

Supporting Information for

O₂ Activation at a Trispyrazolylborato Nickel(II) Malonato Complex

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Table of Contents

Experimental	2
Density Functional Calculations	4
Crystal Structure Analysis	8
References	9

Experimental

All experiments were carried out in a dry argon atmosphere using a MBraun glovebox and/or standard Schlenk techniques. Solvents were purified employing a MBraun Solvent Purification System SPS. All materials were obtained from commercial vendors as ACS reagent-grade or better and used as received. $[\text{Tp}^{\text{Me,Me}}\text{NiOAc}]$ was prepared following literature procedure,¹ $[\text{Tp}^{\text{Ph,Me}}\text{NiBr}]$ was obtained through a modified literature procedure by the reaction of $\text{Tp}^{\text{Me,Ph}}\text{Ti}$ with $\text{NiBr}_2\cdot\text{dme}$.²

NMR spectra were recorded on a Bruker AV 300 NMR spectrometer (^1H 300 MHz). Chemical shifts are reported in ppm relative to residual proton signals of CD_3CN (1.94 ppm). Mass spectra (ESI) were recorded on an Agilent Technologies 6210 Time-of-Flight LC-MS instrument. GC-MS measurements were performed on a Varian GC-3800 equipped with a Varian VF-5ms column and a FID detector. Infrared (IR) spectra were recorded in the region $4000 - 400 \text{ cm}^{-1}$ using solid samples prepared as KBr pellets with a Shimadzu FTIR-8400s spectrometer. Microanalyses were performed on a HEKAtech Euro EA 3000 elemental analyzer. Magnetic susceptibility measurements were carried out using the Evans NMR method. UV/Vis spectra were obtained at variable temperatures with an Agilent 8453 UV/Vis spectrophotometer equipped with an Unisoku USP-203-A cryostat. SUPRASIL Quartz cells from Hellma Analytics with a 10 mm path length were used.

Synthesis of **1**

$[\text{Tp}^{\text{Me,Me}}\text{NiOAc}]$ (100 mg, 241 μmol) in 15 mL thf was added to a solution of PhmLi (58.3 mg, 241 μmol) dissolved in 15 mL thf. The reaction mixture was stirred for 12 h at room temperature and then filtered. The residue was extracted with 5 mL thf and the combined filtrates were evaporated to dryness. The residue was extracted four times with 20 mL hexane and all volatiles were removed in vacuo from the combined extracts to give **1** (60 mg, 42% yield, 102 μmol) as a green solid.

Elemental analysis (%) calc. for $\text{C}_{28}\text{H}_{37}\text{BN}_6\text{NiO}_4$ ($590.23 \text{ g}\cdot\text{mol}^{-1}$): C 56.89, H 6.31, N 14.22; found: C 56.59, H 6.37, N 13.92; IR [KBr]: $\tilde{\nu} = 3124$ (w), 2966 (m), 2926 (m), 2517 (m), 1623 (vs), 1547 (m), 1454 (s), 1430 (m), 1418 (s), 1391 (m), 1371 (s), 1336 (s), 1313 (m), 1306 (m), 1290 (m), 1265 (m), 1207 (m), 1190 (m), 1163 (m), 1110 (m), 1085 (vs), 1070 (s), 1063 (s), 1035 (m), 1005 (m), 857 (m), 824 (m), 809 (m), 801 (m), 791 (m), 779 (m), 696 (m), 647 (m), 467 (m) cm^{-1} ; ^1H NMR (300.13 MHz, CD_3CN): $\delta = 58.1$ (3H, Pz-H), 7.38-6.89 (5H, $-\text{CH}_{\text{Ph}}$), 3.51 (4H, $-\text{CH}_2$), 2.45 (6H, $-\text{CH}_3$), -2.62 (9H, Pz- CH_3), -9.00 (9H, Pz- CH_3) ppm.

Synthesis of **2**

[Tp^{Ph,Me}NiBr] (100 mg, 161 μ mol) was added to PhmalLi (39 mg, 161 μ mol) dissolved in acetonitrile. The reaction mixture was stirred for 12 h at room temperature and then filtered. The residue was extracted three times with 15 mL of hexane and the combined filtrates were evaporated to dryness to give **2** (87 mg, 70% yield, 112 μ mol,) as an ochre colored solid. Crystals of **2** suitable for single crystal X-ray diffraction studies were obtained by slowly evaporating the volatiles from a saturated solution of **2** in acetonitrile.

Elemental analysis (%) calc. for C₄₃H₄₃BN₆NiO₄ (776.28 g·mol⁻¹): C 66.44, H 5.58, N 10.81; found: C 66.46, H 5.85, N 10.31; IR [KBr]: $\tilde{\nu}$ = 3061 (m), 3026 (w), 2976 (m), 2959 (m), 2928 (m), 2868 (w), 2521 (m), 1619 (vs), 1597 (m), 1545 (m), 1506 (m), 1452 (s), 1437 (s), 1411 (s), 1375 (s), 1338 (s), 1326 (m), 1306 (m), 1273 (m), 1262 (m), 1222 (w), 1189 (m), 1183 (m), 1095 (vs), 1066 (s), 1030 (w), 1011 (m), 983 (m), 843 (m), 789 (s), 762 (s), 695 (s), 668 (m), 640 (m), 531 (m) cm⁻¹; MS (EI): m/z = 799.26 [Tp^{Ph,Me}NiPhmal+Na]⁺, 815.24 [Tp^{Ph,Me}NiPhmal+K]⁺.

Reaction of **1** with O₂

A solution of **1** (50 mg, 85 μ mol) in 20 mL acetonitrile was prepared under an argon atmosphere. Subsequently, the atmosphere was exchanged by dioxygen and the solution was stirred for 2 h at room temperature. A 3 M HCl solution (1 mL) was added to the bright green solution, which led to an immediate decoloration. The mixture was stirred for further 30 min. and then passed through a short silica column to remove nickel containing constituents. The organic reaction products were analysed by GC/MS. A control reaction showed that treatment of PhmalLi with O₂ followed by an analogous procedure only provided back HPhmal. No oxidation products were found.

Density Functional Calculations

Geometry optimizations were performed in redundant internal coordinates without symmetry restrictions using the Gaussian09 program package.³ The molecular structure of compound $\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{Phmal})$ (**2**) as determined by X-ray diffraction analysis was used to create a starting structure for $\text{Tp}^{\text{Me,Me}}\text{Ni}(\text{Phmal})$ (**1**) by replacing the phenyl residues by methyl groups. Different starting points for the organoperoxonickel intermediate were generated by adding O_2 in several modes to the ground state structure of $\text{Tp}^{\text{Me,Me}}\text{Ni}(\text{Phmal})$ (**1**) and all were optimized for the singlet, triplet, and quintet state.

The B3LYP functional⁴ was employed together with the Def2-TZVP basis set for all atoms,⁵ as implemented in Gaussian. Very tight convergence criteria were chosen for the SCF procedure and a pruned (99,590) “ultrafine” integration grid was used for numerical integrations. Vibrational frequencies were computed analytically. Visualization of molecular structures was accomplished with the program Gauss View (Gaussian, Inc.).

$\text{Tp}^{\text{Me,Me}}\text{Ni}(\text{Phmal})$ (**1**) has a triplet ground state, the singlet and quintet state have 66.3 and 309.7 kJ/mol higher energies, respectively. The Mulliken spin density at the Ni atom is 1.7.

For the organoperoxonickel intermediate several minimum structures were found, however, in most cases with a weakly coordinated O_2 unit quite far away from the Ni atom. The most favourable structure was found for the triplet state and is shown in the main paper. All other structures of local minima in the singlet, triplet, and quintet state were significantly higher (> 22 kJ/mol) in energy.

The reaction



was calculated to be exothermic with a reaction energy of -13.0 kJ/mol (including correction for the zero-point vibrational energy).

Cartesian coordinates (Å) for the theoretical structure of Tp^{Me,Me}Ni(Phmal) (1):

B3LYP/ Def2-TZVP

Triplet state, E = -3252.78279827 hartree

	x	y	z
Ni	-0.493225	0.001325	-0.426650
B	-3.440314	-0.001061	0.447183
N	-1.929460	-1.416213	-0.993261
N	-3.157601	-1.252581	-0.423298
N	-1.159085	-0.007409	1.510489
N	-1.928331	1.424998	-0.981013
N	-2.509458	-0.006515	1.682882
N	-3.156799	1.257311	-0.413003
O	0.987886	1.384725	-0.395878
O	0.988538	-1.382095	-0.409058
O	3.022215	2.314052	-0.237286
O	3.024212	-2.311925	-0.271201
C	-1.994954	-2.486021	-1.785962
C	-3.284115	-3.035464	-1.716375
C	-0.851061	-2.941036	-2.630458
C	-3.993836	-2.227378	-0.846674
C	-5.416608	-2.348287	-0.410834
C	-0.597161	-0.013710	2.720126
C	-1.992838	2.501519	-1.764682
C	2.233771	1.218059	-0.309783
C	2.234551	-1.215660	-0.323929
C	-2.804430	-0.012115	3.000950
C	-3.992301	2.236101	-0.828511
C	-1.604919	-0.016803	3.693392
C	0.880341	-0.017098	2.930303
C	-3.281716	3.051084	-1.691052
C	-0.848353	2.962899	-2.604939
C	2.943774	0.001192	-0.277191
C	-4.195729	-0.012802	3.542316
C	-5.415174	2.354212	-0.392228
C	4.435982	0.001608	-0.187753
C	2.415398	3.617527	-0.204011
C	2.418513	-3.616185	-0.253411
C	5.222054	0.082797	-1.338869
C	5.084896	-0.078558	1.045938
C	2.047165	4.034884	1.207866
C	2.055393	-4.053214	1.153865
C	6.609980	0.084490	-1.262471
C	6.472370	-0.078441	1.129385
C	7.240927	0.003460	-0.026288
H	-3.651450	-3.904984	-2.235417
H	0.056968	-2.399692	-2.378716
H	-1.069694	-2.784212	-3.689877
H	-0.666236	-4.008539	-2.493482
H	-6.008020	-1.479841	-0.706744
H	-5.501897	-2.446883	0.672802
H	-5.862292	-3.231454	-0.866899
H	-4.578605	-0.002149	0.801669
H	-1.475232	-0.021869	4.762592
H	1.348540	0.863996	2.490564
H	1.345684	-0.892887	2.477171

H	1.104306	-0.025412	3.996514
H	-3.648287	3.925212	-2.202844
H	0.060657	2.423299	-2.352995
H	-0.667147	4.030450	-2.463720
H	-1.064009	2.809168	-3.665445
H	-4.755671	0.868883	3.225421
H	-4.161088	-0.017714	4.631073
H	-4.757901	-0.890188	3.217542
H	-6.007006	1.488656	-0.695676
H	-5.860134	3.241456	-0.841031
H	-5.500859	2.443739	0.692163
H	1.544788	3.635066	-0.856379
H	3.180851	4.275310	-0.615756
H	3.183008	-4.267623	-0.676800
H	1.545681	-3.625535	-0.902931
H	4.735586	0.145524	-2.304795
H	4.491776	-0.142028	1.950137
H	1.685925	5.066067	1.204818
H	2.915590	3.979111	1.866013
H	1.256864	3.400350	1.608594
H	1.694260	-5.084308	1.137743
H	1.266405	-3.424522	1.566254
H	2.926120	-4.006656	1.809701
H	7.199205	0.148439	-2.169337
H	6.953813	-0.141703	2.097865
H	8.322194	0.004119	0.035992

Cartesian coordinates (Å) for the theoretical structure of organoperoxonickel intermediate

Tp^{Me,Me}Ni(Phmal)O₂:

B3LYP/ Def2-TZVP

Triplet state, E = -3403.18122601 hartree

	x	y	z
Ni	-0.745117	0.210035	-0.114464
B	-3.781435	-0.266692	-0.094345
N	-1.735313	-1.195973	-1.223155
N	-3.083691	-1.264459	-1.051550
N	-1.896707	-0.215077	1.573244
N	-2.201974	1.636675	-0.618409
N	-3.219093	-0.444248	1.339180
N	-3.488332	1.181379	-0.562070
O	2.568111	1.313064	1.829954
O	0.808353	-1.186347	0.593710
O	3.263335	2.408661	-0.013515
O	2.867433	-1.778199	1.195754
O	1.842917	0.418000	-1.368993
O	0.697643	1.193983	-0.923170
C	-3.598692	-2.221872	-1.854443
C	-5.052397	-2.555178	-1.921576
C	-1.394488	-2.105723	-2.134862
C	-2.547271	-2.782049	-2.559983
C	0.017296	-2.313285	-2.571992
C	-1.701018	-0.301115	2.889098
C	-2.242395	2.904163	-1.030453

C	2.815913	1.352670	0.648475
C	2.010581	-1.005731	0.555358
C	-3.857950	-0.684437	2.505881
C	-4.338542	2.161494	-0.943306
C	-2.918000	-0.604284	3.518151
C	-0.371191	-0.080182	3.530575
C	-3.578106	3.275397	-1.249091
C	-1.020239	3.747992	-1.182688
C	2.676391	0.120967	-0.285550
C	-5.319843	-0.969532	2.608387
C	-5.821552	1.998652	-1.005613
C	4.037822	-0.300307	-0.843956
C	3.363154	3.661289	0.707755
C	2.327505	-2.858691	2.004476
C	4.164380	-0.652956	-2.185759
C	5.166477	-0.330172	-0.025098
C	4.723916	3.818726	1.355865
C	3.494528	-3.593107	2.620335
C	5.400575	-1.035644	-2.696145
C	6.399678	-0.709151	-0.537658
C	6.521005	-1.066218	-1.876288
H	-2.607765	-3.570307	-3.291617
H	0.599825	-1.400401	-2.460505
H	0.047837	-2.624192	-3.617047
H	0.500851	-3.096567	-1.981746
H	-5.650127	-1.702565	-2.249140
H	-5.441489	-2.872594	-0.952407
H	-5.206300	-3.367850	-2.630564
H	-4.957557	-0.464599	-0.094332
H	-3.091683	-0.738258	4.572856
H	-0.475808	0.564375	4.405322
H	0.338436	0.385627	2.850457
H	0.060053	-1.023353	3.876228
H	-3.940147	4.231309	-1.589169
H	-0.142125	3.131819	-1.370495
H	-0.840650	4.333826	-0.276145
H	-1.149015	4.452685	-2.005729
H	-5.923021	-0.130151	2.257362
H	-5.580805	-1.161244	3.648558
H	-5.604862	-1.843653	2.020257
H	-6.115740	1.208762	-1.699333
H	-6.274380	2.930120	-1.343484
H	-6.245736	1.750577	-0.030841
H	2.561580	3.704287	1.443455
H	3.194345	4.419207	-0.055195
H	1.728366	-3.500847	1.358674
H	1.669141	-2.424272	2.755887
H	3.300752	-0.612308	-2.832737
H	5.085005	-0.061550	1.020285
H	4.794191	4.805122	1.819721
H	5.519710	3.731876	0.614981
H	4.877983	3.067341	2.130257
H	3.122382	-4.417469	3.231303
H	4.080922	-2.931366	3.258576
H	4.149368	-4.004028	1.851348
H	5.484775	-1.305082	-3.741561
H	7.267370	-0.722893	0.110031
H	7.482964	-1.360564	-2.276785

Crystal Structure Analysis

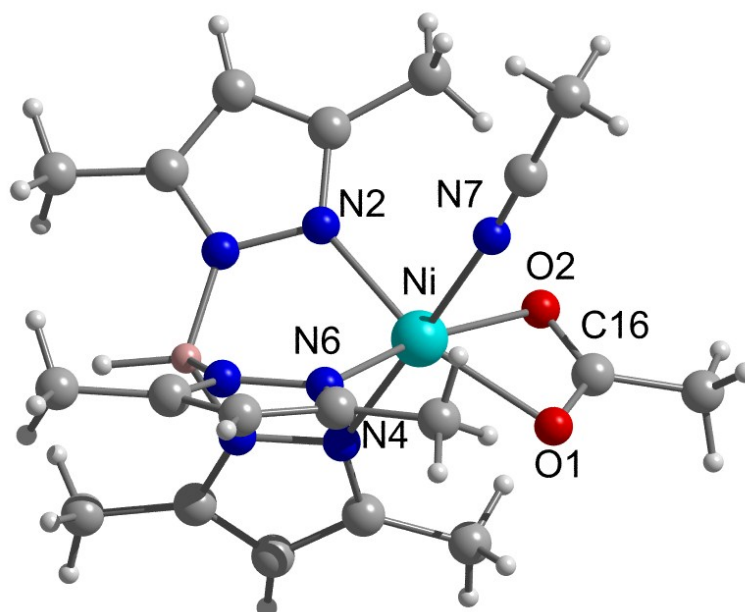
The data collections were performed with a BRUKER D8 VENTURE or a STOE IPDS 2 T diffractometer area detector, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Multi-scan absorption corrections implemented in SADABS⁶ were applied to the data for complex **2**. The structures were solved by intrinsic phasing method (SHELXT-2013)⁷ and refined by full matrix least square procedures based on F^2 with all measured reflections (SHELXL-2013)⁸ with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. CCDC 1582025 (**2**·CH₃CN), 1582026 ([Tp^{Me,Me}NiOAc]·CH₃CN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic Data for 2·CH₃CN:

C₄₃H₄₃BN₆NiO₄·CH₃CN, $M_r = 818.39$, monoclinic, $P2_1/c$, light blue block, 0.38 x 0.26 x 0.24 mm, $a = 10.0918(5) \text{ \AA}$, $b = 19.4765(11) \text{ \AA}$, $c = 20.9089(12) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.711(2)^\circ$, $\gamma = 90^\circ$, $V = 4105.1(4) \text{ \AA}^3$, $Z = 4$, $\rho = 1.324 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.525 \text{ mm}^{-1}$, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), $T = 90(2) \text{ K}$, $\Theta = 2.27 - 28.92^\circ$, $F_{000} = 1720$, reflections collected 87681, reflections unique 10503 [$R_{int} = 0.0481$], Goof = 0.983, $R_1 = 0.0382$, $wR_2 = 0.1137$, largest diff. peak and hole 0.619 / – 0.445 e \AA^{-3} .

Crystallographic Data for [Tp^{Me,Me}NiOAc]·CH₃CN:

C₁₇H₂₅BN₆NiO₂·CH₃CN, $M_r = 456.00$, monoclinic, $P2_1/c$, blue cube, 0.5 x 0.5 x 0.5 mm, $a = 8.5167(3) \text{ \AA}$, $b = 14.3456(3) \text{ \AA}$, $c = 18.3576(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.856(2)^\circ$, $\gamma = 90^\circ$, $V = 2241.70(11) \text{ \AA}^3$, $Z = 4$, $\rho = 1.351 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.895 \text{ mm}^{-1}$, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), $T = 100(2) \text{ K}$, $\Theta = 3.32 - 29.52^\circ$, $F_{000} = 960$, reflections collected 41326, reflections unique 6032 [$R_{int} = 0.0547$], GoF = 1.034, $R_1 = 0.0248$, $wR_2 = 0.0639$, largest diff. peak and hole 0.363 / – 0.544 e \AA^{-3} .



S1 Molecular structure of $[\text{Tp}^{\text{Me,Me}}\text{NiOAc}]\text{-CH}_3\text{CN}$ as determined by single crystal X-ray diffraction; selected bond lengths [Å] and angles [°] : Ni–O1 2.1147(8), Ni–O2 2.1179(8), Ni–N2 2.0462(10), Ni–N4 2.1042(9), Ni–N6 2.0271(9), Ni–N7 2.1163(10), O1–C16 1.2624(14), O2–C16 1.2654(14), N2–Ni–N4 90.43(4), N2–Ni–N6 91.52(4), N4–Ni–N6 86.03(4), N6–Ni–N7 90.83, N2–Ni–N7 89.23(4), N4–Ni–N7 176.83(4), O1–Ni–N2 161.69(3), O1–Ni–N4 96.40(3), O1–Ni–N6 105.86(3), O1–Ni–N7 84.86(3), O2–Ni–N2 100.01(3), O2–Ni–N4 96.51(3), O2–Ni–N6 168.16(4), O2–Ni–N7 86.65(3), O1–Ni–O2 62.41(3), Ni–O1–C1 126.24(10), Ni–O3–C5 126.59(10), O1–Ni–C16 31.20(3), O2–Ni–C16 31.28(3).

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