Organometallic Nickel(II) Complexes Containing Thiolate and Dithiocarbamate Ligands

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The mono(pentafluorophenyl)nickel(II) complexes [Ni(C_6F_5)ClL_2] (L = $PPhMe_2$, PPh_2Me; L_2 = dppe) react with KSR (R = Ph, C_6H_4Me-*p*, C_6H_4OMe-*p*, C_6H_4Cl-*p*, $C_6H_3Cl_2$-2,6, $C_6H_4NO_2$-*p*) at room temperature in acetone/dichloromethane to give the mononuclear thiolate complexes [Ni(C_6F_5)(SR)L_2]. The binuclear μ-thiolate complex [{Ni(C_6F_5)($PPhMe_2$)}$_2$(μ-$SC_6H_4NO_2$-*p*)$_2$] is obtained by reaction of $KSC_6H_4NO_2$-*p* with the same chloro complex in refluxing dichloromethane. A single-crystal X-ray diffraction study of [Ni(C_6F_5)($SC_6H_4NO_2$-*p*)($PPhMe_2$)$_2$] and [{Ni_2(C_6F_5)$_2$($PPhMe_2$)$_2$(μ-$SC_6H_4NO_2$-*p*)$_2$] has established the mononuclear and binuclear nature of the complexes. The dithiocarbamatenickel complexes [Ni(C_6F_5)(S_2CNR_2)L] (L = $PPhMe_2$, PPh_2Me, PEt_3; R = Et, *i*Pr; R_2 = C_5H_{10}, C_4H_8O) have been prepared by reaction of [Ni(C_6F_5)ClL_2] (L = $PPhMe_2$, PPh_2Me, PEt_3) with the alkali metal salt of the corresponding dithioacid. A single-crystal X-ray diffraction study of [Ni(C_6F_5)(S_2CN*i*Pr_2)($PPhMe_2$)] has established the mononuclear nature of the complex, and the geometry around each Ni atom as that of a tetrahedrally distorted square-planar geometry. Analytical (C, H, N), spectroscopic (IR, ^{1}H, and ^{19}F NMR), and mass spectrometry (FAB) data have been used for structural assignments.

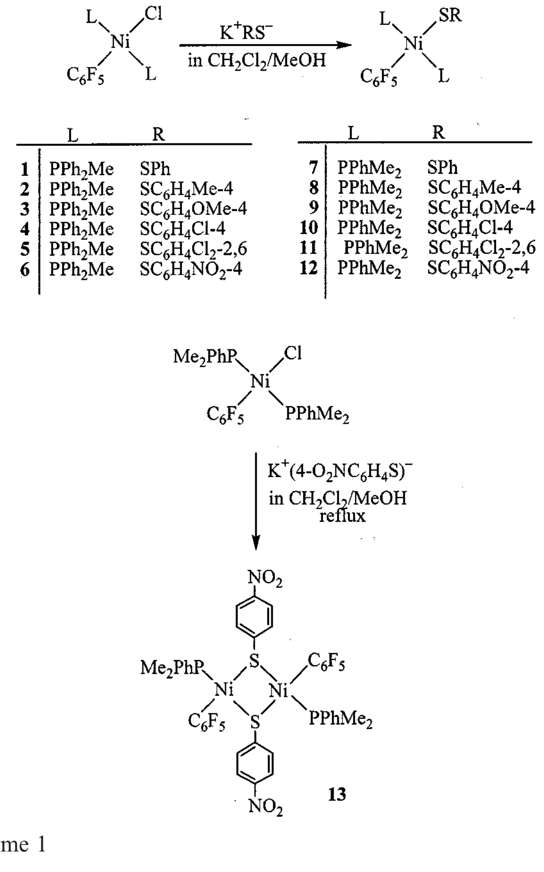
Introduction

Monomeric late transition-metal thiolate complexes have been receiving increasing attention,[1−3] in part because of their relevance as models of biologically redox-active metalloproteins.[4] Nickel complexes with S-donor ligands are present in many hydrogenases.[5] Nickel(II) thiolates are generally square-planar species with a strong tendency to form dimers and oligomers.[6−9] Despite the great amount of work devoted to the study of metal−thiolate complexes,[1] fundamental knowledge of the structures of mononuclear species is relatively sparse.[10,11] Di- and trinuclear pentafluorophenylnickel complexes have been prepared by treating the di-μ-hydroxo-complex $[NBu_4]_2$-[{Ni(C_6F_5)$_2$(μ-OH)}$_2$] with thiols.[12] Considering related complexes with S-donor ligands, mononuclear derivatives such as [Ni(C_6F_5)$_2$(S_2CNR_2)]$^-$,[13] [Ni(S_2CNEt_2)(PPh_3)$_2$]$^+$,[14] and [Ni(S_2COEt)$_2$(PPh_3)][15] have also been studied.

Results and Discussion

Mononuclear Thiolate Complexes

The addition of a methanolic solution of the corresponding alkali metal arylthiolate to a solution of [Ni(C_6F_5)ClL_2] (L = $PPhMe_2$, PPh_2Me) in dichloromethane results in the rapid formation of the mononuclear arylthiolate complexes [Ni(C_6F_5)(SR)L_2] (**1**−**12**) shown in Scheme 1. The forma-



	L	R
1	PPh_2Me	SPh
2	PPh_2Me	SC_6H_4Me-4
3	PPh_2Me	SC_6H_4OMe-4
4	PPh_2Me	SC_6H_4Cl-4
5	PPh_2Me	$SC_6H_3Cl_2$-2,6
6	PPh_2Me	$SC_6H_4NO_2$-4

	L	R
7	$PPhMe_2$	SPh
8	$PPhMe_2$	SC_6H_4Me-4
9	$PPhMe_2$	SC_6H_4OMe-4
10	$PPhMe_2$	SC_6H_4Cl-4
11	$PPhMe_2$	$SC_6H_4Cl_2$-2,6
12	$PPhMe_2$	$SC_6H_4NO_2$-4

Scheme 1

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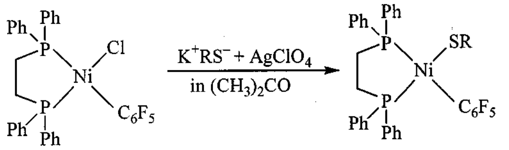
tion of these mononuclear complexes takes place at ambient temperature; on increasing the temperature, loss of a phosphane ligand may occur, and the binuclear μ-arylthiolate would be the reaction product. In fact, when the solution containing [Ni(C_6F_5)Cl($PPhMe_2$)$_2$] and $KSC_6H_4NO_2$-4 was boiled under reflux, the binuclear complex [{Ni(C_6F_5)($PPhMe_2$)}$_2$(μ-$SC_6H_4NO_2$-4)$_2$] (**13** in Scheme 1) was obtained. The *trans* influence of the pentafluorophenyl ligand should favour the dissociation of one phosphane molecule, and the resulting vacant coordination site is occupied by a μ-arylthiolate group.

The ^{19}F NMR spectra of complexes **1−13** show the expected three-resonance signals for a pentafluorophenyl ring freely rotating around the carbon−nickel bond (2 F_o:1 F_p:2 F_m). The experimental NMR pattern consists of a doublet for the *o*-fluorine atoms, a triplet for the *p*-fluorine atom and multiplet for the *m*-fluorine atoms. The observation of a single signal in the ^{31}P NMR spectra indicates that complexes **1−12** all have the *trans* geometry shown in Scheme 1. The same *trans* geometry should also be assigned to complex **13** because only one set of ^1H resonances for the 4-$O_2NC_6H_4S$ group is found in the ^1H NMR spectrum (two doublets for 2,6-H and 3,5-H, respectively, although one doublet is overlapped with the multiplet of the phenyl group.

In acetone, [Ni(C_6F_5)Cl(dppe)] reacts with $AgClO_4$ with elimination of AgCl; on removing the precipitated AgCl, the addition of an alkali metal thiolate (in methanol) to the resulting solution gives the corresponding mononuclear thiolates **14−19** shown in Scheme 2. The ^{19}F NMR spectra of these complexes are qualitatively similar to those of **1−12**, but the ^{31}P NMR spectroscopic data indicate the presence of two nonequivalent phosphorus atoms, one *trans* to S and one *trans* to C, and two ^{31}P resonances are found in the range δ = 50−56; the multiplet structure of the low-field signal is due to coupling to the *o*-fluorine atoms of the pentafluorophenyl group and this signal is consequently assigned to the phosphorus atom *trans* to C_6F_5.



14: R = Ph
15: R = SC_6H_4Me-4
16: R = SC_6H_4OMe-4
17: R = SC_6H_4Cl-4
18: R = $SC_6H_4Cl_2$-2,6
19: R = $SC_6H_4NO_2$-4

Scheme 2

The neutral compounds **1−19** show the characteristic infrared absorptions of the pentafluorophenyl group[16] at ca. 1630m, 1495vs, 1050s, 950vs, and 780s cm^{-1}.

Crystal Structures of Complexes 12 and 13

The X-ray crystal structure determinations carried out for complexes [Ni(C_6F_5)($SC_6H_4NO_2$-4)($PPhMe_2$)$_2$] **(12)** and [{Ni(C_6F_5)($PPhMe_2$)}$_2$(μ-$SC_6H_4NO_2$-4)$_2$] **(13)** show the mono- and di-nuclearity of these complexes. A view of complex **12** is depicted in Figure 1, and relevant bond lengths and bond angles are shown in Table 1. The Ni atom and the four atoms coordinated to it deviate slightly from the plane defined by them. The Ni−C distance is similar to values found in other pentafluorophenylnickel compounds;[17,18] the strong *trans* influence of the C_6F_5 group is manifested by a lengthening of the Ni−S bond, giving a distance of 2.233 Å, which is significantly longer than those found in homoleptic nickel-thiolate complexes.[19]

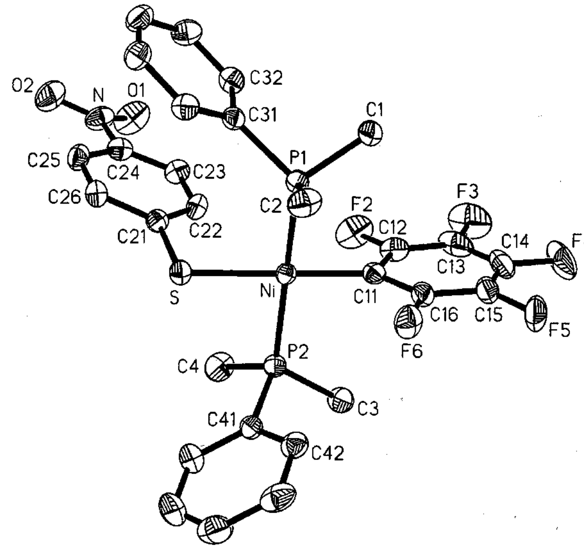


Figure 1. Molecular structure of compound **12**

The structure of complex **13** consists of centrosymmetric binuclear molecules with two Ni atoms bridged by arylthiolate groups (Figure 2). Bond lengths and bond angles are given in Table 1. The nickel atoms have approximately square-planar coordination, the deviation from the ideal geometry being revealed by the S−Ni−S angles. The Ni−S distances, 2.2140(11) and 2.2490(11), are quite similar to those found in the asymmetric binuclear complex [(C_6F_5)$_2$Ni(μ-SPh)$_2$Pd(dppe)] [2.214(2) and 2.2509(14)].[20] In the trinuclear complex [Ni_3(C_6F_5)$_4$(μ-SEt)$_4$] a weighted mean Ni−S distance of 2.203(5) was observed.[12]

Dithiocarbamate Complexes

The addition of a methanolic solution of the alkali metal dithiocarbamate (diethyldithiocarbamate, diisopropyldithiocarbamate, piperidinecarbodithioate, and morpholinecarbodithioate) to a solution of [Ni(C_6F_5)ClL_2] (L = $PPhMe_2$, PPh_2Me, PEt_3) in dichloromethane results in the formation of the dithiocarbamate complexes [Ni(C_6F_5)(S_2CNR_2)L] (**20−31**) with loss of one phosphane molecule (Scheme 3).

The ^{19}F NMR spectra of the dithiocarbamatenickel complexes exhibit the three signals (2 F_o:1 F_p:2 F_m) corresponding to a freely rotating C_6F_5 ring, and the ^{31}P NMR spectra show the single resonance expected for the phosphane ligand. The most relevant IR absorptions of coordinated dithiocarbamate are those originating from the thioureide group. In complexes **20−31**, the C−N and C−S stretching vibrations[21,22,23] are found at 1550−1450 cm^{-1} and 995−970 cm^{-1}, respectively, and the presence of only one

Table 1. Selected bond lengths [Å] and angles [°] for complexes **12**, **13**, and **24**

12		**13**		**24**	
Bond lengths					
Ni−C(11)	1.911(2)	Ni−C(1)	1.899(4)	Ni−C(1)	1.923(2)
Ni−P(1)	2.2087(7)	Ni−S	2.2140(11)	Ni−S(1)	2.2029(5)
Ni−P(2)	2.1905(7)	Ni−P	2.1807(12)	Ni−S(2)	2.2144(5)
Ni−S	2.2335(7)	Ni−S#1	2.2490(11)	Ni−P	2.1683(5)
Bond angles					
C(11)−Ni−P(1)	89.98(7)	C(1)−Ni−P	88.17(14)	C(1)−Ni−P	91.80(5)
C(11)−Ni−P(2)	91.63(7)	P−Ni−S	97.73(4)	C(1)−Ni−S(1)	91.40(5)
P(1)−Ni−S	89.01(2)	C(1)−Ni−S#1	90.53(14)	P−Ni−S(2)	98.11(2)
P(2)−Ni−S	89.42(3)	S−Ni−S#1	83.72(4)	S(1)−Ni−S(2)	78.77(2)

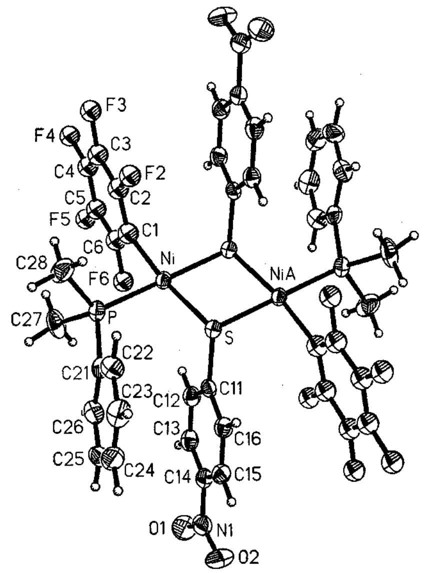


Figure 2. Molecular structure of compound **13**

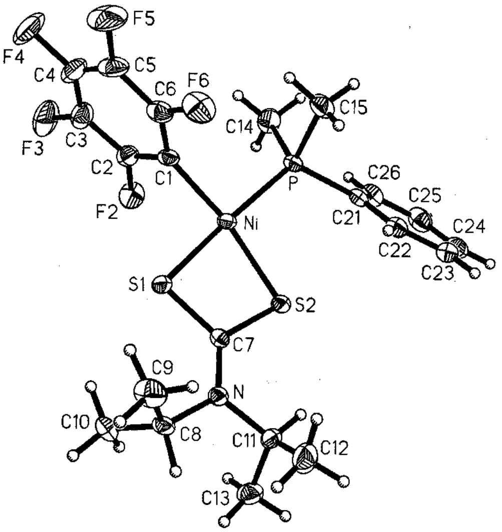
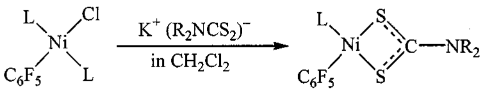


Figure 3. Molecular structure of compound **24**



	L	R		L	R
20	PPh_2Me	Et	**26**	PPh_2Me	C_5H_{10}
21	$PPhMe_2$	Et	**27**	$PPhMe_2$	C_5H_{10}
22	PEt_3	Et	**28**	PEt_3	C_5H_{10}
23	PPh_2Me	*i*Pr	**29**	PPh_2Me	C_4H_8
24	$PPhMe_2$	*i*Pr	**30**	$PPhMe_2$	C_4H_8
25	PEt_3	*i*Pr	**31**	PEt_3	C_4H_8

Scheme 3

band for ν(CS) is consistent with bidentate coordination of the dithiocarbamate.[24,25] Since the C=N and C−N stretching vibrations are usually found at 1690−1640 and 1350−1250 cm^{-1},[25] the thioureide band at 1550−1450 cm^{-1} indicates that the C−N bond in the coordinated $(S_2CNR_2)^-$ has considerable double bond character. However, the ^1H NMR spectra of complexes **20**−**31** indicate that rotation of the NR_2 group around the C−N bond is not hindered.

Crystal Structure of Complex 24

The structure of [Ni(C_6F_5)(S_2CNiPr_2)($PPhMe_2$)] (**24**) has been determined by X-ray crystallography. An ORTEP diagram is provided in Figure 3, and relevant bond lengths and angles are reported in Table 1. The overall coordination geometry about the nickel atom is essentially square planar. The S1−Ni−S2 angle is restricted by the chelate ring to 78.77(2)°. The P−Ni−S2 bond angle compensates to a great extent for the low angle by opening to 98.11(2)° with the C1−Ni−S1 angle at 91.40(5)°. The strong Ni−C_6F_5 bonding is evident in the nonequivalent Ni−S1 and Ni−S2 bond lengths and the *trans* influence exerted by the pentafluorophenyl ring is higher than that of the phosphane ligand lengthening the bond Ni−S2 giving a distance of 2.2144(5) Å, longer than the distance Ni−S1, 2.2029(5).

Conclusion

This work shows that mononuclear Ni-thiolate complexes [Ni(C_6F_5)(SR)L_2] can be conveniently prepared by metathetical reactions carried out with the corresponding chloro complexes [Ni(C_6F_5)ClL_2]. The reaction temperature is a decisive factor in the formation of the mononuclear thiolate complex. At room temperature the mononuclear thiolato complex is the outcome of the metathetical reaction, but if the reaction is carried out in refluxing dichloromethane the binuclear thiolate complex is obtained with the concomitant release of one L molecule. The dithiocarbamate complexes are similarly obtained when [Ni(C_6F_5)ClL_2] is treated with KS_2CNR_2.

Experimental Section

General Methods: C, H, and N analyses were carried out with a Carlo Erba instrument. − Infrared spectra were recorded with a Perkin−Elmer 16F-PC-FT spectrophotometer using Nujol mulls between polyethylene sheets. − ^{1}H, ^{31}P, and ^{19}F 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 solution, $c \approx 5 \times 10^{-4}$ mol·dm^{-3}). − Decomposition temperatures were determined with a Reichert microscope. − All solvents were dried by conventional methods. − The compounds [Ni(C_6F_5)Cl($PPhMe_2$)$_2$],[18] [Ni(C_6F_5)Cl(PPh_2Me)$_2$],[19] [Ni(C_6F_5)Cl(dppe)],[26] and [Ni(C_6F_5)Cl(PEt_2)$_2$][19] were prepared as described elsewhere.

[Ni(C_6F_5)(SR)L_2]; L = PPh_2Me and R = Ph (1), C_6H_4Me-*p* (2), C_6H_4OMe-*p* (3), C_6H_4Cl-*p* (4), $C_6H_4Cl_2$−2,6 (5), $C_6H_4NO_2$-*p* (6); L = $PPhMe_2$ and R = Ph (7), C_6H_4Me-*p* (8), C_6H_4OMe-*p* (9), C_6H_4Cl-*p* (10), $C_6H_4Cl_2$-2,6 (11), $C_6H_4NO_2$-*p* (12): A solution of [Ni(C_6F_5)ClL_2] (0.164 mmol) in dichloromethane (10 mL) was added to a solution of KSR (0.164 mmol) in methanol (10 mL), and the solution was stirred at room temperature for 30 min. It was concentrated under reduced pressure to ca. 5 mL. The addition of water (ca. 1 mL) caused precipitation of a red solid, which was filtered off, washed with hexane and air-dried. The complexes were recrystallized from dichloromethane/hexane.

1: Yield: 72%. − $C_{38}H_{31}F_5NiP_2S$ (735.4): calcd. C 62.1, H 4.2, S 4.4; found C 62.0, H 4.4, S 4.2. − M.p. 156 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.7 (t, 6 H, PPh_2*Me*), 7.0 (m, 3 H, SPh), 7.2 (m, 12 H, P*Ph*$_2$Me), 7.5 (m, 8 H, P*Ph*$_2$Me), 7.7 (d, 2 H, SPh). − ^{19}F NMR ([D$_6$]acetone): δ = −116.7 (d, J_{om} = 25.0 Hz, 2 F_o), −162.3 (t, J_{mp} = 19.8 Hz, 1 F_p), −163.7 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 8.4 (s).

2: Yield: 70%. − $C_{39}H_{33}F_5NiP_2S$ (749.4): calcd. C 62.5, H 4.4, S 4.3; found C 62.2, H 4.5, S 4.6. − M.p. 160 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.7 (t, 6 H, PPh_2*Me*), 2.2 (s, 3 H, SC_6H_4*Me*-*p*), 6.8 (d, 2 H, SC_6H_4Me-*p*), 7.2 (m, 12 H, PPh_2Me), 7.5 (m, 8 H, PPh_2Me), 7.7 (d, 2 H, SC_6H_4Me-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −116.6 (d, J_{om} = 24.6 Hz, 2 F_o), −162.5 (t, J_{mp} = 20.0 Hz, 1 F_p), −163.8 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 8.3 (s).

3: Yield 76%. − $C_{39}H_{33}F_5NiOP_2S$ (765.4): calcd. C 61.2, H 4.3, S 4.2; found C 61.0, H 4.6, S 4.5. − M.p. 155 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.7 (t, 6 H, PPh_2*Me*), 3.7 (s, 3 H, SC_6H_4*MeO*-*p*), 6.5 (d, 2 H, SC_6H_4MeO-*p*), 7.4 (m, 14 H, PPh_2Me), 7.5 (m, 6 H, PPh_2Me), 7.6 (d, 2 H, SC_6H_4MeO-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −116.6 (d, J_{om} = 22.9 Hz, 2 F_o), −162.5 (t, J_{mp} = 21.4 Hz, 1 F_p), −163.8 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 8.3 (s).

4: Yield 77%. − $C_{38}H_{30}ClF_5NiP_2S$ (769.8): calcd. C 59.3, H 3.9, S 4.2; found C 59.5, H 4.2, S 4.4. − M.p. 150 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.7 (t, 6 H, PPh_2*Me*), 6.8 (d, 2 H, SC_6H_4Cl-*p*), 7.2 (m, 14 H, PPh_2Me), 7.4 (m, 6 H, PPh_2Me), 7.6 (d, 2 H, SC_6H_4Cl-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −116.6 (d, J_{om} = 24.8 Hz, 2 F_o), −161.8 (t, J_{mp} = 19.8 Hz, 1 F_p), −163.4 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 8.0 (s).

5: Yield 74%. − $C_{38}H_{29}Cl_2F_5NiP_2S$ (804.3): calcd. C 56.7, H 3.6, S 4.0; found C 56.5, H 3.8, S 4.1. − M.p. 160 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.7 (t, 6 H, PPh_2*Me*), 6.5 (t, 1 H, $SC_6H_4Cl_2$−2,6), 6.9 (d, 2 H, $SC_6H_4Cl_2$-2,6), 7.4 (m, 12 H, PPh_2Me), 8.0 (m, 8 H, PPh_2Me). − ^{19}F NMR ([D$_6$]acetone): δ = −113.6 (d, J_{om} = 26.9 Hz, 2 F_o), −162.3 (t, J_{mp} = 20.8 Hz, 1 F_p), −163.8 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 4.0 (s).

6: Yield 76%. − $C_{38}H_{30}F_5NNiO_2P_2S$ (780.4): calcd. C 58.5, H 3.9, N 1.8, S 4.1; found C 58.7, H 4.1, N 1.9, S 4.3. − M.p. 170 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.6 (t, 6 H, PPh_2*Me*), 7.3 (m, 12 H, PPh_2Me), 7.5 (m, 8 H, PPh_2Me, $SC_6H_4NO_2$-*p*), 7.6 (d, 2 H, SC_6H_4Cl-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −117.2 (d, J_{om} = 23.5 Hz, 2 F_o), −160.9 (t, J_{mp} = 19.7 Hz, 1 F_p), −162.6 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 7.6(s).

7: Yield 79%. − $C_{28}H_{27}F_5NiP_2S$ (611.2): calcd. C 55.0, H 4.5, S 5.2; found C 55.2, H 4.8, S 5.3. − M.p. 120 °C (dec.). − ^{1}H NMR ([D$_6$]acetone)]: δ = 1.3 (t, 12 H, PPh*Me*$_2$), 7.0 (m, 3 H, SPh), 7.3 (m, 10 H, $PPhMe_2$), 7.8 (d, 2 H, SPh). − ^{19}F NMR ([D$_6$]acetone): δ = −117.6 (d, J_{om} = 27.0 Hz, 2 F_o), −161.1 (t, J_{mp} = 19.7 Hz, 1 F_p), −163.3 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = −3.7.

8: Yield 71%. − $C_{29}H_{29}F_5NiP_2S$ (625.3): calcd. C 55.7, H 4.7, S 5.1; found C 55.5, H 4.8, S 5.4. − M.p. 130 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.3 (t, 12 H, PPh*Me*$_2$), 2.2 (s, 3 H, Me), 6.8 (d, 2 H, SC_6H_4Me-*p*), 7.2 (m, 10 H, $PPhMe_2$), 7.7 (d, 2 H, SC_6H_4Me-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −116.6 (d, J_{om} = 26.6 Hz, 2 F_o), −162.5 (t, J_{mp} = 20.0 Hz, 1 F_p), −163.8 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = −3.6 (s).

9: Yield 75%. − $C_{29}H_{29}F_5NiOP_2S$ (641.2): calcd. C 54.3, H 4.6, S 5.0; found C 54.6, H 4.9, S 4.9. − M.p. 135 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.3 (t, 12 H, PPh*Me*$_2$), 3,7 (s, 3 H, MeO), 6.6 (d, 2 H, SC_6H_4MeO-*p*), 7.2 (m, 10 H, $PPhMe_2$), 7.7 (d, 2 H, SC_6H_4MeO-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −117.5 (d, J_{om} = 27.9 Hz, 2 F_o), −161.1 (t, J_{mp} = 20.0 Hz, 1 F_p), −163.3 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = −3.7 (s).

10: Yield 81%. − $C_{28}H_{26}ClF_5NiP_2S$ (645.7): calcd. C 52.1, H 4.1, S 5.0; found C 52.4, H 4.0, S 4.8. − M.p. 130 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.3 (t, 12 H, PPh*Me*$_2$), 6.9 (d, 2 H, SC_6H_4Cl-*p*), 7.2 (m, 10 H, $PPhMe_2$), 7.7 (d, 2 H, SC_6H_4Cl-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −117.7 (d, J_{om} = 24.8 Hz, 2 F_o), −160.7 (t, J_{mp} = 19.8 Hz, 1 F_p), −163.0 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = −3.8.

11: Yield 80%. − $C_{28}H_{25}Cl_2F_5NiP_2S$ (680.1): calcd. C 49.4, H 3.7, S 4.7; found C 49.6, H 3.9, S 4.9. − M.p. 155 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.3 (t, 12 H, PPh*Me*$_2$), 6.7 (t, 1 H, $SC_6H_4Cl_2$-2,6), 7.1 (d, 2 H, $SC_6H_4Cl_2$-2,6), 7.2 (m, 10 H, $PPhMe_2$). − ^{19}F NMR ([D$_6$]acetone): δ = −115.9 (d, J_{om} = 26.9 Hz, 2 F_o), −161.5 (t, J_{mp} = 20.8 Hz, 1 F_p), −163.5 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = −5.8.

12: Yield 83%. − $C_{28}H_{26}F_5NNiO_2P_2S$ (656.2): calcd. C 51.2, H 4.0, N 2.1, S 4.9; found C 51.0, H 4.1, N 2.0, S 4.7. − M.p. 160 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.3 (t, 12 H, PPh*Me*$_2$), 7.2 (m, 12 H, $PPhMe_2$ + $SC_6H_4NO_2$-*p*), 7.7 (d, 2 H, $SC_6H_4NO_2$-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −117.2 (d, J_{om} = 23.5 Hz, 2 F_o), −160.9 (t, J_{mp} = 19.7 Hz, 1 F_p), −162.6 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = −3.8.

[{Ni(C_6F_5)($PPhMe_2$)}$_2$(μ-$SC_6H_4NO_2$-*p*)$_2$] (13): A solution of [Ni(C_6F_5)Cl($PPhMe_2$)$_2$] (0.164 mmol) in dichloromethane (10 mL) was added to a solution of $KSC_6H_4NO_2$-*p* (0.164 mmol) in methanol (10 mL), and the solution was heated under reflux for 5 h.

The solvent was then partly evaporated under reduced pressure to half the original volume, and the addition of diethyl ether caused the precipitation of a red-brown solid, which was filtered off, washed with hexane and air-dried. The complex was recrystallized from dichloromethane/diethyl ether. − Yield: 83%. − $C_{40}H_{30}F_{10}N_2Ni_2O_4P_2S_2$ (1036): calcd. C 46.4, H 2.9, N 2.7, S 6.2; found C 46.1, H 3.1, N 2.6, S 6.5. − M.p. 165 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 1.3 (t, 12 H, PPh*Me*$_2$), 7.3 (m, 14 H, PPhMe$_2$ + SC$_6$H$_4$NO$_2$-*p*), 7.8 (d, 4 H, SC$_6$H$_4$NO$_2$-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −116.2 (d, J_{om} = 30.2, 2 F$_o$), −160.2 (t, J_{mp} = 19.7, 1 F$_p$), −162.4 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = − 5.0.

[Ni(C$_6$F$_5$)(SR)(dppe)]; R = Ph (14), C$_6$H$_4$Me-*p* (15), C$_6$H$_4$OMe-*p* (16), C$_6$H$_4$Cl-*p* (17), C$_6$H$_4$Cl$_2$-2,6 (18), C$_6$H$_4$NO$_2$-*p* (19): AgClO$_4$ (0.157 mmol) was added to a solution of [Ni(C$_6$F$_5$)Cl(dppe)] (100 mg, 0.157 mmol) in acetone (20 mL). After stirring at room temperature for 1 h, the precipitated AgCl was filtered off and the resulting solution was added to a solution of KSR (0.157 mmol) in methanol (10 mL). The solution was then stirred at room temperature for 30 min. It was concentrated under reduced pressure to ca. 5 mL. The addition of water (ca. 1 mL) caused precipitation of a brown solid, which was filtered off, washed with hexane and air-dried. The complexes were recrystallized from dichloromethane/hexane.

14: Yield 77%. − M.p. 215 °C (dec.). − $C_{38}H_{29}F_5NiP_2S$ (733.3): C 62.2, H 4.0, S 4.4; found C 62.0, H 4.2, S 4.6. − ^1H NMR ([D$_6$]acetone): δ = 2.1 (m, 4 H, dppe), 6.6 (m, 3 H, SPh), 7.1 (d, 2 H, SPh), 7.4 (m, 16 H, dppe), 8.0 (m, 4 H, dppe). − ^{19}F NMR ([D$_6$]acetone): δ = −116.9 (m, 2 F$_o$), −164.1 (t, J_{mp} = 21.4, 1 F$_p$), −165.2 (m, 2 F$_m$). $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 50.4 (m, P$_A$), 54.8 (d, ^2J = 40.4, P$_B$).

15: Yield 81%. − $C_{39}H_{31}F_5NiP_2S$ (747.4): calcd. C 62.7, H 4.2, S 4.3; found C 62.4, H 4.3, S 4.5. − M.p. 195 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 2.1 (s, 3 H, SC$_6$H$_4$*Me-p*), 2.5 (m, 4 H, dppe), 6.3 (d, 2 H, SC$_6$H$_4$Me-*p*), 6.8 (d, 2 H, SC$_6$H$_4$Me-*p*), 7.4 (m, 20 H, dppe). − ^{19}F NMR ([D$_6$]acetone): δ = −116.9 (m, 2 F$_o$), −164.7 (t, J_{mp} = 21.4 Hz, 1 F$_p$), −165.4 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 50.5 (m, P$_A$), 54.5 (d, ^2J = 40.4 Hz, P$_B$).

16: Yield 82%. − $C_{39}H_{31}F_5NiOP_2S$ (763.4): calcd. C 61.4, H 4.1, S 4.2; found C 61.5, H 4.4, S 4.3. − M.p. 198 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 2.1 (m, 4 H, dppe), 3.6 (s, 3 H, SC$_6$H$_4$*MeO-p*), 6.3 (d, 2 H, SC$_6$H$_4$MeO-*p*), 7.0 (d, 2 H, SC$_6$H$_4$MeO-*p*), 7.4 (m, 16 H, dppe), 8.0 (m, 4 H, dppe). − ^{19}F NMR ([D$_6$]acetone): δ = −116.9 (m, 2 F$_o$), −164.3 (t, J_{mp} = 21.4 Hz, 1 F$_p$), −165.0 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 50.4 (m, P$_A$), 54.3 (d, ^2J = 40.4 Hz, P$_B$).

17: Yield 84%. − $C_{38}H_{28}ClF_5NiP_2S$ (767.8): calcd. C 59.5, H 3.7, S 4.2; found C 59.8, H 4.0, S 4.3. − M.p. 190 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 2.1 (m, 4 H, dppe), 6.7 (d, 2 H, SC$_6$H$_4$Cl-*p*), 7.0 (d, 2 H, SC$_6$H$_4$Cl-*p*), 7.5 (m, 16 H, dppe), 8.0 (m, 4 H, dppe). − ^{19}F NMR ([D$_6$]acetone): δ = −116.8 (m, 2 F$_o$), −163.2 (t, J_{mp} = 21.4 Hz, 1 F$_p$), −164.8 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 52.1 (m, P$_A$), 56.1 (d, ^2J = 41.4 Hz, P$_B$).

18: Yield 80%. − $C_{38}H_{27}Cl_2F_5NiP_2S$ (802.2): calcd. C 56.9, H 3.4, S 4.0; found C 57.0, H 3.2, S 4.2. − M.p. 205 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 2.2 (m, 4 H, dppe), 6.6 (t, 1 H, SC$_6$H$_3$Cl$_2$-2,6), 6.9 (d, 2 H, SC$_6$H$_3$Cl$_2$-2,6), 7.4 (m, 16 H, dppe), 8.0 (m, 4 H, dppe). − ^{19}F NMR ([D$_6$]acetone): δ = −114.2 (m, 2 F$_o$), −163.8 (t, J_{mp} = 19.8 Hz, 1 F$_p$), −164.5 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 52.0 (m, P$_A$), 54.6 (m, P$_B$).

19: Yield 86%. − $C_{38}H_{28}F_5NNiO_2P_2S$ (778.3): calcd. C 58.6, H 3.6, N 1.8, S, 4.1; found C 58.8, H 3.5, N 2.0, S 4.2. − M.p. 200 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 2.2 (m, 4 H, dppe), 7.2 (d, 2 H, SC$_6$H$_4$NO$_2$-*p*), 7.4 (m, 4 H, dppe), 7.6 (m, 12 H, dppe), 7.9 (m, 4 H, dppe), 8.2 (d, 2 H, SC$_6$H$_4$NO$_2$-*p*). − ^{19}F NMR ([D$_6$]acetone): δ = −116.7 (m, 2 F$_o$), −162.1 (t, J_{mp} = 21.4 Hz, 1 F$_p$), −164.2 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 51.2 (d, ^2J = 42.7 Hz, P$_A$), 56.0 (d, P$_B$).

[Ni(C$_6$F$_5$)(S$_2$CNR$_2$)L]; R = Et and L = PPh$_2$Me (20), PPhMe$_2$ (21), PEt$_3$ (22); R = *i*Pr and L = PPh$_2$Me (23), PPhMe$_2$ (24), PEt$_3$ (25); R = C$_5$H$_{10}$ and L = PPh$_2$Me (26), PPhMe$_2$ (27), PEt$_3$ (28); R = C$_4$H$_8$ and L = PPh$_2$Me (29), PPhMe$_2$ (30), PEt$_3$ (31): Potassium dialkyldithiocarbamate (0.164 mmol) was added to a solution of [Ni(C$_6$F$_5$)ClL$_2$] (0.164 mmol) in acetone (20 mL) and the solution was stirred at room temperature for 15 min. It was concentrated under reduced pressure to ca. 5 mL. The addition of water (1 mL) caused precipitation of an orange solid, which was filtered off, washed with hexane and air-dried. The complexes were recrystallized from dichloromethane/hexane.

20: Yield 82%. − $C_{24}H_{23}F_5NNiPS_2$ (574.2): calcd. C 50.2, H 4.0, N 2.4, S 11.2; found C 50.3, H 3.8, N 2.5, S 11.5. − M.p. 124 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 1.2 (t, 6 H, Et), 1.4 (t, 3 H, PPh$_2$Me), 3.6 (m, 4 H, Et), 7.4 (m, 6 H, PPh$_2$Me), 7.6 (m, 4 H, PPh$_2$Me). − ^{19}F NMR ([D$_6$]acetone): δ = −116.7 (d, 2 F$_o$, J_{om} = 23.7), −161.8 (t, $J_{m,p}$ = 19.7 Hz, 1 F$_p$), −164.3 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 15.4 (s).

21: Yield 79%. − $C_{19}H_{21}F_5NNiPS_2$ (512.7): calcd. C 44.6, H 4.1, N 2.7, S 12.5; found C 44.3, H 3.9, N 2.6, S 12.4. − M.p. 119 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 1.2 (t, 6 H, Et), 1.4 (m, 6 H, PPhMe$_2$), 3.6 (m, 4 H, Et), 7.4 (m, 3 H, PPh$_2$Me), 7.6 (m, 2 H, PPh$_2$Me). − ^{19}F NMR ([D$_6$]acetone): δ = −117.1 (d, J_{om} = 25.8 Hz, 2 F$_o$), −161.5 (t, J_{mp} = 19.2 Hz, 1 F$_p$), −164.3 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 1.4 (s).

22: Yield 72%. − $C_{17}H_{25}F_5NNiPS_2$ (492.2): calcd. C 41.5, H 5.1, N 2.8, S 13.0; found C 41.2, H 5.0, N 2.8, S 13.1. − M.p. 112 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 1.2 (m, 15 H, Et + PEt$_3$), 1.3 (m, 6 H, PEt$_3$), 3.6 (q, 4 H, Et). − ^{19}F NMR ([D$_6$]acetone): δ = −116.3 (d, J_{om} = 25.0, 2 F$_o$), −161.7 (t, J_{mp} = 19.7 Hz, 1 F$_p$), −164.2 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 21.0 (s).

23: Yield 71%. − $C_{26}H_{27}F_5NNiPS_2$ (602.3): calcd. C 51.9, H 4.5, N 2.3, S 10.6; found C 51.6, H 4.4, N 2.4, S 10.4. − M.p. 151 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 1.4 (m, 15 H, *i*Pr + PPh$_2$Me), 4.5 (m, 2 H, *i*Pr), 7.4 (m, 6 H, PPh$_2$Me), 7.6 (m, 4 H, PPh$_2$Me). − ^{19}F NMR ([D$_6$]acetone): δ = −116.4 (d, J_{om} = 23.4 Hz, 2 F$_o$), −162.1 (t, J_{mp} = 19.7 Hz, 1 F$_p$), −164.4 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 15.3 (s).

24: Yield 78%. − $C_{21}H_{25}F_5NNiPS_2$ (540.2): calcd. C 46.7, H 4.6, N 2.6, S 11.9; found C 46.6, H 4.5, N 2.5, S 11.7. − M.p. 136 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 1.4 (m, 18 H, *i*Pr + PPhMe$_2$), 4.5 (m, 2 H, *i*Pr), 7.4 (m, 3 H, PPhMe$_2$), 7.6 (m, 2 H, PPh$_2$Me). − ^{19}F NMR ([D$_6$]acetone): δ = −116.7 (d, J_{om} = 24.0, 2 F$_o$), −161.6 (t, J_{mp} = 19.5 Hz, 1 F$_p$), −164.2 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 1.3 (s).

25: Yield 75%. − $C_{19}H_{29}F_5NNiPS_2$ (520.4): calcd. C 43.9, H 5.6, N 2.7, S 12.3; found C 44.0, H 5.6, N 2.6, S 12.2. − M.p. 115 °C (dec.). − ^1H NMR ([D$_6$]acetone): δ = 1.4 (m, 27 H, *i*Pr + PEt$_3$), 4.5 (m, 2 H, *i*Pr). − ^{19}F NMR ([D$_6$]acetone): δ = −116.2 (d, J_{om} = 25.0 Hz, 2 F$_o$), −161.9 (t, J_{mp} = 19.8 Hz, 1 F$_p$), −164.3 (m, 2 F$_m$). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 20.3 (s).

Table 2. Crystal data and parameter of data collection for complexes **12**, **13**, and **24**

	12	**13**	**24**
Empirical formula	$C_{28}H_{26}F_5NNiO_2P_2S$	$C_{40}H_{30}F_{10}N_2Ni_2O_4P_2S_2$	$C_{21}H_{25}F_5NNiPS_2$
Formula mass	656.21	1036.14	540.22
Temperature	293(2) K	173(2) K	173(2) K
Absorption coefficient	9.30 cm^{-1}	12.18 cm^{-1}	11.08 cm^{-1}
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 15.647(4) Å	a = 10.2451(14) Å	a = 14.6464(12)
	b = 10.4481(14) Å	b = 8.38.01(10) Å	b = 11.9076(10)
	c = 19.035(3) Å	c = 23.523(3) Å	c = 13.8742(12)
	β = 114.21(2)°	β = 97.681(10)°	β = 101.086(6) °
Z; V Å^3	4; 2838.3(9) Å^3	2; 2001.5(5) Å^3	4; 2374.6(3) Å^3
Density (calculated)	1.361 g·cm^{-3}	1.719 g·cm^{-3}	1.511 g·cm^{-3}
Wavelength (Mo-K_α)	0.71073 Å	0.71073 Å	0.71073 Å
F (000)	1344	1048	1112
Independent reflections	4937	3514	4183
Parameters	365	248	286
R1	0.0429	0.0653	0.0283
wR2	0.1011	0.1162	0.0591

26: Yield 77%. − $C_{25}H_{23}F_5NNiPS_2$ (586.26): calcd. C 51.2, H 3.9, N 2.4, S 10.9; found C 51.1, H 4.0, N 2.4, S 10.6. − M.p. 170 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.6 (m, 9 H, C_5H_{10} + PPh_2Me), 3.7 (m, 4 H, C_5H_{10}), 7.4 (m, 6 H, PPh_2Me), 7.6 (m, 4 H, PPh_2Me). − ^{19}F NMR ([D$_6$]acetone): δ = −116.7 (d, J_{om} = 24.0, 2 F_o), −161.8 (t, J_{mp} = 19.8 Hz, 1 F_p), −164.3 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 15.6 (s).

27: Yield 76%. − $C_{20}H_{21}F_5NNiPS_2$ (524.2): calcd. C 45.8, H 4.0, N 2.7, S 11.2; found C 45.6, H 4.1, N 2.7, S 12.0. − M.p. 180 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.2 (t, 6 H, $PPhMe_2$), 1.4 (m, 6 H, $C_5H_{10}N$), 3.7 (m, 4 H, $C_5H_{10}N$), 7.4 (m, 3 H, $PPhMe_2$), 7.6 (m, 2 H, PPh_2Me). − ^{19}F NMR ([D$_6$]acetone): δ = 117.0 (d, J_{om} = 23.5 Hz, 2 F_o), −161.3 (t, J_{mp} = 19.2 Hz, 1 F_p), −164.1 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 1.8 (s).

28: Yield 74%. − $C_{18}H_{25}F_5NNiPS_2$ (504.2): calcd. C 42.9, H 5.0, N 2.8, S 12.7; found C 42.7, H 4.9, N 2.7, S 12.6. − M.p. 160 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.2 (m, 15 H, PEt_3), 1.7 (m, 6 H, C_5H_{10}), 3.7 (m, 4 H, C_5H_{10}). − ^{19}F NMR ([D$_6$]acetone): δ = −116.4 (d, J_{om} = 24.2 Hz, 2 F_o), −161.6 (t, J_{mp} = 19.6 Hz, 1 F_p), −164.2 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 21.3 (s).

29: Yield 75%. − $C_{24}H_{21}F_5NNiOPS_2$ (588.2): calcd. C 49.0, H 3.6, N 2.4, S 10.9; found C 48.9, H 3.7, N 2.3, S 10.7. − M.p. 147 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.6 (m, 3 H, PPh_2Me), 3.7 (m, 8 H, C_4H_8O), 7.4 (m, 6 H, PPh_2Me), 7.6 (m, 4 H, PPh_2Me). − ^{19}F NMR ([D$_6$]acetone): δ = −116.9 (d, J_{om} = 23.5 Hz, 2 F_o), −161.4 (t, J_{mp} = 19.8 Hz, 1 F_p), −164.1 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 15.3 (s).

30: Yield 79%. − $C_{19}H_{19}F_5NNiOPS_2$ (526.16): calcd. C 43.4, H 3.6, N 2.7, S 12.2; found C 43.3, H 3.5, N 2.6, S 12.3. − M.p. 142 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.4 (m, 6 H, $PPhMe_2$), 3.7 (m, 8 H, C_4H_8O), 7.4 (m, 3 H, $PPhMe_2$), 7.6 (m, 2 H, PPh_2Me). − ^{19}F NMR ([D$_6$]acetone): δ = −117.3 (d, J_{om} = 23.8 Hz, 2 F_o), −160.9 (t, J_{mp} = 19.5 Hz, 1 F_p), −163.9 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 1.8 (s).

31: Yield 74%. − $C_{17}H_{23}F_5NNiOPS_2$ (506.2): calcd. C 40.3, H 4.6, N 2.8, S 12.7; found C 40.5, H 4.4, N 2.9, S 12.7. − M.p. 128 °C (dec.). − ^{1}H NMR ([D$_6$]acetone): δ = 1.6 (m, 15 H, PEt_3), 3.7 (d, 4 H, C_4H_8O), 3.8 (d, 4 H, C_4H_8O). − ^{19}F NMR ([D$_6$]acetone): δ = −116.6 (d, J_{om} = 24.0 Hz, 2 F_o), −161.3 (t, J_{mp} = 19.8 Hz, 1 F_p), −164.0 (m, 2 F_m). − ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 21.4 (s).

Determination of the X-ray Crystal Structures of 12, 13, and 24: Single crystals of complexes **12** (approximate dimensions 0.75 × 0.50 × 0.40 mm), **13** (0.50 × 0.30 × 0.20 mm), and **24** (0.60 × 0.50 × 0.30 mm) were mounted on a Siemens P4 diffractometer with LT2 temperature attachment. The crystallographic data are shown in Table 2. The scan method was ω with $2\Theta_{\max} = 50$° for the three cases, empirical Ψ-scan mode absorption was made. The structures were solved by direct methods and refined anisotropically on F^2.[26] The final R factors were 0.0367, 0.0451 and 0.0233 in **12**, **13**, and **24**, respectively {R_w = 0.0986, 0.1091, and 0.058, $w = 1/[\sigma^2(F^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants set by the program} over the observed reflections [$I > 2\sigma(I)$]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-139088 to CCDC-139090. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336-033, E-mail: deposit@chemcrys.cam.ac.uk].

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