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Phosphinooxazolines as assembling ligands in heterometallic complexes

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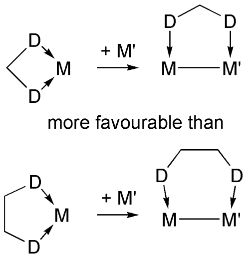
It is shown that phosphinooxazolines such as (2-oxazoline-2-ylmethyl)diphenylphosphine **1** can be used as *P*,*N* assembling ligands for the synthesis of heterometallic complexes. These were obtained in a stepwise manner from the iron carbonyl complexes containing one, [Fe(CO)$_4$(PCH$_2$-oxazoline-*P*)] **2**, or two, *trans*-[Fe(CO)$_3$(PCH$_2$-oxazoline-*P*)$_2$] **6**, P-bound phosphinooxazoline ligands. These metalloligands were then reacted with metal complexes. With **2**, complete ligand transfer from Fe to the second metal (Pd) was sometimes observed. The metal–metal bonded complex [(OC)$_4$Fe(μ-PCH$_2$-oxazoline-*P*,*N*)PdCl$_2$] **3** was of limited stability, whereas the trinuclear complex *trans*-[{(OC)$_4$Fe(μ-PCH$_2$-oxazoline-*P*,*N*)}$_2$CoCl$_2$] **4**, in which **2** functions as a N-donor metalloligand toward the tetrahedral Co(II) centre, was stable and could be fully characterised by X-ray diffraction. This complex catalyses the oligomerization of ethylene to give linear α-olefins in the range C$_4$–C$_{26}$, with a maximum of the Schulz-Flory distribution around C$_6$. The complex [{(OC)$_4$Fe(μ-PCH$_2$-oxazoline-*P*,*N*)}$_2$HgI$_2$] **5** was also prepared from **6**. With the metalloligand **6**, the Fe⟶Pd and Fe⟶Co metal–metal bonded compounds *trans*-[(OC)$_3$Fe(μ-PCH$_2$-oxazoline-*P*,*N*)$_2$Pd(NCMe)](BF$_4$)$_2$ **8** and *trans*-[(OC)$_3$Fe(μ-PCH$_2$-oxazoline-*P*,*N*)$_2$CoCl$_2$] **9** were obtained.

Introduction

One of the major motivations for using assembling ligands in coordination and organometallic chemistry is to allow or facilitate the synthesis of complex molecules with strong, weak or no metal–metal bonding whereas in cluster chemistry, the molecular stability is mainly due to metal–metal bonding.[1,2] Assembling ligands may thus allow greater flexibility in the bonding/non-bonding separation between the metal centres and lead to systems displaying reversible metal–metal bond breaking/formation under mild conditions.[3] This is of considerable relevance to the occurrence of synergistic and bimetallic effects in stoichiometric or catalytic reactivity where irreversible breaking of a polymetallic structure into mononuclear fragments is undesirable.[4]

Among the most often used assembling ligands, one finds small-bite ligands which by supporting a metal–metal bond lead to the formation of stabilised five-membered ring structures, as exemplified with the well-known ligands Ph$_2$PCH$_2$PPh$_2$ (dppm), 2-(diphenylphosphino)pyridine (P–Py) or, more recently, Ph$_2$PNHPPh$_2$ (dppa).[1,5] An efficient method to access these dimetallic five-membered ring structures consists of starting from a thermodynamically less favourable four-membered chelate that will insert the second metal into a metal–phosphorus bond (metal-induced chelate ring opening) (Scheme 1).[6]



Scheme 1 Formation of dinuclear, metal–metal bonded complexes by metal-induced chelate opening (D = donor atom).

Such small-bite bridging ligands are more rarely involved in six-membered ring structures.[5c,7,8] A metal-induced opening of a stable, five-membered ring mononuclear chelate to form a metal–metal bonded six-membered structure is thermodynamically much less attractive than the above transformation from a four-membered chelate to a five-membered, metal–metal bonded system (Scheme 1).

Functional phosphine ligands (*i.e.* phosphine ligands bearing at least one additional, chemically different function) have been much used as assembling ligands between two or more metal atoms, in particular but not exclusively in the context of early–late chemistry where the different electronic properties of the donor groups can lead to very selective binding processes.[9] When metal–metal bonding is present, mostly five-membered metallocycles have been reported,[1] larger bimetallic cycles being less frequent. In the case of (P,O) ligands, we reported some examples of six-membered ring metal–metal bonded systems,[10] and with (P,N) ligands, we reported recently the first six-membered ring metal–metal bonded system.[11] Only one seven-membered cycle has been very recently reported.[12]

Our interest in phosphinooxazoline ligands, which behave either as P-monodentate or P,N-donors in five-membered ring chelate structures (rigid or hemilabile),[13] has led us to explore their potential as bridging ligands, a situation which, to the best of our knowledge, had not been reported before, and examine their ability to support a metal–metal bond in a six-membered ring structure. Preliminary results have been obtained with a Fe–Cu system.[11]

Results and discussion

Following our studies on heterobimetallic systems involving the precursors [Fe(CO)$_4$(dppm-*P*)], [Fe(CO)$_4$(dppa-*P*)] or [Fe{Si(OMe)$_3$}(CO)$_3$(dppm-P)]$^-$,[1e,14] we first prepared the metalloligand [Fe(CO)$_4$(PCH$_2$-oxazoline-*P*)] **2** by reaction of [Fe(CO)$_5$] in THF with the ligand (2-oxazoline-2-ylmethyl)-diphenylphosphine **1** (abbreviated PCH$_2$-oxazoline in the

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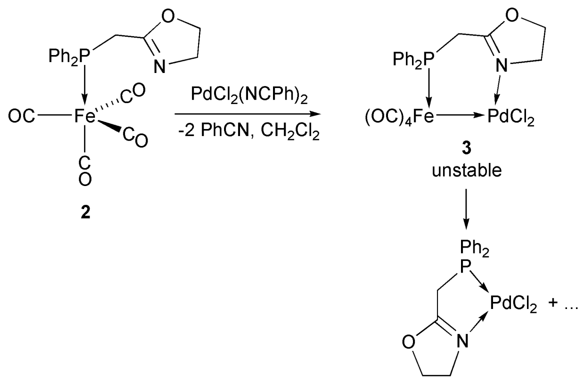
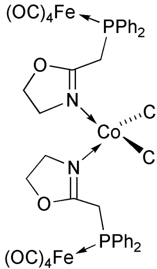
following) in the presence of a catalytic amount of $CoCl_2$.[15] Its reaction with $[PdCl_2(cod)]$ or $[PdCl_2(NCPh)_2]$ resulted in the formation of the desired complex $[(OC)_4Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)PdCl_2]$ **3** which was however too unstable to be fully characterised in the solid-state (eqn. (1)). Its formation was monitored *in situ* by $^{31}P\{^1H\}$ NMR spectroscopy (δ 64.0 ppm) and IR in the $\nu(CO)$ (2021 (vs), 1996 (vs), 1934 (w) cm^{-1}) and $\nu(CN)$ (1632 (m) cm^{-1}) regions.



(1)

This complex rapidly transforms in solution with complete ligand transfer from Fe to Pd and formation of the mononuclear complex $[PdCl_2(PCH_2\text{-oxazoline-}P,N)]$.[16,17a] Similarly, $[PdCl(Me)(PCH_2\text{-oxazoline-}P,N)]$ was formed in the reaction of **2** with [PdCl(Me)(cod)]. Obviously, the phosphine-oxazoline ligand **1** is less suitable than dppm or dppa for the stabilisation of complexes with a dative Fe⟶Pd metal–metal bond.[14]

Reaction of two equiv. of **2** with anhydrous $CoCl_2$ afforded a trinuclear complex *trans*-$[(OC)_4Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2\text{-}CoCl_2]$ **4** in which **2** functions only as a *N*-donor metalloligand toward the tetrahedral Co(II) centre, as indicated by a $\nu(C{=}N)$ absorption at 1630 (w) cm^{-1}.



4

The geometry of this complex was established by X-ray diffraction and confirmed the bridging behaviour of each phosphinooxazoline ligand. A view of the crystal structure is shown in Fig. 1 and selected bond distances and angles are given in Table 1.

The metals are far apart [Fe(1)–Co and Fe(2)–Co separations of 5.111(1) and 5.324(1) Å] and each metal centre is found in its usual coordination environment, trigonal bipyramidal for Fe(0) and tetrahedral for Co(II). The bonding parameters are in the expected range. The Co–Cl distances of 2.232(3) and 2.261(3) Å and the Co–N distances of 2.032(8) and 2.044(7) Å are similar to those found in cobalt oxazoline complexes where the oxazoline moiety is part of a *N,N*, *O,N* or *P,N* chelate,[18] taken for comparison in the absence, to the best of our knowledge, of structural data on Co(II) complexes with monohapto or bridging oxazoline ligands. The Fe–P distances of 2.223(4) and 2.232(3) Å and the ligand arrangement around the Fe centre are similar to those in the mononuclear complex *trans*-$[Fe(CO)_3\text{-}(PCH_2\text{-oxazoline-}P)_2]$ **6** (see below). In view of the catalytic performances of Fe(II) and Co(II) diimine complexes for the oligomerisation of ethylene,[19a,b] preliminary experiments were carried out with **4**. The details are given in the Experimental section. It was found to oligomerise ethylene to give linear α-olefins in the range C_4–C_{26}, with a maximum of the Schulz–Flory distribution around C_6. The turnover frequency of 341 (mol C_2H_4 mol Co^{-1} min^{-1}) is much lower than those observed by Brookhart and co-workers and Gibson and co-workers,[19] although our experiments have not been optimized.

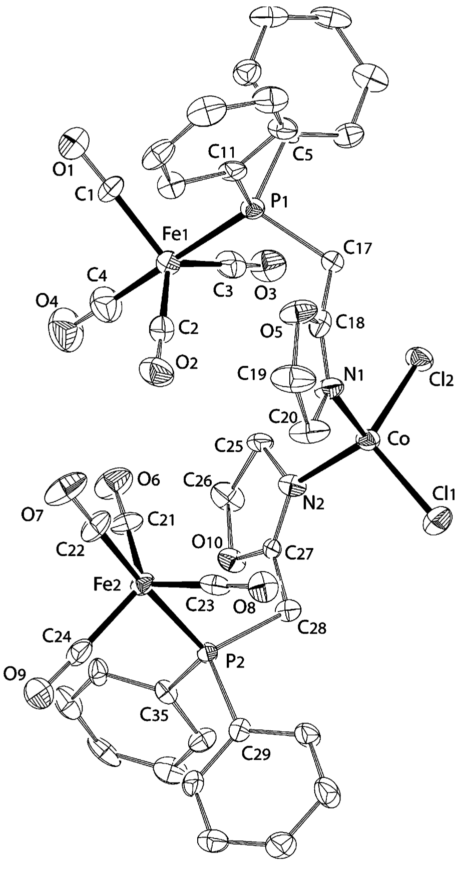
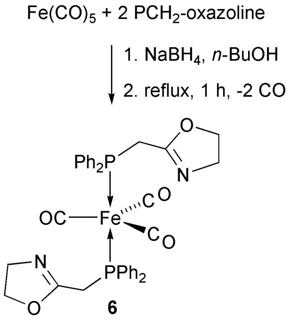


Fig. 1 ORTEP view of the crystal structure of complex **4**. Ellipsoids are shown at the 50% probability level.

Similarly to the synthesis of **4**, the complex $[\{(OC)_4\text{-}Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)\}_2HgI_2]$ **5** was prepared by reaction of HgI_2 with two equiv. of **2** in CH_2Cl_2. The spectroscopic data are consistent with the *P,N*-bridging mode of ligand **1** (see Experimental section).

In view of the very modest stabilization brought about by the bridging ligand **1** in a metal–metal bonded complex of type **3**, and its facile, complete transfer from Fe to Pd, we envisaged to use an iron synthon containing two P,N ligands **1** that could act as a chelating system, *trans*-$[Fe(CO)_3(PCH_2\text{-oxazoline-}P)_2]$ **6**.[11] It was obtained by reaction of $[Fe(CO)_5]$ with two equiv. of **1** in 1-butanol, using the $NaBH_4$ activation procedure (eqn. (2)),[20] whereas addition of one equiv. of **1** to a solution of **2** in CH_2Cl_2 in the presence of Me_3NO led to a mixture of products.

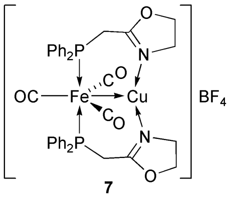


(2)

The *trans*-arrangement of the P donors gives rise to a singlet at δ 77.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum and it was confirmed in the solid-state by an X-ray diffraction study.[11]

Table 1 Selected bond distances (Å) and angles (°) in **4**

Fe(1)–C(1)	1.807(9)	N(1)–C(18)	1.286(11)
Fe(1)–C(2)	1.791(11)	N(1)–C(20)	1.487(10)
Fe(1)–C(3)	1.816(11)	N(2)–C(25)	1.444(11)
Fe(1)–C(4)	1.755(11)	N(2)–C(27)	1.287(10)
Fe(1)–P(1)	2.223(3)	C(1)–O(1)	1.136(12)
Fe(2)–C(21)	1.799(10)	C(2)–O(2)	1.148(12)
Fe(2)–C(22)	1.786(9)	C(3)–O(3)	1.121(12)
Fe(2)–C(23)	1.776(10)	C(4)–O(4)	1.149(12)
Fe(2)–C(24)	1.804(10)	C(17)–C(18)	1.471(12)
Fe(2)–P(2)	2.232(3)	C(18)–O(5)	1.338(10)
Co–N(1)	2.032(8)	C(19)–O(5)	1.435(13)
Co–N(2)	2.044(7)	C(19)–C(20)	1.483(14)
Co–Cl(1)	2.232(3)	C(21)–O(6)	1.145(11)
Co–Cl(2)	2.261(3)	C(22)–O(7)	1.140(11)
P(1)–C(5)	1.808(8)	C(23)–O(8)	1.146(11)
P(1)–C(11)	1.835(9)	C(24)–O(9)	1.121(12)
P(1)–C(17)	1.866(9)	C(25)–C(26)	1.563(13)
P(2)–C(28)	1.860(8)	C(26)–O(10)	1.445(11)
P(2)–C(29)	1.827(9)	C(27)–O(10)	1.324(10)
P(2)–C(35)	1.825(8)	C(27)–C(28)	1.482(11)
C(4)–Fe(1)–C(1)	91.4(5)	C(29)–P(2)–C(35)	101.6(4)
C(4)–Fe(1)–C(2)	91.8(5)	C(28)–P(2)–C(35)	104.9(4)
C(4)–Fe(1)–C(3)	90.3(5)	C(28)–P(2)–Fe(2)	114.0(3)
C(2)–Fe(1)–C(1)	114.7(5)	C(29)–P(2)–Fe(2)	112.7(3)
C(2)–Fe(1)–C(3)	124.2(5)	C(35)–P(2)–Fe(2)	118.3(3)
C(1)–Fe(1)–C(3)	121.0(5)	C(18)–N(1)–C(20)	107.0(7)
C(1)–Fe(1)–P(1)	90.1(3)	C(18)–N(1)–Co	135.5(6)
C(2)–Fe(1)–P(1)	91.6(3)	C(20)–N(1)–Co	117.3(6)
C(3)–Fe(1)–P(1)	85.0(3)	C(25)–N(2)–C(27)	107.9(7)
C(4)–Fe(1)–P(1)	175.2(4)	C(25)–N(2)–Co	116.9(5)
C(21)–Fe(2)–C(22)	87.9(4)	C(27)–N(2)–Co	134.2(6)
C(22)–Fe(2)–C(24)	91.5(5)	O(1)–C(1)–Fe(1)	178.1(10)
C(23)–Fe(2)–C(21)	127.0(4)	O(2)–C(2)–Fe(1)	179.1(9)
C(23)–Fe(2)–C(22)	91.2(4)	O(3)–C(3)–Fe(1)	178.6(9)
C(23)–Fe(2)–C(24)	115.3(4)	O(4)–C(4)–Fe(1)	176.5(12)
C(24)–Fe(2)–C(21)	117.7(4)	C(18)–C(17)–P(1)	113.9(6)
C(21)–Fe(2)–P(2)	92.2(3)	N(1)–C(18)–O(5)	116.2(8)
C(22)–Fe(2)–P(2)	176.4(4)	N(1)–C(18)–C(17)	128.0(8)
C(23)–Fe(2)–P(2)	85.8(3)	O(5)–C(18)–C(17)	115.8(8)
C(24)–Fe(2)–P(2)	91.7(3)	O(5)–C(19)–C(20)	105.5(8)
N(1)–Co–N(2)	113.5(3)	N(1)–C(20)–C(19)	103.9(8)
N(1)–Co–Cl(1)	103.4(2)	O(6)–C(21)–Fe(2)	176.5(9)
N(2)–Co–Cl(1)	110.4(2)	O(7)–C(22)–Fe(2)	179.3(10)
N(1)–Co–Cl(2)	107.2(2)	O(8)–C(23)–Fe(2)	177.8(8)
N(2)–Co–Cl(2)	105.7(2)	O(9)–C(24)–Fe(2)	176.4(9)
Cl(1)–Co–Cl(2)	116.8(1)	N(2)–C(25)–C(26)	103.9(7)
C(5)–P(1)–C(11)	102.3(4)	O(10)–C(26)–C(25)	101.4(7)
C(5)–P(1)–C(17)	102.1(4)	N(2)–C(27)–O(10)	116.4(8)
C(11)–P(1)–C(17)	103.4(4)	N(2)–C(27)–C(28)	127.4(8)
C(5)–P(1)–Fe(1)	112.8(3)	O(10)–C(27)–C(28)	116.2(7)
C(11)–P(1)–Fe(1)	119.2(3)	C(27)–C(28)–P(2)	111.9(6)
C(17)–P(1)–Fe(1)	115.0(3)	C(18)–O(5)–C(19)	107.2(7)
C(28)–P(2)–C(29)	103.8(4)	C(26)–O(10)–C(27)	108.6(6)



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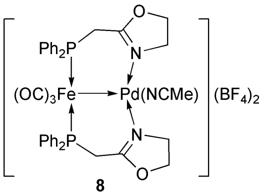

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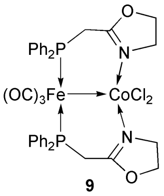

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We have recently shown that **6** can indeed function as a chelating metallodiphosphine since its reaction with $[Cu(NCMe)_4]BF_4$ in CH_2Cl_2 afforded $[(OC)_3Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2Cu]BF_4$ **7**, which has been characterised by X-ray diffraction and shown to contain a dative Fe⟶Cu bond [2.544(7) Å].[11] Reaction of **6** with $[Pd(NCMe)_4](BF_4)_2$ in MeCN afforded an orange compound, *trans*-$[(OC)_3Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2Pd(NCMe)](BF_4)_2$ **8**, which could only be characterised spectroscopically owing to its limited stability. The latter most likely results from the geometrical constraints imposed by the bridging ligands on the Pd(II) coordination geometry. The N–Pd–N angle has to severely depart from the usual 180°, as suggested by the corresponding N–Cu–N angle of 132.7(1)° in **7**.[11]

Reaction of **6** with one equiv. of $CoCl_2$ afforded the paramagnetic complex *trans*-$[(OC)_3Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2CoCl_2]$ **9** and with $[Co(NCMe)_6](BF_4)_2$ a red, paramagnetic compound, formulated as *trans*-$[(OC)_3Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2Co(NCMe)](BF_4)_2$ (IR (MeCN): ν(CO) 1970 (w), 1901 (vs), 1878 (vs); ν(C=N) 1638 (br, m) cm^{-1}; ^1H NMR (acetone-d_6, 298 K): consistent with the paramagnetic nature of the Co(II) centre, signals were observed at: δ 50.5 (vbr), 32.6 (br), 15.2, −17.7; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 72 (br, $w_{1/2} = 51$ Hz)), although no satisfactory elemental analysis could be obtained for this product. When **2** was reacted with $[PdCl_2(cod)]$, $[PdCl(Me)(cod)]$ or $[PtCl_2(cod)]$, no dinuclear complex could be isolated and complete tranfer of the phosphinooxazoline ligand occurred to give the known complexes $[PdCl_2(PCH_2\text{-oxazoline-}P)]$, $[PdCl(Me)(PCH_2\text{-oxazoline-}P)]$ or $[PtCl_2(PCH_2\text{-oxazoline-}P)]$, respectively, which were identified by comparison with authentic samples.[17]

Conclusion

We have shown that the phosphinooxazoline ligand **1** can be used as an assembling ligand for the synthesis of heterometallic complexes. This was demonstrated here by a stepwise approach based on iron carbonyl complexes containing one (**2**) or two (**6**) P-bound phosphinooxazoline ligands as building blocks. These were subsequently reacted with complexes of a second metal. In addition to the nitrogen atom of the pendent oxazoline(s) being available for coordination to a second metal, the filled *d* orbitals of the Fe centre can participate in dative metal–metal bonding, which results in these metalloligands behaving as bidentate or tridentate donors, respectively. In the former case, complete ligand transfer from Fe to the second metal was sometimes observed. The metal–metal bonded Fe⟶Pd complex **3** was of limited stability, whereas the stable, trinuclear Co/Fe_2 complex **4** was fully characterised by X-ray diffraction. This latter complex catalyses the oligomerisation of ethylene to give linear α-olefins in the range C_4–C_{26}, with a maximum of the Schulz–Flory distribution around C_6. With the metalloligand **6**, the Fe⟶Pd and Fe⟶Co metal–metal bonded compounds **8** and **9** were obtained, respectively.

Experimental

All the reactions were performed using Schlenk tube techniques under an inert atmosphere of purified nitrogen. Solvents were freshly distilled under nitrogen from the usual drying agent prior to use. Nitrogen was passed through BASF R3–11 catalyst and molecular sieves columns to remove residual oxygen and water. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a FT Bruker AC 300 instrument. Infrared spectra were recorded in the 4000–400 cm^{-1} range on a IFS-66 FTIR Bruker spectrometer. Samples were prepared as KBr pellets or in solutions using CaF_2 cells. The synthesis of the ligand (2-oxazoline-2-ylmethyl)diphenylphosphine **1** was carried out as described previously.[19a]

Synthesis of the complexes

Synthesis of $[Fe(CO)_4(PCH_2\text{-oxazoline-}P)]$ 2. A toluene solution (30 ml) of the PCH_2-oxazoline ligand **1** (2.70 g, 10 mmol) and a catalytic amount of anhydrous $CoCl_2$ (0.05 g, 0.385 mmol) were refluxed before $[Fe(CO)_5]$ (2.63 ml, 20 mmol) was added. The reaction was monitored by IR in the $\nu(CO)$ region. Reflux was continued until the spectrum remained invariant with time. After cooling to room temperature, the reaction mixture was eluted with toluene through a column containing $CoCl_2·6H_2O$ (5 g)/neutral alumina (20 g)/silica gel (20 g) disposed in three layers from top to bottom, respectively.[15] Solvent and excess $[Fe(CO)_5]$ were then removed under reduced pressure and the product was recrystallized from CH_2Cl_2–hexane. The product was isolated as ochre crystals (3.00 g, 70%). IR (CH_2Cl_2): $\nu(CO)$ 2051 (s), 1975 (m), 1939 (vs); $\nu(C{=}N)$ 1662 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 298 K): δ 7.71–7.33 (m, 10H, aromatics), 4.13 (t, 2H, $^3J_{HH}$ = 9.8 Hz, OCH_2), 3.80 (dt, 2H, $^3J_{HH}$ = 9.8, $^5J_{PH}$ = 4.4 Hz, NCH_2), 3.54 (d, 2H, $^2J_{PH}$ = 10.6 Hz, PCH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 213.5 (d, $^2J_{PC}$ = 19.5 Hz, CO), 161.9 (s, C=N), 132.7–127.9 (aromatics), 68.2 (s, OCH_2), 55.1 (s, NCH_2), 33.5 (d, PCH_2, $^2J_{PC}$ = 25.7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 68.2 (s). Anal. Calc. for $C_{20}H_{16}FeNO_5P$: C, 54.95; H, 3.69; N, 3.20. Found: C, 54.72; H, 3.56; N, 3.00%.

Synthesis of $[\{(OC)_4Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)\}_2CoCl_2]$ 4. Dried $CoCl_2$ (0.043 g, 0.335 mmol) was added to a dichloromethane solution (100 ml) of $[Fe(CO)_4(PCH_2\text{-oxazoline-}P)]$ **2** (0.292 g, 0.667 mmol) at room temperature. After a few minutes of vigorous stirring, the colour of the initial green solution turned sea-blue. The solution was concentrated to half of its volume under reduced pressure. Overnight, blue crystals appeared (0.256 g, 77%). IR (CH_2Cl_2): $\nu(CO)$ 2052 (s), 1978 (m), 1945 (vs), 1933 (sh); $\nu(C{=}N)$ 1630 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 298 K): consistent with the paramagnetic nature of the Co(II) centre, signals were observed at: δ 28.66 (br), 9.9 (br), 8.47–7.25 (aromatics), 3.98 (br), 3.74 (br), 3.48 (br). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 61.7 (br, $w_{1/2}$ = 263 Hz). Anal. Calc. for $C_{40}H_{32}CoCl_2Fe_2N_2O_{10}P_2·1.5CH_2Cl_2$: C, 44.05; H, 3.12; N, 2.48. Found: C, 44.17; H, 2.95; N, 2.47%.

Synthesis of $[\{(OC)_4Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)\}_2HgI_2]$ 5. Dried HgI_2 (0.137 g, 0.30 mmol) was added to a dichloromethane solution (100 ml) of $[Fe(CO)_4(PCH_2\text{-oxazoline-}P)]$ (0.264 g, 0.60 mmol) at room temperature. After a few minutes of vigorous stirring, the colour of the initial orange solution turned deep orange. The solution was concentrated to half of its volume under reduced pressure. Overnight, an orange precipitate appeared which was collected by filtration (0.32 g, 80%). IR (CH_2Cl_2): $\nu(CO)$ 2085 (s), 2002 (vs), 1940 (s), $\nu(C{=}N)$ 1653 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 298 K): 7.40–7.70 (m, 20 H, aromatics), 4.21 (m, 4H, OCH_2), 3.83 (m, 4H, NCH_2), 3.50 (m, 4H, PCH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 65.07.

Synthesis of *trans*-$[(OC)_3Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2Pd(NCMe)](BF_4)_2$ 8. Solid $[Pd(NCMe)_4](BF_4)_2$ (0.058 g, 0.13 mmol) was added to a solution of *trans*-$[Fe(CO)_3(PCH_2\text{-oxazoline-}P)_2]$ **6** (0.089 g, 0.13 mmol) in MeCN at −78 °C. After a few minutes of vigorous stirring, the colour of the initial yellow solution turned orange. The solvent was rapidly evaporated under reduced pressure. Owing to its observed instability, a correct elemental analysis could not be obtained for this complex. IR (CH_2Cl_2): $\nu(CO)$ 2018 (s), 1967 (vs), 1943 (ms); $\nu(C{=}N)$ 1653 (s) cm^{-1}. ^1H NMR (acetone-d_6, 298 K): δ 8.15–7.46 (m, 20H, aromatics), 4.75 (m, 4H, PCH_2), 4.47 (pseudo t, 4H, $^3J_{HH} \approx 9.35$ Hz, OCH_2), 3.95 (pseudo t, 4H, $^3J_{HH} \approx 9.35$ Hz, NCH_2), 2.25 (s, 3 H, CH_3CN). $^{31}P\{^1H\}$ NMR (acetone-d_6, 298 K): δ 71.8 (s).

Synthesis of *trans*-$[(OC)_3Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2CoCl_2]$ 9. Dried $CoCl_2$ (0.191 g, 1.47 mmol) was added to a solution of *trans*-$[Fe(CO)_3(PCH_2\text{-oxazoline-}P)_2]$ **6** (1.00 g, 1.47 mmol) dissolved in 30 ml of previously degassed 1-butanol. The reaction mixture was refluxed for 1 h. The colour of the initial yellow solution turned to pastel green with formation of a pastel green precipitate upon cooling. The mixture was concentrated to half of its volume and the solvent was removed under N_2 *via* canula. The solid was washed with pentane (3 × 50 ml) and dried under vacuum (0.460 g, 39%). IR (CH_2Cl_2): $\nu(CO)$ 1979 (w), 1903 (s), 1876 (vs); $\nu(C{=}N)$ 1642 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 298 K): consistent with the paramagnetic nature of the Co(II) centre, signals were observed at: δ 55.6 (vbr), 41.9 (vbr), 23.8 (br), 16.9, 15.8, −5.5 (vbr). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 66.4 (br, $w_{1/2}$ = 130 Hz). Anal. Calc. for $C_{35}H_{32}CoCl_2FeN_2O_5P_2$: C, 52.01; H, 3.99; N, 3.47. Found: C, 50.72; H, 4.00; N, 3.07%.

Table 2 Crystal data and data collection parameters for **4**

Formula	$C_{40}H_{32}Cl_2CoFe_2N_2O_{10}P_2$
Molecular weight	1004.19
Colour	Blue
Crystal system	Monoclinic
Space group	$P2_1/n$
T/K	173(2)
a/Å	9.619(5)
b/Å	14.350(5)
c/Å	30.846(5)
β/°	92.441(5)
V/Å^3	4254(3)
Z	4
D_c/g cm^{-3}	1.568
μ/mm^{-1}	1.317
Radiation	Mo-Kα graphite-monochromated
λ/Å	0.71069
hkl Limits	−12 to 12, 0–18, 0–40
θ Limit/°	27.485
F(000)	2036
Number of measured data	9638
Number of data ($I > 2\sigma(I)$)	7470
Weighting scheme	$4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$
R^a	0.1220
$R_w{}^a$	0.2314
GOF	1.257

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2]^{1/2}$.

Catalysis

A mechanically stirred 1000 mL Parr autoclave was heated overnight to 100 °C under vacuum and then cooled to 30 °C under an ethylene atmosphere. The autoclave was charged with 200 mL of degased toluene and 5 mL MAO. The autoclave was sealed, and ethylene was added (100 psig). The solution was stirred for 10 min, during which time the desired reaction temperature was established. The ethylene pressure was then released, and a suspension of $[(OC)_4Fe(\mu\text{-}PCH_2\text{-oxazoline-}P,N)_2CoCl_2]$ **4** (0.1 mmol, 0.081 g in 2 mL of toluene) was added to the reaction mixture *via* canula. The reactor was then sealed and pressurised with ethylene to the desired reaction pressure. The reaction mixture was stirred under constant ethylene pressure for 1 h, after which time the reactor was placed in an ice-bath and the pressure was released. After addition of 200 μL of *n*-heptane, an aliquot of the reaction mixture was analyzed by GC–mass spectroscopy to determine the Schulz–Flory α constant. The integrated areas of the C_{12} and C_{14} oligomers were used to calculate the α constant. The GLC conditions used are as follows: injector and detector temperatures, 250 °C; oven temperature program, 100 °C for 4 min, 8 °C min^{-1} ramp, 250 °C/ for 70 min. Oligomer peaks in the range C_4–C_{26} were resolved under these analytical conditions.

X-Ray crystallography

We succeeded in selecting an almost not-twinned crystal, but of sufficient quality for an unambiguous molecular structure resolution. This factor should explain the relative high R values. It was mounted on a Kappa CCD diffractometer. The relevant data are summarized in Table 2. Data were collected using phi-scans and the structure was solved using direct methods and refined against F^2 using SHELX 97 software.[21,22] 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, $U_{11} = 0.04$).

CCDC reference number 192296.

See http://www.rsc.org/suppdata/dt/b3/b300277m/ for crystallographic data in CIF or other electronic format.

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