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Unexpected and then rational synthesis of a new class of anionic phosphino–oxazoline ligands; structure and catalytic properties of a ruthenium complex†

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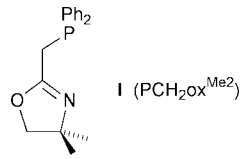
A new class of anionic, hybrid chelating ligands is reported which contain a phosphine moiety covalently linked to an oxazoline of which the nitrogen atom formally carries a partly delocalized negative charge; the first metal complex, a ruthenium derivative, has been characterized by X-ray diffraction and shown to be active in catalytic transfer hydrogenation.

The numerous synthetic pathways to oxazolines make them versatile synthons for ligand design[1] and their availability in enantiomeric pure forms accounts for the increasing use over the last 10 years of oxazoline-based ligands for asymmetric reactions catalyzed by transition metal complexes.[2] We have recently investigated the synthesis of Pd and Ru complexes with the neutral *P,N*-type ligand (oxazolinylmethyl)diphenylphosphine **I** (abreviated PCH_2ox^{Me2}) and studied their catalytic properties for ethylene/CO copolymerization and asymmetric transfer hydrogenation of ketones, respectively.[3]



I (PCH_2ox^{Me2})

We then felt it would be of interest to isolate Ru hydrido complexes of potential catalytic relevance but reactions of $[Ru(H)Cl(PPh_3)_3]$ or $[Ru(H)(OAc)(PPh_3)_3]$ with **I** were not selective and although hydrido species were observed by ^1H NMR spectroscopy, no pure complexes could be isolated. We then reacted $[Ru(OAc)(PCH_2ox^{Me2})_2]Cl$ **1**,† prepared from $[RuCl_2(PCH_2ox^{Me2})_2]$[3b] and Tl(OAc), with CsF in acetone in order to prepare a monofluoride derivative that could be subsequently cleanly transformed into a hydride complex.[4] The $^{31}P\{^1H\}$ NMR spectrum of the only product formed, **2**, exhibited an AB spin system at δ 46.8 and 58.3 with ^2J(PP) 35.8 Hz which, surprinsingly, showed no coupling with a ^{19}F nucleus. The reaction of $[RuCl_2(PCH_2ox^{Me2})_2]$ itself with CsF was found to be less selective and not further investigated. An X-ray diffraction study‡ established the ligand arrangement in **2** and the fact that one of the *P,N*-ligands had unexpectedly been deprotonated. The crystals contain two crystallographically independent, but almost identical, molecules (A and B). A view of the structure of one of them (A) is shown in Fig. 1. Both ligands (excepting for the substituents) are roughly planar, but in the deprotonated one the N(1)C(14)C(13)P(1) moiety is practically planar. The two Ru–N bond distances in the octahedral complexes differ remarkably and the shorter, 2.102(3) Å in (A) and 2.111(3) Å in (B), involves the N(1) atom bearing the partial negative charge. Whereas the double bond is mainly localized on the C–N bond in the PCH_2ox^{Me2} ligand [bond distance 1.281(4) Å in both A and B], electronic delocalization occurs within the N(1)C(14)C(13)P(1) moiety of $PCHox^{Me2}$, as indicated by the values of the C–C [1.370(5) Å in (A) and 1.371(5) Å in (B)], C–N [1.328(4) Å in (A) and 1.317(4) Å in (B)] and P–C [1.753(3) Å in (A) and 1.754(4) Å in (B)] bond distances. Consistently, the IR spectrum of **2** contains two bands at 1618 and 1535 cm^{-1} assigned to the C=N and C⋯N vibrations of PCH_2ox^{Me2} and $PCHox^{Me2}$, respectively. In the ^1H NMR spectrum, each proton in PCH_2ox^{Me2} and $PCHox^{Me2}$ appears as a single resonance in agreement with the lack of any symmetry element in the molecule.

The selective synthesis of **2** was unexpected and found to depend on the nature of the cation associated with the fluoride anion. Thus, reaction of **1** with LiF only afforded a low yield of **2**. A more rational and general access to the anionic chelate in **2** consisted in the reaction of **1** with Bu^tOK in THF and selective deprotonation of only one PCH_2 group was observed [eqn. (1)].

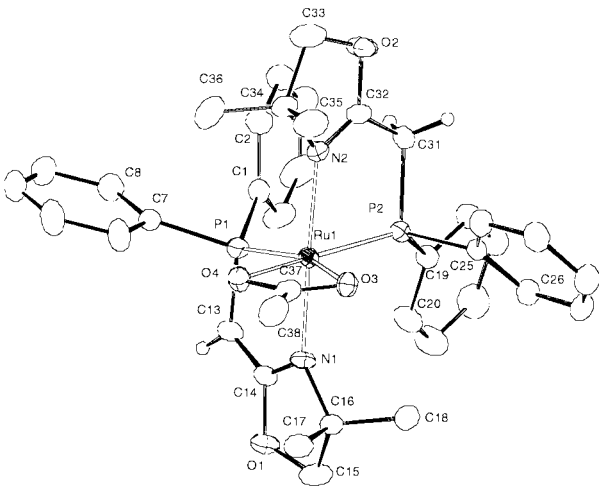


Fig. 1 View of the molecular structure of one (A) of the two crystallographic independent (A and B) molecules $[Ru(OAc)(PCHox^{Me2})(PCH_2ox^{Me2})]$ **3** together with the atomic numbering system. Selected bond distances (Å) and angles (°) in molecule A (values in square brackets refer to molecule B): Ru–P(1) 2.278(2) [2.270(1)], Ru–P(2) 2.226(1) [2.231(1)], Ru–N(1) 2.102(3) [2.111(3)], Ru–N(2) 2.166(3) [2.150(3)], Ru–O(3) 2.236(2) [2.228(2)], Ru–O(4) 2.209(2) [2.222(2)], P(1)–C(13) 1.753(3) [1.754(4)], C(13)–C(14) 1.370(5) [1.371(5)], C(14)–N(1) 1.328(4) [1.317(4)], C(16)–N(1) 1.495(4) [1.479(4)], P(2)–C(31) 1.857(4) [1.851(4)], C(31)–C(32) 1.474(5) [1.481(5)], C(32)–N(2) 1.281(4) [1.281(4)], C(34)–N(2) 1.515(4) [1.499(4)]; Ru–N(1)–C(14) 116.8(2) [116.5(2)], N(1)–C(14)–C(13) 126.3(3) [126.4(3)], C(14)–C(13)–P(1) 111.9(3) [111.7(3)], Ru–N(2)–C(32) 119.8(2) [119.6(2)], N(2)–C(32)–C(31) 124.8(3) [124.7(3)], C(32)–C(31)–P(2) 105.9(2) [106.7(3)].

† Electronic supplementary information (ESI) available: synthesis and spectral characterisation of **1**–**3**, See http://www.rsc.org/suppdata/cc/b0/b002515l/

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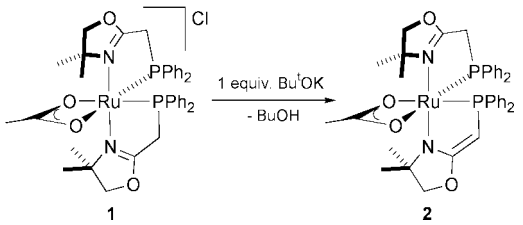
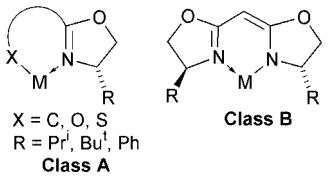
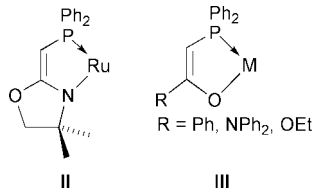


1 2 (1)

Anionic ligands incorporating an oxazoline ring are few compared to their neutral analogs and they belong to two main families. In class **A**, the anionic charge is carried by an exocyclic atom (C^-,[5] O^-,[6] S^- [7]) and the nitrogen atom of the oxazoline formally remains a neutral donor.

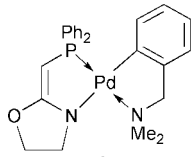


Some of their complexes are catalysts for, *e.g.* ethylene polymerization,[6a] sulfide oxidation,[8] alkyl- and phenyl-zincation of aldehydes[6b,c] and conjugate addition to enones.[7] In the second class of ligands, **B**, the anionic charge is partly localized on the nitrogen atom of the oxazoline but only one representative is known which has led to efficient Ti,[9] Cu,[10] Zn[11] or Mg[12] catalysts for several asymmetric reactions, *e.g.* reduction of ketones,[9b] cyclopropanation of olefins,[10] allylzincation,[11] and hydrocyanation of aldehydes.[12] Although there are two reported X-ray crystal structures of Cu[13] and Rh complexes,[14] the precatalysts were usually prepared *in situ* and not isolated (Zn, Mg, Ti).



The new ligand system in **II** provides an interesting extension to *anionic* four-electron donor phosphino enolate ligands of type **III** currently much investigated. These and related phosphorus/oxygen chelates confer special reactivity to their complexes, as found, *e.g.* in reactions with various organic or inorganic electrophiles[15] or in the highly selective convertion of ethylene into linear α-olefins.[16] The anionic ligand $PCHox^{Me2}$ found in **2** is therefore the first representative of a new class of hybrid ligands which combine some of the aspects of systems **B** and **III** and its chemistry therefore offers considerable potential. Preliminary catalytic studies with complex **2** have been performed for the transfer hydrogenation of aryl alkyl and dialkyl ketones by propan-2-ol, a reaction of current interest.[17] Under standard conditions ([Ru]/[ketone]/[PrⁱONa] = 1:200:5, [ketone] = 0.1 M, T = 82 °C), **2** exhibits very high to high activity for hydrogenation of acetophenone (98% yield in 5 min) and cyclohexylmethyl ketone (91% in 5 h) respectively.§

Access to complexes containing this new anionic *P,N*-ligand can be generalized, as shown with Pd since reaction of [Pd(dmba)Cl(PCH_2ox)] with BuᵗOK in THF afforded [Pd(dmba)(PCHox)] **3** in 84% yield.



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Notes and references

‡ *Crystal data* for **2**: $C_{38}H_{42}N_2O_4P_2Ru$, M = 753.75 monoclinic, space group $P2_1/c$, graphite monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 0.569 mm^{-1}, a = 18.256(4), b = 20.590(5), c = 20.454(5) Å, β = 111.28(6)°, V = 7164(3) $Å^3$, Z = 8, D_c = 1.398 g cm^{-3}. Philips PW 1100 diffractometer, θ–2θ scan technique, room temperature. 20871 Unique reflections measured ($3 < \theta < 30°$) and used in the refinement. All hydrogen atoms placed at their geometrically calculated positions and refined riding on their parent atoms, excepting those bonded to C(31) and C(13), which were localized in the final ΔF map and refined isotropically, wR_2 0.0876 and R_1 [for 8473 reflections with $I > 2\sigma(I)$] 0.0369. All calculations were carried out on the DIGITAL Alpha Station 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica " del CNR, Parma, using the SHELX-97 systems of crystallographic computer programs.[18] CCDC 182/1603. See http://wwww.rsc.org/suppdata/cc/b0/b002515l/ for crystallographic files in .cif format.

§ *Catalytic transfer hydrogenation*: Typical procedure for the catalytic transfer hydrogenation of acetophenone: **2** (0.0052 g, 0.0068 mmol) was dissolved in 13 mL PrⁱOH in a 50 mL two-neck round bottom flask fitted with a reflux condenser. Acetophenone (0.158 mL, 1.36 mmol) was added and the yellow solution was brought to reflux. The solution was stirred for 10 min and 0.36 mL (0.034 mmol) of a solution of PrⁱONa in PrⁱOH (0.1 M) was added. The volume of PrⁱOH was adjusted so that all catalytic runs were performed with an initial concentration in acetophenone of 0.1 M. The addition of PrⁱONa was considered as the starting time of the reaction. Conversion was determined by gas chromatography using a Lipodex A 25 m × 0.25 mm column.

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