Synthesis of Homo- and Hetero-Bimetallic Complexes Containing the $Ni(C_6F_5)_2$ Moiety – Crystal Structure of $[(C_6F_5)_2Ni(\mu\text{-}SPh)_2Pd(dppe)]$

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The compound *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$ has been used as the starting material for the preparation of the bimetallic complexes $[(C_6F_5)_2Ni(\mu\text{-}X)_2Ni(C_6F_5)_2]^{2-}$ (X = SCN, OCN, N_3), $[(C_6F_5)_2Ni(\mu\text{-}SCN)_2Pd(C_6F_5)_2]^{2-}$, $[(C_6F_5)_2Ni(\mu\text{-}NCS)_2Pd(dppe)]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane], and the trimetallic$[(C_6F_5)_2Ni(\mu\text{-}NCS)_2Pd(\mu\text{-}SCN)_2Ni(C_6F_5)_2]^{2-}$. The mononuclear compounds $[(C_6F_5)_2NiLX]$ (L = PPh_3, $P(C_6H_4MeO\text{-}p)_3$; X = SCN, OCN) are obtained by reaction between $[(C_6F_5)_2Ni(\&\mu\text{-}X)_2Ni\text{-}(C_6F_5)_2]^{2-}$ and L. The treatment of *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$ with $[M(SAr)_2(dppe)]$ leads to the formation of the arylthiolate complexes $[(C_6F_5)_2Ni(\mu\text{-}SAr)_2M(dppe)]$ (Ar = Ph, C_6H_4Me-*p*, $C_6H_4NO_2$-*p*; M = Ni, Pd, Pt). The X-ray diffraction study of $[(C_6F_5)_2Ni(\mu\text{-}SPh)_2Pd(dppe)]$ shows that both metal atoms, Ni and Pd, are coordinated in a slightly distorted square-planar geometry and the μ-thiolato groups are in the *syn* conformation.

Introduction

Anionic complexes of the group-10 elements of the type $[M_2R_4(\mu\text{-}X)_2]^{2-}$ (M = Ni, R = C_6F_5, X = F or Cl; M = Pd or Pt, R = C_6F_5, X = Cl, Br, I or SCN; M = Pd, R = $C_6F_3H_2$-2,4,6, X = Cl, Br, I, SCN) have been reported[1][2][3][4]. Labile complexes such as $[MR_2(tht)_2]$ (M = Pd or Pt; R = C_6F_5)[5] and $[PdR_2(PhCN)_2]$ (R = C_6F_5, $C_6F_3H_2$-2,4,6)[6] have shown to be excellent precursors for the synthesis of asymmetric homo- and hetero-bimetallic complexes with halide bridges.

Symmetric or antisymmetric binuclear complexes can be obtained by treating the labile complex R_2ML_2 with the appropriate reagent [Eq. (1) and (2)]. The reaction represented by Eq. (1) was used for the preparation of bis(μ-hydroxo) complexes of nickel[7] and palladium[8] $[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2]^{2-}$ from the reaction between *cis*-$[M(C_6F_5)_2(PhCN)_2]$ and OH^-, but the platinum anologue[9] could not be prepared by this method because the nucleophilic attack of coordinated PhCN by OH^- was competitive. The process represented by Eq. (2) was used for the preparation of bimetallic (Pd−Ni, Pd−Pd, or Pd−Pt) palladium complexes[6]. We report here the preparation and study of a number of new bimetallic pseudohalide-bridged complexes derived from the $Ni(C_6F_5)_2$ starting from the labile complex *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$.

$$2\,R_2ML_2 + 2\,X^- \rightarrow R_2M(\mu\text{-}X)_2M'R_2 + 4\,L \tag{1}$$

$$R_2ML_2 + X_2M'L'_2 \rightarrow R_2M(\mu\text{-}X)_2M'L'_2 + 2\,L \tag{2}$$

The above method has been extended to the preparation of some bimetallic arylthiolate-bridged complexes of nickel. The relevance of transition-metal complexes with aliphatic thiolate ligands as models of biologically redox-active metalloproteins[10] has stimulated interest in the chemistry of metal thiolates[11]. Nickel(II) thiolates are generally square-planar species with a strong tendency to form dimers and oligomers[12][13][14][15]. We have prepared a number of di- and trinuclear nickel(II) complexes with bridging thiolate groups by reaction of $[(C_6F_5)_2Ni(\mu OH)_2Ni(C_6F_5)_2]^{2-}$ with thiols[16]. Now we report the preparation of asymmetric bimetallic complexes of the type $[(C_6F_5)_2Ni(\mu\text{-}SAr)M(dppe)]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane] starting from the precursor *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$.

Results and Discussion

1. Pseudohalide Complexes

The reaction (1:1 molar ratio) between $[Ni(C_6F_5)_2(PhCN)_2]$ and the pseudohalides SCN^-, OCN^-, and $N_3{}^-$ gives the pseudohalide-bridged complexes **1−3** (Scheme 1) in 60−85% yields. The new complexes are air-stable solids and their acetone solutions exhibit conductances in the range 207−217 S cm^2 mol^{-1}, corresponding to 2:1 electrolytes[17]. The infrared spectra of the complexes show bands attributed to the C_6F_5 group[18] at ca. 1630 m, 1495 vs, 1460 vs, 1050 vs, 950 vs, and 780 br., s cm^{-1}. Complex **1** gives a ν(CN) band at 2158 cm^{-1} consistent with the presence of bridged thiocyanate[19] and the ^{19}F-NMR spectrum indicates that there are two sorts of C_6F_5 rings, so the sym-

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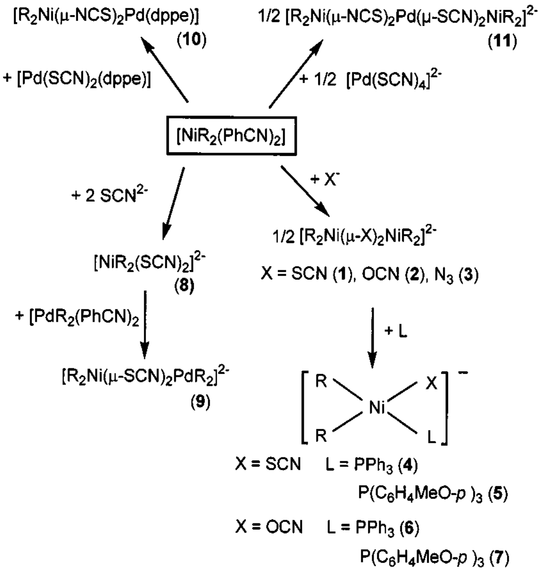
metric structure Ni(SCN)(NCS)Ni is proposed for this complex. The infrared spectrum of the cyanate complex **2** shows a band at 2168 cm^{-1} supporting the bridging character of the cyanate group by means of the nitrogen atom[20]. The ^{19}F-NMR spectrum is consistent with the presence of four equivalent pentafluophenyl groups. The IR[21] and NMR data of complex **3** are consistent with a binuclear structure contaning two azide bridges. The electronic spectra of complexes **1−3** show an absorption band which may be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in a square-planar ligand field[22].

Scheme 1. Pseudohalide complexes (R = C_6F_5)



Complexes **1** and **2** react with triphenylphophane and tris(*p*-methoxyphenyl)phosphane to give the mononuclear complexes $(PPh_4)[Ni(C_6F_5)_2XL]$ [X = SCN, OCN; L = PPh_3, $P(C_6H_4MeO\text{-}p)_3$] (**4-7**) (Scheme 1). However, similar reactions with pyridine or triethylphosphane give a mixture of $[Ni(C_6F_5)_2(SCN)_2]^{2-}$ and $[Ni(C_6F_5)_2L_2]$. The azide-bridged complex **3** does not react with neutral ligands. The IR data of the mononuclear complexes **4−7** are consistent with terminal S-thiocyanate or N-cyanate. The ^{19}F-NMR spectra exhibit six signals corresponding to two inequivalent C_6F_5 rings, one *trans* to the pseudohalide and the other *trans* to the neutral ligand. Their acetone solutions show conductance values (83−95 S cm^2 mol^{-1}) corresponding to 1:1 electrolytes[17]. The elemental analyses of complexes $(PPh_4)[Ni(C_6F_5)_2XL]$ (**4−7**) showed no significant variation when the crystals were twice recrystallized from acetone/diethyl ether and the spectroscopic data also supported that a mixture of $[Ni(C_6F_5)_2L_2]$ and $(PPh_4)_2[Ni(C_6F_5)_2X_2]^{2-}$ should be discarded. For example, $(PPh_4)[Ni(C_6F_5)_2(SCN)(PPh_3)]$ gives a single IR band for the ν(CN) vibration (at 2102 cm^{-1}) while $(PPh_4)_2[Ni(C_6F_5)_2(SCN)_2]$ gives a split band for the same vibrational mode (2112 and 2124 cm^{-1}).

The reaction between $[Ni(C_6F_5)_2(PhCN)_2]$ and SCN^- (molar ratio 1:2) gives the corresponding mononuclear complex $(PPh_4)_2[Ni(C_6F_5)_2(SCN)_2]$ (**8**). However, similar complexes with cyanate and azide anions could not be obtained. Complex **8** behaves as a 2:1 electrolyte in acetone solution (molar conductance 224 S cm^2 mol^{-1}) and the infrared band observed at 2112 cm^{-1} indicates that the thiocyanate ligand is S-bonded[19]. The expected three signals (4 F_o/2 F_p/4 F_m) of two equivalent C_6F_5 groups are observed in the ^{19}F-NMR spectrum. In dichloromethane, complex **8** reacts with the labile *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ to give the binuclear heterobimetallic complex $[(C_6F_5)_2Ni(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(C_6F_5)_2]^{2-}$ (**9**). The IR spectrum shows a band at 2144 cm^{-1} which is consistent with a bridging thiocyanate[19] and four signals observed in the ^{19}F-NMR spectrum for the pentafluorophenyl *ortho*-fluorine atoms indicate that there are four different C_6F_5 rings, in accordance with the structure proposed above.

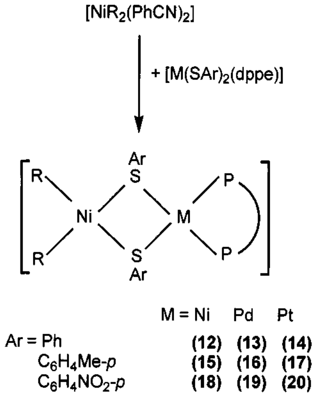
The asymmetric binuclear complex **10** (Scheme 1) is prepared by reaction between the labile nickel complex $[Ni(C_6F_5)_2(PhCN)_2]$ and the thiocyanate palladium complex $[Pd(SCN)_2(dppe)]$. The infrared absorption found at 2158 cm^{-1} for complex **10** is consistent with the presence of bridging thiocyanate[19] and the ^{19}F-NMR spectrum exhibits two signals in the *ortho*-fluorine region attributed to the structure $[(C_6F_5)_2Ni(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(dppe)]$, i.e., one C_6F_5 ring *trans* to N and one C_6F_5 ring *trans* to S.

The trinuclear complex **11** (Scheme 1) is obtained by reaction of *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$ with the thiocyanate complex $[Pd(SCN)_4]^{2-}$. The absorption found at 2146 cm^{-1} for complex **11** indicates the presence of bridging thiocyanate[27]. The ^{19}F-NMR spectrum shows three signals (intensity ratio of 2:1:2) corresponding to the *ortho*-, *para*-, and *meta*-fluorine atoms of four equivalent C_6F_5 rings, in accord with the structure $[(C_6F_5)_2Ni(\mu\text{-}NCS)_2Pd(\mu\text{-}SCN)_2Ni(C_6F_5)_2]^{2-}$.

2. Thiolate Complexes

In methanol, *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$ reacts with $[M(SAr)_2(dppe)]$ (M = Ni, Pd, Pt; Ar = Ph, $C_6H_4Me\text{-}p$, $C_6H_4NO_2\text{-}p$) to give the corresponding asymmetric binuclear thiolate complexes shown in Scheme 2. They are orange or red, air-stable solids which in acetone solution behave as non-electrolytes.

Scheme 2. Arylthiolate complexes (R = C_6F_5)

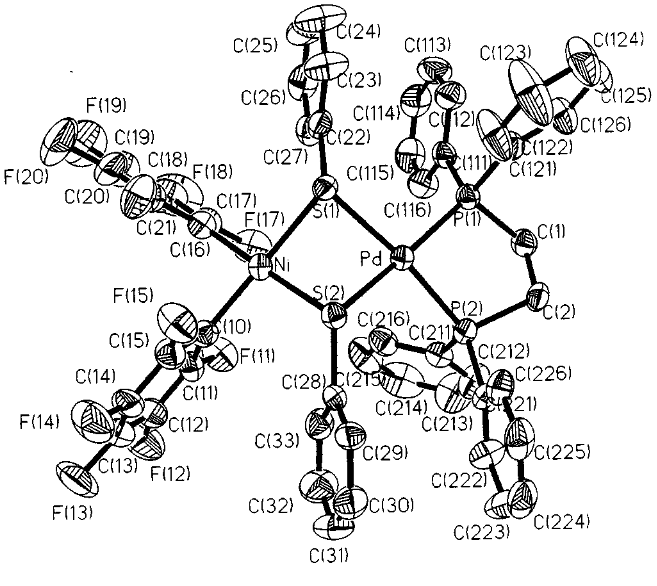


The infrared spectra of these *gem* derivatives show the bands attributed to the C_6F_5 group[18] at ca. 1630 m, 1490 vs, 1050 vs, and 950 vs cm^{-1}, as well as a broad or split band at 780 cm^{-1} for the so-called "X-sensitive" mode of C_6F_5 which is characteristic of the *cis*-$M(C_6F_5)_2$ fragment[23][24]. The ^1H-, ^{19}F-, and $^{31}P\{^1H\}$-NMR data for the binuclear complexes are in agreement with the formula $[(C_6F_5)_2Ni(\mu\text{-}SAr)_2M(dppe)]$. As expected, the ^{31}P-NMR spectra show a single resonance and that of the platinum complexes are flanked by the satellites by coupling to ^{195}Pt, the coupling constant being in the range 2900−3100 Hz. The three signals observed in the ^{19}F NMR correspond to the A_2MX_2 spin system of two equivalent pentafluorophenyl groups freely rotating around the Ni−C bond and with the coupling constant $J_{AX} = 0$. The ^1H-NMR data also give evidence of free rotation of the thiolate aryl group around the C−S bond, although in complexes **18** and **19** the resonance signals of the $C_6H_4NO_2$-*p* substituent are overlapped with the dppe phenyl resonances.

3. Crystal Structure of $[(C_6F_5)_2Ni(\mu\text{-}SPh)_2Pd(dppe)]\cdot Me_2CO$

Figure 1 represents an ORTEP[25] projection of the molecular structure with the atom numbering and Table 1 shows some selected bond lengths and bond angles. Both metal atoms, Ni and Pd, are coordinated in a slightly distorted square-planar geometry and the μ-thiolato groups are in the *syn* conformation.

Figure 1. Molecular structure of compound **13**



The main distortion of the square-planar coordination is a slight twist of de PdS_2 plane relative to the PdP_2 plane, by 9.4°. The Ni−C and Ni−S distances are similar to values reported in the literature[16][26]. The Ni−S and Pd−S distances are also similar to values found in other homonuclear complexes[27][28]. The distortion of the square-planar coordination in the Ni atom is a slight twist of the NiS_2 plane relative to the NiC_2 plane, by 9.6°.

The phosphane has a strong *trans* influence, lengthening the Pd−S bonds. So, the Pd−S distances are 2.356(2) and 2.360(2) Å giving a weighted mean distance of 2.358(2) Å, significantly longer than distances with other ligands[27][28].

Table 1. Selected intramolecular distances [Å] and angles [°] for **13**

a) Distances		b) Angles	
Pd−P(2)	2.2720(14)	P(2)−Pd−P(1)	84.27(5)
Pd−P(1)	2.2973(14)	P(2)−Pd−S(2)	99.76(5)
Pd−S(2)	2.3564(13	P(1)−Pd−S(2)	171.10(4)
Pd−S(1)	2.3597(13)	P(2)−Pd−S(1)	173.40(4)
Pd···Ni	3.1157(10)	P(1)−Pd−S(1)	101.73(5)
Ni−C(10)	1.900(5)	S(2)−Pd−S(1)	74.70(4)
Ni−C(16)	1.906(5)	C(10)−Ni−C(16)	87.0(2)
Ni−S(2)	2.214(2)	C(10)−Ni−S(2)	95.05(14)
Ni−S(1)	2.2509(14)	C(16)−Ni−S(2)	177.82(14)
		C(16)−Ni−S(2)	177.82(14)
		C(10)−Ni−S(1)	169.3(2)
		C(16)−Ni−S(1)	98.46(14)
		S(2)−Ni−S(1)	79.69(5)
		C(10)−Ni−Pd	132.91(14)

The Ni···Pd distance is 3.116(2) Å, showing no significant metal-metal interaction. The NiSPdS ring adopts a hinged square-planar geometry with a dihedral angle of 120.4° along the S···S line.

As expected, the two carbon atoms of the aliphatic chain of dppe ligand lie on each side of the PdP_2 plane. Thus, C(1) lies 0.067 to one side, while C(2) lies 0.640 Å to the other side of the plane, the PdP_2C_2 chelate ring adopting a twist conformation. The non-planarity of the PdP_2C_2 ring is a consequence of the tetrahedral geometry at the carbon and phosphorus atoms and the square-planar coordination of the metal center.

The two pentafluorophenyl rings are planar and rotated 83.5° with respect to each other. The rings present distortions as indicated by the values of the C−C−C angles which range from 112.5(4) to 125.5(5). This type of distortion has already been observed in other fluorophenyl rings[29].

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Experimental Section

General Methods: C, H, N, and S analyses were carried out with a Carlo Erba instrument. − Infrared spectra were recorded with a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. − ^1H-, ^{19}F-, and ^{31}P-NMR spectra were recorded with a Bruker AC 200E or a Varian 300 spectrometer. − Conductance measurements were performed with a Crison 525 conductimeter (in acetone, $c \approx 5\cdot10^{-4}$ mol dm^{-3}). − Decomposition temperatures were determined with a Reichert microscope. − All solvents were dried by conventional methods. − The compounds $[Ni(C_6F_5)_2(PhCN)_2]$[7], $(PPh_4)SCN$[30], KN_3[31], $Pd(dppe)(SCN)_2$[32], $(NBu_4)_2[Pd(SCN)_4]$[33], $[Ni(SAr)_2(dppe)]$[34] and $[M(SAr)_2(dppe)]$ (M = Pd, Pt)[35] were prepared as described elsewhere.

$(PPh_4)_2[Ni_2(C_6F_5)_4(\mu\text{-}SCN)_2]$ (**1**) *and $(PPh_4)_2[Ni(C_6F_5)_2(SCN)_2]$* (**8**): A solution of $(PPh_4)SCN$ (1.33 mmol for **1** and 2.66 mmol for **8**) in dichloromethane (10 ml) was added to a solution of $[Ni(C_6F_5)_2(PhCN)_2]$ (0.8 g, 1.33 mmol) in dichloromethane (15 ml) and the mixture was stirred (**1**) or boiled under reflux (**8**) for

30 min. The solution was then concentrated under reduced pressure to half the original volume. Addition of diethyl ether caused the precipitation of a yellow solid which was filtered off, washed with diethyl ether and air-dried.

1: Yield 84%. − $C_{74}H_{40}F_{20}N_2Ni_2P_2S_2$ (1580.58): calcd. C 56.2, H 2.6, N 1.8, S 4.1; found C 56.7, H 2.3, N 1.8, S 3.7. − M.p. 211°C (dec.). − Λ_M = 193 S cm^2 mol^{-1}. − IR (Nujol): ν = 2158 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 22.6 (1088). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.4 (m, 4 F$_o$), −116.9 (m, 4 F$_o$), −165.2 (t, 2 F$_p$, J_{pm} = 19.7), −165.6 (t, 2 F$_p$, J_{pm} = 21.7 Hz), −167.3 (m, 4 F$_m$), −167.5 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6.

8: Yield 58%. − $C_{62}H_{40}F_{10}N_2NiP_2S_2$ (1187.77): calcd. C 62.7, H 3.4, N 2.4, S 5.4; found C 62.6, H 3.6, N 2.5, S 5.3. − M.p. 189°C (dec.). − Λ_M = 224 S cm^2 mol^{-1}. − IR (Nujol): ν = 2112 cm^{-1}, 2124 (sh) (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 23.4 (752). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.9 (d, 4 F$_o$, J_{om} = 29.9 Hz), −166.9 (t, 2 F$_p$, J_{pm} = 20.3 Hz), −167.9 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6.

$(PPh_4)_2[Ni_2(C_6F_5)_4(\mu\text{-}NCO)_2]$; X = NCO (**2**) *or N_3* (**3**): An acetone (20 ml) solution containing [Ni(C$_6$F$_5$)$_2$(PhCN)$_2$] (100 mg, 0.17 mmol) and KNCO or KN$_3$ (0.17 mmol) was stirred at room temperature for 15 min and then a solution of (PPh$_4$)Cl (62.6 mg, 0.17 mmol) in hot acetone (15 ml) was added. The mixture was stirred at room temperature for 30 min. The KCl formed during the reaction was removed by filtration, and the resulting solution was then concentrated under reduced pressure to ca. 10 ml. Addition of diethyl ether (for **2**) or hexane (for **3**) resulted in the precipitation of an orange solid. This was filtered off, washed with water and diethyl ether (**2**) or ethanol and hexane (**3**) and air-dried. Complexes **2** and **3** were recrystallized from acetone/diethyl ether and acetone/hexane respectively.

2: Yield 61%. − $C_{74}H_{40}F_{20}N_2Ni_2O_2P_2$ (1548.45): calcd. C 57.4, H 2.6, N 1.8; found C 57.5, H 2.7, N 1.8. − M.p. 187°C (dec.). − Λ_M = 207 S cm^2 mol^{-1}. − IR (Nujol): ν = 2168 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 21.6 (798). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.4 (d, 8 F$_o$, J_{om} 29.1 Hz), −165.9 (t, 4 F$_p$, J_{pm} 20.0), −167.7 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6.

3: Yield 79%. − $C_{72}H_{40}F_{20}N_6Ni_2P_2$ (1548.45): calcd. C 55.9, H 2.6, N 5.4; found C 55.9, H 2.9, N 5.5. − M.p. 196°C (dec.). − Λ_M = 217 S cm^2 mol^{-1}. − IR (Nujol): ν = 2063 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 21.7 (1165). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.3 (d, 8 F$_o$, J_{om} = 29.1), −165.1 (t, 4 F$_p$, J_{pm} = 19.2 Hz), −167.2 (m, 8 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6.

$(PPh_4)[Ni(C_6F_5)_2XL]$; X = SCN, L = PPh_3 (**4**) *or $P(C_6H_4CH_3O\text{-}p)_3$* (**5**); *X = NCO, L = PPh_3* (**6**) *or $P(C_6H_4CH_3O\text{-}p)_3$* (**7**): A solution of (PPh$_4$)$_2$[Ni$_2$(C$_6$F$_5$)$_4$(μ-X)$_2$] (X = SCN or NCO; 0.094 mmol) and the corresponding neutral ligand (PPh$_3$ or P(C$_6$H$_4$CH$_3$O-*p*)$_3$; 0.22 mmol) in dichloromethane (15 ml) was stirred at room temperature for 30 min. The resulting solution was concentrated under reduced pressure to half the original volume. Addition of diethyl ether precipitated a yellow solid which was filtered off, washed with diethyl ether and air-dried.

4: Yield 79%. − $C_{55}H_{35}F_{10}NNiP_2S$ (1052.58): calcd. C 62.8, H 3.4, N 1.3, S 3.1; found C 62.9, H 3.4, N 1.5, S 3.2. − M.p. 190°C (dec.). − Λ_M = 91 S cm^2 mol^{-1}. − IR (Nujol): ν = 2102 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 24.9 (868). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −116.2 (m, 2 F$_o$), −117.7 (m, 2 F$_o$), −166.2 (t, 1 F$_p$, J_{pm} = 19.7 Hz), −166.9 (m, 1 F$_p$ + 2 F$_m$), −167.4 (m, 2 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6, 23.1.

5: Yield 77%. − $C_{58}H_{41}F_{10}NNiO_3P_2S$ (1141.69): calcd. C 61.0, H 3.6, N 1.2, S 2.8; found C 61.3, H 3.4, N 1.4, S 2.9. − M.p. 171°C (dec.). − Λ_M = 94 S cm^2 mol^{-1}. − IR (Nujol): ν = 2106 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 25.0 (931). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.6 (m, 2 F$_o$), −116.9 (m, 2 F$_o$), −165.8 (t, 1 F$_p$, J_{pm} = 22.6 Hz), −166.4 (m, 1 F$_p$ + 2 F$_m$), −166.8 (m, 2 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6, 19.5.

6: Yield 75%. −$C_{55}H_{35}F_{10}NNiOP_2$ (1036.51): calcd. C 63.7, H 3.4, N 1.4; found C 63.6, H 3.6, N 1.3. − M.p. 175°C (dec.). − Λ_M = 95 S cm^2 mol^{-1}. − IR (Nujol): ν = 2222 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 24.2 (572). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.6 (m, 2 F$_o$), −117.1 (m, 2 F$_o$), −167.1 (m, 2 F$_p$ + 2 F$_m$), −167.7 (m, 2 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6, 22.7.

7: Yield 65%. − $C_{58}H_{41}F_{10}NNiO_4P_2$ (1126.59): calcd. C 61.8, H 3.7, N 1.2; found C 61.6, H 3.5, N 1.3. − M.p. 98°C (dec.). − Λ_M = 83 S cm^2 mol^{-1}. − IR (Nujol): ν = 2218 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 24.5 (663). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.6 (m, 2 F$_o$), −116.9 (m, 2 F$_o$), −167.1 (m, 2 F$_p$), −167.7 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6, 18.9.

$(PPh_4)_2[(C_6F_5)_2Ni(\mu\text{-}SCN)_2Pd(C_6F_5)_2]$ (**9**): A solution of (**8**) (0.15 g, 0.126 mmol) and [Pd(C$_6$F$_5$)$_2$(PhCN)$_2$] (81.6 mg, 0.126 mmol) in dichloromethane (15 ml) was stirred at room temperature for 30 min. The resulting solution was concentrated under reduced pressure to half the original volume. Addition of hexane precipitated a yellow solid which was filtered off, washed with hexane and air-dried. The compound was recrystallized from dichloromethane/hexane. − Yield 84%. − $C_{74}H_{40}F_{20}N_2NiP_2PdS_2$ (1628.31): calcd. C 54.6, H 2.5, N 1.7, S 3.9; found C 54.3, H 2.2, N 1.7, S 3.8. − M.p. 221°C (dec.). − Λ_M = 197 S cm^2 mol^{-1}. − IR (Nujol): ν = 2144 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 22.8 (731). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −113.2 (d, 2 F$_o$, J_{om} = 29.6 Hz), −114.4 (m, 2 F$_o$), −114.8 (m, 2 F$_o$), −116.3 (m, 2 F$_o$), −164.2 (m, 2 F$_p$), −164.7 (t, 1 F$_{p,\,Jpm}$ = 19.2 Hz), −165.1 (t, 1 F$_p$, J_{pm} = 19.7 Hz), −165.7 (m, 1 F$_m$), −166.2 (m, 1 F$_m$), −166.7 (m, 1 F$_m$), −167.0 (m, 1 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 24.6.

$[(C_6F_5)_2Ni(\mu\text{-}SCN)_2Pd(dppe)]$ (**10**): A solution of [Pd(SCN)$_2$(dppe)] (0.134 g, 0.21 mmol) and [Ni(C$_6$F$_5$)$_2$(PhCN)$_2$] (0.129 g, 0.21 mmol) in dichloromethane (20 ml) was stirred at room temperature for 20 min. The resulting solution was concentrated under reduced pressure to half the original volume. Addition of diethyl ether precipitated a yellow solid which was filtered off, washed with diethyl ether and air-dried. The compound was recrystallized from dichloromethane/diethyl ether. − Yield 73%. − $C_{40}H_{24}F_{10}N_2NiP_2PdS_2$ (1013.82): calcd. C 47.4, H 2.4, N 2.8, S 6.3; found C 47.1, H 2.5, N 2.9, S 6.2. − M.p. 177°C (dec.). − Λ_M = 6 S cm^2 mol^{-1}. − IR (Nujol): ν = 2158 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 29.7 (7564). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −116.2 (m, 2 F$_o$), −117.6 (m, 2 F$_o$), −164.3 (t, 1 F$_p$, J = 19.7 Hz), −164.8 (t, 1 F$_p$, J = 19.7 Hz), −167.0 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 71.5 (br.).

$[NBu_4]_2[(C_6F_5)_2Ni(\mu\text{-}SCN)_2Pd(\mu\text{-}SCN)_2Ni(C_6F_5)_2]$ (**11**): A solution of [NBu$_4$]$_2$[Pd(SCN)$_4$] (0.130 g, 0.15 mmol) and [Ni(C$_6$F$_5$)$_2$(PhCN)$_2$] (0.2 g, 0.33 mmol) (molar ratio 1:2.2) in acetone (10 ml) was stirred at room temperature for 20 min. The re-

sulting solution was concentrated under reduced pressure to half the original volume. Addition of diethyl ether precipitated a red solid which was filtered off, washed with diethyl ether and air-dried. The compound was recrystallized from dichloromethane/diethyl ether. − Yield 54%. − $C_{60}H_{72}F_{20}N_6Ni_2PdS_4$ (1609.31): calcd. C 44.8, H 4.5, N 5.2, S 8.0; found C 45.1, H 4.7, N 5.4, S 7.7. − M.p. 180°C (dec.). − Λ_M = 164 S cm^2 mol^{-1}. − IR (Nujol): ν = 2146 cm^{-1} (CN str). − UV/Vis (acetone): λ_{max} [cm^{-1} × 10^{-3}] (ε) = 29.7 (10320). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −117.4 (m, 8 F$_o$), −164.9 (m, 4 F$_p$), −167.1 (m, 8 F$_m$).

[(dppe)M(μ-SAr)$_2$Ni(C$_6$F$_5$)$_2$] (**12−20**) (see Scheme 2): Complexes **12−20** were obtained by treating *cis*-[Ni(C$_6$F$_5$)$_2$(PhCN)$_2$] with [M(SAr)$_2$(dppe)] (molar ratio 1:1) in MeOH according to the following general method. To a MeOH (10 ml) solution of the *cis*-[Ni(C$_6$F$_5$)$_2$(PhCN)$_2$] (0.174 mmol) was added [M(SAr)$_2$(dppe)] (0.174 mmol), and the solution was stirred at room temperature for 30 min. It was concentrated under reduced pressure to ca. one fifth of the initial volume obtaining an orange or red precipitate, which was filtered off, washed with hexane and air-dried.

12: Yield 75%. − $C_{50}H_{34}F_{10}Ni_2P_2S_2$ (1068.27): calcd. C 56.2, H 3.2, S 6.0; found C 55.9, H 3.1, S 5.8. − M.p. 215°C (dec.). − ^{1}H NMR ([D$_6$]acetone, TMS): δ = 2.5 (d, 4 H, dppe), 6.7 (t, 4 H, Ph), 6.9 (t, 2 H, Ph), 7.3 (d, 4 H, Ph), 7.5 (m, 12 H, dppe), 7.9 (m,8 H, dppe). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.2 (d, 4 F$_o$, J_{om} = 28.8 Hz), −165.3 (t, 2 F$_p$, J_{pm} = 19.7 Hz), −166.6 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 58.7.

13: Yield 68%. − $C_{50}H_{34}F_{10}NiP_2PdS_2$ (1116): calcd. C 53.8, H 3.1, S 5.8; found C 53.5, H 3.3, S 5.6. − M.p. 119°C (dec). − ^{1}H NMR ([D$_6$]acetone, TMS): δ = 2.6 (d, 4 H, dppe), 6.7 (t, 4 H, Ph), 6.9 (t, 2 H, Ph), 7.3 (d, 4 H, Ph), 7.5 (m, 12 H, dppe), 7.9 (m, 8 H, dppe). −^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.3 (d, 4 F$_o$, J_{om} = 28.3), −165.6 (t, 2 F$_p$, J_{pm} = 19.8), −166.8 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 58.6.

14: Yield 65%. − $C_{50}H_{34}F_{10}NiP_2PtS_2$ (1204.66): calcd. C 49.9, H 2.8, S 5.3; found C 49.8, H 3.0, S 5.2. − M.p. 235°C (dec.). − ^{1}H NMR ([D$_6$]acetone, TMS): δ = 2.7 (d, H, dppe), 6.6 (t, 4 H, Ph), 6.8 (t, 2 H, Ph), 7.2 (d, 4 H, Ph), 7.5 (m, 12 H, dppe), 7.8 (m, 8 H, dppe). − ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −116.9 (d, 4 F$_o$, J_{om} = 24.5 Hz), −164.4 (m, 2 F$_p$), −166.2 (m, 2 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 43.3 [J(PPt) = 3076.5 Hz].

15: Yield 73%. − $C_{52}H_{38}F_{10}Ni_2P_2S_2$ (1096.32): calcd. C 57.0, H 3.5, S 5.9; found C 56.7, H 3.4, S 5.7. − M.p. 213°C (dec.). − ^{1}H NMR ([D$_6$]acetone, TMS): δ = 2.1 (s, 6 H, C$_6$H$_4$Me-*p*), 2.4 (d, 4 H, dppe), 6.5 (d, 4 H, C$_6$H$_4$Me-*p*), 7.2 (d, 4 H, C$_6$H$_4$Me-*p*), 7.5 (m, 8 H, dppe). −^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = −115.4 (d, 4 F$_o$, J_{om} = 28.8 Hz), −166.0 (t, 2 F$_p$, J_{pm} = 19.7 Hz), −167.1 (m, 4 F$_m$). − ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 57.9.

16: Yield 89%. − $C_{52}H_{38}F_{10}NiP_2PdS_2$ (1144.05): calcd. C 54.6, H 3.4, S 5.6; found C 54.5, H 3.3, S 5.5. − M.p. 224°C (dec.). − ^{1}H NMR (CDCl$_3$, TMS): δ = 2.1 (s, 6 H, C$_6$H$_4$Me-*p*), 2.3 (d, 4 H, dppe), 6.4 (d, 4 H, C$_6$H$_4$Me-*p*), 7.2 (d, 4 H, C$_6$H$_4$Me-*p*), 7.4 (m, 12 H, dppe), 7.6 (m, 8 H, dppe). − ^{19}F NMR (CDCl$_3$, CFCl$_3$): δ = −115.6 (d, 4 F$_o$, J_{om} = 28.8 Hz), −166.2 (t, 2 F$_p$, J_{pm} = 20.0 Hz), −167.3 (m, 4 F$_m$). − ^{31}P NMR (CDCl$_3$, H$_3$PO$_4$): δ = 57.8.

17: Yield 81%. − $C_{52}H_{38}F_{10}NiP_2PtS_2$ (1232.71): calcd. C 50.7, H 3.1, S 5.2; found C 50.8, H 3.3, S 5.1. − M.p. 205°C (dec.). − ^{1}H NMR (CDCl$_3$, TMS): δ = 1.5 (s, 6 H, C$_6$H$_4$Me-*p*), 2.2 (d, 4 H, dppe), 6.4 (d, 4 H, C$_6$H$_4$Me-*p*), 7.1 (d, 4 H, C$_6$H$_4$Me-*p*), 7.4 (m, 12 H, dppe), 7.6 (m, 8 H, dppe). − ^{19}F NMR (CDCl$_3$, CFCl$_3$): δ = −116.9 (d, 4 F$_o$, J_{om} = 29.1 Hz), −164.6 (t, 2 F$_p$, J_{pm} = 19.7 Hz), −166.3 (m, 4 F$_m$). − ^{31}P NMR (CDCl$_3$, H$_3$PO$_4$): δ = 46.3 [J(PPt) = 2899.2 Hz].

18: Yield 88%. − $C_{50}H_{32}F_{10}N_2Ni_2O_4P_2S_2$ (1158.27): calcd. C 51.9, H 2.8, N 2.4, S 5.5; found C 51.7, H 3.1, N 2.6, S 5.4. − M.p. 184°C (dec.). − ^{1}H NMR (CDCl$_3$, TMS): δ = 2.1 (d, 4 H, dppe), 7.4 (m, 20 H, dppe + C$_6$H$_4$NO$_2$-*p*), 7.8 (m, 8 H, dppe). − ^{19}F NMR (CDCl$_3$, CFCl$_3$): δ = −116.9 (d, 4 F$_o$, J_{om} = 27.6 Hz), −162.5 (t, 2 F$_p$, J_{pm} = 19.7 Hz), −165.0 (m, 4 F$_m$). − ^{31}P NMR (CDCl$_3$, H$_3$PO$_4$): δ = 59.0.

19: Yield 70%. − $C_{50}H_{32}F_{10}N_2NiO_4P_2PdS_2$ (1205.99): calcd. C 49.8, H 2.7, N 2.3, S 5.3; found C 49.9, H 2.5, N 2.4, S 5.1. − M.p. 180°C (dec.). − ^{1}H NMR (CDCl$_3$, TMS): δ = 2.4 (d, 4 H, dppe), 7.4 (m, 28 H, dppe + C$_6$H$_4$NO$_2$-*p*). − ^{19}F NMR (CDCl$_3$, CFCl$_3$): δ = −117.1 (d, 4 F$_o$, J_{om} = 27.3 Hz), −162.7 (t, 2 F$_p$, J_{pm} = 19.7 Hz), −165.1 (m, 4 F$_m$). − ^{31}P NMR (CDCl$_3$, H$_3$PO$_4$): δ = 58.9.

20: Yield 70%. −$C_{50}H_{32}F_{10}N_2NiO_4P_2PtS_2$ (1294.65): calcd. C 46.4, H 2.5, N 2.2, S 5.0; found C46.3, H 2.7, N 2.4, S 4.9. − M.p. 207°C (dec.). − ^{1}H NMR (CDCl$_3$, TMS): δ = 2.4 (d, 4 H, dppe), 7.2 (d, 4 H, C$_6$H$_4$NO$_2$-*p*), 7.3 (d, 4 H, C$_6$H$_4$NO$_2$-*p*), 7.5 (m, 12 H, dppe), 7.6 (m, 8 H, dppe). − ^{19}F NMR (CDCl$_3$, CFCl$_3$): δ = −117.2 (d, 4 F$_o$, J_{om} = 27.3 Hz), −162.5 (t, 2 F$_p$, J_{pm} = 19.6 Hz), −165.0 (m, 4 F$_m$). − ^{31}P NMR (CDCl$_3$, H$_3$PO$_4$): δ = 45.4 [J (PPt) = 3103.2 Hz].

Determination of the X-ray Crystal Structure of **13**: A single crystal of complex **13** (approximate dimensions 0.42 × 0.35 × 0.20 mm) was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator for Mo-K_α radiation. The crystallographic data are shown in Table 2. Accurate cell parameters were determined by least-squares fitting of 25 high-angle reflections. The scan method was ω-2Θ with the range of *hkl* ($-16 \le h \le 16$, $-19 \le k \le 19$, $0 \le l \le 22$) corresponding to $2\Theta_{max}$ = 60.88°. Empirical ψ-scan mode absorption was made. The structure was solved by heavy-atom methods SHELXS-86[36] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms. Hydrogen atoms were introduced in calculated positions and were refined during the last stages of the refinement. The final R factor was 0.0539 [R_w = 0.0984, where $w = 1/\sigma^2(F_o^2) + (0.0465\ P)^2$ and $P = (F_o^2 + 2\ F_c^2)/3$] over 5879 ob-

Table 2. Crystal data and structure refinement for complex **13**

Empirical formula	$C_{50}H_{34}F_{10}NiP_2$ PdS2·C3H6O
Formula weight	1174.02
Temperature	293(2) K
Wavelength (Mo-*Ka*)	0.71073 A
Crystal system	Triclinic
Space group	*P*1
Unit cell dimensions	a = 11.803(2) A; α = 95.86(3)° b = 13.541(3) A; β = 93.86(3)° c = 15.739(3) A; γ = 94.05(3)°
Volume, *Z*	2489.0(9) A^3, 2
Density (calculated)	1.566 Mg/m^3
Absorption coefficient	0.964 mm^{-1}
F(000)	1184
h range for data collection	2.39−30.44°
Limiting indices	$-16 \le h \le 16$, $-19 \le k \le 19$, $0 \le l \le 22$
Reflections collected	15576
Observed reflections	5879
Independent reflections	15074 (R_{int} = 0.0681)
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	15074/0/635
Goodness-of-fit on F^2	0.833
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0539, $wR2$ = 0.0984
R indices (all data)	$R1$ = 0.2690, $wR2$ = 0.1231
Largest diff. peak and hole	0.708 and −1.921 eA^{-3}

served reflections [$I > 2\sigma(I)$]. The residual peaks in the final Fourier difference synthesis were located close to the metal atoms. Scattering factors were taken from the literature[37]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100812. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(0)1223/336-033, e-mail: deposit@ccdc.cam.ac.uk].

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