Preparation and solid-state characterization of nickel(II) complexes with 1′-(diphenylphosphino)ferrocenecarboxylic acid

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1′-(Diphenylphosphino)ferrocenecarboxylic acid (Hdpf) reacts with nickel(II) halides and nickel(II) thiocyanate to give the paramagnetic complexes $[NiX_2(Hdpf\text{-}\kappa P)_2]$ (X = Cl, **1**; Br, **2**; I, **3**) and the diamagnetic planar isothiocyanato complex $[Ni(SCN\text{-}\kappa N)_2(Hdpf\text{-}\kappa P)_2]$ (**4**), respectively. *In situ* neutralization of Hdpf followed by reaction with nickel(II) sulfate affords the salt $[Ni(dpf)_2]$ (**5**). The halide complexes **1**–**3** easily undergo dissociative decomposition in polar donor solvents; compound **5** is insoluble in all common solvents. All compounds were characterized by IR and UV/vis spectroscopies and magnetic measurements in the solid state. The solid-state structure of the solvate $\mathbf{4} \cdot 2CHCl_3$ was determined by single-crystal X-ray diffraction. A series of complexes, including the ligand Hdpf and its Ca salt (**6**) as reference compounds, were further studied by X-ray photoelectron spectroscopy. Spectral data and magnetic measurements indicate compound **5** contains the dpf^- anion as a P,O-coordinated ligand.

Introduction

Nickel compounds are frequently used catalysts. Their unique properties result from the easy interconversion of the Ni(II) and Ni(0) oxidation states, from a wide range of accessible coordination geometries and the possibility of tuning the metal centre properties by changing the attached ligands. Among the numerous applications of nickel complexes in catalysis, carbon–carbon bond formation reactions are of particular importance. Representitive examples include cross-coupling reactions,[1] oligomerization of ethyne and butadiene,[2] alkene and ethyne polymerizations[3] and oligomerization of ethene into linear 1-alkenes (Shell higher olefin process, SHOP).[4] In attempts to optimize the course of the latter process, various complexes bearing O,P-chelating phosphinocarboxylates(1−) and phosphinocarboxylic esters,[5] phosphinoenolates and phosphinoalcoholates (phosphinophenolates)[6] as the ligands have been tested as catalyst precursors.

We have recently reported the preparation of another type of hybrid phosphinocarboxylic donor, 1′-(diphenylphosphino)-ferrocenecarboxylic acid (Hdpf)[7]—an organometallic analogue of the archetypal ligand, (diphenylphosphino)acetic acid, which has been used for the preparation of model SHOP catalysts.[5a] We have also demonstrated that Hdpf binds soft transition metals as a simple phosphine whose carboxyl functionality remains uncoordinated and takes part in hydrogen bonding [Pd(II), Pt(II),[8] Cu(I)[9] and Hg(II)[10]]. A deprotonated form of Hdpf, dpf^-, coordinates alkali earth metals as an O-donor.[11] In the case of Rh(I), complexes containing both P-Hdpf and O,P-chelating dpf^- ligands were obtained. In a mixed Hdpf-dpf^- complex, *trans*-[Rh(CO)(dpf-κ*O*,*P*)(Hdpf-κ*P*)], the ferrocene ligands undergo a fast proton exchange, thus demonstrating the ability of Hdpf to act as a hemilabile hybrid donor.[12] This prompted us to study the coordination behaviour of Hdpf towards nickel(II) since the location of nickel metal at the borderline between typically hard and soft transition metals renders the coordination bonds to both hard and soft donor atoms comparably stable.

In this paper we describe the synthesis of nickel(II) Hdpf complexes $[NiX_2(Hdpf\text{-}\kappa P)_2]$ (X = Cl, Br, I and NCS) and $[Ni(dpf)_2]$ and their characterization in the solid state by IR, UV/vis and X-ray photoelectron spectroscopies and magnetic measurements. The crystal structure of *trans*-$[Ni(NCS\text{-}\kappa N)_2(Hdpf\text{-}\kappa P)_2] \cdot 2CHCl_3$ is also reported.

Results and discussion

Synthesis and spectral characterization

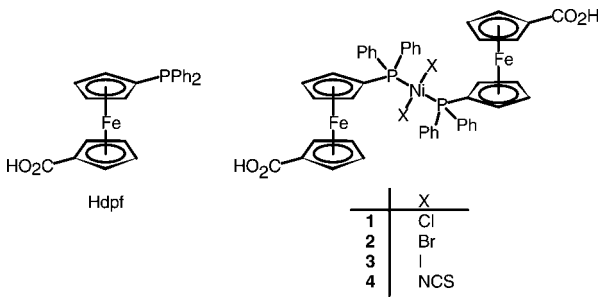
Complexes $[NiX_2(Hdpf\text{-}\kappa P)_2]$, where X = Cl (**1**), Br (**2**) and I (**3**), were prepared by mixing stoichiometric amounts of Hdpf and the appropriate hydrated nickel(II) salt in ethanol and evaporating the solvent. Because of their easy dissociative decomposition in solution (see below), the complexes cannot be recrystallized. The halide complexes are dark green (**2**) or brown (**1** and **3**) and their magnetic properties and UV/vis spectra imply tetrahedral coordination in all cases (Table 1). The magnetic moments observed for **1**–**3** are in accordance with the values expected for a tetrahedral $[NiA_2B_2]$ donor set, which is usually found within the lower part of the 3.0–3.9 μ_B interval typical for tetrahedral Ni(II) complexes.[13] In the electronic spectra, the halide complexes exhibit bands assignable to $^3A_2 \leftarrow {}^3T_1(F)$ and $^3T_1(P) \leftarrow {}^3T_1(F)$ transitions and strong CT bands located predominantly within the ferrocene moiety (electronic transitions of tetrahedral complexes **1**–**3** are labelled as if belonging to the T_d symmetry throughout this text). The bands exhibit shoulders due to the splitting of energy levels on lowering the idealized local symmetry of the complex molecule from T_d to D_{2h}. The observed shift of the d–d transitions in the $[NiX_2(Hdpf\text{-}\kappa P)_2]$ complexes to higher wavenumbers in the sequence I < Br < Cl corresponds to the position of the halide ligands in the spectrochemical and nephelauxetic series. The halide complexes are insoluble in

Table 1 Diffuse reflectance UV/vis spectral[a] and magnetic data for complexes **1**–**5**

Complex	$\tilde{\nu}/10^3$ cm^{-1}	χ_M[b]/10^{-6} cm^3 mol^{-1}	T/K	μ/μ_B[c]
1	21.7,[d] 11.1–17.2[e]	4283	294.3	3.18
2	23.3,[d] 16.7, 14.3sh;[f] 10.6, 8.62[g]	4295	292.9	3.17
3	22.2,[d] 17.5sh; 13.5;[f] 9.26, 7.81sh[g]	4215	293.8	3.15
4	23.3, 20.4[h]	−403	294.4	diamg
5	25.6, 21.3; 14.7sh, 11.9	2015	293.2	2.18

[a] Tentative assignment. [b] Hdpf: found $\chi_M = -252 \times 10^{-6}$ cm^3 mol^{-1} at 294.5 K; calculated from Pascal constants -240×10^{-6} cm^3 mol^{-1}. [c] $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}. [d] CT bands. [e] $^3A_2 \leftarrow {}^3T_1(F)$ and $^3T_1(P) \leftarrow {}^3T_1(F)$. [f] $^3T_1(P) \leftarrow {}^3T_1(F)$. [g] $^3A_2 \leftarrow {}^3T_1(F)$. [h] CT bands and $^1B_{1g} \leftarrow {}^1A_{1g}$. *Cf.* data for a $CHCl_3$ solution: strong band at 24 570 cm^{-1} (ε_M 2220 M^{-1} cm^{-1}) and a shoulder at *ca.* 20 800 cm^{-1}.

non-polar organic solvents but dissociate extensively in polar solvents (chloroform, acetic acid, acetone and acetonitrile), as follows from the increased molar conductivity of the solutions. Hence, no direct comparison of their solution and solid-state electronic spectra are feasible.



IR spectra of complexes **1**–**3** exhibit strong bands due to ν_a(COO) and ν_s(COO) at *ca.* 1670 and 1290 cm^{-1}, respectively, similar to the values of uncoordinated Hdpf, thus indicating that the ligand behaves as a simple P-donor without participation of its carboxyl group in bonding to the central atom.

The brick red, diamagnetic planar complex [Ni(NCS)$_2$(Hdpf-κ*P*)$_2$] (**4**) was prepared similarly to its halide analogues **1**–**3**. The position of the IR bands due to the SCN ligand [ν(CN) 2089 and ν(CS) 872 cm^{-1}] points to its coordination by the nitrogen atom.[14] This assumption was confirmed by X-ray diffraction analysis (see below). In its UV/vis spectrum, complex **4** possesses two bands above 20 000 cm^{-1}, which cannot unequivocally be assigned to CT and $^1B_{1g} \leftarrow {}^1A_{1g}$ bands. Unlike the halide complexes **1**–**3**, compound **4** does not dissociate in chloroform solution (Λ_M 0.03 S cm^{-2} mol^{-1}). As the solid-state and chloroform solution spectra are similar, it is obvious that the planar coordination sphere remains intact in solution. In polar donor solvents, such as acetone or acetonitrile, however, the complex partially dissociates as indicated by the increased conductivity of the solutions.

Another type of complex with the composition [Ni(dpf)$_2$] was obtained by metathesis of nickel(II) sulfate with *in situ* generated Nadpf. Compound **5** is probably polymeric as indicated by its very low solubility in all common organic solvents and in water. The IR spectrum of complex **5** corroborates the assumed presence of a deprotonated carboxyl group by showing carboxylate bands at 1609 and 1358 cm^{-1} [ν_a(COO) and ν_s(COO), respectively]. Based on the value $\Delta\nu = \nu_a - \nu_s$ of *ca.* 250 cm^{-1}, which is rather high compared to other carboxylates,[15] it can be concluded that the carboxylate is probably bonded as an O-unidentate, κ^1*O*,κ^2*O*′-bridge or κ^1*O*,κ^2*OO*′-bridge with only a low ionic contribution to the Ni–O bond [*cf.* Δν *ca.* 185 cm^{-1} for ionic Ca(II), Sr(II) and Ba(II) salts of Hdpf[7]]. The magnetic moment per nickel atom in **5** is only 2.18 μ_B, around half of the maximum value expected for tetrahedral but lower than values typical of octahedral Ni(II) complexes. Thus, one may anticipate that about half of the nickel centres are low-spin and planar while the rest are high-spin. In the UV/vis spectrum of complex **5**, no bands due to planar nickel(II) sites could be identified because of the presence of strong CT bands. However, the spectrum can be interpreted in terms of a tetrahedral coordination arrangement of the high-spin nickel ion. Both elemental analysis and spectral methods exclude the presence of further donors like coordination-capable solvents in the structure of compound **5**. Therefore, we expect the compound to form a polymeric structure in which the dpf$^-$ anion builds up coordination polyhedra around different nickel centres by combining the simple P-donation with a multidentate, preferably bridging, O-coordination of the deprotonated carboxyl group. Unfortunately, more accurate information about the structure of compound **5** could not be obtained since all attempts to isolate a solid crystalline sample or a monomeric species failed. As all the complexes studied are insoluble in non-polar solvents but decompose upon dissolution in polar solvents, they are not suitable for catalytic applications.

X-Ray photoelectron spectra

With the aim of gaining further information about the bonding and charge distribution in complexes **1**–**5**, the complexes were studied by X-ray photoelectron spectroscopy (XPS). As a comparison, the XPS spectra of Hdpf and anhydrous Ca(dpf)$_2$ (**6**)[7] were also recorded. The measured core level binding energy values (E_b), along with the widths of the photoemission lines are given in Table 2.

The binding energy of the Fe 2p$_{3/2}$ electrons (707.9 ± 0.1 eV) does not change in the series of samples studied and lies between the values reported for ferrocene (707.7 eV)[16] and 1,1′-ferrocenedicarboxylic acid (708.4 eV).[17] The P 2p binding energy (Table 2, Fig. 1) measured for Hdpf (and also for complexes **1** and **5**) is similar to the values published for free triphenylphosphine (130.8 ± 0.1 eV)[18] while all data correspond well to the data reported for analogous nickel(II) compounds—for instance [NiX$_2$(PPh$_2$Et)$_2$], X = Br: 131.0 (tetrahedral), 131.2 (planar); X = I: 131.4 eV (tetrahedral).[19] The P 2p binding energy in homologous tetrahedral complexes **1**–**3** decreases in the order **3** > **2** > **1** as the result of decreasing donation of the phosphorus lone pair to the nickel atom and, thus, increased electron density at the phosphorus atom. Such a trend is in accordance with the decreasing stability of the complexes towards dissociative decomposition. For compound **4**, the S 2p and N 1s binding energies compare well to the values reported for [Ni(SCN)$_2$(PPh$_3$)$_2$] of 126.6 and 398.5 eV, respectively.[19]

In accordance with the results of magnetic measurements revealing that all complexes except for compound **4** are paramagnetic, Ni 2p$_{3/2}$ spectra of **1**–**3** and **5** show characteristic shake-up satellite structures (see Fig. 2).[20] Considering a correlation between the Ni 2p$_{3/2}$ binding energy and charge on the nickel atom in a series of nickel compounds as reported by Matienzo *et al.*,[20] we can conclude that the positive charge on the nickel centre increases in the order **2** ≈ **4** < **3** < **5** < **1** with the covalency of the compounds increasing in the reverse sequence.

Table 2 X-Ray photoelectron spectra

Compound	E_b(FWHM)[a]/eV				
	P 2p	O 1s[b]	Fe $2p_{3/2}$	Ni $2p_{3/2}$	Other
Hdpf	130.5(2.0)	531.8(2.2), 533.2	708.0(1.6)		
1	130.6(2.5)	531.6(2.4), 533.2	708.0(1.9)	856.0(3.4)	199.2(3.2)[c]
2	131.2(2.5)	531.5(2.4), 532.8	707.8(1.6)	854.8(3.2)	
3	132.5(1.9)	531.3(2.3), 532.8	707.9(1.8)	855.2(3.8)	
4	131.5(2.7)	531.4(2.5), 533.2	707.8(1.9)	854.8(2.2)	398.2(2.0)[d] 162.7(2.5)[e]
5	130.8(2.2)	531.3(2.2)	7.7.9(1.7)	855.6(2.7)	
6	130.8(2.8)	531.4(2.3)	708.1(1.8)		347.3(2.0)[f]

[a] Binding energies are corrected to the C 1s value (E_b = 284.6 eV). FWHM is full width at half maximum intensity. [b] Signals due to O 1s electrons were fitted with the same FWHM. [c] Cl 2p. [d] N 1s. [e] S 2p. [f] Ca $2p_{3/2}$.

With the exception of complexes **5** and **6**, two components are observed in the spectra of O 1s electrons (Fig. 3), which can be assigned to C=*O* (lower E_b) and C–*O* bonds of the carboxyl group (*cf.* O 1s spectra of phthalic acid[21] or *p*-$ClC_6H_4CO_2H$[22]). In most cases, the intensity of the component due to C=O is higher than that due to the C–O oxygen although a 1 : 1 ratio can be expected from the stoichiometry of the unsolvated complexes. The non-equality very likely arises from an overlap of the C=*O* bands with bands coming from ethanol used as the solvent, which remains adsorbed on the surface of the samples (O 1s binding energies of alcohols are *ca.* 532.5 eV, lower than E_b of water, *ca.* 535 eV[23]). Further support for this assumption is obtained from the deviation of the *surface* elemental analysis, inferred from photoelectron spectra, from the calculated values,[24] which increase with increasing intensity of the lower E_b component of the O 1s doublet.

XPS further completes the data obtained for complex **5**. The Ni $2p_{3/2}$ binding energy in **5** differs significantly from the E_b(Ni $2p_{3/2}$) reported for $NiCl_2$ (856.4 eV),[19] showing that the paramagnetism of **5** is an inherent property of the prepared compound and is not due to an admixture of the starting nickel(II) salt. Furthermore, the obtained Ni $2p_{3/2}$ binding energy value rules out[20] the presence of octahedrally coordinated nickel(II) centres in **5**. However, as the E_b(Ni $2p_{3/2}$) in planar and tetrahedral Ni(II) complexes do not differ significantly,[20] it is not possible to decide which type of coordination centres are present in the solid-state structure of complex **5**. Comparison of O 1s spectra of compounds **5** and **6** indicates deprotonation of the carboxyl group since the spectra show only a one-component signal characteristic for deprotonated carboxylic acids.[22] As the presence of solvating donor molecules is excluded by traditional as well as by XPS elemental analysis, it is obvious that the carboxylate dpf^- has to coordinate nickel(II) cations not only as a P-donor but also as an O-ligand, as suggested on the basis of IR spectra.

Crystal structure of complex 4

Complex **4** crystallizes from its chloroform solution as the solvate **4**·$2CHCl_3$. The molecular structure of the complex and the atom labelling scheme is shown in Fig. 4; selected geometric parameters are listed in Table 3. The central atom resides on a crystallographic inversion centre in a unit cell with $P\bar{1}$ symmetry, which renders only one half of the molecule crystallographically independent. As a result of the

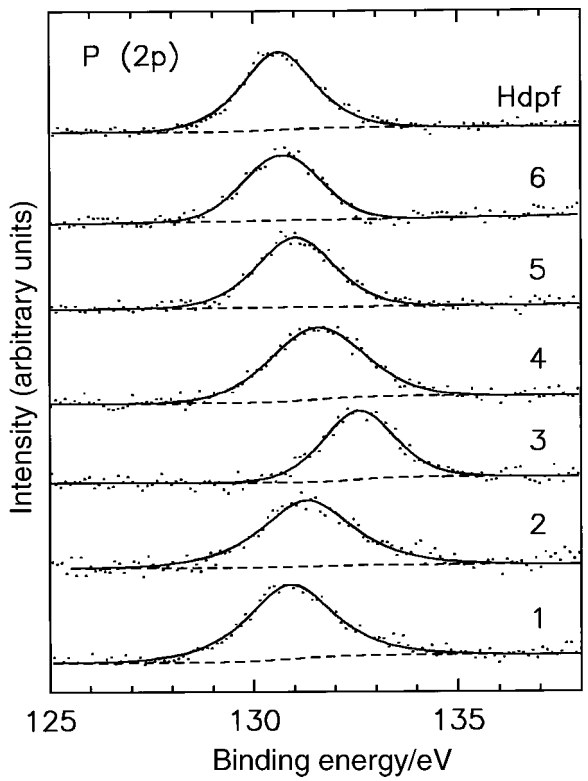


Fig. 1 X-Ray photoelectron spectra of P 2p electrons for compounds **1**–**6** and Hdpf.

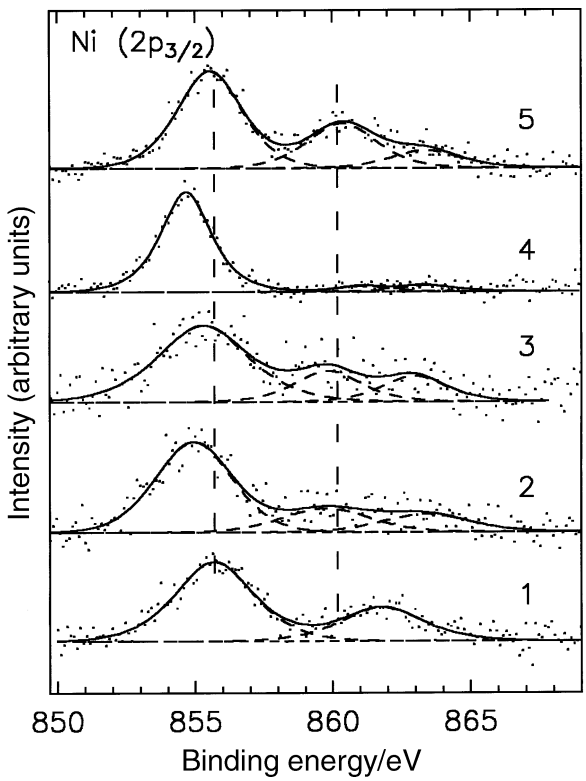


Fig. 2 X-Ray photoelectron spectra of Ni $2p_{3/2}$ electrons for complexes **1**–**5**.

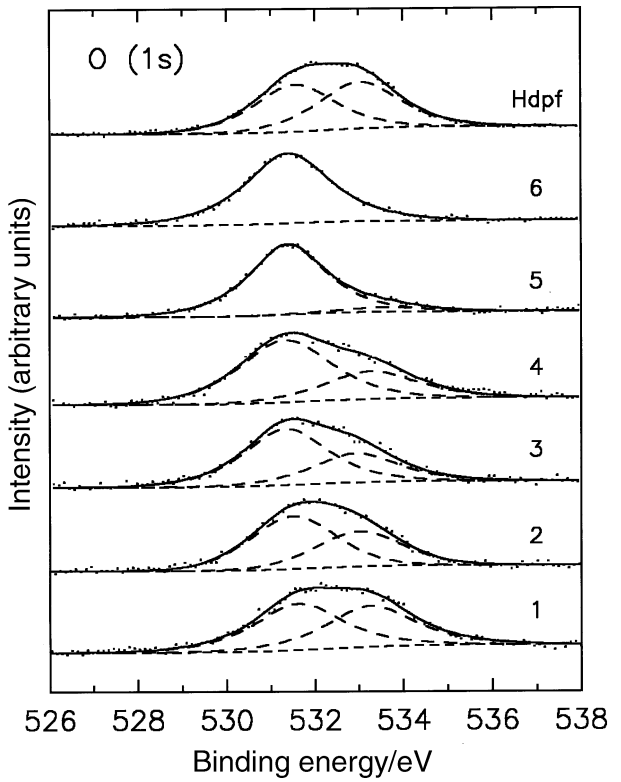


Fig. 3 X-Ray photoelectron spectra of O 1s electrons for **1**–**6** and Hdpf.

imposed symmetry, the nickel atom has a perfectly planar environment with the corresponding angles N–Ni–P and N^{i}–Ni–P differing slightly from the right angle expected for an ideal square arrangement due to the steric demands of the bulky phosphine ligand. For the same reason, the isothiocyanato ligand, which itself is almost exactly linear [N–C(24)–S 178.8(7)°], is oriented to a less sterically hindered site and displays a slight bending at the nitrogen atom [Ni–N–C(24) 173.1(5)°]. A similar deformation can be traced in the structures of the analogous complexes $[Ni(PPh_3)(NCS\text{-}\kappa N)_2]$[25] and $[Ni(PMePh_2)(NCS\text{-}\kappa N)_2]$.[26]

The Ni–S distance in **4** does not differ significantly from the values reported for the above mentioned complexes. On the other hand, the Ni–P distance of 2.263(2) Å is slightly longer than the analogous distances in the aforementioned complexes [2.245(1) and 2.240(1) Å, respectively].

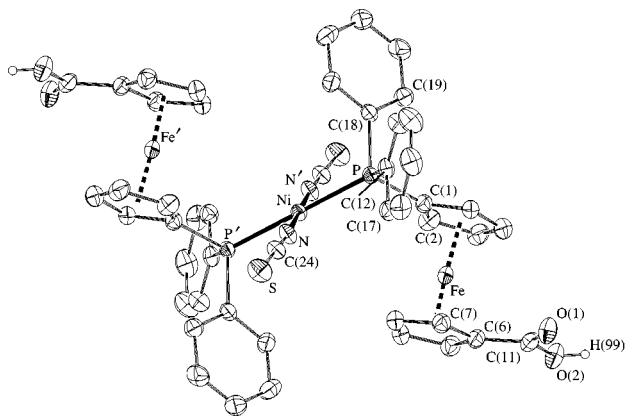


Fig. 4 Molecular diagram of $4 \cdot 2CHCl_3$ with thermal ellipsoids drawn at 30% probability level. The molecule of solvating chloroform and hydrogen atoms [except the carboxylic proton H(99)] are not shown for clarity. Prime labelled atoms are generated by the $(2 - x, -y, -z)$ symmetry transformation.

Table 3 Selected bond lengths (Å) and bond and dihedral angles of least-squares planes[a] (°) for $4 \cdot 2CHCl_3$

Ni–N	1.819(5)	N–Ni–P	93.8(2)
Ni–P	2.263(2)	N^{i}–Ni–P	86.3(2)
S–C(24)	1.599(7)	Ni–N–C(24)	173.1(5)
P–C(01)	1.809(7)	N–C(24)–S	178.8(7)
P–C(12)	1.819(6)	C(01)–P–C(12)	103.9(3)
P–C(18)	1.819(6)	C(01)–P–C(18)	105.2(3)
N–C(24)	1.174(8)	C(12)–P–C(18)	105.2(3)
O(1)–C(11)	1.228(9)	O(1)–C(11)–O(2)	124.8(7)
O(2)–C(11)	1.286(9)	O(1)–C(11)–C(06)	120.1(7)
Fe–C (Cp)[b]	2.04(1)	O(2)–C(11)–C(06)	115.0(7)
C–C (Cp)[b]	1.41(1)	C–C–C (Cp)[b]	108.0(7)
C–C (Ph)[b]	1.38(1)	C–C–C (Ph)[b]	120.0(8)
Cp1 *vs.* Cp2	4.5(6)	Cp2 *vs.* CO_2	7(2)
Cp1 *vs.* Ph1	79.6(3)	Ph1 *vs.* Ph2	71.5(2)
Cp1 *vs.* Ph2	74.2(3)		

[a] Symmetry operation: (i) $2 - x, -y, -z$. The least-squares planes are defined as follows: Cp1: C(1–5), Cp2: C(6–10), Ph1: C(12–17), Ph2: C(18–23) and CO_2: C(11), O(1), O(2). [b] Average values.

Compared to uncoordinated Hdpf,[7] the carboxyphosphine part undergoes only a marginal deformation of the bond lengths and angles upon coordination. The perpendicular distances of the iron atom to both cyclopentadienyl ring centroids are 1.646(3) Å. The rings are tilted at a dihedral angle of 4.5(6)° and adopt a perfect *anti*-eclipsed conformation [compare the torsion angle defined by C(1), ring centroids and C(6) of −143.7(5)° with the ideal value of −144°]. The conformation is very likely the result of the solid-state packing, in which the uncoordinated carboxyl groups of adjacent molecules of the complex are linked by centrosymmetric double hydrogen bonds [$O(2)\cdots O(1)^{ii}$ 2.632(9) Å, (ii) $3 - x, 1 - y, -1 - z$] into infinite chains. The hydrogen bonding influences the conformation of the ferrocene framework by bringing the carboxyl groups in the complex molecule into mutually opposite positions. However, it does not deviate the carboxyl group from a coplanar arrangement with its adjacent cyclopentadienyl ring [dihedral angle of the corresponding least-squares planes is only 7(2) Å].

Experimental

Materials and methods

All reactions were carried out under an argon atmosphere using solvents dried by the appropriate drying agents[27] and distilled under an argon atmosphere. Water, methanol and azeotropic ethanol were degassed with argon. Triethylamine was distilled from sodium. Nickel(II) thiocyanate was prepared by reacting an excess of basic nickel(II) carbonate with aqueous HSCN and characterized as the hydrate $Ni(SCN)_2 \cdot 3/2H_2O$ on the basis of complexometric titration [found: $w(Ni) = 29.1\%$]. $NiBr_2 \cdot 3H_2O$ [found: $w(Ni) = 21.5\%$] and $NiI_2 \cdot 5/2H_2O$ [found: $w(Ni) = 16.4\%$] were prepared similarly. Hdpf[7] and its solvated calcium salt[11] were prepared by literature methods.

IR spectra were recorded on an Mattson Genesis FT IR instrument (range 400–4000 cm^{-1}). UV/vis spectra of the solid samples were measured on a Varian Cary 17D instrument equipped with a diffuse reflectance accessory in the range 350–1400 nm. The samples were diluted with MgO (1 : 3, w/w) and magnesium oxide was used as the reference. Solution UV/vis spectra were recorded on a Unicam UV 300 instrument in the range 350–1100 nm. Conductivity measurements were carried out on a Radiometer CDM 3 conductometer. Magnetic susceptibilities were determined by the Faraday method using modified Curie–Chéneveau balances.[28]

X-Ray photoelectron spectra (XPS) were measured on an ESCA 310 (Gammadata Scienta, Sweden) electron spectro-

meter equipped with an Al-Kα X-ray source (1486.6 eV) and operated in the fixed analyzer transmission mode. The powder samples were spread on a gold plate, which was mounted onto a sample stub by means of metal clips. During the spectral acquisition the X-ray source was operated at 14 kV and 300 mA. The pass energy of the hemispherical electron analyzer was set to 150 eV. The curve fitting of high resolution spectra was carried out using a Gaussian–Lorentzian line shape and a damped non-linear least-squares fitting procedure. Quantification of the concentrations of elements was accomplished by correcting the photoelectron peak areas for their cross-sections[29] and by taking into account the dependence of the photoelectron mean free path and analyzer transmission on the electron kinetic energy.[30]

Syntheses

***trans*-[NiCl$_2$(Hdpf-κ*P*)$_2$] 1.** A solution of $NiCl_2 \cdot 6H_2O$ (47.5 mg, 0.20 mmol) in ethanol (2 cm^3) was added to a solution of Hdpf (166.0 mg, 0.40 mmol) in the same solvent (15 cm^3). After stirring for 15 min at room temperature, the solution was filtered and evaporated under reduced pressure to leave a light brown solid. Yield: 176.3 mg, 92%. Anal. found: Ni, 5.8; $C_{46}H_{38}Cl_2Fe_2NiO_4P_2$ requires Ni, 6.1%. M.p. 200 °C (dec.). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3519 w, 3428 w, 2633 w, 1667 s, 1295 s, 1163 m, 1097 w, 1026 m, 935 w, 827 m, 744 s, 693 s, 636 w, 597 w, 564 m, 497 m, 471 w, 447 w.

***trans*-[NiBr$_2$(Hdpf-κ*P*)$_2$] 2.** A solution of $NiBr_2 \cdot 3H_2O$ (54.6 mg, 0.20 mmol) in ethanol (4 cm^3) was added to a solution of Hdpf (165.6 mg, 0.40 mmol) in the same solvent (15 cm^3). After stirring for 15 min at room temperature, the solution was filtered and evaporated under reduced pressure. Washing the resulting green solid with toluene (5 × 2 cm^3) and hexane (6 × 2 cm^3), then drying *in vacuo* (4 h, 1 Torr) afforded **2** as a dark green solid. Yield: 190.0 mg, 91%. Anal. found: C, 52.2; H, 4.1; Ni, 5.6; $C_{46}H_{38}Br_2Fe_2NiO_4P_2$ requires C, 52.8; H, 3.8; Ni, 5.6%. M.p. dec. above 210 °C. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3376 w, 2637 w, 1665 s, 1293 m, 1162 m, 1091 w, 1033 w, 1026 w, 936 w, 827 w, 744 m, 695 m, 565 w, 497 w.

***trans*-[NiI$_2$(Hdpf-κ*P*)$_2$] 3.** A mixture of $NiI_2 \cdot 5/2H_2O$ (89.5 mg, 0.25 mmol) and Hdpf (207.0 mg, 0.50 mmol) was dissolved in ethanol (33 cm^3). The reaction mixture was stirred for 15 min, filtered and evaporated *in vacuo*. The residue was extracted with hot dichloromethane (20 cm^3). The resulting dark brown extract was filtered and evaporated under reduced pressure, leaving a solid that was washed with diethyl ether (6 × 2 cm^3) and hexane (3 × 2 cm^3), then dried at 75 °C for 3 h to give **3** as a dark brown solid. Yield: 190.0 mg, 91%. Anal. found: C, 48.9; H, 3.5; I, 21.7; Ni, 4.9; $C_{46}H_{38}Fe_2I_2NiO_4P_2$ requires C, 48.4; H, 3.4; I, 22.3; Ni, 5.1%. M.p. dec. above 225 °C. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3320 w, 2630 w, 1676 s, 1283 m, 1142 s (composite), 1095 m, 1032 m, 998 w, 913 w, 837 m, 746 m, 725 s, 693 w, 570 m, 534 m, 489 w.

***trans*-[Ni(Hdpf-κ*P*)$_2$(NCS-κ*N*)$_2$] 4.** A solution of $Ni(SCN)_2 \cdot 3/2H_2O$ (40.6 mg, 0.20 mmol) in ethanol (6 cm^3) was added to a solution of Hdpf (165.6 mg, 0.40 mmol) in the same solvent (20 cm^3). The resulting orange solution was stirred for 15 min at room temperature, filtered and evaporated under reduced pressure. The residue was washed with toluene (5 × 2 cm^3) and hexane (6 × 2 cm^3), and finally dried *in vacuo* (2 h, 1 Torr) to give a powdery red solid. Yield: 178.4 mg, 89%. Anal. found: C, 59.0; H, 4.2; N, 2.6; S, 6.1; Ni, 5.8; $C_{48}H_{38}Fe_2N_2NiO_4P_2S_2$ requires C, 57.5; H, 3.8; N, 2.8; S, 6.4; Ni, 5.8%. M.p. 190 °C (dec.). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3430 w, 2635 w, 2089 vs, 1680 s, 1294 m, 1164 m, 1098 m, 1036 w, 999 w, 935 w, 872 w, 839 w, 742 m, 696 m, 627 w, 541 w, 508 w, 492 w.

[Ni(dpf)$_2$] 5. At 40 °C, a solution of sodium hydrogen carbonate (42.0 mg, 0.50 mmol) in water (10 cm^3) was added to a solution of Hdpf (207.0 mg, 0.50 mmol) in ethanol (10 cm^3). After stirring the resulting yellow solution for 2 min, aqueous $NiSO_4$ solution (0.185 cm^3, 1.371 M, 0.25 mmol) was added, whereupon deposition of a yellow precipitate started immediately. The mixture was brought to boiling, cooled slowly to room temperature and stirred for a further 12 h. The precipitate was filtered off, washed with water, ethanol and hexane (4 × 1.5 cm^3 each) and dried in air to give **5** as an ochre–brown powder. Yield: 157.0 mg, 71%. Anal. found: C, 62.3; H, 4.1; Ni, 6.7; $C_{46}H_{36}Fe_2NiO_4P_2$ requires C, 62.4; H, 4.1; Ni, 6.6%. M.p. dec. above *ca.* 180 °C. IR (Nujol): $\tilde{\nu}$/cm^{-1} 1609 s, 1392 s, 1358 s, 1192 m, 1173 m, 1161 m, 1097 w, 1053 w, 1028 m, 922 w, 831 w, 789 m, 744 m, 694 m, 636 w, 492–529 m (composite), 465 w.

Compound **5** can also be prepared by metathesis of solvated Ba(dpf)$_2$ with a $NiSO_4$ solution or by *in situ* deprotonation of a Hdpf–$NiCl_2$ mixture with triethylamine but the product is difficult to separate from side products ($BaSO_4$ and ammonium dpf$^-$ salts, respectively).

X-Ray crystallography

Crystal data and data collection parameters for 4·2CHCl$_3$. $C_{50}H_{40}Cl_6Fe_2N_2NiO_4P_2S_2$, $M = 1242.0$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.724(1)$, $b = 11.0215(6)$, $c = 12.758(1)$ Å; $\alpha = 73.832(5)$, $\beta = 73.892(4)$, $\gamma = 71.608(4)°$, $U = 1344.2(2)$ Å^3 (determined by least-squares from 5956 diffractions with $2.0° \leqslant 2\theta \leqslant 50.0°$ at $T = 296$ K), graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $Z = 1$, $D_c = 1.359$ g cm^{-3}, $F(000) = 630$, μ(Mo-Kα) = 1.36 mm^{-1}, orange–red plate grown by slow evaporation from a chloroform solution, dimensions 0.03 × 0.25 × 0.25 mm^3, Nonius KappaCCD image plate diffractometer: 108 frames measured (2° oscillation and 120 s counting time each, 10 558 integrated diffractions) and the data were analyzed by the HKL program package;[31] data collection range $0 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 13$, $-14 \leqslant l \leqslant 15$ ($2\theta_{max} = 50°$); 4744 unique diffractions were used in all calculations. The diffraction data were corrected for Lorentz polarization effects and for absorption (diffractometer-implemented multiscan routine: $T_{min} = 0.906$, $T_{max} = 0.966$).

Structure solution and refinement. The structure was solved by direct methods (SIR92[32]) and refined by full-matrix least-squares on F^2 (SHELXL97[33]). Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$, $w_1 = 0.0890$ and $w_2 = 0.9300$ was applied. All non-hydrogen atoms were refined anisotropically. The carboxylic hydrogen atom was indentified on a diference electron density map and isotropically refined. All other hydrogen atoms were included in calculated positions and refined with fixed C–H bond lengths (0.93 Å aromatic, 0.98 Å $CHCl_3$) and $U_{iso}(H) = 1.2\,U_{eq}(C)$. Final $R = 0.068$ and $wR = 0.165$ for 2929 observed diffractions [$F_o > 4\sigma(F_o)$]; $R = 0.120$ and $wR = 0.192$ (all data); 317 parameters, largest Δ/σ 0.001, goodness of fit 1.05, extremes on the residual electron density map +1.59 and −1.17 e Å^{-3}.

CCDC reference number 161110. See http://www.rsc.org/suppdata/nj/b1/b104780a/ for crystallographic data in CIF or other electronic format.

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