

Supplemental Material for:

Synthesis and Characterization of Side-Bound Aryldiazo and End-Bound Nitrosyl Complexes of Nickel

Vlad M. Iluc, Alexander J. M. Miller and Gregory L. Hillhouse*

Experimental Details

General Considerations. Unless otherwise stated, all reactions were carried out under an inert atmosphere, using either an MBraun *Lab Master* glove box with purified dinitrogen atmosphere, or Schlenk techniques under an argon atmosphere. Anhydrous diethyl ether was purchased from Fischer, stirred over sodium metal, and filtered through activated alumina. Hexanes, petroleum ether, and toluene were dried by passage through activated alumina and Q-5 columns. C₆D₆ and CD₂Cl₂ were purchased from Cambridge Isotope Laboratories, degassed by freeze-pump-thaw cycles, and dried over CaH₂ or activated 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated by evacuation overnight at 180°C. [(dtbpe)Ni]C₆H₆ (**1**)¹ and [(dtbpe)NiCl]₂ (**3**)² were prepared by the literature methods. All other chemicals were used as received. Infrared data (CaF₂ plates and Fluorolube S-20 mull) were measured using a Nicolet 670-FT-IR instrument. Elemental analyses were performed by Desert Analytics (Tucson, AZ). ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on Bruker 400 or 500 MHz spectrometers. ¹H and ¹³C NMR resonances are reported with reference to solvent resonances: residual C₆D₅H in C₆D₆, at δ_H = 7.16 and δ_C = 128.0; residual CDHCl₂ in CD₂Cl₂ at δ_H = 5.32 and δ_C = 53.8. ³¹P NMR spectra are reported with reference to an external 85% H₃PO₄ solution, with δ_P = 0; residual C₄H₇DO in THF-*d*₈ at δ_H = 3.58 and δ_C = 67.57. X-Ray diffraction data were collected on a Siemens Platform goniometer with a Charged

Coupled Device (CCD) detector. Structures were solved by direct methods using the SHELXTL (version 5.1) program suite (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).

Preparation of [(dtbpe)Ni(N₂C₆H₄OCH₃)] [PF₆] (2). To a solution of **1** (100 mg, 0.12 mmol) in 10 mL of Et₂O cooled to -35°C was added a 5 mL Et₂O solution of [N₂C₆H₄OCH₃] [PF₆] (68 mg, 0.24 mmol). The reaction mixture was stirred for 1 h at room temperature. After removing of solvent under vacuum the residue was triturated with n-pentane (3x5 mL) and the product was recrystallized from a 1:1 THF:n-pentane mixture yielding pure red crystalline **2** (138 mg, 83%). For **2**: ¹H-NMR (298K, 400.1 MHz, THF-*d*₈): δ 8.00 (d, 2H, J_{HH} = 9 Hz, Ar), 7.27 (d, 2H, J_{HH} = 9 Hz, Ar), 3.94 (s, 3H, OCH₃), 3.62 (m, 2H, CH₂CH₂O), 2.22 (m, 4H, CH₂P), 1.78 (m, 2H, CH₂CH₂O), 1.48 (d, 18H, J_{HP} = 13 Hz, C(CH₃)₃), 1.44 (d, 18H, J_{HP} = 13 Hz, C(CH₃)₃). ¹³C{¹H} NMR (298K, 100.62 MHz, THF-*d*₈): δ 165.64 (s, Ar), 130.59 (s, Ar), 126.38 (s, Ar), 116.77 (s, Ar), 68.21 (s, CH₂CH₂O), 56.67 (s, OCH₃), 36.63 (d, J_{CP} = 18Hz, C(CH₃)₃), 35.15 (d, J_{CP} = 18Hz, C(CH₃)₃), 30.75 (d, J_{CP} = 4Hz, C(CH₃)₃), 30.36 (d, J_{CP} = 4Hz, C(CH₃)₃), 26.37 (s, CH₂CH₂O), 23.53 (dd, J_{CP} = 24Hz, J_{CP} = 9Hz, CH₂P), 22.78 (dd, J_{CP} = 24Hz, J_{CP} = 9Hz, CH₂P). ³¹P{¹H} NMR (298K, 162MHz, THF-*d*₈): δ 94.68 (d, J_{PP} = 25 Hz), 93.75 (d, J_{PP}=25 Hz), -143.74 (sept., J_{PF} = 710 Hz). IR (Fluorolube mull, CaF₂): 1602 (s, ν_{N=N}), 1481 cm⁻¹. Anal. Calcd. for **2**•**0.5 THF**, C₂₇H₅₁F₆N₂NiO_{1.5}P₃: C, 46.77; H, 7.41; N, 4.04 %. Found: C, 46.59; H, 7.26; N, 3.50 %.

Preparation of (dtbpe)Ni(OTf) (4). 0.205 g (0.249 mmol) [(dtbpe)NiCl]₂ (**3**) was dissolved in 8 mL THF, and the light-orange solution was cooled to -35°C. A 5 mL cold clear solution of 0.175 g (0.248 mmol) TlOTf was added to the solution of **3**, and the

resultant mixture immediately turns cloudy orange. After 1.5 h, the cloudy tan solution was filtered, leaving white TiCl_3 solid. The filtered clear brown solution is dried and extracted with 6 mL toluene, again leaving white solid. The clear brown toluene solution is cooled to -35°C and left in the freezer overnight, yielding 0.081 g (0.154 mmol, 76%) paramagnetic (1.98 μB) **4**. ^1H NMR (22°C , 400 MHz, C_6D_6): δ 10.5 (br, $\Delta\nu_{1/2} = 752$ Hz), δ -11.5 (br, $\Delta\nu_{1/2} = 476$ Hz). Anal. Calcd. for $\text{C}_{19}\text{H}_{40}\text{F}_3\text{NiO}_3\text{P}_2\text{S}$: C, 43.37; H, 7.66 %. Found: C, 42.89; H, 7.19 %.

Preparation of (dtbpe)Ni(NO)(OTf) (5). In a 100 mL Schlenk flask (dtbpe)NiOTf (**4**; 0.092 g, 0.174 mmol) was dissolved in 15 mL toluene. The golden brown toluene solution was cooled to -78°C . Added 0.174 mmol NO gas via syringe to the cooled solution, which causes a fast color change to blue-green. The reaction was stirred at -78°C for 15 min, and became a bright blue color. The reaction mixture was then warmed to room temperature while stirring for 45 minutes. The Schlenk flask was evacuated and the solution was concentrated under reduced pressure to 2 mL, with blue precipitate. The Schlenk flask was cycled into the glove box, where an additional 3 mL toluene was used to dissolve the blue precipitate. The 5 mL blue solution was filtered, and cooled to -35°C and left in the freezer overnight. Blue crystals of **7** formed, in a crop of 0.085 g (0.154 mmol, 86%). ^1H NMR (22°C , 400 MHz, CD_2Cl_2): δ 2.01 (d, CH_2CH_2 , 4H), 1.27 (d, tBu, 36H). $^{31}\text{P}\{^1\text{H}\}$ NMR (22°C , 400 MHz, CD_2Cl_2): δ 92.5 (s, dtbpe). $^{13}\text{C}\{^1\text{H}\}$ NMR (22°C , 400 MHz, CD_2Cl_2): δ 35.7 (m, $\text{C}-(\text{CH}_3)_3$), 29.8 (br, CH_3), 26.4 (m, CH_2CH_2). IR (CaF_2 , Fluorolube): 2948, 2309, 1764 (ν_{NO}) cm^{-1} . Anal. Calcd. for $\text{C}_{19}\text{H}_{40}\text{F}_3\text{NNiO}_4\text{P}_2\text{S}$: C, 41.03; H, 7.25; N, 2.52 %. Found: C, 40.69; H, 7.10; N, 2.24 %.

Preparation of [(dtbpe)Ni(NO)][BAr^F₄] (6). In the dry-box, a scintillation vial was charged with **5** (0.040 g, 0.0726 mmol) dissolved in 5 mL diethyl ether, chilled to -35°C, and added to a cold suspension of NaBAr^F₄ (0.060 g, 0.070 mmol) in diethyl ether. The mixture was stirred for 30 min, and darkened to a blue-green color, with a white precipitate. The reaction mixture was filtered, dried in vacuo, and washed with toluene, affording a jade-green solid. The green product **6** was extracted with chlorobenzene, and crystallized from a chlorobenzene/ petroleum ether solution, giving 0.060 g (91 %) yield. ¹H NMR (22°C, 500 MHz, CD₂Cl₂): δ 7.72 (s, 8H, BAr^F₄), 7.56 (s, 4H, BAr^F₄), 1.58 (d, 4H, CH₂Cl₂), 1.53 (d, 36H, *t*-butyl). ³¹P{¹H} NMR (22°C, 500 MHz, CD₂Cl₂): δ 78.7 (s, dtbpe). ¹³C{¹H} NMR (22°C, 400 MHz, CD₂Cl₂): δ 162.0 (q, CF₃), 134.9 (s), 129.1 (d), 126.0 (s), 123.3(s), 117.6 (s), 36.25 (m, C-(CH₃)₃), 30.97 (br, CH₃), 20.2 (m, CH₂CH₂). IR (CaF₂, Fluorolube): 1832 cm⁻¹ (ν_{NO}). Anal. Calcd. for C₅₀BH₅₂F₂₄NNiOP₂: C, 47.27; H, 4.13; N, 1.10 %. Found: C, 48.02; H, 3.83; N, 1.00 %.

References:

- (1) I. Bach, K. -R. Pörschke, R. Goddard, C. Kopsike, C. Krüger, A. Rufinska and K. Seevogel, *Organometallics*, 1996, **15**, 4959.
- (2) D. J. Mindiola, R. Waterman, D. M. Jenkins and G. L. Hillhouse, *Inorg. Chim. Acta*, 2003, **345**, 299.