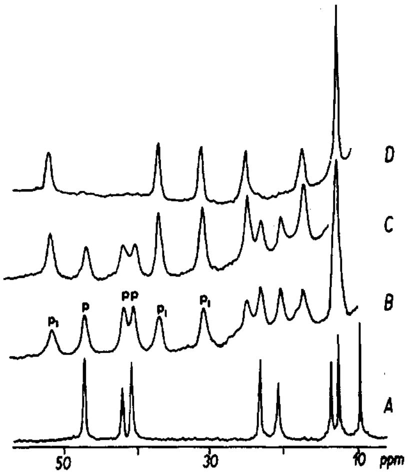

Figure 3. Titration of (N-CH_3TPP)CoCl with 1-methylimidazole (solvent $CDCl_3$, concentration of complex 12.8 mM, 25 °C). Concentration of 1-methylimidazole: (A) 0; (B) 0.45 M; (C) 0.6 M; (D) 2 M. Abbreviations: p, pyrrole resonances of **1**; p_1, pyrrole resonances of **3**. The remaining part of the spectrum is obscured by 1-MeIm resonances.

The plots of shift vs. T^{-1} for **1** (Figure 2) and **2** present a noticeable deviation from Curie law, particularly for pyrrole and NCH_3 resonances (extrapolated intercepts for pyrroles are 3.09, −8.3, 0.1, and −3.2 ppm and 41.5 ppm for NCH_3). This clearly implies the existence of thermal equilibrium between closely situated electronic states of high-spin Co(II).[1,18] The methylated nitrogen is approximately sp^3 hybridized;[1] therefore only a σ delocalization mechanism is available for the N-methyl group. For this type of delocalization one would expect to observe a large downfield shift[19] for the methyl resonance. The observed large upfield shift of the N-methyl group is consistent only with a predominant dipolar contribution to the isotropic shift.

When axial symmetry geometric factors are used to account roughly for dipolar shifts of the phenyl resonances, good linear correlations with isotropic shifts are achieved for several different orientations of the main magnetic axis. Therefore, its exact orientation remains unknown and the separation of the dipolar and contact shifts will require further detailed study of the magnetic tensor orientation and components.

The experimental line width ratios 1:1.18:1.14:1.25 (−60 °C) for H_b:H_c:H_d:H_a protons respectively are slightly different from those theoretically predicted on the basis of the dominating dipolar contribution to the relaxation mechanism,[7] i.e. 1:1.08:1.123:1.25 (r^{-6} values were calculated from the crystallographic data[1]). However, the considerably large differences between experimental and theoretical values have been observed at 20 °C. Due to the specific orientational dependence of the magnetic susceptibility tensor, an angular dependence of T_1 and T_2 can account for the difference.[21,22] This angular dependence is usually neglected for regular porphyrins as all pyrrole protons have a similar orientation with respect to the main magnetic axis. The tentative assignment of pyrrole resonances is presented in Figure 1.

The thermodynamic parameters for rotation of the phenyl groups of **1** were determined by ^1H NMR. Similar $\Delta G^{\ddagger}$ values for both (nonequivalent by geometry) sets of phenyl groups were determined on the basis of ln (line width) $= f(T^{-1})$ analysis.[23] The following values have been found ($CDCl_3$ solution): o_1 proton, $\Delta H^{\ddagger} = 9.0 \mp 0.4$ kcal, $\Delta S^{\ddagger}/R = -13.2 \mp 0.6$, $\Delta G^{\ddagger}_{298} = 16.9 \mp 0.8$ kcal; o_2 proton, $\Delta H^{\ddagger} = 11.4 \mp 0.6$ kcal, $\Delta S^{\ddagger}/R = -8.5 \mp 1.0$, $\Delta G^{\ddagger}_{298} = 16.5 \mp 1.3$ kcal. The measured values are similar to those reported previously for a large variety of non-N-substituted tetraphenylporphyrins and their complexes (*meso*-tetrakis(*o*-hydroxyphenyl)porphyrin,[24] $\Delta G^{\ddagger}_{298} = 24$ kcal; (TPP)Ni^{II}, $\Delta G^{\ddagger}_{463} > 26$ kcal;[25] TPP complexes of ruthenium, titanyl, and indium,[26] $\Delta H^{\ddagger} = 11.2$–$17.5$ kcal, $\Delta S^{\ddagger}/R = -3.7$ to -12.4, $\Delta G^{\ddagger}_{298} = 14.3$–$18.6$ kcal). The different positions of phenyls with respect to the N-methyl-substituted pyrrole ring are probably responsible for differences in the respective $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.

The addition of 1-methylimidazole to **1** resulted in the formation of a new set of resonances corresponding to the five-coordinate species (N-CH_3TPP)Co^{II}(1-MeIm) (**3**) (Figure 3). The stability constant calculated from the pyrrole intensity ratio analysis equals 2.1 M (25 °C, $CDCl_3$), which remains in good agreement with reported values for other high-spin Co(II) complexes.[27,28] The resonances of the coordinated 1-MeIm have not been observed due to the fast exchange with uncoordinated ligands.

The identity of observed pyrrole resonances has been confirmed by the spectrum of (N-CH_3TPP-d_8)Co(1-MeIm). The spread of pyrrole resonances increases upon 1-MeIm coordination probably due to the preferred orientation of the 1-MeIm plane, which leads to preferential π spin density distribution.[31]

Other paramagnetic complexes with less pronounced dipolar contributions are being studied in order to elucidate the spin density distribution and spin-transfer mechanism.

Acknowledgment. This work was supported by the Polish Academy of Sciences (MR I.9 project).

Registry No. 1, 51552-52-4; 2, 94499-87-3; 3, 94499-88-4; 1-MeIm, 616-47-7.

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Coordination Chemistry of Higher Oxidation States. 12.[1] Synthesis and Complexes of the Bis(phosphine) 1,2-Bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene, o-$C_6F_4(PMe_2)_2$

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Recent studies[2-5] have shown that ligands of the type o-$C_6H_4(EMe_2)(E'Me_2)$ (E, E′ = P, As, Sb) (L–L) are particularly effective at stabilizing high formal oxidation states of the transition

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metals, $[M(L\text{-}L)_2X_2]^{n+}$ (X = Cl, Br), where M for example is Ni(III), Ni(IV), Pd(IV), or Fe(IV). This has been attributed to the combination of good σ donor properties and small steric requirements, while the rigid o-C_6H_4– backbone resists dissociation from the metal. However, as always, clarification of the relative importance of steric and electronic properties is difficult, and in order to probe these effects further we have synthesized the new ligand[6] o-$C_6F_4(PMe_2)_2$ (F–diphos), which has very similar steric properties to o-$C_6H_4(PMe_2)_2$(diphos) but is expected to be a weaker σ donor to the –I effect of the fluorines. It has been previously found that in normal oxidation state chemistry, ligands with hydrocarbon and fluorocarbon backbones behave in significantly different ways: e.g., o-$C_6H_4(PPh_2)_2$ readily forms five-coordinate $[Ni(L\text{-}L)_2X]^+$ ions,[7] but o-$C_6F_4(PPh_2)_2$ does not,[8] while S-demethylation at Ni(II) or Pd(II) is much more facile in o-$C_6F_4(PPh_2)(SMe)$ than in o-$C_6H_4(PPh_2)(SMe)$.[9]

Experimental Section

Details of the techniques and instrumentation are given in previous parts of this series. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM 360 spectrometer. Shifts are relative to 85% H_3PO_4–high-frequency positive δ scale.

o-$C_6F_4(PMe_2)_2$. Under nitrogen, the apparatus consisting of a 250-cm^3 three-necked flask, fitted with nitrogen inlet, "Suba seal" septum cap, and reflux condenser, was charged with dry diethyl ether (100 cm^3) and 1,2-dibromotetrafluorobenzene (5 g, 0.016 mol). The mixture was cooled to −85 °C and n-BuLi (10.9 cm^3 of a 1.49 M solution) added dropwise via a syringe over a period of ca. 20 min. After warming to −20 °C for 5 min, the mixture was cooled to −85 °C and Me_2PCl (1.56 g, 0.016 mol) added slowly via a syringe, the mixture becoming red in color. After stirring for 30 min, the mixture was allowed to warm to room temperature. The mixture was cooled again to −85 °C and treated successively with n-BuLi (11 cm^3) and Me_2PCl (1.7 g) and allowed to warm over ca. 1 h. Hydrolysis was effected with deoxygenated aqueous NH_4Cl solution (35 cm^3) at 0 °C, the organic layer separated, and the aqueous layer extracted with diethyl ether (25 cm^3), and the combined organic layers were dried (Na_2SO_4). The ether was distilled off and the residue fractionated in vacuo. After a short forerun (bp 51–54 °C (0.4 mmHg)) the main fraction boiled at 60–85 °C (0.5 mmHg); 1.9 g (43%). Redistillation gave bp 73 °C (0.5 mm). Mass spectrum: m/z 270 (11, P^+), 255 (100, $P - Me^+$), 240 (23, $P - 2\,Me^+$). ^1H NMR $[(CD_3)_2SO]$: δ 1.50 (m). $^{31}P\{^1H\}$: δ −39.9. $^{19}F\{^1H\}$ $[(CD_3)_2SO]$: δ 8.75 (m), 32.3 (m) (relative to C_6F_6).

Methiodide. o-$C_6F_4(PMe_2)_2$ (0.135 g, 0.5 mmol) was added to a warm acetone solution (30 cm^3) of MeI (0.3 g, 2 mmol). The solvent was evaporated in vacuo and the white product recrystallized from acetone/diethyl ether. Anal. Calcd for $C_{11}H_{15}F_4IP_2$: C, 32.0; H, 3.7. Found: C, 31.8; H, 3.7. Mp: 174–177 °C (dec.) ^1H NMR $[(CD_3)_2SO]$: δ 1.4 (d, J = 5 Hz, 6 H), 2.28 (d, J = 14 Hz, 9 H) (both show evidence of further coupling under high resolution). $^{31}P\{^1H\}$: δ +31.75 (Me_3P^+–), −34.6 (Me_2P–).

Dichlorobis[1,2-bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene]nickel(II), $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]$. The ligand (0.27 g, 1.0 mmol) was added to a deoxygenated solution of $Ni(H_2O)_6Cl_2$ (0.12 g, 0.5 mmol) in ethanol (40 cm^3) and the mixture refluxed for 5 min, cooled, and concentrated to ca. 5 cm^3. Diethyl ether (30 cm^3) was added with rapid stirring and the mixture cooled to −20 °C overnight. The resulting green precipitate was filtered off, washed with diethyl ether (5 cm^3), and dried in vacuo; 0.073 g (22%). After the filtrate was concentrated and cooled, dark orange crystals were obtained, which were isolated in a similar manner; 0.098 g (29%).

Data for the green form: Anal. Calcd for $C_{20}H_{24}Cl_2F_4NiP_4$: C, 35.9; H, 3.6. Found: C, 35.7; H, 3.7. Electronic spectrum (diffuse reflectance; 10^3 cm^{-1}): 13.9, 15.1, 16.6 sh, 24.9, 30.7.

Data for the orange form: Anal. Found: C, 35.4; H, 3.5. Electronic spectrum (CH_2Cl_2 solution; 10^3 cm^{-1} (ϵ_{mol}, dm^3 cm^{-1} mol^{-1})): 24.3 (900), 32.3 (3800); (diffuse reflectance) 21.2 sh, 23.4. $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Br_2]$ was isolated in a similar manner as orange-brown crystals, 0.322 g (85%). Anal. Calcd for $C_{20}H_{24}Br_2F_4NiP_4$: C, 31.7; H, 3.2. Found: C, 32.0; H, 3.2. Electronic spectrum (CH_2Cl_2 solution; 10^3 cm^{-1} (ϵ_{mol}, dm^3 cm^{-1} mol^{-1})): 20.5 sh, 25.3 (1030), 30.5 (6300); (diffuse reflectance) 19.3 sh, 24.2, 26.5, 30.3.

Bis[1,2-bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene]nickel(II) Perchlorate. $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2](ClO_4)_2$. The ligand (0.54 g, 2 mmol) was syringed into a warm solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.4 g, 1.1 mmol) in propan-1-ol (50 cm^3) with stirring, and a yellow precipitate appeared immediately. This was filtered off, washed with propan-2-ol and diethyl ether, and dried in vacuo. It was recrystallized from acetonitrile/propan-2-ol (1/1 v/v); 0.71 g (89%). Anal. Calcd for $C_{20}H_{24}Cl_2F_8NiO_8P_4$: C, 30.1; H, 3.0. Found: C, 30.5; H, 3.0. ^1H NMR $[(CD_3)_2SO]$: δ 2.22 (br s).

Dichlorobis[1,2-bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene]nickel(III) Perchlorate, $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2](ClO_4)$. To a solution of $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]$ (0.065 g, 0.1 mmol) and $LiClO_4$ (0.01 g, 0.1 mmol) in ethanol (25 cm^3)/MeCN (7 cm^3) was added a small excess of Cl_2/CCl_4 solution, to produce a grass green solution. This was concentrated in vacuo to yield a green precipitate that was filtered off, rinsed with cold propan-2-ol and diethyl ether, and dried in vacuo; 0.05 g (78%). Anal. Calcd for $C_{20}H_{24}Cl_3F_8NiO_4P_4$: C, 31.2; H, 3.15. Found: C, 31.4; H, 3.3. IR ν(Ni–Cl) = 235 cm^{-1}. Electronic spectrum (MeCN solution; 10^3 cm^{-1} (ϵ_{mol}, dm^3 cm^{-1} mol^{-1})): 14.53 (130), 27.8 (14 500). Magnetic moment (Evans' method, MeCN): 1.94 μ_B. $[Ni[o\text{-}C_6F_4(PMe_2)_2]Br_2]ClO_4$ was made similarly from $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Br_2]$, $LiClO_4$ (1/1 mole ratio), and Br_2 in ethanol and isolated as a brick red solid, 88%. Anal. Calcd for $C_{20}H_{24}Br_2ClF_8NiO_4P_4$: C, 28.0; H, 2.8. Found: C, 28.2; H, 2.8. IR: ν(Ni–Br) = 183 cm^{-1}. Electronic spectrum (MeCN; 10^3 cm^{-1} (ϵ_{mol}, dm^3 cm^{-1} mol^{-1})): 14.28 (42), 21.20 (800), 27.30 (4750). Magnetic moment (Evans' method, MeCN): 1.98 μ_B.

Dichlorobis[1,2-bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene]palladium(II), $[Pd[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]$. The ligand (0.27 g, 1 mmol) was added to a gently refluxing solution of Na_2PdCl_4 (0.15 g, 0.5 mmol) in ethanol (40 cm^3). After the mixture was stirred for 1 h, the solvent was removed and the residue recrystallized from CH_2Cl_2/diethyl ether; 0.27 g (75%). Anal. Calcd for $C_{20}H_{24}Cl_2F_4P_4Pd$: C, 33.5; H, 3.3. Found: C, 32.9; H, 3.1. Electronic spectrum (diffuse reflectance; 10^3 cm^{-1}): 25.6 sh, 29.4 sh, 31.7. ^1H NMR spectrum $[(CD_3)_2CO]$: δ 2.20 (br).

Dichlorobis[1,2-bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene]palladium(IV) Perchlorate, $[Pd[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2](ClO_4)_2$. $[Pd[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]$ (0.36 g, 0.5 mmol) was dissolved in the minimum volume of concentrated HNO_3 at 0 °C with magnetic stirring, giving a deep yellow solution. The product was precipitated by the slow dropwise addition of chilled 70% $HClO_4$ (CARE)[10] as a yellow solid, filtered, washed with 10% $HClO_4$, and dried in vacuo; 0.34 g (76%). Anal. Calcd for $C_{20}H_{24}Cl_4F_8O_8P_4Pd$: C, 26.2; H, 2.6. Found: C, 26.4; H, 2.7. IR: ν(Pd–Cl) = 380 cm^{-1}. Electronic spectrum (CF_3CO_2H; 10^3 cm^{-1} (ϵ_{mol}, dm^3 cm^{-1} mol^{-1})): 24.51 (ca. 1800).

Dichlorobis[1,2-bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene]cobalt(III) Chloride, $[Co[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]Cl$. The ligand (0.27 g, 1 mmol) was added to a solution of $[Co(H_2O)_6]Cl_2$ (0.12 g, 0.5 mmol) in warm propan-2-ol (20 cm^3). After the mixture was cooled to room temperature, light green crystals precipitated. These were rinsed with diethyl ether and dried in vacuo. They were finely powdered, suspended in dry CCl_4 (ca. 5 cm^3), and treated with a small excess of chlorine. After the mixture was allowed to stand for 2 h, the resulting light purple powder was filtered off, washed with CCl_4 (10 cm^3), and dried in vacuo; 0.2 g (50%). Anal. Calcd for $C_{20}H_{24}Cl_3CoF_8P_4$: C, 34.1; H, 3.4. Found: C, 34.3; H, 3.4. IR: ν(Co–Cl) = 399 cm^{-1}. Electronic spectrum (MeCN; 10^3 cm^{-1} (ϵ_{mol}, dm^3 cm^{-1} mol^{-1})): 17.86 (100), 27.17 (3240).

Dichlorobis[1,2-bis(dimethylphosphino)-3,4,5,6-tetrafluorobenzene]iron(III) Tetrafluoroborate. The ligand (0.27 g, 1 mmol) was added to a solution of anhydrous $FeCl_3$ (0.195 g, 1.2 mmol) in ethanol (25 cm^3) with stirring. The red precipitate was filtered off and air-dried. It was then dissolved in acetone (20 cm^3), and tetrafluoroboric acid (5 cm^3, 30% by volume) was filtered into the solution. After concentration to ca. 15 cm^3, dark red crystals precipitated. These were filtered off and dried in vacuo; 0.3 g (40%). Anal. Calcd for $C_{20}H_{24}BCl_2F_8FeP_4$: C, 35.4; H, 3.6. Found: C, 35.3; H, 3.6. IR: ν(Fe–Cl) = 382 cm^{-1}. Electronic spectrum (MeCN; 10^3 cm^{-1} (ϵ_{mol}, dm^3 cm^{-1} mol^{-1})): 18.18 (2150), 26.88 sh (780), 29.24 (4400). Magnetic moment (Evans' method, CH_3CN): 2.21 μ_B.

The syntheses of the corresponding complexes of o-$C_6H_4(PMe_2)_2$ have been described elsewhere.[2-4]

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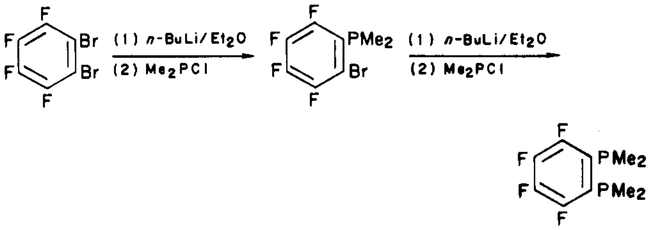
Table I. Redox Potentials[a]

	Ni(II) → Ni(III)	Ni(III) → Ni(IV)		Fe(II) → Fe(III)	Fe(III) → Fe(IV)
$[Ni(diphos)_2Cl_2]^{n+}$	+0.36	+1.18	$[Fe(diphos)_2Cl_2]^{n+}$	+0.045	+1.43
$[Ni(F\text{-}diphos)_2Cl_2]^{n+}$	+0.47	+1.40	$[Fe(F\text{-}diphos)_2Cl_2]^{n+}$	+0.345	+1.69

[a] ±0.01 V in MeCN with 0.1 M $n\text{-}Bu_4NBF_4$ as supporting electrolyte; carbon electrodes vs. standard calomel electrode.

Scheme I



Results and Discussion

The ligands $o\text{-}C_6H_4(EMe_2)(E'Me_2)$ are made by reaction of EMe_2^- nucleophiles with $o\text{-}C_6H_4Cl_2$ (E = E′) or $o\text{-}C_6H_4Br\text{-}(E'Me_2)$,[11] but an analogous route cannot be used for the title ligand since the C–F bonds are attacked.[12] F–diphos was obtained as in Scheme I in ca. 43% yield, as a colorless oil that is less air sensitive than $o\text{-}C_6H_4(PMe_2)_2$.

The ^{31}P NMR resonance in F-diphos (−39.9 ppm) is shifted ca. 16 ppm to high frequency from that in diphos (−56 ppm),[11] and since the bond angles at P are assumed to be very similar, this indicates significant electron density changes at the phosphorus.

The Ni(II), Co(III), and Fe(III) complexes of F–diphos (Experimental Section) are generally similar to their diphos analogues, the most notable difference being that while diphos only gives the planar solid $Ni(diphos)_2Cl_2$,[2] $Ni(F\text{–}diphos)_2Cl_2$ can be obtained as both brown-planar (P_4) and green pseudooctahedral (P_4Cl_2) forms. Both dissolve in polar solvents to give a mixture of $[Ni(F\text{–}diphos)_2]^{2+}$ and $[Ni(F\text{–}diphos)_2Cl]^+$. Moreover, the ready synthesis of relatively stable $[Pd^{IV}(F\text{–}diphos)_2Cl_2](ClO_4)_2$ and $[Ni^{III}(F\text{–}diphos)_2X_2]ClO_4$[2-4] shows the ability of the ligand to stabilize high oxidation states. In order to probe differences between F–diphos and diphos complexes we have used cyclic voltammetry.[13] As shown in Table I the F–diphos complexes of Ni(III) and Fe(III) are much less readily oxidized to the M(IV) states than those of diphos, while the oxidation of Fe(II) → Fe(III) is considerably harder with F–diphos. The Ni(II) → Ni(III) potentials are less strictly comparable; unlike the other systems they are not electrochemically reversible, as they involve a change in coordination number (4 or 5 in Ni(II), 6 in Ni(III)). Similar trends are present in the corresponding bromide complexes.[5] It is notable that the redox potential differences between corresponding F–diphos and diphos complexes are much greater than between those of diphos and $o\text{-}C_6H_4(AsMe_2)_2$.[2,5]

Conclusions

The electrochemical data demonstrate that diphos and F–diphos have significantly different abilities to stabilize high oxidation states, reflecting different *electronic* properties. Since both have excellent coordinating abilities toward transition-metal ions, they offer a means of probing (or modifying) the electronic effects, while steric changes are minimized, and hence should be valuable in a wide range of coordination/organometallic systems.

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Registry No. $o\text{-}C_6F_4(PMe_2)_2$, 95045-52-6; $o\text{-}C_6F_4(Br)_2$, 827-08-7; Me_2PCl, 811-62-1; $o\text{-}C_6F_4(PMe_2)_2$ methiodide, 95045-53-7; $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]$, 95045-54-8; $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2]Cl_2$, 95045-68-4; $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Br_2]$, 95045-55-9; $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2](ClO_4)_2$, 95045-57-1; $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2](ClO_4)$, 95045-59-3; $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Br_2](ClO_4)$, 95045-61-7; $[Pd[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]$, 95045-62-8; $[Pd[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2](ClO_4)_2$, 95045-64-0; $[Co[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]Cl$, 95045-65-1; $[Fe[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2](BF_4)$, 95045-67-3; $[Fe[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]$, 95045-69-5; $[Fe[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]^{2+}$, 95045-70-8; $[Ni[o\text{-}C_6F_4(PMe_2)_2]_2Cl_2]^{2+}$, 95045-71-9.

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(13) Analysis of the electronic spectra is precluded since an insufficient number of metal-centered transitions (d–d bands) are resolved, due to the presence of charge-transfer transitions at low energy in the high oxidation state complexes.

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Synthesis of (Trimethylsilyl)- and (Trimethylgermyl)allylphosphine

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Trialkylsilyl-substituted phosphines [e.g. $[(CH_3)_3Si]_{3-m+n}P(H)_mR_n$; $m + n = 1, 2$; R = an organo moiety] are valuable synthons for the preparation of new organophosphorus and organophosphorus-metal compounds. Recent examples include the syntheses of novel nickel- and cobalt-phosphorus cluster complexes[1] and primary and secondary organophosphines[2,3] such as $\{Co_4(\mu_3\text{-}PC_6H_5)_4[P(C_6H_5)_3]_4\}$ and $[(C_6H_5)_2PCH_2CH_2]_2PH$, respectively. In the former case, advantage is taken of facile Si–P bond cleavage in $[(CH_3)_3Si]_2PC_6H_5$ by metal halides. In the latter case, since Si–P bonds resist radical reaction, a two-step synthesis involving initial addition of $(CH_3)_3SiPH_2$ to the olefin followed by hydrolytic removal of $(CH_3)_3Si$ groups can be exploited.

Previous syntheses of $(CH_3)_3Si$-substituted organophosphines have been limited to cases where R = alkyl and aryl; only recently have four-carbon or greater alkenyl-substituted compounds been prepared.[2,3] Lower homologues, e.g. $(CH_3)_3SiP(H)CH_2CHCH_2$, could not be prepared. We have now investigated alternate syntheses of these and find that $(CH_3)_3SiI$ or $(CH_3)_3GeBr$ with $CH_2CHCH_2PH_2$ in the presence of $(C_2H_5)_3N$ yield the new (trimethylsilyl)- and (trimethylgermyl)allylphosphines. This work is described below.

Results and Discussion

Trimethyliodosilane and $(CH_3)_3GeBr$ react with $CH_2CHCH_2PH_2$ in CH_2Cl_2 in the presence of $(C_2H_5)_3N$ to afford the unsymmetrically substituted (silyl)- and (germyl)allylphosphines, $(CH_3)_3SiP(H)CH_2CHCH_2$ (1) and $(CH_3)_3GeP(H)CH_2CHCH_2$ (3), respectively (eq 1). Reactions involve initial adduct formation

$$(CH_3)_3EX + CH_2CHCH_2PH_2 + (C_2H_5)_3N \rightarrow (CH_3)_3EP(H)CH_2CHCH_2 + (C_2H_5)_3NHX \quad (1)$$

$$E, X = Si, I; Ge, Br$$

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