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Contrasting bonding modes of a tridentate bis(oxazoline)phosphine ligand in cobalt and iron *vs.* palladium complexes: unprecedented *N*,*N*-coordination for a N,P,N ligand†‡§

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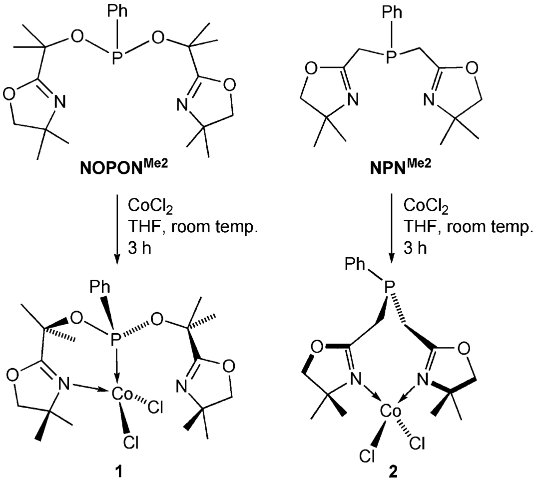
Unexpected *N*,*N*-coordination of the potentially tridentate *N*,*P*,*N*-ligand bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine occurs in Co(II) and Fe(II) complexes, in contrast to the *P*,*N*- or *N*,*P*,*N*-coordination modes observed in Pd(II) complexes; this leads to the formation of unprecedented eight-membered ring chelates.

Complexes containing oxazoline heterocycles are much used in asymmetric catalysis[1–5] and *P*,*N*-chelating phosphino-oxazoline ligands form metal complexes, with *e.g.* Ru(II), Ni(II) and Pd(II), which are efficient precatalysts in a number of reactions.[1,6,7] A pentacoordinated Ni(II) complex containing a tridentate *N*,*P*,*N*-ligand of the type bis(oxazolinyl)phenylphosphonite, NOPON^{Me2} (Scheme 1), catalyses ethylene oligomerisation.[8]



Scheme 1 *N*,*P*,*N* ligands and their use for the synthesis of the Co(II) complexes.

Square-planar palladium(II) complexes coordinated by this ligand display either a fluxional chelating *P*,*N*-coordination mode with chlorides or chloride and alkyl or η^1-allyl groups as co-ligands or a tridentate *N*,*P*,*N*-coordination mode when BF_4^- is a counter anion.[9] A related study on cationic Ru(II) benzene complexes also confirmed the role played by the counter anion on the coordination behaviour of the *N*,*P*,*N*-ligand bis(2-oxazolin-2-ylmethyl)phenylphosphine.[10]

The current interest in cobalt complexes with tridentate ligands for olefin oligomerization and polymerization[11–15] has led us to use the ligands NOPON^{Me2} and bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine (NPN^{Me2}) for the synthesize of new cobalt complexes (Scheme 1). The reactions of $CoCl_2$ with NOPON^{Me2} or NPN^{Me2} in a 1 : 1 molar ratio afforded complexes **1** and **2**, respectively.¶ Their magnetic moments of 3.8 and 4.0 μ_B, respectively, were determined by the Evans method[16,17] in CD_2Cl_2 and are slightly lower than expected for high spin d^7 Co(II) ions. As observed in the IR spectra of the corresponding Pd(II) complexes,[9] **1** presents two bands for the $\nu_{C=N}$ vibrations at 1682 and 1627 cm^{-1} which correspond to the uncoordinated and coordinated oxazolines, respectively. The crystal structure of **1** in $\mathbf{1}\cdot 0.5C_7H_8$ (Fig. 1) was determined by X-ray diffraction‖ and establishes the non-coordination of one oxazoline arm. The metal centre adopts a distorted tetrahedral coordination geometry in contrast to the square-planar geometry observed for Pd(II) complexes with this ligand, either when it behaves as a *P*,*N*-chelate or a *N*,*P*,*N*-tridentate ligand.[9] The Ni(II) and Ru(II) complexes with this ligand, [NiCl$_2$(NOPON^{Me2})][8] and [RuCl$_2$(NOPON^{Me2})][18] are pentacoordinated, with a coordination

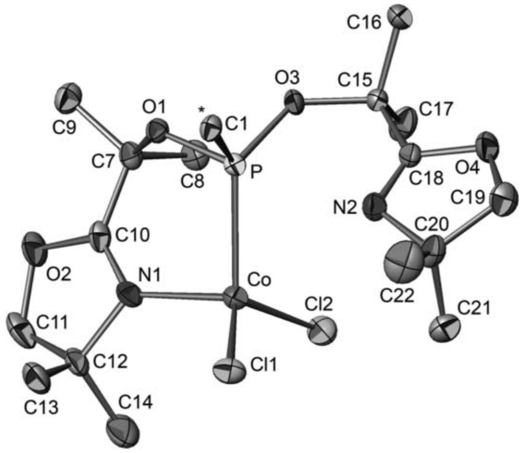


Fig. 1 ORTEP view of the molecular structure of **1** in $\mathbf{1}\cdot 0.5C_7H_8$. Ellipsoids enclose 50% of the electron density. Only the *ipso* carbon C1 of the phenyl group attached to P is shown for clarity. Hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [°]: Co–N1 2.038(3), Co–P 2.358(1), Co–Cl1 2.238(1), Co–Cl2 2.240(1); N1–Co–P 92.93(9), N1–Co–Cl1 109.2(1), N1–Co–Cl2 108.4(1), P–Co–Cl1 113.44(4), P–Co–Cl2 112.95(4), Cl1–Co–Cl2 117.06(4).

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‡ CCDC reference numbers 659280–659282. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717021c

§ Electronic supplementary information (ESI) available: Detailed experimental procedures for all new compounds. See DOI: 10.1039/b717021c

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geometry intermediate between trigonal-bipyramidal and square-base pyramidal. This illustrates the bonding versatility of this ligand. The Co–Cl1 (2.238(1) Å), Co–Cl2 (2.240(1) Å), Co–P 2.358(1) and Co–N1 (2.038(3) Å) distances are similar to those in Co(II) complexes with a distorted tetrahedral geometry and containing phosphinito-oxazoline ligands.[19]

In contrast to the *P*,*N*-chelating behaviour of the NOPON$^{\mathrm{Me2}}$ ligand in **1**, the crystal structure of **2** in **2**·0.5C_7H_8 (Fig. 2) revealed ligand chelation by coordination of the two nitrogen atoms of the tridentate ligand, without the expected coordination of the phosphorus atom.

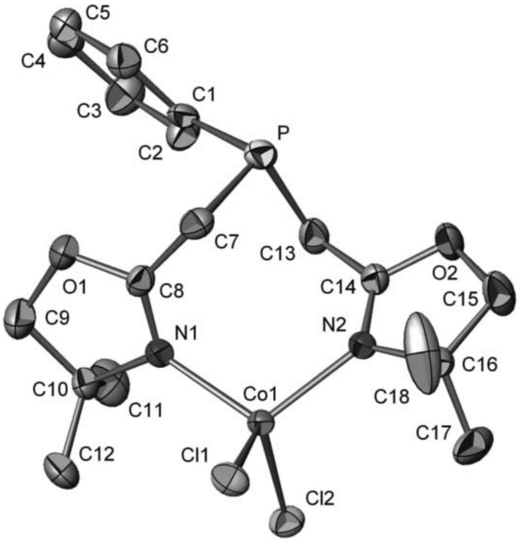


Fig. 2 ORTEP view of the molecular structure of **2** in **2**·0.5C_7H_8. Ellipsoids enclose 50% of the electron density. Hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [°]: Co–Cl1 2.2447(10), Co–Cl2 2.2459(10), Co–N1 2.036(3), Co–N2 2.049(3); N1–Co–N2 108.8(1), N1–Co1–Cl1 105.4(1), N2–Co1–Cl1 111.47(9), N1–Co1–Cl2 111.14(9), N2–Co1–Cl2 108.54(9), Cl1–Co1–Cl2 111.53(4).

The Co–P separation of 4.307(1) Å is very long and the phosphorus lone pair is not properly oriented to coordinate the metal centre. The N1–Co and N2–Co distances of 2.036(3) and 2.049(3) Å respectively, are similar to those in tetrahedral cobalt complexes coordinated by *N*,*N*-diimine ligands but the N1–Co–N2 angle of 108.8(1)° is significantly larger.[20,21]

Iron complexes are also of current interest in olefin oligomerization and polymerization catalysis where their performances depend very much on the ligand used and may be very significant.[13,14,22–24] We thus reacted NPN$^{\mathrm{Me2}}$ with $FeCl_2$ and obtained a complex formulated as [$FeCl_2$(NPN$^{\mathrm{Me2}}$)] **3**. Its crystal structure established that the *N*,*P*,*N* ligand again only functioned as a *N*,*N* chelate (Fig. 3) as observed for **2** in **2**·0.5C_7H_8. The crystal structure of **3** shows a distorted tetrahedral geometry around the Fe(II) centre. The N1–Fe and N2–Fe distances (2.088(2) and 2.094(2) Å, respectively) are slightly longer than the N1–Co and N2–Co distances found in **2**·0.5C_7H_8. The separation of 4.340(2) Å between the Fe centre and the P atom rules out any bonding interaction between these atoms. In both the structures of **2**·0.5C_7H_8 and of **3**, the marked torsion of the *N*,*P*,*N* ligand is noteworthy.

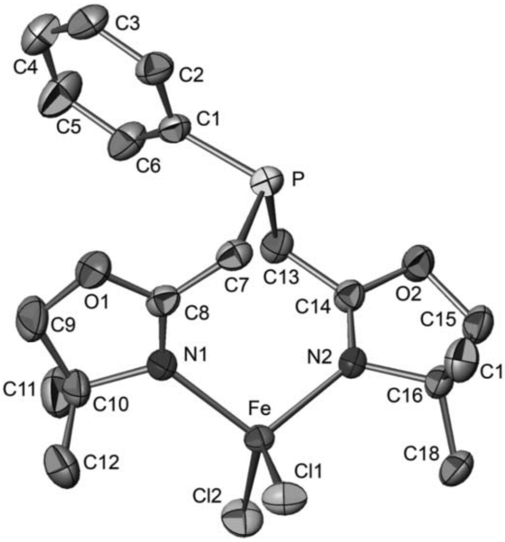
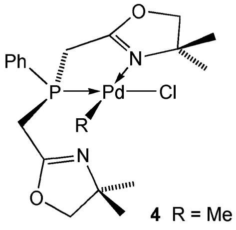


Fig. 3 ORTEP view of the molecular structure of **3**. Ellipsoids enclose 50% of the electron density. Hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [°]: Fe–Cl1 2.2607(8), Fe–Cl2 2.2586(8), Fe–N1 2.088(2), Fe–N2 2.094(2); N1–Fe–N2 105.80(9), N1–Fe–Cl1 104.79(8), N1–Fe–Cl2 113.21(7), N2–Fe–Cl1 110.91(7), N2–Fe–Cl2 104.39(7), Cl1–Fe–Cl2 117.29(3).

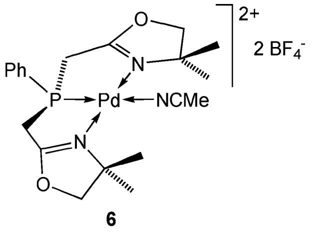
To the best of our knowledge, this *N*,*N*-chelating mode of a *N*,*P*,*N* ligand in **2** and **3** is unprecedented and also results, according to the CCDC, in the first transition metal complexes with a *N*,*P*,*N* ligand forming an eight-membered ring. One example has been reported with gallium[25a] and another theoretical structure recently calculated for niobium.[25b]

The molecular structures of **2**·0.5C_7H_8 and **3** indicate that the occurrence of a *N*,*N*-chelating mode for a *N*,*P*,*N* ligand in transition metal coordination chemistry may be more general than originally considered and could play a significant role in explaining the catalytic properties of such complexes.

For comparison, we reacted the ligand NPN$^{\mathrm{Me2}}$ with one equiv. of [Pd(Me)Cl(COD)] (COD = 1,5-cyclooctadiene), [$PdCl_2(NCPh)_2$] or [$Pd(NCMe)_4$]$(BF_4)_2$ in CH_2Cl_2 and obtained complexes **4–6**, respectively (see ESI§).



4 R = Me
5 R = Cl



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In contrast to the situation in **2** and **3**, coordination of the phosphorus atom to the metal centre is clearly indicated in the $^{31}P\{^1H\}$ NMR spectra by the shift from δ −24.8 ppm for the free ligand to 26.6 ppm for the coordinated ligand in **4** and 19.9 ppm in **5**. The $^{13}C\{^1H\}$ NMR spectra of **4** and **5** contain two signals for the C=N oxazoline carbon: a doublet at 169.6 ppm ($^2J_{PC}$ of 18.5 Hz, complex **4**) or at 173.9 ppm ($^2J_{PC}$ of 23.9 Hz, complex **5**) corresponding to a coordinated oxazoline and a singlet at 159.4 ppm (complex **4**) or a doublet at 158.2 ppm ($^2J_{PC}$ of 7.6 Hz, complex **5**) corresponding to an uncoordinated oxazoline. The

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^{1}H NMR spectra confirm the presence of the coordinated and uncoordinated oxazoline with two distinct ABX spin systems (A = H, B = H, X = P) for PCH^{A}H^B and two distinct AB spin systems for OCH^{A}H^B. Two ν(C=N) vibrations for the uncoordinated and coordinated oxazolines appear in the IR spectrum at 1659 and 1630 cm^{-1} for **4** and 1659 and 1614 cm^{-1} for **5**, respectively.

The ^{31}P{^{1}H} NMR spectrum of **6** established again the coordination of the phosphorus donor atom to the metal centre, in marked contrast with the situation encountered above with **2** and **3**. As expected and in contrast to **4** and **5**, the ^{13}C{^{1}H} NMR spectrum of **6** presented only a doublet for the C=N oxazoline at 174.7 ppm ($^2J_{PC}$ = 19.8 Hz). Coordination of the two oxazoline moieties was also confirmed by ^{1}H NMR spectroscopy with the presence of only one ABX spin system for the PCH^{A}H^B protons and one AB spin system for the OCH^{A}H^B protons and by IR spectroscopy with the presence of a unique band for the ν(C=N) vibration at 1613 cm^{-1}.

The ligands NOPON^{Me2} and NPN^{Me2} thus present a similar coordination behaviour in their Pd(II) complexes and always behave as P donor ligands. The tetrahedral geometry of the cobalt and iron complexes does not readily explain why *N*,*N*-coordination is so much favored in **2** and **3** instead of the *P*,*N*-coordination observed in complex **1** and further work is in progress.

Preliminary studies on catalytic ethylene oligomerisation showed activities up to 17700 mol$_{C_2H_4}$ mol$_{Co}$$^{-1}$ h^{-1} for **1** with 6 equiv. of AlEtCl$_2$ as cocatalyst under an ethylene pressure of 30 bar at 80 °C. Further catalytic tests are in progress.

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Notes and references

¶ **1**: Anhydrous CoCl$_2$ (0.14 g, 1.1 mmol) was added to a solution of NOPON^{Me2} (0.46 g, 1.1 mmol) in 30 mL of THF. The blue solution was stirred for 3 h at room temp. THF was removed under reduced pressure and the blue powder was dried overnight under vacuum (yield: 0.58 g, 1.05 mmol, 97%). Data in ESI.§
2: Anhydrous CoCl$_2$ (0.24 g, 1.85 mmol) was added to a solution of NPN^{Me2} (0.62 g, 1.85 mmol) in 50 mL of THF. The blue solution was stirred for 3 h at room temp. After filtration of the solution and elimination of THF under reduced pressure, the blue powder was dried overnight under vacuum (yield: 0.81 g, 1.75 mmol, 94%). Data in ESI.§
3: To a solution of NPN^{Me2} (1.99 g, 6.0 mmol) in 50 mL of CH$_2$Cl$_2$ was added a CH$_2$Cl$_2$ solution of FeCl$_2$·4H$_2$O (1.19 g, 6.0 mmol) and the mixture was stirred at room temp. overnight. The solvent was then eliminated under reduced pressure and 50 mL of diethyl ether was added to precipitate the white complex which was recovered by filtration, washed with diethyl ether and dried under vacuum (yield: 2.40 g, 5.2 mmol, 87%). Data in ESI.§
|| Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[26] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C–H}$ = 0.95 Å, U_{11} = 0.04). Crystallographic data for **1**·0.5C$_7$H$_8$. C$_{22}$H$_{33}$Cl$_2$CoN$_2$O$_4$P·0.5(C$_7$H$_9$), M = 596.37, triclinic, space group $P\bar{1}$, T = 173(2) K, a = 9.1010(4) Å, b = 9.1930(4) Å, c = 17.5460(9) Å, α = 79.9750(15)°, β = 84.2710(15)°, γ = 83.173(3)°, V = 1430.62(11) Å^3, Z = 2, reflections: measured/independent/observed = 10153/6620/4065, R_{int} = 0.044, $R\,[F^2 > 2\sigma(F^2)]$ = 0.061, $wR\,(F^2)$ = 0.180, S = 1.01.
Crystallographic data for **2**·0.5C$_7$H$_8$. C$_{18}$H$_{25}$Cl$_2$CoN$_2$O$_2$P·0.5(C$_7$H$_9$), M = 1015.53, monoclinic, space group $P2_1/c$, T = 173(2) K, a = 9.1785(2) Å, b = 12.1326(5) Å, c = 23.4657(7) Å, β = 111.606 (2)°, V = 2429.51(13) Å^3, Z = 2, reflections: measured/independent/observed = 14007/5541/3981, R_{int} = 0.040, $R\,[F^2 > 2\sigma(F^2)]$ = 0.058, $wR\,(F^2)$ = 0.175, S = 1.07.
Crystallographic data for **3**. C$_{18}$H$_{25}$Cl$_2$FeN$_2$O$_2$P, M = 459.12, monoclinic, space group $P2_1/c$, T = 173(2) K, a = 12.7240(13) Å, b = 12.3190(15) Å, c = 15.5250(19) Å, β = 113.772(5)°, V = 2227.0(4) Å^3, Z = 4, reflections: measured/independent/observed = 10818/6465/4953, R_{int} = 0.029, $R\,[F^2 > 2\sigma(F^2)]$ = 0.057, $wR\,(F^2)$ = 0.162, S = 1.08.

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