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Article

Size Matters: Room Temperature P–C Bond Formation Through C–H Activation in *m*-Terphenyldiiodophosphines

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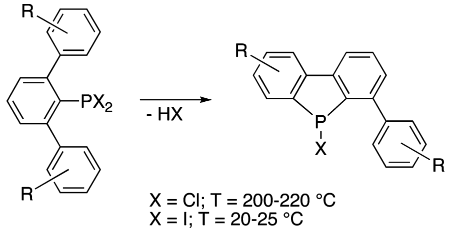
m-Terphenyl- and biphenyl-2-diiodophosphines, $TerphPI_2$ and $BiphPI_2$, have been obtained by halide exchange from the chloro derivatives $TerphPCl_2$ and $BiphPCl_2$ and excess LiI in a benzene solution at room temperature. Whereas $BiphPI_2$ compounds are stable, the $TerphPI_2$ species undergo intramolecular C–H activation at room temperature and cyclize to form unsymmetrical 9-iodo-9-phosphafluorenes 1-(3,5-dimethylphenyl)-6,8-dimethyl-9-iodo-9-phosphafluorene, **4**; 1-(4-*t*-butylphenyl)-7-*t*-butyl-9-iodo-9-phosphafluorene, **5**; and 1-(2-methylphenyl)-5-methyl-9-iodo-9-phosphafluorene, **6**, albeit the latter reaction is rather slow due to unfavorable steric interactions. Cyclization of the alkyl-substituted 4,4′-di-*tert*-butyl-biphenyl-2-diiodophosphine, **11**, is slow in refluxing benzene solution, but faster than that for the parent biphenyl-2-diiodophosphine. Ab initio and density functional theory calculations are in agreement with an electrophilic aromatic substitution mechanism that is facilitated by steric strains in the terphenyl compounds $2,6\text{-}(3,5\text{-}Me_2C_6H_3)_2C_6H_3PI_2$, **1**; $2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3PI_2$, **2**; and $2,6\text{-}(2\text{-}MeC_6H_4)_2C_6H_3PI_2$, **3**. All new compounds have been characterized by multinuclear NMR spectroscopy and direct analysis in real time mass spectrometry. 9-Iodo-9-phosphafluorene, **12**, was also analyzed by X-ray diffraction.

Introduction

The common procedure for the formation of aryl phosphines involves the reaction of an aryl lithium or aryl Grignard reagent with a P(III) halide, alkoxide, or aryloxide.[1] Simple phosphines such as phenyl- or tolyldichlorophosphines $ArPCl_2$ can also be obtained via a Friedel–Crafts-type reaction between PCl_3 and the arene in the presence of $AlCl_3$.[2]Direct phosphination of an arene with PCl_3 is possible but requires exceedingly high temperatures. For instance, 600 °C is needed for the formation of $PhPCl_2$ from PCl_3 and benzene.[1] We have recently reported the formation of unsymmetrical 9-phosphafluorenes from *m*-terphenyldichlorophosphines, $TerphPCl_2$, by a simple thermolysis route at only 200–220 °C (eq 1, X = Cl).[3] In other words, the reaction temperature can be lowered significantly under certain conditions such as a close proximity of the phosphorus center and the targeted C–H bond, for example, in a cyclophosphination.

 (1)

Here, we report that the reaction temperature can be further reduced to room temperature through the employment of the iodo precursors, $TerphPI_2$ (eq 1, X = I). We have also investigated the extension toward biphenyl-2-diiodophosphines and have supported our findings with ab initio and density functional theory (DFT) calculations.

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Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies or Vacuum Atmospheres drybox. Solvents were freshly distilled under N_2 from sodium, potassium, a sodium/potassium alloy, or calcium hydride and degassed twice prior to use, or they were dispensed from a commercial Grubbs-type solvent purification system. Compounds 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3PCl_2$, **14**;[3] 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3PCl_2$;[4] 2,6-(2-$MeC_6H_4)_2C_6H_3PCl_2$;[4] and 2-bromo-4,4′-di-*tert*-butylbiphenyl[5] were prepared according to literature procedures. All other chemicals were purchased and used as received with the exception of lithium iodide, which was dried at 60 °C under reduced pressure for 3 h before use. NMR spectra were recorded on a Varian Mercury 300 MHz, a Varian Unity Plus 400 MHz, a Bruker AMX 360 MHz, a Bruker Avance 400 MHz, or a JEOL ECX-300 spectrometer. ^1H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or $CDCl_3$ as an internal reference ($\delta = 7.15$ or 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent signal ($\delta = 128.0$ or 77.0 ppm) and ^{31}P NMR spectra to external 85% H_3PO_4. Mass spectra were recorded with a JEOL AccuTOF direct analysis in real time spectrometer. Melting points were determined in Pyrex capillary tubes sealed under nitrogen with a Mel-Temp apparatus and are uncorrected.

1-(3,5-Dimethylphenyl)-6,8-dimethyl-9-iodo-9-phosphafluorene, 4[6]. Benzene (20 mL) was added to a mixture of 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3PCl_2$ (0.50 g, 1.3 mmol) and finely powdered LiI (0.40 g, 3.0 mmol), and the reaction mixture was stirred at room temperature for 24 h. The yellow suspension was filtered, and the volatile material was removed under reduced pressure to afford a yellow solid, which was recrystallized from hexanes. Yield: 0.49 g, 86%. Mp: 195–200 °C. ^1H NMR (C_6D_6, 400.13 MHz): δ 7.49 (m, H-3, 1H), 7.38 (s, *o*-H(xylyl), 2H), 7.28 (s, H-5 or H-7, 1H), 7.20 (m, H-2, H-4, 2H), 6.88 (s, *p*-H(xylyl), 1H), 6.6 (d, $J_{PH} = 4.4$ Hz, H-5 or H-7, 1H), 2.33 (s, CH_3-8, 3H), 2.23 (s, *m*-CH_3, 6H), 2.12 (s, CH_3-6, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz): δ 147.29 (d, $J_{PC} = 18.9$ Hz), 145.71, 144.90, 141.78 (d, $J_{PC} = 19.4$ Hz), 141.50 (d, $J_{PC} = 22.6$ Hz), 139.91 (d, $J_{PC} = 29.4$ Hz), 138.24 (*m*-C(xylyl)), 136.83 (d, $J_{PC} = 26.9$ Hz), 131.58 (C-2 or C-4), 130.59 (d, $J_{PC} = 2.3$ Hz, C-5 or C-7), 129.87 (*p*-C(xylyl)), 128.97 (d, $J_{PC} = 1.5$ Hz, C-2 or C-4), 126.63 (d, $J_{PC} = 5.3$ Hz, *o*-C(xylyl)), 121.03 (C-3), 120.75 (C-5 or C-7), 21.49 (CH_3-6), 21.41 (CH_3(xylyl)), 21.03 (d, $J_{PC} = 8.1$ Hz, CH_3-8). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.47 MHz): δ 11.4. Mass spectrometry: *m*/*z* 443.04025 (M + H^+). Calcd for $C_{22}H_{21}IP^+$: 443.04256.

1-(4-*t*-Butylphenyl)-7-*t*-butyl-9-iodo-9-phosphafluorene, 5. A solution of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3PCl_2$ (0.50 g, 1.1 mmol) in benzene (30 mL) was added to finely ground LiI (0.45 g, 3.4 mmol), and the mixture was stirred at room temperature for 20 h. The yellow-orange supernatant liquor was decanted via canula from the colorless solid (LiI and LiCl). The volatile material was removed in vacuo to afford a yellow-orange solid. Recrystallization from hexanes at room temperature for 2 days gave yellow crystals of **5**. Yield: 0.27 g, 47%. Mp: 151–154 °C. ^1H NMR (C_6D_6, 400.13 MHz): δ 7.89 (dd, $J = 4.1$ Hz, 1.7 Hz; 1H), 7.73 (d, $J = 8.3$ Hz, *o*-H(4-*t*BuC_6H_4), 2H), 7.49 (m, 2H), 7.40 (d, $J = 8.3$ Hz, *m*-H(4-*t*BuC_6H_4), 2H), 7.22 (m, 3H), 1.23 (s, CH_3(4-*t*BuC_6H_4), 9H), 1.12 (s, CH_3, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz): δ 152.07 (d, $J_{PC} = 5.3$ Hz, C-7), 151.06 (*p*-C(4-*t*-BuC_6H_4)), 147.06 (d, $J_{PC} = 18.8$ Hz), 145.40, 141.79, 141.70 (d, $J_{PC} = 25.5$ Hz), 139.58 (d, $J_{PC} = 31.0$ Hz), 138.95, 131.84, 128.92, 128.48 (d, $J_{PC} = 5.4$ Hz, *o*-C(4-*t*-BuC_6H_4)), 126.00 (*m*-C(4-*t*-BuC_6H_4)), 122.09, 120.72, 34.85 (7-*C*($CH_3)_3$), 34.62 (*p*-*C*($CH_3)_3$), 31.36 (*p*-C($CH_3)_3$), 31.22 (7-C($CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.47 MHz): δ 11.1. Mass spectrometry: *m*/*z* 499.10318 (M + H^+). Calcd for $C_{26}H_{29}IP^+$: 499.10516.

1-(2-Methylphenyl)-5-methyl-9-iodo-9-phosphafluorene, 6. A solution of 2,6-(2-$MeC_6H_4)_2C_6H_3PCl_2$ (0.17 g, 0.5 mmol) in benzene (10 mL) was added to finely ground LiI (0.20 g, 1.5 mmol), and the mixture was stirred at room temperature for 5 days. The red-orange supernatant liquor was transferred via canula from the colorless solid (LiI and LiCl). The volatile material was removed in vacuo to afford a viscous orange oil, which still contained approximately 30% of the unreacted precursor. The oil was heated at 73 °C for 53 min to afford an orange oil which partially solidified after standing at room temperature for 1 day. Crystallization from a CH_2Cl_2/hexane solution (2 mL) at −20 °C gave **6** as a yellow crystalline solid. Yield: 0.085 g, 41%. Mp: 114–124 °C. ^1H NMR (C_6D_6, 400.13 MHz): δ 7.70 (t, $J = 9.4$ Hz, 1H), 7.50 (s, broad, 1.3 H), 7.32 (d, $J = 6.6$ Hz, 0.6H), 7.19 (d, $J = 4.9$ Hz, 2H), 6.98 (dd, $J = 7.4$ Hz, 4.2 Hz, 1 H), 6.85 (td, $J = 7.3$ Hz, 3.0 Hz, 1H), 6.81 (d, $J = 7.2$ Hz, 1H), 2.29 (s, 5-CH_3, 3H), 2.28 (s, CH_3(2-methylphenyl), 1.8H), 2.06 (s, CH_3(2-methylphenyl), 1.2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz): δ 146.9 (m), 142.3 (m), 140.9 (m), 135.56, 135.46, 135.29, 134.19, 131.78, 130.94 (d, $J_{PC} = 18.4$ Hz), 130.39 (d, $J_{PC} = 29.8$ Hz), 129.89 (d, $J_{PC} = 28.4$ Hz), 129.67 (d, $J_{PC} = 2.8$ Hz), 129.97, 128.62, 126.16, 126.09, 125.22, 125.06, 22.44 (5-CH_3), 20.98 (2-*methyl*-phenyl), 20.03 (d, $J_{PC} = 8.0$ Hz (2-*methyl*-phenyl)).$^{31}P\{^1H\}$ NMR (C_6D_6, 121.65 MHz): δ 8.3 (65%), 7.9 (35%): syn and anti mixture. Mass spectrometry: *m*/*z* 415.00919 (M + H^+). Calcd for $C_{20}H_{17}IP^+$: 415.01126.

Reaction of (2-biphenyl)MgBr with PCl_3. A solution of 2-bromobiphenyl (2.61 g, 11.2 mmol) in tetrahydrofuran (THF; 20 mL) was dried by heating over calcium hydride at 58 °C for 2 days. After cooling to room temperature and filtration, the solution was added to magnesium turnings (0.30 g, 12.5 mmol), which had been activated by grinding and stirring in vacuo for 2 h. After the addition of half of the solution, 1,2-dibromoethane (30 μL, 0.35 mmol) was added, and the mixture was briefly heated to reflux with a heat gun. After 1–2 min, a colorless solid began to precipitate, indicating that the reaction had begun. The mixture was stirred for 1 h, after which time the remaining half of the 2-bromo-biphenyl solution was added. Stirring overnight afforded a thick, colorless suspension which was diluted with THF (10 mL). The Grignard suspension was separated from the unreacted magnesium by transfer via canula into a clean flask, cooled to −78 °C, and freshly distilled PCl_3 (2.0 mL, 23 mmol) was added dropwise via syringe over a period of 3 min. No reaction was observed. The mixture was held at −78 °C for 30 min, slowly warmed to room temperature, and stirred overnight to give a clear, pale yellow solution. The volatile material was removed in vacuo, affording a pale yellow, sticky solid, which was extracted with hexanes (60 mL). After filtration and removal of the solvent in vacuo, a pale yellow, mobile liquid was obtained, which was identified by ^{31}P NMR spectroscopy as a 1.4:2.2:1 mixture of (2-biphenyl)PCl_2, **7a** ($\delta_P = 159.7$ ppm); (2-biphenyl)PClBr, **7b** ($\delta_P = 156.8$ ppm); and (2-biphenyl)PBr_2, **7c** ($\delta_P = 152.6$ ppm). Yield: 2.04 g, 61% based on 2-bromobiphenyl. ^1H NMR (C_6D_6, 400.13 MHz): δ 8.40 (ddd, $J = 7.8$ Hz, 3.0 Hz,

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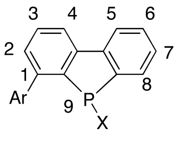
(6) Numbering scheme:



1.0 Hz, H-3, **7c**), 8.31 (ddd, $J = 7.8$ Hz, 3.3 Hz, 1.0 Hz, H-3, **7b**), 8.26 (ddd, $J = 7.7$ Hz, 3.6 Hz, 1.1 Hz, H-3, **7a**).

Reaction of (4,4′-*t*-Bu$_2$-2-biphenyl)MgBr with PCl$_3$. Freshly distilled PCl$_3$ (1.57 g, 11.4 mmol) was added dropwise to a solution of (4,4′-*t*-Bu$_2$-2-biphenyl)MgBr [generated from 4,4′-*t*-Bu$_2$-2-biphenylbromide (1.69 g, 3.8 mmol) and Mg turnings (0.13 g, 5.5 mmol) in THF at room temperature in analogy to **7**] in THF (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 1 h. The volatile material was removed under reduced pressure, and the orange residue was extracted with warm hexanes (50 mL, 62 °C). Removal of the solvent afforded a pale yellow viscous oil, which was identified by ^{1}H NMR spectroscopy as a 1:2.2:1.5 mixture of three phosphorus-containing compounds, most likely (4,4′-*t*-Bu$_2$-2-biphenyl)PCl$_2$, **8a**; (4,4′-*t*-Bu$_2$-2-biphenyl)PBr$_2$, **8c**; and (4,4′-*t*-Bu$_2$-2-biphenyl)PClBr, **8b**. This characterization is based on the presence of three signals due to the hydrogen next to the PX$_2$ group (H-3) at 8.74 (dd, $J =$ 3.3 Hz, 2.0 Hz), 8.67 (dd, $J = 3.6$ Hz, 2.0 Hz), and 8.61 (dd, $J =$ 3.9 Hz, 2.0 Hz). The mixture also contained approximately 10–15% 4,4′-*t*-Bu$_2$-biphenyl.

9-Bromo(chloro)-9-phosphafluorene, 9. Mixture **7** (1.26 g, 4.2 mmol) was placed in a Schlenk flask and subsequently heated at 224–228 °C for 50 min, during which time a color change to dark yellow was observed. The yellow oil solidified upon cooling to room temperature and was purified by crystallization from hexanes (100 mL) at −20 °C. Yield: 0.80 g, 72%. Mp: 88–95 °C. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 7.52 (dd, $J = 7.4$ Hz, J_{HP}= 3.7 Hz, H-1, H-8, 2H), 7.29 (d, $J = 7.7$ Hz, H-4, H-5, 2H), 7.00 (t, $J = 7.5$ Hz, H-3, H-6, 2H), 6.90 (tdd, $J = 7.4$ Hz, $J_{HP} = 3.2$ Hz, $J = 1.0$ Hz, H-2, H-7, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 100.61 MHz): δ 144.19, 141.51 (d, $^1J_{PC} = 26.5$ Hz), 131.93 (d, $J_{PC} = 26.7$ Hz, C-1, C-8), 131.30 (C-4, C-5), 128.67 (d, $J_{PC} = 6.0$ Hz, C-2, C-7), 121.82 (C-4, C-5). ^{31}P{^{1}H} NMR (C_6D_6, 145.79 MHz): δ 67.9 (9-chloro-9-phosphafluorene,[7] **9a**, 3%), 48.7 (9-bromo-9-phosphafluorene, **9b**, 97%). Mass spectrometry: *m/z* 262.96143, 264.95999 (M + H$^+$). Calcd for $C_{12}H_9BrP^+$: 262.96252 and 264.96048.

Biphenyl-2-diiodophosphine, 10. A solution of the remainder of mixture **7** (maximal 10.3 mmol) in benzene (40 mL) was added to finely ground LiI powder. The solution turned yellow after a few minutes; stirring was continued for 3 days. Filtration followed by removal of the solvent under reduced pressure afforded an orange-golden oil. Dissolution into hexanes (100 mL), filtration, and concentration to ca. 30 mL resulted in the separation of a small amount of an orange oil. Cooling at −20 °C for 2 days gave yellow crystals (1.63 g), and a second crop was obtained from the concentrated mother liquor at −20 °C. Yield: 1.81 g, 40% based on biphenylbromide. Mp: 65–67 °C. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 8.50 (d, $J = 7.8$ Hz, 1H), 7.16 (m, Ph-H, obscured by C_6D_6), 7.07 (m, Ph-H, 3H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.85 (td, $J = 7.6$ Hz, 1.0 Hz, 1H), 6.76 (t, $J = 6.9$ Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 100.61 MHz): δ 143.46 (d, $J_{PC} = 39.9$ Hz), 140.10 (d, $J_{PC} = 9.6$ Hz), 133.85 (d, $J_{PC} = 68.9$ Hz), 132.01, 129.09 (d, $J_{PC} = 2.1$ Hz), 129.03, 128.76, 128.69, 128.63, 128.58. ^{31}P{^{1}H} NMR (C_6D_6, 145.78 MHz): δ 101.2 (s). Mass spectrometry: *m/z* 438.85996 (M + H$^+$). Calcd for $C_{12}H_{10}I_2P^+$: 438.86096.

4,4′-Di-*tert*-butyl-biphenyl-2-diiodophosphine, 11. A solution of mixture **8** (1.07 g, max. 2.9 mmol) in benzene (15 mL) was added to LiI powder (1.18 g, 8.8 mmol), upon which the solution immediately changed color to yellow. After 5 h, the volatile material was removed in vacuo, and the oily residue was extracted with hexanes (30 mL). Filtration, concentration to 4–5 mL, and cooling at −20 °C overnight afforded dark, yellow-brown crystals of **11**. These crystals were contaminated with ca. 5% di-*tert*-butyl-biphenyl, which could not be removed by recrystallization. Yield: 0.91 g, 57%. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 8.83 (s, broad, $w_{1/2} = 6.2$ Hz, 3-H, 1H), 7.30 (dd, $J = 8.2$ Hz, $J_{HP} = 2.9$ Hz, *o*-H(C_6H_4-*t*-Bu-4), 2H), 7.24 (d, $J =$ 8.2 Hz, *m*-H(C_6H_4-*t*-Bu-4), 2H), 7.10 (dd, $J = 8.0$ Hz, 1.8 Hz, 5-H, 1H), 6.94 (dd, $J = 8.0$ Hz, $J_{HP} = 6.8$ Hz, 6-H, 1H), 1.27 (s, 4-C(C*H*$_3$)$_3$, 9H), 1.18 (s, C(C*H*$_3$)$_3$(C_6H_4-*t*-Bu-4), 9H). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): 151.63 (4-C or *p*-C(C_6H_4-*t*-Bu-4)), 151.48 (4-C or *p*-C(C_6H_4-*t*-Bu-4)), 140.91 (d, $J_{PC} = 40.6$ Hz, 1-C), 137.78 (2-C), 137.41 (d, J_{PC} = 40.6 Hz, *i*-C(C_6H_4-*t*-Bu-4)), 133.58 (d, $J_{PC} = 68.8$ Hz, 2-C), 129.81 (5-C), 129.03 (d, $J_{PC} = 2.3$ Hz, 6-C), 128.66 (d, $J_{PC} = 6.7$ Hz, *o*-C(C_6H_4-*t*-Bu-4)), 125.76 (*m*-C(C_6H_4-*t*-Bu-4)), 35.17 (*p*-*C*(CH$_3$)$_3$(C_6H_4-*t*-Bu-4)), 34.62 (4-*C*(CH$_3$)$_3$), 31.30 (*p*-C(*C*H$_3$)$_3$(C_6H_4-*t*-Bu-4)), 31.13 (4-C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 121.65 MHz): δ 108.3. Mass spectrometry: *m/z* 550.98305 (M + H$^+$). Calcd for $C_{20}H_{26}I_2P^+$: 550.98616.

9-Iodo-9-phosphafluorene, 12. A Schlenk flask containing **10** (0.52 g, 1.2 mmol) was placed into a 170 °C oil bath. The solid melted, and a smooth gas evolution commenced after ca. 2 min and lasted for 15 min. The flask was removed from the oil bath and cooled to room temperature, and the volatile material (HI) was pumped off to afford a yellow-red solid. Crystallization from hexanes at −20 °C for 2 days gave orange crystals of **12**. Yield: 0.23 g, 62%. Mp: 105–107 °C. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 7.56 (dd, $J = 7.4$ Hz, $J_{HP} = 3.5$ Hz, H-1, H-8, 2H), 7.33 (d, $J =$ 7.7 Hz, H-4, H-5, 2H), 6.99 (t, $J = 7.5$ Hz, H-3, H-6, 2H), 6.90 (tdd, $J = 7.4$ Hz, $J_{HP} = 3.2$ Hz, $J = 0.8$ Hz, H-2, H-7, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 100.61 MHz): δ 144.10, 141.14 (d, $^1J_{PC} = 26.9$ Hz), 131.82 (d, $J_{PC} = 26.1$ Hz, C-1, C-8), 130.76 (C-3, C-6), 128.54 (d, $J_{PC} = 5.9$ Hz, C-2, C-7), 122.13 (C-4, C-5). ^{31}P{^{1}H} NMR (C_6D_6, 121.65 MHz): δ 5.2. Mass spectrometry: *m/z* 310.94694 (M + H$^+$). Calcd for $C_{12}H_9IP^+$: 310.94866.

9-Iodo-2,7-di-*tert*-butyl-9-phosphafluorene, 13. A Schlenk flask was charged with **11** (0.51 g, 0.9 mmol) and placed into a preheated oil bath at 180 °C. The crystals melted within 30 s and turned dark red; a smooth gas evolution commenced after 2 min and stopped after 10 min more. The product was cooled to room temperature, the HI byproduct was pumped off, and the dark red solid was dissolved in warm hexanes (15–20 mL). Cooling at −20 °C afforded a small amount of a dark solid, which was separated. The remaining orange-gold solution was concentrated to ca. 3 mL and cooled at −20 °C for 2 days to give a fine ochre powder, which was identified as **13** contaminated with approximately 15% di-*tert*-butyl-biphenyl. Further purification by either fractional crystallization or vacuum sublimation was unsuccessful. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 7.92 (dd, $J_{HP} = 4.2$ Hz, $J = 1.6$ Hz, H-1,8, 2H), 7.47 (d, $J = 8.1$ Hz, H-4,5, 2H), 7.25 (dd, $J = 8.1$ Hz, $J = 1.6$ Hz, H-3,6, 2H), 1.16 (s, C(C*H*$_3$)$_3$, 18H). ^{13}C{^{1}H} NMR (C_6D_5Br, 100.61 MHz): δ 151.40 (d, $J_{CP} = 5.2$ Hz, C2,7), 141.47 (C4A, 5A), 140.54 (d, J_{CP} = 26.2 Hz, C1A, 8A), 128.43 (d, $J_{CP} = 26.0$ Hz, C1,8), 126.78 (C3,6), 121.69 (C4,5), 34.84 (*C*(CH$_3$)$_3$), 31.37 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 121.65 MHz): δ 8.3. Mass spectrometry: *m/z* 423.07104 (M + H$^+$). Calcd for $C_{20}H_{25}IP^+$: 423.07386.

X-Ray Crystallography. Crystals of **12** were obtained by vacuum sublimation at 70 °C. The crystals were covered with a layer of hydrocarbon oil inside a drybox. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream. The data were collected at 95(2) K on a Bruker Apex diffractometer using Mo Kα ($\lambda = 0.710\ 73$ Å) radiation. An absorption correction using a multiscan method from equivalent reflections was applied. The structure was solved by the direct method using SHELXTL program suite version 6.12[8] and refined by full-matrix least-squares on F^2, including all

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(7) Teunissen, H. T.; Hansen, C. B.; Bickelhaupt, F. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1996**, *118*, 309–312.

(8) *SHELXTL*; Bruker ASX: Madison, WI.

Table 1. Crystallographic Data for **12**

	12
chemical formula	$C_{12}H_8IP$
fw	310.05
space group	$P2(1)/n$ (No. 14)
a	8.4166(14) Å
b	8.9856(15) Å
c	14.101(2) Å
β	91.757(3)°
V	1066.0(3) Å^3
Z	4
T	95(2) K
λ	0.71073 Å
D_{calcd}	1.932 g/cm^3
μ	3.108 mm^{-1}
$R_1{}^a$ [I > $2\sigma(I)$]	0.0285
$wR_2{}^b$ [I > $2\sigma(I)$]	0.0764

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

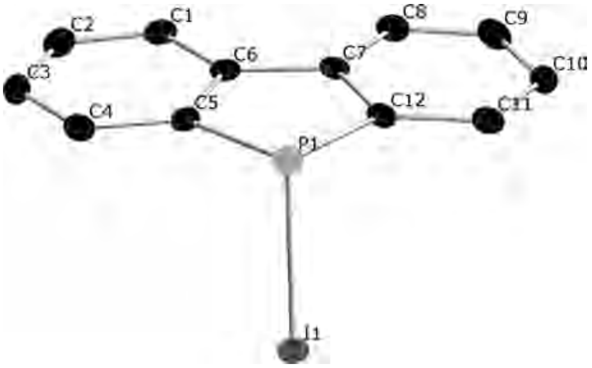

Figure 1. Thermal ellipsoidal (50% ellipsoids) plot of **12**. Selected bond distances (Å) and angles (deg): I(1)−P(1) 2.4980(4), P(1)−C(12) 1.8228(10), P(1)−C(5) 1.8245(10), C(5)−C(6) 1.4110(14), C(6)−C(7) 1.4581(15), C(7)−C(12) 1.4116(13), C(5)−P(1)−I(1) 99.98(3), C(12)−P(1)−I(1) 98.71(3), C(12)−P(1)−C(5) 89.70(5), C(6)−C(5)−P(1) 111.72(8), C(5)−C(6)−C(7) 113.29(9), C(12)−C(7)−C(6) 113.20(9), C(7)−C(12)−P(1) 111.81(7).

Table 2. Comparison of Experimental and Calculated Structural Data, Bond Distances (Å) and Angles (deg)

	12 (exptl.)	**12** (calcd.)	p-t-BuTerphPCl$_2$ (exptl.)^a	p-t-BuTerphPCl$_2$ (calcd.)
d(P−I)	2.4980(4)	2.510		
d(P−Cl)			2.0612(9)	2.052
			2.0723(9)	2.074
d(P−C)	1.8228(10)	1.818	1.837(2)	1.835
	1.8245(10)	1.818		
d(P···C)			3.165	3.319
d(Cl···H)			2.800	2.901
			2.957	3.338
C−P−C	89.70(5)	89.67		
C−P−I	99.98(3)	101.38		
	98.71(3)	101.30		
Cl−P−Cl			100.11(4)	101.1
P−C−C			111.4(2)	112.6
			128.2(2)	128.6

^{a} p-t-BuTerphPCl$_2$ = 2,6-(4-t-Bu$C_6H_4)_2C_6H_3PCl_2$.

reflections. All of the non-hydrogen atoms were refined anisotropically, and all of the hydrogen atoms were included with idealized parameters. The crystals were twinned and required SHELXTL twin refinement with HKLF 5 type data containing two components in a 70:30 ratio. Some details of the crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in the figure legend of Figure 1 and in Table 2. X-ray crystallographic data are available in the Supporting Information.

Computational Methods. The geometries of the reactants, products, and transition states were fully optimized at the 3-21G Hartree–Fock level.[9] Vibrational frequencies were computed to confirm there were no imaginary frequencies for the reactants and products and exactly one imaginary frequency for each transition state. The imaginary frequency corresponds to a normal coordinate in which the primary motion is rotation of one of the flanking phenyl rings toward coplanarity with the i-phenyl ring and the approach of the phosphorus and an ortho carbon on a flanking arene to form the five-membered ring. One phosphorus−halide bond is becoming perpendicular to the phosphafluorene plane while the other phosphorus−halide bond and the carbon−hydrogen bond are stretching. As shown later in Table 2, the computed geometries are in very good agreement with experimental results. The single-point energy for each optimized structure was calculated using B3LYP[10,11] density functional theory with the 6-311G* basis set. All computations were performed with Spartan ’06 software.[12]

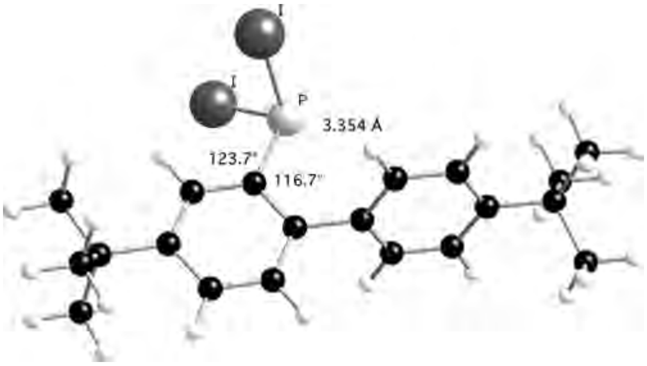

Figure 2. Calculated structure of **11**.

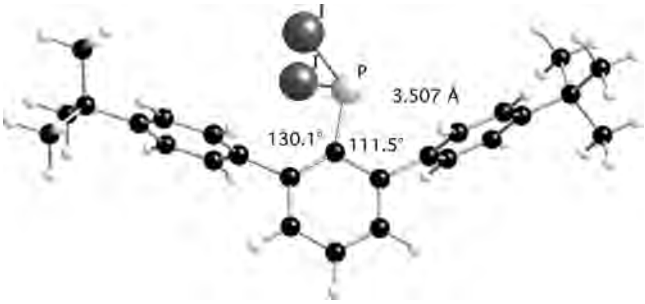

Figure 3. Calculated structure of **2**.

Results

9-Phosphafluorene **4** was first observed as a minor side product during the synthesis of 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3PCl_2$ from 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3Li$ and PCl_3.[3] Its formation was eventually traced back to the presence of some LiI in improperly purified lithium reagent, which was generated from TerphI and BuLi.

Essentially quantitative yields of the 9-iodo-9-phosphafluorenes **4** and **5** have been obtained by stirring a solution of the m-terphenyldichlorophosphines with an excess of dry, finely divided LiI powder in benzene. The progress of the reaction can be monitored conveniently by ^{31}P NMR spectroscopy. For example, after 2.5 h at room temperature, the reaction mixture of the reaction of 2,6-(4-tBu$C_6H_4)_2C_6H_3PCl_2$ with 3 equiv of

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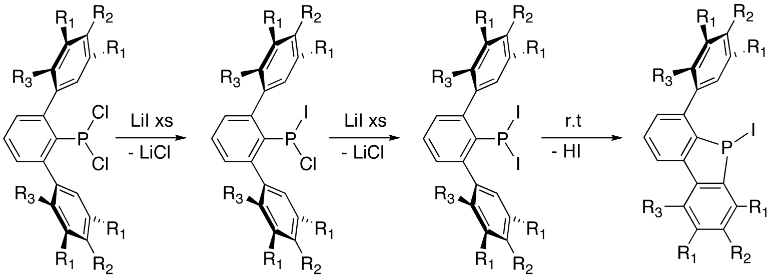
[9] Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797–2803.

[10] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

[11] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[12] *Spartan ’06*; Wavefunction Inc.: Irvine, CA.



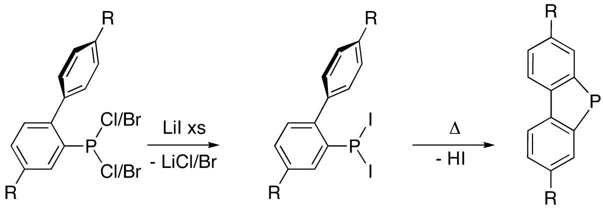
R$_1$ = Me; R$_2$, R$_3$ = H; **1**
R$_1$, R$_3$ = H; R$_2$ = *t*-Bu; **2**
R$_1$, R$_2$ = H; R$_3$ = Me; **3**

R$_1$ = Me; R$_2$, R$_3$ = H; **4**
R$_1$, R$_3$ = H; R$_2$ = *t*-Bu; **5**
R$_1$, R$_2$ = H; R$_3$ = Me; **6**

(2)

LiI in benzene contained no starting material but an approximately 1:4 ratio of the chloroiodo- and diiodophosphines 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$PClI ($\delta_P = 136$ ppm) and 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$PI$_2$ ($\delta_P = 92$ ppm). After an additional 2 h, the mixture contained only the diodophosphine and iodophosphafluorene ($\delta_P = 10.6$ ppm) in a 9:1 ratio. The reaction was complete after 27 h. The intermediates TerphPClI and TerphPI$_2$ were identified according to their ^{31}P NMR chemical shifts.[13,14] Similar to the 9-chloro-9-phosphafluorene formation,[3] the reaction of the *o*-tolyl substituted *m*-terphenylphosphine 2,6-(2-Me-C$_6$H$_4$)$_2$C$_6$H$_3$PCl$_2$ with LiI required either an extended reaction time of more than 5 days at room temperature or heating at 73 °C for about 1 h. The 9-iodo-9-phosphafluorenes **4**−**6** were obtained as yellow crystalline moisture-sensitive powders after crystallization from hexanes.

In order to gain insight into the mechanism and the scope of this reaction, the reactivity of the biphenyl compounds biphenyl-2-diiodophosphine, **10**, and 4,4′-di-*tert*-butyl-biphenyl-2-diiodophosphine, **11**, toward ring closure was investigated. The reaction of the 2-biphenyl Grignard reagents biphenyl-2-magnesium bromide and 4,4′-di-*tert*-butyl-biphenyl-2-magnesium bromide with a 2-fold excess of PCl$_3$ at −78 °C afforded a mixture of biphenyl chloro- and bromophosphines, that is, BiphPCl$_2$, **7a** and **8a**; BiphPClBr, **7b** and **8b**; and BiphPBr$_2$, **7c** and **8c**. An alternative approach, the reaction of 2-biphenyllithium with excess PCl$_3$, gave a mixture of biphenyl-2-PCl$_2$ and the biarylated (biphenyl-2-)$_2$-PCl, which could not be separated. Formation of a 3:97 mixture of the known 9-chloro-9-phosphafluorene, **9a**,[7] and the new 9-bromo-9-phosphafluorene, **9b**, from the reactant mixture **7** required a thermolysis temperature of 224–228 °C, similar to that reported for the thermolysis of TerphPCl$_2$.[3] Contrary to TerphPCl$_2$, the reaction of the reactant mixtures **7** and **8** with LiI afforded the room-temperature-stable crystalline diiodophosphines, biphenyl-2-diiodophosphine, **10**, and 4,4′-di-*tert*-butyl-biphenyl-2-diiodophosphine, **11**. Ring closure of **10** to the 9-iodo-9-phosphafluorene **12** commences slowly around 105 °C in solution, but it is complete within minutes at 170 °C in the absence of a solvent. Conversion of the more electron-rich **11** to 9-iodo-2,7-di-*tert*-butyl-9-phosphafluorene, **13**, is faster: 2 weeks in C$_6$D$_6$ solution at 80–83 °C, 4 h in C$_6$D$_5$Br solution at 119–122 °C, or minutes in the absence of a solvent at 178 °C. The conversion of **11** at temperatures above 90 °C is accompanied by competing P−C cleavage and the formation of 4,4′-di-*tert*-butyl-biphenyl. For example, the reaction at 119–122 °C gave 17% 4,4′-di-*tert*-butyl-biphenyl and 83% **13**, and the reaction of neat **11** at 178 °C afforded a mixture of 75% **13** and 25% of the biphenyl.



R = H; **7**
R = *t*-Bu; **8**

R = H; **10**
R = *t*-Bu; **11**

R = H; **12**
R = *t*-Bu; **13**

(3)

Crystals of **12** have been obtained by vacuum sublimation at 70 °C or by crystallization from hexane solution. The structure of **12** consists of a planar 9-phosphafluorene ring system (deviation from the mean plane: 0.022 Å) with a strongly pyramidal phosphorus at the 9 position. The P−C distances with values of 1.8228(10) and 1.8245(10) Å are close to those of previously reported 9-phosphafluorenes.[3,15,16] The C(12)−P(1)−C(5) angle is narrow at 89.70(5)°, and the sum of the angles at P(1) is 288.39°. The P−I distance of 2.4980(4) Å is also in line with those observed for the iodophosphines (Me$_5$C$_5$)$_2$PI (2.494 Å),[17] 1,2-bisiodo-1,2-diphospha-acenaphthalene (2.499 Å),[18] and MesP(I)P(I)Mes (2.472 Å, Mes = 2,4,6-Me$_3$C$_6$H$_2$).[19] Molecules of **12** are loosely associated into dimers via long (4.397 Å) P···I contacts, which are longer than the sum of the van der Waals radii (3.80–3.97 Å)[20] and also longer than those in the acenaphthalene derivative (3.970 Å).

Discussion

P−I bonds are longer and weaker than P−Cl bonds (d(P−Cl) = 2.03−2.09 Å,[4,20] D_0(P−Cl) = 78 kcal/mol; d(P-

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

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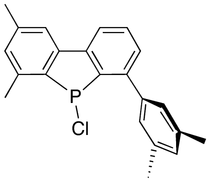
I) = 2.50 Å, D_0(P−I) = 44 kcal/mol[20]). This is reflected, for example, in the ability of iodophosphines to cleave ethers at room temperature,[21] whereas chlorophosphines do not react under comparable conditions. Although the reactivity pattern of the terphenyldiiodophosphines **1**−**3** and biphenyl-2-diiodophosphine **10** was in agreement with an electrophilic aromatic substitution pathway with a partially positively charged phosphorus center as the electrophile, the low reactivity of the *tert*-butyl derivative **11** was unexpected. Ab initio and DFT calculations were performed to better understand the experimental results.

The calculated structures of the diiodophosphines **1**−**3**, **10**, and **11** already hinted at the reasons for the observed reactivity differences between the terphenyl- and the biphenyldiiodophosphines. Whereas the structures of the biphenyl compounds **10** and **11** are practically strain-free (Figure 2), the additional phenyl substituent in **1**−**3** leads to a distortion of the environment around phosphorus and the ipso carbon of the terphenyl substituent (Figure 3) presumably due to steric repulsion between the large iodide substituents and one of the flanking aromatic rings. The two P−C−C angles differ now significantly (130.1° and 111.5°), resulting in the leaning of the phosphorus toward one of the flanking aromatic rings. Since similar distortions have been observed experimentally for the related *m*-terphenyldichlorophosphines,[4,22,23] for example, 128.2(2)° and 111.4(2)° in 2,6-(4-tBu$C_6H_4)_2C_6H_3PCl_2$,[4] and can also be found to a lesser degree in the calculated structures of biphenyldiiodophosphines, for example, 123.7° and 117.1° in **10** and 123.7° and 116.7° in **11**, an additional attractive interaction between the partially electrophilic phosphorus and the electron-rich aromatic ring may also play a role. This so-called Menshutkin interaction[24] is usually observed for the interaction of tin, lead, antimony, or bismuth halides with aromatics.[15,25] The shortening observed here of the P···C distance between the phosphorus and an ortho carbon of one of the flanking arenes of the substituent upon simple rotation around the aryl−aryl bond in **1**−**3** versus that in **10** and **11** predisposes the system toward cyclization. The accuracy of the calculated structures is supported by the close agreement with experimental data (Table 2).

The activation energies (Table 3) and the transition-state geometries are consistent with an electrophilic aromatic substitution process "S_E"[26] facilitated by the long P−I bond and the steric strains in **1**−**3**. The calculated activation energies reflect the observed reactivity patterns. The lowest values were obtained for the terphenyl derivatives **1** with two alkyl substituents and **2** with with one alkyl substituent on each of the flanking arene rings, with values of 17.8 and 20.0 kcal/mol, respectively. An intermediate value of 22.2 kcal/mol was calculated for **3**, which just as **2** has one alkyl substituent but suffers from steric repulsion of the hydrogen and methyl substituents in the 4 and 5 positions in the product **6**. The loss of steric strain in the biphenyl compounds **10** and **11** resulted in higher activation energies with values of 27.6 and 25.9 kcal/mol, respectively. Again, the species with the alkylated substituent **11** features the lower activation energy. Significantly higher activation energies were calculated for the chlorophosphines 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3PCl_2$ and **7**, in agreement with experimental data. The activation energies exceeded those of their iodo counterparts by 8.1 and 7.6 kcal/mol, respectively.

Table 3. Calclulated activation energies for the conversion of $TerphPX_2$ and $BiphPX_2$ into 9-phosphafluorenes

reactant	product	E_a (kcal/mol)
2,6-(3,5-$Me_2C_6H_3)_2C_6H_3PI_2$, **1**	**4**	17.8
2,6-(4-t-Bu$C_6H_4)_2C_6H_3PI_2$, **2**	**5**	20.0
2,6-(2-Me$C_6H_4)_2C_6H_3PI_2$, **3**	**6**	22.2
4,4′-t-Bu_2-biphenyl-2-PI_2, **11**	**13**	25.9
biphenyl-2-PI_2, **10**	**12**	27.6
2,6-(3,5-$Me_2C_6H_3)_2C_6H_3PCl_2$, **14**	**15**[a]	25.9
biphenyl-2-PCl_2, **7**	**9**	35.2

[a]  = **15**

Summary

Large *m*-terphenyl substituents significantly reduce the activation barrier and hence the reaction temperature for the 9-phosphafluorene formation from *m*-terphenyldiiodophosphines via intramolecular cyclization. Iodide substituents contribute ca. 8 kcal/mol to the reduction of the activation barrier compared to chloride substituents, according to quantum mechanical calculations. The reactivity pattern corresponds to an electrophilic aromatic substitution mechanism.

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

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