt. This strategy allowed the development of efficient



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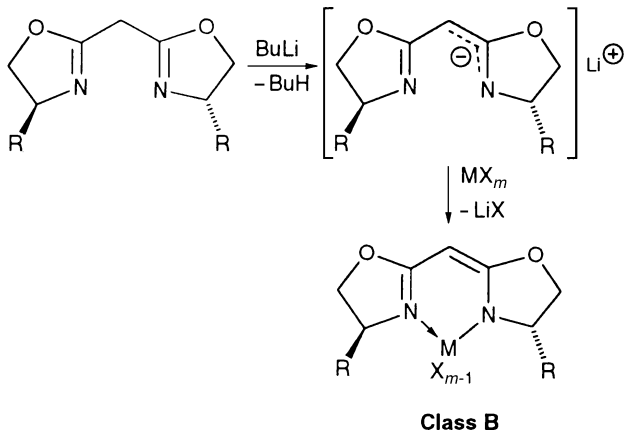
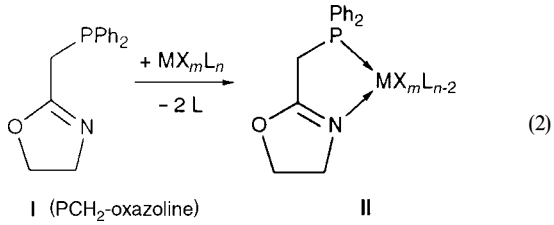


(1)

Ti,[19,20] Cu,[21,22] Rh,[23] Zn[24,25] or Mg[26] catalysts for several asymmetric reactions such as reduction of ketones,[20] cyclopropanation of olefins,[21,22] allylzincation,[24,25] and hydrocyanation of aldehydes.[26] The precatalysts are usually prepared *in situ* and not isolated (Zn, Mg, Ti) and only three crystal structures have been determined by X-ray diffraction, for the Cu,[27] Rh[23] and Y[28] complexes.

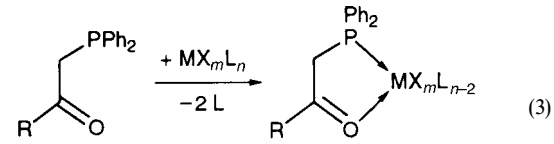
We have previously reported the synthesis of Pd and Ru complexes of type **II** bearing the neutral *P*,*N*-type ligand (oxazolinylmethyl)diphenylphosphine **I** (abreviated PCH_2-oxazoline) [eqn. (2)] and studied their catalytic properties for ethylene/CO copolymerization and asymmetric transfer hydrogenation of ketones, respectively.[29,30]



(2)

I (PCH_2-oxazoline) II

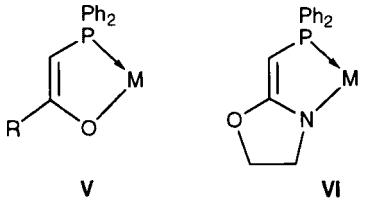
This provided an extension to work carried out by several groups, including ours, on bifunctional phosphorus ligands and more specifically on phosphorus/oxygen *P*,*O*-type ligands **III** [eqn. (3)].[2,31–37]



(3)

III R = Ph, OEt, NPh_2 IV

The often encountered hemilabile character of such neutral ligands in complexes of type **IV** allows for the temporary protection and facile generation of reactive sites in the coordination sphere of their complexes and several of them have been used in homogeneous catalysis. An additional feature of these *P*,*O*-type ligands is that the acidity of their PCH_2 protons allows facile deprotonation of this group to form an *anionic* 4-electron donor phosphino enolate ligand, with loss of the hemilabile behaviour. These strong chelates confer special reactivity to their complexes **V**, as found, for example, in the reversible CO_2 fixation by palladium complexes,[38,39] the rhodium-catalysed transfer dehydrogenation of cyclooctane[40] and the highly selective nickel-catalysed conversion of ethylene into linear α-olefins.[41–47]



V VI

This dramatic change in reactivity observed when going from neutral to anionic *P*,*O*-type ligands triggered our interest for new anionic *P*,*N*-type ligands derived from **I**, in which the acidity of the PCH_2 protons should also allow easy deprotonation, particularly after coordination to a metal centre. Here we report the synthesis of such complexes containing a phosphine moiety covalently linked to an oxazoline, whose nitrogen atom formally carries the partly delocalised negative charge, thus resulting in the formation of a covalent rather than dative N–M bond, as depicted in **VI**. The corresponding ligand, abreviated PCH-oxazoline, is the first representative of a new class of hybrid ligands, which combines some of the features of B and **V** type systems. In addition to the synthesis of palladium(II) complexes, we present a comparison of the catalytic activity of ruthenium(II) complexes containing PCH_2-oxazoline (type **II**) or PCH-oxazoline (type **VI**) ligands for transfer hydrogenation of acetophenone in propan-2-ol. A preliminary communication on related systems where the oxazoline carries two methyl groups on the carbon α to nitrogen has appeared.[48]

Results and discussion

Complexes with the neutral PCH_2-oxazoline ligand I

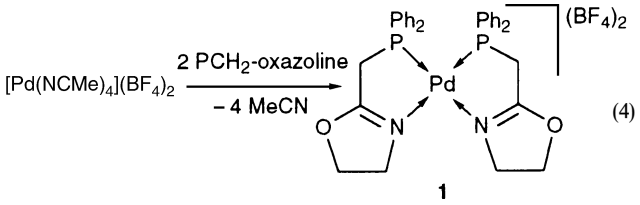
Mixing 2 equiv. of PCH_2-oxazoline with 1 equiv. of $[Pd(NCMe)_4](BF_4)_2$ in CH_2Cl_2 [eqn. (4)] led to the formation

Table 1 Selected NMR and IR data

	NMR[a]			IR/cm^{-1} (CH_2Cl_2)	
Complex	^1H[b]	$^{13}C\{^1H\}$[c] ($^1J_{PC}$/Hz)	$^{31}P\{^1H\}$[d]	ν(C=N)	ν(C≡C≡N)
***cis*-[Pd(PCH_2-oxazoline)$_2$](BF_4)$_2$, 1**	3.75 (d) PCH_2[e]	—	29.7[e]	1633	—
[Pd(dmba)Cl(PCH_2-oxazoline)], **2**	3.65 (d) PCH_2[e]	31.5 (25.2)	32.6[e]	1660, 1631	—
Pd(dmba)(PCH_2-oxazoline)][PF_6), **3**	3.45 (d) PCH_2[e]	—	32.8[e]	1635	—
[RuCl(η^6-*p*-cymene)(PCH_2-oxazoline)]Cl, **4**	3.30 (dd), 3.40 (dd), PCH_2	30.5 (34.0)	50.5	1641	—
cis-[Pd(PCH-oxazoline)$_2$], **6**	2.60 (s) PCH	41.2 (78.5)	20.5	—	1538
[Pd(dmba)(PCH-oxazoline)], **7**	2.82 (s) PCH	40.7 (82.5)	24.4	—	1537
[RuCl(η^6-*p*-cymene)(PCH-oxazoline)], **8**	3.10 (s) PCH	37.0 (78.8)	40.5	—	1546

[a] In CD_2Cl_2, unless otherwise stated. [b] 300.13 MHz. [c] 75.4 MHz. [d] 121.5 MHz. [e] In $CDCl_3$.

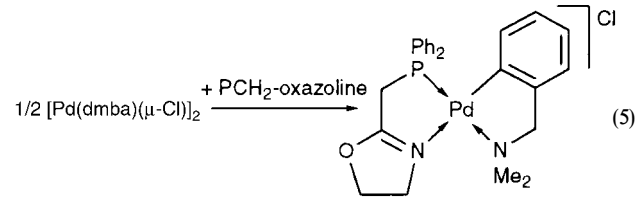
of [Pd(PCH_2-oxazoline)$_2$](BF_4)$_2$ (**1**) in high yield (95%).



(4)

1

The spectroscopic data (Table 1) are consistent with the coordination of the ligand in a static bidentate fashion.[29] The *cis* arrangement of the P atoms is deduced from the $^{31}P\{^1H\}$ NMR chemical shift and from the doublet observed in the ^1H NMR spectrum for the PCH_2 protons. Such an arrangement for two atoms of large *trans* influence is thermodynamically favoured.[49,50] Moreover, the related Ni complex [Ni(phosphinoaryloxazoline)$_2$]$^{2+}$ has been recently shown to have a *cis* structure, both in solution and in the solid state.[51]



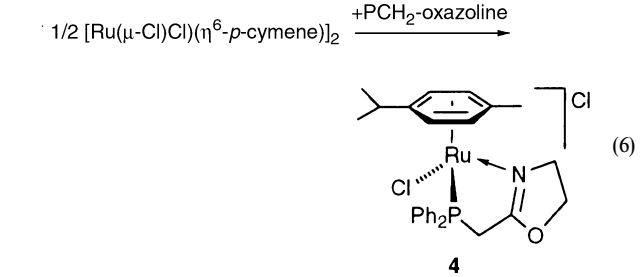
(5)

2

Reaction of PCH_2-oxazoline with [Pd(dmba)(μ-Cl)]$_2$ afforded **2** *via* opening of the chloride bridges [eqn. (5)].

The IR spectrum of **2** in CH_2Cl_2 shows two bands at 1660 and 1631 cm^{-1}, assigned to the C=N vibrations of the uncoordinated and coordinated oxazolines, respectively, by analogy with the values for the free ligand (1660 cm^{-1})[29] and for **1**. For comparison, we prepared the PF_6 analogue of **2** by carrying out the reaction in the presence of NH_4PF_6 (see Experimental). As expected, its IR spectrum in CH_2Cl_2 exhibits only one band at 1635 cm^{-1}. Therefore, the existence of coordinated and uncoordinated oxazolines in solutions of **1** suggests competition between the oxazoline nitrogen and the chloride for coordination to palladium. Comparison of the $^{31}P\{^1H\}$ and ^1H NMR spectra with those of the free ligand confirms that PCH_2-oxazoline forms a *P,N*-chelate, but the broad resonances of the oxazoline protons are again consistent with a hemilabile behaviour of the ligand through reversible oxazoline nitrogen (de)coordination. For the first time, this ligand is shown to display a hemilabile behaviour.[2]

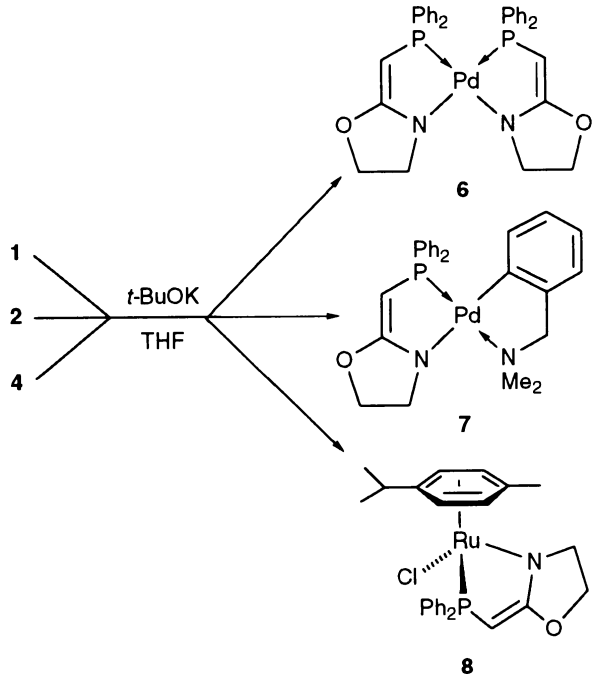
Reaction of 2 equiv. of PCH_2-oxazoline with 1 equiv. of [Ru(μ-Cl)Cl(η^6-*p*-cymene)]$_2$ in refluxing EtOH [eqn. (6)] led to the isolation of [RuCl(η^6-*p*-cymene)(PCH_2-oxazoline)]Cl (**4**) in good yield (89%).



(6)

4

In contrast to **2**, which also has Cl^- as a counter ion, the IR spectrum of **4** exhibits only one C=N vibration band at 1641 cm^{-1}, which corresponds to a coordinated oxazoline. The ^1H NMR spectrum shows that the protons of the PCH_2-oxazoline ligand appear at six distinct resonances and are thus diastereotopic. This is consistent with the ruthenium centre becoming a stereogenic centre upon chelation of PCH_2-oxazoline. The PCH_2 protons exhibit an ABX spin system with two different $^2J_{PH}$ coupling constants (8.5 and 13.0 Hz).



Scheme 1

The analogous complex, [RuCl(η^6-C_6H_6)(PCH_2-oxazoline)](O_3SCF_3) (**5**), was prepared for catalytic purposes in order to allow comparison with related complexes containing a tridentate NPN ligand (see below). Its spectroscopic properties are very similar to those of **4** (see Experimental).

These cationic PCH_2-oxazoline complexes were mainly used as precursors for the synthesis of complexes containing the anionic PCH-oxazoline ligand (see below).

Complexes with the anionic PCH-oxazoline ligand

The deprotonation of the PCH_2 group in complexes **1**, **2** and **4** in THF was achieved in 78–86% yields, by reaction with Bu^{t}OK (Scheme 1).[48] This simple and efficient methodology has been reported before with β-ketophosphines of the type $R^1_2PCH_2C(O)R^2$ coordinated to Re,[52] Fe,[53] Ru,[54–56] Rh,[40,57] Pd,[58] or Pt,[59] using various bases.

In all cases, the typical ν(C=N) IR absorption band of the coordinated oxazoline in the precursor complex is replaced by a strong absorption in the range 1537–1546 cm^{-1} (see Table 1). This is consistent with the IR data of a Cu complex described by Lehn *et al.*, which shows an absorption band at 1530 cm^{-1}.[27] The shift towards lower energy by about 100 cm^{-1} on going from PCH_2-oxazoline to anionic PCH-oxazoline is consistent with previous observations made with *P,O*-ligands when going from **IV** to **V**. The PCH carbon appears in the $^{13}C\{^1H\}$ NMR spectrum as a doublet downfield shifted (6.5–9 ppm) compared to the corresponding PCH_2 and exhibits a larger $^1J_{PC}$ coupling constant, 78.5–82.5 Hz *vs.* 25.2–34.0 Hz, respectively. This increase is attributed to the change in hybridisation of the carbon atom α to P from sp^3 in the neutral chelate to sp^2 in the anionic one. While the PCH_2 protons of complexes **1**–**5** exhibit in the ^1H NMR spectrum a doublet, the PCH proton of **6**–**8** exhibits only a singlet. Complexes **6**–**8** are air-stable and, in contrast to their precursors, they react with $CDCl_3$ to give uncharacterised side products. An X-ray diffraction study on single crystals of **6** confirmed that the two phosphorus atoms occupy *cis* positions (Fig. 1 and Table 2). The coordination around the metal centre approximates a square planar geometry with a slight displacement of the Pd–N(2) vector from the plane defined by the two phosphorus, two nitrogen and palladium atoms [0.150(3) Å]. The non-ideal geometry is also reflected by the angles P(1)–Pd–P(2) and N(1)–Pd(1)–N(2) of 102.16(4)° and

Table 2 Selected bond lengths (Å) and angles (°) for *cis*-[Pd(PCH-oxazoline)$_2$], (**6**)

Pd(1)–P(1)	2.286(1)	N(1)–C(2)	1.335(4)
Pd(1)–P(2)	2.293(1)	C(2)–C(1)	1.370(5)
Pd(1)–N(1)	2.074(3)	C(1)–P(1)	1.737(4)
Pd(1)–N(2)	2.073(3)	C(2)–O(1)	1.380(4)
N(1)–Pd(1)–N(2)	94.40(11)	N(1)–C(2)–C(1)	125.6(3)
N(2)–Pd(1)–P(2)	81.42(8)	C(2)–C(1)–P(1)	112.1(3)
P(2)–Pd(1)–P(1)	102.16(4)	C(1)–P(1)–Pd(1)	102.0(1)
P(1)–Pd(1)–N(1)	82.20(8)	O(1)–C(2)–C(1)	121.3(3)
Pd(1)–N(1)–C(2)	116.2(2)	O(1)–C(2)–N(1)	113.1(3)

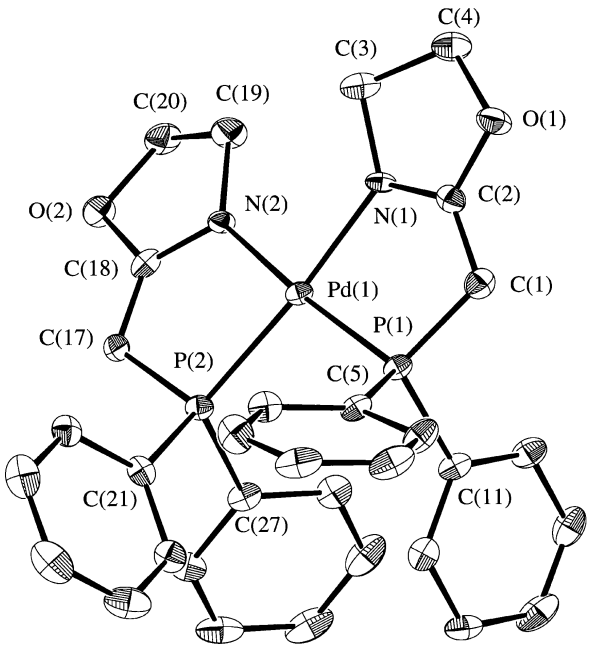
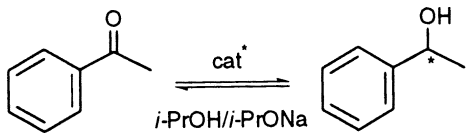


Fig. 1 ORTEP view of the crystal structure of *cis*-[Pd(PCH-oxazoline)$_2$] (**6**).

94.40(1)°, respectively. The two planes defining the backbone of the *P*,*N*-chelates, Pd(1), P(1), N(1), C(1), C(2) and Pd(1), P(2), N(2), C(17), C(18), form a dihedral angle of 1.9°. However, the angle between the two planes O(1), N(1), C(2), C(3), C(4) and O(2), N(2), C(18), C(19), C(20), corresponding to the two oxazolines, form a dihedral angle of 28.8°, which results in a staggered arrangement for the NCH_2 protons. It is interesting to compare the distances and angles of PCHox in **6** with those of the neutral PCH_2-oxazoline-Me_2 ligand in [$PdCl_2$(PCH_2-oxazoline-Me_2)] where PCH_2-oxazoline-Me_2 is similar to PCH_2-oxazoline but has two methyl substituents on the carbon α to the nitrogen atom.[29] Of special interest are the bond lengths and angles within the five-membered ring chelates. The C–C bond distance decreases on going from the neutral to the anionic ligand [1.480(4) to 1.370(5) Å, respectively] and this latter value is close to the average length of a C=C (sp^2–sp^2) bond (1.34 Å). At the same time, the C–N bond length increases from 1.276(4) to 1.335(4) Å, which is in favour of a single C–N bond [average $d(C_{sp^2}–N) = 1.36$ Å]. Even though it is likely that electron delocalisation occurs within the chelate ring, we prefer to describe the bonding within the five-membered *P*,*N*-chelate as involving a pronounced C=C double bond character. The X-ray crystal structure of **6** is significant since there are only three reported X-ray crystal structures of an anionic oxazoline in a class **B** complex (M = Cu,[27] Rh,[23] Y[28]) although this bonding mode is often invoked, and the only example with a PCH-oxazoline-type ligand.[48]

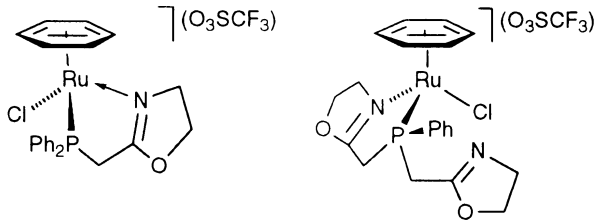
Catalytic study

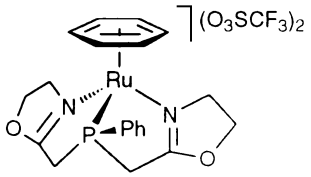
As part of our interest in the properties of multidentate ligands that contain both phosphine and oxazoline in a chelating array,[2] we have tested their ruthenium complexes in the catalytic transfer hydrogenation of ketones by propan-2-ol [eqn. (7)].[30,48,60,61] There is considerable current research activity around this reaction in order to both develop new classes of catalysts and to understand the different steps involved in the overall catalytic process.[62–67]



(7)

We recently described a precursor catalyst for this reaction, [RuCl(η^6-C_6H_6)(*N*,*P*-NPN)](O_3SCF_3) (**9**) where NPN is a bis(oxazoline)phosphine that forms a bidentate *P*,*N*-chelate.[60] It was shown that the dangling oxazoline arm of this ligand tends to have a detrimental effect on the catalytic activity, possibly owing to the formation of a bis-chelating system of type **10**.[60] This is now further supported by the observation that complex **5** is more active than **9** and **10** (see Table 3).





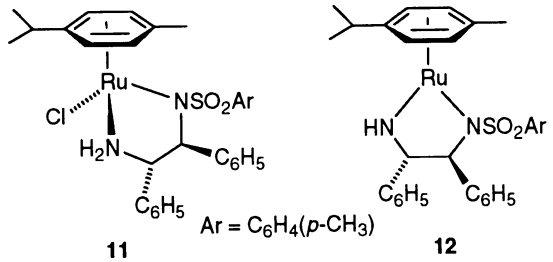
In light of our synthetic route to prepare complexes bearing the anionic ligand, it is likely that under catalytic conditions, the Pr^{i}ONa base, which is present in a 5-fold excess to Ru, reacts with the precursor catalyst **4** to form compound **8**. To test this hypothesis we used **8** as the catalyst precursor. Whereas the conversion obtained after 6 h at reflux temperature in propan-2-ol was identical to that observed with **4** (94% yield), the turnover frequency (TOF) was higher with [RuCl(η^6-*p*-cymene)(PCH-oxazoline)] than with [RuCl(η^6-*p*-cymene)(PCH_2-oxazoline]Cl during the first hour (Table 3). This may correspond to an induction period to form the catalyst **8**. Although it appears that **4** gives **8** under catalytic conditions, we cannot rule out that both **4** and **8** may be independently active catalysts for transfer hydrogenation. Noyori *et al.* have recently published[67] the structure of a preformed catalyst precursor **11**, which upon *in situ* deprotonation of the NH group generates the true catalyst **12** which is to date among the best catalysts for transfer hydrogenation of ketones.[68,69] These results emphasise the spectacular conse-

Table 3 Transfer hydrogenation of acetophenone in propan-2-ol catalyzed by Ru(II) complexes[a]

Catalyst	Time/h	Yield[b] (%)	Turnover/h^{-1}
4	0.25	5	40
	1	34	68
	3	75	50
	6	94	32
5	0.25	23	184
	1	61	122
8	0.25	25	200
	1	49	98
	3	86	58
	6	94	32
8[c]	8	16	4
9[d]	0.25	13.5	108
	1	54	108
10[d]	0.25	11	88
	1	45	90

[a] The reactions were carried out in refluxing propan-2-ol using a 0.1 M substrate concentration and a 0.1 M solution of Pr^iONa as a base and a 1 : 200 : 5 Ru–ketone–base ratio. [b] Chemical yields determined by GC analysis of the crude reaction mixture at the reported time. [c] Reaction carried out in propan-2-ol at 30 °C. [d] Taken from ref. 60 with a 1:200:24 Ru–ketone–base ratio.

quences that ligand deprotonation may have on the catalytic properties of the metal complex.



Compound [RuCl(η⁶-*p*-cymene)(PCH-oxazoline)] (**8**) is very similar to **11** with the difference that the PCHox ligand in **8** cannot be further deprotonated to form species analogous to **12**.[67a] This could account for the higher reactivity of **11** compared to **8**. Nevertheless, our results are encouraging and complexes analogous to [RuCl(η⁶-*p*-cymene)(PCH-oxazoline)] with a chiral version of PCH_2-oxazoline should be synthesised in the future. Furthermore, Noyori *et al.* have shown that the arene ligand has a strong influence on the reactivity and enantioselectivity of the catalysts, suggesting that complexes containing other arene ligands such as benzene or 1,3,5-trimethylbenzene should also be evaluated.[70]

Conclusion

The versatility of the PCH_2-oxazoline ligand allows its coordination as hemilabile or static neutral *P*,*N*- or static anionic *P*,*N*-type ligand. It was shown that in the latter case its structural and electronic properties induce higher reactivity in the catalytic transfer hydrogenation of acetophenone in propan-2-ol than its neutral analogue. This finding should lead to further investigations with chiral versions of PCH-oxazoline in order to study their influence on the enantioselectivity of this catalytic reaction. Also as an extension to this work, it would be interesting to evaluate our Ru-phosphinooxazoline complexes in Diels–Alder reactions, since a [Ru(H_2O)(η⁶-*p*-cymene)-phosphinoaryloxazoline]$^{2+}$ complex has been recently reported to be a good catalyst for such reactions.[71]

Experimental

General procedures

All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13, 75.4 and 121.5 MHz, respectively, on an FT Bruker AC300 instrument, $^1H\{^{31}P\}$ NMR at 500.13 MHz on an FT Bruker ARX500 instrument, chemical shifts are positive downfield from external TMS for ^1H and ^{13}C, and from H_3PO_4 (85% in H_2O) for ^{31}P. IR spectra were recorded in the 4000–400 cm^{-1} range on a Bruker IFS66 FT spectrometer.

Syntheses

The compounds [Pd(dmba)(μ-Cl)]$_2$,[72] [Ru(μ-Cl)Cl(η⁶-*p*-cymene)]$_2$,[73] and [Pd(NCMe)$_4$](BF$_4$)$_2$[74] were prepared according to literature procedures.

***cis*-[Pd(PCH_2-oxazoline)$_2$](BF$_4$)$_2$ (1).** In a 100 mL Schlenk flask were placed together the ligand PCH_2-oxazoline (0.715 g, 2.660 mmol) and [Pd(NCMe)$_4$](BF$_4$)$_2$ (0.590 g, 1.330 mmol) in CH_2Cl_2 (40 mL). The pale yellow solution was stirred for 12 h and the volume reduced under vacuum to about 5 mL. Addition of pentane afforded a white solid, which was further washed with Et_2O (2 × 10 mL) and dried *in vacuo*. The product was obtained as a white solid (1.035 g, yield 95%). ^1H NMR ($CDCl_3$, 300.13 MHz): δ 3.75 (d, 4 H, $^2J_{PH}$ = 11.9 Hz, PCH_2), 4.40 (t, 4 H, $^3J_{HH}$ = 9.5 Hz, NCH_2), 4.80 (t, 4 H, $^3J_{HH}$ = 9.5 Hz, OCH_2), 7.30–7.65 (m, 20 H, aryl). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 29.7. Anal. calc. for $C_{32}H_{32}B_2F_8N_2O_2P_2Pd$: C, 46.95; H, 3.94; Found: C, 47.22; H, 3.68%.

[Pd(dmba)(PCH_2-oxazoline)]Cl (2). In a 100 mL Schlenk flask were placed together the phosphine oxazoline ligand PCH_2-oxazoline (1.095 g, 4.070 mmol) and [Pd(dmba)(μ-Cl)]$_2$ (1.120 g, 2.03 mmol) in CH_2Cl_2 (30 mL). The pale yellow solution was stirred for 1 h after which the volume was reduced under vacuum to about 3 mL. Addition of hexane led to the precipitation of a colourless oil, which was triturated with Et_2O (2 × 5 mL); the solid thus obtained was washed with hexane (2 × 30 mL) and dried under vacuum. The product was obtained as a white powder (1.995 g, 90%). ^1H NMR ($CDCl_3$, 300.13 MHz): δ 2.90 [s, 6 H, $N(CH_3)_2$], 3.65 (d, 2 H, $^2J_{PH}$ = 8.4 Hz, PCH_2), 4.05 [overlapping s and m, 4 H, $(CH_3)_2NCH_2$ and oxazoline NCH_2], 4.45 (t, 2 H, $^3J_{HH}$ = 9.4 Hz, OCH_2), 6.30–7.00 (m, 4 H, aryl from dmba), 7.40–7.90 (m, 10 H, aryl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 31.5 (d, $^1J_{PC}$ = 25.2 Hz, PCH_2), 51.0 [s, $N(CH_3)_2$], 54.7 (s, NCH_2), 69.5 [s, $(CH_3)_2NCH_2$], 73.0 (s, OCH_2), 123.2–149.5 (m, aryl), 167.7 (d, $^2J_{PC}$ = 10.9 Hz, C=N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 32.6. Anal. calc. for $C_{25}H_{28}ClN_2OPPd$: C, 55.06; H, 5.18; N, 5.14. Found: C, 55.20; H, 5.17; N, 5.04%.

[Pd(dmba)(PCH_2-oxazoline)](PF$_6$) (3). In a 100 mL Schlenk flask were placed together [Pd(dmba)(PCH_2-oxazoline)]Cl (**2**) (0.400 g, 0.737 mmol) and NH_4PF_6 (0.122, 0.740 mmol) in CH_2Cl_2 (30 mL). The pale yellow solution was stirred for 2 h after which the solution was filtered through Celite and its volume reduced under vacuum to about 2 mL. Addition of pentane led to the precipitation of a pale yellow solid, which was further washed with Et_2O (2 × 10 mL) and dried *in vacuo*. The product was obtained as a pale yellow solid (0.438 g, 91%). ^1H NMR ($CDCl_3$, 300.13 MHz): δ 2.90 [s, 6 H, $N(CH_3)_2$], 3.45 (d, 2 H, $^2J_{PH}$ = 10.5 Hz, PCH_2), 4.00 [s, 2 H, $(CH_3)_2NCH_2$], 4.05 (t, 2 H, $^3J_{HH}$ = 11.1 Hz, oxazoline NCH_2), 4.60 (t, 2 H, $^3J_{HH}$ = 11.1 Hz, OCH_2), 6.40–7.00 (m, 4 H, aryl from dmba), 7.40–7.90 (m, 10 H, aryl). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 32.8. Anal. calc. for $C_{25}H_{28}N_2OP_2Pd$: C, 45.85; H, 4.31. Found: C, 45.61; H, 4.22%.

Table 4 Selected crystallographic data for complex *cis*-[Pd(PCH-oxazoline)$_2$], **6**

Formula	$C_{32}H_{30}N_2O_2P_2Pd$
FW	642.95
Crystal system	Monoclinic
Space group	$P21/n$ (no. 14)
T/K	180(1)
a/Å	17.293(2)
b/Å	9.7528(13)
c/Å	17.6784(6)
β/°	115.2840
U/Å^3	2695.9(4)
Z	4
μ/mm^{-1}	8.42
No. of reflections collected	24477
No. of unique reflections	6934
No. of variable parameters	352
No. of reflections [$I > 3\sigma(I)$]	4082
Residuals (R, R_w)[a]	0.037, 0.031

[a] $R = \Sigma_{hkl}(\| F_{obs} \| - \| F_{calc} \|)/\Sigma_{hkl} \| F_{obs} \|$; $R_w = [\Sigma_{hkl} w(\| F_{obs} \| - \| F_{calc} \|)^2/\Sigma_{hkl} w F_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$.

[RuCl(η^6-*p*-cymene)(PCH$_2$-oxazoline)]Cl (4). In a 100 mL Schlenk flask fitted with a reflux condenser were placed together the ligand PCH$_2$-oxazoline (0.138 g, 0.513 mmol) and [Ru(μ-Cl)Cl(η^6-*p*-cymene)]$_2$ (0.157 g, 0.256 mmol) in EtOH (15 mL). The yellow solution was heated to reflux temperature for 1.5 h, then cooled to room temperature and the solvent was removed under vacuum. The solid was partially dissolved in THF (2 mL) and precipitated by addition of pentane (15 mL). This procedure was repeated twice and afforded the product as a yellow powder (0.260 g, yield: 89%). ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 1.15 [d, 3 H, $^2J_{HH} = 6.8$ Hz, CH(C*H*$_3$)(CH$_3$)], 1.25 [d, 3 H, $^2J_{HH} = 6.8$ Hz, CH(CH$_3$)(C*H*$_3$)], 1.50 (s, 3 H, *p*-CH$_3$), 2.50 [sept, 1 H, $^2J_{HH} = 6.8$ Hz, C*H*(CH$_3$)$_2$], ABX spin system δ_A 3.30 (dd, 1 H, $^2J_{HH} = 17$ Hz, $^2J_{PH} = 8.5$ Hz, PC*H*$_A$H), δ_B 3.40 (dd, 1 H, $^2J_{HH} = 17$ Hz, $^2J_{PH} = 13.0$ Hz, PCH*H*$_B$), 4.10 (dd, 1 H, $^2J_{HH} = 21.0$ Hz, $^3J_{HH} = 10.4$ Hz, OC*H*H), 4.75 (dd, 1 H, $^2J_{HH} = 14.2$ Hz, $^3J_{HH} = 7.5$ Hz, NC*H*H), 5.10 (dd, 1 H, $^2J_{HH} = 21.0$ Hz, $^3J_{HH} = 10.4$ Hz, OCH*H*), 5.20 (m, 1 H, NCH*H*), 5.60 (d, 1 H, $^3J_{HH} = 5.8$ Hz, *p*-cymene), 5.70 (d, 1 H, $^3J_{HH} = 5.8$ Hz, *p*-cymene), 6.15 (d, 1 H, $^3J_{HH} = 6.0$ Hz, *p*-cymene), 6.25 (d, 1 H, $^3J_{HH} = 6.0$ Hz, *p*-cymene), 7.30 (m, 2 H, aryl), 7.40–7.70 (m, 8 H, aryl H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.4 MHz): δ 17.4 (s, *p*-CH$_3$), 21.8 [s, CH(*C*H$_3$)(CH$_3$)], 22.8 [s, CH(CH$_3$)(*C*H$_3$)], 30.5 (d, $^1J_{PC} = 34$ Hz, PCH$_2$), 31.2 [s, *C*H(CH$_3$)$_2$], 58.6 (s, NCH$_2$), 73.5 (s, OCH$_2$), 84.7 (s, aromatic *p*-cymene), 87.3 (d, $J_{PC} = 6.6$ Hz, aromatic *p*-cymene), 89.3 (d, $^2J_{PC} = 6.9$ Hz, aromatic *p*-cymene), 101.4 (s, aromatic *p*-cymene), 117.1 (d, $J_{PC} = 4.7$ Hz, aromatic *p*-cymene), 126.2–135.5 (m, aryl), 175.6 (d, $^2J_{PC} = 16.9$ Hz, C=N). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 50.5. Anal. calc. for $C_{26}H_{30}NOPCl_2Ru$: C, 54.20; H, 5.21; N, 2.43. Found: C, 54.17; H, 5.31; N, 2.27%.

[RuCl(η^6-benzene)(PCH$_2$-oxazoline)](O$_3$SCF$_3$) (5). In a 100 mL Schlenk flask were placed together the ligand PCH$_2$-oxazoline (0.210 g, 0.78 mmol) and [Ru(μ-Cl)Cl(η^6-benzene)]$_2$ (0.195 g, 0.39 mmol) in CH_2Cl_2 (15 mL). The dark orange solution obtained was stirred for 1 h at room temperature and then filtered through a canula 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$_3$) (0.200 g, 0.78 mmol) and 20 mL of CH_2Cl_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 volume of the orange filtrate was reduced under vacuum to *ca.* 2 mL. Addition of Et_2O afforded a yellow solid, which was further washed with 10 mL of hexane and Et_2O. Pure **5** was obtained by crystallisation from 1 : 3 CH_2Cl_2–hexane (0.375 g, 75%). ^{1}H NMR ($CDCl_3$, 300.13 MHz): ABX spin system δ_A 3.25 (dd, 1 H, $^2J_{HH} = 17.5$ Hz, $^2J_{PH} = 8.5$ Hz, PC*H*$_A$H), δ_B 3.40 (dd, 1 H, $^2J_{HH} = 17.5$ Hz, $^2J_{PH} = 12.5$ Hz, PCH*H*$_B$), 4.15 (m with appearance of overlapping dt, 1 H, $J_{HH} = 10.2$ Hz, $J_{HH} = 10.5$ Hz, OC*H*H), 4.75 (m, 1 H, NC*H*H), 4.90 (m, NCH*H*), 5.20 (m with appearance of overlapping dt, 1 H, $J_{HH} = 8.5$ Hz, $J_{HH} = 9.6$ Hz, OCH*H*), 5.80 (s, 6 H, η^6-benzene), 7.30 (m, 2 H, aryl), 7.50–7.80 (m, 8 H, aryl H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 48.4. Anal. calc. for $C_{24}H_{26}ClF_3NO_4PSRu$: C, 44.38; H, 4.04; N, 2.16. Found: C, 44.49; H, 3.95; N, 2.27%.

***cis*-[Pd(PCH-oxazoline)$_2$] (6).** In a 100 mL Schlenk flask were placed together *cis*-[Pd(PCH$_2$-oxazoline)$_2$](BF$_4$)$_2$ (1.005 g, 1.228 mmol) and Bu^{t}OK (0.305 g, 2.700 mmol) in THF (30 mL). The colourless suspension turned red–orange within 15 min with formation of a white precipitate; the reaction mixture was then stirred for 12 h. The solvent was removed under reduced pressure and CH_2Cl_2 (30 mL) was added. The white precipitate was filtered off by means of a canula fitted with glass fiber filter paper. The volume of the solution was reduced under vacuum to about 4 mL; addition of Et_2O afforded an orange solid, which was further washed with Et_2O (2 × 20 ml) and dried *in vacuo*. The product was obtained as an orange powder (0.616 g, yield 78%). ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 2.60 (s, 1 H, PCH), 3.90 (t, 2 H, $^3J_{HH} = 7.9$ Hz, NCH$_2$), 4.35 (t, 2 H, $^3J_{HH} = 7.9$ Hz, OCH$_2$), 7.00–7.40 (m, 20 H, aryl). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.4 MHz): δ 41.2 (d, $^1J_{PC} = 78.5$ Hz, PCH), 52.7 (s, NCH$_2$), 70.1 (s, OCH$_2$), 126.5–135.0 (m, aryl), 180.5 (d, C=N). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 20.5. Anal. calc. for $C_{32}H_{30}N_2O_2P_2Pd$: C, 59.78; H, 4.70; N, 4.36. Found: C, 60.04; H, 4.62; N, 4.18%.

[Pd(dmba)(PCH-oxazoline)] (7). In a 100 mL Schlenk flask were placed together complex [Pd(dmba)Cl(PCH$_2$-oxazoline)] (1.020 g, 1.875 mmol) and Bu^{t}OK (0.220 g, 1.970 mmol) in THF (20 mL). The colourless suspension turned yellow within 5 min with formation of a white precipitate; the reaction mixture was stirred then for 12 h. The solvent was removed under reduced pressure and CH_2Cl_2 (30 mL) was added. The white precipitate was filtered off by means of a canula fitted with glass fiber filter paper. The volume of the solution was reduced under vacuum to about 4 mL; addition of pentane afforded a yellow solid, which was further washed with hexane (2 × 20 mL) and dried *in vacuo*. The product was obtained as a yellow powder (0.800 g, yield 84%). ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 2.80 [s, 6 H, N(CH$_3$)$_2$], 2.82 (s, 1 H, PCH), 3.70 (t, 2 H, $^3J_{HH} = 7.9$ Hz, oxazoline NCH$_2$), 3.95 [s, 2 H, (CH$_3$)$_2$NC*H*$_2$], 4.30 (t, 2 H, $^3J_{HH} = 7.9$ Hz, OCH$_2$), 6.55–7.00 (m, 4 H, aryl from dmba), 7.40–7.70 (m, 10 H, aryl). ^{13}C{^{1}H} (CD_2Cl_2, 75.4 MHz): δ 40.7 (d, $^1J_{PC} = 82.5$ Hz, PCH), 50.9 [s, N(CH$_3$)$_2$], 52.2 (s, oxazoline NCH$_2$), 69.3 [s, (CH$_3$)$_2$NCH$_2$], 73.3 (s, OCH$_2$), 122.8–149.5 (m, aryl). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 24.4. Anal. calc. for $C_{25}H_{27}N_2OPPd$: C, 59.01; H, 5.35; N, 5.50. Found: C, 58.79; H, 5.22; N, 5.46%.

[RuCl(η^6-*p*-cymene)(PCH-oxazoline)] (8). In a 100 mL Schlenk flask were placed together [RuCl(η^6-*p*-cymene)-(PCH$_2$-oxazoline)]Cl (0.440 g, 0.765 mmol) and Bu^{t}OK (0.090 g, 0.800 mmol) in THF (20 mL). The yellow solution turned orange within 5 min with formation of a white precipitate; the reaction mixture was then stirred for 12 h. The solvent was removed under reduced pressure and CH_2Cl_2 (30 mL) was added. The white precipitate was filtered off by means of a canula fitted with glass fiber filter paper. The volume of the deep orange solution was reduced under vacuum to about 4

mL; addition of Et_2O afforded a brown–orange solid, which was further washed with Et_2O (2 × 20 ml) and dried *in vacuo*. The product was isolated as a brown–orange powder (0.355 g, yield: 86%). ^1H NMR (CD_2Cl_2, 500.13 MHz): δ 0.95 [d, 3 H, $^2J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)(CH$_3$)], 1.10 [d, 3 H, $^2J_{HH}$ = 6.9 Hz, CH(CH$_3$)(C*H*$_3$)], 2.10 (s, 3 H, *p*-CH$_3$), 2.20 [sept, 1 H, $^2J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$], 3.10 (s, 1 H, PCH), 3.70 (m with appearance of t of d, $^2J_{HH}$ = 9.0 Hz, $^3J_{HHcis}$ = 9.0 Hz, $^3J_{HHtrans}$ = 3.6 Hz, OC*H*H), 3.85 (m with appearance of overlapping dt, 1 H, J_{HH} = 10.2 Hz, J_{HH} = 9.0 Hz, NC*H*H), 4.25 (m with appearance of overlapping dt, 1 H, J_{HH} = 10.2 Hz, J_{HH} = 7.8 Hz, OCH*H*), 4.25 (overlapping m, 1 H, J_{HH} = 1.2 Hz, *p*-cymene), 4.35 (m with appearance of t of d of d, $^2J_{HH}$ = 7.8 Hz, $^3J_{HHcis}$ = 7.8 Hz, $^3J_{HHtrans}$ = 3.6 Hz, $^5J_{HH}$ = 1.2 Hz, NCH*H*), 5.20 (d, 1 H, $^3J_{HH}$ = 6.2 Hz, *p*-cymene), 5.40 (d, 1 H, $^3J_{HH}$ = 5.7 Hz, *p*-cymene), 5.70 (d, 1 H, $^3J_{HH}$ = 6.2 Hz, *p*-cymene), 7.30–7.40 (m, 6 H, aryl), 7.50–7.70 (m, 4 H, aryl H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 18.4 (s, CH$_3$), 22.0 [s, CH(*C*H$_3$)(CH$_3$)], 23.0 [s, CH(CH$_3$)(*C*H$_3$)], 31.4 [s, *C*H(CH$_3$)$_2$], 37.0 (d, $^1J_{PC}$ = 78.8 Hz, PCH), 55.4 (s, NCH$_2$), 69.3 (s, OCH$_2$), 83.5 (s, Pr^i–C···CH from *p*-cymene), 84.5 (s, Me–C···CH from *p*-cymene), 88.6 (d, J_{PC} = 5.9 Hz, Pr^i–C···CH from *p*-cymene), 93.3 (d, J_{PC} = 5.9 Hz, Me–C···CH from *p*-cymene), 97.4 (s, quat C *p*-cymene), 103.1 (s, quat C *p*-cymene), 126.8–142.2 (m, aryl), 179.3 (d, $^2J_{PC}$ = 43.4 Hz, C=N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 40.5. Anal. calc. for $C_{26}H_{29}NOPRuCl$: C, 57.88; H, 5.38; N, 2.59. Found: C, 57.65; H, 5.29; N, 2.56%.

X-Ray structural analysis[75]

The intensity data were collected on a Rigaku/ADSC CCD diffractometer at 180(1) K in 0.50° oscillations with 35.0 s exposures. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions with C–H = 0.98 Å. Selected data are given in Table 4.

CCDC reference number 440/211. See http://www.rsc.org/suppdata/nj/b0/b004786o/ for crystallographic files in cif format.

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