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Transition Metal Complexes of Phosphinous Acids Featuring a Quasichelating Unit: Synthesis, Characterization, and Hetero-bimetallic Complexes

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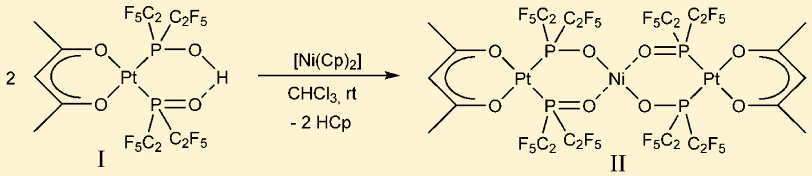
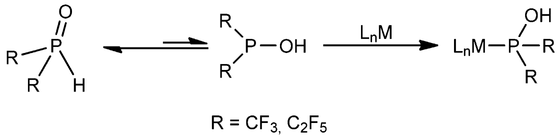
Supporting Information



ABSTRACT: Diorganophosphane oxides were employed as preligands for the synthesis of catalytically active transition metal complexes of the phosphinous acids $(CF_3)_2POH$ and $(C_2F_5)_2POH$. Their reactions with solid $PtCl_2$ and $PdCl_2$ led to the formation of mononuclear phosphinous acid complexes $[Cl_2M\{P(R^f)_2OH\}_2]$ (M = Pd, Pt; $R^f = C_2F_5, CF_3$), which can be crystallized, for example, as its pyridinium salts, $2[HPy]^+[Cl_2Pd\{P(CF_3)_2O\}_2]^{2-}$. In vacuo HCl is liberated from the neutral palladium complexes affording mixtures of di- and polynuclear complexes. Moreover, $(C_2F_5)_2POH$ was reacted with several β-diketonato complexes of palladium, platinum, and nickel yielding air- and moisture-stable complexes $[(acac)M\{[P(R^f)_2O]_2H\}]$, featuring a quasichelating phosphinous acid phosphinito unit $\{P(R^f)_2O\cdots H\cdots O(R^f)_2P\}^-$. Treatment of $[Ni(Cp)_2]$ (Cp = cyclopentadienyl) and $[(cod)RhCl]_2$ (cod = 1,5-cyclooctadiene) with $(C_2F_5)_2POH$ leads to the substitution of one Cp or chloro ligand by a quasichelating unit. The novel coordination compounds were characterized by NMR and IR spectroscopies, mass spectrometry, and X-ray diffraction analysis. The platinum complex $[(acac)Pt\{[P(C_2F_5)_2O]_2H\}]$ (acac = acetylacetonato) was used for the construction of hetero-bimetallic complexes by the treatment with $[(cod)RhCl]_2$ and $[Ni(Cp)_2]$. The trinuclear bimetallic complex $[\{(acac)Pt[P(C_2F_5)_2O]_2\}_2Ni]$ is the first structurally characterized hetero-bimetallic species containing a bis(perfluoroalkyl)phosphinito bridge.

■ INTRODUCTION

Phosphane ligands PR_3 exhibit a fascinating range of applications in coordination chemistry. By the variation of the electronic and steric properties of the substituents R it is possible to influence the properties of the corresponding transition metal complexes $[L_nMPR_3]$. Particularly with regard to the synthesis of catalytically active complexes, numerous studies have been carried out. A drawback, however, is the high sensitivity toward oxidation of trialkyl phosphanes. An alternative source of trivalent phosphorus ligands are secondary phosphane oxides. Diorganophosphane oxides $R_2P(O)H$ are in a tautomeric equilibrium with the corresponding phosphinous acid R_2POH. For aryl and alkyl substituents the equilibrium is, in general, completely shifted to the phosphane oxide. But, via the employment of the highly electron-withdrawing groups such as CF_3 and C_2F_5, it is possible to shift the tautomeric equilibrium completely to the side of the phosphinous acid.[1−5] In the case of the less strongly electron-withdrawing C_6F_5 and 2,4-$(CF_3)_2C_6H_3$ groups a solvent-dependent tautomeric equilibrium is observed.[5]



(1)

Chatt and Heaton demonstrated that phosphinous acids with electron-donating substituents can be stabilized or trapped by coordination to suitable transition metals.[6a] Transition metal complexes of phosphinous acids[6b,c] are frequently applied in homogeneous catalysis.[7] Figure 1 shows some commercially available palladium(II) complexes of phosphinous acids. The complexes POPd1, Ph1-Phoxide, and POPd7 exhibit a so-called phosphinous acid phosphinito quasichelating unit—a phosphinito ion $[R_2PO]^-$ and a phosphinous acid R_2POH fused via a strong hydrogen bridge.[7]

Comparable complexes were synthesized employing the bis(pentafluoroethyl)phosphinous acid. The reaction of $(C_2F_5)_2POH$ with palladium(II) chloride led to the formation of the mononuclear complex $[Cl_2Pd\{P(C_2F_5)_2OH\}_2]$ and the dinuclear complex $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)_2O]_2H\}_2]$ [cf. Scheme

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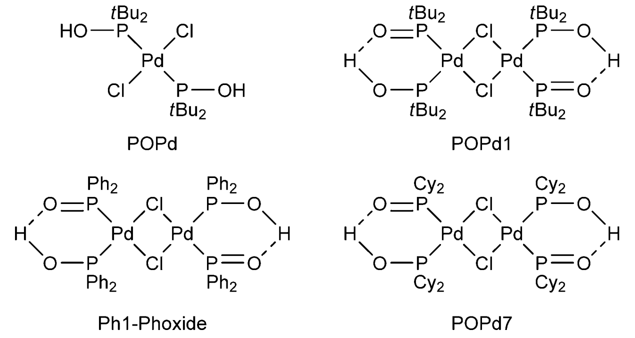
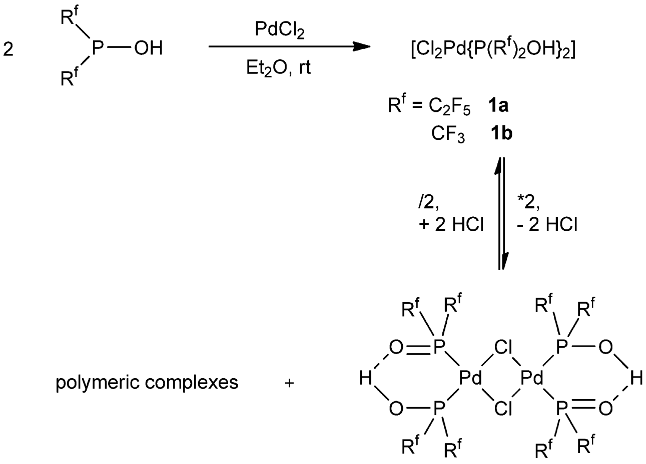


Figure 1. Palladium complexes commercialized by Combiphos.

1].[8a,8b] Transition metal complexes of phosphinous acids with the electron-withdrawing group 2,4-$(CF_3)_2C_6H_3$ exhibit an impressive catalytic activity in Suzuki type reactions.[9]

Scheme 1. Coordination of $(R^f)_2POH$ (R^f = C_2F_5, CF_3) to $PdCl_2$ and Equilibrium between Mononuclear and Polynuclear Complexes



The present paper describes the rich coordination chemistry of bis(perfluoroalkyl)phosphinous acids. Efficient syntheses of mononuclear complexes featuring a quasichelating phosphinic acid phosphinito unit, $[R^f_2PO\cdots H\cdots OPR^f_2]^-$, will be described. These kinds of complexes will be employed to mimic acac ligands leading to the synthesis of hetero-bimetallic complexes [cf., for example, Scheme 3].

RESULTS AND DISCUSSION

Addition of $(C_2F_5)_2POH$ to a slurry of palladium(II) chloride in diethyl ether smoothly afforded one product, as evidenced by a complex multiplet in the ^{31}P NMR spectrum at 84.7 ppm. Attempts to isolate this material by removal of all volatile compounds in vacuo resulted in mixtures of different components. Mass spectrometric analysis of the residue allows the detection of a dinuclear species. When a solution of the residue in diethyl ether was treated with gaseous hydrogen chloride, the initially formed complex was recovered. These observations are explained by the smooth formation of the mononuclear palladium complex $[Cl_2Pd\{P(C_2F_5)_2OH\}_2]$, **1a**, which upon concentration in vacuo undergoes a reversible condensation reaction yielding di- and polynuclear species.

A similar situation was observed for the reaction of $(CF_3)_2POH$ with $PdCl_2$. The initially formed $[Cl_2Pd\{P(CF_3)_2OH\}_2]$, **1b**, is also prone to condensation reactions in vacuo. If pyridine (py) is condensed onto a freshly prepared mixture of $(CF_3)_2POH$ and $PdCl_2$ in diethyl ether, single crystals of the adduct **1b**·2 py slowly separate. The X-ray structure analysis of the crystals [Figure 2] disclosed the presence of two different species in the unit cell. In the first molecule both phosphinito units are cis-orientated with both oxygen atoms clasping the hydrogen atom at N1 of a pyridinium cation (with N1). Thereby the atoms Pd1, P1, P2, O1, and O2 are located in the same plane with a separation O1···O2 of 291.5(1) pm. The second pyridinium ion (with N2) resides on the opposite side of the metal atom (Cl2···H2 248.9 pm). In the second, independent molecule each phosphinito unit is linked to one pyridinium ion by hydrogen bonding O3···H···N3 (267.4 pm) and O4···H···N4 (268.5 pm) resulting in a longer O3···O4 distance of 306.7 pm.

The reaction of solid platinum(II) chloride with $(C_2F_5)_2POH$ in diethyl ether selectively affords one product. In keeping with this the ^{31}P NMR spectrum exhibits one single resonance at 79.5 ppm with a $^1J(Pt,P)$ coupling constant of 3279 Hz, characteristic of phosphorus ligands in a trans-disposition. The product *trans*-$[Cl_2Pt\{P(C_2F_5)_2OH\}_2]$, **2**, was isolated in 37% yield after sublimation at 50 °C (Scheme 2).

Single crystals were obtained from a mixture of **2** and 2,2,6,6-tetramethylpiperidine (TMP). The molecular structure [Figure 3] shows a contact ion triple consisting of a central platinate unit located at a twofold axis and two piperidinium ions. Twofold deprotonation of the coordinated phosphinous acids leads to a shortening of the P1−O1 distance to 150.1(2) pm.

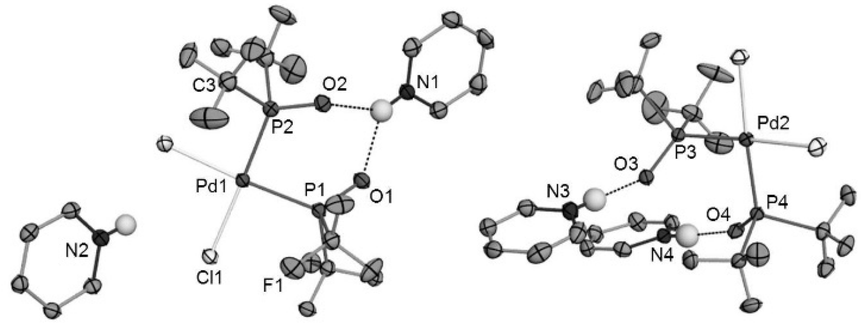


Figure 2. Molecular structure of two isomers of $2[HPy]^+[Cl_2Pd\{P(CF_3)_2O\}_2]^{2-}$, 50% probability amplitude displacement ellipsoids are shown; H atoms omitted for clarity. Selected bond lengths [pm] and angles [deg]: P1−O1 148.8(2), P2−O2 149.4(2), P3−O3 150.6(2), P4−O4 149.9(2), O1−N1 275.4(2), O2−N2 271.5(2), O3−N3 267.4(2), O4−N4 268.5(2), P1−Pd1−P2 89.31(2), P3−Pd2−P4 89.77(2); disorder of CF_3 groups on two positions.

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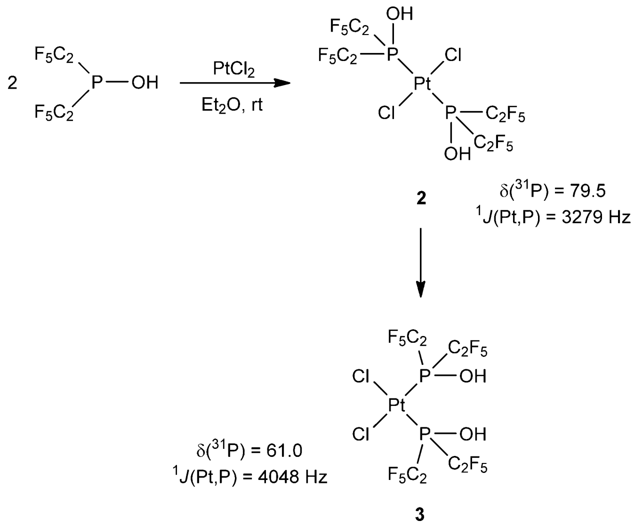
Scheme 2. Synthesis of *trans*-[$Cl_2Pt\{P(C_2F_5)_2OH\}_2$], 2, and Rearrangement to *cis*-[$Cl_2Pt\{P(C_2F_5)_2OH\}_2$], 3



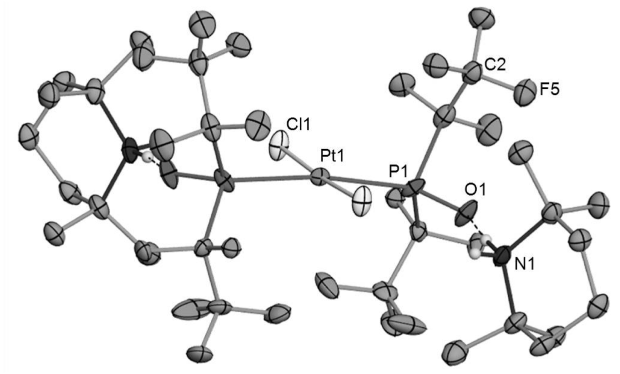
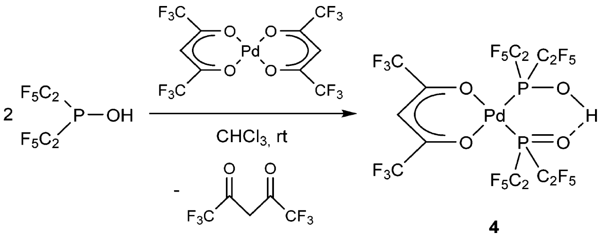


Figure 3. Molecular structure of $2[HTMP]^+[Cl_2Pt\{P(C_2F_5)_2O\}_2]^{2-}\cdot 2THF$, 50% probability amplitude displacement ellipsoids are shown; H atoms, minor distorted parts, and solvent molecules omitted for clarity. Selected bond lengths [pm] and angles [deg]: Pt1−Cl1 229.95(5), Pt1−P1 229.63(5), P1−O1 150.1(2), P1−C1 191.1(2), Cl1−Pt1−P1 91.82(2), O1−P1−C1 103.97(9); disorder of C_2F_5 group on two positions, disorder of the cation on two positions, disorder of C16 on two positions.

The cations are ligated to the oxygen atoms of the phosphinito units via intermolecular hydrogen bridging with an O1···N1 distance of 274.9(1) pm. A similar compound, featuring 2,4-bis(trifluoromethyl)phenyl substituents at the phosphorus atom, was published in 2011.[9] The bond lengths are virtually identical.

In solution as well as in the solid state, *trans*-[$Cl_2Pt\{P(C_2F_5)_2OH\}_2$], **2**, rearranges into cis-configured complex **3**, evidenced by an increase of the ^1J(Pt,P) coupling constant from 3279 Hz for **2** to 4048 Hz for **3**. The mass spectrum of **3** reveals peaks of a dinuclear species, which points to the condensation of **2** under HCl elimination. This seems, however, to be linked to the conditions within the mass spectrometer, because **3** was inert toward added HCl gas. Therefore, the cis-configurated complex observed in solution is best formulated as the mononuclear complex *cis*-[$Cl_2Pt\{P(C_2F_5)_2OH\}_2$], **3**.

The phosphane oxide $Ph_2P(O)H$ readily reacted with [$Pd(acac)_2$] (acac = acetylacetonato) affording the phosphinous acid complex [$(acac)Pd\{(PPh_2O)_2H\}$] bearing a phosphinous acid phosphinito quasichelating unit $\{PPh_2O\cdots H\cdots OPh_2P\}^-$.[10] This result motivated us to investigate the reactivity of $(CF_3)_2POH$ and $(C_2F_5)_2POH$ toward *β*-diketonato complexes of palladium, platinum and nickel. Bis(hexafluoroacetylacetonato)palladium(II) was selected as a starting material due to the NMR spectroscopic activity of the CF_3 groups. Addition of $(C_2F_5)_2POH$ to a chloroform solution of [$Pd(F_6acac)_2$] led to the precipitation of a colorless solid and the formation of free hexafluoroacetylacetone (eq 2).



(2)

The crude product was isolated and further purified by sublimation at room temperature. The ^{31}P NMR spectrum displays a multiplet at 82.2 ppm for coordinated phosphinous acids, whereas both the ^1H NMR and the ^{19}F NMR spectrum reveal resonances belonging to a coordinated hexafluoroacetylacetonato ligand ($\delta(^1H) = 6.5$, $\delta(^{19}F) = -74.8$). Table 1shows selected NMR data of several compounds. The NMR spectroscopic and electrospray ionization (ESI) mass spectrometric data agree with the proposed structure of [$(F_6acac)Pd\{[P(C_2F_5)_2O]_2H\}$], **4**. One hexafluoroacetylacetonato ligand of the precursor was protonated under formation of a quasichelating unit, $\{P(C_2F_5)_2O\cdots H\cdots O(C_2F_5)_2P\}^-$. The reaction is highly selective, and complex **4** remains inert toward an excess of the phosphinous acid.

Table 1. Selected NMR Spectroscopic Data of 1a, 1b, 2, 3, 4, 5, 6a, 6b, and 7

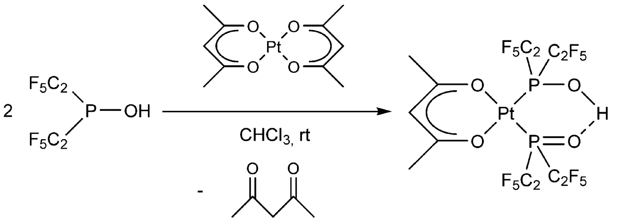
	$\delta(^1H)$	$\delta(^{31}P)$	^2J(M,P)
[$Cl_2Pd\{P(C_2F_5)_2OH\}_2$], **1a**	12.7[a]	84.7[b]	
[$Cl_2Pd\{P(CF_3)_2OH\}_2$], **1b**[b]	11.8	78.7	
tr.-[$Cl_2Pt\{P(C_2F_5)_2OH\}_2$], **2**[b]	14.0	79.5	3279
cis-[$Cl_2Pt\{P(C_2F_5)_2OH\}_2$], **3**[b]		61.0	4048
[$(F_6acac)Pd\{[P(C_2F_5)_2O]_2H\}$], **4**	11.0[c]	82.2[c]	
[$(acac)Pt\{[P(C_2F_5)_2O]_2H\}$], **5**[c]	11.0	55.2	4125
[$(Cp)Ni\{[P(C_2F_5)_2O]_2H\}$], **8a**[d]	11.4	127.3	
[$(Cp)Ni\{[P(CF_3)_2O]_2H\}$], **8b**[c]	7.4	114.0	
[$(cod)Rh\{[P(C_2F_5)_2O]_2H\}$], **7**[c]		105.9	184

[a] [D_6]acetone. [b] Et_2O. [c] [D]chloroform. [d] [D_6]benzene.

Walther et al. also described the reaction of $Ph_2P(O)H$ with [$Pt(acac)_2$] and [$Ni(acac)_2$] yielding [$Pt\{(PPh_2O)_2H\}_2$] and [$(acac)Ni\{(PPh_2O)_2H\}$], respectively.[10]

Treatment of a solution of [$Pt(acac)_2$] with a slight excess of $(C_2F_5)_2POH$ results in the liberation of acetylacetone, as indicated by ^1H NMR spectroscopy.

The ^{31}P NMR spectrum is characterized by a resonance at 55.2 ppm with a ^1J(Pt,P) coupling constant of 4125 Hz, characteristic of cis-orientated phosphorus-containing ligands. Furthermore, the ^{195}Pt NMR spectrum reveals a triplet of multiplets, indicating the coordination of two phosphinous acids. Single crystals of **5** were grown from diethyl ether solution. According to eq 3 one acac ligand was substituted by a phosphinous acid phosphinito quasichelating unit under the



(3)

5

formation of [(acac)Pt{[P(C_2F_5)$_2$O]$_2$H}], **5**. Complex **5** crystallizes in the monoclinic space group *Pn* (No. 7) with two independent molecules per unit cell. Because of similar structural parameters only the molecule at Pt1 will be discussed. The molecular structure in the solid phase, depicted in Figure 4, reveals a square planar platinum center coordinated by one acetylacetonato ligand and a quasichelating unit with a characteristic O3···O4 distance of 242.0(1) pm and Pt1–P–O angles of ~119.5° (cf. Table 2).

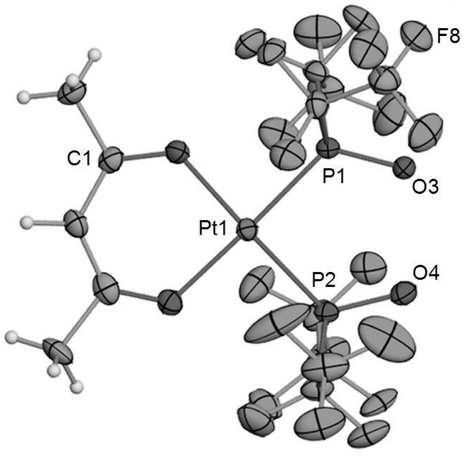


Figure 4. Molecular structure of [(acac)Pt{[P(C_2F_5)$_2$O]$_2$H}], **5**, 50% probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [deg]: Pt1–P1 221.3(2), Pt1–P2 221.6(2), P1–O3 151.8(6), P2–O4 152.7(7), P1–Pt1–P2 91.9(8), Pt1–P1–O3 119.4(2).

Table 2. Selected Structural Parameters of Bis(perfluoroorganyl)phosphinous Acid and Bis(perfluoroorganyl)phosphinito Complexes

	d(O···O)[a], pm	d(P–O), pm	∠M–P–O, deg
[Cl_2Pd{P(CF_3)$_2$O}$_2$]$^{2-}$		148.8(2)/ 149.4(2)	
[Cl_2Pt{P(C_2F_5)$_2$O}$_2$]$^{2-}$		150.1(2)	
[(acac) Pt{[P(C_2F_5)$_2$O]$_2$H}]	242.0(1)	151.8(6)/ 152.7(7)	119.4(2)/ 119.5(2)
[{(acac) Ni[P(CF_3)$_2$O]$_2$}$_2$ Ni$_2$(acac)$_2$]	285.7(1)	150.6(2)/ 150.7(2)	125.3(1)/ 126.4(1)
[{(acac) Pt[P(C_2F_5)$_2$O]$_2$}$_2$Ni]	283.5(1)	150.0(2)/ 150.1(2)	125.5(1)/ 125.6(1)
[(Cp) Ni{[P(CF_3)$_2$O]$_2$H}]	242.8(1)	153.9(2)/ 153.3(2)	119.5(1)/ 119.6(1)
[(cod) Rh{[P(C_2F_5)$_2$O]$_2$H}]	241.0(1)	154.3(2)/ 154.1(2)	122.0(1)/ 121.5(1)

[a] O···O distance of the {P(R^f)$_2$O···H···O(R^f)$_2$P}$^-$ unit.

The platinum complex [(acac)Pt{[P(C_2F_5)$_2$O]$_2$H}], **5**, is a promising starting material for the synthesis of heterobimetallic complexes. It is stable against air and moisture, easily accessible, and the ^1J(Pt,P) coupling constant is valuable to probe the coordination of an additional metal center at the quasichelating unit.

The reaction of two equiv of [(acac)Pt{[P(C_2F_5)$_2$O]$_2$H}], **5**, with one equiv of [{(cod)RhCl}$_2$] leads to the formation of a light yellow solid. Mass spectrometric analysis indicates the formation of the dinuclear bimetallic complex [(acac)Pt{P(C_2F_5)$_2$O}$_2$Rh(cod)], **6**, Scheme 3. Accordingly, the ^{1}H NMR spectrum reveals the characteristic signals of a coordinated acetylacetonato (δ(^{1}H) = 2.5, 5.8) and cyclooctadiene ligand (δ(^{1}H) = 2.1, 4.3 ppm). The resonance of the phosphorus atom at 48.8 ppm experiences a slight upfield shift with an increased ^1J(Pt,P) coupling constant of 4471 Hz. The ^{31}P{^{19}F} NMR spectrum shows an additional doublet splitting of 4 Hz, which may be due to a ^2J(Rh,P) coupling along the oxygen atom.

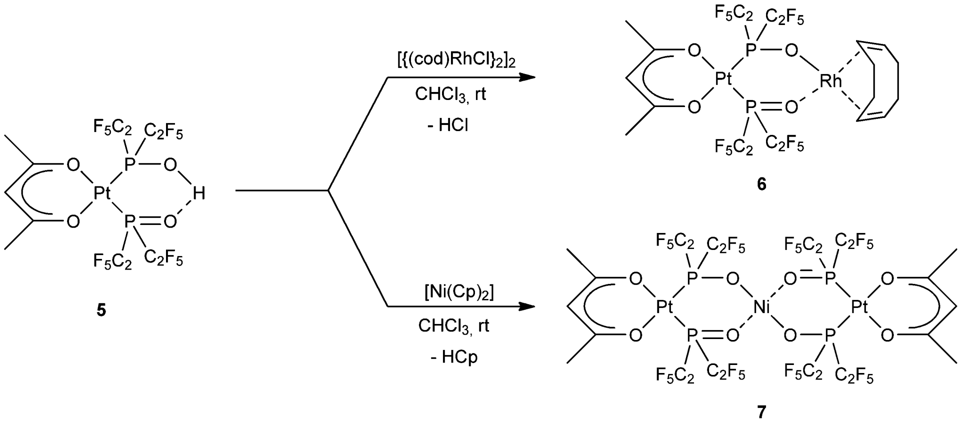
A trinuclear platinum nickel complex **7** is accessible by treatment of two equiv of [(acac)Pt{[P(C_2F_5)$_2$O]$_2$H}], **5**, with one equiv of [Ni(Cp)$_2$] in a diethyl ether/*n*-hexane mixture. After removal of all volatile compounds and recrystallization from chloroform dark yellow crystals were obtained. According to NMR measurements the product is paramagnetic. The structural characterization was accomplished by means of X-ray diffraction analysis. The molecular structure [cf. Figure 5] gives the picture of a trinuclear hetero-bimetallic platinum nickel complex. Therein the structure of the platinum precursor is virtually unaffected and coordinates to a nickel atom via the oxygen atoms of the quasichelating unit. Because of the coordination of the nickel atom the O3···O4 distance is elongated to 283.5(1) pm and the Pt1–P–O angles are opened to 125.5°. The nickel center exhibits an octahedral coordination sphere with two quasichelating units and two water ligands. In the solid compound **7** exists as a paramagnetic nickel high-spin complex.

Attempts to synthesize a mononuclear phosphinous acid nickel complex were made starting from trimeric [Ni(acac)$_2$], which was suspended in tetrahydrofuran (THF) and treated with (CF_3)$_2$POH, whereupon the green slurry turned into a yellow solution. Evaporation of all volatile compounds afforded a bright yellow solid. However, no resonances could be detected in the ^{1}H, ^{19}F, or ^{31}P NMR spectra of the product, which might be due to the paramagnetism of the resulting complex. NMR spectroscopic investigations of the volatile reaction products reveal the liberation of acetylacetone (cf. eq 4).

Recrystallization of the obtained reaction product from THF solution yielded bright yellow single crystals. The product crystallized in the triclinic space group $P\bar{1}$ (No. 2). The analysis revealed a tetranuclear phosphinous acid nickel complex [see Figure 6] with an inversion center between Ni1 and Ni1#. Ni2 is coordinated square planar by one acetylacetonato ligand and two phosphinito ligands via the phosphorus atoms P1 and P2. The phosphinito ligands coordinate a second nickel center Ni1 via the oxygen atoms O1 and O2. The nickel atom Ni1 exhibits an octahedral coordination sphere with bridging acetylacetonato ligands resulting in a Ni1···Ni1# distance of 316.09(2) pm. In comparison, the Ni···Ni distances in the trimeric [Ni(acac)$_2$]$_3$ are 288.7 and 289.6 pm.[11] The coordination sphere of Ni1 is completed by a THF molecule.

β-Diketonato complexes of palladium and platinum are ideal starting materials for the synthesis of mononuclear phosphi-

Scheme 3. Synthesis of [(acac)Pt{P(C_2F_5)$_2$O}$_2$Rh(cod)], 6, and [{(acac)Pt{P(C_2F_5)$_2$O}$_2$}$_2$Ni], 7



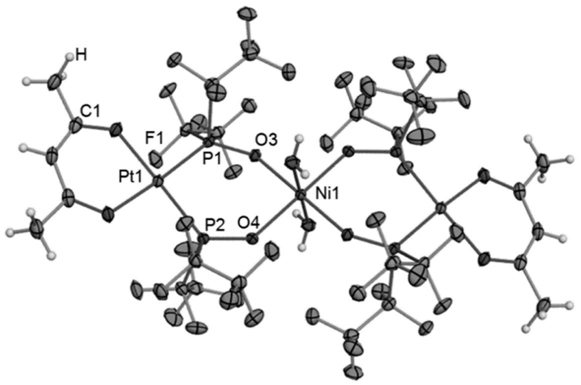


Figure 5. Molecular structure of [{(acac)Pt[P(C_2F_5)$_2$O]$_2$}$_2$Ni]·2H_2O, 7·2H_2O, 50% probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [deg]: Pt1−P1 221.22(7), Pt1−P2 220.65(7), P1−O3 150.0(2), P2−O4 150.1(2), Ni1−O3 203.9(2), Ni1−O4 201.6(2), P1−Pt1−P2 93.62(2), Pt1−P1−O3 125.49(7), Pt1−P2−O4 125.60(7), O3−Ni1−O4 88.73(7).

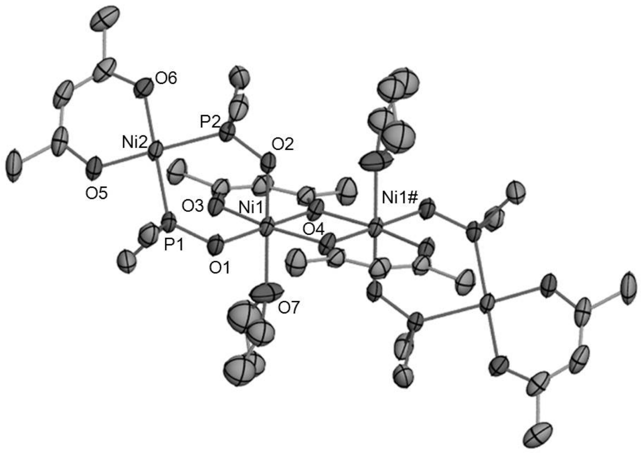
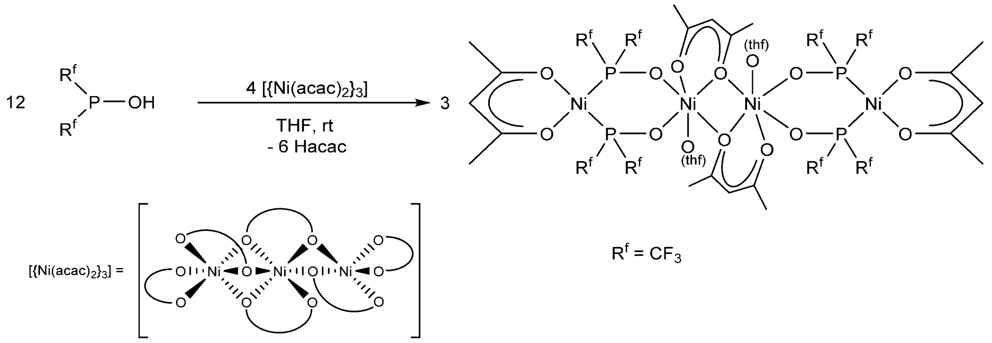


Figure 6. Molecular structure of [{(acac)Ni[P(CF_3)$_2$O]$_2$}$_2$Ni$_2$(acac)$_2$]·2THF, 50% probability amplitude displacement ellipsoids are shown; H and F atoms omitted for clarity. Selected bond lengths [pm] and angles [deg]: Ni1−O1 204.5(2), Ni1−O2 205.2(2), Ni1−O3 199.0(2), Ni1−O4 202.6(2), Ni1−O7 205.3(2), Ni2−O5 185.4(2), Ni2−P1 214.64(8), Ni2−P2 215.35(7), P1−O1 150.6(2), P2−O2 150.7(2), O1−Ni1−O2 88.44(8), P1−Ni2−P2 93.11(3), Ni2−P1−O1 125.33(8); disorder of the THF molecule on two positions.

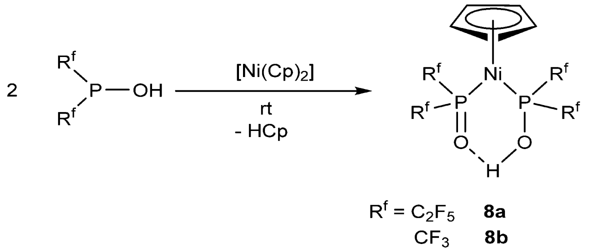
nous acid complexes. Even with an excess of (C_2F_5)$_2$POH selectively one acetylacetonato ligand is substituted by a {(C_2F_5)$_2$P−O···H···O−P(C_2F_5)$_2$}$^-$ unit. In strong contrast [Ni(acac)$_2$] forms a tetranuclear product on treatment with (CF_3)$_2$POH. The product formation could be described via a fast reaction of in situ formed [(acac)Ni{P(R^f_2PO}$_2$H] (R^f = CF_3, C_2F_5) with [{Ni(acac)$_2$}$_3$]. The trimeric nature of the precursor leads to the coordination of a dinuclear nickel unit bridged by acac ligands (cf. eq 4).

For the synthesis of a mononuclear phosphinous acid nickel complex the change of the starting material from trimeric [{Ni(acac)$_2$}$_3$] to monomeric nickelocene seemed promising. The solvent-free reaction of [Ni(Cp)$_2$] with (C_2F_5)$_2$POH affords a yellow solid, which was purified by recrystallization from *n*-hexane. The ^{31}P NMR spectrum reveals one multiplet at 127.3 ppm indicating the coordination of a phosphinous acid moiety. The ^{1}H NMR spectrum exhibited characteristic signals of a cyclopentadienyl ligand at 4.9 ppm. Substitution of one cyclopentadienyl ligand by a phosphinous acid phosphinito quasichelating unit yielded [(Cp)Ni{[P(C_2F_5)$_2$O]$_2$H}], **8a** (cf.



(4)

eq 5). The corresponding CF_3 derivative is also accessible following the above-described synthetic protocol. Single crystals suitable for X-ray analysis were grown from *n*-hexane solution. Complex **8b** crystallizes in the orthorhombic space group *Pbca* (No. 61). The molecular structure (Figure 7) underlines that one Cp ligand was substituted by a $\{P(CF_3)_2O\cdots H\cdots O(CF_3)_2P\}^-$ unit with an O1···O2 distance of 242.8(1) pm.



(5)

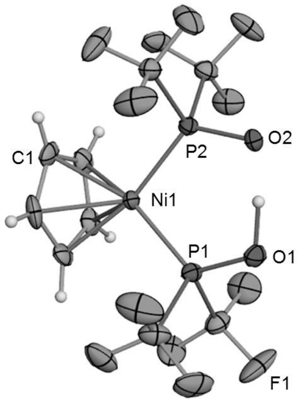
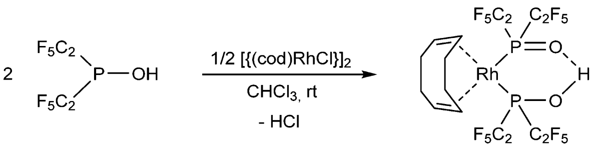


Figure 7. Molecular structure of $[(Cp)Ni\{P(CF_3)_2O\}_2H]$, **8b**, 50% probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [deg]: Ni1–C1 208.3(3), Ni1–P1 211.48(7), Ni1–P2 211.61(7), P1–O1 153.9(2), P2–O2 153.3(2), Ni1–P1–O1 119.49(7), Ni1–P2–O2 119.60(7).

To get a deeper insight into the reactivity of $(C_2F_5)_2POH$ toward transition metal complexes featuring alkene ligands, the dimeric rhodium complex $[\{(\text{cod})\text{RhCl}\}^2]$ was allowed to react with bis(pentafluoroethyl)phosphinous acid, $(C_2F_5)_2POH$. The mixture of the reactants in chloroform evolved HCl. After 4 h volatile components were removed, and the crude product was sublimated at 1×10^{-3} mbar and 50 °C to afford a yellow crystalline solid. Rhodium has a nuclear spin of 1/2. While the NMR sensitivity of ^{103}Rh is very low, couplings to the phosphorus atoms of phosphane ligands can be observed.[12] The ^{31}P NMR spectrum exhibits one resonance at 105.9 ppm with a high ordered multiplet. The $^{31}P\{^{19}F\}$ NMR spectrum, however, reveals a doublet with a $^{1}J(\text{Rh,P})$ coupling constant of 184 Hz. Mass spectrometry and single-crystal analysis confirmed the formation of $[(\text{cod})Rh\{[P(C_2F_5)_2O]_2H\}]$, **9** (Figure 8 and eq 6).



(6)

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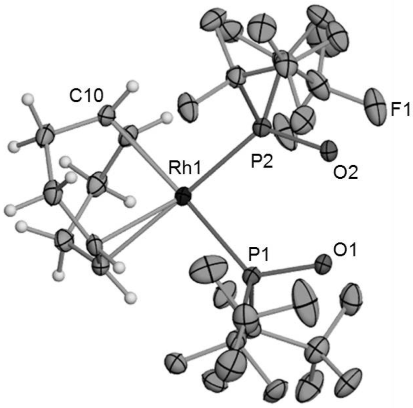

Figure 8. Molecular structure of $[(cod)Rh\{[P(C_2F_5)_2O]_2H\}]$, **9**, 50% probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [deg]: Rh1–C10 235.6(2), Rh1–P1 223.11(6), Rh1–P2 224.83(6), P1–O1 154.3(2), P2–O2 154.1(2), Rh1–P1–O1 122.03(7), Rh1–P2–O2 121.47(7).

The molecular structure in the solid phase is characterized by a $\{P(C_2F_5)_2O\cdots H\cdots O(C_2F_5)_2P\}^-$ unit with an O1···O2 distance of 241.0(1) pm and a Rh–P–O angle of averaged 121.8°, which is virtually identical to the values obtained for the platinum complex **5** and the nickel complex **8b**. The remaining cod ligand exhibits two short C–C bonds between the carbon atoms coordinated by the rhodium center of 136.7 pm, which is not unexceptional for a C–C double bond.

■ CONCLUSION

This work demonstrates the rich coordination chemistry of the electron-deficient bis(perfluoroalkyl)phosphinous acids R^f_2POH ($R^f = CF_3$, C_2F_5). The recently reported palladium complexes, synthesized from $PdCl_2$ and $(CF_3)_2POH$ or $(C_2F_5)_2POH$, are prone to form di- and polynuclear condensates. These condensation reactions are reversible, and the equilibrium can be shifted to the precursors by the addition of hydrogen chloride. The reaction of $PtCl_2$ with $(C_2F_5)_2POH$ initially yields *trans*-$[Cl_2Pt\{P(C_2F_5)_2OH\}_2]$. However, the trans configured complex is not stable toward a trans–cis isomerization.

Mononuclear complexes bearing a phosphinous acid phosphinito quasichelating unit are accessible from β-diketonato, cyclopentadienyl, or halide complexes. Several complexes featuring palladium, platinum, rhodium, or nickel centers were synthesized and fully characterized using NMR and IR spectroscopies, mass spectrometric methods, and X-ray diffraction analysis. The $\{P(R^f)_2O\cdots H\cdots O(R^f)_2P\}^-$ unit exhibits in the solid state a characteristic O···O distance of ~242 pm and a widened M–P–O angle of ~120°. The substitution of the hydrogen atom by a nickel atom leads to an increased O···O distance of ~285 pm and a widened M–P–O angle of ~126°. The efficient synthesis of the mononuclear complexes featuring a quasichelating unit opens the door to their implementation in catalysis as well as the synthesis of further heterometallic complexes with novel synthetic applications. As a consequence, the trinuclear bimetallic complex $[\{(acac)Pt[P(C_2F_5)_2O]_2\}_2Ni]$ represents the first structurally characterized hetero-bimetallic species containing a bis(perfluoroalkyl)phosphinito bridge.

■ EXPERIMENTAL SECTION

All chemicals were obtained from commercial sources and used without further purification. $(CF_3)_2POH$[2] and $(C_2F_5)_2POH$[4] were synthesized according to literature methods. Standard high-vacuum techniques were employed throughout all preparative procedures. Nonvolatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (^{31}P 111.92 MHz; ^{19}F 282.40 MHz; ^{13}C 75.47 MHz, ^{1}H 300.13 MHz) with positive shifts being downfield from the external standards (85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F) and TMS (^{1}H)). IR spectra were recorded on an Alpha-FT-IR spectrometer (Bruker) using a gas cell with KBr windows. ESI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Nitrogen was generated by a Bruker nitrogen generator NGM 11. Helium served as the cooling gas for the ion trap and collision gas for mass spectrometry (MS) experiments. The spectra were recorded with a Bruker Daltonik esquireNT 5.2 esquireControl software by the accumulation and averaging of several single spectra. Data analysis software 3.4 was used for processing the spectra. C, H, and N analyses were performed with a HEKAtech Euro EA 3000. The crystal data for compounds $2[HPy]^+[Cl_2Pd\{P(CF_3)_2O\}_2]^{2-}$, $2[HTMP]^+[Cl_2Pt\{P(C_2F_5)_2O\}_2]^{2-}\cdot 2THF$, **5**, **7**, **8b**, and **9** were collected on a Bruker Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 71.073 pm). Data collection for X-ray structure determination for compound $[\{(acac)Ni[P(CF_3)_2O]_2\}_2Ni_2(acac)_2]\cdot 2THF$ was performed on a Bruker AXS X8 Prospector Ultra with APEX II using Cu Kα radiation (λ = 154.178 pm). Suitable crystals were selected, coated with paratone oil, and mounted onto the diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares cycles (programs SHELXS-97 and SHELXL-97 (Sheldrick, G. M. SHELXL-97; Programs for Crystal Structure Analysis, University of Göttingen, 1997)[13]). The CCDC depositions numbers for all complexes are given in Tables S1 and S2 in the Supporting Information, where additional crystallographic information is available.

Synthesis of $[Cl_2Pd\{P(C_2F_5)_2OH\}_2]$, 1a. A sample of $(C_2F_5)_2POH$ (1.5 g, 5.1 mmol) was added to a slurry of $PdCl_2$ (0.3 g, 1.7 mmol) in diethyl ether (30 mL). After 3 h the yellow solution was filtered under inert conditions. The solution was investigated by NMR spectroscopy. ^{1}H NMR ([D_6]acetone, room temperature (rt)): δ = 12.7 ppm (s, $[Cl_2Pd\{P(C_2F_5)_2O\boldsymbol{H}\}_2]$); $^{13}C\{^{1}H\}$ NMR (Et_2O, rt): δ = 113.1 (m, $[Cl_2Pd\{P(CF_2\boldsymbol{C}F_3)_2OH\}_2]$), 118.0 ppm (m, $[Cl_2Pd\{P(\boldsymbol{C}F_2CF_3)_2OH\}_2]$); ^{19}F NMR (Et_2O, rt): δ = −116.9 (d, d, m, $^{2}J(F^a,F^b)$ = 313 Hz, $^{2}J(P,F^b)$ = 48 Hz, 1 F, $[Cl_2Pd\{P(CF^a\boldsymbol{F^b}CF_3)_2OH\}_2]$), −112.0 (d, d, m, $^{2}J(F^a,F^b)$ = 313 Hz, 1 F, $^{2}J(P,F^b)$ = 89 Hz, $[Cl_2Pd\{P(C\boldsymbol{F^a}F^bCF_3)_2OH\}_2]$), −80.5 ppm (s, 3 F, $[Cl_2Pd\{P(CF_2C\boldsymbol{F}_3)_2OH\}_2]$), ^{31}P NMR (Et_2O, rt): δ = 84.7 ppm (m, $[Cl_2Pd\{\boldsymbol{P}(C_2F_5)_2OH\}_2]$). Removal of all volatile compounds yielded 0.9 g of a mixture of a yellow and colorless solid. EI-MS (20 eV): *m/z* (%): 1103 (100) $[ClPd_2\{P(C_2F_5)_2O\}_2\{P(C_2F_5)_2OH\}]^+$, 1068 (14) $[Pd_2\{P(C_2F_5)_2O\}_2\{P(C_2F_5)_2OH\}]^+$, 700 (18) $[ClPd_2\{P(C_2F_5)_2OH\}\{P(C_2F_5)OH\}]^+$.

Synthesis of $[Cl_2Pd\{P(CF_3)_2OH\}_2]$, 1b. Addition of $(CF_3)_2POH$ (1.3 g, 6.9 mmol) to a slurry of $PdCl_2$ (0.4 g, 2.3 mmol) in 30 mL of diethyl ether yielded after 3 h a yellow solution. After filtration under inert conditions the solution was investigated by NMR spectroscopy. ^{1}H NMR (Et_2O, rt): δ = 11.8 ppm (s, $[Cl_2Pd\{P(CF_3)_2O\boldsymbol{H}\}_2]$); ^{13}C NMR (Et_2O, rt): δ = 121.1 ppm (m, $[Cl_2Pd\{P(\boldsymbol{C}F_3)_2OH\}_2]$); ^{19}F NMR (Et_2O, rt): δ = −64.5 ppm (d, $^{2}J(P,F)$ = 93 Hz, $[Cl_2Pd\{P(C\boldsymbol{F}_3)_2OH\}_2]$); ^{31}P NMR (Et_2O, rt): δ = 78.7 ppm (sept, $^{2}J(P,F)$ = 93 Hz, $[Cl_2Pd\{\boldsymbol{P}(CF_3)_2OH\}_2]$). Removal of all volatile compounds yielded 0.9 g of a mixture of a yellow and colorless solid. EI-MS (20 eV): *m/z* (%): 1025 (13) $[Cl_2Pd_2\{P(CF_3)_2O\}_3\{P(CF_3)_2OH\}]^+$, 804 (48) $[ClPd_2\{P(CF_3)_2O\}_2\{P(CF_3)_2OH\}]^+$, 653 (36) $[Cl_2Pd_2\{P(CF_3)_2O\}\{P(CF_3)_2OH\}]^+$, 514 (4) $[ClPd\{P(CF_3)_2OH\}_2]^+$.

Synthesis of $[Cl_2Pt\{P(C_2F_5)_2OH\}_2]$. $PtCl_2$ (1.3 g, 4.9 mmol) was suspended in 30 mL of diethyl ether, and $(C_2F_5)_2POH$ (2.8 g, 9.8 mmol) was added. After 3 d a yellow solution was obtained. Filtration under inert conditions, removal of the solvent, and sublimation at 50 °C yielded 1.5 g (1.8 mmol, 37%) of yellow oily *trans*-$[Cl_2Pt\{P(C_2F_5)_2OH\}_2]$. ^{1}H NMR (Et_2O, rt): δ = 14.0 ppm (s, *trans*-$[Cl_2Pt\{P(C_2F_5)_2O\boldsymbol{H}\}_2]$); ^{19}F NMR (Et_2O, rt): δ = −118.3 (m, $^{2}J(F^a,F^b)$ = 315 Hz, 1 F, *trans*-$[Cl_2Pt\{P(CF^a\boldsymbol{F^b}CF_3)_2OH\}_2]$), −114.2 (m, $^{2}J(F^a,F^b)$ = 315 Hz, 1 F, *trans*-$[Cl_2Pt\{P(C\boldsymbol{F^a}F^bCF_3)_2OH\}_2]$), −80.2 ppm (s, 3 F, *trans*-$[Cl_2Pt\{P(CF_2C\boldsymbol{F}_3)_2OH\}_2]$); ^{31}P NMR (Et_2O, rt): δ = 79.5 ppm (m, $^{1}J(Pt,P)$ = 3279 Hz, *trans*-$[Cl_2Pt\{\boldsymbol{P}(C_2F_5)_2OH\}_2]$); ^{195}Pt NMR (Et_2O, rt): δ = −3939.6 (t, m, $^{1}J(Pt,P)$ = 3279 Hz, *trans*-$[Cl_2\boldsymbol{Pt}\{P(C_2F_5)_2OH\}_2]$). Storing for several weeks at rt afforded a colorless solid *cis*-$[Cl_2Pt\{P(C_2F_5)_2OH\}_2]$. ^{19}F NMR (Et_2O, rt): δ = −118.3 (m, $^{2}J(F^a,F^b)$ = 316 Hz, 1 F, *cis*-$[Cl_2Pt\{P(CF^a\boldsymbol{F^b}CF_3)_2OH\}_2]$), −113.4 (m, $^{2}J(F^a,F^b)$ = 316 Hz, 1 F, *cis*-$[Cl_2Pt\{P(C\boldsymbol{F^a}F^bCF_3)_2OH\}_2]$), −80.4 ppm (s, 3 F, *cis*-$[Cl_2Pt\{P(CF_2C\boldsymbol{F}_3)_2OH\}_2]$); ^{31}P NMR (Et_2O, rt): δ = 61.0 ppm (m, $^{1}J(Pt,P)$ = 4048 Hz, *cis*-$[Cl_2Pt\{\boldsymbol{P}(C_2F_5)_2OH\}_2]$); ^{195}Pt NMR (Et_2O, rt): δ = −4269.8 (t, m, $^{1}J(Pt,P)$ = 4048 Hz, *cis*-$[Cl_2\boldsymbol{Pt}\{P(C_2F_5)_2OH\}_2]$); EI-MS (20 eV): *m/z* (%): 1482 (100) $[Cl_2Pt_2\{P(C_2F_5)_2O\}_2\{P(C_2F_5)_2OH\}\{P(C_2F_5)OH\}]^+$, 718 (8) $[Cl_2Pt\{P(C_2F_5)_2OH\}\{P(C_2F_5)OH\}]^+$.

Synthesis of $[(F_6acac)Pd\{[P(C_2F_5)_2O]_2H\}]$, 4. $(C_2F_5)_2POH$ (0.48 g, 1.67 mmol) was added to a solution of $[Pd(F_6acac)_2]$ (0.26 g, 0.50 mmol) in 10 mL of chloroform and stirred at room temperature until the yellow color disappeared. All volatile compounds were removed in vacuo. Sublimation at 1 × 10^{-3} mbar and room temperature yielded 0.32 g (0.36 mmol, 72%) of light yellow solid **4**. ^{1}H NMR ([D]chloroform, rt): δ = 6.5 (s, 1 H, $[(C_5\boldsymbol{H}F_6O_2)Pd\{[P(C_2F_5)_2O]_2H\}]$), 11.0 ppm (s, 1 H, $[(C_5HF_6O_2)Pd\{[P(C_2F_5)_2O]_2\boldsymbol{H}\}]$); ^{19}F NMR ([D]chloroform, rt): δ = −115.8 (m, 1 F, $[(C_5HF_6O_2)Pd\{[P(CF^a\boldsymbol{F^b}CF_3)_2O]_2H\}]$), −113.9 (m, 1 F, $[(C_5HF_6O_2)Pd\{[P(C\boldsymbol{F^a}F^bCF_3)_2O]_2H\}]$), −79.1 (s, 3 F, $[(C_5HF_6O_2)Pd\{[P(CF_2C\boldsymbol{F}_3)_2O]_2H\}]$), −74.8 ppm (s, 3 F, $[(C_5H\boldsymbol{F}_6O_2)Pd\{[P(C_2F_5)_2O]_2H\}]$); ^{31}P NMR ([D]chloroform, rt): δ = 82.2 ppm (m, $\boldsymbol{P}$), $^{31}P\{^{19}F\}$ NMR ([D]chloroform, rt): δ = 82.2 ppm (s, $\boldsymbol{P}$); EI-MS (70 eV): *m/z* (%): 885 (15) $[M + H]^+$, 765 (21) $[M\text{-}C_2F_5]^+$, 677 (19) $[M\text{-}F_6acac]^+$; ESI-MS (CH_2Cl_2): *m/z* (%): 883 (100) $[M\text{-}H]^-$; IR (ATR): $\tilde{\nu}$ = 425 (m), 462 (m), 505 (m), 550 (w), 567 (w), 597 (w), 633 (w), 682 (w), 707 (w), 750 (m), 804 (m), 838 (m), 959 (m), 999 (m), 1023 (m), 1073 (s), 1133 (s), 1204 (s), 1262 (w), 1297 (m), 1447 (w), 1639 (w).

Synthesis of $[(acac)Pt\{[P(C_2F_5)_2O]_2H\}]$, 5. $[Pt(acac)_2]$ (0.27 g, 0.69 mmol) was dissolved in 10 mL of chloroform, and $(C_2F_5)_2POH$ (0.59 g, 2.08 mmol) was added. The reaction mixture was stirred at room temperature for 2 h, and all volatile compounds were removed in vacuo. Sublimation at 1 × 10^{-3} mbar and 70 °C yielded 0.43 g (0.50 mmol, 73%) of light yellow solid **5**. ^{1}H NMR ([D]chloroform, rt): δ = 2.1 (s, 6 H, $C\boldsymbol{H}_3$), 5.8 (s, 1 H, $C\boldsymbol{H}$), 11.0 ppm (s, 1 H, $[(acac)Pt\{[P(C_2F_5)_2O]_2\boldsymbol{H}\}]$); $^{13}C\{^{1}H\}$ NMR ([D]chloroform, rt): δ = 26.5 (s, $\boldsymbol{C}H_3$), 102.9 (s, $\boldsymbol{C}H$), 206.2 ppm (s, $\boldsymbol{C}O$); $^{13}C\{^{19}F\}$ NMR ([D]chloroform, rt): δ = 111.9 (s, $\boldsymbol{C}F_3$), 118.7 ppm (d, $^{1}J(C,P)$ = 48 Hz, $\boldsymbol{C}F_2$); ^{19}F NMR ([D]chloroform, rt): δ = −118.6 (m, 1 F, $(acac)Pt\{[P(CF^a\boldsymbol{F^b}CF_3)_2O]_2H\}]$), −116.6 (m, 1 F, $[(acac)Pt\{[P(C\boldsymbol{F^a}F^bCF_3)_2O]_2H\}]$), −79.3 ppm (m, 3 F, $[(acac)Pt\{[P(CF_2C\boldsymbol{F}_3)_2O]_2H\}]$); ^{31}P NMR ([D]chloroform, rt): δ = 55.2 ppm (m, $^{1}J(Pt,P)$ = 4125 Hz, $\boldsymbol{P}$); $^{195}Pt\{^{1}H\}$ NMR ([D]chloroform, rt): δ = −3924.9 ppm (t, m, $^{1}J(Pt,P)$ = 4158 Hz, $\boldsymbol{Pt}$); EI-MS (70 eV): *m/z* (%): 866 (33) $[MH^+]$, 746 (100) $[M^+\text{-}C_2F_5]$; ESI-MS (CH_2Cl_2): *m/z* (%): 864 (100) $[M\text{-}H^-]$; IR (ATR): $\tilde{\nu}$ = 379 (w), 423 (m), 463 (s), 504 (w), 533 (w), 553 (m), 598 (w), 629 (w), 651 (w), 689 (m), 752 (m), 774 (w), 804 (m), 941 (w), 970 (s), 1023 (w), 1080 (m), 1139 (s), 1210 (s), 1296 (m), 1359 (w), 1390 (w), 1426 (w), 1529 (m), 1561 (m).

Synthesis of $[(acac)Pt\{P(C_2F_5)_2O\}_2Rh(cod)]$, 6. $[(acac)Pt\{[P(C_2F_5)_2O]_2H\}]$, **5**, was dissolved in chloroform, and $[\{(cod)RhCl\}^2]$, dissolved in chloroform, was added. The reaction mixture was stirred at rt for 30 min. All volatile compounds were removed in vacuo yielding orange solid **6**. ^{1}H NMR ([D]chloroform, rt): δ = 2.1 (s, 6 H,

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Inorg. Chem. 2015, 54, 7945−7952

$\mathrm{C}\boldsymbol{H}_3$ (acac)), 2.5 (m, 8 H, $\mathrm{C}\boldsymbol{H}_2$ (cod), 4.3 (s, 1 H, $\mathrm{C}\boldsymbol{H}$ (acac)), 5.8 ppm (s, 4 H, $\mathrm{C}\boldsymbol{H}$ (cod)); $^{31}\mathrm{P}\{^{19}\mathrm{F}\}$ NMR ([D]chloroform, rt): $\delta = 48.8$ ppm (d, $^{2}J(\mathrm{Rh,P}) = 4$ Hz, $^{2}J(\mathrm{Pt,P}) = 4471$ Hz, $\boldsymbol{P}$); EI-MS (70 eV): m/z (%): 1075 (71) $[M]^+$, 210 (100) $[(\mathrm{cod})\mathrm{Rh}]^+$, 182 (44) $[(\mathrm{C_2F_5})_2\mathrm{P(O)_2H}]^+$.

Synthesis of $[\{(\mathrm{acac})\mathrm{Pt}[\mathrm{P(C_2F_5)_2O}]_2\}_2\mathrm{Ni}]\cdot 2\mathrm{H_2O}$, 7. $[\mathrm{Ni(Cp)_2}]$ (0.016 g, 0.101 mmol) was dissolved in 3 mL of *n*-hexane and added to a solution of **5** (0.108 g, 0.125 mmol) in 3 mL of chloroform. After the solution was stirred for 12 h at room temperature all volatile compounds were removed in vacuo. Recrystallization from chloroform yielded 0.062 g (0.035 mmol, 56%) of dark yellow crystalline 7.

Synthesis of $[(\mathrm{Cp})\mathrm{Ni}\{[\mathrm{P(C_2F_5)_2O}]_2\mathrm{H}\}]$, 8a. In a Young valve flask $(\mathrm{C_2F_5})_2\mathrm{POH}$ (0.49 g, 1.73 mmol) was added to nickelocene (0.13 g, 0.69 mmol). The green reaction mixture was stirred at rt until the color turned to yellow. All volatile compounds were removed in vacuo. Recrystallization from *n*-hexane yielded 0.23 g (0.33 mmol, 48%) of yellow crystalline **8a**. $^{1}\mathrm{H}$ NMR ([D$_6$]benzene, rt): $\delta = 4.9$ (s, 5 H, $[(\mathrm{C_5}\boldsymbol{H}_5)\mathrm{Ni}\{[\mathrm{P(C_2F_5)_2O}]_2\mathrm{H}\}]$), 11.4 ppm (s, 1 H, $[(\mathrm{C_5H_5})\mathrm{Ni}\{[\mathrm{P(C_2F_5)_2O}]_2\boldsymbol{H}\}]$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ([D$_6$]benzene, rt): $\delta = 95.4$ ppm (s, $[(\boldsymbol{C}_5\mathrm{H_5})\mathrm{Ni}\{[\mathrm{P(C_2F_5)_2O}]_2\mathrm{H}\}]$); $^{13}\mathrm{C}\{^{19}\mathrm{F}\}$ NMR ([D$_6$]benzene, rt): $\delta = 113.7$ (m, $\boldsymbol{C}\mathrm{F_3}$), 118.8 ppm (m, $\boldsymbol{C}\mathrm{F_2}$); $^{19}\mathrm{F}\{^{31}\mathrm{P}\}$ NMR ([D$_6$]benzene, rt): $\delta = -120.7$ (pseudo-d, $^{2}J(\mathrm{F^a,F^b}) = 320$ Hz, 1 F, $[(\mathrm{Cp})\mathrm{Ni}\{[\mathrm{P(CF^a}\boldsymbol{F}^{\mathbf{b}}\mathrm{CF_3)_2O}]_2\mathrm{H}\}]$), -116.7 (pseudo-d, $^{2}J(\mathrm{F^a,F^b}) = 320$ Hz, 1 F, $[(\mathrm{Cp})\mathrm{Ni}\{[\mathrm{P(C}\boldsymbol{F}^{\mathbf{a}}\mathrm{F^bCF_3)_2O}]_2\mathrm{H}\}]$), -78.1 ppm (s, 3 F, $[(\mathrm{Cp})\mathrm{Ni}\{[\mathrm{P(CF_2C}\boldsymbol{F}_3\mathrm{)_2O}]_2\mathrm{H}\}]$); $^{31}\mathrm{P}$ NMR ([D$_6$]benzene, rt): $\delta = 127.3$ ppm (m, $[\mathrm{CpNi}\{[\boldsymbol{P}\mathrm{(CF_2CF_3)_2O}]_2\mathrm{H}\}]$), $^{31}\mathrm{P}\{^{19}\mathrm{F}\}$ NMR ([D$_6$]benzene, rt): $\delta = 127.3$ ppm (s, $[(\mathrm{Cp})\mathrm{Ni}\{[\boldsymbol{P}\mathrm{(CF_2CF_3)_2O}]_2\mathrm{H}\}]$); EI-MS (70 eV): m/z (%): 815 (2) $[M_2\text{-}[\mathrm{P(C_2F_5)_2O}]_2\mathrm{H}\}]^+$, 694 (7) $[M]^+$, 409 (21) $[M\text{-}(\mathrm{C_2F_5})_2\mathrm{POH}]^+$, 189 (28) $[\mathrm{Ni(Cp)_2}]^+$, 123 (100) $[\mathrm{Ni(Cp)}]^+$, 67 (24) $[\mathrm{Cp}]^+$; IR (ATR): $\tilde{\nu} = 425$ (m), 459 (m), 533 (w), 549 (m), 596 (w), 628 (w), 641 (w), 692 (w), 750 (m), 817 (m), 837 (w), 938 (w), 962 (m), 1052 (w), 1127 (s), 1201 (s), 1294 (m), 1407 (w); Anal. Calcd (%) for $\mathrm{C_{13}H_6F_{20}NiO_2P_2}$: C 22.48, H 0.87; found: C 23.19, H 0.97.

Synthesis of $[\mathrm{CpNi}\{[\mathrm{P(CF_3)_2O}]_2\mathrm{H}\}]$, 8b. In a Young valve flask $(\mathrm{CF_3})_2\mathrm{POH}$ (0.67 g, 3.59 mmol) was added to nickelocene (0.27 g, 1.44 mmol). The green reaction mixture was stirred at room temperature until the color turned to red. All volatile compounds were removed in vacuo. Recrystallization from *n*-hexane yielded 0.50 g (1.01 mmol, 70%) of deep red crystalline **8b**. $^{1}\mathrm{H}$ NMR ([D]chloroform, rt): $\delta = 5.7$ (s, 5 H, $[(\mathrm{C_5}\boldsymbol{H}_5)\mathrm{Ni}\{[\mathrm{P(CF_3)_2O}]_2\mathrm{H}\}]$), 7.4 ppm (s, 1 H, $[(\mathrm{C_5H_5})\mathrm{Ni}\{[\mathrm{P(CF_3)_2O}]_2\boldsymbol{H}\}]$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ([D]chloroform, rt): $\delta = 95.2$ ppm (s, $[(\boldsymbol{C}_5\mathrm{H_5})\mathrm{Ni}\{[\mathrm{P(CF_3)_2O}]_2\mathrm{H}\}]$); $^{13}\mathrm{C}\{^{19}\mathrm{F}\}$ NMR ([D]chloroform, rt): $\delta = 122.0$ ppm (m, $\boldsymbol{C}\mathrm{F_3}$); $^{19}\mathrm{F}$ NMR ([D]chloroform, rt): $\delta = -69.0$ ppm (s, $[(\mathrm{Cp})\mathrm{Ni}\{[\mathrm{P(C}\boldsymbol{F}_3\mathrm{)_2O}]_2\mathrm{H}\}]$); $^{31}\mathrm{P}$ NMR ([D]chloroform, rt): $\delta = 114.0$ ppm (m, $[(\mathrm{Cp})\mathrm{Ni}\{[\boldsymbol{P}\mathrm{(CF_3)_2O}]_2\mathrm{H}\}]$); $^{31}\mathrm{P}\{^{19}\mathrm{F}\}$ NMR ([D]chloroform, rt): $\delta = 114.0$ ppm (s, $[(\mathrm{Cp})\mathrm{Ni}\{[\boldsymbol{P}\mathrm{(CF_3)_2O}]_2\mathrm{H}\}]$); EI-MS (70 eV): m/z (%): 616 (2) $[M_2\text{-}\{[\mathrm{P(CF_3)_2O}]_2\mathrm{H}\}]^+$, 494 (8) $[M]^+$, 308 (23) $[\mathrm{M}\text{-}(\mathrm{C_2F_5})_2\mathrm{POH}]^+$, 189 (28) $[\mathrm{Ni(Cp)_2}]^+$, 123 (100) $[\mathrm{Ni(Cp)}]^+$; IR (ATR): $\tilde{\nu} = 429$ (m), 483 (w), 529 (m), 545 (m), 578 (m), 705 (w), 752 (w), 815 (m), 825 (m), 838 (m), 908 (w), 940 (w), 1045 (m), 1116 (s), 1140 (s), 1197 (m), 1362 (w), 1402 (w), 1459 (w), 1620 (w); Anal. Calcd (%) for $\mathrm{C_9H_6F_{12}NiO_2P_2}$: C 21.87, H 1.22; found: C 21.94, H 1.34.

Synthesis of $[(\mathrm{cod})\mathrm{Rh}\{[\mathrm{P(C_2F_5)_2O}]_2\mathrm{H}\}]$, 9. $(\mathrm{C_2F_5})_2\mathrm{POH}$ (0.18 g, 0.64 mmol) was added to a solution of $[(\mathrm{cod})\mathrm{RhCl}]_2$ (0.08 g, 0.16 mmol) in 4 mL of chloroform and stirred at room temperature for 2 h. Removal of all volatile compounds and sublimation at 1×10^{-3} mbar and 50 °C yielded 0.15 g (0.19 mmol, 59%) of yellow solid **9**. $^{1}\mathrm{H}$ NMR ([D]chloroform, rt): $\delta = 2.5$ (m, 2 H, $\mathrm{C}\boldsymbol{H}$), 5.9 ppm (s, 4 H, $\mathrm{C}\boldsymbol{H}_2$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ([D]chloroform, rt): $\delta = 29.8$ (s, $\boldsymbol{C}\mathrm{H_2}$), 106.9 ppm (m, $\boldsymbol{C}\mathrm{H}$); $^{13}\mathrm{C}\{^{19}\mathrm{F}\}$ NMR ([D]chloroform, rt): $\delta = 118.4$ ppm (s, $\boldsymbol{C}\mathrm{F_3}$); $^{19}\mathrm{F}$ NMR ([D]chloroform, rt): $\delta = -118.5$ (m, 1 F, $[(\mathrm{cod})\mathrm{Rh}\{[\mathrm{P(CF^a}\boldsymbol{F}^{\mathbf{b}}\mathrm{CF_3)_2O}]_2\mathrm{H}\}]$), -116.8 (m, 1 F, $[(\mathrm{cod})\mathrm{Rh}\{[\mathrm{P(C}\boldsymbol{F}^{\mathbf{a}}\mathrm{F^bCF_3)_2O}]_2\mathrm{H}\}]$), -79.2 ppm (m, 3 F, $[(\mathrm{cod})\mathrm{Rh}\{[\mathrm{P(CF_2C}\boldsymbol{F}_3\mathrm{)_2O}]_2\mathrm{H}\}]$); $^{31}\mathrm{P}\{^{19}\mathrm{F}\}$ NMR ([D]chloroform, rt): $\delta = 105.9$ ppm (d, $^{1}J(\mathrm{Rh,P}) = 184$ Hz, $\boldsymbol{P}$); IR (ATR): $\tilde{\nu} = 423$ (m), 458 (m), 510 (m), 547 (w), 595 (w), 627 (w), 672 (w), 697 (w), 747 (m), 807 (m), 899 (w), 952 (s), 1112 (s), 1196 (s), 1261 (s), 1294 (m), 1378 (w), 1458 (w), 1781 (w), 2852 (w), 2922 (m).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01038. CCDC contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray data and structure, compound **1a** (CIF)
X-ray data and structure, compound **1b** (CIF)
X-ray data and structure, compound **2** (CIF)
X-ray data and structure, compound **3** (CIF)
X-ray data and structure, compound **5** (CIF)
X-ray data and structure, compound **7** (CIF)
X-ray data and structure, compound **9** (CIF)
Crystal data and refinement characteristics for compounds **2**, **5**, **7**, **8b**, and **9** (PDF)

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Notes

The authors declare no competing financial interest.

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