Heteroatom Chemistry
Volume 00, Number 0, 2012

On the Intramolecular Interactions of Si/P in 1,2-Phenylene Frameworks

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Received 7 May 2012; revised 26 June 2012

ABSTRACT: *The synthesis and structure of 1-diphenylphosphino-2-(fluorodiphenylsilyl) benzene* **1** *and 1-diphenylphosphino-2-(difluorophenylsilyl)-benzene* **2** *are reported. An X-ray crystal structure analysis of* **1** *shows a weak interaction between the silicon and phosphorus moieties, producing a hypervalent state at the silicon. The hypervalent state of the silicon is also supported by a natural bond orbital calculation. However, despite having a difluorosilyl group,* **2** *does not show a hypervalent state for the silicon, based on an X-ray crystal structure analysis.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 00:1–5, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21044

INTRODUCTION

The chemistry of hypervalent organosilicon compounds has been extensively explored over the past two decades [1]. This is because hypervalent derivatives are involved as models for the intermediate/transition-state structures in S_N reactions and show unique structural features and dynamic intramolecular interactions. For example, organosilicon compounds substituted with hard *N*- or *O*-groups at the adjacent position in the molecule usually show unique intramolecular interactions because of their Lewis acidic or basic nature. However, there are few examples of hypervalent organosilicon compounds with soft phosphine donors to date. Tamao et al. reported phosphine-coordinated fluorodisilanes based on the structurally rigid 1,8-naphthylene backbone [2]. Walter et al. reported the synthesis of 1-dimethylphosphino-2-fluorodimethylsilylbenzene; however, the Si/P interaction in this molecule was not determined [3]. Alternatively, Breit et al. prepared 1-diphenylphosphino-2-chlorodi(isopropyl)silylbenzene and found a Si/P interaction from its X-ray crystal structure [4]. The degree of hypervalent state of the Si atom was quite low, probably because the four-membered ring structure for the formation of the Si–P bridge is unfavorable. Very recently, a Sn/P interaction in a 1,2-phenylene backbone was reported by Lin et al. [5]. However, when the silicon becomes more positive by substitution with electronegative groups on the silicon atom, the silicon center would be an acceptable hypervalent state [6]. Here, we report the synthesis of 1-diphenylphosphino-2-fluorosilylbenzenes **1** and **2** (Chart 1) and discuss their ability to form Si/P interactions.

RESULTS AND DISCUSSION

1 - Diphenylphosphino - 2 - (fluorodiphenylsilyl)benzene **1** was synthesized by the reaction of lithiated triphenylphosphine derived from **3** and dichlorodiphenylsilane followed by fluorination with HF•pyridine (Scheme 1). 1-Diphenylphosphino-2-(difluorophenylsilyl)benzene **2** was also prepared by the reaction of the lithiated

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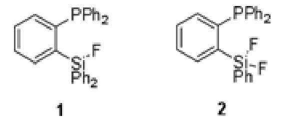
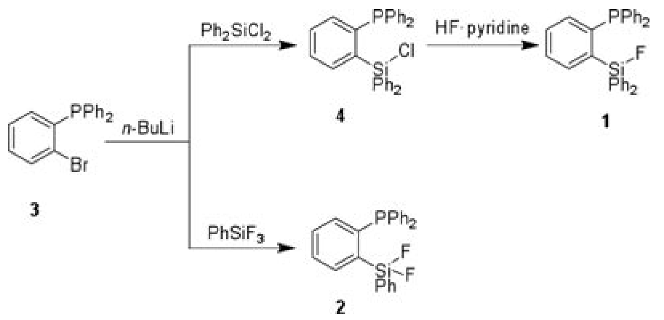


CHART 1



SCHEME 1

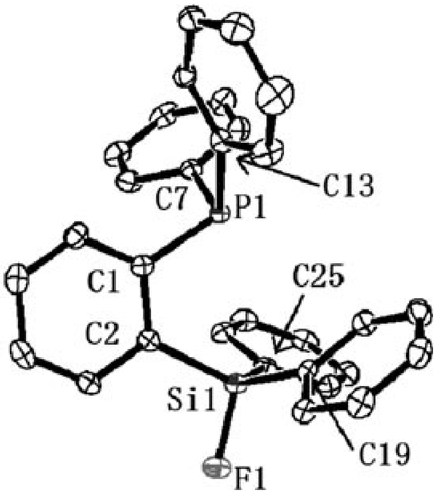


FIGURE 1 An ORTEP drawing of **1** at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): P1· · ·Si1 = 3.243, Si1–F1 = 1.618, ∠F1–Si1· · ·P = 160.73, ∠C2–Si1–F1 = 102.52, ∠C19–Si1–F1 = 104.31, ∠C25–Si1–F1 = 107.56, ∠C2–Si1–C19 = 114.22, ∠C19–Si1–C25 = 113.69, ∠C25–Si1–C2 = 113.23.

triphenylphosphine and trifluorophenylsilane. The products were fully characterized by spectroscopic methods.

The structure of **1** was identified from single-crystal X-ray analysis (Fig. 1). As expected, the X-ray crystal structure suggests an electronic interaction between the phosphorus and the silicon atom. Thus, the distance between P(1) and Si(1) is rather small (3.24(3) Å), which is well within the sum of the van der Waals radii of the two elements (3.90 Å). The Si(1)–F(1) bond distance is 1.61(8) Å, where the standard Si–F bond length is 1.58 Å. In the structure, additionally, the P(1)–Si(1)–F(1) angle is 160.73°. When the silicon atom adopts a distorted trigonal bipyramidal (TBP) geometry, the %TBP$_a$ and %TBP$_e$ [7] calculated from the X-ray analysis are 24 and 40, respectively. The values are quite small compared with the %TBP when the silicon atom in the five-coordinated state adopts a distorted TBP geometry, but larger than those reported for 1-diphenylphosphino-2-chlorosilylbenzene (%TBP$_a$ = 24 and %TBP$_e$ = 34) [4]. This is due to the substitution of the electronegative fluorine group on the Si atom. These data show that Si(1) in **1** has the ability to form the weak Si/P interactions to form the five-coordinated state.

To support the donor–acceptor interaction between the phosphorus and silicon atoms of the compound, the natural bond orbital (NBO) analysis [8] was examined. In the calculation, the structure obtained from the X-ray analysis was used as an optimized structure (Gaussian 09 program [9] with a B3LYP/6-31G* basis set). The analysis shows that the hybrid orbital order of Si(1) is sp$^{2.17}$, and an n(P)–σ^*(Si) orbital interaction is feasible. Although the coordination of the lone pair electrons on P1 to the σ^* orbital of the Si1–F1 bond is not effective in the structure, the contribution to the stability of the molecule by the n(P)–σ^*(Si) interaction is calculated to be 7.7 kcal/mol in **1**.

In solution, the ^{29}Si chemical shift appeared at −5.7 ppm with $^1J_{\text{Si–F}}$ = 281 Hz, which is slightly shifted upfield to that observed for triphenylfluorosilane (–3.3 ppm with $^1J_{\text{Si–F}}$ = 281 Hz) [10,11]. The Si–P coupling was found in **1** ($J_{\text{Si–P}}$ = 7.2 Hz), but not in 1-diphenylphosphino-2-(chlorodiphenylsilyl)benzene, which is further smaller than that observed for reported phosphine-coordinated fluorodisilanes [2]. The NMR study shows almost no interaction of Si–P atoms in **1** occurred in solution at room temperature, although further studies are required.

Next, the structure of **2** was determined by single-crystal X-ray analysis (Fig. 2). However, **2** does not show a hypervalent state for the silicon; nevertheless, the Si with two F atoms is more positive than the Si in **1**. The distance between P(1) and Si(1) is 3.29(2) Å, which is within the sum of the van der Waals radii of the two elements (3.90 Å); however, the Si–F bond distance (1.59 Å) is almost the same as the standard Si(1)–F(1 or 2) bond length. The P(1)· · ·Si(1)–F(1) angle is 163.55°. The %TBPs calculated from the X-ray analysis are rather low (%TBP$_a$ = 17 and %TBP$_e$ = 28). The NBO calculation shows that the hybrid orbital order of the Si(1) atoms is sp$^{1.44}$, and the stabilization of the molecule by n(P)–σ^*(Si) is rather small (ca. 4.5 kcal/mol). Thus, the coordination of the lone pair electrons on P1 to the

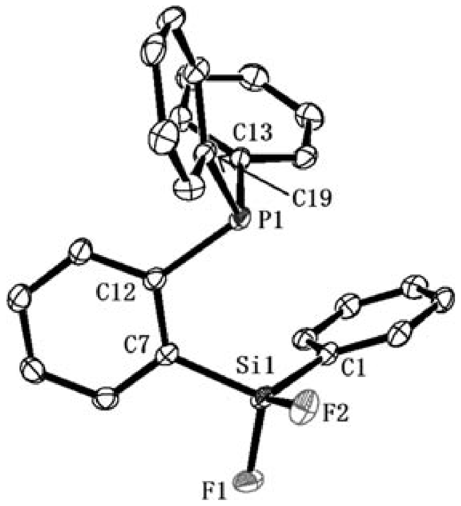


FIGURE 2 An ORTEP drawing of **2** at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): P1···Si1 = 3.292, Si1–F1 = 1.590, Si1–F2(eq) = 1.588, $\angle$F1–Si1···P = 163.55, $\angle$C7–Si1–C1 = 117.97, $\angle$C7–Si1–F2(eq) = 111.20, $\angle$C1–Si1–F2(eq) = 108.13, $\angle$F1(ap)–Si1–F2(eq) = 104.44, $\angle$F1(ap)–Si1–C7 = 105.17, $\angle$F1(ap)–Si1–C1 = 109.05.

σ^* orbital of the Si1–F1 bond is not effective in the structure. These data suggest that Si(1) in **2** is not in the five-coordinated state. This may be due to the structural stability in the crystal packing of **2**, although further study is required. In solution, the ^{29}Si NMR showed no interactions of the Si and P atoms (–31.2 ppm with $J_{\text{Si–P}} = 7.2$ Hz and $J_{\text{Si–F}} = 290.0$ Hz).

CONCLUSION

The results reported here show that, even with the rigidity of the 1,2-phenylene backbone, the phosphine and silicon groups of **1** are involved in the weak intramolecular Si/P interaction, and the silicon atom has the ability to be is in a hypervalent state. However, despite having a difluorosilyl group, **2** does not show a hypervalent state for the silicon, based on an X-ray crystal structure analysis. This observation is also supported by the NBO calculations. Although further studies are required, the Lewis acidity of the silicon and also the structural motif are important factors governing the ability to form the hypervalent state on the silicon, even in the same structural framework. Furthermore, this study may provide a principle to design main group element containing molecules with a combination of Lewis acids and bases, because cooperation between Lewis acids and Lewis bases in frustrated Lewis pairs has attracted considerable interest recently and has been shown to exhibit unique chemical behavior [12]. Further study is currently in progress.

EXPERIMENTAL

General

^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded using a Bruker BioSpin GmbH (Rheinstetten, Germany) DPX 300 NMR spectrometer at 300, 75.4, 282, and 60 MHz, respectively. ^{31}P NMR spectra were recorded on a Bruker BioSpin GmbH Avance 400 spectrometer at 162 MHz. ^{1}H and ^{13}C chemical shifts were referenced to solvent residues. ^{19}F, ^{29}Si, and ^{31}P NMR chemical shifts were referenced to external $CFCl_3$, Me_4Si, and aq. 85% H_3PO_4, respectively. High-resolution mass spectra were obtained with a JEOL (Tokyo, Japan) JMS-700 mass spectrometer. Melting points were measured on a micromelting point apparatus IA9100 (AsOne, Tokyo, Japan). All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry nitrogen. 1-Bromo-2-(diphenylphosphino)benzene [4] and phenyltrifluorosilane [13] were prepared according to the literature.

Synthesis of 1-Diphenylphosphino-2-(chlorodiphenylsilyl)benzene

1.65 M *n*-butyllithium in hexane (4.2 mL, 5.47 mmol) was added at room temperature to a solution of 1-bromo-2-(diphenylphosphino)benzene (1.92 g, 5.63 mmol) in toluene (30 mL) and Et_2O (15 mL). The mixture was stirred at the same temperature for 25 min. Dichlorodiphenylsilane (3.14 g, 12.4 mmol) was added to the reaction mixture, and then the reaction mixture was stirred overnight. After filtration with Celite, the solution was removed under reduced pressure. The residue (4.61 g) was recrystallized from a hexane (60 mL)/toluene (13 mL) mixed solvent at −30°C to afford the title compound in 87% yield (2.36 g, 4.92 mmol) as colorless crystals: mp 158.9–160.0°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.97–7.05 (m, 4H), 7.17–7.58 (m, 15H), 7.70–7.80 (m, 4H), 7.99–8.07 (m, 1H); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 127.9, 128.2, 128.3, 129.2, 130.2, 131.3, 133.2 (d, J = 18.0 Hz), 134.7 (d, J = 18.1 Hz), 135.4 (d, J = 2.8 Hz), 136.1, 137.1 (d, J = 10.6 Hz), 137.6 (d, J = 16.1 Hz), 140.8 (d, J = 47.5 Hz), 144.0 (d, J = 11.3 Hz); ^{29}Si{^{1}H} NMR ($CDCl_3$, 60 MHz) δ 6.0; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ −11.2; HRMS (EI–DI, 70 eV) calcd for $C_{24}H_{19}F_2PSi$ (value for $[M]^+$) *m/z* 478.1073, found 478.1069.

Synthesis of 1-Diphenylphosphino-2-(fluorodiphenylsilyl)benzene **1**

70% HF•pyridine complex (57.0 mg, 1.51 mmol) was added at room temperature to a solution of

1-diphenylphosphino-2-(chlorodiphenylsilyl)benzene (711 mg, 1.48 mmol) in dichloromethane. The mixture was stirred at the same temperature for 4 h, and then the solution was removed under reduced pressure. Toluene (15 mL) was added to the residue, and any supernatant liquid was decanted off. The residual solid was washed with toluene (5 mL × 2). The combined solution was removed under reduced pressure (659 mg) followed by recrystallization from hexane (3 mL) at −30°C to afford **1** in 60% yield (415 mg, 0.89 mmol) as colorless crystals: mp 95.0–97.9°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.97–7.05 (m, 4H), 7.15–7.60 (m, 15H), 7.68–7.85 (m (d-like), J = 6.6 Hz, 4H), 7.92–7.98 (m, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 127.8, 128.2, 128.3, 129.1, 130.4, 131.1, 133.2 (d, $J = 18.0$ Hz), 133.8 (dd, $J = 17.1$ Hz, $J = 3.0$ Hz), 135.4, 135.5 (dd, $J = 3.6$ Hz, $J = 1.6$ Hz), 136.4 (dd, $J = 18.2$ Hz, $J = 4.6$ Hz), 137.2 (d, $J = 10.2$ Hz), 141.6 (dd, $J = 16.7$ Hz, $J = 50.8$ Hz), 143.9 (dd, $J = 2.5$ Hz, $J = 10.2$ Hz); $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 60 MHz) δ −5.7 (dd, $^3J_{Si-P} = 12.9$ Hz, $^1J_{Si-F} = 281.2$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ −9.25 (d, $^4J_{P-F} = 28.3$ Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −163.7 (d, $^4J_{F-P} = 28.2$ Hz); HRMS (EI–DI, 70 eV) calcd for $C_{24}H_{19}F_2PSi$ (value for $[M]^+$) m/z 462.1369, found 462.1374.

Synthesis of 1-Diphenylphosphino-2-(difluorophenylsilyl)benzene **2**

1.65 M n-butyllithium in hexane (5.2 mL, 8.5 mmol) was added at room temperature to a solution of 1-bromo-2-(diphenylphosphino)benzene (2.73 g, 8.02 mmol) in Et_2O (35 mL). The mixture was stirred at the same temperature for 15 min. Phenyltrifluorosilane (1.97 g, 12.2 mmol) was added to the reaction mixture at −78°C. The reaction mixture was stirred at the same temperature for 1 h, at −58°C for 3 h and then at room temperature overnight. After filtration with Celite, the solution was removed under reduced pressure. The residue (4.61 g) was recrystallized from a hexane (60 mL)/toluene (13 mL) mixed solvent at −30°C to afford **2** in 87% yield (2.36 g, 4.92 mmol) as colorless crystals: mp 74.1–74.8°C (760 mmHg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.19 (t-like, $^3J_{H-H} = 7.5$ Hz, 4H, Ar–H), 7.20–7.30 (m, 6H, Ar–H), 7.32 (s, 1H, Ar–H), 7.34–7.40 (m, 2H, Ar–H), 7.41–7.49 (m, 1H, Ar–H), 7.45–7.55 (m, 2H, Ar–H), 7.65–7.75 (d-like, $J = 7.0$ Hz, 2H, Ar–H), 7.97–8.02 (m, 1H, Ar–H); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 128.1, 128.4, 128.5, 128.7, 129.2, 130.6 (td, $J = 3.5$ Hz, $J = 19.1$ Hz), 132.0 (d, $J = 60.8$ Hz), 133.3 (d, $J = 19.8$ Hz), 134.5 (m), 135.0, 136.2 (dt, $J = 18.3$ Hz, $J = 2.3$ Hz), 136.6 (d, $J = 8.8$ Hz), 137.4 (dt, $J = 52.3$ Hz, $J = 16.8$ Hz), 144.9 (d, $J = 10.7$ Hz); $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 60 MHz) δ −31.2 (dt, $^3J_{Si-P} = 7.2$ Hz, $^1J_{Si-F} = 290.0$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ −7.10 (t, $^4J_{P-F} = 40.5$ Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −139.1 (d, $^4J_{F-P} = 40.5$ Hz); HRMS (EI–DI, 70 eV) calcd for $C_{24}H_{19}F_2PSi$ (value for $[M]^+$) m/z 404.0962, found 404.0964.

X-Ray Measurements

The crystallographic measurements were performed at −160 ± 1°C using a Rigaku (Tokyo, Japan) Saturn AFC7R CCD diffractometer with Mo Kα radiation (λ = 0.7107 Å). The structure was solved by direct methods and refined by full-matrix least squares on F^2.

Single crystals of **1** were obtained by recrystallization from a toluene/hexane (v/v = 1/12) solution. A colorless chip crystal (0.30 × 0.30 × 0.30 mm^3) was used. Crystal data for **1**: $C_{30}H_{24}SiFP$, M = 462.58, orthorhombic,P_{bca} (#61), a = 17.893(10) Å, b = 14.546(8) Å, c = 18.660(10) Å, V = 4857(5) Å^3, Z = 8, D(calc) = 1.265, F_{000} = 1936.00. Total reflections collected = 25700 (unique = 5333, R_{int} = 0.151), GOF = 1.302, Max S/E = 0.010, R/P ratio = 17.84, $R(I > 2.00\sigma(I)) = 0.1097$, Rw (all reflections) = 0.1117.

Single crystals of **2** were obtained by recrystallization from a pentane solution. A colorless chip crystal (0.30 × 0.20 × 0.20 mm^3) was used. Crystal data for **2**: $C_{24}H_{19}PSiF_2$, M = 404.47, orthorhombic, P_{-1} (#2), a = 9.663(7) Å, b = 11.084(9) Å, c = 11.773(9) Å, α = 115.974(10)°, β = 91.5949(18)°, γ = 114.911(10)°, V = 992.7(13) Å^3, Z = 2, D(calc) = 1.353, F_{000} = 420.00. Total reflections collected = 7183 (unique = 4192, R_{int} = 0.111), GOF = 0.651, Max S/E = 0.000, R/P ratio = 16.50, R ($I > 2.00\,\sigma(I)$) = 0.0665, Rw (all reflections) = 0.1705.

SUPPLEMENTARY MATERIAL

CCDC-876980 (**1**) and CCDC-876981 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

SUPPORTING INFORMATION

NMR for new compounds and NBO analysis are available in the Supporting Information.

ACKNOWLEDGMENTS

This work was performed under the Cooperative Research Program of “Network Joint Research Center for Materials and Devices" and supported by Special Education and Research Expenses (Nano-Macro Materials, Devices and System Research Alliance) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We also thank the Center for Advanced Materials Analysis, Technical Department, Tokyo Tech.

REFERENCES

[1] (a) Chuit, C.; Corriu, R. J. P.; Reye, C. Chemistry of Hypervalent Compounds; Akiba, K.-y., Ed.; Wiley-VCH: New York, 1999; pp. 81–146; (b) Kira, M.; Zhang, L.-C. Chemistry of Hypervalent Compounds; Akiba, K.-y., Ed.; Wiley-VCH: New York, 1999; pp. 147–169; (c) Kost, D.; Kalikhman, I. The Chemistry of Organic Silicon Compounds, Volume 2, Part 2; Patai, S., Apeloig, Y., Eds.; Wiley: Chichester, UK, 1998; pp. 1339–1445.

[2] Toshimitsu, A.; Saeki, T.; Tamao, K. J Am Chem Soc 2001, 123, 9210.

[3] Grobe, J.; Hildebrandt, W.; Martin, R.; Walter, A. Z. Anorg Allg Chem 1991, 592, 121.

[4] Quintard, D.; Keller, M.; Breit, B. Synthesis 2004, 905.

[5] Lin, T. P.; Gualco, P.; Ladeira, S.; Amgoune, A.; Bourissou, D.; Gabbaï, F. P. C R Chimie 2010, 13, 1168.

[6] (a) Tamao, K.; Asahara, M.; Saeki, T.; Toshimitsu, A. J Organomet Chem 2000, 600, 118; (b) Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C. J Organomet Chem 1994, 470, 43.

[7] Kano, N.; Komatsu, F.; Yamamura, M.; Kawashima, T. J Am Chem Soc 2006, 128, 7097.

[8] Foster, J. P.; Weinhold, F. J Am Chem Soc 1980, 102, 7211.

[9] Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc.: Wallingford, CT, 2010.

[10] Cory, D.; Woong, A.; Ritchey, W. M. J Organomet Chem 1982, 235, 277.

[11] Farooq, O. J Chem Soc, Perkin Trans 1 1998, 661.

[12] For recent reviews, see: (a) Stephan, D. W. Chem Commun 2010, 46, 8526; (b) Stephan, D. W.; Erker, G. Angew Chem, Int Ed 2010, 49, 46.

[13] Powell, D. A.; Fu, G. C. J Am Chem Soc 2004, 126, 7788.