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Synthesis and Characterization of Electron-Rich Nickel Tris-Carbene Complexes

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Supplementary Information:

Experimental Section

Methods and Procedures:

Manipulation of air-sensitive compounds was performed under a controlled dry nitrogen atmosphere using standard Schlenk techniques and inert-gas glove boxes (MBraun Labmaster by M. Braun, Inc.). Solvents were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA) and transferred to the glove box without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. All NMR spectra were recorded at room temperature ($20^{o}C$) in d_6-benzene, d_3-acetonitrile and d_6-DMSO solutions on Varian spectrometers operating at 400/300 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) and referenced to residual solvent peaks unless otherwise noted (δ in ppm). Cyclic voltammetric measurements were performed on Bioanalytical Systems equipment (BAS, CV-50W) in acetonitrile or THF solutions containing 0.1 M $[N(n\text{-}Bu)_4](ClO_4)$ as electrolyte (working electrode: platinum; auxiliary electrode: platinum wire; reference electrode: $Ag/AgNO_3$ in acetonitrile). Potentials are reported relative to the ferrocene/ferrocenium couple (Fc/Fc^+). Solid-state magnetization measurements of powdered samples were recorded on a SQUID magnetometer (Quantum Design) at 10 kOe between 5 and 300 K. Magnetic susceptibility data were corrected for background and underlying diamagnetic contributions using tabulated Pascal constants ($\chi_{dia} = 3.61 \cdot 10^{-4}$ cm^3 mol^{-1}).[1] Data reproducibility was carefully checked in multiple individual measurements of independently synthesized samples. X-band EPR spectra of dilute complex solutions in acetonitrile were recorded on a Bruker Elexsys E500 Spectrometer equipped with a helium flow cryostat (Oxford 900). Elemental analyses were performed by Kolbe Microanalytical Laboratory (Muelheim a. d. Ruhr/Germany).

Starting Materials:

Tris[2-(3-tert-butylimidazol-2-ylidene)ethyl]amine (TIMEN$^{t\text{-}Bu}$) was prepared as describe before.[2] Bis(1,5-cyclooctadiene)nickel(0) was obtained from commercial sources (Strem Chemicals, Inc.) and used as received.

Synthesis of Complexes:

Ni(TIMEN$^{t\text{-Bu}}$) (1): A solution of Ni(COD)$_2$ (0.18 g, 0.67 mmol) in THF was added dropwise to a solution of TIMEN$^{t\text{-Bu}}$ (0.31 g, 0.67 mmol) in 2 mL THF. Upon addition, the solution turned into deep red immediately. The reaction mixture was stirred for one hour and then evaporated under vacuum. The red precipitate was collected by filtration, washed with 5 ml cold diethyl ether, and dried in vacuum (0.20 g; Yield: 58%). Red crystals suitable for X-ray diffraction analysis were grown from a saturated diethyl ether solution of **1** at –35$^{\text{o}}$C.

^{1}H NMR (300 MHz, d$_6$-benzene, 20 °C): δ = 6.71 (s, 3H), 6.30 (s), 3.92 (t, ^3J(H,H) = 12 Hz , 3H), 3.04 (d, ^3J(H,H) = 12 Hz, 3H), 2.82 (d, ^3J(H,H) = 12 Hz, 3H), 2.42 (t, ^3J(H,H) = 12, 3H), 1.87 (s, 27H). ^{13}C NMR (100 MHz, d$_6$-benzene, 20 $^{\text{o}}$C): δ = 194.9, 116.4, 114.3, 64.0, 56.5, 52.9, 30.8ppm. Elemental analysis (%) calcd for C$_{27}$H$_{45}$N$_7$Ni**:** C 61.60, H 8.61, N 18.63; found: C 61.53, H 8.56, N 18.71.

[Ni(TIMEN$^{t\text{-Bu}}$)]Cl (2): 1 mL of dichloromethane was added to **1** (58 mg, 0.11 mmol). The resulting yellow solution was stirred for 5 minutes, and then 5 mL of diethyl ether was added to precipitate **2** as a yellow solid. The solid was collected by filtration, washed with diethyl ether, and dried in vacuum (42 mg; Yield: 68%). Yellow crystals suitable for X-ray diffraction analysis were grown by diffusion of diethyl ether into an acetonitrile solution of **2** at room temperature.

^{1}H NMR (300 MHz, d$_3$-acetonitrile, 20 °C): δ = 31.1 (s, 3H, $\Delta v_{1/2}$ = 20 Hz), 20.4 (s, 3H, $\Delta v_{1/2}$ = 13 Hz), 12.7 (s, 3H, $\Delta v_{1/2}$ = 11 Hz), 11.1 (s, 9H, $\Delta v_{1/2}$ = 22 Hz), 10.8 ppm (s, 3H, $\Delta v_{1/2}$ = 15 Hz), 6.5 ppm (s, 27H, $\Delta v_{1/2}$ = 30 Hz), -6.1 ppm (s, 3H, $\Delta v_{1/2}$ = 11 Hz). Elemental analysis (%) calcd for C$_{27}$H$_{45}$N$_7$NiCl**:** C 57.72, H 8.07, N 17.45; found: C 57.41, H 8.06, N 17.52.

Crystallographic details for Ni(TIMEN$^{t\text{-Bu}}$) (1): A crystal of dimensions 0.26 x 0.22 x 0.20 mm^3 was mounted on a glass fiber. A total of 17469 reflections (-9 $\leq$ h $\leq$ 17, -18 $\leq$ k $\leq$ 18, - 17 $\leq$ l $\leq$ 18) were collected at T = 100(2) K in the range of 2.05 to 27.46$^{\text{o}}$ of which 2123 were unique (R_{int} = 0.0227); Mo$_{K\alpha}$ radiation (λ= 0.71073 Å). The structure was solved by direct methods (Shelxtl Version 6.10, Bruker AXS, Inc., **2000**). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The residual peak and hole of electron densities were 0.36 and –0.12 eA^{-3}. The absorption coefficient was 0.732 mm^{-1}. The least squares refinement converged with residuals of $R(F)$ =0.0225, $wR(F^2)$ = 0.0555 and a GOF = 1.113(I>2σ(I)). C$_{27}$H$_{45}$N$_7$Ni, space group $P2_1$3, Cubic, a = 14.0195(4), α = 90.00$^{\text{o}}$, V = 2755.48(10) A^3, Z = 4, ρ_{calcd} = 1.269 Mg/m^3.

Crystallographic details for [Ni(TIMEN$^{t\text{-Bu}}$)]Cl (2): A crystal of dimensions 0.50 x 0.08 x 0.08 mm^3 was mounted on a glass fiber. A total of 16993 reflections (-15 $\leq$ h $\leq$ 15, -15 $\leq$ k $\leq$ 15, - 15 $\leq$ l $\leq$ 15) were collected at T = 100(2) K in the range of 1.46 to 22.50$^{\text{o}}$ of which 7554 were unique (R_{int} = 0.0519); Mo$_{K\alpha}$ radiation (λ= 0.71073 Å). The structure was solved by direct methods (Shelxtl Version 6.10, Bruker AXS, Inc., **2000**).

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron of densities were 0.741 and –0.352 e$\AA^{-3}$. The absorption coefficient was 0.791 mm^{-1}. The least squares refinement converged normally with residuals of $R(F) = 0.0495$, $wR(F^2) = 0.1078$ and a GOF = 0.960 ($I > 2\sigma(I)$). $C_{27}H_{45}N_7NiCl$, space group P-1, Triclinic, $a = 14.5847(8)$, $b = 14.7332(9)$, $c = 14.7698(9)$ Å, $\alpha = 103.2710(10)°$, $\beta = 99.4650(10)$, $\gamma = 105.2760(10)$, $V = 2893.1(3)$ A^3, $Z = 4$, $\rho_{calcd} = 1.290$ Mg/m^3.

Reference

(1)   O'Connor, C. J. *Progress in Inorganic Chemistry* **1982**, *29*, 203-283.

(2)   Hu, X.; Castro-Rodriguez, I.; Meyer, K. *Journal of the American Chemical Society* **2003**, *125*, 12237-12245.

Figure S1. Cyclic voltammogram of [Ni(TIMEN$^{t\text{-Bu}}$)] (**1**) recorded in THF solution containing 0.1 M [N(*n*-Bu)$_4$](ClO$_4$) as electrolyte.

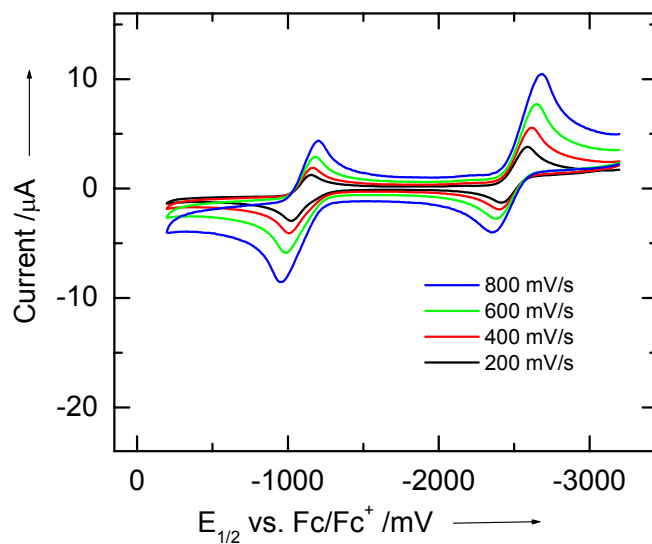**Figure S2.** Cyclic voltammogram of [Ni(TIMEN$^{t\text{-Bu}}$)]Cl (**2**) recorded in THF solution containing 0.1 M [N(*n*-Bu)$_4$](ClO$_4$) as electrolyte.
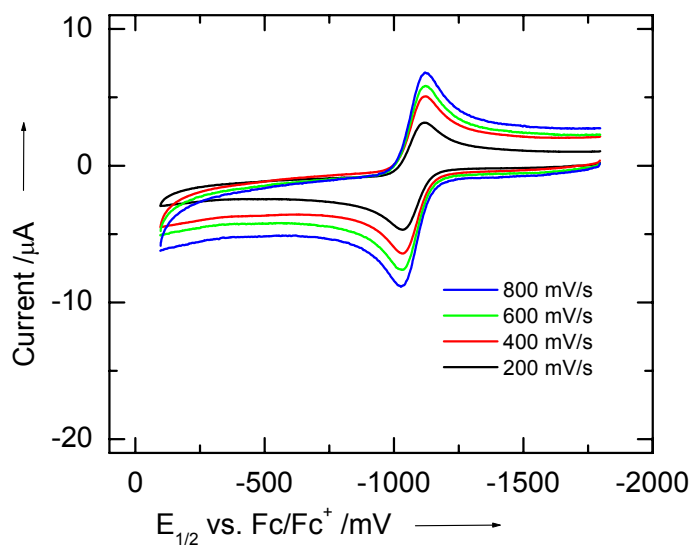
Figure S3. Plot of the effective magnetic moment, μ_{eff}, versus temperature from SQUID magnetization measurements for two independently prepared samples of **2** (m = 16.7 mg, m = 22.4 mg, χ_{dia} = 3.61 · 10^{-4} cm^3 mol^{-1}). The observed temperature behavior of the magnetic moment indicates weak antiferromagnetic spin-spin coupling in the solid state, which is sample dependent and, thus, may account for discrepancy between two independently synthesized microcrystalline samples.
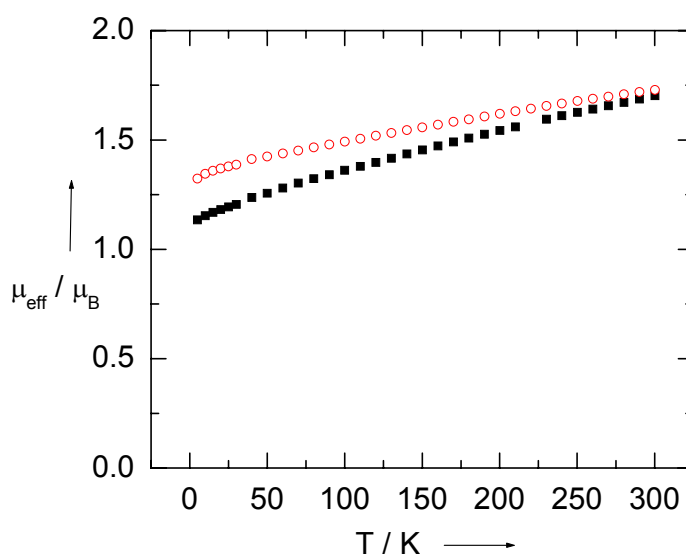
Figure S4. EPR spectrum of complex 2 recorded in frozen acetonitrile solution at 8 K. Experimental condition: microwave frequency, 9.465697 GHz; power, 0.6362 mW; modulation amplitude, 10G. The spectrum is different from those of conventional Ni(I) species, but it is highly reproducible and thus rules out the possibility of sample contamination.