Supplementary Material (ESI) for Dalton Transactions

Supporting Information for the Paper Entitled

"Facile Entry to Late Transition Metal Boryl Complexes and Spectroscopic Observation of an Intermediate in the Alkoxide-Boryl Metathesis"

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Experimental

General Considerations. Unless otherwise stated, all operations were performed in an M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under a nitrogen atmosphere. Anhydrous ^{n}hexane, ^{n}pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18L) and dried by passage through two columns of activated alumina and a Q-5. Diethylether and CH_2Cl_2 were dried by passage through a column of activated alumina. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal. Distilled THF was transferred into an inert atmosphere using vacuum reservoirs. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 ºC. All other chemical were used as received unless otherwise stated. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded on Varian 300 and 400 MHz NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported with reference to solvent resonances of C_6D_6 at 7.16 ppm and 128.0 ppm, respectively. ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (aqueous solution, δ 0.0 ppm). ^{11}B NMR chemical shifts are reported with respect to external standard $BF_3{\cdot}OEt_2$ (δ 0.0 ppm). High resolution mass spectrometry experiment was performed on the MAT-95 XP mass spectrometer at Indiana University Chemistry Department Mass Spectrometry Facility. CHN analyses were performed by Midwest Microlabs, Indianapolis, IN. X-ray diffraction data were collected on APEX II Kappa Duo (Bruker) system under a stream of N_2 (g)

at low temperatures. PNP = N[2-P($CHMe_2$)$_2$-4-methylphenyl]$_2^-$,[1] (PNP)NiCl,[2] and (PNP)CoCl[3] were all synthesized according to published procedure in the literature. (PNP)Ni[B(catechol)] was independently prepared by a published protocol for referencing purposes.[4] All other chemical were used as received except for KO^{t}Bu which was washed with anhydrous hexane and dried in vacuum under an inert atmosphere.

Synthesis of (PNP)Ni(O^{t}Bu) (1). In a vial (PNP)NiCl (300 mg, 0.57 mmol) was taken in 5 ml of THF and cooled to −35 ^{o}C. An analogously cooled solution of KO^{t}Bu (64.3 mg, 0.57 mmol) was added dropwise to the cooled solution of (PNP)NiCl. After 30 minutes the color of the reaction mixture changed to blue. The reaction mixture was stirred for 2 hours and then dried in vacuo. The dried mass was extracted with pentane 5 mL to afford a blue color solution which upon storing at −45 ^{o}C yielded blue crystals of **1**. The crystalline product was collected on a medium porosity frit via vacuum filtration. Yield 79 % (252 mg, 0.449 mmol). ^{1}H NMR (25 ^{o}C, 399.8 MHz, C_6D_6): δ 7.34 (d, C_6H_3, 2H), 7.06 (s, C_6H_3, 2H), 6.65(d, C_6H_3, 2H), 2.36 (septet, C*H*Me$_2$, 4H), 2.14(s, *Me*Ar, 6H), 1.60 (q, CH*Me*$_2$, 12H), 1.35(dd, overlapped with s, CH*Me*$_2$ and O^t*Bu* resonances overlapped, 21H). ^{13}C NMR (25 ^{o}C, 100.6 MHz, C_6D_6): δ 162.26 (aryl), 131.87 (aryl), 131.74 (aryl), 124.34 (aryl), 121.28 (aryl), 117.46 (aryl), 66.83 (O*C*(CH$_3$)$_3$), 35.89 (OC(*C*H$_3$)$_3$) 24.45 (*C*HMe$_2$), 20.59(*Me*Ar), 19.39 (CH*Me*$_2$), 17.34 (CH*Me*$_2$). ^{31}P NMR (25 ^{o}C, 121.5 MHz, C_6D_6): δ 17.23. Anal. Calcd. for $C_{30}H_{49}NNiOP_2$: C, 64.30; H, 8.81; N, 2.50. Found: C, 64.10; H, 8.75; N, 2.32.

Synthesis of (PNP)Co(O^{t}Bu) (2). In a 20 mL vial, (PNP)CoCl (201 mg, 0.38 mmol) was dissolved in ethereal solution (4 mL). To this vial was added dropwise KO^{t}Bu (43 mg, 0.38

mmol) in an ethereal solution (2 mL) with a glass pipette at room temperature causing a change in color of the solution from dark blue to dark green. After 2.5 h, all volatiles were removed and the crude product extracted into 5 mL pentane and filtered through a fiber glass plug containing celite. The resulting filtrate was reduced in volume and storing at −35 ^{o}C afforded dark green blocks of crystals. The crystalline product was collected on a medium porosity frit, washed with cold pentane, and dried under reduced pressure. Yield = 86 % (180 mg, 0.33 mmol). ^{1}H NMR (25 °C, 300 MHz, C_6D_6): δ 40.3 ($\Delta\upsilon_{1/2}$ = 72 Hz), 34.4 ($\Delta\upsilon_{1/2}$ = 36 Hz), 29.2 ($\Delta\upsilon_{1/2}$ = 67 Hz), 28.8 ($\Delta\upsilon_{1/2}$ = 45 Hz), 19.9 ($\Delta\upsilon_{1/2}$ = 54 Hz), 16.8 ($\Delta\upsilon_{1/2}$ = 250 Hz), 2.5 ($\Delta\upsilon_{1/2}$ = 190 Hz), 0.84 ($\Delta\upsilon_{1/2}$ = 142 Hz), −16.7 ($\Delta\upsilon_{1/2}$ = 104 Hz), −34.8 ($\Delta\upsilon_{1/2}$ = 132 Hz). μ_{eff} = 2.16 μ_B (25 °C) (Evans' method). Anal. Calcd. for $C_{30}H_{49}CoNOP_2$: C, 64.27; H, 8.81; N, 2.50. Found: C, 64.35; H, 8.98; N, 2.56.

Synthesis of (PNP)Ni[B(catechol)] (3). In a 20 mL scintillation vial was charged solid B_2cat_2 (85.0 mg, 0.357 mmol) and the solid dissolved with 5 mL diethyl ether. To this solution was added dropwise an 5 mL ethereal solution (PNP)Ni(O^tBu) (200 mg, 0.357 mmol) at –37 °C. The solution mixture changed to red a solution, then yellow over 10h. The diethyl ether solution was reduced in volume via dynamic vacuum and stored at –37 °C producing yellow crystalline compound. The yellow product was collected by vacuum filtration on a medium porosity frit and dried under vacuum. Yield = 85% (184 mg, 0.304 mmol). The spectroscopic detail and the X-ray structure of **3** have been communicated elsewhere.[4]

Synthesis of (PNP)Co[B(pinacol)] (**4**). In a 20 mL scintillation vial was charged solid B_2pin_2 (90.6 mg, 0.357 mmol) and dissolved in 3 mL of diethyl ether. To this solution was added

(PNP)Co(O^{t}Bu) (200 mg, 0.357 mmol) dissolved in 10 mL of diethyl ether via a glass pipette at –37 °C. The solution mixture gradually changed from dark green to reddish brown over 2 h. The reaction was allowed to stir an additional 8 h to ensure completion. All volatiles were removed under reduced pressure and the crude waxy solid was extracted into 5 mL of pentane and an additional 2 mL of diethyl ether and filtered through a medium porosity frit containing celite. The resulting filtrate solution was reduced to 3 mL and stored at –37 °C producing red crystalline product which was collected by vacuum filtration on a medium porosity frit, washed with cold pentane and the red crystals dried under reduced pressure. Yield = 65% (142 mg, 0.232 mmol). ^{1}H NMR (25 °C, 300 MHz, C_6D_6): δ 39.7 ($\Delta\upsilon_{1/2}$ = 40 Hz), 35.1 ($\Delta\upsilon_{1/2}$ = 83 Hz), 23.4 ($\Delta\upsilon_{1/2}$ = 14 Hz), 14.1 ($\Delta\upsilon_{1/2}$ = 23 Hz), 12.4 ($\Delta\upsilon_{1/2}$ = 210 Hz), 4.9 ($\Delta\upsilon_{1/2}$ = 19 Hz), –9.6 ($\Delta\upsilon_{1/2}$ = 39 Hz), –17.7 ($\Delta\upsilon_{1/2}$ = 44 Hz) . μ_{eff} = 2.25 μB (25 °C) (Evans' method). CI-HRMS: Anal. Calcd. for $C_{32}H_{52}BCoNO_2P_2$: 614.2898. Found: 614.2867. Multiple attempts to obtain satisfactorily elemental analysis on crystalline samples of **4** gave unsatisfactory results.

Single Crystal X-ray Crystallography: General Parameters and Refinement.

Inert-atmosphere techniques were used to place the crystal onto the tip of a glass capillary (0.06-0.20 mm diameter) mounted on a SMART6000 (Bruker) at 113(2) K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20-30 frames. The data collection was carried out using graphite-monochromated Mo Kα radiation with a frame time of 3 s and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ωat different φsettings with the detector set at -43° in 2θ. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration

(SAINT).[5] The structure was solved using SHELXS-97 and refined with SHELXL-97.[6] A direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were refined with isotropic displacement parameters (unless otherwise specified). Some intensity data were corrected for absorption (SADABS).[7]

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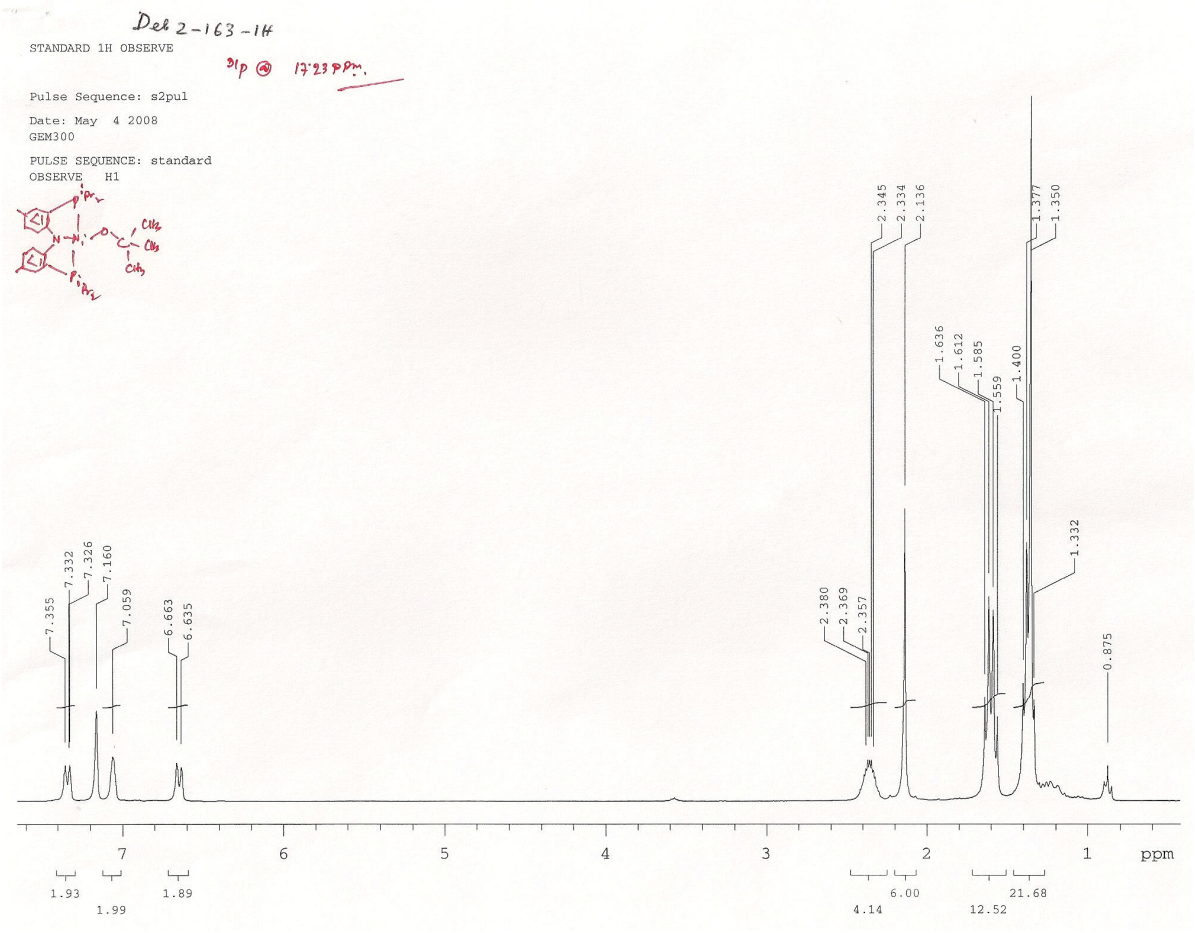

Figure S1. The ^{1}H NMR spectrum of (PNP)Ni(O^{t}Bu) **(1)** recorded in C_6D_6 at 25 °C.

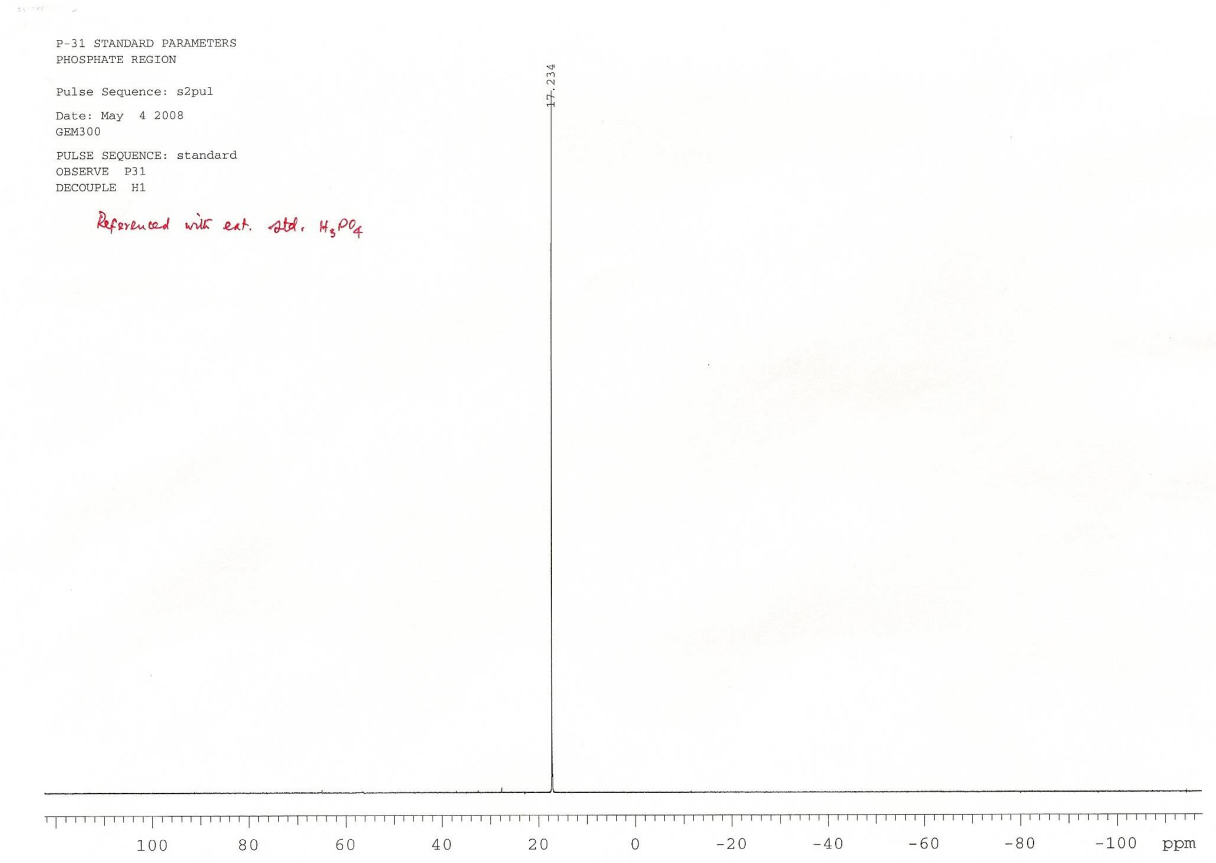

Figure S2. The $^{31}P\{^{1}H\}$ NMR spectrum of compound **1** recorded in C_6D_6 at 25 °C.

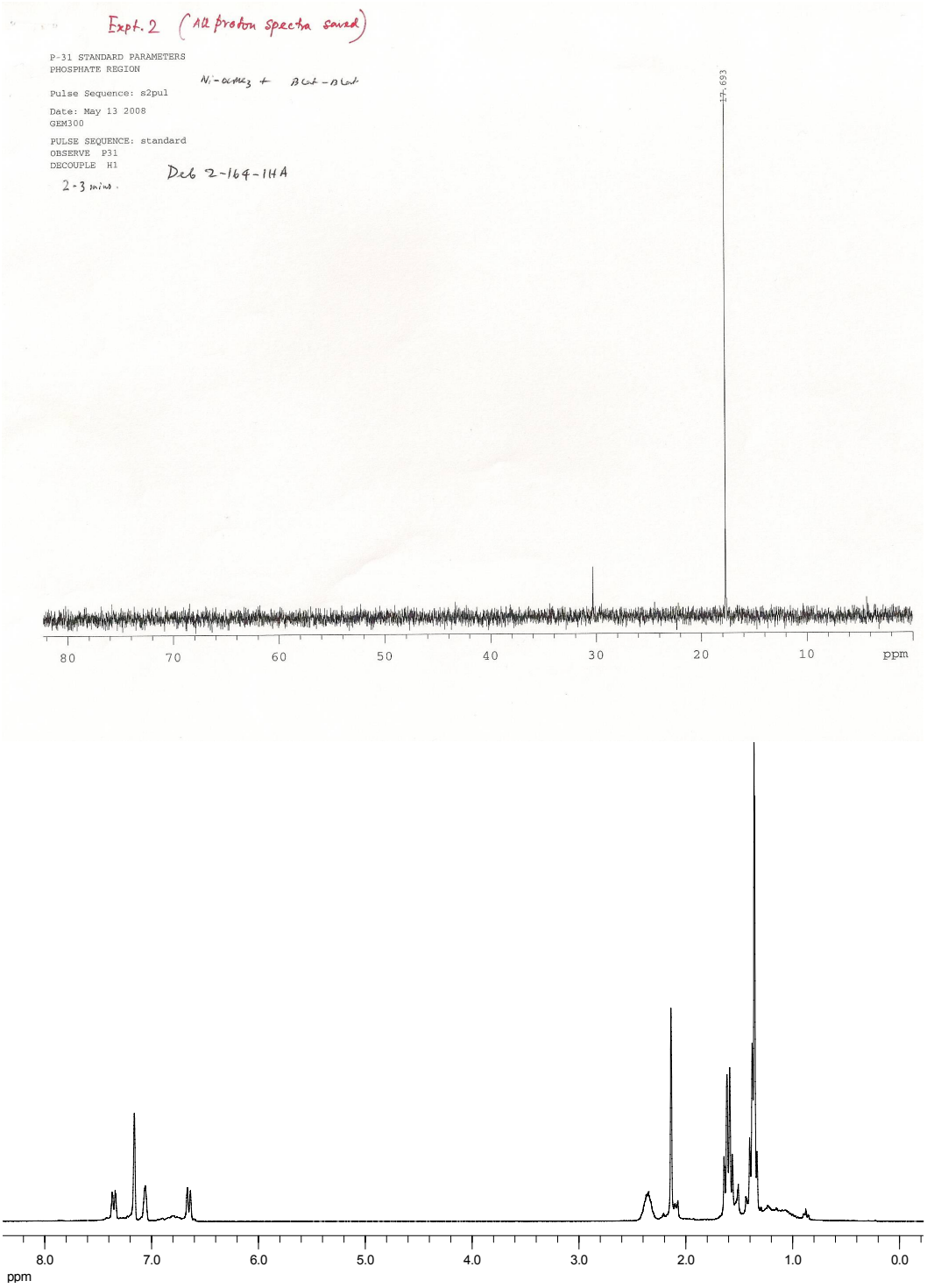

Figure S3. The addition of B_2cat_2 and complex (PNP)Ni(O^{t}Bu) **(1)** monitored by $^{31}P\{^1H\}$ (top) and ^1H (bottom) NMR in C_6D_6 at 25 °C. The dominant resonance corresponds to **1** and the minor resonance at ~30 ppm is the intermediate.

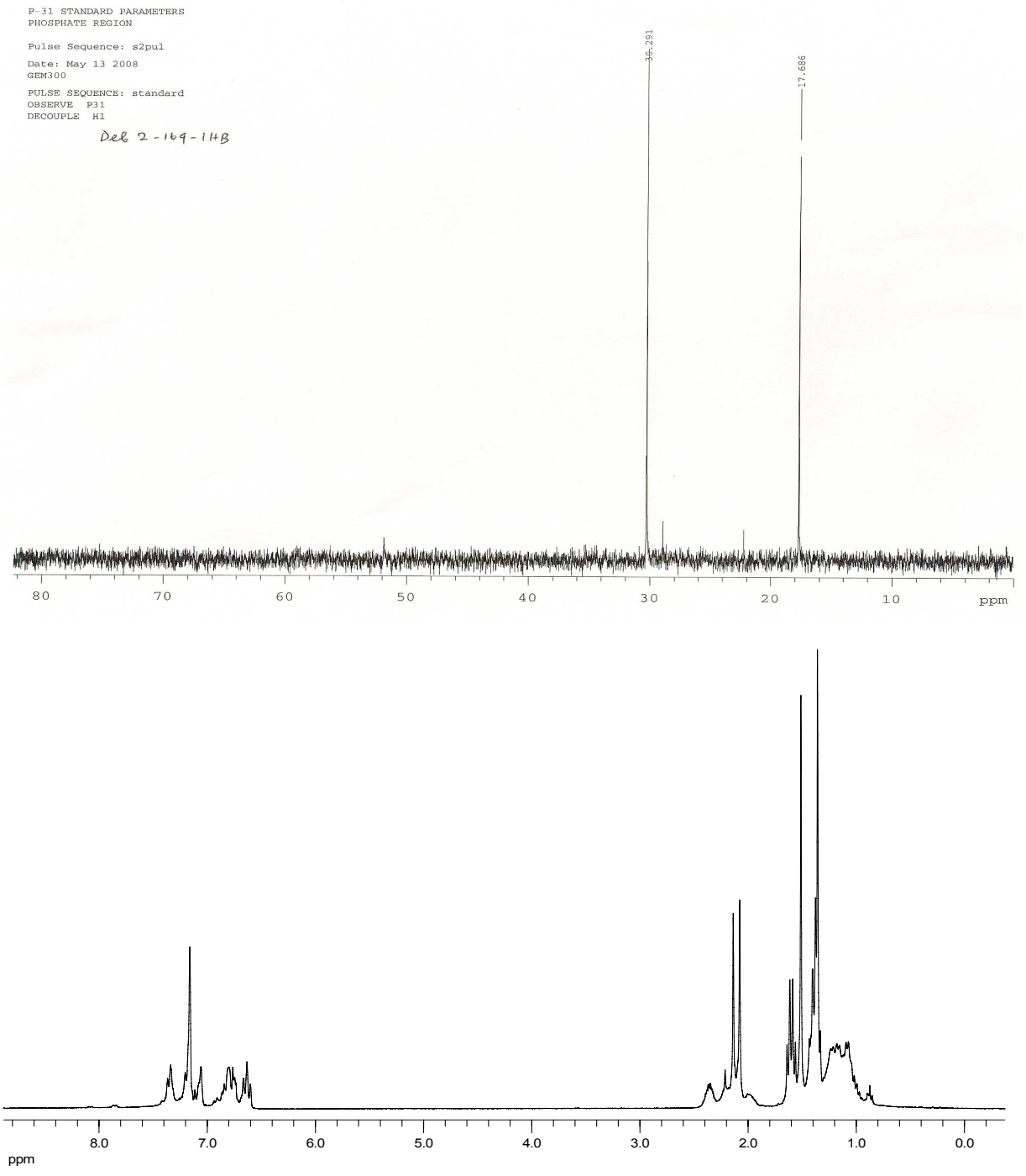

Figure S4. Expanded regions of the reaction of B_2cat_2 and complex (PNP)Ni(O^{t}Bu) **(1)** monitored by $^{31}P\{^1H\}$ (top) and ^1H (bottom) NMR in C_6D_6 at 25 °C. The disappearance of **1** and the growing in of the intermediate at ~30 ppm after 5 min. Some minor product, **3**, is observed along with other unrecognizable by products. The ^1H NMR also reveals two products in solution.

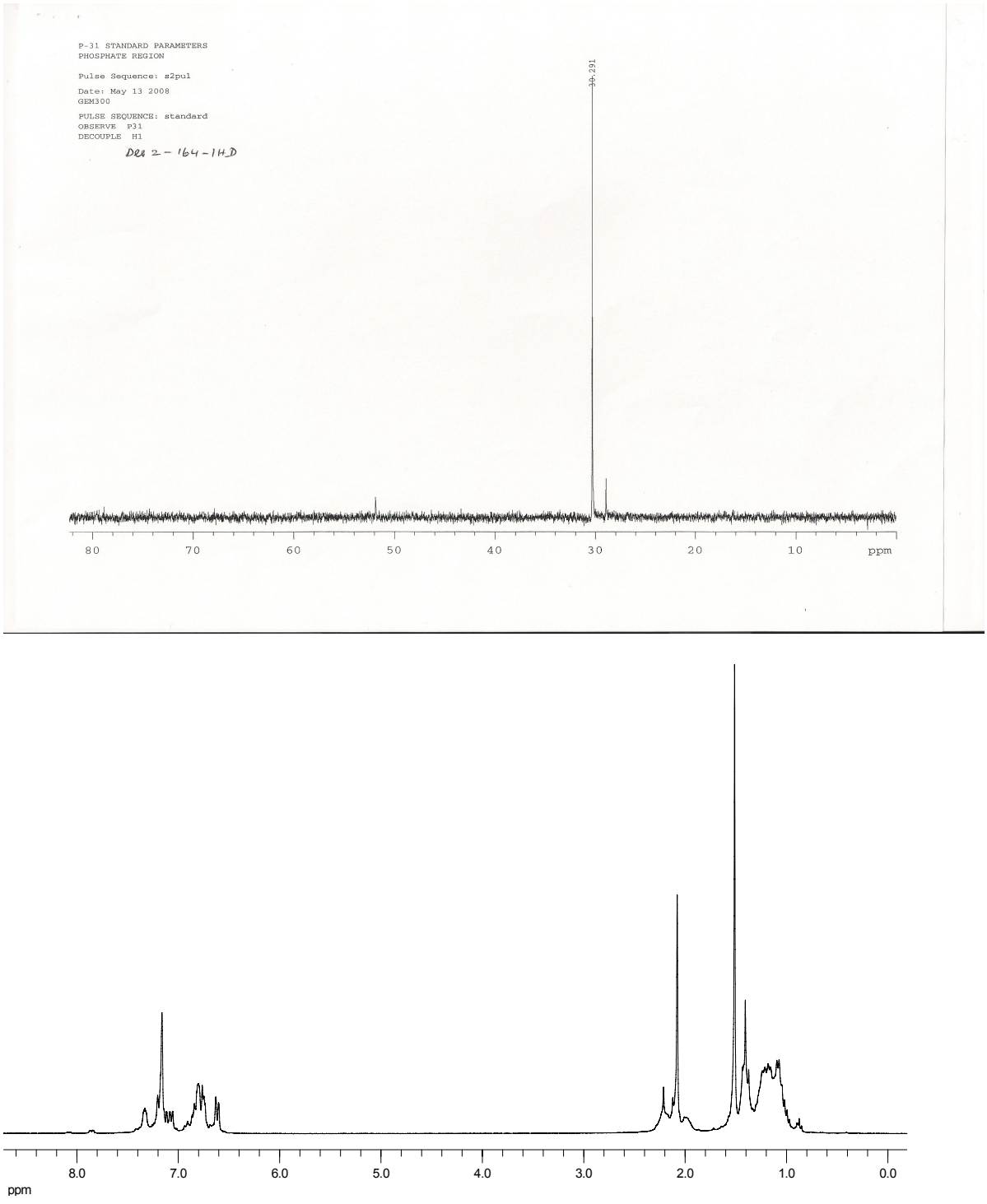

Figure S5. The reaction of B_2cat_2 and complex (PNP)Ni(O^tBu) **(1)** monitored by $^{31}P\{^1H\}$ (top) and ^1H (bottom) NMR in C_6D_6 at 25 °C. Complete conversion to the intermediate at 30 ppm after 0.5h and the minor resonance at ~ 52 ppm attributed to (PNP)Ni[B(catechol)] **(3)** which has been independently synthesized. ^1H spectrum also shows new features, in which the OtBu resonance shifted.

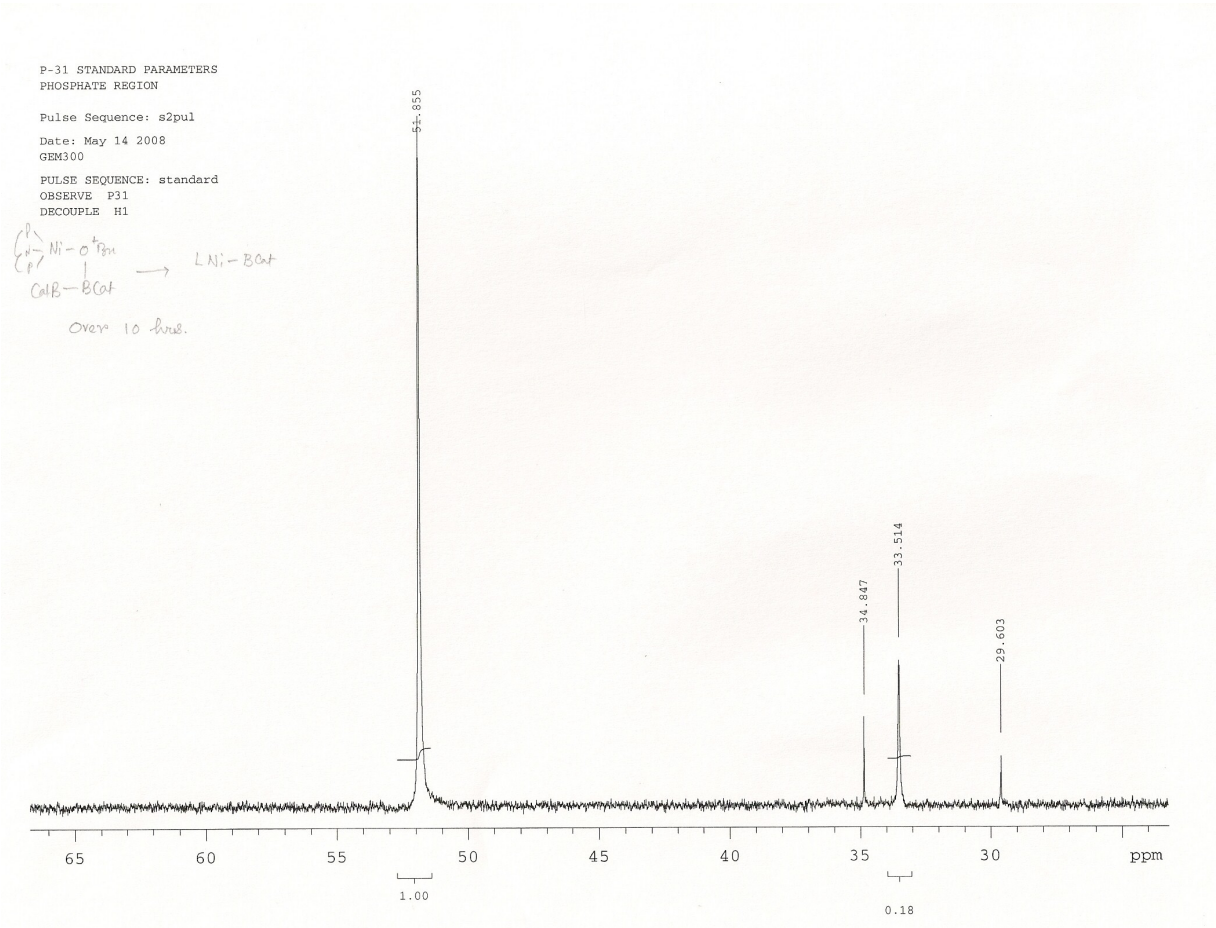

Figure S6. The reaction of B_2cat_2 and complex (PNP)Ni(O^{t}Bu) **(1)** monitored by $^{31}P\{^1H\}$ NMR in C_6D_6 at 25 °C. After 10 h, the intermediate has converted mostly to the product **3**, which is at ~52 ppm. However, there are unidentified minor side products at 33 and 35 ppm.

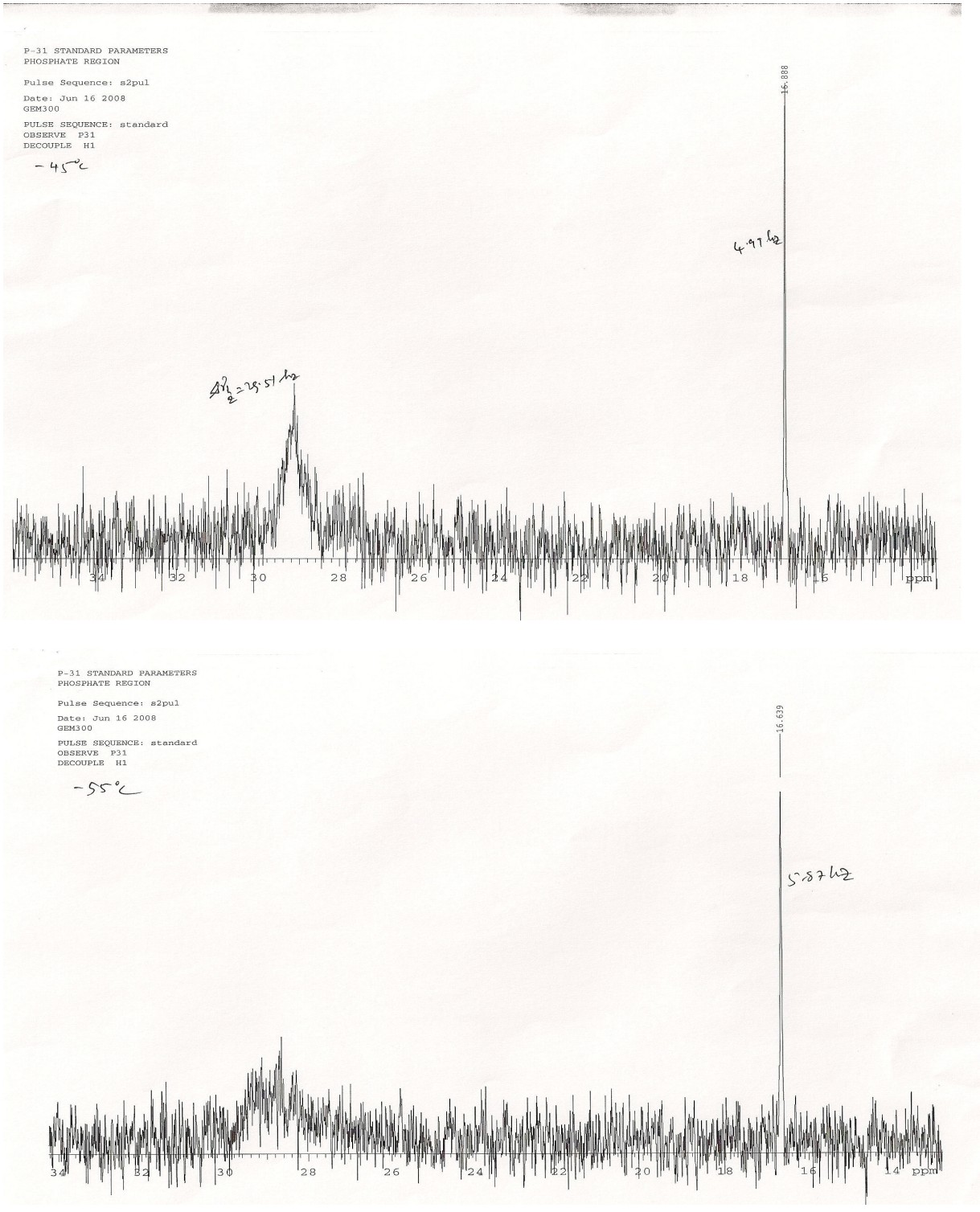

Figure S7. The reaction of B_2cat_2 and complex (PNP)Ni(O^{t}Bu) **(1)** monitored by $^{31}P\{^1H\}$ NMR in C_6D_6 at –45 °C (**top**) and at –55 °C (**bottom**). The broad peak at ~ 30 ppm corresponds to the intermediate and has broadened at lower temperature compared to the room temperature recording.

Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 6.0 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2-5] and the 6-31G** basis set with no symmetry restrictions. Transition metals were represented using the Los Alamos LACVP basis[6,7]. The NMR chemical shift calculation was computed by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set[8] cc-pVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis. Vibrational calculations were carried out on the structures of intermediates **A** and **B** to indeed confirm that they are true minima.

The models used in this study consist of up to ~100 atoms, which represent the non-truncated substrates that were also used in the related experimental work. These calculations challenge the current state of computational capabilities, and the numerical efficiency of the Jaguar program allows us to accomplish this task in a bearable time frame.

References

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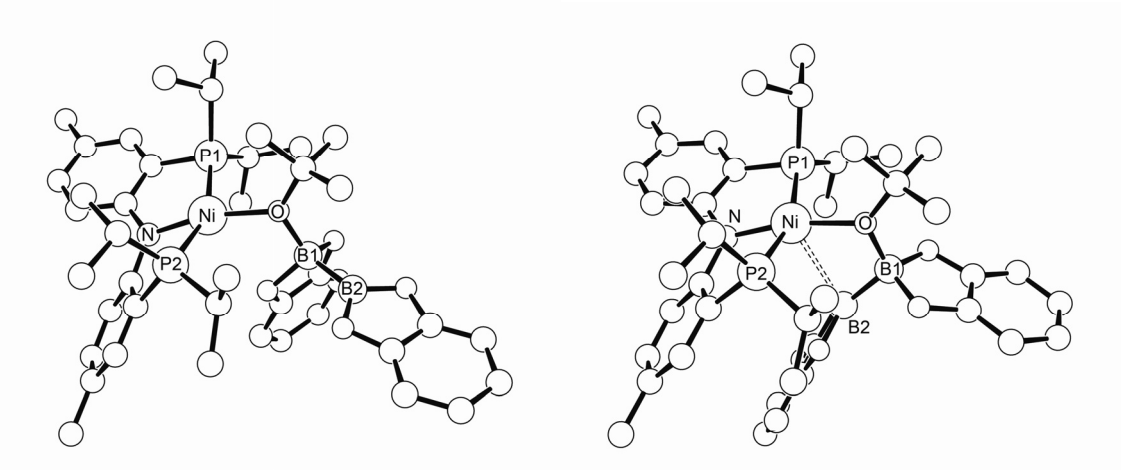
Figure S8. Two candidates (isomers) for the intermediate observed.



A (0.00*) **B** (-5.17)

* Relative electronic energy in kcal/mol.

Select bond lengths (Å) and bond angles (°).

Isomer A		Isomer B	
Ni-P1	2.396	Ni-P1	2.399
Ni-P2	2.341	Ni-P2	2.337
Ni-N	1.909	Ni-N	1.905
Ni-O	2.036	Ni-O	1.978
Ni-B2	4.416	Ni-B2	2.741
O-B1	1.517	O-B1	1.525
B1-B2	1.736	B1-B2	1.747
P1-Ni-P2	157.3	P1-Ni-P2	160.7
N-Ni-O	166.3	N-Ni-O	167.3
Ni-O-B1	107.4	Ni-O-B1	104.0
O-B1-B2	119.4	O-B1-B2	113.9

Discussion of data.
1) According to the computed energies, **B** is the more plausible candidate for the observed intermediate.
2) Computed ^{11}B NMR chemical shifts:
Isomer A: B1 7.9 ppm, B2 36.3 ppm
Isomer B: B1 8.0 ppm, B2 32.8 ppm
Chemical shifts of **A** and **B** are rather close, and can not be used to justify which is the more plausible one.

3) Computed ^{31}P NMR chemical shifts:
(PNP)NiO^{t}Bu: P1 43.4 ppm, P2 19.7 ppm. Average: 31.5 ppm
Isomer A: P1 78.7 ppm, P2 14.3 ppm. Average: 46.5 ppm
Isomer B: P1 75.4 ppm, P2 17.2 ppm. Average: 46.3 ppm

(PNP)Ni[B(cat)]: P1 65.9 ppm, 52.9 ppm. Average: 59.4 ppm

S9. Optimized structures.

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isomer **A**

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Ni	5.117476662	9.976035816	2.243345685
P	6.884459086	10.627446932	3.633257569
N	4.106539298	10.319338473	3.825815523
P	2.972658341	10.111339110	1.184572453
C	6.103741948	10.086988555	5.185604138
C	8.536351432	9.771823363	3.322900423
C	7.232788488	12.467135193	3.868562229
C	4.702872406	9.962696663	5.042358641
C	2.822320300	10.852627396	3.799104014
C	2.063786817	10.777220336	2.608692894
C	2.868082450	11.478239870	-0.132878304
C	1.871942331	8.713787528	0.566634685
H	9.606299292	9.795851057	5.248116430
H	2.432760564	13.180139767	1.162919132
C	6.721087919	9.808987599	6.414199847
H	8.237219038	8.978480163	2.639888500
C	9.530025698	10.680032178	2.578656288
C	9.222109250	9.082422497	4.510484612
H	7.779857175	12.768793067	2.966797281
C	8.100102018	12.766404589	5.102970624
C	5.919230450	13.261055420	3.925835703
C	3.981792488	9.439926071	6.140017511
C	2.214819283	11.509486160	4.900548125
C	0.730317223	11.213367038	2.577020381
H	3.650080869	11.216591185	-0.853142041
C	1.542012108	11.575562627	-0.903875618
C	3.222836643	12.840820180	0.487687771
C	2.423820785	8.035976842	-0.695849876
H	0.920641850	9.202799814	0.317938195
C	1.604899952	7.707269533	1.697745699
H	7.790043285	9.950816334	6.522595803
C	5.997892539	9.343075434	7.513163845
H	9.960348587	11.445547936	3.231745653
H	9.085854865	11.185277823	1.716663221
H	10.355059690	10.064251077	2.204026241
H	10.074619540	8.511259610	4.125963130
H	8.557690995	8.377582128	5.012542536
H	8.313376980	13.841041333	5.154764713
H	9.058122105	12.239712388	5.087813195
H	7.576055268	12.487883250	6.022487015
H	5.320665982	12.971516930	4.795319415
H	5.306391887	13.104298803	3.035239439
H	6.135882034	14.332559245	4.009955987
C	4.619552352	9.142426545	7.335960925
H	2.916557544	9.262959719	6.041815632
H	2.779493423	11.655329709	5.814299740
C	0.906297362	11.961027469	4.834564189
C	0.116885259	11.800407434	3.682621817
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H	1.631463240	12.352067379	-1.673157629
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H	2.521546690	7.220102486	2.035910446
H	1.737469618	7.241304934	-1.011495238
H	2.519100125	8.734856444	-1.534220768
H	1.128677587	8.186664883	2.557458707
C	6.668767263	9.032085748	8.831622613
H	4.030719506	8.736109314	8.156369189
H	0.480362015	12.456257519	5.705546707
C	-1.322793564	12.257217523	3.652365611
H	6.616087476	7.961985215	9.068609017
H	6.193487691	9.566913420	9.662846257
H	7.726123432	9.313609087	8.818074762
H	-1.955975005	11.641428635	4.303920225
H	-1.739591300	12.200614817	2.642131526
H	-1.424785529	13.293557379	3.996549995
O	6.298894568	9.193739967	0.780869412
B	6.475804293	7.717358055	1.083381052
C	6.727573129	9.804103669	-0.475216512

C	8.190699584	9.464845815	-0.809736393
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H	5.878418714	8.227722813	-1.703153660
H	8.532300454	10.121188803	-1.617400245
H	8.304853450	8.438449381	-1.159366578
H	8.843313971	9.619237528	0.049743022
H	6.797455029	11.833319642	-1.239886652
H	7.342749909	11.681061537	0.437313642
H	5.619910272	11.593734176	0.062162359
O	6.104688158	7.612843605	2.542983016
C	5.262785848	6.540578913	2.638647674
C	4.891407838	6.090413514	1.356874458
O	5.445064798	6.867218864	0.388687071
B	8.019190114	6.970727059	0.810423861
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C	9.513133534	5.513348573	0.022106487
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C	11.351167358	5.856895555	1.575450688
C	10.192991104	4.534164039	-0.681669818
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C	11.484746161	4.220824440	-0.234791515
H	13.051916586	4.594404486	1.191231198
H	12.054278770	3.456299714	-0.755304230
H	3.787204194	4.642651476	0.209669084
C	3.588297346	4.354885656	2.364647111
C	3.941406284	4.816085274	3.631307294
H	5.079122825	6.294561078	4.767782280
H	3.565435090	4.307278721	4.515096583
H	2.939464643	3.488069890	2.269161513

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isomer **B**

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Ni	5.123089267	10.038613178	2.243875562
P	6.913220904	10.651911119	3.615467286
N	4.093211820	10.403103967	3.804372001
P	3.005471314	10.107738426	1.118315340
C	6.092712558	10.268837922	5.189719461
C	8.516968385	9.666120872	3.364263218
C	7.380732723	12.477682748	3.755425765
C	4.690094629	10.151707924	5.050785466
C	2.782850464	10.875916289	3.724346884
C	2.040860392	10.698308007	2.531700721
C	2.945336991	11.564563760	-0.101880332
C	1.925263710	8.782109510	0.320242280
H	9.494098810	9.613661458	5.336170970
H	2.551377236	13.170616526	1.323177194
C	6.708298602	10.072417565	6.436138650
H	8.198546950	8.897246268	2.655994857
C	9.629874481	10.486982259	2.686220726
C	9.071822799	8.929313539	4.591929854
H	7.961711135	12.697446962	2.852291899
C	8.244586893	12.784152340	4.991695553
C	6.123158507	13.358739184	3.755402018
C	3.970112603	9.710767197	6.186837999
C	2.128621022	11.578410208	4.770414711
C	0.685300875	11.056251899	2.465519106
H	3.722848471	11.333853600	-0.837470288
C	1.617876182	11.744767879	-0.854324193
C	3.328190818	12.868496962	0.614380098
C	2.556746113	8.173814385	-0.939675916
H	1.017489588	9.327091906	0.029665511
C	1.522052286	7.693057984	1.324213905
H	7.780834340	10.200733958	6.528326976
C	5.983001912	9.701042179	7.567066416
H	10.072778330	11.224607670	3.362382962
H	9.297181001	11.009755555	1.786303933
H	10.430816379	9.803776432	2.381338388
H	9.881889135	8.269862292	4.258647698
H	8.313130657	8.305840471	5.064784340
H	8.557382491	13.835150491	4.969350001
H	9.148816658	12.172007522	5.046447276
H	7.674738047	12.626388225	5.912155648
H	5.476323800	13.125553764	4.607256118
H	5.534752641	13.230793306	2.845118458
H	6.408737574	14.414729097	3.830409161
C	4.603711855	9.497864040	7.401118037

H	2.908038624	9.514908873	6.102130902
H	2.676887450	11.827654808	5.670877421
C	0.796135260	11.946921631	4.671395524
C	0.024826407	11.661894067	3.531764222
H	0.127604235	10.857409626	1.553541506
H	0.794742889	11.973470715	-0.170102603
H	1.342113489	10.869161679	-1.447546536
H	1.709545664	12.592053152	-1.544869182
H	3.453830089	13.674268940	-0.117960719
H	4.263217316	12.771120658	1.171037459
H	3.479974864	7.638978435	-0.701305381
H	0.802836704	7.017932520	0.844817005
H	2.384779339	7.105785404	1.642411336
H	1.853870498	7.458288935	-1.382910109
H	2.777480862	8.926196250	-1.703844578
H	1.044057990	8.114819444	2.213090103
C	6.648432171	9.485451917	8.907067927
H	4.011392014	9.148421221	8.244596779
H	0.336986286	12.474611668	5.505549865
C	-1.442425288	12.014936207	3.468698116
H	6.522534252	8.453322582	9.257583930
H	6.223020349	10.137838085	9.679647860
H	7.722621128	9.688529537	8.857836502
H	-2.042941108	11.359828155	4.112888470
H	-1.833459291	11.920067784	2.451025351
H	-1.624657463	13.043644670	3.801371989
O	6.253044293	9.271832493	0.812882271
B	6.255717949	7.776095478	1.108216224
C	6.807817457	9.897138867	-0.400533533
C	8.253311860	9.443603139	-0.665939849
C	6.795722396	11.408572687	-0.151798868
C	5.951543054	9.565436780	-1.631300962
H	6.351113018	10.089725879	-2.507331938
H	4.916871778	9.881071031	-1.492631519
H	5.952541547	8.494911066	-1.834036858
H	8.676834082	10.077343907	-1.453890693
H	8.304273296	8.409802963	-1.008179936
H	8.875642653	9.537998492	0.223952520
H	7.122177877	11.941770697	-1.050496368
H	7.470929722	11.680814157	0.663261855
H	5.793181545	11.757620129	0.105130719
O	5.605324430	7.000645063	0.009389781
C	6.506882787	6.083161223	-0.430321418
C	7.725712540	6.217134847	0.261347705
O	7.650512086	7.226974461	1.166451015
B	5.524273094	7.355648760	2.638297796
C	6.336937074	5.119626974	-1.409907820
C	8.801829377	5.389519897	-0.012900013
O	4.299819557	6.675596908	2.765368893
C	4.257054168	6.152644486	4.033655680
C	5.432074430	6.495703571	4.702559808
O	6.219829975	7.244327202	3.861433041
C	3.268235927	5.386921468	4.627947589
C	5.680695544	6.080447152	5.999856660
C	3.506643643	4.965238668	5.943941627
H	2.360958176	5.123230544	4.094269521
H	6.598750362	6.347106330	6.512494047
C	4.687935780	5.302633740	6.613514537
H	2.760314384	4.359305315	6.449884177
H	4.841986915	4.952654253	7.630397022
H	9.736503436	5.499334437	0.528833678
C	8.632495734	4.404123051	-1.004002148
C	7.425930730	4.272519439	-1.688160104
H	5.390299056	5.022476645	-1.933215754
H	7.318179179	3.501487606	-2.446347897
H	9.457245582	3.734778588	-1.233404225

S10 . Computed vibrational frequencies(**cm^{-1}**)

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isomer A

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21.41 23.93 27.27 31.44 33.38 42.86
46.94 49.29 54.45 60.59 63.04 67.61
70.86 71.94 76.60 80.98 87.13 87.99
89.30 97.30 99.82 107.31 108.39 116.66
119.71 125.96 132.44 139.91 143.42 145.63
155.96 167.58 171.28 188.88 198.81 202.73
213.84 217.67 221.10 225.09 225.55 234.78
235.35 236.84 239.74 246.66 248.17 249.19
251.36 259.79 262.68 268.95 273.81 277.05
279.17 287.44 289.43 292.18 298.05 301.64
311.60 314.46 316.73 321.08 338.29 339.32
344.10 358.31 359.15 369.04 376.79 388.35
398.63 407.99 411.20 421.81 434.09 437.26
441.73 446.37 452.59 463.25 464.76 478.43
482.94 491.06 505.54 511.83 529.48 533.58
553.84 555.12 557.41 566.76 584.43 587.79
601.70 604.76 607.19 608.17 622.25 625.20
641.11 644.18 659.12 703.68 710.89 712.69
739.59 740.19 747.15 752.16 756.55 760.03
762.55 780.25 807.57 830.91 834.11 844.27
853.92 854.47 860.12 865.87 866.40 876.75
882.70 886.87 889.05 889.75 894.09 896.37
902.17 903.91 909.63 914.25 918.07 927.04
927.59 931.25 937.02 939.35 939.94 946.93
950.48 951.12 964.42 966.55 967.21 970.44
973.50 974.36 975.81 983.03 984.57 1018.51
1021.14 1031.89 1033.02 1050.40 1054.55 1056.66
1059.13 1062.53 1064.69 1064.79 1071.71 1076.86
1082.38 1084.19 1104.29 1107.21 1119.81 1120.67
1130.06 1136.76 1178.50 1178.86 1179.18 1183.69
1186.51 1189.31 1192.63 1194.74 1214.97 1226.17
1237.55 1238.06 1239.50 1240.85 1257.48 1265.10
1273.57 1279.42 1281.96 1282.68 1286.85 1293.17
1293.68 1300.49 1303.92 1306.48 1318.19 1320.81
1332.07 1339.42 1341.77 1343.47 1346.07 1350.41
1406.71 1407.92 1408.61 1410.02 1412.06 1413.19
1415.58 1422.98 1426.03 1427.89 1429.80 1432.46
1433.48 1436.15 1438.74 1443.10 1444.62 1484.09
1492.71 1494.30 1495.86 1497.04 1497.16 1497.57
1499.99 1500.80 1502.83 1504.26 1504.76 1506.46
1507.46 1507.68 1508.70 1510.30 1510.43 1511.01
1514.06 1515.47 1516.38 1517.48 1517.94 1520.26
1521.49 1522.12 1522.48 1525.74 1527.06 1532.54
1538.72 1586.95 1600.13 1646.60 1650.91 1654.62
1658.26 1662.46 1672.57 3029.50 3031.26 3033.16
3039.27 3040.98 3042.38 3045.27 3045.97 3048.73
3049.25 3051.45 3053.59 3056.18 3060.42 3068.59
3075.17 3081.27 3083.43 3098.87 3102.21 3108.12
3112.64 3112.90 3113.54 3115.11 3116.08 3116.73
3118.42 3125.02 3128.79 3133.48 3135.25 3136.53
3140.64 3141.20 3144.26 3145.36 3151.45 3158.56
3163.30 3165.80 3167.64 3169.30 3171.52 3174.28
3175.85 3184.30 3184.36 3186.54 3198.28 3199.78
3204.60 3211.13 3211.71 3215.91 3216.86 3219.58

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Isomer B

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18.11 23.15 25.00 28.44 38.64 46.20
47.47 54.30 61.38 65.46 70.97 71.71
73.34 75.22 80.38 84.96 85.37 91.02
92.80 98.41 105.39 110.27 114.81 118.53
123.51 124.05 136.08 137.71 143.76 151.58
163.32 173.14 180.75 194.09 198.62 202.68
208.94 214.46 217.34 228.60 233.08 237.64
240.10 243.71 244.34 245.54 252.54 253.04
257.28 263.11 264.52 267.49 272.68 281.05
286.25 286.37 293.80 296.53 298.76 305.27
313.92 316.81 318.31 321.80 340.04 342.54
346.49 360.60 363.30 374.36 379.00 390.18
405.90 410.64 414.45 424.77 433.62 435.14
438.75 440.56 450.46 461.92 464.01 476.76
485.49 493.32 505.87 513.34 533.63 536.07
552.58 553.55 559.75 567.50 583.15 586.66
600.20 608.12 609.31 622.21 623.67 624.80
632.27 642.42 664.47 704.93 713.74 718.52
738.09 741.65 746.18 749.06 751.11 752.83
758.43 787.15 818.17 828.81 836.38 844.36

852.47 854.47 854.60 860.00 866.64 871.53
878.25 887.79 890.88 892.89 896.27 897.80
898.52 902.85 909.14 911.28 914.71 916.89
922.50 928.32 929.78 937.54 940.91 944.92
946.80 959.57 964.23 964.36 969.29 973.25
975.00 976.12 985.43 985.94 986.56 1018.97
1021.73 1034.14 1034.53 1051.77 1057.36 1057.86
1061.61 1064.32 1064.95 1069.02 1075.96 1078.28
1079.98 1086.59 1104.55 1107.90 1118.96 1122.08
1133.10 1137.54 1178.66 1179.39 1180.71 1183.97
1185.32 1189.27 1190.48 1200.60 1207.33 1229.84
1235.79 1239.68 1240.01 1241.47 1244.49 1257.35
1275.68 1279.81 1280.94 1284.04 1288.35 1289.93
1293.35 1304.99 1306.99 1313.97 1319.01 1322.36
1331.49 1339.14 1342.32 1343.47 1347.31 1354.57
1405.47 1407.97 1410.44 1412.79 1413.95 1414.58
1417.28 1425.64 1427.56 1428.98 1430.20 1432.33
1433.29 1437.01 1441.70 1442.73 1450.13 1481.98
1490.78 1491.36 1493.74 1497.05 1497.20 1500.02
1500.38 1500.98 1502.98 1505.18 1506.38 1507.42
1508.00 1508.68 1509.86 1510.19 1510.66 1513.32
1514.54 1514.93 1516.97 1518.73 1520.42 1521.18
1522.55 1523.82 1526.24 1526.64 1528.27 1531.98
1539.76 1585.75 1598.78 1651.67 1652.98 1658.65
1659.20 1659.59 1672.63 3030.16 3030.41 3035.28
3039.01 3040.85 3042.33 3042.93 3045.94 3046.76
3048.36 3050.31 3053.59 3056.69 3061.58 3066.15
3075.85 3081.73 3083.47 3094.78 3101.83 3106.79
3106.86 3110.01 3113.65 3113.73 3115.39 3115.52
3117.20 3121.50 3128.36 3134.35 3135.49 3136.91
3137.90 3141.92 3142.17 3145.31 3150.18 3154.20
3164.59 3167.21 3168.25 3168.33 3173.39 3177.35
3180.49 3181.49 3183.13 3187.65 3196.59 3199.54
3205.15 3213.55 3214.81 3217.11 3218.72 3224.36