# Supporting information for

# Facile displacement of η<sup>5</sup>-cyclopentadienyl ligands from half-sandwich alkyl,NHC-nickel complexes: an original route to robust *cis*-C,C-nickel square planar complexes

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## **General information**

All reactions were carried out using standard Schlenk or glovebox techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon. Solution NMR spectra were recorded at 298 K on FT-Bruker Ultra Shield 300 and FT Bruker Spectrospin 400 spectrometers operating at 300.13 or 400.14 MHz for <sup>1</sup>H and at 75.47 or 100.61 MHz for <sup>13</sup>C{<sup>1</sup>H}. <sup>1</sup>H 2D COSY spectra were obtained for complexes **2a** and **3a**,**b** to help in the <sup>1</sup>H signal assignments. The assignments of  ${}^{13}C{}^{1}H$  NMR spectra were made with the aid of DEPT <sup>13</sup>C spectra for all compounds. The chemical shifts are referenced to the residual deuterated or <sup>13</sup>C solvent peaks. Chemical shifts ( $\delta$ ) and coupling constants (J) are expressed in ppm and Hz respectively. Chemical shifts and full NMR spectra of 2a are given for  $[2a] \sim 3.10^{-2}$  mol.L<sup>-1</sup> in CD<sub>3</sub>CN. IR spectra of solid samples of all compounds were recorded on a FT-IR Nicolet 380 spectrometer equipped with a diamond SMART-iTR ATR. Vibrational frequencies are expressed in cm<sup>-1</sup>. Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, Institut de Chimie, Université de Strasbourg. Commercial compounds were used as received.  $[Ni{Mes-NHC-(CH_2)_2CH(CN)}Cp]$ **1**a.<sup>1</sup> [Ni{Me-NHC-CH<sub>2</sub>CH(CN)}Cp] **1b**<sup>2</sup>  $[Ni{(Mes)_2NHC}(CH_3)Cp]$  4a<sup>3</sup> and  $[Ni{(Mes)_2NHC}(CH_2CN)Cp]$  4b<sup>1</sup> were prepared according to the published methods.

#### Synthesis of [Ni{Mes-NHC-(CH<sub>2</sub>)<sub>2</sub>CH(CN)}(NCCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (2a)

To a dark green suspension of **1a** (300 mg, 0.798 mmol) and KPF<sub>6</sub> (147 mg, 0.799 mmol) in acetonitrile (5 mL) at room temperature was added drop-wise an equimolar amount of aqueous HCl (37%) diluted in acetonitrile to 1.0 M (0.80 mL, 0.800 mmol). The reaction mixture readily turned ochre yellow and was stirred for 10 min before filtration on a Celite pad, which was subsequently rinsed with acetonitrile until the washings were colourless. Volatiles were evaporated under vacuum, and the resulting solid was washed with pentane (3 x 10 mL), diethyl ether (3 x 10 mL) and dried under vacuum at 50°C to afford 2a as a dark yellow solid (325 mg, 0.604 mmol, 76%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.13 MHz):  $\delta = 7.32$  (d, <sup>3</sup>J = 1.8, 1H, NCH), 7.24 (s, 1H, m-H), 7.05 (s, 1H, m-H), 7.03 (d,  ${}^{3}J = 1.8$ , 1H, NCH), 4.13 and 4.03 (2m, 2 x 1H, NCH<sub>2</sub>), 2.56 (s, 3H, p-Me), 2.38 (s, 3H, o-Me), 2.33, (m, 1H, CHCN), 2.03 (s, 3H, o-Me), 1.69 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>), 1.08 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>). Free CH<sub>3</sub>CN that results from exchange with CD<sub>3</sub>CN is seen as a singlet (at 1.96 ppm) on the downfield side of the multiplet due to residual CHD<sub>2</sub>CN observed at 1.94 ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 100.61 MHz):  $\delta = 156.1$  (br., NCN); 140.3 (*p*- or *ipso*-C<sub>Ar</sub>), 136.5, 136.2, 135.7 (*ipso*- or *p*-C<sub>Ar</sub>, *o*-C<sub>Ar</sub>) and CHCN), 130.4 and 130.0 (m-C<sub>Ar</sub>), 125.4 and 123.6 (NCH), 50.6 (NCH<sub>2</sub>), 29.2 (NCH<sub>2</sub>CH<sub>2</sub>), 21.1 (*p*-Me), 19.2 and 18.3 (*o*-Me), -2.0 (br., CHCN). IR [ATR]: v(C<sub>sp2</sub>-H) 3176 (w), 3145 (w); v(C<sub>sp3</sub>-H) 2923 (w), 2861 (w); v(CH<sub>3</sub>CN) 2352(w), 2322 (w), 2293 (w);  $v(C \equiv N)$  2234 (m); v(P-F) 826 (s).



# NMR spectra of [Ni{Mes-NHC-(CH<sub>2</sub>)<sub>2</sub>CH(CN)}(NCCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (2a)<sup>a</sup>

<sup>*a*</sup> [2a] ~  $3.10^{-2}$  mol.L<sup>-1</sup> for the <sup>1</sup>H NMR spectrum

### Concentration dependence of the <sup>1</sup>H NMR spectrum of (2a).

The <sup>1</sup>H NMR spectrum of **2a** is concentration dependent. Thus, while both *meta*-protons of the mesityl ring each appear as two relatively sharp singlets when  $[2a] \sim 3.10^{-2} \text{ mol.L}^{-1}$ , one signal of the *m*-protons shifts significantly to lower field when  $[2a] \sim 0.15 \text{ mol.}L^{-1}$ , and then appears as a very broad singlet (Figure S1A). Similar behaviour is observed for the two ortho-methyls of the mesityl ring. Thus, while both appear as two relatively sharp singlets when  $[2a] \sim 3.10^{-2}$  mol.L<sup>-1</sup>, one significantly shifts to lower field when  $[2a] \sim 0.15$  mol.L<sup>-1</sup>, and then appears as a very broad singlet (Figure S1B). Apart from the CHCN proton, whose chemical shift is also concentration dependent, all the other protons give well-resolved sharp signals and hardly change upon concentration variation. The exact reason of this behaviour is not well understood, but may well originate from enhanced intermolecular interactions at higher concentrations and/or from a fluxional process involving mesityl group rotation, that could be linked to the rate of acetonitrile exchange. The presence of free CH<sub>3</sub>CN as a singlet on the downfield side of the multiplet due to residual CHD<sub>2</sub>CN (Figure S1B) indicates that CH<sub>3</sub>CN/CD<sub>3</sub>CN exchange is indeed occuring, and a VT NMR experiment run in CD<sub>3</sub>CN from +27°C to +75°C on a diluted solution of 2a indeed allowed to observe a slight broadening at high temperature (at +70 and +75°C) of the mesityl methyl groups that resonate at 2.6 and 2.1 ppm.

Figure S1A. Aromatic area of the <sup>1</sup>H NMR spectra (CD<sub>3</sub>CN, 298 K) of 2a at [2a]  $\sim 3.10^{-2}$ 

 $mol.L^{-1}$  (bottom) and 0.15  $mol.L^{-1}$  (top)



Figure S1B. Mesityl methyl groups area of the <sup>1</sup>H NMR spectra (CD<sub>3</sub>CN, 298 K) of 2a at  $[2a] \sim 3.10^{-2} \text{ mol.L}^{-1}$  (bottom) and 0.15 mol.L<sup>-1</sup> (top)



#### Deuterium labelling experiment; reaction of (1a) with DCl

To a dark green suspension of **1a** (50 mg, 0.133 mmol) and KPF<sub>6</sub> (25 mg, 0.133 mmol) in CD<sub>3</sub>CN (2 mL) (C ~ 7.10<sup>-2</sup> mol.L<sup>-1</sup>) at room temperature was added drop-wise a solution of DCl (35 wt.% in D<sub>2</sub>O) diluted in CD<sub>3</sub>CN to 1.0 M. The addition was stopped as soon as a colour change from dark green to ochre yellow was observed. The reaction mixture was then stirred for 5 min, before it was allowed to settle and a sample was removed with a syringe and directly analyzed by <sup>1</sup>H NMR. The obtained spectrum shows the presence of [Ni{Mes-NHC-(CH<sub>2</sub>)<sub>2</sub>CH(CN)}(NCCD<sub>3</sub>)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub> **2a-D** and mono-deuterated cyclopentadiene C<sub>4</sub>H<sub>4</sub>CHD in a 1:1 ratio. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.13 MHz):  $\delta$  = 7.33 (s, 2H, NCH and *m*-H), 7.07 (s, 1H, *m*-H), 7.04 (s, 1H, NCH), 6.56 and 6.48 (2d, <sup>3</sup>J n.r, 2 x 2H, C<sub>4</sub>H<sub>4</sub>CHD), 4.11 and 4.02 (2m, 2 x 1H, NCH<sub>2</sub>), 2.95 (br. s, 1H, C<sub>4</sub>H<sub>4</sub>CHD), 2.56 (s, 3H, *p*-Me), 2.41 (br. s, 4H, *o*-Me and CHCN), 2.03 (s, 3H, *o*-Me), 1.66 (br. s, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 1.05 (br. s, 1H, NCH<sub>2</sub>CH<sub>2</sub>).



## Synthesis of [Ni{Mes-NHC-(CH<sub>2</sub>)<sub>2</sub>CH(CN)}(acac)] (3a)

To a dark green suspension of 1a (1.00 g, 2.66 mmol) and KPF<sub>6</sub> (490 mg, 2.66 mmol) in acetonitrile (20 mL) at room temperature was added drop-wise an equimolar amount of aqueous HCl (37%) diluted in acetonitrile to 1.0 M (2.66 mL, 2.66 mmol). The reaction mixture turned yellow and was stirred for 10 min before filtration on a Celite pad, which was subsequently rinsed with acetonitrile until the washings were colourless. Potassium acetylacetonate (368 mg, 2.66 mmol) was then added to the filtrate and the reaction mixture was stirred for 30 min. The resulting light green suspension was filtered through Celite and the solvent evaporated under vacuum. Recrystallization from a thf/pentane mixture then afforded **3a** as light green microcrystals (650 mg, 1.46 mmol, 55%) that were washed with pentane (3 x 10 mL) and dried under vacuum. Anal. Calcd for C<sub>21</sub>H<sub>25</sub>N<sub>3</sub>NiO<sub>2</sub>•<sup>1</sup>/<sub>2</sub>C<sub>4</sub>H<sub>8</sub>O: C, 61.91; H, 6.55; N, 9.42. Found: C, 61.99; H, 6.60; N, 9.30. [The crystals contain half a molecule of thf per formula unit, as shown by the NMR data and the X-ray diffraction study]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400.14 MHz):  $\delta = 7.04$  (d, <sup>3</sup>J = 1.8, 1H, NCH), 7.04 (s, 1H, *m*-H), 6.88 (s, 1H, m-H), 6.70 (d,  ${}^{3}J = 1.8$ , 1H, NCH), 5.11 (s, 1H, CH[C(O)Me]<sub>2</sub>), 4.13 (m, 1H, NCH<sub>2</sub>), 4.01 (m, 1H, NCH<sub>2</sub>), 3.68 (m, 2H, 0.5 thf), 2.59 (s, 3H, o-Me), 2.31 (s, 3H, p-Me), 2.10 (s, 3H, o-Me), 1.82 (m, 2H, 0.5 thf), 1.78-1.71 (m, 2H, CHCN and NCH<sub>2</sub>CH<sub>2</sub>), 1.74 (s, 3H, C(O)*Me*), 1.27 (s, 3H, C(O)*Me*), 1.15 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400.14 MHz):  $\delta = 7.22$  (d,  ${}^{3}J = 1.8$ , 1H, NCH), 7.07 (s, 1H, m-H), 6.94 (s, 1H, m-H), 6.83 (d,  ${}^{3}J = 1.8$ , 1H, NCH), 5.15 (s, 1H, CH[C(O)Me]<sub>2</sub>), 4.07 (2m, 2 x 1H, NCH<sub>2</sub>), 3.65 (m, 2H, 0.5 thf), 2.51 (s, 3H, o-Me), 2.31 (s, 3H, p-Me), 2.08 (s, 3H, o-Me), 1.80 (m, 2H, 0.5 thf), 1.75 (dd,  ${}^{3}J = 8.8, {}^{3}J$ = 7.6, 1H, CHCN, 1.70 (s, 3H, C(O)Me), 1.65 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>), 1.31 (s, 3H, C(O)Me), 1.01 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 75.47 MHz):  $\delta = 187.8$  and 186.8 (CO), 163.1 (NCN), 138.9 (*p*- or *ipso*- $C_{Ar}$ ), 138.1 (*ipso*- or *p*- $C_{Ar}$ ), 136.3 (*o*- $C_{Ar}$ ), 135.7 (CHCN),

129.6 (*m*-C<sub>Ar</sub>), 124.4 and 122.5 (NCH), 100.7 (CH[C(O)Me]<sub>2</sub>), 68.3 (thf), 50.9 (NCH<sub>2</sub>), 30.8 (NCH<sub>2</sub>CH<sub>2</sub>), 27.0 and 25.2 (C(O)*Me*), 26.3 (thf), 21.1 (*p*-Me), 18.9 (*o*-Me), -2.2 (CHCN). IR [ATR]:  $\nu(C_{sp2}$ -H) 3152 (w), 3121 (w), 3093 (w);  $\nu(C_{sp3}$ -H) 2966 (w), 2916 (w), 2858 (w);  $\nu(C\equiv N)$  2187 (m);  $\nu(C=O) + \nu(C=C)$  1581 (m), 1520 (s).



NMR spectra of [Ni{Mes-NHC-(CH<sub>2</sub>)<sub>2</sub>CH(CN)}(acac)] (3a)



#### Synthesis of [Ni{Me-NHC-CH<sub>2</sub>CH(CN)}(acac)] (3b)

To a dark green suspension of **1b** (300 mg, 1.16 mmol) and  $\text{KPF}_6$  (214 mg, 1.16 mmol) in acetonitrile (5 mL) at room temperature was added drop-wise an equimolar amount of aqueous HCl (37%) diluted in acetonitrile to 1.0 M (1.16 mL, 1.16 mmol). The reaction mixture turned yellow and was stirred for 10 min before filtration on a Celite pad, which was subsequently rinsed with acetonitrile until the washings were colourless. Potassium acetylacetonate (160 mg, 1.16 mmol) was then added to the filtrate and the reaction mixture was stirred for 30 min. The resulting light brown-green suspension was filtered through Celite and the solvent evaporated under vacuum. The residue was then redissolved in THF (5 mL), filtered through Celite again, and precipitated from a thf/pentane (1:4) mixture to afford **3b** as a yellow powder (235 mg, 0.805 mmol, 69%) that was washed with pentane (3 x 10 mL) and dried under vacuum. Anal. Calcd for C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>NiO<sub>2</sub>: C, 49.37; H, 5.18; N, 14.39. Found: C, 49.47; H, 5.37; N, 14.10. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz):  $\delta = 6.78$  (d, <sup>3</sup>J = 1.8, 1H, NCH), 6.58 (d,  ${}^{3}J = 1.8$ , 1H, NCH), 5.38 (s, 1H, CH[C(O)Me]<sub>2</sub>), 3.79 (dd,  ${}^{2}J = 12.2$ ,  ${}^{3}J = 12.2$ 8.1, 1H, NCH<sub>2</sub>), 3.72 (s, 3H, NCH<sub>3</sub>), 3.51 (dd,  ${}^{2}J = 12.2$ ,  ${}^{3}J = 3.3$ , 1H, NCH<sub>2</sub>), 2.20 (dd,  ${}^{3}J =$ 8.1,  ${}^{3}J = 3.3$ , 1H, CHCN), 1.88 (s, 3H, C(O)Me), 1.84 (s, 3H, C(O)Me).  ${}^{13}C{}^{1}H$  NMR  $(CDCl_3, 75.47 \text{ MHz})$ :  $\delta = 187.5$  and 185.9 (CO), 160.8 (NCN), 136.3 (CHCN), 123.8 and 117.3 (NCH), 100.5 (CH[C(O)Me]<sub>2</sub>), 52.4 (NCH<sub>2</sub>), 35.5 (NCH<sub>3</sub>), 27.2 and 26.5 (C(O)Me), 4.0 (CHCN). IR [ATR]: v(C<sub>sp2</sub>−H) 3147 (w), 3116 (w); v(C<sub>sp3</sub>−H) 2940 (w); v(C≡N) 2185 (m); v(C=O) + v(C=C) 1575 (m), 1518 (s).



# NMR spectra of [Ni{Me-NHC-CH<sub>2</sub>CH(CN)}(acac)] (3b)

#### Synthesis of [Ni(Mes<sub>2</sub>NHC)(CH<sub>3</sub>)(acac)] (5a)

To a brownish suspension of 4a (300 mg, 0.677 mmol) and KPF<sub>6</sub> (125 mg, 0.679 mmol) in acetonitrile (5 mL) at room temperature was added drop-wise an equimolar amount of aqueous HCl (37%) diluted in acetonitrile to 1.0 M (0.68 mL, 0.680 mmol). The reaction mixture turned yellow and was stirred for 10 min before filtration on a Celite pad, which was subsequently rinsed with acetonitrile until the washings were colourless. Potassium acetylacetonate (94 mg, 0.680 mmol) was then added to the filtrate and the reaction mixture was stirred for 30 min at room temperature. The resulting light brown suspension was filtered through Celite and the solvent evaporated under vacuum. The residue was then extracted in toluene (5 mL) and filtered through Celite again. Solvent evaporation afforded 5a as a yellow solid (228 mg, 0.478 mmol, 71%) that was washed with pentane (3 x 10 mL) and dried under vacuum. Anal. Calcd for C<sub>27</sub>H<sub>34</sub>N<sub>2</sub>NiO<sub>2</sub>: C, 67.95; H, 7.18; N, 5.87. Found: C, 67.98; H, 7.35; N, 5.65. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.13 MHz):  $\delta = 7.12$  (s, 4H, *m*-H), 7.10 (s, 2H, NCH), 5.06 (s, 1H, CH[C(O)Me]<sub>2</sub>), 2.40 (s, 6H, p-Me), 2,17 (s, 12H, o-Me), 1.54 (s, 3H, C(O)Me), 1.51 (s, 3H, C(O)Me), -1.13 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 75.47 MHz):  $\delta = 186.6$  and 186.1 (CO), 179.5 (NCN), 139.6 (p- or ipso-C<sub>Ar</sub>), 137.9 and 136.4 (br. o-C<sub>Ar</sub>), 137.7 (ipso- or p-C<sub>Ar</sub>), 129.9 (*m*-C<sub>Ar</sub>), 124.3 (NCH), 100.0 (CH[C(O)Me]<sub>2</sub>), 27.2 and 26.5 (C(O)Me), 21.2 (*p*-Me), 18.6 (br. *o*-Me), -13.7 (CH<sub>3</sub>). IR [ATR]:  $\nu$ (C<sub>sp2</sub>-H) 3164 (w), 3134 (w), 3079 (w);  $v(C_{sp3}-H)$  2951 (m), 2917 (m), 2854 (m); v(C=O) + v(C=C) 1578 (s), 1515 (s).



# NMR spectra of [Ni(Mes<sub>2</sub>NHC)(CH<sub>3</sub>)(acac)] (5a)

#### Synthesis of [Ni(Mes<sub>2</sub>NHC)(CH<sub>2</sub>CN)(acac)] (5b)

To a dark green suspension of 4b (500 mg, 1.07 mmol) and KPF<sub>6</sub> (197 mg, 1.07 mmol) in acetonitrile (10 mL) at room temperature was added drop-wise an equimolar amount of aqueous HCl (37%) diluted in acetonitrile to 1.0 M (1.07 mL, 1.07 mmol). The reaction mixture turned yellow and was stirred for 10 min before filtration on a Celite pad, which was subsequently rinsed with acetonitrile until the washings were colourless. Potassium acetylacetonate (148 mg, 1.07 mmol) was then added to the filtrate and the reaction mixture was stirred for 30 min. The resulting greenish suspension was filtered through Celite and the solvent evaporated under vacuum. The residue was then redissolved in THF (5 mL), filtered through Celite again, and recrystallized from a thf/pentane (1:4) mixture at 4°C to afford 5 as a yellow-green solid (378 mg, 0.753 mmol, 70%) that was washed with pentane (3 x 10 mL) and dried under vacuum. Anal. Calcd for C<sub>28</sub>H<sub>33</sub>N<sub>3</sub>NiO<sub>2</sub>: C, 66.96; H, 6.62; N, 8.37. Found: C, 67.12; H, 6.64; N, 8.26. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.13 MHz):  $\delta = 7.17$  (s, 6H, *m*-H and NCH), 5.18 (s, 1H, CH[C(O)Me]<sub>2</sub>), 2.41 (s, 6H, p-Me), 2,16 (br. s, 12H, o-Me), 1.60 (s, 3H, C(O)Me, 1.59 (s, 3H, C(O)Me), -0.13 (s, 2H, CH<sub>2</sub>CN). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz):  $\delta =$ 7.10 (s, 4H, *m*-H), 6.95 (s, 2H, NCH), 5.06 (s, 1H, CH[C(O)Me]<sub>2</sub>), 2.41 (s, 6H, *p*-Me), 2,23 (s, 12H, o-Me), 1.66 (s, 3H, C(O)Me), 1.53 (s, 3H, C(O)Me), -0.02 (s, 2H, CH<sub>2</sub>CN).<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 75.47 MHz):  $\delta$  = 187.0 and 186.9 (CO), 169.8 (NCN), 140.1 (*p*- or *ipso*-C<sub>Ar</sub>), 137.6 and 136.0 (br. o-C<sub>Ar</sub>), 136.7 (ipso- or p-C<sub>Ar</sub>), 130.1 (m-C<sub>Ar</sub>), 125.2 (NCH), 100.6 (CH[C(O)Me]<sub>2</sub>), 26.9 and 26.1 (C(O)Me), 21.3 (p-Me), 18.4 (br. o-Me), -22.4 (CH<sub>2</sub>CN). IR [ATR]: v(C<sub>sp2</sub>-H) 3171 (w), 3128 (w), 3079 (w); v(C<sub>sp3</sub>-H) 2957 (m), 2918 (m), 2859 (w); v(C=N) 2193 (m); v(C=O) + v(C=C) 1578 (s), 1519 (s).



# NMR spectra of [Ni(Mes<sub>2</sub>NHC)(CH<sub>2</sub>CN)(acac)] (5b)

#### X-ray Diffraction Studies. Structure Determination and Refinement

A single crystal of **3a** suitable for X-ray diffraction studies was selected from a batch of crystals obtained at -28 °C from a thf/pentane solution. Diffraction data were collected at 173(2) K on a Bruker APEX II DUO KappaCCD area detector diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A summary of crystal data, data collection parameters and structure refinements is given in Table S1 (see the Supporting Information). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)<sup>4</sup> from reflections taken from three sets of twelve frames, each at ten s exposure. The structure was solved using direct methods with SHELXS-97 and refined against  $F^2$  for all reflections using the SHELXL-97 software.<sup>5</sup> A semi-empirical absorption correction was applied using SADABS in APEX2.<sup>4</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters, using weighted full-matrix least-squares on  $F^2$ . Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters.

Complex	3a
Empirical formula	$2(C_{21}H_{25}N_3NiO_2)\bullet C_4H_8O$
Formula weight	892.40
Crystal system	Tetragonal
Space group	I -4
<i>a</i> (Å)	18.4575(4)
<i>c</i> (Å)	13.1542(4)
$V(\text{\AA}^3)$	4481.36(19)
Ζ	4
$D_{\text{calcd}}$ (Mg.m <sup>-3</sup> )	1.323
Absorp coeff (mm <sup>-1</sup> )	0.891
Crystal habit, color	block, yellow
Crystal size (mm)	$0.20\times0.15\times0.10$
$h, k, l_{\max}$	24, 23, 17
$T_{\min}, T_{\max}$	0.842, 0.916
Reflns collected	29009
$R \left[ I > 2\sigma(I) \right]$	0.0259
$wR^2$ (all data)	0.0677
GOF on $F^2$	1.048

**Table S1**. X-Ray Crystallographic Data and Data Collection Parameters for 3a

Table S2. Selected 1	Bond Lengths	(Å) and Angles	(°) for Compl	exes $\mathbf{1a}^{1,2}$ and	<b>3a</b> with Esd's
in Parentheses					
	<b>1a</b> <sup><i>a</i></sup>	$\mathbf{3a}^{a}$			

	1a	Ja
Ni-C1	1.8560(19)	1.8686(19)
Ni-C2	1.9718(19)	1.961(2)
Ni-O1	_	1.8835(14)
Ni-O2	_	1.8968(14)
C2–C3	1.438(3)	1.447(3)
C3-N3	1.143(3)	1.145(3)
C1-Ni-C2	93.95(8)	91.91(8)
O1-Ni-O2	_	93.29(6)
C1-Ni-O2	_	89.71(7)
C2-Ni-O1	_	84.97(7)
Ni-C2-C3	106.91(15)	107.00(13)
C2-C3-N3	177.7(3)	178.0(2)

<sup>*a*</sup> The geometric parameters of the nickelacycle of 3a are almost identical to those of its half-sandwich precursor 1a.

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