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Supporting Information

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Supporting Information

for

The Low Basicity of Phosphabenzenes: First Examples of Protonation, Alkylation and Silylation Reactions

by

Yun Zhang, Fook S. Tham, John F. Nixon, Charlotte Taylor, Jennifer C. Green, and Christopher A. Reed

(9 pages)

Synthetic Procedures

General. Air sensitive materials were handled in a He atmosphere Vac. Atm. Corp. glove box (O_2, H_2O < 2 ppm). All reactions outside of the dry box were carried out under dry nitrogen in Schlenk tubes with Teflon stopcocks. High purity dichloromethane (Omisolv), benzene, o-dichlorobenzene, and n-hexane were purchased from EM science. Solvents were dried over Na/K, P_2O_5, or CaH and distilled prior to use. NMR spectra were record on a Varian Inova 400, 500 or Bruker 300 spectrometers for ^{1}H, ^{13}C, and ^{31}P (referenced externally to 85% H_3PO_4).

All carborane reagents were freshly prepared. $Et_3Si(CHB_{11}Me_5Br_6)$,[1] $Et_3Si(CHB_{11}Me_5Cl_6)$,[1] arenium ion salts $[H(arene)][CHB_{11}Me_5Cl_5]$ (arene = mesitylene, *o*-xylene and toluene),[1] and $CH_3(CHB_{11}Me_5Br_6)$[2] were prepared by literature methods.

(1) Reed, C. A.; Kim, K-C.; Stoyanov, E. S.; Stasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2003**, *125*, 1796-1804.
(2) Kato, T.; Stoyanov, E.; Geier, J.; Grutzmacher, H.; Reed, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 12451.

$[H(C_3P_3{}^tBu_3)][CHB_{11}Me_5Br_6]$, 6. Freshly prepared $Et_3Si(CHB_{11}Me_5Br_6)$ (148 mg, 0.185 mmol) was combined with $(C_3P_3{}^tBu_3)$, **4** (55.4 mg, 0.185 mmol), in a 5 mL vial with a stir bar. Approximately 1 mL of benzene was added to yield a pale yellow solution. A white powdery precipitate was formed when 3 drops of TfOH (~2 eq) was added to this solution. Dry *n*-hexane (~2 mL) was added to ensure complete precipitation of the product. The resulting white precipitate was filtered off, washed with dry *n*-hexane (~2 mL) and dried under vacuum (153 mg, 84 %). The final product was re-dissolved in CH_2Cl_2 and layered with *n*-hexane to yield X-ray quality crystals. ^{1}H NMR (Figure S1) in (300 MHz, δ, CD_2Cl_2, 25 ºC): 0.11 (s, 15H, BCH_3), 1.54 (bs, 1H, BCH), 1.84 (s, 27H, tBu), 9.46 (d, 1H, $^1J_{H\text{-}P}$ = 595 Hz, PH). ^{31}P NMR (Figure S2) (122 MHz, δ, CD_2Cl_2, 25 ºC): 85.11 (dt, 1P, $^2J_{P\text{-}P}$ = 49.0 Hz, $^1J_{P\text{-}H}$ = 592 Hz), 304.49 (d, 2P, $^2J_{P\text{-}P}$ = 49.2 Hz).). ^{31}P NMR (^{1}H-Dec, 122 MHz, δ, CD_2Cl_2, 25 ºC): 85.07 (t, 1P, $^2J_{P\text{-}P}$ = 48.7 Hz), 304.47 (d, 2P, $^2J_{P\text{-}P}$ = 48.9 Hz).

$[H(C_3P_3{}^tBu_3)][CHB_{11}Cl_{11}]$. This was prepared in an analogous manner to **6** from **4** and $Et_3Si(CHB_{11}Me_5Cl_6)$. ^{1}H NMR (Figure S3) (300 MHz, δ, d_4-*o*-dichlorobenzene, 25 ºC): 1.54 (s, 18H, tBu), 1.60 (s, 9H, tBu), 2.98 (bs, 1H, BCH), 9.22 (d, 1H, $^1J_{H\text{-}P}$ = 586 Hz, PH). ^{31}P NMR (122 MHz, δ, CD_2Cl_2, 25 ºC): 81.68 (dt, 1P, $^2J_{P\text{-}P}$ = 48.3 Hz, $^1J_{P\text{-}H}$ = 590 Hz), 302.69 (d, 2P, $^2J_{P\text{-}P}$ = 48.3 Hz). ^{31}P NMR (^{1}H-Dec, 122 MHz, δ, d_4-*o*-dichlorobenzene, 25 ºC): 81.88 (t, 1P, $^2J_{P\text{-}P}$ = 48.8 Hz), 302.91 (d, 2P, $^2J_{P\text{-}P}$ = 48.5 Hz).

$[H(PC_5H_2t\text{-}Bu_3)][CHB_{11}Me_5Cl_6]$, 7. This was prepared in an analogous manner to **6** from **5** and $Et_3Si(CHB_{11}Me_5Cl_6)$. X-ray crystals were grown from CD_2Cl_2/hexanes. ^{1}H NMR (Figure S5) (300 MHz, δ, CD_2Cl_2 25 °C): 0.13 (15H_{Me}, *s*), 1.48 (9H_{But}, *s*), 1.61 (18H_{But}, *s*), 8.45 (1H, *dd*, $^3J_{PH}$ = 36, $^4J_{HH}$ = 4.6 Hz), 9.32 (1H, *dt*, $^4J_{HH}$ = 4.6Hz, $^1J_{PH}$ = 627 Hz) ppm. ^{31}P NMR (Figure S6) (122 MHz, δ, CD_2Cl_2, 25 ºC) 60.2 (*dt*, $^1J_{PH}$ = 625 *Hz*, $^3J_{PH}$ = 36 *Hz*). ^{31}P NMR (^{1}H-Dec, 122 MHz, δ, CD_2Cl_2, 25 ºC): 60.2 (s).

$[Me(C_3P_3{}^tBu_3)][CHB_{11}Me_5Br_6]$, 8. Freshly prepared $CH_3(CHB_{11}Me_5Br_6)$ (50.1 mg, 0.073 mmol) was combined with $(C_3P_3{}^tBu_3)$ **5** (19.5 mg, 0.065 mmol) in a 5 mL vial with a stir bar. The reaction vial was cooled down to dry ice temperature before addition of 2 mL cold CH_2Cl_2 (-90 ºC). The reaction was allowed to warm up to room temperature with stirring before all volatiles were removed by vacuum. The resulting pale yellow solid (59 mg, 83 %) was re-dissolved in CD_2Cl_2 for NMR spectroscopic analysis. ^{1}H NMR (400 MHz, δ, 25 ºC): 0.11 (s, 15H, BCH_3), 1.55 (bs, 1H, CH), 1.82 (s, 27H, tBu), 3.50 (d, 3H, CCH_3, $^2J_{H\text{-}P}$ = 18.6 Hz). ^{31}P NMR (Figure S7) (122 MHz, δ, 25 ºC): 133.8 (tq, 1P, $^2J_{P\text{-}P}$ = 52.0 Hz, $^2J_{P\text{-}H}$ = 19.0 Hz), 302.6 (d, 2P, $^2J_{P\text{-}P}$ = 52.0 Hz).). ^{31}P NMR (^{1}H-Dec, 122 MHz, δ, CD_2Cl_2, 25 ºC): 133.4 (t, 1P, $^2J_{P\text{-}P}$ = 52.2 Hz), 302.2 (d, 2P, $^2J_{P\text{-}P}$ = 52.0 Hz).

Figure S1. ^1H NMR spectrum of $[H(C_3P_3{}^tBu_3)][CHB_{11}Me_5Br_6]$ **6** in CD_2Cl_2.

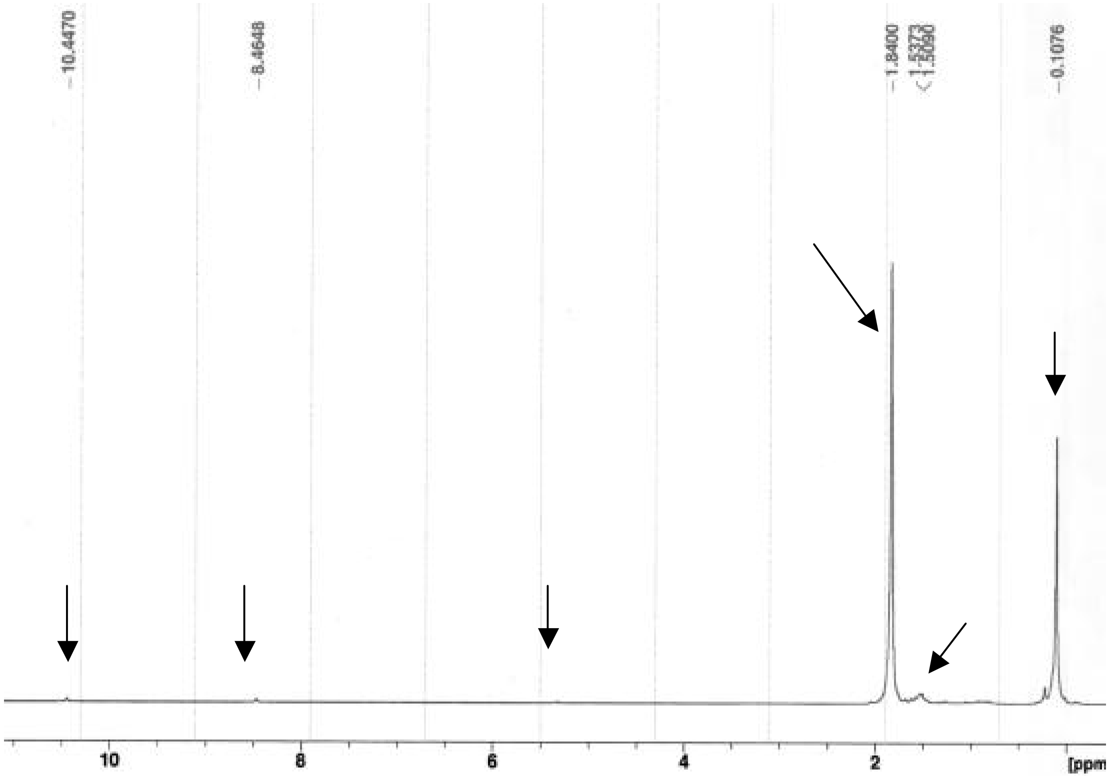


Figure S2. ^{31}P and ^{31}P{^{1}H} NMR spectrum of [H($C_3P_3{}^tBu_3$)][$CHB_{11}Me_5Br_6$] **6** in CD_2Cl_2.

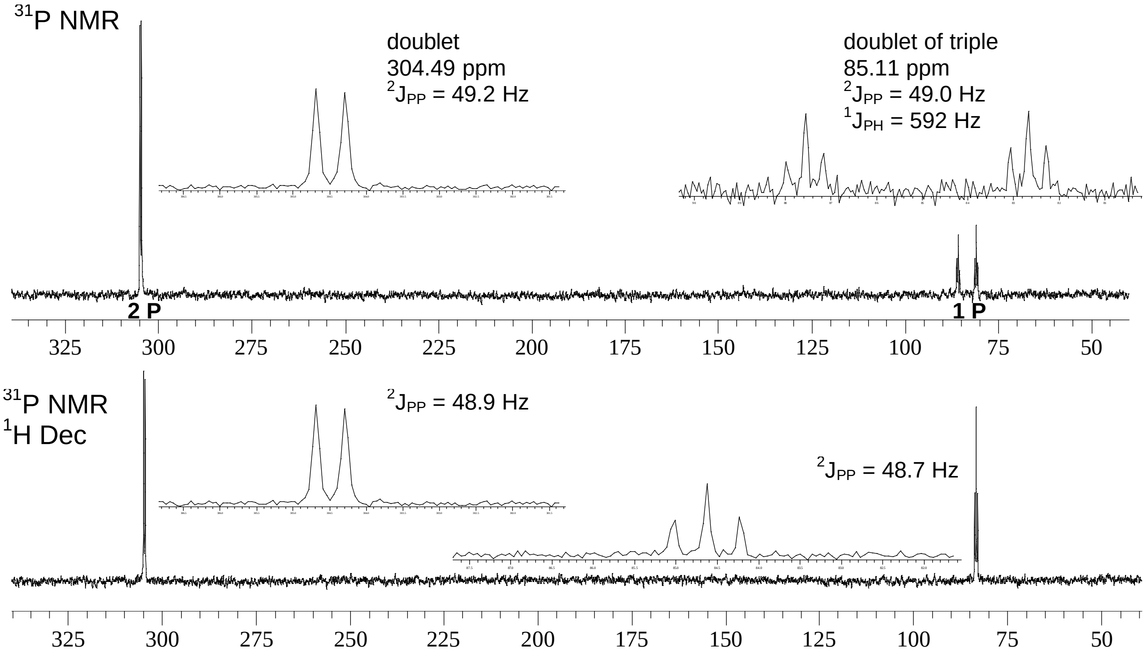


Figure S3. ^{1}H NMR spectrum of $[H(C_3P_3{}^tBu_3)][CHB_{11}Cl_{11}]$ in *d4*-ODCB.

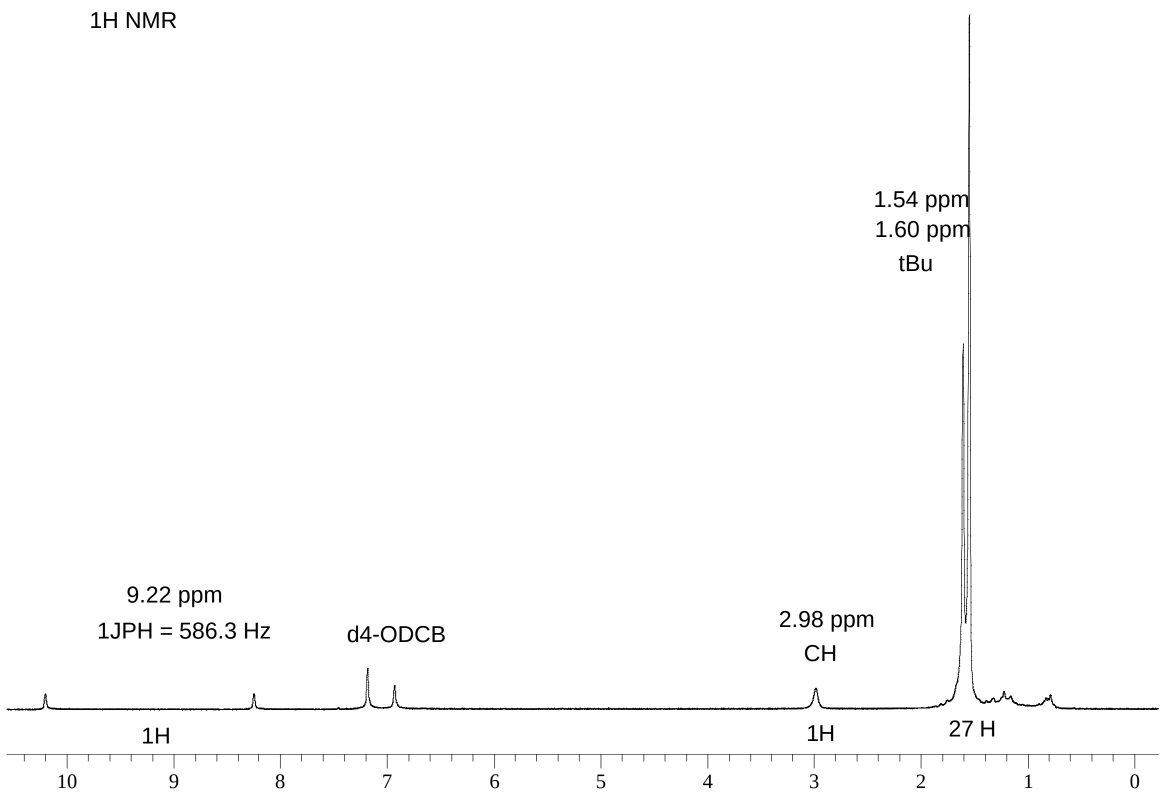


Figure S4. ^{31}P and ^{31}P{^{1}H} NMR spectrum of [H($C_3P_3{}^tBu_3$)][$CHB_{11}Cl_{11}$] in *d4*-ODCB.

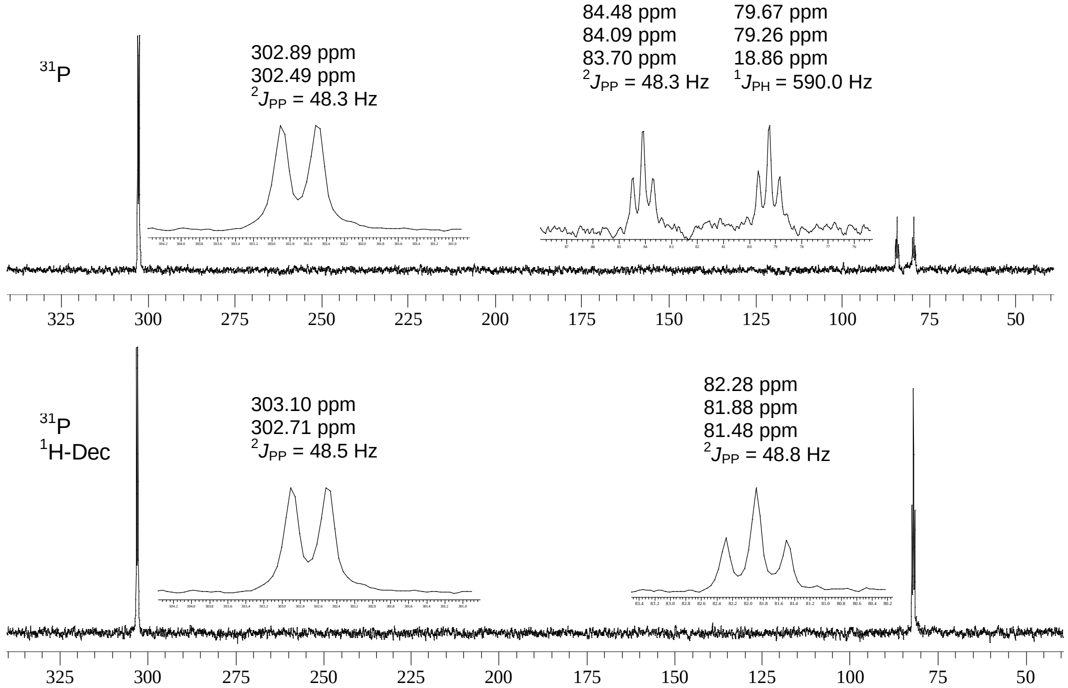


Figure S5. ^{1}H NMR spectrum of $[H(PC_5H_2{}^tBu_3)][CHB_{11}Me_5Cl_6]$, **7,** in CD_2Cl_2.

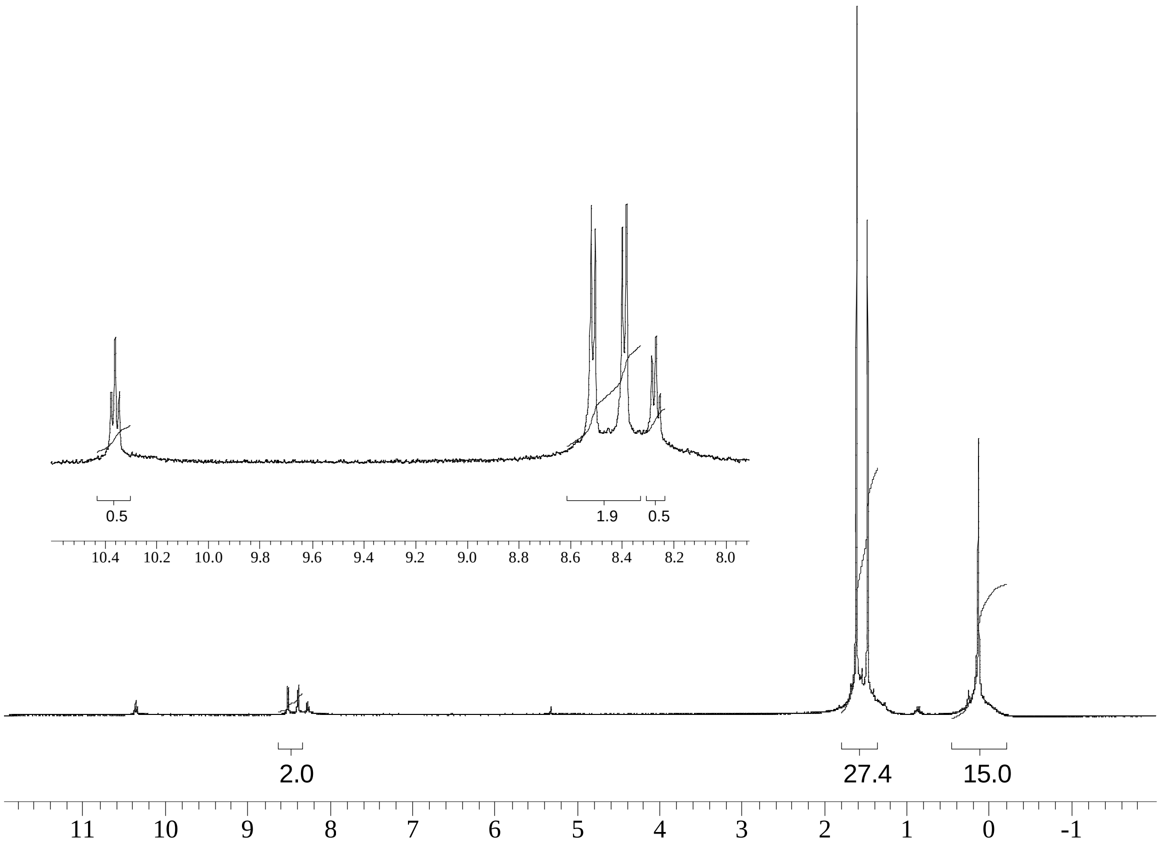
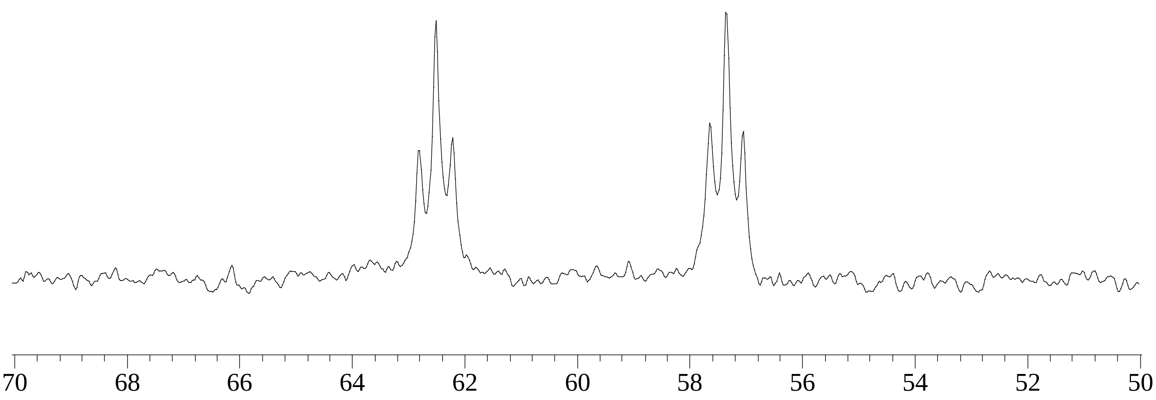


Figure S6. ^{31}P and $^{31}P\{^1H\}$ NMR spectrum of $[H(PC_5H_2{}^tBu_3)][CHB_{11}Me_5Cl_6]$, **7,** in CD_2Cl_2.

31P



$^{31}P\{^1H\}$

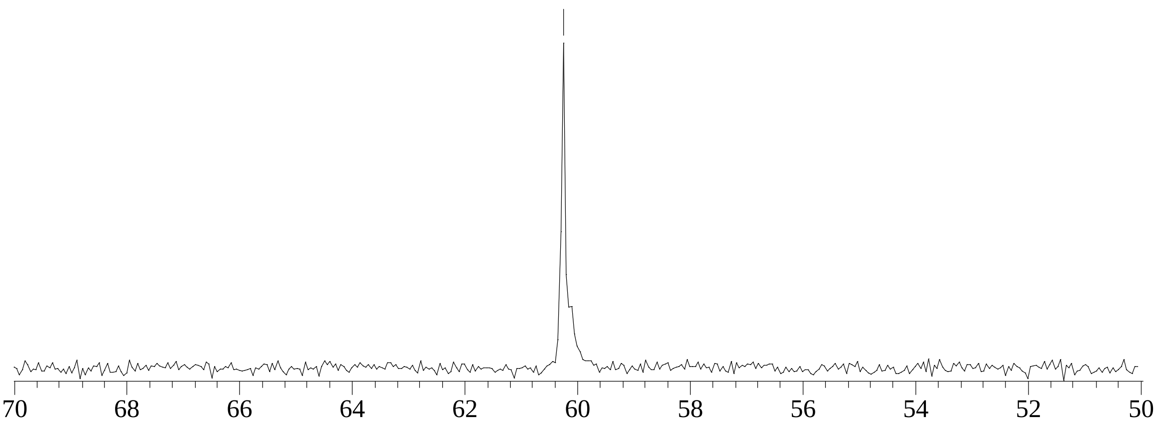


Figure S7. ^{31}P and ^{31}P{^{1}H} NMR spectrum of [Me(C$_3$P$_3{}^t$Bu$_3$)][CHB$_{11}$Me$_5$Br$_6$], **8**, in CD$_2$Cl$_2$ at room temperature.