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Ni→B Interactions in Nickel Phosphino-Alkynyl-Borane Complexes

Xiaoxi Zhao, Edwin Otten, Datong Song, and Douglas W. Stephan^{*[a]}

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Experimental Methods

General Considerations

All preparations and manipulations were performed on a double manifold N₂/vacuum line with Schlenk-type glassware or in a N₂-filled M-Braun glove box. Solvents (Aldrich) were dried using an Innovative Technologies solvent system. NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer and spectra were referenced to residual solvent (¹H, ¹³C) or externally (¹¹B; BF₃OEt₂, ¹⁹F; CFCl₃, ³¹P; 85% H₃PO₄). NMR solvents were purchased from Cambridge Isotopes, dried over CaH₂ or Na/benzophenone, vacuum distilled prior to use and stored over 4Å molecular sieves in the glovebox. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. B(C₆F₅)₃ was generously provided by Nova Chemicals. Combustion analysis was performed in house on a Perkin-Elmer CHN Analyzer.

Synthesis of tBu₂PHC=CBCl(C₆F₅)₂ 1 To a solution of ClB(C₆F₅)₂ (733 mg, 1.93 mmol) in toluene (2 mL) was added a solution of HCCPtBu₂ (328 mg, 1.93 mmol) in toluene (8 mL) at -35 °C. The reaction was stirred for 1 h, during which time the solution color turned yellow. After the solvent was completely pumped off, pentane (12 mL) was added and the mixture was stirred until an off-white solid formed. The supernatant liquid was decanted and the solid product was washed with pentane. Drying *in vacuo* afforded an off-white powder. This product was used in the subsequent reactions without further purification. Yield: 761 mg, 72%. ¹H NMR: 5.80 (d, 1H, ¹J_{HP} = 469 Hz, PH), 1.51 (d, 18H, ³J_{HP} = 18.8 Hz, tBu). ¹¹B{¹H} NMR: -12.80 (s). ¹³C{¹H} NMR: 148.26 (dm, ¹J_{CF} = 243 Hz, o-C₆F₅), 145.18 (br, C=CB), 140.07 (dm, ¹J_{CF} = 251 Hz, p-C₆F₅), 137.57 (dm, ¹J_{CF} = 248 Hz, m-C₆F₅), 119.81 (br, quat-C₆F₅), 67.43 (d, ¹J_{CP} = 155 Hz, C=CP), 35.41 (d, ¹J_{CP} = 42 Hz, quat-tBu), 26.99 (d, ²J_{CP} = 2.5 Hz, tBu). ¹⁹F NMR: -133.09 (m, 4F, o-C₆F₅), -160.50 (t, 2F, ³J_{FF} = 20 Hz, p-C₆F₅), -166.08 (m, 4F, m-C₆F₅). ³¹P {¹H} NMR: 25.50 (s). Anal. Calcd. for C₂₂H₁₉BClF₁₀P: C, 47.99; H, 3.48. Found: C, 47.87; H, 3.80 %.

Synthesis of tBu₂PHC=CBH(C₆F₅)₂ 2 Compound 1 (368 mg, 0.668 mmol) was stirred with Me₂SiHCl (1.0 g, 5.83 mmol) overnight in CH₂Cl₂. After confirming full conversion to the product by NMR of the reaction mixture, all the volatiles were completely pumped off. The residue was dissolved in toluene and passed through neutral alumina to eliminate high molecular weight impurities. The filtrate was dried and the product was recrystallized by layering CH₂Cl₂ solution with pentane at RT overnight. The product colorless crystals were separated from the supernatant, from which more product was recrystallized using CH₂Cl₂/pentane. The combined product was dried *in vacuo*. Yield: 273 mg, 79%. Single crystals suitable for X-ray diffraction were grown by layering a CH₂Cl₂ solution of the product with pentane at 25°C. ¹H NMR: 5.70 (dd, 1H, ¹J_{HP} = 464 Hz, ⁵J_{HH} = 2.0 Hz, PH), 3.25 (q, 1H, ¹J_{HB} = 91 Hz, BH), 1.48 (d, 18H, ³J_{HP} = 18.8 Hz, tBu). ¹¹B{¹H}: -29.15 (s). ¹³C{¹H} NMR: 147.98 (dm, ¹J_{CF} = 235 Hz, o-C₆F₅), 138.77 (dm, ¹J_{CF} = 245 Hz, p-C₆F₅), 136.93 (dm, ¹J_{CF} = 261 Hz, m-C₆F₅), 120.90 (br, quat-C₆F₅), 64.37 (d, ¹J_{CP} = 158 Hz, C=CP), 34.72 (d, ¹J_{CP} = 44 Hz, quat-tBu), 26.70 (d, ²J_{CP} = 2.6 Hz, tBu). C=CB was not observed. ¹⁹F NMR: -133.23 (dm, 4F, ³J_{FF} = 21 Hz, o-C₆F₅), -162.79 (t, 2F, ³J_{FF} = 20 Hz, p-C₆F₅), -166.67 (m, 4F, m-C₆F₅). ³¹P{¹H} NMR : 24.18 (s). IR (CH₂Cl₂, cm⁻¹): 2125

($\nu(\text{C}=\text{C})$). Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{BF}_{10}\text{P}$: C, 51.19; H, 3.91. Found: C, 51.35; H, 4.02 %.

Synthesis of $(t\text{Bu}_2\text{PC}=\text{CB}(\text{C}_6\text{F}_5)_2)\text{Ni}(\text{COD})\cdot 0.5\text{C}_7\text{H}_8$ 4 This compound was obtained in via two synthetic routes. Method 1: To a toluene (1.0 mL) solution of **2** (100 mg, 0.19 mmol) was added a mixture of $\text{B}(\text{C}_6\text{F}_5)_3$ (99 mg, 0.19 mmol) and PtBu_3 (39 mg, 0.19 mmol) dissolved in toluene (2.0 mL) at RT. The reaction mixture immediately turned orange-yellow, and became cloudy upon stirring for 1 h. Hexanes (10 mL) were added, and the reaction was left standing at -35°C for 3 h. The mixture was then filtered through Celite and washed with cold hexanes. Upon addition of the combined filtrate to a mixture of $\text{Ni}(\text{COD})_2$ (50 mg, 0.18 mmol) and 1,5-cyclooctadiene (190 mg, 1.8 mmol), the reaction immediately started to turn orange, and became red in 15 min. After 6 h of stirring, the solution was pumped down and some toluene was added to dissolve all the red precipitate. The mixture was then filtered through Celite to eliminate small amount of Ni metal that precipitated out of the reaction. The filtrate was further pumped down until a red precipitate started to form. Upon addition of pentane (8 mL) and cooling at -35°C overnight, the supernatant liquid was removed to afford an orange-red fine crystalline product, which was washed with pentane and dried *in vacuo*. The isolated product was stored at -35°C to avoid decomposition. Yield: 86 mg, 65 %.

Method 2: **2** (100 mg, 0.19 mmol), $\text{Ni}(\text{COD})_2$ (53 mg, 0.19 mmol) and 1,5-cyclooctadiene (210 mg, 1.9 mmol) were mixed together in toluene (5 mL). The initially yellow solution turned deep red upon overnight stirring at RT. The reaction work up was the same as method 1. Yield: 101 mg, 72 %. The crystalline product was suitable for X-ray diffraction. ^1H NMR (C_6D_6): 7.13 (m, 1.5H, *o/p*-Ph, toluene), 7.02 (m, 1H, *m*-Ph, toluene), 5.50 (br, 2H, $=\text{CH}$, cod), 4.88 (br, 2H, $=\text{CH}$, cod), 2.11 (s, 1.5H, CH_3 , toluene), 1.90 (m, 4H, CH_2 , cod), 1.67 (m, 4H, CH_2 , cod), 1.22 (d, 18H, $^3J_{\text{HP}} = 12.3$ Hz, *t*Bu). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): 6.98 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 147.89 (dm, $^1J_{\text{CF}} = 241$ Hz, *o*- C_6F_5), 140.49 (dm, $^1J_{\text{CF}} = 247$ Hz, *p*- C_6F_5), 137.96 (dm, $^1J_{\text{CF}} = 250$ Hz, *m*- C_6F_5), 137.90 (s, *i*-Ph, toluene), 129.34 (s, *o*-Ph, toluene), 128.69 (s, *m*-Ph, toluene), 125.68 (s, *p*-Ph, toluene), 120.70 (d, $^1J_{\text{CP}} = 57$ Hz, $\text{C}=\text{CP}$), 108.62 (d, $^3J_{\text{CP}} = 11.2$ Hz, $=\text{CH}$, cod), 98.70 (s, $=\text{CH}$, cod), 33.03 (d, $^1J_{\text{CP}} = 25$ Hz, quat-*t*Bu), 31.03 (s, CH_2 , cod), 29.60 (d, $^2J_{\text{CP}} = 14$ Hz, *t*Bu), 28.31 (s, CH_2 , cod), 21.42 (s, CH_3 , toluene). $\text{C}=\text{CB}$ and quat- C_6F_5 carbons were not observed. ^{19}F NMR (C_6D_6): -129.32 (m, 4F, *o*- C_6F_5), -154.85 (t, 2F, $^3J_{\text{FF}} = 21$ Hz, *p*- C_6F_5), 163.13 (m, 4F, *m*- C_6F_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 6.86 (s). IR (thin film from CH_2Cl_2 , cm^{-1}): 1881 ($\nu(\text{C}=\text{C})$). Anal. Calcd. for $\text{C}_{30}\text{H}_{30}\text{BF}_{10}\text{PNi}\cdot\text{C}_{3.5}\text{H}_4$: C, 55.34; H, 4.71. Found: C, 55.35; H, 5.00 %.

Synthesis of $[(t\text{Bu}_2\text{PC}=\text{CB}(\text{C}_6\text{F}_5)_2)\text{Ni}(\text{NCMe})]_2$ 5 Compound **4** (24 mg, 0.033 mmol) and acetonitrile (50 μL , 0.96 mmol) were mixed in benzene (2 mL). Dark brown crystals formed out of the reaction mixture overnight at RT. The crystals were isolated and washed with benzene (2 x 1 mL) and pentane (2 mL). Yield: 9 mg, 45 %. The crystalline product was suitable for X-ray diffraction. ^1H NMR (THF-d_8): 2.52 (br), 2.18 (s), 1.28 (br, m). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF-d_8): no signal was observed. ^{19}F NMR (THF-d_8): -130.33 (m, 8F, *o*- C_6F_5), -159.68 (t, 4F, $^3J_{\text{FF}} = 20$ Hz, *p*- C_6F_5), -165.97 (m, 8F, *m*- C_6F_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-d_8): 53.16 (s). IR

(KBr, cm^{-1}): 2269 ($\nu(\text{N}=\text{C})$), 1838 ($\nu(\text{C}=\text{C})$). Anal. Calcd. for $\text{C}_{48}\text{H}_{42}\text{B}_2\text{F}_{20}\text{N}_2\text{P}_2\text{Ni}_2$: C, 46.96; H, 3.45; N, 2.28. Found: C, 47.22; H, 3.51; N, 2.82 %.

Computational Methods

DFT calculations were performed using Gaussian 03.^(ref) Geometry optimization was carried out using the B3PW91 method^(ref) and 6-311G** basis set implemented in Gaussian 03 software. Frequency analysis performed after geometry optimization confirmed that no imaginary frequency was present.

Optimized atomic coordinates for **3_{calc}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	0.597677	8.859701	5.585688
2	9	0	-0.178444	5.680712	2.408723
3	9	0	2.370649	4.820945	7.374146
4	9	0	-0.172882	1.959481	4.589355
5	9	0	2.944153	2.418310	3.828907
6	9	0	-0.348069	0.191678	6.591622
7	9	0	3.348418	1.716938	1.277529
8	9	0	2.183798	3.036807	9.355262
9	9	0	0.828574	0.715547	8.981047
10	9	0	0.243404	4.960117	-0.130367
11	9	0	2.003572	2.978959	-0.714079
12	6	0	0.938422	7.175646	5.301282
13	6	0	1.367017	4.083592	3.233408
14	6	0	0.429750	2.257267	5.745054
15	6	0	1.035921	5.978360	5.046246
16	6	0	1.104417	3.470817	5.892235
17	6	0	0.903654	4.348163	0.850086
18	6	0	0.320082	1.328737	6.768139
19	6	0	0.707022	4.709987	2.174109
20	6	0	2.251435	3.061630	2.882975
21	6	0	1.682281	3.699650	7.142266
22	6	0	2.482711	2.684542	1.569575
23	6	0	2.999277	9.091586	3.959790
24	1	0	3.458470	9.575229	3.089070
25	1	0	2.950423	8.018770	3.760186
26	1	0	3.661477	9.249542	4.811993

27	6	0	0.917176	1.595909	7.992849
28	6	0	1.308569	9.148497	7.330269
29	6	0	1.799441	3.331340	0.548413
30	6	0	1.605539	2.786657	8.182579
31	6	0	1.604805	9.679875	4.184874
32	5	0	1.166988	4.527266	4.729267
33	6	0	1.697576	11.185389	4.453670
34	1	0	2.093778	11.684909	3.562474
35	1	0	2.372992	11.414676	5.281548
36	1	0	0.719315	11.625004	4.670835
37	6	0	0.747797	9.442025	2.931375
38	1	0	1.248849	9.883222	2.062125
39	1	0	-0.239971	9.901628	3.024093
40	1	0	0.608792	8.376249	2.732156
41	6	0	0.851339	10.540277	7.790359
42	1	0	1.143621	10.686482	8.836143
43	1	0	-0.235711	10.644330	7.728680
44	1	0	1.303312	11.345669	7.208335
45	6	0	0.631801	8.096115	8.220931
46	1	0	0.883686	8.303210	9.267225
47	1	0	0.971910	7.086694	7.984029
48	1	0	-0.458144	8.124774	8.128075
49	6	0	2.827567	9.016907	7.446028
50	1	0	3.120194	9.110413	8.499023
51	1	0	3.351742	9.801057	6.894295
52	1	0	3.175979	8.044882	7.088517

LUMO for **3_{calc}**

Optimized Coordinates For **4_{calc}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	28	0	-1.341268	5.711959	4.899160
2	15	0	-0.038203	8.898303	5.242692
3	9	0	-0.345384	5.486743	2.161535
4	9	0	1.642663	5.084433	7.514333
5	9	0	0.098536	1.717551	4.558929
6	9	0	2.988001	2.760760	4.149430
7	9	0	0.230477	-0.063235	6.546818
8	9	0	3.886222	2.125777	1.725436
9	9	0	1.755507	3.288996	9.477144
10	9	0	1.053489	0.702609	9.024365
11	9	0	0.577094	4.836167	-0.239390
12	9	0	2.700441	3.149245	-0.498787
13	6	0	0.022527	7.106451	5.096431
14	6	0	1.253715	4.131200	3.286608
15	6	0	0.516298	2.149569	5.760547
16	6	0	0.625050	5.993554	5.027455
17	6	0	0.855110	3.490947	5.939023
18	6	0	1.161781	4.323785	0.844471
19	6	0	-2.512803	4.076715	5.483326
20	1	0	-1.817371	3.500769	6.088151
21	6	0	0.574970	1.204109	6.772483
22	6	0	0.701759	4.641377	2.113548
23	6	0	-2.334468	4.028985	4.119982
24	1	0	-1.549455	3.378169	3.745929
25	6	0	2.343547	3.279898	3.095898
26	6	0	1.272730	3.830620	7.225825
27	6	0	2.838879	2.940384	1.844900
28	6	0	2.320641	8.609727	3.517203
29	1	0	2.757888	8.889689	2.550915
30	1	0	2.143762	7.532477	3.504896
31	1	0	3.063252	8.822501	4.286688
32	6	0	0.993857	1.591532	8.037433
33	6	0	0.887994	9.154423	6.896717
34	6	0	2.240805	3.463881	0.708458
35	6	0	1.345677	2.913799	8.265319
36	6	0	1.023569	9.391205	3.726264
37	6	0	-3.026404	6.792855	4.260267
38	1	0	-2.574417	7.612395	3.705293
39	5	0	0.776633	4.547036	4.756393
40	6	0	-2.945256	6.876842	5.629890
41	1	0	-2.466189	7.765901	6.031311
42	6	0	-3.765811	4.541311	6.192696
43	1	0	-4.636850	4.384282	5.553444
44	1	0	-3.920950	3.915428	7.076055

45	6	0	1.318562	10.893447	3.810468
46	1	0	1.716581	11.238046	2.848994
47	1	0	2.068036	11.122305	4.571724
48	1	0	0.417719	11.477108	4.024732
49	6	0	-3.954612	5.891169	3.477245
50	1	0	-4.870048	5.716687	4.046653
51	1	0	-4.261290	6.413299	2.566769
52	6	0	-3.666939	6.013581	6.628904
53	1	0	-3.117945	6.070989	7.574127
54	1	0	-4.666155	6.422242	6.833478
55	6	0	0.090807	9.139619	2.529884
56	1	0	0.588053	9.463017	1.607902
57	1	0	-0.844068	9.700482	2.622430
58	1	0	-0.148315	8.078788	2.420524
59	6	0	-3.292428	4.554522	3.083123
60	1	0	-2.728097	4.696601	2.158725
61	1	0	-4.060304	3.800591	2.861233
62	6	0	0.780726	10.642610	7.258922
63	1	0	1.176309	10.797636	8.269504
64	1	0	-0.259076	10.982687	7.249890
65	1	0	1.351800	11.281792	6.583046
66	6	0	0.084858	8.353955	7.933894
67	1	0	0.483553	8.562499	8.933429
68	1	0	0.158563	7.278946	7.760810
69	1	0	-0.971984	8.640423	7.934692
70	6	0	2.346204	8.700557	6.925990
71	1	0	2.723776	8.753499	7.954660
72	1	0	2.984706	9.342089	6.314748
73	1	0	2.457005	7.668450	6.586470

LUMO

HOMO

HOMO-1

HOMO-2

Reference:

Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E., Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.