Supplementary data:

Synthesis and Reactivity of Nickel-Hydride Amino-*bis*-Phosphinimine Complexes

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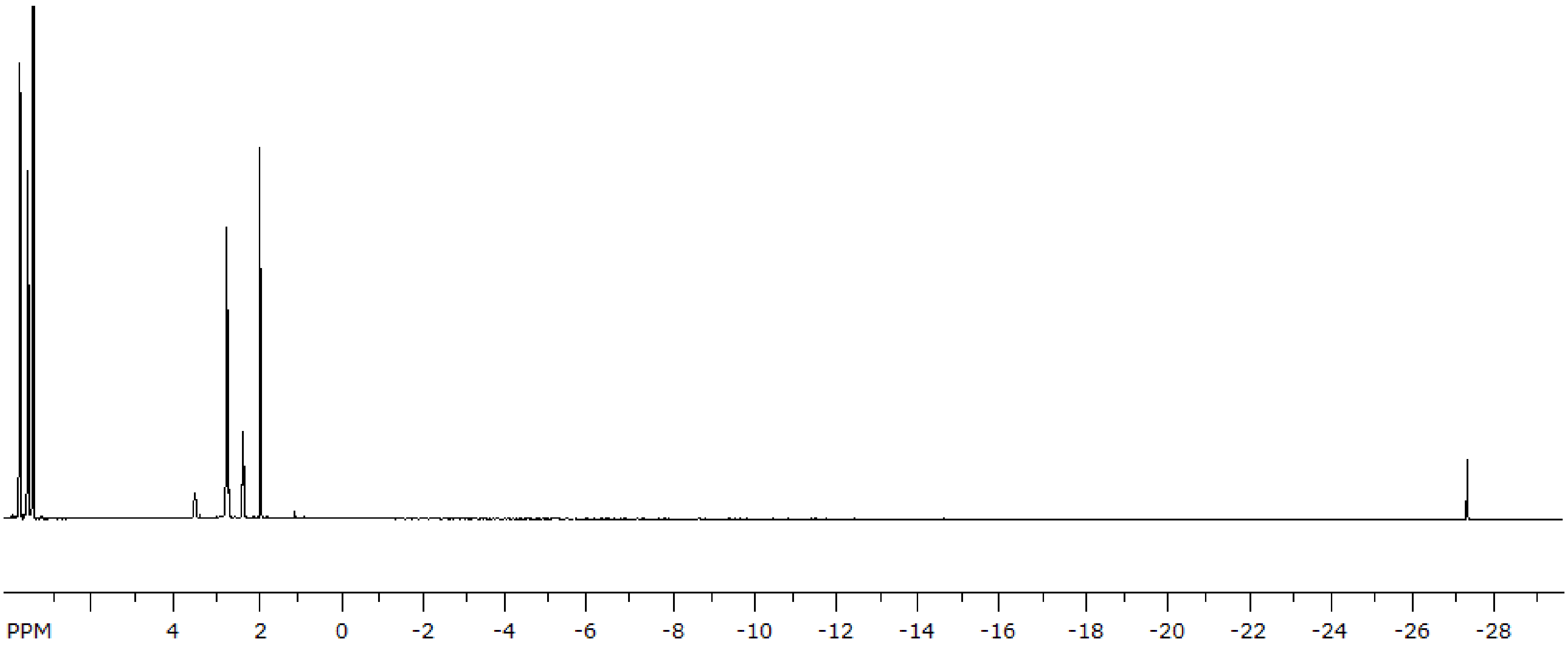
Experimental Section

All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing an Innovative Technology glove box and a Schlenk vacuum-line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, toluene, CH_2Cl_2), or were dried over the appropriate agents and distilled. All solvents were thoroughly degassed after purification (repeated freeze-pump-thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly (CD_2Cl_2). Toluene and pentane were stored over potassium mirrors, while bromobenzene and dichloromethane were stored over 4Å molecular sieves. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C on Varian 400 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residue solvent signal (^{1}H, ^{13}C) or relative to an external standard (^{31}P: 85% H_3PO_4). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Compound **1** and **2** were synthesised according to reported literature procedures.[1] $LiHBEt_3$ (1M in THF) was purchased from Aldrich and used as received.

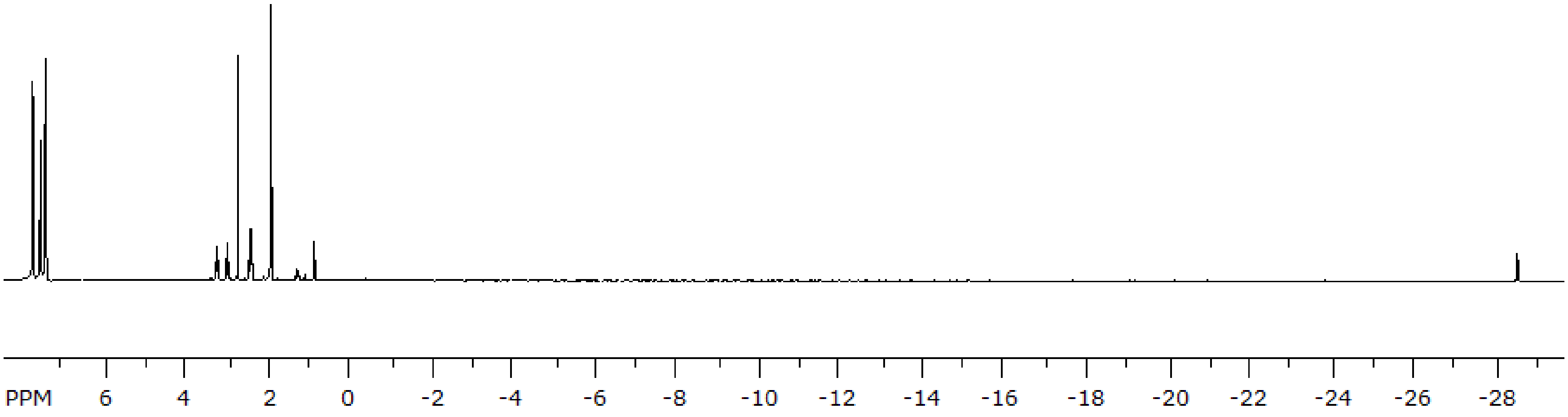
Synthesis of [HN(1,2-CH_2CH_2N=PPh_3)$_2$NiH][PF_6] 3: A 1M in THF solution of $LiHBEt_3$ (0.14 mL, 0.14 mmol) was added dropwise at -35°C to [HN(1,2-CH_2CH_2N=PPh_3)$_2$Ni-Cl][PF_6] (120 mg, 0.14 mmol) in CH_2Cl_2 (2 mL).The resulting dark orange solution was stirred for 5 min at -35°C and cold Et_2O was added slowly to precipitate the compound. The resulting solid was washed twice with 5 mL of cold Et_2O and dried under vacuo. The solid was redissolved in THF (1mL) and cooled to -35°C and $LiHBEt_3$ (0.07mL, 0.07 mmol) was added dropwise. The mixture was allowed to warm up to room temperature for 20 min which led to the formation of precipitate. The orange solid was isolated by filtration over a pad of Celite and washed with Et_2O. The orange compound was dissolved in CH_3CN, filtered through Celite and the solvent was evaporated affording red crystals. Yield 60 mg (52%). ^{1}H NMR (CD_3CN): 7.85 (dd, 12H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$= 11.9 Hz, C_6H_5), 7.64 (t, 6H, C_6H_5), 7.51 (m, 12H, C_6H_5), 3.58 (s br, 1H, N-*H*), 2.79 (m, 6H, C*H*$_2$), 2.39 (t br, 2H, $^3J_{HH}$ = 7.2 Hz, C*H*$_2$), -27.33 (s, 1H, Ni-*H*). ^{31}P{^{1}H} NMR: 31.9 (s, N=PPh_3), -144.6 (sept, PF_6). ^{13}C{^{1}H} NMR (CD_3CN): 133.9 (d, *C*H, $^3J_{CP}$ = 9.4 Hz), 133.2 (d, *C*H, $^4J_{CP}$ = 2.3 Hz), 129.4 (d, *C*H, $^2J_{CP}$ = 12.5 Hz), 129.2 (d, $^1J_{CP}$ = 102.2 Hz, *C*q), 52.1 (s, *C*H$_2$), 51.3 (d, *C*H$_2$, $^2J_{CP}$ = 15.9 Hz).Anal. Calcd for $C_{40}H_{40}F_6N_3NiP_3.CH_3CN$ (869.42): C, 58.02; H, 4.99; N, 6.44. Found: C, 57.94; H, 4.93; N, 6.58.



Synthesis of [HN(1,2-CH$_2$CH$_2$N=PPh$_3$)$_2$NiD][PF$_6$] 3*d*$_1$: Similar procedure to that described for **3** using LiDBEt$_3$
^{1}H NMR (C$_6$D$_5$Br): 7.67 (dd, 12H, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$= 11.7 Hz, C$_6$*H*$_5$), 7.28 (m, 8H, C$_6$*H*$_5$), 7.19 (m, 10H, C$_6$*H*$_5$), 4.04 (t br, 1H, N-*H*), 3.04 (t br, 2H, C*H*$_2$), 2.67 (m br, 2H, C*H*$_2$), 2.49 (m br, 2H, C*H*$_2$), 2.17 (m br, 2H, C*H*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_5$Br): 32.4 (s, N=PPh$_3$), -141.9 (sept, PF$_6$). ^{2}H NMR (C$_6$H$_5$Br): -27.10 (Ni-*D*). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br): 133.5 (*C*q), 133.1 (d, *C*H, J_{CP} = 9.4 Hz), 131.8 (s, *C*H), 128.3 (d, *C*H, J_{CP} = 12.5 Hz), 52.5 (s br, *C*H$_2$), 52.0 (d, *C*H$_2$, $^2J_{CP}$ = 16.7 Hz). Anal. Calcd. for C$_{40}$H$_{39}$DF$_6$N$_3$NiP$_3$.CH$_3$CN (870.43): C, 57.95; H, 5.09; N, 6.44. Found: C, 57.61; H, 4.88; N, 6.30.

Synthesis of [MeN(1,2-CH$_2$CH$_2$N=PPh$_3$)$_2$NiH][PF$_6$] 4 and [MeN(1,2-CH$_2$CH$_2$N=PPh$_3$)$_2$Ni-D][PF$_6$] 4*d*$_1$: These compounds were prepared in a similar manner and thus only one preparation is detailed. LiHBEt$_3$ (0.23 ml, 0.23 mmol) was added room temperature to a suspension of **2** (100 mg, 0.11 mmol) in bromobenzene (2 mL). The reaction was stirred for 1h and a precipitate formed, the

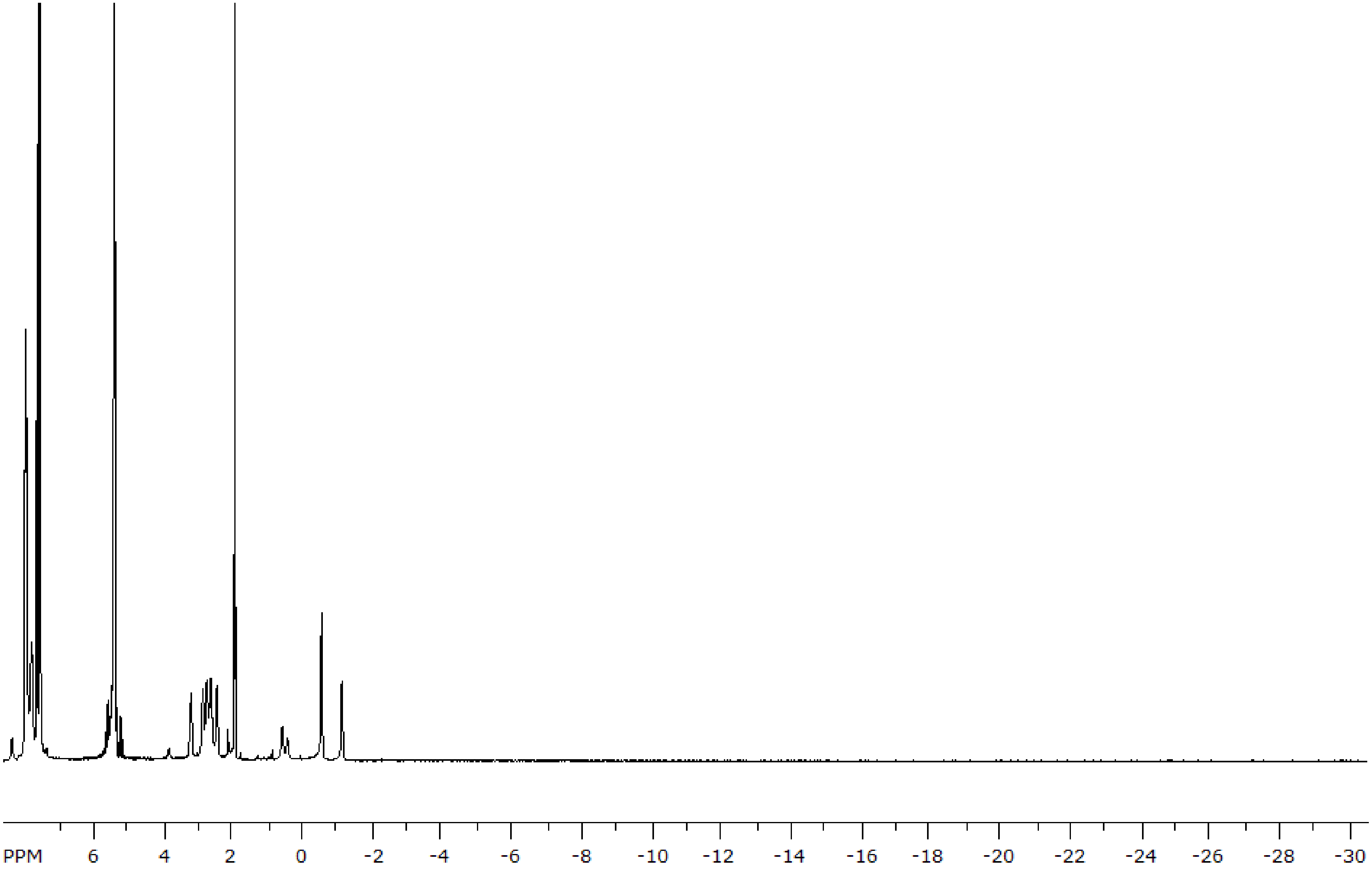
precipitate collected on a plug of Celite and washed with Et_2O. The orange solid was dissolved in CH_3CN and filtered. Volatiles were evaporated under vacuum affording orange crystals. Yield 84 mg (84%)
4: ^{1}H NMR (CD_3CN): 7.81 (dd, 12H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$= 11.9 Hz, C_6H_5), 7.64 (t, 6H, $^3J_{HH}$ = 7.6 Hz, C_6H_5), 7.51 (td, 12H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.8 Hz. C_6H_5), 3.31 (dt, 2H, CH_2), 3.01 (tt, 2H, CH_2), 2.80 (s, 3H, N-CH_3), 2.48 (m, 4H, CH_2), -28.65 (s, 1H, Ni-*H*). ^{31}P{^{1}H} NMR: 32.3 (s, N=PPh_3), -144.6 (sept, PF_6). ^{13}C{^{1}H} NMR (CD_3CN): 134.0 (d, $^3J_{CP}$ = 9.5 Hz, *C*H), 133.3 (d, $^4J_{CP}$ = 2.7 Hz, *C*H), 129.5 (d, $^2J_{CP}$ = 12.2 Hz, *C*q), 129.3 (d, $^1J_{CP}$ = 102.4 Hz, *C*q), 62.2 (d, $^2J_{CP}$ = 15.2 Hz, CH_2), 51.4 (CH_2), 40.1 (N-CH_3). Anal. Calcd. for $C_{41}H_{42}F_6N_3NiP_3.CH_3CN$ (883.45): C, 58.46; H, 5.13; N, 6.34. Found: C, 58.71; H, 5.38; N, 6.77.



***4d*$_1$**: ^{1}H NMR (CD_3CN): 7.81 (dd, 12H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$= 11.9 Hz, C_6H_5), 7.64 (t, 6H, $^3J_{HH}$ = 7.6 Hz, C_6H_5), 7.51 (td, 12H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.8 Hz. C_6H_5), 3.31 (dt, 2H, CH_2), 3.01 (tt, 2H, CH_2), 2.80 (s, 3H, N-CH_3), 2.48 (m, 4H, CH_2). ^{2}H NMR: -28.65 (s, 1H, Ni-*D*). ^{31}P{^{1}H} NMR: 32.3 (s, N=PPh_3), -144.6 (sept, PF_6). ^{13}C{^{1}H} NMR (CD_3CN): 134.0 (d, $^3J_{CP}$ = 9.5 Hz, *C*H), 133.3 (d, $^4J_{CP}$ = 2.7 Hz, *C*H), 129.5 (d, $^2J_{CP}$ = 12.2 Hz, *C*q), 129.3 (d, $^1J_{CP}$ = 102.4 Hz, *C*q), 62.2 (d, $^2J_{CP}$ = 15.2 Hz, CH_2), 51.4 (CH_2), 40.1 (N-CH_3). Anal. Calcd. for $C_{41}H_{42}F_6N_3NiP_3.CH_3CN$ (883.45): C, 58.39; H, 5.24; N, 6.33. Found: C, 58.22; H, 5.28; N, 6.59.

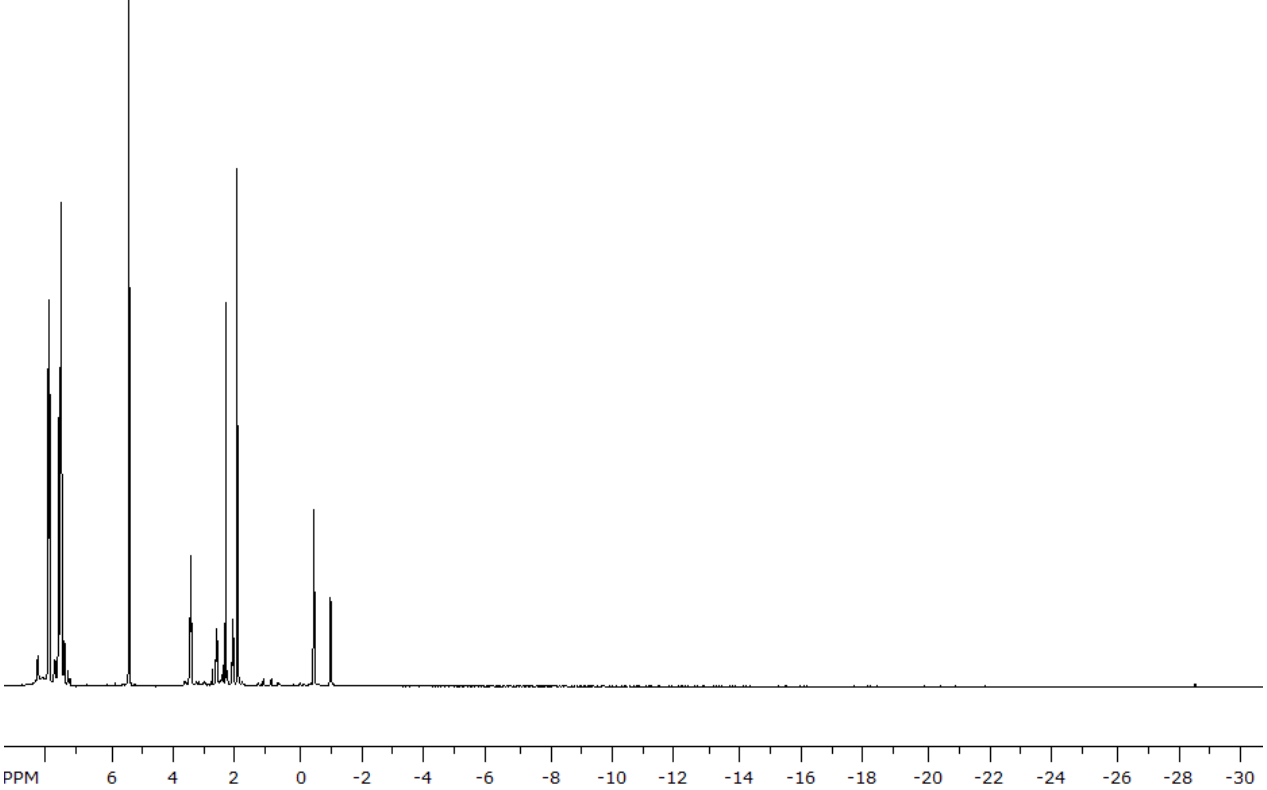
Generation of [HN(1,2-CH_2CH_2N=PPh_3)$_2$NiEt][PF_6] 5: 3 (30 mg, 0.036 mmol) in CD_3CN is transferred to a J-Young's NMR tube, degassed and the atmosphere is replaced by an atmosphere of ethylene. NMR is acquired after 10 minutes and shows 96% conversion to the **7**. Monitoring the reaction for two hours did not show further conversion.

^{1}H NMR (CD_3CN): 7.99 (m br, 12H, C_6H_5), 7.68 (m br, 6H, C_6H_5), 7.60 (m br, 12H, C_6H_5), 3.26 (s br, 2H, CH_2), 2.91 (s br, 2H, CH_2), 2.68 (s br, 2H, CH_2), 2.50 (s br, 2H, CH_2), -0.49 (t br, 3H, Ni-CH_2CH_3), -1.08 (q br, 2H, Ni-CH_2CH_3). ^{31}P{^{1}H} NMR (CD_3CN): 33.4 (N=PPh_3), -144.5 (sept, PF_6). ^{13}C{^{1}H}NMR (CD_3CN): 134.1 (d, $^3J_{CP}$ = 9.0 Hz, *C*H), 133.8 (d, $^4J_{CP}$ = 3.1 Hz, *C*H), 129.6 (d, $^2J_{CP}$ = 12.0 Hz, *C*H), 128.7 (d, $^1J_{CP}$ = 100 Hz, *C*q), 50.8 (CH_2), 50.0 (d, Jcp = 11.6 Hz, CH_2), 14.3 (Ni- CH_2CH_3), -7.3 (Ni-CH_2CH_3).



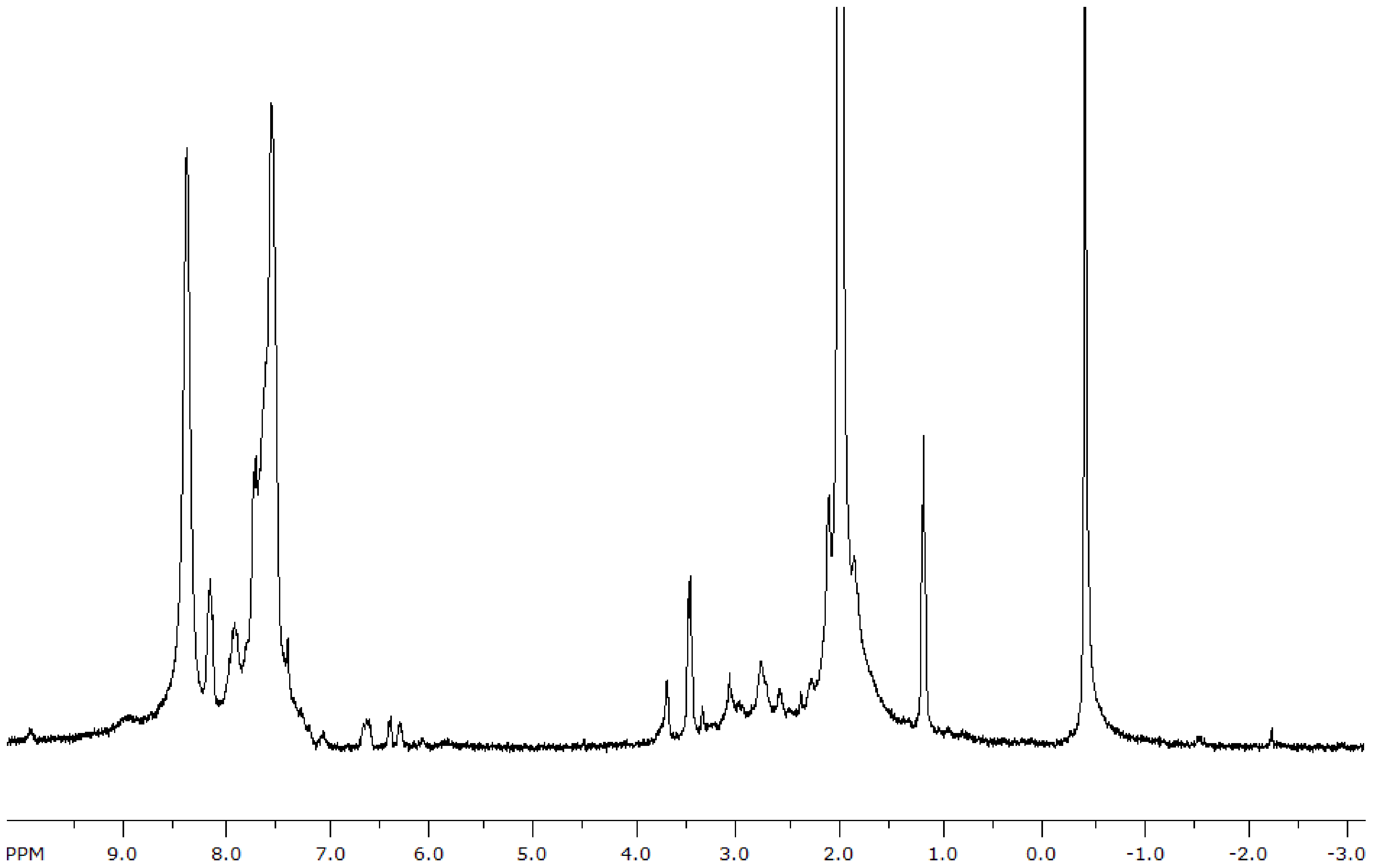
Generation of [MeN(1,2-CH_2CH_2N=PPh_3)$_2$NiEt][PF_6] 6: 4 (0.030g, 0.034 mmol) in CD_3CN is transferred to a J-Young's NMR tube, and degassed and the atmosphere is replaced by an atmosphere of ethylene.

^{1}H NMR (CD_3CN): 8.00 (dd, 12H, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 11.7 Hz, Ar*H*), 7.67 (m, 6H, Ar*H*), 7.61 (m, 12H, Ar*H*), 3.47 (m, 4H, CH_2), 2.64 (m, 2H, CH_2), 2.35 (s, 3H, N-CH_3), 2.12 (m, 2H, CH_2), -0.44 (t, 3H, $^3J_{HH}$ = 7.3 Hz, Ni-CH_2CH_3), -0.98 (q, 2H, $^3J_{HH}$ = 7.3 Hz, Ni-CH_2CH_3). ^{31}P{^{1}H} NMR (CD_3CN): 34.2 (N=PPh_3), -144.5 (sept, PF_6). ^{13}C{^{1}H}NMR (CD_3CN): 134.2 (d, $^3J_{CP}$ = 9.7 Hz, *C*H), 133.6 (d, $^4J_{CP}$ = 3.0 Hz, *C*H), 129.8 (d, $^2J_{CP}$ = 12.4 Hz, *C*H), 128.3 (d, $^1J_{CP}$ = 98.9 Hz, *C*q), 58.7 (d, $^2J_{CP}$ = 12.7 Hz, CH_2), 48.3 (CH_2), 44.4 (N-CH_3), 15.2 (Ni-CH_2CH_3), -7.1 (Ni-CH_2CH_3).



Thermolysis of [HN(1,2-CH_2CH_2N=PPh_3)$_2$NiH][PF_6] at 80°C

3 (15 mg, 0.017 mmol) was dissolved in CD_3CN, transferred to a J-Young's NMR tube and placed at 80°C for 3 hours. NMR was acquired at room temperature. ^{1}H NMR (CD_3CN) selected: 6.62 (m, 2H, C_6H_4), 6.40 (m, 1H, C_6H_4), 6.30 (m, 1H, C_6H_4),
^{31}P{^{1}H} NMR (CD_3CN): 44.7, 36.7, -144.5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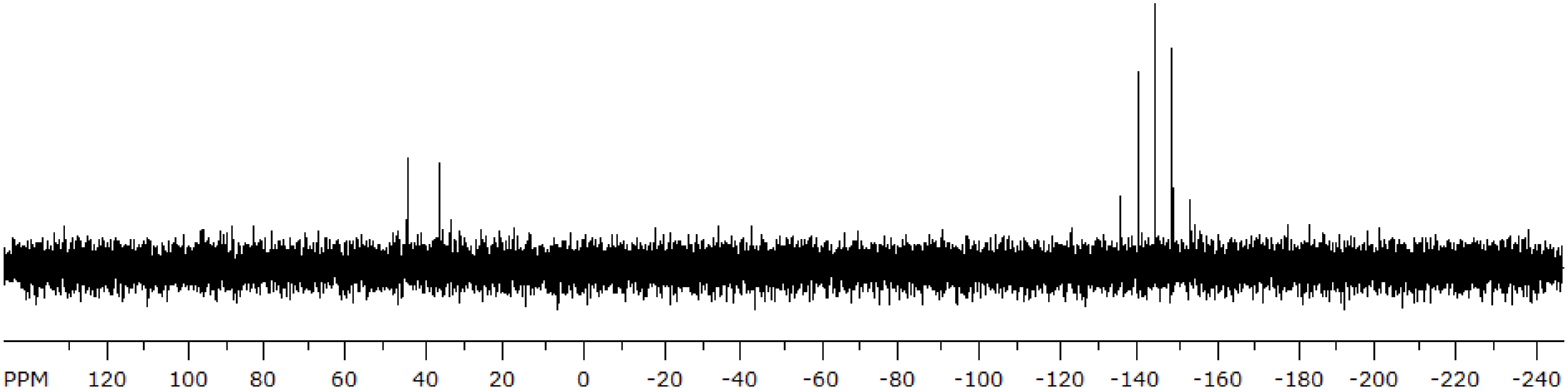
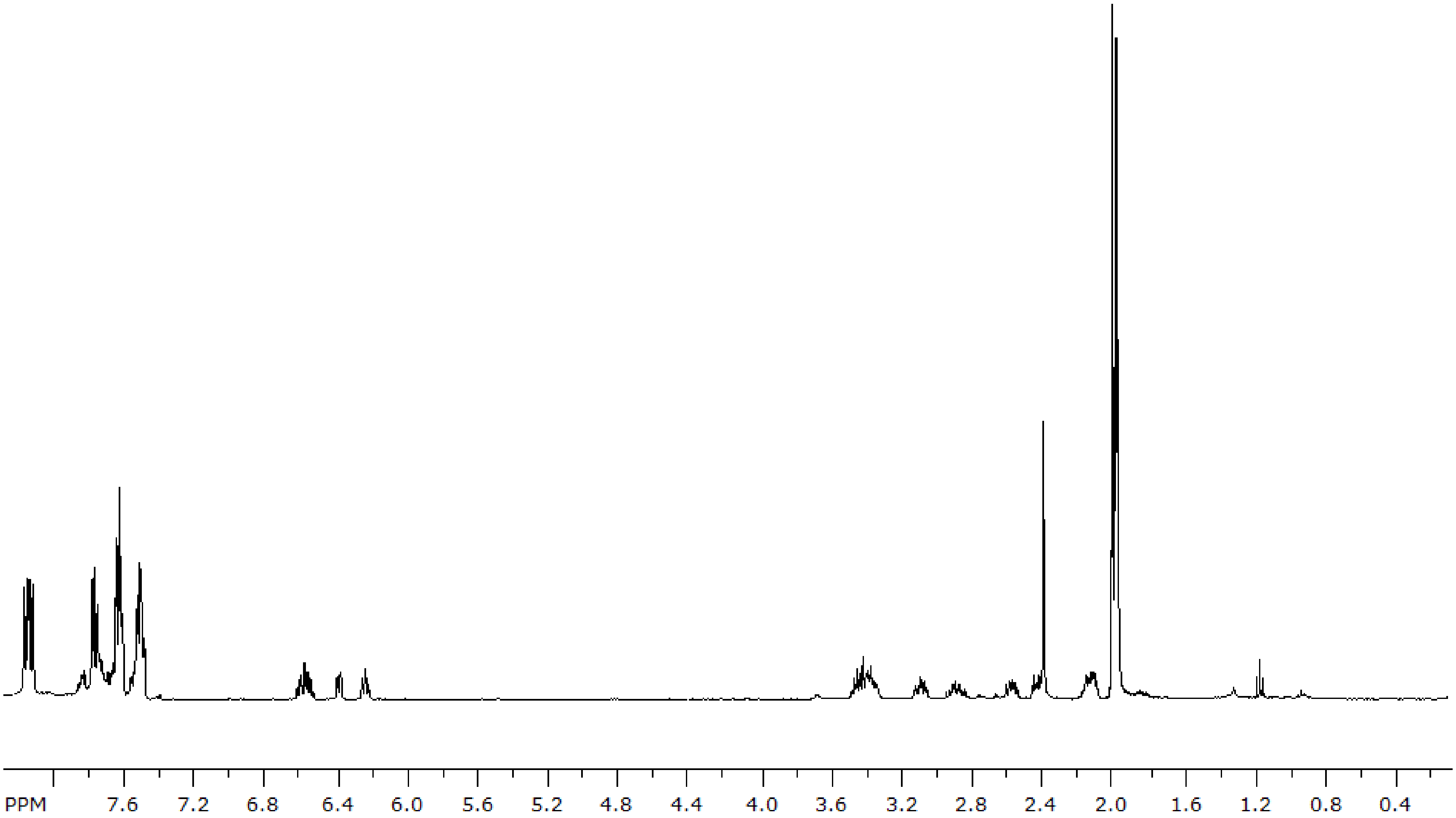


Synthesis of [MeN(CH_2CH_2N=PPh_3)(CH_2CH_2N=$PPh_2(C_6H_4)$Ni][PF_6] 8: Compound **4** (20 mg, 0.023 mmol) was dissolved in CD_3CN, transferred to a J-Young's NMR tube and placed at 80°C for 3 hours. NMR was acquired at room temperature.
^{1}H NMR (CD_3CN): 8.15 (dd, 6H, $^3J_{HH}$ = 7.9 Hz, J_{HP} =11.6 Hz, C_6H_5), 7.85 (m, 1H, C_6H_5), 7.78 (m, 5H, C_6H_5), 7.64 (m, 6H, C_6H_5), 7.52 (dt, 6H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.6 Hz, C_6H_5), 6.58 (m, 2H, C_6H_4), 6.39 (d, 1H, $^3J_{HH}$ = 7.4 Hz, C_6H_4), 6.24 (t, 1H, $^3J_{HH}$ = 7.0 Hz, C_6H_4), 3.41 (m, 2H, CH_2), 3.08 (m, 1H, CH_2), 2.88 (m, 1H, CH_2), 2.56 (m, 1H, CH_2), 2.42 (m, 1H, CH_2), 2.39 (s, 3H, N-CH_3), 2.12 (m, 2H, CH_2). ^{31}P{^{1}H} NMR (CD_3CN): 45.7, 35.9, -144.5. ^{13}C{^{1}H}NMR (CD_3CN): 141.1 (d, $^2J_{CP}$ = 16.1 Hz, *C*H), 134.9 (d, J_{CP} = 9.6 Hz, *C*H), 134.1 (dt, J_{CP} = 15.4 Hz, J_{CP} = 3.0 Hz, *C*H), 133.4 (d, J_{CP} = 10.2 Hz, *C*H), 133.1 (d, J_{CP} = 10.2 Hz, *C*H), 132.7 (d, J_{CP} = 9.6 Hz, *C*q)130.4 (d, J_{CP} = 4.0 Hz, *C*H), 130.2 (d, J_{CP} = 4.0 Hz, *C*H), 129.7 (d, J_{CP} = 12.3 Hz, *C*H), 128.7 (d, J_{CP} = 3.1 Hz, *C*H), 128.4 (d, J_{CP} = 2.9 Hz, *C*H), 128.2 (*C*q) 127.6 (*C*q), 126.5 (*C*q), 123.5 (d, $^2J_{CP}$ = 14.8 Hz, *C*H), 63.9 (d, $^2J_{CP}$ = 14.5 Hz, CH_2), 60.6 (d, $^2J_{CP}$ = 10.8 Hz, CH_2), 49.2 (CH_2), 45.2 (CH_2), 41.9 (N-CH_3).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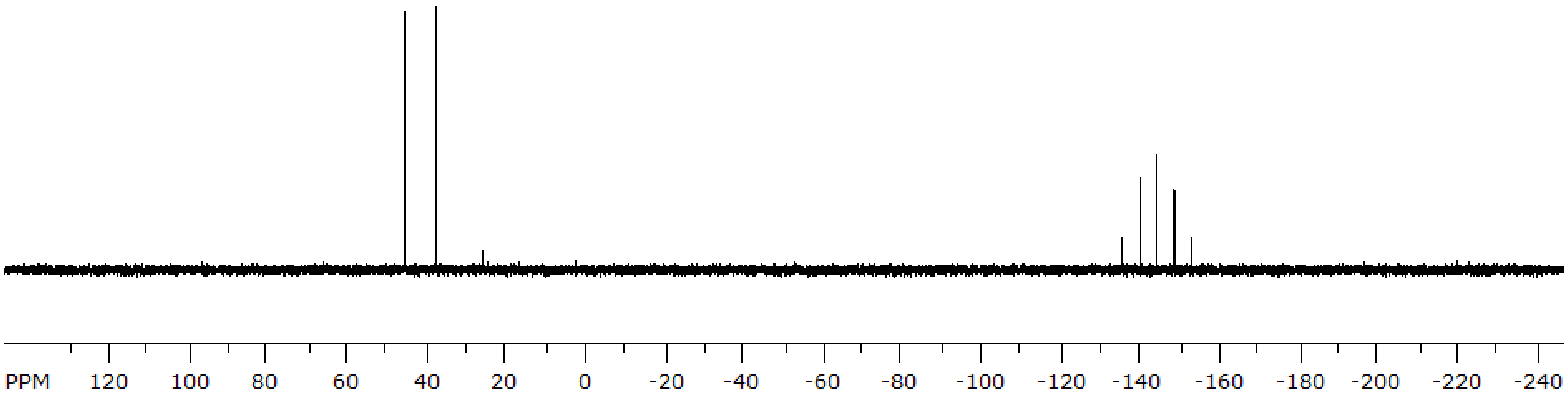
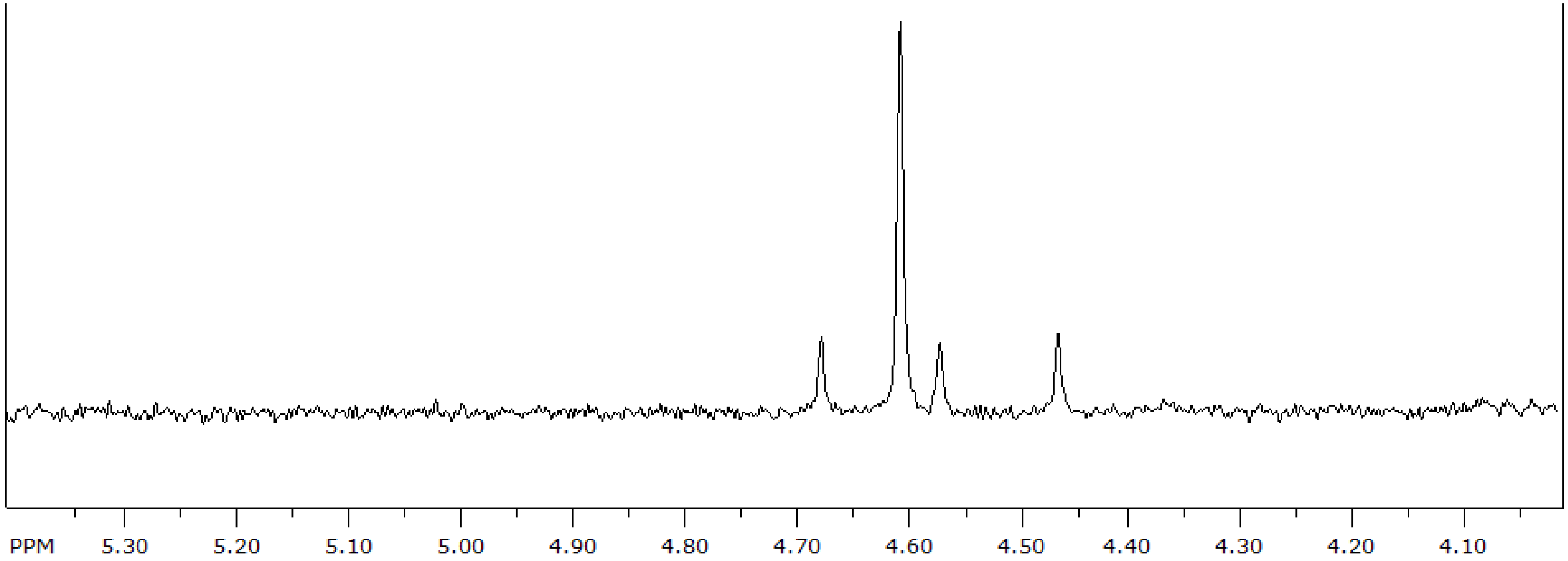


Reaction of [HN(1,2-$CH_2CH_2N{=}PPh_3)_2$Ni-H][PF_6] and [MeN(1,2-$CH_2CH_2N{=}PPh_3)_2$Ni-H][PF_6] with $LiHBEt_3$ forming 9 and 10: In the glovebox, **3** (20 mg, 0.023 mmol) were dissolved in C_6D_5Br and transferred to a J-Young's NMR tube and cooled to -35°C. $LiHBEt_3$ (0.023 ml, 0.023 mmol) (1M in THF) was added dropwise to the solution of **3**. A darkening of the solution is observed as well as H_2 gas evolution. ^{1}H NMR reveals the presence of H_2 as a singlet at 4.60 ppm, and $^{11}B\{^1H\}$ shows the formation of BEt_3 at 80.0 ppm.. The product was identified as characterized **9**, its NMR spectrum as already been reported.^{ref}
$^{31}P\{^1H\}$ NMR (C_6D_5Br): 35.6 (N=PPh_3), -143.2 (sept, PF_6).
10: $^{31}P\{^1H\}$ NMR (C_6D_5Br): 36.8 (N=PPh_3), -143.2 (sept, PF_6).

Reaction of [HN(1,2-$CH_2CH_2N{=}PPh_3)_2$Ni-D][PF_6] and [MeN(1,2-$CH_2CH_2N{=}PPh_3)_2$Ni-D][PF_6] with $LiHBEt_3$: Similar reaction procedure using **3*d*$_1$** and **4*d*$_1$**. $LiHBEt_3$ (18 µl, 0.018 mmol, 1M in THF) was added to a J-Young's NMR tube containing a frozen solution of [HN(1,2-$CH_2CH_2N{=}PPh_3)_2$Ni-D][PF_6] (16 mg, 0.018 mmol) in 0.5 ml of C_6D_5Br at -45°C. The solution was then warmed up to room temperature. The orange solution slowly darkens and gas evolution is observed. Full conversion to [RN(1,2-$CH_2CH_2N{=}PPh_3)_2$Ni-C_6D_5][PF_6] was achieved in 45 minutes. $^{31}P\{^1H\}$ NMR (C_6D_5Br): 35.7 (N=PPh_3), -142.1 (PF_6). ^{1}H NMR (C_6H_5Br): 4.60 (s, H_2), 4.57 (t, $^1J_{HD}$ = 42.4 Hz, HD)



^{1}H NMR spectrum of HNNi-H and LiDBEt$_3$

REFERENCES

(1) (a) Cariou, R.; Dahcheh, F.; Graham, T. W.; Stephan, D. W. *Dalton Trans.* **2011**, *40*, 4918; (b) Cariou, R.; Graham, T. W.; Dahcheh, F.; Stephan, D. W. *Dalton Trans.* **2011**, *40*, 5419.