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Note

Formation of donor–acceptor Fe(0)–Hg(II) bond in separation and stabilization of optically active iron(0) phosphine complexes. Absolute configuration of (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$

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Abstract

The chiral phosphine ligand 2-(ethylphenylphosphino)pyridine (EtPhPpy, *R*/*S* mixture) reacts with $Fe(CO)_5$ to give racemic (±)-$Fe(CO)_4$(EtPhPpy-*P*), which undergoes an addition reaction with $HgCl_2$ to afford the optically active binuclear Fe(0)–Hg(II) complexes (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ and (−)-(*S*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$, which can be separated manually in crystalline form. The absolute configuration of (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ has been determined by single crystal X-ray analysis.

Keywords: Crystal structures; Iron complexes; Mercury complexes; Chiral phosphine complexes

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1. Introduction

Many chiral phosphorus compounds have interesting biological properties connected closely with the absolute configuration at the phosphorus centre [1], and transition metal complexes of optically active phosphines have been used successfully as efficient catalysts in asymmetric synthesis [2]. Several transformation methods have been developed to synthesize optically pure *P*-chiral phosphines [3,4], which were the first to be used for asymmetric hydrogenation [5,6]. However, published reports about the absolute configuration of *P*-chiral phosphines are few in number, some known examples being [{(+)-(1*R*,5*R*)-η^3-pinenyl}Ni{(S_p)-PMe^{t}BuPh)}] [7], (+)-[η^4-(1,5-cod)Rh{(R_p)-PMe(men)Ph}](BF_4) [8] and (−)-[FeCoMo(μ-S)Cp$(CO)_7$-{(R_p)-PMePrPh)}] [9], as well as [S_p-4-4-1(*R*),4(*S*)]-bromo[1-[(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]-[1-(benzylthio)-2-(methylphosphino)ethane-*P*]palladium(II) [10].

Recent work from our laboratories has demonstrated that neutral 18-electron organometallic compounds, such as *trans*-$Fe(CO)_3(Ph_2Ppy)_2$ and $Fe(CO)_4(Ph_2Ppy$-*P*), can react with Lewis acids to form heterobinuclear complexes that are consolidated by a donor–acceptor metal–metal bond [11–16]. A study of the catalytic behaviour of a number of heterobinuclear complexes of this class showed that when the complex FeRh(μ-$Ph_2Ppy)_2(CO)_4Cl$ is used as a homogeneous catalyst for the carbonylation of ethanol and iodoethane to form ethyl propionate, the reaction activity and selectivity are superior to $Rh(Ph_3P)_3Cl$ [11].

We have prepared previously the asymmetrical phosphine ligand EtPhPpy as a racemic mixture [16]. We report here the reaction of racemic (±)-Fe$(CO)_4$(EtPhPpy-*P*) with $HgCl_2$ that leads to the sepa-

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ration and stabilization of optical isomers of iron(0) phosphine complexes. The absolute configuration of (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ has been determined by X-ray analysis.

2. Results and discussion

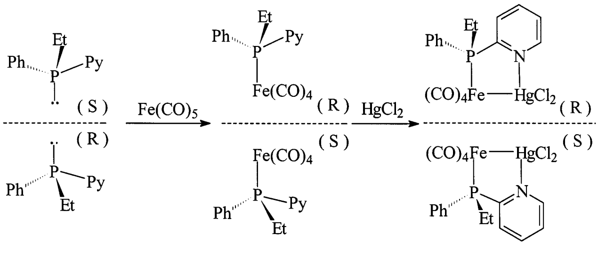
By the oxygen-atom transfer reaction, racemic (±)-$Fe(CO)_4$(EtPhPpy-*P*) was obtained from $Fe(CO)_5$, (±)-EtPhPpy [16] and $Me_3NO{\cdot}2H_2O$ [15].

$$Fe(CO)_5 + Me_3NO{\cdot}2H_2O + (\pm)\text{-EtPhPpy} \rightarrow (\pm)\text{-}Fe(CO)_4(\text{EtPhPpy-}P) + Me_3N + CO_2 + 2H_2O$$

This complex decomposed slowly in CH_2Cl_2 even under a N_2 atmosphere at room temperature, which may be due to the decarbonylation reaction. Treatment of a solution of racemic (±)-$Fe(CO)_4$(EtPhPpy-*P*) in CH_2Cl_2 with $HgCl_2$ at room temperature readily yielded binuclear Fe(0)–Hg(II) complexes (±)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$. By layering MeOH on the reaction solution, (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ was obtained as orange plate-like crystals and (−)-(*S*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ as orange needle-shaped microcrystals, which were separated manually under a microscope (Scheme 1).

The binuclear Fe(0)–Hg(II) complexes are stable in solution and in the solid state even on exposure to air, which indicates that the formation of a donor–acceptor Fe(0)–Hg(II) bond leads to stabilization of unstable electron-rich iron(0) complexes. The change of electron density at the iron centre can be gauged from the observed carbonyl stretching vibrations. The IR spectrum of (±)-$Fe(CO)_4$(EtPhPpy-*P*) shows $\nu(CO)$ at 2045.7, 1980.5 and 1930.4 cm^{-1}, while that of (±)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ shifted to higher frequencies at 2097.4, 2046.5, 2015.4 cm^{-1}, which is consistent with a decrease in electron density at the iron(0) centre.

The $^{31}P\{^1H\}$ NMR spectrum of (±)-$Fe(CO)_4$(EtPhPpy-*P*) exhibits a singlet at 83.62 ppm, while that of (±)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ shows a triplet at 95.18 ppm with $^{2+3}J(^{199}Hg-^{31}P) = 417$ Hz. Such a coupling constant has also been found in $ClFe(CO)_2(\mu\text{-}Ph_2Ppy)_2HgCl$ ($^{2+3}J(^{199}Hg-^{31}P) = 419$ Hz) [17] and *mer*-$[\{(MeO)_3Si\}(CO)_3Fe(\mu\text{-dppm})HgCl\{Ph_2CH_2C(O)Ph\}]$ ($^{2+3}J(^{199}Hg-^{31}P) = 397$ Hz) [18].



Scheme 1.

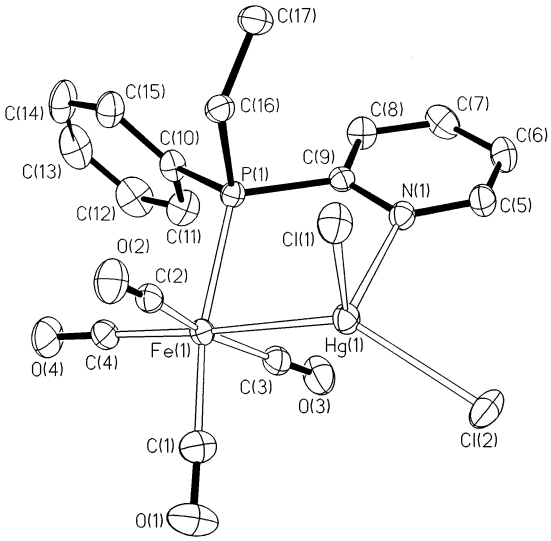


Fig. 1. ORTEP drawing (35% thermal ellipsoids) showing the molecular structure of (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$. Pertinent bond lengths (Å) and angles (°): Fe(1)–Hg(1) 2.608(1), Hg(1)–Cl(1) 2.549(1), Hg(1)–Cl(2) 2.445(1), Hg(1)–N(1) 2.530(4), Fe(1)–P(1) 2.297(1); P(1)–Fe(1)–C(1) 169.1(2), C(2)–Fe(1)–C(3) 163.3(2), C(4)–Fe(1)–Hg(1) 176.0(2), Hg(1)–Fe(1)–C(2) 80.4(2), C(2)–Fe(1)–C(4) 96.2(2), C(4)–Fe(1)–C(3) 100.5(2), C(3)–Fe(1)–Hg(1) 82.9(2), Fe(1)–Hg(1)–Cl(1) 114.8(1), Fe(1)–Hg(1)–Cl(2) 138.7(1), Fe(1)–Hg(1)–N(1) 90.0(1), Cl(1)–Hg(1)–Cl(2) 100.8(1).

The molecular structure of (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ is depicted in Fig. 1. The chiral phosphorus atom exhibits an *R* configuration. However, as the phosphorus atom coordinates to the iron centre through its lone-pair electrons, the absolute configuration of the original phosphine ligand can be deduced as *S* (Scheme 1). The iron and mercury centres are linked by an EtPhPpy-*P*,*N* bridge supported by a donor–acceptor metal–metal bond. The coordination geometry of the Fe(1) centre is distorted octahedral with bond angles P(1)–Fe(1)–C(1) = 169.1(2), C(2)–Fe(1)–C(3) = 163.3(2) and C(4)–Fe(1)–Hg(1) = 176.0(2)°. The sum of the Hg(1)–Fe(1)–C(2), C(2)–Fe(1)–C(4), C(4)–Fe(1)–C(3), and C(3)–Fe(1)–Hg(1) bond angles is 360°, indicating that the atoms of this C_3FeHg fragment are co-planar. The P(1) atom deviates from the perpendicular to the above fragment, with a somewhat acute bond angle of P(1)–Fe(1)–Hg(1) = 83.3(1)°. The Hg centre exhibits a distorted tetrahedral coordination geometry, with bond angles Fe(1)–Hg(1)–Cl(1) = 114.8(1), Fe(1)–Hg(1)–Cl(2) = 138.7(1), Fe(1)–Hg(1)–N(1) = 90.0(1) and Cl(1)–Hg(1)–Cl(2) = 100.8(1)°. The Fe–Hg distance of 2.608(1) is comparable to 2.546(1) Å in $Cl_2HgFe(CO)_2(PMe_2Ph)_2(CS_2C_2(CO_2Me)_2)$ [19] and 2.570(2) Å in $(CO)_4Fe(\mu\text{-}Ph_2Ppy)_2Hg(\mu\text{-}Cl)_2HgCl_2$ [8]. The Hg–N distance of 2.530(4) is somewhat longer than 2.483(11) Å in $(CO)_4Fe(\mu\text{-}Ph_2Ppy)_2Hg(\mu\text{-}Cl)_2HgCl_2$.

The crystallization of enantiomeric forms of $(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ in easily distinguishable habits is a most unusual phenomenon. Thus far we have had no success in our attempt to recover the enantiopure (−)-EtPhPpy ligand from the reaction of (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ with bis(diphenylphosphino)methane(dppm), 1,2-bis(diphenylphosphino)ethane (dppe), HCl or NaOH in DMF solution, and also failed to obtain the enantiopure phosphine oxide EtPhP(O)py by treating the binuclear complex with concentrated HNO_3 and H_2O_2.

3. Experimental

3.1. General

All reactions were carried out under nitrogen using Schlenk techniques. The solvents were purified by standard methods. Infrared spectra were recorded on a Perkin–Elmer 1600 spectrometer as KBr discs. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX-500 spectrometer at 202.5 MHz using 85% H_2PO_3 as the external standard and $CDCl_3$ as solvent.

3.2. Preparation of (±)-Fe(CO)$_4$(EtPhPpy-P)

$Me_3NO\cdot H_2O$ (0.55 g, 0.05 mol) dissolved in 20 ml ethanol was added slowly, over a period of 30 min, to a mixture of $Fe(CO)_5$ (0.67 ml, 0.05 mol) and (±) EtPhPpy (1.08 g, 0.05 mol) in 20 ml ethanol under N_2 at room temperature, and stirred for a further 5 h. The solvent was removed in vacuo to give an orange residue, which was then purified by column chromatography using 1:1 hexane/dichloromethane as the eluent under N_2. The product was obtained as a yellow powder (1.60 g, 83% yield). IR (KBr disc): ν(CO) 2045.7, 1980.5, 1930.4 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 83.62 ppm. *Anal.* Found: C, 53.70; H, 3.79; N, 3.30. Calc. for $C_{17}H_{14}NFeO_4P$: C, 53.26; H, 3.66; N, 3.66%.

3.3. Preparation of (+)-(R)-(CO)$_4$Fe(μ-EtPhPpy)-HgCl$_2$ and (−)-(S)-(CO)$_4$Fe(μ-EtPhPpy)HgCl$_2$

$HgCl_2$ (0.22 g, 8 mmol) was added to a solution of (±)-$Fe(CO)_4$(EtPhPpy-*P*) (0.30 g, 8 mmol) in 20 ml dichloromethane and stirred for 30 min at room temperature. After filtration, MeOH (20 ml) was added to the filtrate and it was cooled to −10°C for 12 h. (+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ was obtained as orange plate-like crystals (0.15 g, 57% yield). [α] [20] +18.16° (*c* 0.019, DMF) and (−)-(*S*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$ were obtained as orange needle-like microcrystals (0.12 g, 46% yield). [α] [20] −17.44° (*c* 0.019, DMF). IR (KBr disc): ν(CO) 2097.4, 2046.5, 2015.4 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 95.18 ppm. *Anal.* Found: C, 30.84; H, 2.16; N, 1.77. Calc. for $C_{17}H_{14}NFeHgO_4P$: C, 31.16; H, 2.14; N, 2.14%.

3.4. X-ray crystallography

(+)-(*R*)-$(CO)_4Fe(\mu\text{-EtPhPpy})HgCl_2$, $C_{17}H_{14}Cl_2FeHgNO_4P$, $M = 654.6$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 10.224(1)$, $b = 10.455(1)$, $c = 19.780(1)$ Å, $V = 2114.2(1)$ Å^3, $Z = 4$, $D_c = 2.057$ Mg m^{-3}, $F(000) = 1240$, orange plate with dimensions 0.28 × 0.10 × 0.08 mm, μ(Mo Kα) = 8.289 mm^{-1}. A total of 19 570 reflections with $2\theta \leq 55°$ were measured on a Smart CCD system at 20°C using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), and empirical absorption correction was applied using the SADABS [20] program. Refinement of 245 parameters for 27 non-hydrogen atoms and 5740 observed ($|F_o| > 4\sigma(F_o)$ out of 7776 ($R_{int} = 4.69\%$) unique data converged to $R(F) = 0.038$ and $wR(F^2) = 0.056$ with $w^{-1} = \sigma^2(F_o^2)$ and goodness-of-fit = 0.933. The Flack *x* parameter [21], which refined to a value of 0.010(5), was used to establish the absolute structure.

4. Supplementary material

The atomic parameters have been deposited at the Cambridge Crystallographic Data Centre as CCDC Ref. No. 116304.

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