Tertiary Phosphines and *P*-Chiral Phosphinites Bearing a Fullerene Substituent

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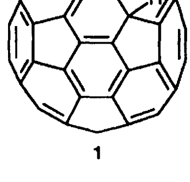
The reaction of a lithiated phosphine–borane or a posphinite borane with C_{60} followed by removal of the BH_3 group affords a phosphine or a phosphinite bearing a fullerene substituent, which undergoes complexation with BH_3 and $PtCl_2$ selectively on the phosphorus atom with 1 : 1 and 2 : 1 stoichiometry.

We report here the synthesis of a new class of tertiary phosphines **1**, including *P*-chiral derivatives **8** and **11**, which can serve as potential candidates for new design of metal ligands for asymmetric synthesis. The synthesis was achieved in a straightforward manner by the addition of a metalated phosphine–borane to C_{60} followed by removal of the borane group from the adduct with DABCO (Scheme 1). The $C_{60}H$ group in **1** is an unusual sp^3 alkyl substituent with steric bulk, photoactivity[1] and potential to bind to certain metal atoms.[2] The fullerene–phosphines have considerable thermal stability, and, notably, the *P*-chiral phosphinite **8** was also found to be configurationally stable. The $C_{60}H$ group brings about considerable steric congestion and creates a novel coordination sphere in the metal complex.

The borane complex of a secondary phosphine **4** is air-stable and easy to handle.[3] The proton attached to the phosphorus atom in **4** can be easily deprotonated to give the corresponding anion **5**.[4] We found that **5** readily adds across the strained and electron-deficient double bond of [60]fullerene. Thus, addition of $Ph_2PLi{\cdot}BH_3$, prepared by BuLi-deprotonation of $Ph_2PH{\cdot}BH_3$ (457 mg, 2.2 mmol) in 5 ml of THF in the presence of HMPA (394 mg, 4.4 mmol), to a 650 ml toluene solution of C_{60} (800 mg, 1.1 mmol) took place at −78 °C (1 h) to give the adduct **3a** in 82% isolated yield (830 mg) after quenching with HCl in ethyl acetate and purification by silica gel chromatography.† The reaction of $MePhPLi{\cdot}BH_3$ also took place smoothly, albeit slowly, at −40 °C to give the adduct **1b** in 46% yield. The borane complexes were found to be stable in air at room temperature for months.[5]

The structure of the phosphine–borane **3a** was assigned by ^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectroscopy, which indicated that the addition to C_{60} took place at the 6,6-ring junction. In the ^{1}H NMR spectrum of **3a**, the proton on C_{60} appears as doublet at δ 6.94. (J_{P-H} 25.7 Hz). The large P–H coupling is consistent with the vicinal and *cis* relative stereochemistry between the proton and the phosphorus atom[6]

The $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum of **3a** ($CDCl_3$–CS_2; $CDCl_3$ at δ 77.0) showed 30 sp^2 signals and two sp^3 signals in the C_{60} region, indicating the C_s symmetry of the molecule. The doublet at δ 66.5 in the $^{13}C\{^{1}H\}$ NMR spectrum is coupled strongly (32.4 Hz) to the phosphorus atom and hence assigned to the carbon connected to the phosphorus atom. Another sp^3 carbon at δ 58.2 with small coupling (J_{P-C} 9.5 Hz) was assigned to the carbon connected to the hydrogen. The $^{11}B\{^{1}H\}$ NMR ($CDCl_3$–CS_2; H_3BO_3 at δ 0.3) spectrum showed a single broad signal at δ −58.74, and the $^{31}P\{^{1}H\}$ NMR ($CDCl_3$–CS_2; 85% H_3PO_4 at δ 0.0) spectrum also showed a single signal appearing at δ 39.98 (J_{B-P} = *ca.* 44.2 Hz). The relatively small J_{B-P} [*cf.* $Ph_3P{\cdot}BH_3$; $J(^{11}B-P)$ = 57 Hz][7] suggests[8] that the $C_{60}H$ group is a stronger electron-withdrawing group than a phenyl group.



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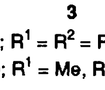

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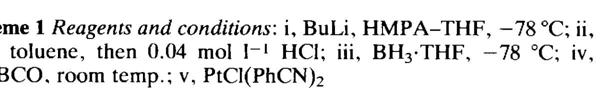
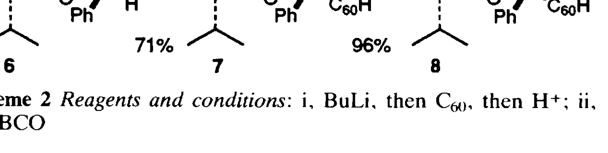
a; $R^1 = R^2 = Ph$
b; $R^1 = Me, R^2 = Ph$

Teatment of the borane complex **3a** with DABCO (20 equiv.) at room temp. for 1.5 h under nitogren removed the borane group to give quantitatively the phosphine **1a** as black power. The removal of the borane group caused a systematic upfield shift of the ^{1}H NMR signals owing to the decreased electron withdrawal by the phosphorus atom. Thus, the proton on C_{60} was shifted upfield to δ 6.82 (J_{PH} = 15.6 Hz). Treatment of **1a** with MCPBA (1 equiv.) gave the phosphine oxide **2a**.‡ The reaction of **1a** with 1 equiv. of $BH_3{\cdot}THF$ at −78 °C selectively took place on the phosphorus atom to give back **3a** in quantitative yield.[9]

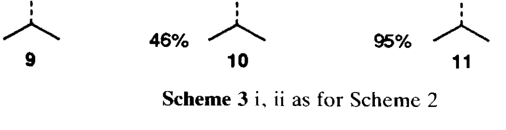
Finally, we describe the synthesis of *P*-chiral fullerene–phosphines and their transition metal complexes. Thus, the (+)-menthyl phosphinite–borane[4] **6** (2 equiv.) was lithiated and added to C_{60} in a manner described above. The adduct **7** was isolated in 71% yield [C(C_{60}–H), δ 7.17, J_{P-H} 26.0 Hz] (Scheme 2). Alternatively, the lithium salt of the diastereoisomeric phosphinite–borane **9** gave **10** in 46% yield [C(C_{60}–H), δ 7.00, J_{P-H} 26.0 Hz] (Scheme 3). The two adducts were shown to be diastereoisomerically pure by ^{1}H NMR, indicating that the addition took place stereospecifically (most likely with retention of the *P* chirality).[5] The B–P bond in a phosphinite–borane complex is so strong that it is generally difficult to remove the BH_3 group by amine treatment. However, the free phosphines **8** [C(C_{60}–H), δ 6.86, J_{P-H} 13.7 Hz) and **11** [C(C_{60}–H), δ 6.81, J_{P-H} 14.2 Hz] could be obtained in *ca.* 90% yield by treatment with 100–120 equiv. of DABCO at room temperature for 15 h with complete retention of the phosphorus chirality. The chirality at phosphorus of the phosphinite **8** was found to be remarkably stable (no sign of epimerization upon heating for 14 h at 80 °C in degassed toluene).



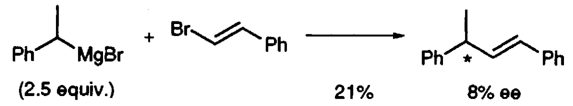
Scheme 1 *Reagents and conditions*: i, BuLi, HMPA–THF, −78 °C; ii, C_{60}, toluene, then 0.04 mol l^{-1} HCl; iii, $BH_3{\cdot}THF$, −78 °C; iv, DABCO, room temp.; v, $PtCl(PhCN)_2$



Scheme 2 *Reagents and conditions*: i, BuLi, then C_{60}, then H^+; ii, DABCO



Scheme 3 i, ii as for Scheme 2

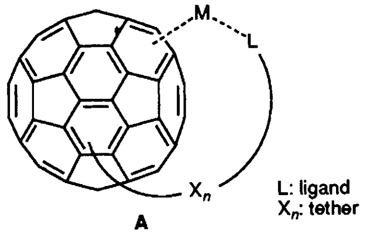


Scheme 4 *Reagents and conditions*: **8** (0.4 equiv.) + $PdCl_2(PhCN)_2$ (0.2 equiv.), Et_2O, 0 °C, 21 h

The phospinite **8** formed a complex with $PtCl_2$. Treatment of **8** with $PtCl_2(PhCN)_2$ (0.5 equiv.) in toluene afforded a clear solution, which yielded an analytically pure complex, $PtCl_2{\cdot}(\mathbf{8})_2$, as a brown powder after concentration and precipitation from $CHCl_3$ with hexane. The ^{31}P NMR spectrum of the complex showed a single phosphorus signal at δ 90.7 with J_{P-Pt} 4.90 kHz, indicating that the metal is coordinated selectively to the phosphorus atom.

A palladium complex of **8**, prepared by treatment of **8** with 0.5 equiv. of $PdCl_2(PhCN)_2$, catalysed, albeit in low optical yield (8% ee), the asymmetric cross coupling of 1-phenylethylmagnesium chloride and β-bromostyrene to afford 1,3-diphenylbut-1-ene (Scheme 4).[10] The observed chirality induction suggests that **8** remains coordinated to the palladium metal during catalytic turnover.

In summary, we have synthesized the first and the simplest member of tailor-made C_{60}-containing metal ligands as represented by the general structure in **A**. Suitable adjustment of the oxygenation level of compounds such as **8** may also be useful for biochemical investigations of buckminsterfullerenes.[11,12]



A

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Footnotes

† Selected physical properties of **3a**: R_f 0.21 (20% toluene in hexane); IR ν_{max}/cm^{-1} ($CHCl_3$) 3020, 2400, 1440, 1225, 1210, 790, 530; ^1H NMR (400 MHz, CS_2–$CDCl_3$) δ 1.50–2.30 (br m, 3 H, BH_3), 6.94 (d, $^3J_{PH}$ 25.7 Hz, 1 H, $C_{60}H$), 7.61–7.68 (m, 6 H, *m*- and *p*-C_6H_5), 8.51 (ddd, *J* 14.2, 8.2, 1.7 Hz, 4 H, *o*-C_6H_5); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ 58.21 (d, $^2J_{CP}$ 9.5 Hz, C_{60}), 65.46 (d, $^1J_{CP}$ 32.4 Hz, C_{60}), 125.30 (d, $^1J_{CP}$ 50.2 Hz, C_6H_5, 2 C), 129.01 (d, $^2J_{CP}$ 10.5 Hz, C_6H_5, 4 C), 132.54 (d, $^4J_{CP}$ 2.9 Hz, C_6H_5, 2 C), 134.82 (d, $^3J_{CP}$ 8.6 Hz, C_6H_5, 4 C), 135.79 (d, J_{CP} 2.0 Hz, C_{60}, 2 C), 137.25 (d, J_{CP} 4.8 Hz, C_{60}, 2 C); 139.20, 140.36, 141.20, 141.21, 141.36, 141.66, 141.77, 141.90, 142.04, 142.46, 142.64, 143.21, 144.22, 144.72, 145.32, 145.35, 145.45, 145.67, 146.16, 146.24, 146.34, 146.40, 146.51, 146.54 (all C_{60}, 2 C); 147.13 (C_{60}), 147.23 (C_{60}), 149.76 (d, J_{CP} 4.8 Hz, C_{60}, 2 C), 152.54 (d, J_{CP} 5.7 Hz, C_{60}, 2 C); ^{31}P NMR (162 MHz, CS_2–$CDCl_3$) δ 39.98; ^{11}B NMR (128 MHz, CS_2–$CDCl_3$) δ −58.74; FAB MS *m/z* 921 (M^+ + 1), 720–724 (C_{60}).

‡ The solid phosphine **1a** is moderately air-sensitive, but can be handled in air without oxidation to **2a**.

References

1 J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Phys. Chem.*, 1991, **95**, 11.

2 P. Fagan, J. C. Calabrese and B. Malone, *Acc. Chem. Res.*, 1992, **25**, 134.

3 T. Imamoto, *J. Synth. Org. Chem., Jpn.*, 1987, **45**, 592.

4 T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto and K. Sato, *J. Am. Chem. Soc.*, 1990, **112**, 5244.

5 BH_3 is known to react with C_{60} above 0 °C: C. C. Henderson and P. A. Cahill, *Science*, 1993, **259**, 1885.

6 A. A. Bothner-By and R. H. Cox, *J. Phys. Chem.*, 1969, **73**, 1830; M. Tsuboi, S. Takahashi, Y. Kyogoku, H. Hayatsu, R. Ukita and M. Kainosho, *Science*, 1969, **166**, 1504.

7 K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, 1969, **8**, 2671.

8 A. H. Cowley and M. C. Damasco, *J. Am. Chem. Soc.*, 1971, **93**, 6815; R. W. Rudolph and C. W. Schultz, *J. Am. Chem. Soc.*, 1971, **93**, 6821.

9 *Cf.* S. Yamago, H. Tokuyama, E. Nakamura, M. Prato and F. Wudl, *J. Org. Chem.*, 1993, **58**, 4796.

10 T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika and M. Kumada, *J. Am. Chem. Soc.*, 1982, **104**, 180.

11 R. Sijbesma, G. Srdanov, F. Wudl, J. A. Castoro, C. Wilkins, S. H. Friedman, D. L. DeCamp and G. L. Kenyon, *J. Am. Chem. Soc.*, 1993, **115**, 6506; R. F. Schinazi, R. Sijbesma, G. Srdanov, C. L. Hill and F. Wudl, *Antimicro. Agents Chemo.*, 1993, **37**, 1707.

12 H. Tokuyama, S. Yamago, E. Nakamura, T. Shiraki and Y. Sugiura, *J. Am. Chem. Soc.*, 1993, **115**, 7918.