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Facile Synthesis of Unsymmetrical 9-Phospha- and 9-Arsafluorenes

Armando A. Diaz,[†] Jackie D. Young,[†] Masood A. Khan,[†] and Rudolf J. Wehmschulte*[,‡]

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Room 208, Norman, Oklahoma 73019, and Department of Chemistry, Florida Institute of Technology, 150 West University Boulevard, Melbourne, Florida 32901

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Unsymmetrical 9-chloro-9-phosphafluorenes (dibenzophospholes) and 9-chloro-9-arsafluorenes (dibenzoarsoles) have been obtained by simple thermolysis of *m*-terphenyldichlorophosphines and -arsines in close to quantitative yields. The reaction temperatures are about 200 °C for the phosphines and 140 °C for the arsine, and the reactions are complete within 5 min. Alternatively, these compounds can be synthesized through an $AlCl_3$-catalyzed Friedel–Crafts type ring-closure reaction at low temperatures, but this method suffers from difficult workup procedures. The P(As)–Cl functionality is readily alkylated. Methylation of *m*-xylyl derivative **4** afforded 1-(3,5-dimethylphenyl)-6,8,9-trimethyl-9-phosphafluorene, **11**. The latter compound formed the complexes **11**·$Fe(CO)_4$, **12**, and **11**·$RuCl_2(\eta^6$-*p*-cymene), **13**, indicating its good donor properties. The new compounds have been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy; mass spectrometry; and single-crystal X-ray crystallography in the case of **11**, **12**, and **13**.

Introduction

9-Phosphafluorenes (dibenzophospholes) constitute an interesting class of compounds,[1] and their transition-metal complexes have been known for more than 30 years.[2−4] Whereas the donor/acceptor properties of 9-phosphafluorenes are very similar to those of the corresponding diarylphosphines, 9-phosphafluorenes are generally smaller because of the constrained geometry of the 9-phosphafluorene unit. This led, for instance, to the formation of five-coordinate complexes L_3NiX_2 of 9-methyl-9-phosphafluorene with various nickel salts,[3] whereas related phosphine $MePPh_2$ formed only four-coordinate compounds L_2NiX_2.[5] The coordination properties of 9-phenyl-9-phosphafluorene and its derivatives have been studied intensively by Nelson and co-workers.[6,7] In recent years, the applicability of the 9-phosphafluorene unit in connection with a chiral backbone for asymmetric catalysis has been investigated by various groups.[8,9] The 9-phosphafluorene unit has been incorporated into polymers for the preparation of luminescence devices,[10] and unsymmetrical 9-phosphafluorene oxides are of interest for *P*-chiral liquid crystals.[11] Recently, a rigid bidentate ligand based on the 9-phosphafluorene framework was found to support the palladium-catalyzed Suzuki−Miyaura reaction.[12] A potential obstacle for the more widespread use of 9-phosphafluorenes as ligands may be found in the scarcity of simple synthetic procedures. Typically, 9-phosphafluorenes are obtained by the reaction of 2,2′-dilithium biphenyls with $RPCl_2$.[1,13] Disadvantages of this method include the high reactivity of

* To whom correspondence should be addressed. Fax: 1 321 674 8951. E-mail: rwehmsch@fit.edu.
† University of Oklahoma.
‡ Florida Institute of Technology.

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the dilithium species and the limited availability of 2,2′-dibromo- or diodobiphenyl precursors. An alternative one-pot synthesis for 9-phenyl-9-phosphafluorene starting from Ph_4PBr could not be generalized.[14] Prompted by the observation by Power and co-workers that the *m*-terphenyldichlorophosphine 2,6-$Trip_2C_6H_3PCl_2$ is cleanly converted into an unsymmetrical 9-phosphafluorene, 5,7,9-triisopropyl-1-(2,4,6-triisopropylphenyl)-9-phosphafluorene, upon magnesium reduction,[15] we have begun to investigate the potential of the *m*-terphenyldichlorophosphines as readily available precursors for the preparation of unsymmetrical, bulky 9-phosphafluorenes. It has since been shown that the above-mentioned reductive approach is limited to electron-rich *m*-terphenyldichlorophosphines.[16] Similarly, our attempts to generate 9-phosphafluorenes via phosphinidenes from thermal decomposition of *m*-terphenylbisazidophosphines led to dimeric and trimeric *m*-terphenylazidophosphazenes instead.[17] Here, we report (i) the preparation of unsymmetrical, bulky 9-phosphafluorenes by simple Friedel−Crafts chemistry and thermolysis, (ii) the extension of this method to 9-arsafluorenes, and (iii) the synthesis of iron and ruthenium complexes of one of the new bulky 9-phosphafluorenes.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies drybox. Solvents were freshly distilled under N_2 from sodium, potassium, sodium/potassium alloy, or calcium hydride and degassed twice prior to use. PCl_3, $AsCl_3$, *n*-butyllithium (1.6 M in hexanes), MeLi (1.6 M in Et_2O), and MeMgBr (1.0 M in THF) were obtained from commercial suppliers. Compounds 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3PCl_2$, **3**;[17] 2,6-$Mes_2C_6H_3PCl_2$, **6** (Mes = 2,4,6-$Me_3C_6H_2$);[18] 2,6-(2-$MeC_6H_4)_2C_6H_3PCl_2$, **9**;[17] 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Br$;[19] and 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3I$[20,21] were synthesized according to literature methods. NMR spectra were recorded on a Varian Mercury 300 MHz, a Varian Unity Plus 400 MHz, a Bruker AMX 360, or a Bruker Avance 400 MHz spectrometer, and ^1H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or $CDCl_3$ as internal reference (δ = 7.15 or 7.26). ^{13}C NMR spectra were referenced to the solvent signal (δ = 128.0 or 77.0) and ^{31}P NMR spectra to external 85% H_3PO_4. Infrared spectra were recorded in the range 4000−400 cm^{-1} using a Nicolet Nexus 470 FTIR spectrometer. Electron impact mass spectra were recorded with a Finnigan MAT Polaris spectrometer and electrospray mass spectra with a Micromass Q-ToF spectrometer. Melting points were determined in Pyrex capillary tubes (sealed under nitrogen where appropriate) with a Mel-Temp apparatus and are uncorrected.

2,6-(3,5-$Me_2C_6H_3)_2C_6H_3PCl_2$, 1. A suspension of 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3I$ (4.40 g, 10.0 mmol) in hexanes (50 mL) was treated with *n*-BuLi solution (1.6 M in hexane, 6.9 mL, 11.0 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. After filtration, the solvent was distilled off under reduced pressure, and the remaining off-white solid was suspended in hexanes (50 mL). The suspension was cooled to −78 °C, and freshly distilled PCl_3 (0.9 mL, 10.0 mmol) was added via syringe. The dry ice/ethanol bath was removed after 10 min, and the reaction mixture was warmed to room temperature and stirred overnight. The fine colorless precipitate was removed by filtration, and the clear yellow filtrate was concentrated to ca. 20 mL to induce crystallization. Large, well-shaped crystals of **1** were obtained after 2 days at room temperature. Yield: 74%, 2.86 g. Mp: 115−122 °C. ^1H NMR (400 MHz, C_6D_6): δ 7.19 (s, *o*-H(xylyl), 4H), 7.16 (dd, J = 6.4 Hz, J_{PH} = 2.8 Hz, *m*-H, 2H), 7.09 (t, J = 6.4 Hz, *p*-H, 1H), 6.85 (s, *p*-H(xylyl), 2H), 2.20 (s, Me, 12H). $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6): δ 149.55 (d, J_{PC} = 28.3 Hz), 140.77 (d, J_{PC} = 8.4 Hz), 137.64, 136.02 (d, J_{PC} = 77.0 Hz), 131.57, 130.76, 130.07, 128.57 (d, J_{PC} = 3.8 Hz), 21.32 (Me). $^{31}P\{^1H\}$ NMR (161.90 MHz, C_6D_6): δ 157.9 (s).

2,6-(4-*t*-$BuC_6H_4)_2C_6H_3AsCl_2$, 2. A suspension of 2,6-(*t*-$BuC_6H_4)_2C_6H_3Li$ (generated from 2,6-(*t*-$BuC_6H_4)_2C_6H_3Br$ (3.94 g, 9.35 mmol) and *n*-BuLi) in hexanes (60 mL) was treated with freshly distilled $AsCl_3$ (1.85 g, 0.85 mL, 10.2 mmol) at −78 °C. The mixture was kept at −78 °C for 1 h, slowly warmed to room temperature, and stirred overnight. The pale yellow supernatant solution (ca. 30 mL) was decanted, concentrated to ca. 10 mL, and left standing at room temperature for 1 day to give large colorless plates (0.55 g). The remaining slurry of the reaction mixture (ca. 20 mL) was extracted with warm hexanes (50 mL) and filtered through a medium-porosity glass frit. Concentration of the colorless filtrate to ca. 30 mL followed by standing at room temperature for 1 day gave a second batch of large colorless crystals (1.25 g). The combined mother liquors were concentrated to 30 mL to afford a third batch of crystals after 3 days at room temperature (0.82 g). Yield: 57%, 2.62 g. Mp: 133−140 °C with gas evolution. ^1H NMR (C_6D_6, 400 MHz): δ 7.57 (d, J = 8.2 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 4H), 7.35 (d, J = 8.2 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 4H), 7.18 (d, J = 7.6 Hz, *m*-H, 2H), 7.08 (t, J = 7.6 Hz, *p*-H, 1H), 1.22 (s, CH_3, 18H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.57 MHz): δ 151.74, 148.80, 142.28, 137.64, 131.43, 130.81, 130.30 (*o*- or *m*-C(4-*t*-BuC_6H_4)), 125.55 (*o*- or *m*-C(4-*t*-BuC_6H_4)), 34.62 ($C(CH_3)_3$), 31.34 ($C(CH_3)_3$).

1-(3,5-Dimethylphenyl)-6,8-dimethyl-9-chloro-9-phosphafluorene, 4.[22] Method A: A solution of $AlCl_3$ (0.35 g, 2.6 mmol) in dichloromethane (20 mL) was added to a solution of **1** (1.00 g, 2.6 mmol) in dichloromethane (20 mL) at −78 °C. The yellow color of the dichloromethane solution of **1** changed to orange upon $AlCl_3$ addition. The reaction mixture was slowly warmed to room temperature (ca. 45 min), and pyridine (0.42 mL, 5.2 mmol) was added to give a pale yellow solution. After removal of the solvent

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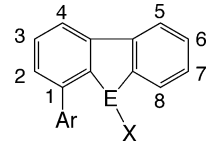

under reduced pressure, the remaining sticky solid was extracted with hexanes (30 mL). The extract was concentrated to about half its original volume and cooled at −40 °C for 24 h to afford colorless crystals of **4**. Yield: 29%, 0.26 g.

Method B: A Schlenk flask was charged with **1** (1.78 g, 4.6 mmol) and placed into a preheated oil bath at 200 °C. After ca. 1 min, the crystals began to melt, and a gentle gas evolution commenced. The liquid turned yellow, and the reaction was complete after 10 min. Before cooling down the liquid, we removed the eliminated HCl gas under reduced pressure. The yellow liquid solidified into a pale yellow glass upon being cooled to room temperature. Yield: >97%, >1.56 g. Mp: 152−171 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.43 (m, 3H), 7.22 (m, 3H), 6.86 (s, br, $w_{1/2}$ = 5 Hz, H-5 or H-7, 1H), 6.61 (d, br, $w_{1/2}$ = 4 Hz, J_{PH} = 4.8 Hz, H-5 or H-7, 1H), 2.40 (s, CH_3-6 or CH_3-8, 3H), 2.22 (s, *m*-CH_3-(xylyl), 6H), 2.09 (s, Me-6 or Me-8, 3H). ^{13}C{^{1}H} NMR (100.57 MHz, C_6D_6): δ 147.66, 147.45, 145.65, 144.49, 142.20, 141.53, 138.14, 132.13, 130.88, 129.89, 129.39, 127.22 (d, J_{PC} = 3.8 Hz), 120.60, 120.28, 21.49 (*C*H_3-6), 21.39 (*C*H_3(xylyl)), 20.78 (d, J_{PC} = 15.0 Hz, *C*H_3-8). ^{31}P{^{1}H} NMR (121.47 MHz, C_6D_6): δ 67.1 (s).

1-(4-*tert*-Butylphenyl)-7-*tert*-butyl-9-chloro-9-phosphafluorene, 5. Method A: $AlCl_3$ (0.75 mmol, 0.10 g) was added via a solids-addition funnel to a solution of **3** (0.75 mmol, 0.33 g) in CH_2Cl_2 (45 mL) at −78 °C. The reaction mixture was held at that temperature for 30 min, slowly warmed to room temperature, and stirred overnight. The resulting clear, yellow solution was concentrated (2−3 mL) and cooled to −28 °C for 1 week. As no crystals formed, the volatile materials were removed under reduced pressure. The resulting yellow solid was suspended in hexanes (15 mL) and treated with pyridine (0.2 mL); the colorless, cloudy mixture was stirred for 12 h. Filtration, concentration, and subsequent cooling to −28 °C for 4 days afforded small colorless crystals. Yield: 43%, 0.13 g.

Method B: A Schlenk flask was charged with **3** (69 mg, 0.15 mmol) and placed into a preheated oil bath at 250 °C. After ca. 1 min, the crystals began to melt, and a gentle gas evolution commenced after two more minutes. The liquid turned yellow, and the reaction was complete after 10 min. Before cooling the liquid down, we removed the eliminated HCl gas under reduced pressure. The yellow liquid solidified into a pale yellow glass upon being cooled to room temperature and was identified as pure **5**. Yield: >95%, >0.058 g. Mp: 125−130 °C. ^{1}H NMR (400, MHz, C_6D_6): δ 7.81 (s, 1H), 7.80 (d, J = 8.0 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 2H), 7.43 (m, 2H), 7.41 (d, J = 8.0 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 2H), 7.25 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 1.21 (s, CH_3, 9H), 1.10 (s, CH_3, 9H). ^{13}C{^{1}H} NMR (100.57 MHz, C_6D_6): δ 152.33 (d, J_{PC} = 5.3 Hz), 151.02, 147.33 (d, J_{PC} = 20.6 Hz), 145.44, 142.53 (d, J_{PC} = 21.3 Hz), 141.56, 140.47 (d, J_{PC} = 29.0 Hz), 138.76, 132.45, 129.42 (d, J_{PC} = 1.5 Hz), 129.08 (d, J = 3.8 Hz), 128.74, 128.49, 125.90, 121.60, 120.31, 34.84 (*C*(CH$_3$)$_3$), 34.58 (*C*(CH$_3$)$_3$), 31.33 (C(*C*H$_3$)$_3$), 31.17 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (161.91 MHz, C_6D_6): δ 70.5.

2,6-Mes$_2$C$_6$H$_3$P(Cl)Ph, 7. $AlCl_3$ (0.10 g, 0.75 mmol) was added via a solids-addition funnel to a solution of **6** (0.31 g, 0.75 mmol) in benzene (45 mL) with cooling in an ice bath. The reaction mixture was warmed to room temperature after 30 min and stirred overnight. Concentration to 3−4 mL followed by cooling at 4 °C for 2 days afforded a yellow oil. The oil was isolated and suspended in hexanes; pyridine (0.2 mL) was added to the mixture to give a cloudy colorless solution after stirring for 24 h at room temperature. Filtration and subsequent removal of the solvent under reduced pressure resulted in the isolation of a viscous oily material, which was identified as a mixture of **7** and silicon grease by ^{1}H and ^{31}P-{^{1}H} spectroscopy. Recrystallization from hexanes (2 mL) at −30 °C for 1 week yielded colorless crystals of **7**. Yield: 14%, 0.050 g. Mp: 107−108 °C. ^{1}H NMR (400, MHz, C_6D_6): δ 7.12 (m, 3H), 6.83 (m, 7H), 6.58 (s, *m*-H(Mes), 2H), 2.19 (s, CH_3, 3H), 2.18 (s, CH_3, 3H), 1.84 (s, CH_3, 3H). ^{13}C{^{1}H} NMR (100.57 MHz, C_6D_6): δ 148.61 (d, J_{PC} = 22.8 Hz), 138.30 (d, J_{PC} = 6.1 Hz), 136.94, 136.32 (d, J_{PC} = 36.6 Hz), 136.28 (d, J_{PC} = 2.3 Hz), 134.55 (d, J_{PC} = 52.7 Hz), 132.03, 131.22, 130.92, 130.45 (d, J_{PC} = 2.3 Hz), 128.48, 128.42, 127.56 (d, J_{PC} = 7.6 Hz), 21.85 (*C*H_3), 21.23 (*C*H_3), 21.12 (*C*H_3). ^{31}P{^{1}H} NMR (161.91 MHz, C_6D_6): δ 79.7 (s). MS (ESI, MeCN solution): *m*/*z* 457.1854 (calcd 457.1852).

1-(4-*tert*-Butylphenyl)-7-*tert*-butyl-9-chloro-9-arsafluorene, 8. A Schlenk flask was charged with **2** (0.81 g, 1.7 mmol) and placed into a preheated oil bath at 145 °C. After ca. 2 min, the crystals began to melt, and a gentle gas evolution commenced. The liquid turned pale yellow, and the reaction was complete after three more minutes. Before cooling down the liquid, we removed the eliminated HCl gas under reduced pressure. The yellow liquid solidified into a pale yellow glass upon being cooled to room temperature. Yield: >95%, >0.73 g. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.83 (d, J = 8.4 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 2H), 7.66 (d, J = 2.1 Hz, 1H), 7.44 (d, J = 8.4 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 2H), 7.43 (d, peak overlap, J ≈ 7.8 Hz, 2H), 7.29 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 7.24 (dd, J = 8.1 Hz, 2.1 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 1.22 (s, CH_3, 9H), 1.12 (s, CH_3, 9H). ^{13}C{^{1}H} NMR (C_6D_6, 75.45 MHz): δ 152.33, 151.00, 147.32, 147.26, 146.62, 145.32, 143.59, 139.88, 132.26, 129.12, 129.09, 128.71, 126.01, 122.34, 120.98, 35.03 (*C*(CH$_3$)$_3$), 34.76 (*C*(CH$_3$)$_3$), 31.52 (C(*C*H$_3$)$_3$), 31.37 (C(*C*H$_3$)$_3$).

1-(2-Methylphenyl)-6-methyl-9-chloro-9-phosphafluorene, 10. A Schlenk flask was charged with **9** (0.82 g, 2.3 mmol) and placed into a preheated oil bath at 230 °C. After ca. 2 min, the crystals began to melt, and a gentle gas evolution commenced. The liquid turned pale yellow, and the reaction was complete after 15 more minutes. Before cooling down the liquid, we removed the eliminated HCl gas under reduced pressure. The yellow liquid solidified into a pale yellow glass upon being cooled to room temperature (0.55 g) and consisted of **10** in about 84% purity according to ^{31}P NMR spectroscopy. ^{1}H NMR (300 MHz, C_6D_6): δ 7.63 (t, J = 7.8 Hz, 1H), 7.49 (m, 0.5H), 7.39 (m, 1.5H), 7.14 (m, 4H), 6.98 (m, 1H), 6.85 (m, 2H), 2.25 (s, 5-CH_3, 3H), 2.20 and 2.08 (s, syn and anti 2-CH_3C$_6$H$_4$, 3H, ratio ≈ 48:52). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): δ quaternary carbons 147.45, 147.12, 146.89, 146.34, 146.20, 143.32, 143.05, 142.17, 142.02, 140.81, 140.47, 137.32, 136.66, 136.34, 135.02; aromatic C−H 134.77, 132.11, 131.52, 131.24, 130.56, 130.42, 130.03, 129.64, 129.41, 128.80, 128.78, 128.56, 128.20, 126.02, 125.86, 124.62; methyl 22.37, 20.82, 20.39. ^{31}P{^{1}H} NMR (121.47 MHz, C_6D_6): δ 66.3 and 66.0 (s), syn and anti mixture, ratio ≈ 48:52.

1-(3,5-Dimethylphenyl)-6,8,9-trimethyl-9-phosphafluorene, 11. MeMgBr (3 M in THF, 1.5 mL, 4.5 mmol) was added to a solution of **4** (1.37 g, 3.9 mmol) in toluene (20 mL) at −78 °C, whereupon the yellow color faded. After warming to room temperature and stirring overnight, the reaction mixture was filtered; the filtrate was concentrated to ca. 5 mL and cooled to −30 °C for several days. As no crystals had formed, the solution was concentrated further (ca. 2 mL), and hexane was added (8 mL); the resulting solution was concentrated to ca. 2 mL to afford large, well-shaped, colorless crystals of **11** after 3 days at room temperature. Yield: 80%, 1.03 g. Mp: 105−108 °C. ^{1}H NMR (300, MHz, C_6D_6): δ 7.77 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.55 (s, 1 H), 7.45 (s, *o*-H(xylyl), 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.29 (ddd, J = 7.5 Hz, 1.5 Hz, J_{PH} = 3.6 Hz, 1H), 6.85 (s, 1H), 6.77 (d, J_{PH} = 4.2 Hz, 1H), 2.31 (s, CH_3,

3H), 2.24 (s, Me, 3H), 2.21 (s, *m*-C*H*$_3$, 6H), 1.04 (d, J_{PH} = 2.4 Hz, PC*H*$_3$, 3H). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): δ 144.93 (d, J_{PC} = 14.3 Hz), 144.69, 144.63 (d, J_{PC} = 4.3 Hz), 144.02 (d, J_{PC} = 2.0 Hz), 142.49, 141.48 (d, J_{PC} = 4.6 Hz), 139.21 (d, J_{PC} = 18.0 Hz), 138.61, 138.14, 129.52 (d, J_{PC} = 4.3 Hz), 129.35, 129.12, 127.73 (d, J_{PC} = 3.7 Hz), 126.84 (d, J_{PC} = 4.5 Hz), 120.72, 120.28, 21.73 (*C*H$_3$), 21.60 (*C*H$_3$ (xylyl)), 21.36 (d, J_{PC} = 9.1 Hz, *C*H$_3$), 9.63 (d, $^1J_{PC}$ = 22.9 Hz, P*C*H$_3$). ^{31}P{^{1}H} NMR (121.47 MHz, C_6D_6): δ −28.2 (s). MS (EI, 70 eV, 120 °C): *m*/*z* 330.2 (M^+, 100), 315.2 (M^+ − Me, 90).

11·Fe(CO)$_4$, 12. $Fe_2(CO)_9$ (1.04 g, 2.9 mmol) was added via a solid-addition funnel to a solution of **11** (0.90 g, 2.7 mmol) in benzene (15 mL) at room temperature. After stirring for 12 h, we removed the volatile material under reduced pressure and redissolved the resulting solid in benzene (20 mL). Filtration followed by concentration to 8 mL and cooling at 3−4 °C for 1 week afforded a fine yellow crystalline solid (0.71 g). A second batch was obtained upon concentration of the mother liquor (0.32 g). Yield: 76%, 1.03 g. Mp: 194−202 °C. FTIR (KBr, hexane solution): 2051, 1975, 1952, 1942 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 7.52 (d, 2- or 4-H, *J* = 7.2 Hz, 1H), 7.31 (s, 5-H, 1H), 7.18 (m, 3-H, 2- or 4-H, 2H), 7.06 (s, *o*-H, 2H), 6.92 (s, *p*-H, 1H), 6.68 (d, J_{PH} = 3.9 Hz, 1H), 2.36 (s, 8-C*H*$_3$, 3H), 2.26 (s, *m*-C*H*$_3$, 6H), 2.11 (s, 6-C*H*$_3$, 3H), 1.58 (d, J_{PH} = 9.3 Hz, P−C*H*$_3$, 3H). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): δ 216.81 (d, J_{PC} = 14.6 Hz, *C*O), quarternary carbons 146.41 (d, J_{PC} = 11.8 Hz), 141.38 (d, J_{PC} = 23.3 Hz), 141.42 (d, J_{PC} = 1.7 Hz), 141.38, 140.49 (d, J_{PC} = 2.9 Hz), 139.59 (d, J_{PC} = 74.4 Hz), 139.53 (d, J_{PC} = 11.8 Hz), 137.92 (*m*-*C*), 135.96 (d, J_{PC} = 51.5 Hz); CH carbons 131.89 (d, J_{PC} = 8.6 Hz), 131.04 (d, J_{PC} = 1.7 Hz), 130.70 (d, J_{PC} = 8.1 Hz), 130.00 (*p*-*C*), 127.44 (*o*-*C*), 120.50 (d, J_{PC} = 19.9 Hz), 120.42 (d, J_{PC} = 20.1 Hz), 21.35 (6-*C*H$_3$), 21.27 (*m*-*C*H$_3$), 20.45 (d, J_{PC} = 4.3 Hz, 8-*C*H$_3$), 17.41 (d, J_{PC} = 25.6 Hz, P-*C*H$_3$). ^{31}P{^{1}H} NMR (121.47 MHz, C_6D_6): δ 37.4 (s).

11·RuCl$_2$(η^6-*p*-cymene), 13. A mixture of **11** (0.16 g, 0.48 mmol) and [RuCl$_2$(η^6-*p*-cymene)]$_2$ (0.15 g, 0.24 mmol) was dissolved in dichloromethane (30 mL) and stirred for 12 h at room temperature. Concentration of the clear orange solution to 4−5 mL and subsequent cooling at −40 °C for 2 days afforded orange crystals of **13**. Yield: 68%, 0.208 g. Mp: 164−168 °C (dec). ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.99 (d, 2- or 4-H, *J* = 7.7 Hz, 1H), 7.70 (s, 5-H, 1H), 7.56 (td, 3-H, *J* = 7.6 Hz, J_{HP} = 1.2 Hz, 1H), 7.29 (dd, 2- or 4-H, *J* = 7.5 Hz, J_{HP} = 4.2 Hz, 1H), 7.07 (d, 7-H, J_{PH} = 3.8 Hz, 1H), 6.96 (s, *p*-H, 1H), 6.85 (s, *o*-H, 2H), 4.74 (d, C*H*(cymene), *J* = 5.9 Hz, 1H), 4.68 (d, C*H*(cymene), *J* = 5.9 Hz, 1H), 4.61 (d, C*H*(cymene), *J* = 5.9 Hz, 1H), 4.50 (d, C*H*(cymene), *J* = 5.9 Hz, 1H), 2.69 (s, 6- or 8-C*H*$_3$, 3H), 2.49 (s, 6- or 8-C*H*$_3$, 3H), 2.32 (s, *m*-C*H*$_3$, 6H), 2.08 (sept, C*H*Me$_2$(cymene), *J* = 6.9 Hz, 1H), 1.95 (d, J_{PH} = 12.6 Hz, P−C*H*$_3$, 3H), 1.66 (s, C*H*$_3$-(cymene), 3H), 0.95 (d, CH*Me*$_2$(cymene), *J* = 6.9 Hz, 3H), 0.92 (d, CH*Me*$_2$(cymene), *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (90.57 MHz, $CDCl_3$): δ 147.49 (d, J_{PC} = 10 Hz), 141.94 (d, J_{PC} = 12 Hz), 141.71 (d, J_{PC} = 12 Hz), 141.10 (d, J_{PC} = 2 Hz), 140.94 (d, J_{PC} = 11 Hz), 140.81 (d, J_{PC} = 1 Hz), 138.69 (d, J_{PC} = 45 Hz), 136.95, 135.45 (d, J_{PC} = 47 Hz), 131.85 (d, J_{PC} = 10 Hz), 131.58 (d, J_{PC} = 8 Hz), 130.44, 129.61, 128.00, 119.61 (d, J_{PC} = 6 Hz), 119.20 (d, J_{PC} = 6 Hz), 106.06 (*C*-Me(cymene)), 98.34 (*C*CHMe$_2$-(cymene)), 88.74 (d, C*H*(cymene), J_{PC} = 6 Hz), 86.89 (d, C*H*(cymene), J_{PC} = 4 Hz), 85.99 (d, C*H*(cymene), J_{PC} = 5 Hz), 85.30 (d, C*H*(cymene), J_{PC} = 5 Hz), 29.87 (*C*HMe$_2$(cymene)), 22.31 (*C*H$_3$), 22.12 (*C*H$_3$), 21.87 (*C*H$_3$), 21.50 (*C*H$_3$), 21.37 (*m*-*C*H$_3$), 9.00 (d, P-*C*H$_3$, J_{PC} = 25 Hz). ^{31}P{^{1}H} NMR (121.47 MHz, C_6D_6): δ 24.6 (s). MS (ESI, $CHCl_3$ solution): *m*/*z* 601.14 (calcd 601.14 for M − Cl$^-$).

X-ray Crystallography. Crystals of **11** were obtained by crystallization from a concentrated hexanes/toluene solution of **11** at room temperature, crystals of **12** from benzene solution at 3−4 °C, and crystals of **13**·$CHCl_3$ from chloroform solution at room temperature. The crystals (**11** and **12**) were removed from the Schlenk tube under a stream of N_2 gas and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[23] The data for **11** were collected at 173(2) K on a Siemens P4 diffractometer and those for **12** and **13**·$CHCl_3$ at 120(2) and 153(2) K, respectively, on a Bruker Apex diffractometer using Mo K$_\alpha$ (λ = 0.71073 Å) radiation. The data were corrected for Lorentz and polarization effects. Absorption corrections using a multiscan method from equivalent reflections were applied for **12** and **13**·$CHCl_3$. The structures were solved by direct methods using the SHELXTL program suite, version 5.1, for **11** and version 6.1[24] for **12** and **13**·$CHCl_3$; the structures were refined by full-matrix least-squares on F^2, including all reflections. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in the refinement with idealized parameters. Phosphafluorene **11** crystallized in the space group $P\bar{1}$ with two independent molecules in the symmetric unit. As both molecules are essentially identical, the discussion in the text focuses on one of the two molecules. The data for the second molecule can be obtained from the Supporting Information. Some details of the crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Tables 2−4. Further details are given in the Supporting Information.

Results and Discussion

Ligand Synthesis. The new terphenyldichlorophosphine 2,6-(3,5-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$PCl$_2$, **1**, and the terphenyldichloroarsine 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$AsCl$_2$, **2**, have been synthesized in good to moderate yields by the reaction of the corresponding *m*-terphenylithium precursor with PCl_3 or $AsCl_3$ as colorless to pale yellow crystalline solids following established procedures.[15,17,18] Contrary to dichlorophosphines, the dichloroarsine **2** is stable toward air and moisture. After we[17] and others[15,25] found that phosphinidene-based schemes for the synthesis of unsymmetrical 9-phosphafluorenes are limited to very few examples, we began to investigate Friedel−Crafts type chemistry as a means for P−C bond formation. In fact, $PhPCl_2$ has been prepared by the reaction of PCl_3 with benzene in the presence of $AlCl_3$.[26] Test reactions on the NMR tube scale involving the reactions of dichlorophosphines **1** or 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$PCl$_2$, **3**,[17] in C_6D_6 solution with 1 equiv of $AlCl_3$ at room temperature resulted in the rapid separation of a yellow to yellow-orange oil at the bottom of the NMR tube. Subsequent addition of excess pyridine led to the complete dissolution of the oil, and the ^{1}H NMR and ^{31}P NMR spectra showed the formation

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Table 1. Crystal Data and Structural Refinement Details for **11**, **12**, and **13**·$CHCl_3$

	11	**12**	**13**·$CHCl_3$
empirical formula	$C_{23}H_{23}P$	$C_{27}H_{23}FeO_4P$	$C_{34}H_{38}Cl_5PRu$
fw	330.38	498.27	755.93
T (K)	173(2)	120(2)	120(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.069(4)	7.7148(3)	11.0207(16)
b (Å)	11.6728(15)	10.8237(5)	12.3536(18)
c (Å)	15.0716(17)	14.6848(6)	12.8898(18)
α (deg)	81.312(8)	80.1070(10)	79.197(2)
β (deg)	69.950(18)	81.8550(10)	76.300(2)
γ (deg)	81.96(2)	77.3020(10)	76.714(2)
V (Å^3)	1800.2(7)	1171.53(9)	1642.8(4)
Z	4	2	2
D_{calcd} (Mg/m^3)	1.219	1.413	1.528
μ(Mo Kα) (mm^{-1})	0.153	0.743	0.956
F(000)	704	516	772
crystal size (mm^3)	0.52 × 0.48 × 0.46	0.38 × 0.26 × 0.22	0.58 × 0.44 × 0.34
cryst color and habit	colorless prism	yellow prism	red prism
$2\theta_{max}$ (deg)	50.00	53.00	53.00
no. of observations	6319	4759	6745
no. of variables	444	303	378
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0387	0.0777	0.0250
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.1042	0.0781	0.0667
GOF on F^2	1.018	1.029	1.065
largest diff. peak (e Å^{-3})	0.313	0.468	0.697

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **11**

P(1)−C(14)	1.8335(18)	C(14)−P(1)−C(22)	89.99(8)
P(1)−C(22)	1.8170(18)	C(14)−P(1)−C(23)	101.46(8)
P(1)−C(23)	1.8464(19)	C(22)−P(1)−C(23)	102.62(8)
C(13)−C(14)	1.411(2)	C(13)−C(14)−P(1)	111.01(13)
C(13)−C(15)	1.470(2)	C(14)−C(13)−C(15)	113.49(15)
C(15)−C(22)	1.403(3)	C(13)−C(15)−C(22)	113.02(15)
		C(15)−C(22)−P(1)	112.18(13)

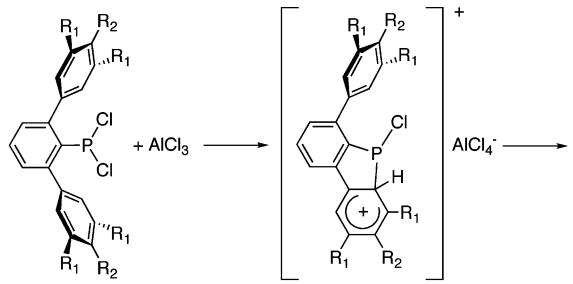
Table 3. Selected Bond Lengths (Å) and Angles (deg) for **12**

Fe(1)−C(24)	1.7933(18)	C(24)−Fe(1)−C(26)	122.22(7)
Fe(1)−C(25)	1.7923(18)	C(24)−Fe(1)−P(1)	117.70(6)
Fe(1)−C(26)	1.7748(15)	C(26)−Fe(1)−P(1)	120.07(5)
Fe(1)−C(27)	1.7961(17)	C(25)−Fe(1)−C(27)	175.21(7)
P(1)−C(14)	1.8275(14)	C(14)−P(1)−C(22)	91.28(6)
P(1)−C(22)	1.8216(14)	C(14)−P(1)−C(23)	104.95(6)
P(1)−C(23)	1.8307(14)	C(22)−P(1)−C(23)	102.19(6)
		C(14)−P(1)−Fe(1)	118.80(4)
		C(22)−P(1)−Fe(1)	117.25(5)
		C(23)−P(1)−Fe(1)	118.11(5)

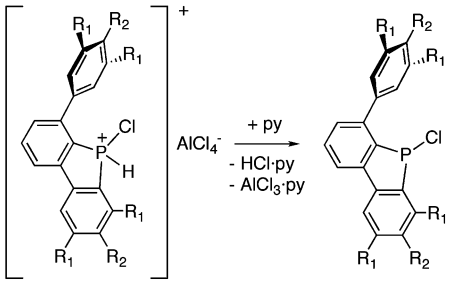
Table 4. Selected Bond Lengths (Å) and Angles (deg) for 13·$CHCl_3$

Ru(1)−P(1)	2.3593(5)	P(1)−Ru(1)−Cl(1)	87.313(18)
Ru(1)−Cl(1)	2.4022(5)	P(1)−Ru(1)−Cl(2)	88.391(19)
Ru(1)−Cl(2)	2.4066(5)	Cl(1)−Ru(1)−Cl(2)	84.44(2)
Ru(1)−C_{cymene}	2.213(29)avg.	C(14)−P(1)−C(22)	91.61(9)
P(1)−C(14)	1.8335(18)	C(14)−P(1)−C(23)	111.10(9)
P(1)−C(22)	1.8279(19)	C(22)−P(1)−C(23)	105.82(9)
P(1)−C(23)	1.8151(19)	C(14)−P(1)−Ru(1)	110.44(6)
		C(22)−P(1)−Ru(1)	117.09(6)
		C(23)−P(1)−Ru(1)	117.76(6)

of corresponding 9-phosphafluorenes **4** and **5** as the only phosphorus-containing species (eq 1). Evidence for the formulation of the benzene insoluble oil (clathrate) being a phosphonium salt is found in the presence of a doublet with a P−H coupling constant of 618 Hz in the ^{31}P NMR spectrum ($\delta = 30.1$) of the oil derived from **1** and $AlCl_3$ after isolation and redissolution in $CDCl_3$. $^1J_{PH}$ coupling constants in the range of 436−642 Hz have been observed for tertiary phosphonium salts.[27]



R_1 = Me, R_2 = H, **1**
R_1 = H, R_2 = *t*-Bu, **3**



(1)

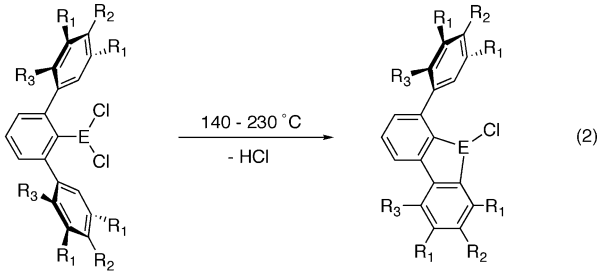
R_1 = Me, R_2 = H, **4**
R_1 = H, R_2 = *t*-Bu, **5**

Whereas the NMR scale experiments indicated selective and essentially quantitative formation of the 9-phosphafluorenes, scaling to the 1−5 mmol scale was less successful. This is mainly due to the practical difficulties in separating the 9-phosphafluorenes from the side products, HCl·py and $AlCl_3$·py. Nevertheless, this method allowed for a relatively convenient synthesis of unsymmetrical 9-phosphafluorenes

(27) *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press: Boca Raton, FL, 1991.

from readily available *m*-terphenyldichlorophosphines. We also reacted 2,6-$Mes_2C_6H_3PCl_2$, **6**, (Mes = 2,4,6-$Me_3C_6H_2$)[18] with $AlCl_3$ in benzene solution. As **6** does not possess hydrogen atoms in the o- or o′′-position, putative phosphenium intermediate $[2,6\text{-}Mes_2C_6H_3PCl]^+[AlCl_4]^-$ reacted with the solvent, and phenyl-substituted phosphine 2,6-$Mes_2C_6H_3P$(Cl)Ph, **7**, was isolated after the addition of excess pyridine. This reaction was also performed as an NMR scale experiment using C_6D_6 as solvent; in this case, phosphonium salt $[2,6\text{-}Mes_2C_6H_3P(D)(Cl)(C_6D_5)]^+[AlCl_4]^-$ was sufficiently soluble to allow the detection of its signal, a 1:1:1 triplet with $^1J_{PD}$ = 86 Hz at 27.2 ppm, in the ^{31}P NMR spectrum. Similar to the 9-phosphafluorene synthesis discussed before, the isolated yields of **7** were low because of the difficulty in removing the side products.

It has been reported that a 9-arsafluorene can be obtained by simple refluxing of a mixture of $AsCl_3$ and 3,3′-dimethoxybiphenyl.[28] Apparently, $AsCl_3$ is reactive enough to attack activated aromatic systems with As−C bond formation. Reasoning that **2** corresponds to the $AsCl_2$-substituted biphenyl intermediate in the above reaction, we investigated the thermolysis of **2**. Heating of **2** to above its melting point at ca. 140 °C caused gas evolution and a color change to yellow. The resulting yellow solid was identified as the 9-arsafluorene **8** (eq 2). Interestingly, the same reaction also takes place in solution at 70 °C over a period of 3−4 h. The analogous 9-phosphafluorene formation has not been reported to date. However, knowing that $PhPCl_2$ can be prepared by the reaction of PCl_3 with benzene in the gas phase at the relatively high temperature of 600 °C,[29] we then investigated the thermolysis of the dichlorophosphines **1**, **3**, and 2,6-$(2\text{-}MeC_6H_4)_2C_6H_3PCl_2$, **9**. Indeed, 9-phosphafluorene formation took place, albeit at somewhat higher temperatures (200−230 °C) than those for the arsenic compound **2**.



E = P; R_1 = Me; R_2, R_3 = H; **1**
E = As; R_1, R_3 = H; R_2 = *t*-Bu; **2**
E = P; R_1, R_3 = H; R_2 = *t*-Bu; **3**
E = P; R_1, R_2 = H; R_3 = Me; **9**

E = P; R_1 = Me; R_2, R_3 = H; **4**
E = As; R_1, R_3 = H; R_2 = *t*-Bu; **8**
E = P; R_1, R_3 = H; R_2 = *t*-Bu; **5**
E = P; R_1, R_2 = H; R_3 = Me; **10**

As was the case for the related 9-borafluorenes,[30] the C−H activation in dichlorophosphine **9** possessing flanking *o*-tolyl groups requires a higher temperature (230 °C) and longer reaction time (20 min) than those for **1** and **3**, presumably because of steric repulsion brought about by the neighboring hydrogen in the 4-position and methyl in the 5-position in **10**.

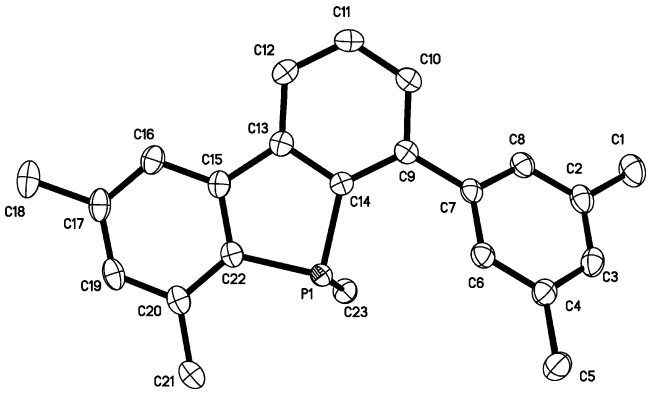


Figure 1. Thermal ellipsoid plot (40% probability level ellipsoids) showing the molecular structure of one of the two independent molecules of **11**. Hydrogen atoms are omitted for clarity.

The P−Cl bond in the 9-phosphafluorenes is reactive and thus easily substituted. As an initial example, we report here the synthesis of the methyl derivative 1-(3,5-dimethylphenyl)-6,8,9-trimethyl-9-phosphafluorene, **11**, and its application as a ligand in iron and ruthenium complexes. Reaction of **4** with MeLi or MeMgBr in toluene or hexane solution afforded the 9-methyl-9-phosphafluorene **11** in good yield. Compound **11** was also characterized by X-ray diffraction, and the structure is shown in Figure 1. Compound **11** features an almost-planar (deviation from the mean plane: 0.0246 Å) 9-phosphafluorene unit with a strongly pyramidal phosphorus, as illustrated by the sum of the angles at P(1) with a value of 294.1(2)° and an angle between the P(1)−C(23) vector and the phosphafluorene plane of 69.9°. The $P-C_{Ar}$ bond distances of 1.8170(18) and 1.8335(18) Å are shorter than the $P-C_{Me}$ distance of 1.8468(19) Å, which may be explained by the difference in carbon radii depending on the hybridization (here, sp^2 vs sp^3). Similar metric parameters have been found for the other two *m*-terphenyl-derived 9-phosphafluorenes whose structures have been reported to date: 1-(2,4,6-triisopropylphenyl)-5,7,9-triisopropyl-9-phosphafluorene[15] and 9,9′-bis-[1-(2,6-dichlorophenyl)-5-chloro-9-phosphafluorene].[31] The flanking C(1)−C(8) aryl group in **11** is rotated out of the 9-phosphafluorene plane by 38.2° but is freely rotating in solution, as shown by the equivalence of the C(1) and C(5) methyl groups and the *o*-hydrogens (H(6A) and H(8A) in the ^{1}H NMR spectra).

Complex Formation. 9-Methyl-9-phosphafluorene **11** readily reacts with $Fe_2(CO)_9$ and $[(\eta^6\text{-cymene})RuCl_2]_2$ at room temperature to afford the complexes **11**·$Fe(CO)_4$, **12**, and **11**·$Ru(\eta^6\text{-cymene})Cl_2$, **13** (eq 3).

Yellow crystals of **12** were obtained by crystallization from benzene (Figure 2). The phosphine ligand occupies an equatorial position in the slightly distorted $(CO)_4FeL$ trigonal bipyramid. This is rather unusual for a phosphine, because this position tends to favor π-acids such as olefins,[32] phosphaalkenes,[33] and diphosphenes.[34] A search of the

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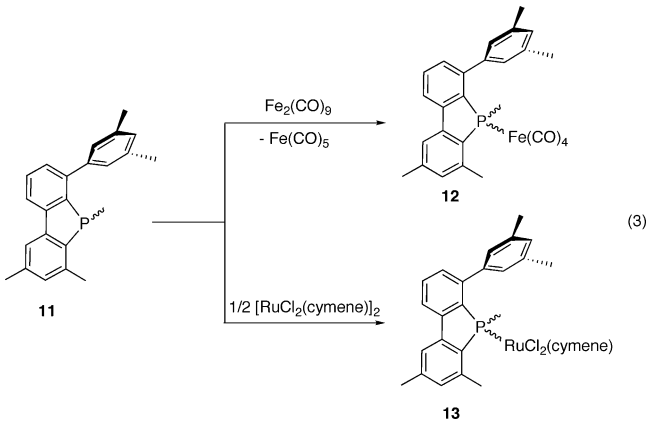

Cambridge Structural Database resulted in only six examples of (phosphine)$Fe(CO)_4$ complexes in which the phosphine ligand occupies the equatorial position, and in most of these cases, the large size of the ligand may have favored this less-crowded coordination site.[35−38] The plane of the phosphafluorene unit is rotated by 57.8° out of the Fe equatorial plane in order to minimize ligand···CO contacts. In fact, the shortest ligand···CO distances are C(25)···H(23B) and O(2)···H(3B), with values of 2.845 and 2.970 Å, respectively. The Fe(1)−P(1) distance of 2.2336(4) Å is typical for this type of complex, as are the Fe−C distances, with an average value of 1.789 Å.[35,37,39] The C(25)−Fe(1)−C(27) angle is close to linear, with a value of 175.21(7)°, and the angles in the equatorial plane deviate only slightly from the ideal 120°. The observation of only one doublet at 216.65 ppm with $^2J_{PC} = 14.9$ Hz for the carbonyl carbons in the $^{13}C\{^1H\}$ NMR spectrum of **12** at room temperature indicates structural fluxionality in solution, a common property of this type of complex.[40] The CO stretching frequency (A_1) with a value of 2050.6 cm^{-1} is close to those reported for $Ph_3PFe(CO)_4$ (2050.5 cm^{-1}), $Me_2PhPFe(CO)_4$ (2050.5 cm^{-1}), or $Bu_3PFe(CO)_4$ (2046.7 cm^{-1}),[32] suggesting donor properties similar to those of phosphafluorene **11**.

Ruthenium complex **13** was crystallized from chloroform. Unlike **12**, complex **13** is air stable. It is only slightly soluble in hydrocarbons but readily dissolves in dichloromethane or chloroform. Its solid-state structure (Figure 3) features the piano stool arrangement typical for (η^6-arene)$RuCl_2$(phosphine) complexes.[41,42] The P(1)−Ru(1) distance with a value of 2.3593(5) Å is slightly longer than those reported previously

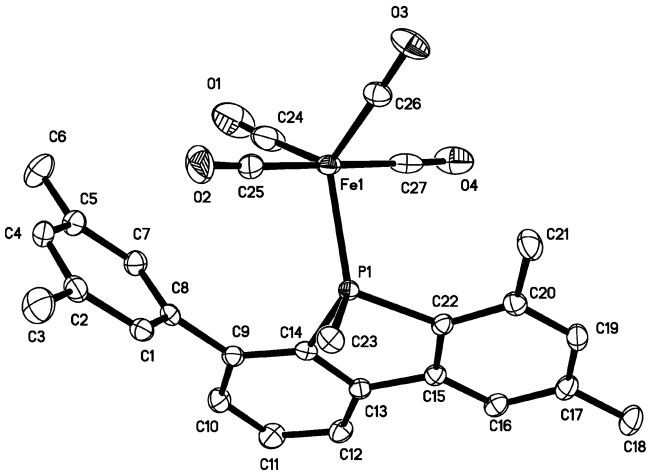

Figure 2. Thermal ellipsoid plot (40% probability level ellipsoids) showing the molecular structure of **12**. Hydrogen atoms are omitted for clarity.

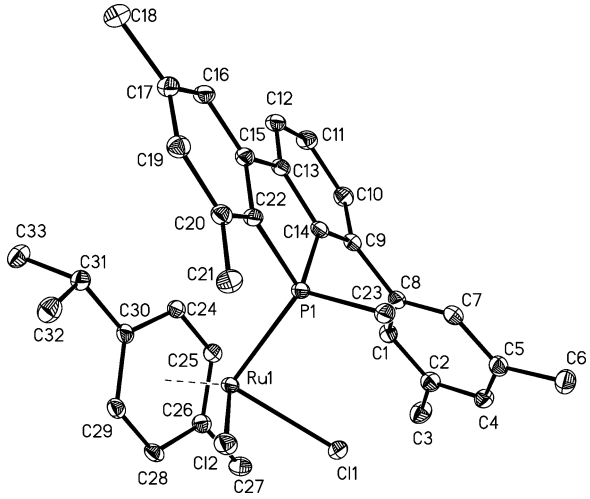

Figure 3. Thermal ellipsoid plot (30% probability level ellipsoids) showing the molecular structure of **13**. Hydrogen atoms are omitted for clarity.

(2.317−2.347 Å),[41−43] whereas the average Ru−Cl and Ru−C distances, with values of 2.404 and 2.213 Å, are within the normal range (Table 4). Contrary to the structure of **12**, the phosphafluorene framework is not planar. The two annulated aromatic rings are rotated by 3.3° around their connecting C(13)−C(15) bond, and P(1) is displaced from the C(14)−C(13)−C(15)−C(22) plane by 0.228 Å. In addition, the *p*-cymene ring and the other ligands are in a mutually eclipsed rather than the more commonly found staggered conformation. These features may be due to the steric influences of the relatively large phosphafluorene ligand.

Summary

Simple thermolysis of readily accessible *m*-terphenyldichlorophosphines and -arsines afforded unsymmetrical 9-chloro-9-phosphafluorenes and -9-arsafluorenes in close to quantitative yields. After methylation, resulting unsym-

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metrical 9-methyl-9-phosphafluorene **11** was shown to be a good ligand for iron and ruthenium complexes. Investigations of the mechanism and scope of the P(As)−C bond formation are in progress.

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Supporting Information Available: X-ray crystallographic data in CIF format. The material is available free of charge via the Internet at http://pubs.acs.org.

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