The Role of the 2,4,6-Tris(trifluoromethyl)phenylamino Group in Stabilizing New Phosphorus-, Arsenic-, and Germanium-Containing Main-Group Compounds and Transition-Metal Derivatives☆

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The reactions of potassium R_f-amide [R_f = tris(trifluoromethyl)phenyl] (**2**) with PCl_3, $AsCl_3$, and $GeCl_2 \cdot$dioxane yield new four-membered inorganic heterocycles $[R_fNPCl]_2$ (**3**), $[R_fNAsCl]_2$ (**4**), and $[R_fNGe]_2$ (**5**), respectively. On the other hand, the reaction of R_f-amide **2** with two equivalents of R_fPCl_2 leads to the formation of the imino-λ^3-phosphane $R_fN{=}PR_f$ (**6**) and the diamino-λ^3-phosphane $(R_fNH)_2PR_f$ (**7**). The iminophosphane **6** reacts with $Ni(CO)_2(PPh_3)_2$ and forms the complex $[Ni(PPh_3)_2(R_fN{=}PR_f)]$ (**9**), in which the iminophosphane coordinates to the metal through the phosphorus lone pair. Treatment of lithium amide **2** with transition metal chlorides $ZnCl_2$ and $FeCl_2$ yields the imido/amido spirocyclic metal derivatives **9** and **10**, respectively. Compounds **3**−**10** have been extensively characterized by their analytical and mass, IR, and NMR (^1H, ^{19}F, and ^{31}P) spectroscopy. Further, the molecular structures of all the compounds have been unambiguously determined by single-crystal X-ray diffraction studies. The diazadigermetidine **5** crystallizes in a fluorescent-yellow orthorhombic and a yellow monoclinic crystal modification. The results obtained reveal the role of R_f group in stabilizing new multiple bonded systems and inorganic heterocycles. A skeletal rearrangment of the R_f ligand is observed in the reactions leading to compounds **9** and **10**. Moreover, the preparation of compounds **9** and **10** indicates the limitation of the use of this ligand in the preparation of new metal-amide systems, especially where the metal atoms have a strong tendency for the formation of strong M−F bonds.

Introduction

The chemistry of low-coordinate multiple bonded main-group systems and new inorganic heterocycles has been a fertile area of research over the last few decades. During this period, several multiple bonded species and heterocycles have been synthesized and spectroscopically and structurally characterized. It has been shown that in many of these systems, the organic substituent attached to these compounds plays a major role in determining the nature of the resulting products in terms of the conformation, isomerization, and the steric and electronic properties.

We have been concentrating over the years on the use of 2,4,6-tris(trifluoromethyl)phenyl ligand (abbreviated as R_f) in stabilizing a wide variety of transition-metal and main-group compounds[1]. Most of these low-coordinated systems contain the hetero elements also in their low oxidation states. It is interesting to note that the steric requirement imposed by the R_f ligand significantly differs from that imposed by a mesityl group. For example, owing to the bulkiness of the R_f group, compounds such as $R_fP{=}PR_f$[2], $(R_f)_2M$ (M= Sn, Pb)[3], and $(R_fOM)_2$ (M = In, Tl)[4] have been prepared. Apart from steric stabilization, this ligand also offers considerable electronic stabilization. Unlike the other bulky ligands known in the literature, the three CF_3 groups on the phenyl ring impose a strong electron-withdrawing effect on the R_f ligand. Another less obvious but more important advantage of using the R_f ligands is the ability of the fluorine atoms of the CF_3 groups to interact with the metals, thereby forming short metal−fluorine interactions. Continuing our efforts in this area, in this contribution, we wish to report on the use of R_f-amino ligand in stabilizing new main-group and transition-metal derivatives.

Results and Discussion

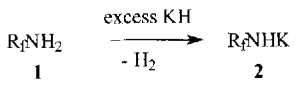
Cyclic Four-Membered Rings Based on the R_f Ligand

The reaction of 2,4,6-tris(trifluoromethyl)phenylamine (**1**) with 1.5 equivalents of KH in THF at 0°C readily yields the monoamide R_fNHK (**2**) in a nearly quantitative yield (Scheme 1). The R_f-amide **2** was used as the starting material in all the subsequent reactions with various main-group and transition-metal halides described in this paper.

Treatment of PCl_3 with two equivalents of the R_f amide **2** leads to the isolation of colorless 2,4-dichloro-1,3-bis[2,4,6-tris(trifluoromethyl)phenyl]-1,3,2λ^3,4λ^3-diazadiphos-

0009−2940/97/0808−1113 $ 17.50+.50/0

Scheme 1

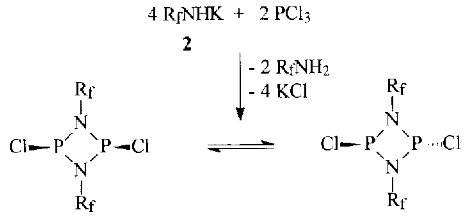


$$\underset{\mathbf{1}}{R_fNH_2} \xrightarrow[-\,H_2]{\text{excess KH}} \underset{\mathbf{2}}{R_fNHK}$$

R_f = 2,4,6-Tris(trifluoromethyl)phenyl

phetidine $[R_fNPCl]_2$ (**3**) in a 65% isolated yield (Scheme 2). The ^{31}P-NMR spectrum of **3** exhibits two septets at δ = 293.3 [^5J(P,F) = 84 Hz] and δ = 214.3 [^5J(P,F) = 84 Hz] which are assignable to the *cis* and the *trans* isomers, respectively. The difference in the chemical shifts between the *cis* and the *trans* isomers (79 ppm) falls in the range that has been observed for several other diazadiphosphetidines. Moreover, the strong electron withdrawing nature of the R_f ligands in **3** causes a shift of the phosphorus resonances into the region where normally resonances due to two-coordinate phosphorus centers are observed. The ^{19}F-NMR spectrum of the *cis*/*trans* isomeric mixture of **3** exhibits doublets at δ = −56.1 (*cis*) and δ = −59.3 (*trans*) corresponding to the resonances of the *ortho*-CF_3 groups on R_f ligand; the resonances due to the *para*-CF_3 groups are observed as singlets at δ = −63.7 and δ = −63.9, respectively.

Scheme 2



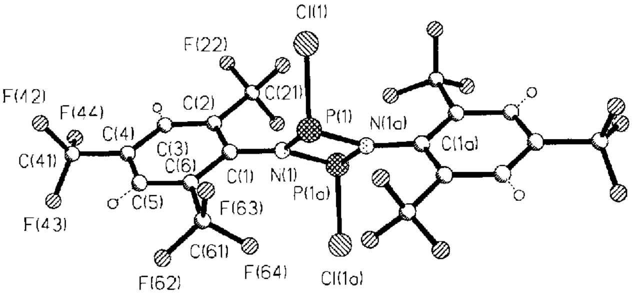
3 (cis) 3 (trans)

At room temperature, an isomer ratio of 4:1 between the *trans* and *cis* isomers was observed by ^{31}P-NMR spectroscopy. The reaction mixture prepared at 0°C also shows the same pattern. Also, heating this isomeric mixture to 60°C for one hour does not markedly change the isomer ratio. Although the chemistry of diazadiphosphetidines have been extensively studied, their geometrical isomerization behavior is not fully understood[5].

Slow and fractional crystallization of **3** from hexane leads to the deposition of the *trans* isomer as colorless blocks, which crystallizes with two half molecules in the asymmetric unit. The molecular structure of one of the molecules with atom numbering scheme is shown in Figure 1. There are no significant differences between the two molecules in terms of the conformation and geometrical parameters. The four-membered P_2N_2 ring is perfectly planar, as observed in most other *trans*-cyclodiphosphazanes. The aryl rings make an angle of 58.2 or 59.8°, respectively, at the heterocycle. The geometry around all the ring nitrogen atoms is trigonal planar with the angles around them summing to ca. 360°. The average P−N distances (172.8 pm) and P−N−P (80.1°) and N−P−N angles (99.9°) observed in **3** are typical for cyclodiphosphazane molecules[1g].

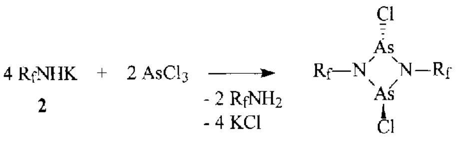
The synthesis of the corresponding arsenic analogue, 2,4-dichloro-1,3-bis[2,4,6-tris(trifluoromethyl)phenyl]-1,3,2λ^3,4λ^3-diazadiarsetidine $[R_fNAsCl]_2$ (**4**) has been achieved by using a similar procedure (Scheme 3). In contrast to **3**, the product contains only one isomer, and no isomerization behavior is observed in the NMR spectroscopy. In the ^{1}H-NMR spectrum of **4**, there is only one singlet observed at δ = 8.2, corresponding to the *trans* isomer. Similarly, the ^{19}F-NMR spectrum also shows signals due to only one isomer with singlets at δ = −55.7 and δ = −63.6, corresponding to *ortho*- and *para*-CF_3 groups. Crystallization of **4** from toluene yields colorless crystals suitable for X-ray diffraction studies. The compound crystallizes with two half molecules of **4** along with one half molecule of solvent toluene in the asymmetric unit. The molecular structure of **4** along with the atom numbering scheme is shown in Figure 2. The structure of **4** is isomorphous to **3**, and does not show any abnormalities in its structure.

Figure 1. Molecular structure of one of the molecules of **3**[a]



[a] Selected bond lengths [pm] and angles [°]. – Molecule 1: P(1)−N(1) 172.7(3), P(1)−N(1a) 173.0(3), P(1)−Cl(1) 208.0(2), N(1)−C(1), 142.1(5); N(1)−P(1)−N(1a) 80.0(2), P(1)−N(1)−P(1a) 100.0(2), N(1)−P(1)−Cl(1) 103.6(1), N(1a)−P(1)−Cl(1) 103.9(1), C(1)−N(1)−P(1) 129.3(2), C(1)−N(1)−P(1a) 130.7(2). – Molecule 2: P(2)−N(2) 172.5(3), P(2)−N(2a) 173.0(3), P(2)−Cl(2) 207.8(2), N(2)−C(11) 141.8(5); N(2)−P(2)−N(2a) 80.1(2), N(2)−P(2)−Cl(2) 102.6(1), N(2a)−P(2)−Cl(2) 103.7(1), C(11)−N(2)−P(2) 129.5(3), C(11)−N(2)−P(2a) 130.6(2).

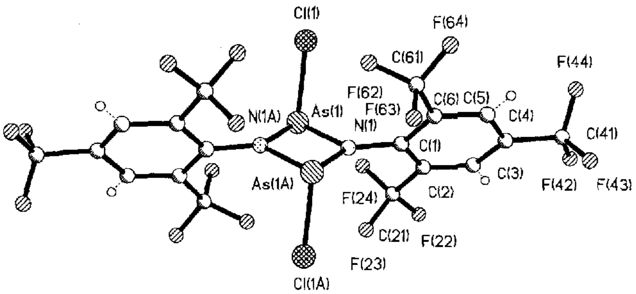
Scheme 3



4 (trans)

Recent interest in Ge−N cyclic systems, and the fact that such systems are extremely rare[6,7], has prompted us to extend this approach for the preparation of new R_f ligand based Ge−N systems. Accordingly, we treated the R_f-amide **2** with one equivalent of $GeCl_2 \cdot$dioxane, which resulted in the ready formation of 1,3-bis[2,4,6-tris(trifluoromethyl)-phenyl]-1,3,2λ^2,4λ^2-diazadigermetidine $[R_fNGe]_2$ (**5**) (Scheme 4). The product is best purified by the sublimation of the reaction residue resulting in analytically pure **5** in 65% yield as a yellow solid. Crystallization of **5** from hexane results in two different modifications of the compound. While the yellow form of **5** decomposes on heating at 127°C, the fluorescent-yellow modification **5a** turns yellow at 85°C. However both the forms are spectroscopically identical and show a single line in the ^{1}H-NMR spectrum at

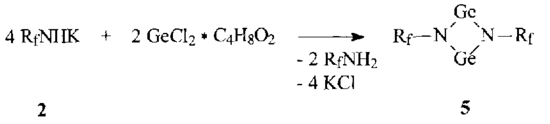
Figure 2. Molecular structure of one of the molecules of 4[a]



[a] Selected bond lengths [pm] and angles [°]: As(1)–N(1A) 185.2(3), As(1)–N(1) 186.5(3), As(1)–Cl(1) 221.6(1), As(2)–N(2A) 185.8(3), As(2)–N(2) 185.8(3), As(2)–Cl(2) 221.8(1); N(1A)–As(1)–N(1) 78.9(1), N(1A)–As(1)–Cl(1) 103.4(1), N(1)–As(1)–Cl(1) 100.4(1), N(2A)–As(2)–N(2) 78.5(2), N(2A)–As(2)–Cl(2) 100.9(1), N(2)–As(2)–Cl(2) 103.4(1), C(1)–N(1)–As(1A) 127.8(2), C(1)–N(1)–As(1) 130.3(2), As(1A)–N(1)–As(1) 101.1(1), C(11)–N(2)–As(2A) 130.8(3), As(2A)–N(2)–As(2) 101.5(2).

$\delta = 7.76$ for the aryl ring protons. The ^{19}F-NMR spectrum contains only two singlets at $\delta = -57.6$ and $\delta = -62.2$ corresponding to the *ortho-* and *para*-CF_3 groups, respectively, also indicating that there are no structural isomers present in solution.

Scheme 4

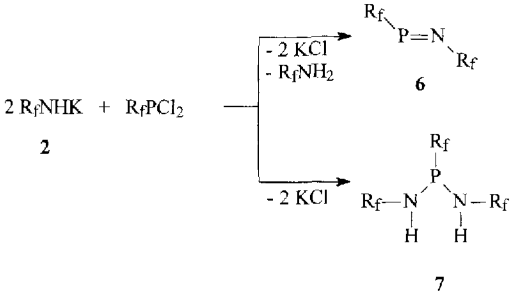


The molecular structure of both the modifications (**5** and **5a**) have been determined by single crystal X-ray diffraction studies. While **5a** crystallizes in orthorhombic *Pccn* space group with one molecule in the asymmetric unit, modification **5** crystallizes in the monoclinic $P2_1/c$ with half a molecule in the asymmetric unit. However in the final refined structures, there are no significant differences between the molecules of the two different modifications. Hence, only the structure of **5** is discussed here and its molecular structure along with selected bond lengths and angles are shown in Figure 3. The Ge–N bonds in Ge_2N_2 ring of **5** are nearly equal [av. 188.0(3) pm], and are comparable to those found in the 2,4,6-*tert*-butylphenyl-substituted diazadigermetidine [184.4(3) and 185.5(3) pm][6].

Imino- and Aminophosphanes Derived from the R$_f$ Ligand

The ability of the R_f ligand to stabilize the species of the type $R_fP{=}PR_f$ prompted us to extend this chemistry to the preparation of other low coordinated main-group species. Toward this direction, we recently reported the synthesis and X-ray crystal structure of the first iminoarsine [$R_fN{=}AsR_f$] starting from **2** and R_fAsCl_2[1h]. On the other hand, the reaction between R_fPCl_2 and two equivalents of **2** results in the formation of two different products, namely, the imino-λ^3-phosphane [$R_fN{=}PR_f$] (**6**, 38%) and the diaminophosphane [$R_fP(NHR_f)_2$] (**7**, 52%), as shown in Scheme 5. It is logical to assume that both the formation of **6** and **7** would have proceeded via the aminochlorophosphane intermediate [$R_fPCl(NHR_f)$]. Efforts to increase the selectivity of the formation of **6** and **7** by means of varying reaction conditions, such as working at low temperature or inverse addition, did not alter the ratio of the products formed.

Scheme 5

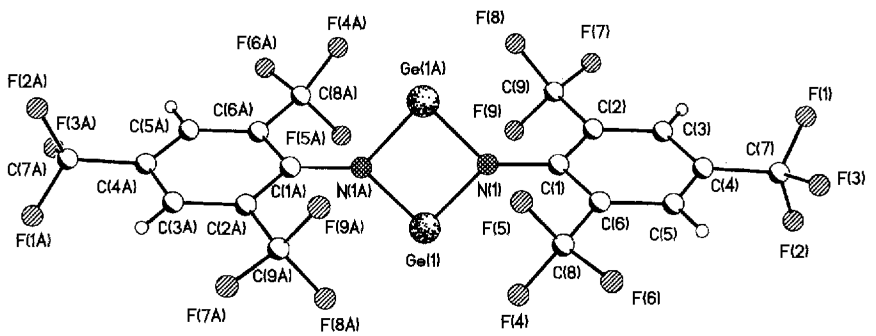


Compound **6** melts at 74°C and also can be sublimed under reduced pressure without any detectable decomposition. The observed exceptional properties of **6** could again be attributed to the strong electron-withdrawing R_f substituents. As a consequence, there is a decrease in the electron density of the P–N double bond, thereby reducing the reactivity of the molecule. While the ^{1}H-NMR spectrum shows two singlets for aromatic protons, the ^{19}F- and ^{31}P-NMR spectra exhibit a A_6B_6X coupling between the *ortho*-CF_3 flourine atoms and the phosphorus center. The A and B part of the ^{19}F-NMR spectrum appear as doublets of septuplets at $\delta = -54.6$ [^4J(F,P) = 36 Hz, ^9J(F,F) = 4.2 Hz] and $\delta = -60.9$ [^5J(F,P) = 19 Hz, ^9J(F,F) = 4.2 Hz], respectively. The ^{31}P-NMR spectrum shows the X part as a septuplet of septuplet at $\delta = 406.9$ [^4J(P,F) = 36 Hz, ^5J(P,F) = 19 Hz].

Crystallization of the sublimed sample of **6** from hexane leads to the isolation of orange prisms suitable for an X-ray diffraction study. Compound **6** crystallizes in the monoclinic space group $P2_1/c$ with one molecule per asymmetric unit. Molecular structure of **6** along with selected structural parameters and atom numbering scheme is shown Figure 4. The R_f groups adopt a *trans* configuration with respect to each other. The P=N bond length [156.1(2) pm] agrees well with the corresponding bond distances observed for other iminophosphanes[8]. The phenyl ring planes form a twist angle of 39.1°. The C(11)–N(1)–P(1) and N(1)–P(1)–C(21) angles are 130.2(2) and 99.8(1)° respectively. In other reported iminophosphanes, the angle around the nitrogen is 120°, while the angle at phosphorus ranges between 100 and 110°.

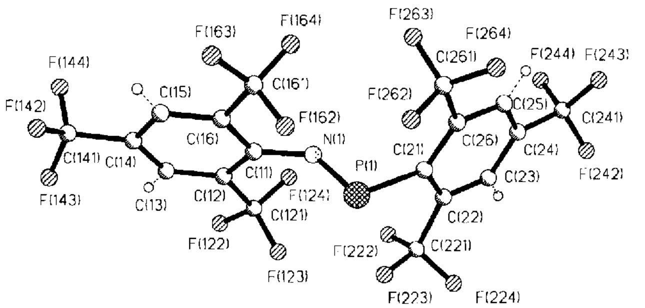
The residual material after the sublimation of **6** and the filtrate obtained during the preparation of **6** were combined and heated under reflux in toluene to obtain **7**. It is interesting to note that there are only a very few diaminophosphanes known in the literature. Among them, only tris(2,4,6-tri-*tert*-butylphenyl)diaminophosphane has been structurally characterized[9]. Also a few diaminophosphane complexes containing group 6 metals have been reported[9a,b].

Figure 3. Molecular structure of **5**[a]



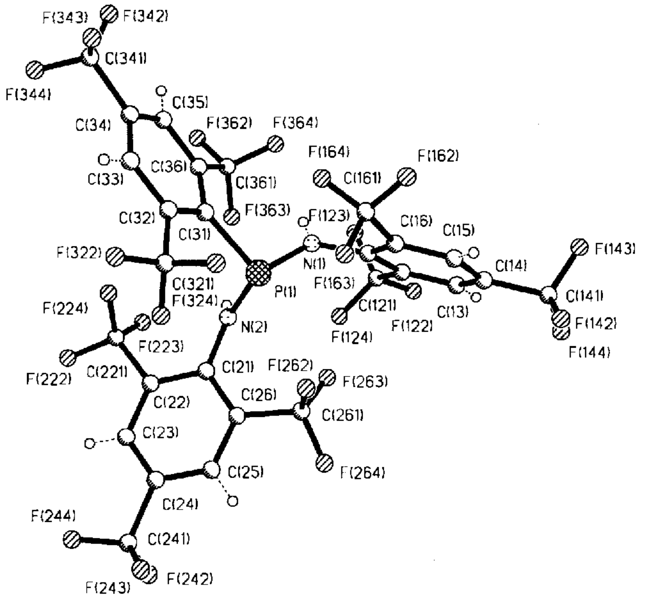
[a] Selected bond lengths [pm] and angles [°]: Ge(1)–N(1A) 187.8(2), Ge(1)–N(1) 188.2(2), N(1)–C(1) 139.4(3); N(1A)–Ge(1)–N(1) 81.1(1), C(1)–N(1)–Ge(1) 130.5(2), Ge(1A)–N(1)–Ge(1) 98.9(1).

Figure 4. Molecular structure of **6**[a]



[a] Selected bond lengths [pm] and angles [°]: P(1)–N(1) 156.1(2), N(1)–C(11) 139.6(3), P(1)–C(21) 188.3(3), N(1)–P(1)–C(21) 99.8(1), C(11)–N(1)–P(1) 130.2(2).

Figure 5. Molecular structure of **7**[a]



[a] Selected bond lengths [pm] and angles [°]: P(1)–N(1) 169.9(4), P(1)–N(2) 170.8(4), P(1)–C(31) 188.2(4), N(1)–C(11) 139.7(5), N(1)–H(1N) 76(3), N(2)–C(21) 140.5(5), N(2)–H(2N) 75(3); N(1)–P(1)–N(2) 103.2(2), N(2)–P(1)–C(31) 101.7(2), N(1)–P(1)–C(31) 102.7(2), C(11)–N(1)–P(1) 122.6(3), H(1N)–N(1)–C(11) 111(3), H(1N)–N(1)–P(1) 120(3), C(21)–N(2)–P(1) 123.9(3), H(2N)–N(2)–C(21) 117(3), H(2N)–N(2)–P(1) 112(3). Hydrogen Bonds: H(1N)···F(123) 227 pm, N(1)–H(1N)···F(123) 138°, N(1)···F(123) 287.5 pm, H(2N)···F(363) 233 pm, N(2)–H(2N)···F(363) 135°, N(2)···F(363) 291.7 pm.

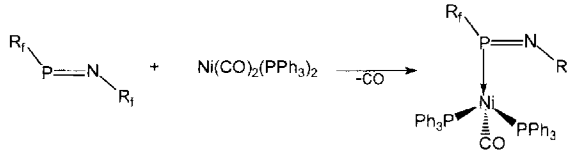
The ^{1}H-NMR spectrum of **7** shows two single resonances due to the aromatic protons at $\delta = 7.93$ (R_fN) and $\delta = 7.67$ (R_fP). A broad signal observed at $\delta = 6.3$ is ascribed to the NH protons. In the ^{19}F-NMR spectrum, the fluorine atoms of the *ortho* positions of the R_f resonate as two doublets at $\delta = -54.4$ [^4J(F,P) = 78 Hz] and $\delta = -59.1$ [^5J(F,P) = 31 Hz]. However, no F–F couplings are observed in the ^{19}F-NMR spectrum. The ^{31}P-NMR spectrum exhibits a quartet of tridecet centered at $\delta = 70.7$.

Single crystals of **7** suitable for diffraction studies were obtained from a hot saturated hexane solution. The molecular structure of the compound with the atom labeling scheme and selected structual parameters is shown in Figure 5. The tetrahedral angles around the phosphorus atom are considerably reduced (av. 102.6°, sum of the angles 307.7°), indicating that the geometry around phosphorus has undergone a considerable pyramidal → trigonal-bipyramidal distortion. There are several hydrogen bonds in the molecule resulting from the interaction of N–H bonds with the neighboring F atoms of the CF_3 groups (see Figure 5).

Iminophosphane 6 as a Ligand for Low-Valent Metal Ions

How strong would be the interaction of the electron deficient iminophosphane **6** with low-valent transition-metal ions? Since most of the coordination chemistry known using this type of ligands is essentially based on electron rich iminophosphanes[10], we wanted to evaluate the coordination behavior of **6**. Interaction of **6** with the zero-valent $Ni(CO)_2(PPh_3)_2$[11] in toluene at room temperature results in the elimination of one equivalent of CO and the formation of the dark-red iminophosphane complex [Ni(CO)$(PPh_3)_2$($R_fP{=}NR_f$)] (**8**) as shown in Scheme 6.

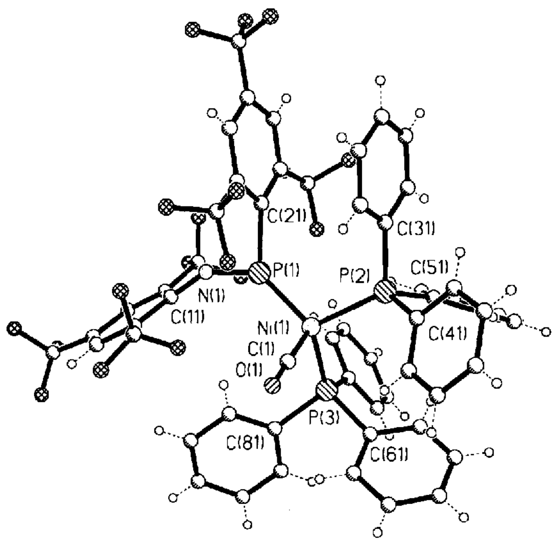
Scheme 6



The ^{1}H-NMR spectrum of **8** shows two singlets due to the R_f protons (δ = 7.62 and 7.53), and a multiplet due to the PPh_3 protons centered around δ = 6.75. In the ^{19}F-NMR spectrum, there are two multiplets at δ = −52.6 (*o*-CF_3) and −60.0 (*o*-CF_3), and two singlets at δ = −61.8 (*p*-CF_3) and −63.3 (*p*-CF_3), respectively. The ^{31}P signal of the coordinated phosphorus is upfield shifted with respect to **6** and appears as a multiplet at δ = 267.3. The resonances due to PPh_3 ligands appear as singlets at δ = 28.9 and 28.6, respectively.

Compound **8** is crystallized by cooling a hot saturated hexane solution to room temperature. The molecular structure of the compound with the atom labeling scheme and selected structural parameters is shown in Figure 6. The coordination environment around nickel atoms is distorted tetrahedral. The phosphorus atom of the iminophosphane ligand shows a η^1-coordination to the metal center. While the Ni(1)−P(1) bond length is 207.0(1) pm, the other two Ni−P bonds originating from PPh_3 groups are ca. 20 pm longer. In the other iminophosphane complexes described in the literature[11a,11b,12] the ligand coordinates to the metal either in η^1- or η^2-fashion, resulting in a tetrahedral or square-planar geometry around the metal, respectively.

Figure 6. Molecular structure of **8**[a]

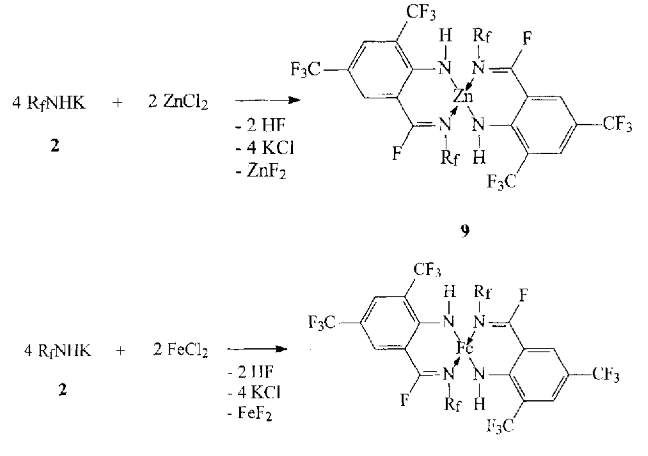


[a] Selected bond lengths [pm] and angles [°]: Ni(1)−C(1) 177.9(5), Ni(1)−P(1) 207.0(1), Ni(1)−P(2) 226.2(1), Ni(1)−P(3) 226.3(1), P(1)−N(1) 155.5(4), P(1)−C(21) 190.4(4), N(1)−C(11) 135.8(5); C(1)−Ni(1)−P(1) 107.6(1), C(1)−Ni(1)−P(2) 106.3(2), C(1)−Ni(1)−P(3) 99.5(2), P(1)−Ni(1)−P(2) 112.0(1), P(1)−Ni(1)−P(3) 121.2(1), P(2)−Ni(1)−P(3) 108.6(1), N(1)−P(1)−C(21) 94.2(2), N(1)−P(1)−Ni(1) 137.2(2), C(21)−P(1)−Ni(1) 126.9(1), C(11)−N(1)−P(1) 146.8(3).

Reactions of R_f-Amide with Transition Metal Halides

In order to extend the reactions of R_f-amide with main-group halides to the transition metals, we further investigated the reactions of **2** with a few transition-metal dihalides. As expected, the reactivity pattern of **2** toward the transition-metal halides is quite different from that of reagents such as PCl_3 or $AsCl_3$. As depicted in Scheme 7, the reactions of **2** with $ZnCl_2$ or $FeCl_2$ do not yield the expected acyclic products $M(NHR_f)_2$ or cyclic $(MNR_f)_2$. Instead, these reactions lead to the formation of the spirocyclic products **9** and **10**, resulting from the rearrangement of the R_f-amide **2**. The rearranged ligand in these compounds possess an imino and an amino functionalities.

Scheme 7



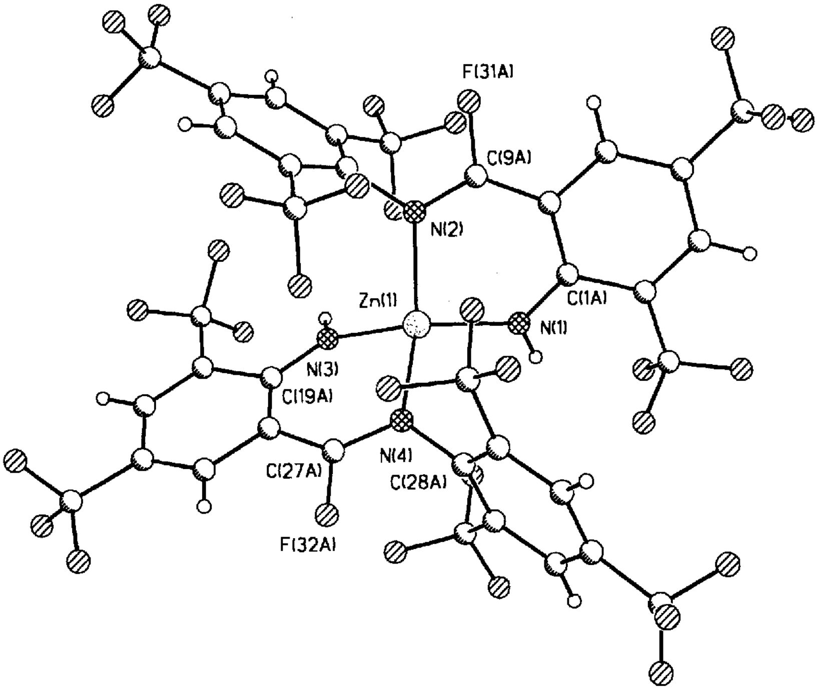
10

The fluorescent-yellow crystals for **9** have been obtained from the reaction mixture. The ^{1}H-NMR spectrum of **9** shows two singlets for aromatic protons (δ = 8.03 and 7.71) and a broad signal due to the NH protons. The ^{19}F-NMR contains a septet for the two fluorine atoms that are bonded at the amino groups [δ = −22.7, ^6J(F,F) = 5.3 Hz]. The corresponding doublet resonates at δ = −62.8. All the other fluorine centers exhibit singlets at δ = −62.0, −62.7, and −63.9, respectively.

Compound **9** crystallizes in the centrosymmetric triclinic space group with two independent molecules in the asymmetric unit which do not show any significant differences between them. The molecular structure of the compound with the atom labeling scheme of molecule 1 and selected structural parameters is shown in Figure 7. The zinc atom shows two types of interactions with the surrounded nitrogen atoms. The shorter Zn−N distance to N(1) and N(3) [190(1) and 192(1) pm, respectively] suggest that these atoms are involved in a σ-bonding to the metal. The longer Zn(1)−N(2) and Zn(1)−N(4) bonds [208.2(9) and 206(1) pm] are indicative of weak coordinate bonds from these nitrogen atoms to the central metal atom. The heteroallyl zinc complexes prepared in our laboratory exhibit similar Zn−N distances (av. 203.8 pm)[13]. The coordination sphere around the zinc atom is distorted tetrahedral. The six-membered heterocycles in the molecule are twisted like propellers.

The iron derivative **10**, due to its paramagnetic nature, shows only broad signals in the NMR spectra, thus rendering them only of little use in the structural elucidation. The ^{1}H-NMR spectrum shows the signals of the aromatic protons at δ = 8.0 ($\nu_{1/2}$ = 510 Hz) and for the coordinated THF molecule at δ = 3.53 and 1.74 ($\nu_{1/2}$ = 510 Hz), respectively. The signal of the NH protons probably overlap with those of THF protons. In the ^{19}F-NMR spectrum,

Figure 7. Molecular structure of one of the molecules of **9**[a]



[a] Selected bond lengths [pm] and angles [°]: Zn(1)–N(1) 190(1), Zn(1)–N(2) 208.2(9), Zn(1)–N(3) 192(1), Zn(1)–N(4) 206(1), N(1)–C(1A) 135(2), N(2)–C(9A) 130(1), N(2)–C(10A) 146(2), N(3)–C(19A) 132(2), N(4)–C(27A) 133(1), N(4)–C(28A) 144 (1); N(1)–Zn(1)–N(2) 92.3(4), N(1)–Zn(1)–N(3) 144.8(5), N(1)–Zn(1)–N(4) 101.4(4), N(2)–Zn(1)–N(4) 128.5(3), N(2)–Zn(1)–N(3) 104.3(4), N(3)–Zn(1)–N(4) 92.2(4), C(1A)–N(2)–Zn(1) 127.5(8), C(9A)–N(2)–Zn(1) 120.0(8), C(19A)–N(3)–Zn(1) 127.0(9), C(27A)–N(4)–Zn(1) 120.4(7).

only two broad signals were found at $\delta = -23.5$ (F–C=N, $\nu_{1/2} = 312$ Hz) and -60.7 (CF_3, $\nu_{1/2} = 601$ Hz).

Dark-red crystals of **10** were grown from warm (40°C) saturated toluene solution. The molecular structure of the compound with the atom labeling scheme and selected structural parameters is shown in Figure 8. The central Fe^{2+} ion binds to two imino nitrogens, two amino nitrogens, and a THF molecule, resulting in a trigonal-bipyramidal coordination sphere. Atoms N(1) and N(3) occupy axial positions, while N(2), N(4), and O(1) atoms are in the equatorial positions. Similar to the structural characteristics of **9**, there are two types of Fe–N distances observed in **10**.

Conclusion

In summary, it has been shown that the potassium tris(trifluoromethyl)phenylamide (**2**) is a very useful starting material for the preparation of a variety of main-group and transition-metal heterocycles. Moreover its exceptional electronic and steric stabilization characteristics make the isolation of low-coordinated iminophosphanes and their arsenic analogues possible. In the case of reaction of **2** with transition-metal halides, a skeletal rearrangement of the R_f ligand resulting in a amino–imino hybrid ligand is observed. This result clearly indicates the limitation of using **2** as the starting material with metals which have a strong tendency to form M–F bonds.

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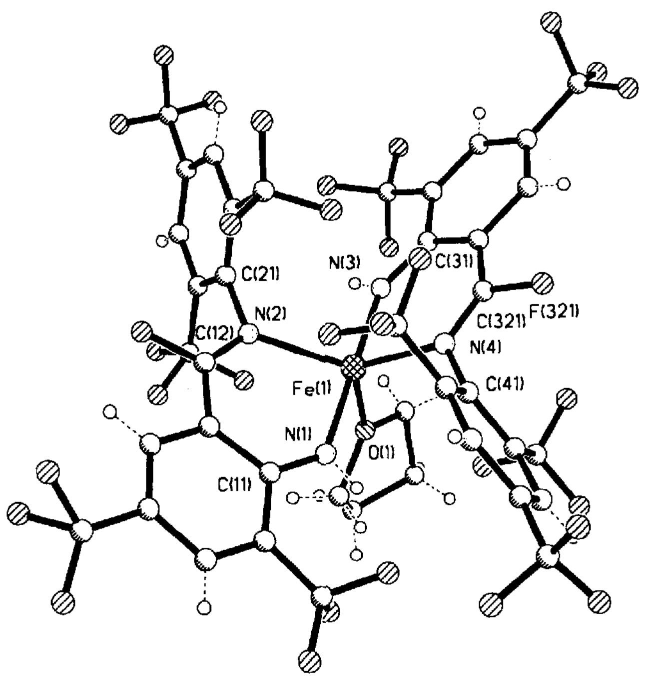
Experimental Section

Reactions were performed and worked up using standard Schlenk techniques, and products were handled under dry oxygen-free nitrogen. Solvents were dried, distilled, and stored using standard procedures. Infrared spectra were obtained using a Bio-Rad FTS7 spectrometer, NMR spectra were recorded with Bruker AM250, WP80SY, and MSL400 spectrometers (used standards ^1H NMR): TMS, ^{19}F NMR: $CFCl_3$, ^{31}P NMR: 85% H_3PO_4), and mass spectra with Finnigan MAT8230, MAT95, and Varian CH5 spectrometers. Microanalyses were performed at the analytical laboratories of the University of Göttingen.

Potassium Tris(trifluoromethyl)phenylamide (**2**): A solution of **1** (2 g, 6.8 mmol), dissolved in THF (10 ml), was added dropwise to a slurry of KH (0.4 g, 10 mol) in THF (10 ml) at 0°C. The mixture turned yellow. After the addition was complete, the mixture was stirred at room temperature for 1 h. The excess of KH was removed by filtration.

2,4-Dichloro-1,3-bis[2,4,6-tris(trifluoromethyl)phenyl]-1,3,2λ^3,4λ^3-diazadiphosphetidine (**3**): A solution of potassium amide **2** (2.00 g, 6.8 mmol) in THF (20 ml) was added dropwise to a solution of PCl_3 (0.46 g, 3.4 mmol) in THF (10 ml) at 0°C. After the addition was complete, the mixture was stirred at room temperature for 2 h. The volatiles were removed in vacuo. The residue was treated in refluxing hexane (10 ml) and the resulting solid was filtered off. The solution was partially concentrated to yield colorless crystals of **3** (0.78 g, 65%). M.p. 156°C. – IR (nujol): $\tilde{\nu} = 3104$ w, 1630 vs, 1279 vs, 1135 vs, 919 s, 684 s. – *trans* isomer: ^1H NMR (200 MHz, $CDCl_3$): $\delta = 8.25$ (s, aromatic H). – $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$): $\delta = -56.1$ [d, 12 F, $^5J(F,P) = 84$ Hz, *o*-CF_3], -63.7 (s, 6 F, *p*-CF_3), – $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 293.3$ [sept, $^5J(P,F) = 84$ Hz]. – *cis* isomer: ^1H NMR (200 MHz,

Figure 8. Molecular structure of **10**[a]



[a] Selected bond lengths [pm] and angles [°]: Fe(1)–N(1) 202.0(5), Fe(1)–N(2) 220.2(4), Fe(1)–N(3) 201.1(5), Fe(1)–N(4) 218.7(4), Fe(1)–O(1) 216.3(4), N(1)–C(11) 133.7(7), N(2)–C(121) 127.7(7), N(2)–C(21) 143.8(7), N(3)–C(31) 133.1(7), N(4)–C(41) 144.5(7), N(4)–C(321) 127.6(7), N(1)–Fe(1)–N(2) 84.6(2); N(2)–Fe(1)–N(3) 96.1(2), N(1)–Fe(1)–O(1) 89.3(2), N(1)–Fe(1)–N(4) 95.5(2), N(2)–Fe(1)–O(1) 115.3(2), N(3)–Fe(1)–O(1) 89.8(2), N(3)–Fe(1)–N(4) 84.7(2), N(1)–Fe(1)–N(3) 179.0(2), N(2)–Fe(1)–N(4) 126.1(2), N(4)–Fe(1)–O(1) 118.6(2), C(11)–N(1)–Fe(1) 135.4(4), C(21)–N(2)–Fe(1) 118.9(3), C(121)–N(2)–Fe(1) 124.0(3), C(121)–N(2)–C(21) 117.1(4), C(31)–N(3)–Fe(1) 137.1(4), C(41)–N(4)–Fe(1) 119.2(3), C(321)–N(4)–C(41) 116.6(4), C(321)–N(4)–Fe(1) 124.2(3).

$CDCl_3$): δ = 8.14 (s, aromatic H). – $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$): δ = −59.3 [d, 12 F, ^5J(F,P) = 35 Hz, *o*-CF_3], −63.3 (s, 6 F, *p*-CF_3), – $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 214.3 [sept, ^5J(P,F) = 35 Hz]. – MS (70 eV); *m/z* (%): 722 (4) [M^+], 361 (50) [$M/2^+$], 326 (100) [$M/2^+$ – Cl]. – $C_{18}H_4Cl_2F_{18}N_2P_2$ (723.07): calcd: C 29.90, H 0.57, F 47.30 N 3.75; found: C 30.7, H 0.8, F 47.0, N 4.1.

2,4-Dichloro-1,3-bis[2,4,6-tris(trifluormethyl)phenyl]-1,3,2λ^3,4λ^3-diazadiarsetidine (**4**): A solution of $AsCl_3$ (0.79 g, 3.4 mmol) in THF (10 ml) was treated with potassium amide **2** (2.00 g, 6.8 mmol) under the conditions described for the synthesis of **3**. The solution was partially concentrated to yield colorless crystals of **4** (0.79 g, 58%). M.p. 179°C. – IR (nujol): $\tilde{\nu}$ = 3107 w, 1629 s, 1275 vs, 1136 vs, 919 s, 683 s. – ^1H NMR (200, MHz, $CDCl_3$): δ = 8.20 (s, aromatic H). – $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$): δ = −55.7 (s, 12 F, *o*-CF_3), −63.6 (s, 6 F, *p*-CF_3). – MS (70 eV); *m/z* (%): 810 (3) [M^+], 405 (50) [$M/2^+$], 238 (100) [$C_9H_2F_6N$]. – $C_{18}H_4Cl_2F_{18}N_2P_2$ (810.97) calcd: C 26.66, H 0.50, F 42.17, N 3.46; found: C 26.3, H 0.6, F 41.5, N 3.3.

1,3-Bis[2,4,6-tris(trifluoromethyl)phenyl]-1,3,2λ^2,4λ^2-diazadigermetidine (**5**): The reaction of $GeCl_2 \cdot C_4H_8O_2$ (0.77 g, 3.4 mmol) with the potassium amide **2** (2.00 g, 6.8 mmol) at 0°C results in **5**. After stirring of the reaction mixture for 12 h at room temperature, the volatiles were removed in vacuo. The residue was sublimed in vacuo (5 · 10^{-6} bar) at 60°C. The yellow product **5** was obtained in 65% yield (0.81 g). M.p. 127°C (dec.). – IR (nujol): $\tilde{\nu}$ = 3099 w, 1626 m, 1275 vs, 1135 vs, 916 s, 682 s. – ^1H NMR (200 MHz, C_6D_6): δ = 7.76 (s, aromatic H). – $^{19}F\{^1H\}$ NMR (188 MHz, C_6D_6): δ = −57.6 (s, 12 F, *o*-CF_3), −62.2 (s, 6 F, *p*-CF_3). – MS (70 eV); *m/z* (%): 736 (10) [M^+], 349 (20) [$M/2^+$ – 2 F], 238 (100) [$C_9H_2F_6N$]. – $C_{18}H_4F_{18}Ge_2N_2$ (735.41) calcd: C 29.40, H 0.55, F 46.51, N 3.81; found: C 29.3, H 0.9, F 45.2, N 3.8.

P,N-Bis[tris(trifluoromethyl)phenyl]iminophosphane (**6**): To a solution of R_fPCl_2 (1.29 g, 3.4 mmol) in THF (10 ml) was added dropwise the potassium amide **2** (2.00 g, 6.8 mmol) at 0°C. After stirring of the reaction mixture for 12 h at room temperature, the volatiles were removed in vacuo. The orange residue was washed with a small amount of ice-cold hexane (10 ml) until the filtrate became colorless. The solvent was removed in vacuo and the crude product purified by sublimation (5 · 10^{-6} bar, 50°C). Yield: 0.78 g (38%) of orange **6**. M.p. 76°C. – IR (nujol): $\tilde{\nu}$ = 3100 w, 1633 s, 1337 vs, 1142 vs, 915 vs, 682 s. – ^1H NMR (200 MHz, $CDCl_3$): δ = 8.20 (s, 2H, aromatic H), 8.08 (s, 2H, aromatic H). – $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$): δ = −54.6 [dsept, 6 F, ^4J(F,P) = 36 Hz, ^9J(F,F) = 4.8 Hz, *o*-CF_3], −60.9 [dsept, 6 F, ^5J(F,P) = 19 Hz, ^9J(F,F) = 4.8 Hz, *o*-CF_3], −63.1 (s, 3 F, *p*-CF_3), −64.1 (s, 3 F, *p*-CF_3). – $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 404.5 [septsept, ^4J(P,F) = 36 Hz, ^5J(P,F) = 19 Hz]. – MS (70 eV); *m/z* (%): 607 (30) [M^+], 326 (25) [$C_9H_2F_9NP$], 238 (100) [$C_9H_2F_6N$]. – $C_{18}H_4F_{18}NP$ (607.19) calcd: C 35.60, H 0.66, F 56.33, N 2.31; found: C 35.6, H 0.9, F 55.8, N 2.4.

P,N,N'-Tris[tris(trifluoromethyl)phenyl]diaminophosphane (**7**): The residue of the sublimation and filtration of **6** was treated in refluxing toluene (20 ml). The solvent was removed in vacuo and the residue washed with hexane (5 ml). Filtration yielded 1.58 g (52%) colorless crystalline **7**. M.p. 128°C. – IR (nujol): $\tilde{\nu}$ = 3463 m, 3423 m, 3103 w, 1635 m, 1292 vs, 1132 vs, 916 s, 685 s. – ^1H NMR (200 MHz, C_6D_6): δ = 7.92 (s, 2H, aromatic H), 7.67 (s, 4H, aromatic H), 6.30 (s, br, 2H, NH). – $^{19}F\{^1H\}$ NMR (235 MHz, C_6D_6): δ = −54.5 [d, 3 F, ^4J(F,P) = 78 Hz, *o*-CF_3], −56.3 (s, 3 F, *o*-CF_3), −59.1 [d, 12 F, ^5J(F,P) = 31 Hz, *o*-CF_3], −62.6 (s, 6 F, *p*-CF_3), −63.5 (s, 3 F, *p*-CF_3). – $^{31}P\{^1H\}$ NMR (101 MHz, THF/C_6D_6): δ = 70.7 [qtd, ^4J(P,F) = 78 Hz, ^5J(P,F) = 31 Hz]. – MS (70 eV); *m/z* (%): 904 (20) [M^+], 608 (100) [$C_{18}H_5F_{18}NP$], 262 (70) [$C_9H_2F_8$]. – $C_{27}H_8F_{27}N_2P$ (904.32) calcd: C 35.86, H 0.89, F 56.73, N 3.10; found: C 35.7, H 1.0, F 55.9, N 3.0.

Nickel Complex **8**: Compound **6** (1.0 g, 1.6 mmol) was stirred together with $Ni(CO)_2(PPh_3)_2$[11] (1.05 g, 1.6 mmol) in toluene (10 ml) at ambient temperature for 18 h. Solvent was removed in vacuo to afford a brown solid which was dissolved using refluxing hexane (20 ml), cooling to room temperature leads to dark red blocks of complex **8** in 85% yield (1.65 g). M.p. 181°C. IR (nujol): $\tilde{\nu}$ = 3060 w, 2008 vs, 1631 s, 1282 vs, 1188 vs, 915 s, 694 s. – ^1H NMR (200 MHz, C_6D_6): δ = 7.62 (s, 2H, aromatic H), 7.53 (s, 2H, aromatic H), 6.75 (m, 30H, aromatic H). – $^{19}F\{^1H\}$ NMR (188 MHz, C_6D_6): δ = −52.6 (m, 6 F, *o*-CF_3), −60.0 (m, 6 F, *o*-CF_3), −61.8 (s, 3 F, *p*-CF_3), −63.3 (s, 3 F, *p*-CF_3). – $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ = 267.3 (m, 1 P, P=N), 28.9 (s, 1 P, PPh_3), 28.6 (s, 1 P, PPh_3). – MS (10 eV); *m/z*: 607 [R_fP=NR_f]. – $C_{55}H_{34}F_{18}NNiOP_3$ (1218.45) calcd: C 54.22, H 2.81, F 28.06, N 1.15; found: C 53.5, H 2.7, F 28.3, N 1.6.

Spirocycle **9**: $ZnCl_2$ (0.46 g, 3.4 mmol) was dissolved in THF (10 ml) and the potassium amide **2** (2.00 g, 6.8 mmol) was added dropwise. The color of the mixture turned to fluorescent yellow. The reaction was allowed to go for completion by stirring the mixture for an additional 24 h. The reaction mixture was evaporated to dryness. The residue was treated in refluxing hexane (15 ml), filtered and washed a few times using the same solvent. The solution

Table 1. Crystallographic data for compounds **3**–**10**

Compound	**3**	**4**	**5**	**5a**	**6**	**7**	**8**	**9**	**10**
Formula	$C_{18}H_4Cl_2F_{18}N_2P_2$	$C_{18}H_4As_2Cl_2F_{18}N_2 \cdot 0.5\ C_7H_8$	$C_{18}H_4F_{18}Ge_2N_2$	$C_{18}H_4F_{18}Ge_2N_2$	$C_{18}H_4F_{18}NP$	$C_{27}H_8F_{27}N_2P$	$C_{55}H_{34}F_{18}NNiOP_3$	$C_{36}H_{10}F_{32}N_4Zn$	$C_{42}H_{22}F_{32}FeN_4O_{1.5}$
M	723.07	857.04	735.41	735.41	607.19	904.32	1218.45	1171.85	1270.49
Data collection at T [K]	153(2)	153(2)	153(2)	153(2)	153(2)	223(2)	213(2)	193(2)	213(2)
Cystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$Pccn$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [pm]	913.2(5)	904.7(1)	1249.8(2)	2676.3(9)	1657.6(5)	918.6(2)	1164.3(1)	1300.0(3)	1240.7(2)
b [pm]	1103.1(6)	1195.2(2)	924.5(1)	978.0(6)	1364.7(6)	1345.4(2)	2463.3(5)	1505.9(3)	1306.6(3)
c [pm]	1446.7(9)	1376.9(4)	1023.8(1)	1755.7(10)	924.4(3)	1392.4(3)	1872.7(2)	2217.1(4)	1617.7(4)
α [°]	68.11(3)	82.56(1)				98.74(2)		108.46(3)	87.50(2)
β [°]	74.04(3)	76.27(1)	102.01(1)		101.71(4)	96.22(1)	101.76(1)	91.66(3)	86.86(2)
γ [°]	67.13(1)	79.21(1)				105.15(1)		96.16(3)	74.67(2)
U [nm^3]	1.232(1)	1.4151(4)	1.1570(3)	4.595(4)	2.048(1)	1.6219(6)	5.258(1)	4.084(1)	2.5242(9)
Z	2	2	2	8	4	2	4	4	2
D [Mg m^{-3}]	1.950	2.011	2.111	2.126	1.970	1.852	1.539	1.906	1.672
μ [mm^{-1}]	0.544	2.687	2.755	2.774	0.306	0.266	0.565	0.784	0.457
$F(000)$	704	826	704	2816	1184	884	2456	2288	1256
Crystal size [mm]	1.0 × 0.5 × 0.4	0.8 × 0.3 × 0.2	0.6 × 0.5 × 0.5	0.4 × 0.4 × 0.4	1.0 × 1.0 × 1.0	0.7 × 0.7 × 0.3	1.0 × 0.4 × 0.2	0.5 × 0.4 × 0.2	0.6 × 0.4 × 0.2
2 θ range for data collection	7 – 45	7 – 45	7 – 45	8 – 50	7 – 50	7 – 50	7 – 50	8 – 43	7 – 45
Reflections collected	5163	3878	4339	4794	3588	5584	7249	10811	7274
Independent reflections	3157, R_{int} = 0.0399	3712, R_{int}= 0.0154	1499, R_{int} = 0.0361	4033, R_{int} = 0.0367	3578, R_{int} = 0.1140	4354, R_{int} = 0.0393	7217, R_{int} =0.0104	9372, R_{int} = 0.2666	6586, R_{int} = 0.0682
Max. and min transmission	–	0.488, 0.276	0.629, 0.397	0.490, 0.358	–	–	–	–	0.491, 0.422
Data / restraints / parameters	3157 / 156 / 399	3712 / 134 / 453	1498 / 42 / 191	4033 / 156 / 381	3578 / 156 / 363	4354 / 157 / 542	7217 / 156 / 732	9372 / 1365 / 1387	6586 / 589 / 830
Goodness of fit on F^2	1.053	1.068	1.090	1.054	1.082	1.049	1.027	1.031	1.024
$R1$, w$R2$ [$I > 2\sigma(I)$]	0.0430, 0.1190	0.0317, 0.0828	0.0239, 0.0605	0.0555, 0.0920	0.0455, 0.1169	0.0520, 0.1232	0.0465, 0.1011	0.0906, 0.2137	0.0688, 0.1781
$R1$, w$R2$ (for all data)	0.0462, 0.1238	0.0339, 0.0853	0.0264, 0.0631	0.1168, 0.1146	0.0518, 0.1233	0.0663, 0.1350	0.0638, 0.1134	0.1613, 0.2642	0.0910, 0.2016
Extinction coefficient	–	0.0053(9)	–	–	–	0.006(1)	–	–	–
Largest difference map peak and hole[e $\ast$ nm^{-3}]	688, – 349	813, -668	325, –514	520, –491	348, –318	491, –359	862, –467	1004, –805	947, –491

was allowed to cool to room temperature to yield 0.82 g (41%) of fluorescent-yellow **9**. M.p. 207°C (dec.). – IR (nujol): $\tilde{\nu}$ = 3433 m, 1640 s, 1557 s, 1279 vs, 1121 vs, 915 s, 686 s. – ^1H NMR (250 MHz, C_6D_6): δ = 8.03 (s, 4H, aromatic H), 7.71 (s, 4H, aromatic H), 6.15 (s, br, 2H, NH). – $^{19}F\{^1H\}$ NMR (188 MHz, C_6D_6): δ = −22.7 [sept, 2 F, ^6J(F,F) = 5.3 Hz, FC=N], −62.0 (s, 6 F, CF_3), −62.7 (s, 6 F, CF_3), −62.8 [d, 12 F, 6J(F,F) = 5.3 Hz, o-CF_3] 63.9 (s, 6 F, CF_3). – MS (70 eV); m/z (%): 1170 (5) [M^+], 554 (30) [$C_{18}H_6F_{16}N_2$], 534 (100) [$C_{18}H_5F_{15}N_2$]. – $C_{36}H_{10}F_{32}N_4Zn$ (1171.85) calcd: C 36.90, H 0.86, F 51.88, N 4.78; found: C 36.4, H 1.4, F 52.4, N 4.4.

Spirocycle **10**: A solution of potassium amide **2** (2.00 g, 6.8 mmol) in 20 ml of THF was added dropwise to a slurry of $FeCl_2$ (0.21 g, 3.4 mmol) in THF (10 ml). The mixture turned reddish-brown. The residue was extracted using warm toluene (10 ml, 40°C) four times. When the filtrate became almost colorless, it was concentrated to ca. 5 ml and cooled to room temperature and stored for 48 h to yield 0.93 g (45%) of compound **10** as dark red plates. M.p. 75°C (dec.). – IR (nujol): $\tilde{\nu}$ = 3403 m, 3103 w, 1638 vs, 1553 vs, 1272 vs, 1158 vs, 918 s, 686 s. – ^1H NMR (200 MHz, C_6D_6): δ = 1.74 [4H, $(CH_2)_2$, $\nu_{1/2}$ = 270 Hz], 3.53 [6H, $(CH_2)_2O$, 2 NH, $\nu_{1/2}$ = 270 Hz], 8.00 (8H, aromatic H, $\nu_{1/2}$ = 500 Hz). – $^{19}F\{^1H\}$ (188 MHz, C_6D_6): δ = −23.5 (2 F, FC=N, $\nu_{1/2}$ = 312 Hz), −60.7 (30 F, CF_3, $\nu_{1/2}$ = 610 Hz). – MS (70 eV); m/z (%): 1162 (10) [M^+ – THF], 534 (100) [$C_{18}H_5F_{15}N_2$], 515 (60) [$C_{18}H_5F_{14}N_2$]. – $C_{40}H_{18}F_{32}FeN_4O$ (1234.43) calcd: C 38.92, H 1.47, F 49.25, N 4.54; found: C 39.1, H 1.9, F 49.4, N 4.5.

Crystal-Structure Determination of Compounds **3**–**10**: Details of data collection, structure solution, and refinement for compounds **3**–**10** are summarised in Table 1. Intensity data were collected on a Stoe-Siemens-AED2-diffractometer with monochromated Mo-K_α radiation (λ = 71.073 pm) using $\omega/2\Theta$ scans following the learnt-profile method[14]. For structures **4**, **5**, **5a**, and **10**, a semiempirical absorption correction from ψ-scans was applied[15]. The structures were solved by direct methods[16]. All non-hydrogen atoms were refined anisotropically[17]. For the hydrogen atoms bonded to carbon atoms, a riding model was used. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2\ F_c^2)/3$. The R values are defined as $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $wR2 = [\Sigma w(F_o^2) - F_c^2)^2 / \Sigma w F_o^4]^{0.5}$.

In structures **7**, **9**, and **10** the hydrogen bonds to nitrogen were refined with distance restraints. In all structures nearly all p-CF_3 groups were found to be disordered. For all the disordered CF_3 groups two positions were refined with distance restraints and rigid bond restraints. The U values of the fluorine atoms lying opposite to each other were fixed to be the same. In structure **4** a disordered half toluene molecule was found on the inversion center. This solvent molecule was refined with distance restraints, the planarity restraint and restraints for the anisotropic displacement parameters. Due to the poor quality of the crystals of **9**, the obtained data quality was rather low. Hence, the structure has to be refined using a large number of restraints to obtain reasonable structural parameters. In structure **10**, a severely disordered half molecule of THF was found on the inversion center. The oxygen atom of this THF molecule could not be distinguished from the carbon atoms. Therefore the THF was refined with two positions of a cyclopentane ring using distance restraints and restraints for the anisotropic displacement parameters.

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[1] [1a] M. Witt, H. W. Roesky, *Prog. Inorg. Chem.* **1992**, *40*, 353–444. – [1b] F. T. Edelmann, *Comments Inorg. Chem.* **1992**, *12*, 259–284. – [1c] D. Stalke, K. H. Whitmire, *J. Chem. Soc., Chem. Commun.* **1990**, 833–834. – [1d] D. Labahn, S. Brooker, G. M. Sheldrick, H. W. Roesky, *Z. Anorg. Allg. Chem.* **1992**, *610*, 163–168. – [1e] D. Labahn, F. M. Bohnen, R. Herbst-Irmer, E. Pohl, D. Stalke, H. W. Roesky, *Z. Anorg. Allg. Chem.* **1994**, *620*, 41–47. – [1f] H. Voelker, U. Pieper, H. W. Roesky, G. M. Sheldrick, *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 255–257. – [1g] T. Lübben, H. W. Roesky, H. Gornitzka, A. Steiner, D. Stalke, *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 121–130. – [1h] J.-T. Ahlemann, A. Künzel, H. W. Roesky, M. Noltemeyer, L. Markovskii, H.-G. Schmidt, *Inorg. Chem.* **1996**, *35*, 6644.

[2] M. Scholz, H. W. Roesky, D. Stalke, K. Keller, F. T. Edelmann, *J. Organomet. Chem.* **1989**, *366*, 73–85.

[3] [3a] H. Grützmacher, H. Pritzkow, F. T. Edelmann, *Organometallics* **1991**, *10*, 23–25. – [3b] S. Brooker, J.-K. Buijink, F. T. Edelmann, *Organometallics* **1991**, *10*, 25–26.

[4] [4a] H. W. Roesky, M. Scholz, M. Noltemeyer, F. T. Edelmann, *Inorg. Chem.* **1989**, *28*, 3829–3830. – [4b] M. Scholz, M. Noltemeyer, H. W. Roesky, *Angew. Chem.* **1989**, *101*, 1419–1420; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1383.

[5] [5a] R. Keat in *The Chemistry of Inorganic Homo- and Heterocycles*, vol. 2 (Ed.: I. Haiduc, D. B. Sowerby), Academic Press, London. **1987**, chapter 19. – [5b] G. Bulloch, R. Keat, *J. Chem. Soc., Dalton Trans.* **1974**, 2010–2014. – [5c] W. Zeiß, W. Andres, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33*, 467–468. – [5d] W. Zeiß, C. Feldt, J. Weis, G. Dunkel, *Chem. Ber.* **1978**, *111*, 1181–1194. – [5e] V. S. Reddy, S. S. Krishnamurthy, M. Nethaji, *J. Chem. Soc., Dalton Trans.* **1994**, 2661–2667. – [5f] K. W. Muir, *J. Chem. Soc., Dalton Trans.* **1975**, 259–162. – [5g] H.-J. Chen, R. C. Haltiwanger, T. G. Hill, M. L. Thompson, D. E. Coons, *Inorg. Chem.* **1985**, *24*, 4725–4730.

[6] B. Hitchcock, M. F. Lappert, A. J. Thorne, *J. Chem. Soc., Chem. Commun.* **1990**, 1587–1589.

[7] A. Bartlett, P. P. Power, *J. Am. Chem. Soc.* **1990**, *112*, 3660–3661.

[8] [8a] V. D. Romanenko, A. B. Drapailo, A. V. Ruban, L. N. Markovskii, *Zh. Obshch. Khim.* **1986**, *56*, 2792–2793 (*Chem. Abstr.* **1988**, *108*, 6093c). – [8b] L. N. Markovskii, V. D. Romanenko, V. D. Ruban, A. B. Drapailo, A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, *Zh. Obshch. Khim.* **1988**, *58*, 291–295 (*Chem. Abstr.* **1989**, *110*, 135342y). – [8c] D. Gudat, H. M. Schiffner, M. Nieger, D. Stalke, A. J. Blake, H. Grondey, E. Niecke, *J. Am. Chem. Soc.* **1992**, *114*, 8857–8862.

[9] [9a] E. G. Bent, R. Schaeffer, R. C. Haltiwanger, A. D. Norman, *Inorg. Chem.* **1990**, *29*, 2608–2613. – [9b] E. Lindner, H. Rauleder, W. Hiller, *Z. Naturforsch., B: Angew. Chem., Org. Chem.* **1983**, *38B*, 417–425.

[10] [10a] D. Gudat, E. Niecke, *J. Chem. Soc., Chem. Commun.* **1987**, 10–11. – [10b] O. J. Scherer, R. Walter, P. Bell, *Chem. Ber.* **1987**, *120*, 1885–1890.

[11] S. Meriwether, M. L. Fiene, *J. Am. Chem. Soc.* **1959**, *80*, 4200–4208.

[12] O. J. Scherer, R. Walter, W. S. Sheldrick, *Angew. Chem.* **1985**, *97*, 525–527; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 525.

[13] U. Wirringa, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Angew. Chem.* **1993**, *105*, 1680–1681; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1628–1630.

[14] W. Clegg, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor., Gen. Crystallogr.* **1981**, *A37*, 22–28.

[15] *SHELXTL PLUS*, Siemens Analytical Instruments, Madison, WI, **1990**.

[16] G. M. Sheldrick, *SHELXS 90*, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *A46*, 467–473.

[17] G. M. Sheldrick, *SHELXL 93*, University of Göttingen, **1993**.

[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100281. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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