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Supplementary Material**for**Re(III) and Re(V) Complexes that Contain the (C₆F₅NCH₂CH₂)₃N Ligand

by

Brigitte Neuner and Richard R. Schrock*

All syntheses were carried out under dinitrogen in a drybox using solvents that had been dried and purified in standard ways. (C₆F₅NCH₂CH₂)₃N¹ (F₅TREN), Ta(CH-t-Bu)Br₃(THF)₂,² and [NEt₄]₂[ReOCl₅]^{3,4} were synthesized as described in the literature.

[(C₆F₅NCH₂CH₂)₂NCH₂CH₂NHC₆F₅]Re(O)Cl (**1**). A THF solution (40 mL) containing 600 mg of [NEt₄]₂[ReOCl₅] (0.936 mmol), 603 mg of F₅TREN (0.936 mmol), and 400 mg of NEt₃ (3.82 mmol) was stirred for 12 hours at room temperature. The pale brown precipitate was filtered off and the emerald green solution was concentrated in vacuo. The resulting green residue was recrystallized from minimal methylene chloride by adding pentane and cooling the mixture to -40°C; total yield 643 mg (78%): ¹H NMR (CD₃CN) δ 2.15 - 4.70 (br, NH), 3.39 and 3.53 (m, 6), 3.82 (m, 4), 4.19 (m, 2); ¹³C NMR (CD₃CN) δ 42.1 (br, CH₂), 61.5 (br, 2 CH₂), 66.4 (br, CH₂), 69.7 (br, 2 CH₂), 133 - 147 (C_{aryl}); ¹⁹F NMR (CD₃CN) δ -173.9 (tt, ³J_{FF} = 21, ⁴J_{FF} = 6.2), -166.8 (m), 166.4 (t, ³J_{FF} = 19), -162.4 (t, ³J_{FF} = 21), -160.3 (d, ³J_{FF} = 23), -150.4 (dd, ³J_{FF} = 23, ⁴J_{FF} = 6.2), -149.9 (m); IR cm⁻¹ 910 (Re=O). Calcd for ReOC₂₄H₁₃N₄ClF₁₅: C, 32.76; H, 1.49; N, 6.37. Found: C, 32.44; H, 1.52; N, 6.21.

[(C₆F₅NCH₂CH₂)₃N]ReBr₂ (**2**). A solution of Ta(CH-t-Bu)Br₃(THF)₂ (699 mg, 1.16 mmol, 1.05 equiv) in 5 mL of toluene was slowly added to a suspension of **1** (970 mg, 1.10 mmol) in 15 mL of toluene at room temperature. After stirring the solution overnight, the volume was reduced to 3 mL and the green-brown precipitate was filtered off and washed twice with toluene.

The precipitate was recrystallized from a mixture of methylene chloride and pentane at -40°C to yield 814 mg olive green crystals (0.81 mmol, 74%): ^1H NMR (CD_3CN) δ -34 (very broad), -138 (very broad); ^{19}F NMR (CD_3CN) δ -132.1 (br s), -151.2 (br s), -156.9 (br s); MS 907 ($\text{M}^+ - \text{Br}$). Calcd for $\text{ReC}_{24}\text{H}_{12}\text{N}_4\text{F}_{15}\text{Br}_2$: C, 29.20; H, 1.22; N, 5.67. Found: C, 29.73; H, 1.19; N, 5.43.

$[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]\text{Re}(\text{N}_2)$ (**3**). An ether solution of methyllithium (0.357 mmol) was added to a stirred solution of **2** (167 mg, 0.17 mmol) in 5 mL of THF under an atmosphere of dinitrogen. The green-brown solution turned dark purple immediately, and then faded to orange-brown over a period of one hour. The solvent was evaporated in vacuo and the oily orange was dissolved in minimal methylene chloride. The extract was filtered, pentane was added, and the mixture was cooled to -40°C to yield orange cubes; yield 104 mg (0.12 mmol, 72%): ^1H NMR (THF-d_8) δ 3.13 (t, 6, $^3\text{J} = 5.6$), 3.95 (t, 6, $^3\text{J} = 5.6$); ^1H NMR (CD_3CN) δ 3.07 (t, 6, $^3\text{J} = 5.6$), 3.90 (t, 6, $^3\text{J} = 5.6$); ^{19}F NMR (THF-d_8) δ -152.90 (m), -164.90 (t, $\text{J} = 21$), -166.59 (t, $\text{J} = 20$); ^{19}F NMR (CD_3CN) δ -152.5 (m), -164.7 (t, $^3\text{J} = 21$), -166.5 (t, $^3\text{J} = 19$); ^{13}C NMR (THF-d_8) δ 57.7 (t, CH_2 , $^1\text{J} = 139$), 63.2 (t, CH_2 , $^1\text{J} = 139$), 135 - 145 (C_{aryl}); ^{15}N (CD_3CN) δ 281.3 and 332.0 (each a d, $\text{J}_{\text{NN}} = 5.5$); IR cm^{-1} 2004 ($\text{N}=\text{N}$, vs), 1935 ($^{15}\text{N}=\text{N}^{15}$, vs); MS: 856 (M^+), 828 ($-\text{N}_2$). Calcd for $\text{ReC}_{24}\text{H}_{12}\text{N}_6\text{F}_{15}$: C, 33.69; H, 1.41; N, 9.82. Found: C, 32.52; H, 1.66; N, 9.48.

The reaction was repeated with 168 mg **2** in the presence of $^{15}\text{N}_2$ to yield 105 mg of the ^{15}N labeled compound (72%).

General procedure for reduction with methyllithium. A THF solution of **2** (10 mL THF per 100 mg) and LiMe (in 10 mL ether per 2.1 equivalents) were separately degassed three times by freeze-pump-thaw cycles. The reaction vessel was then filled with the desired gas and the solutions were combined. The product (**4**, **5**, or **6**) was isolated in a manner analogous to the manner in which **3** was isolated.

$[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]\text{Re}(\text{CO})$ (**4**). Addition of methyllithium to 100 mg **2** (0.101 mmol) under an atmosphere of CO did not yield a purple intermediate; the reaction mixture turned immediately dark green. After 5 minutes the reaction mixture turned red and after stirring overnight a bright yellow. Workup yielded 67 mg (0.0791 mmol, 78%) of product. The reaction

was repeated with 50 mg **2** under ^{13}C to give the ^{13}C labelled product in the same yield: ^1H NMR (CD_2Cl_2) δ 3.16 (t, 6, $^3J = 5.7$), 3.95 (t, 6, $^3J = 5.4$); ^{19}F NMR (CD_2Cl_2) δ -152.0 (m), -163.7 (t, $^3J = 22$), -165.6 (m); ^{13}C NMR (THF- d_8) δ 55.5 (CH_2), 62.6 (CH_2), 135 - 145 (C_{aryl}); ^{13}C NMR (CD_2Cl_2) δ 199.5 ($^{13}\text{C}=\text{O}$); IR (DME solution) cm^{-1} 1875 cm^{-1} ($\text{C}=\text{O}$), 1830 ($^{13}\text{C}=\text{O}$). Calcd for $\text{ReC}_{25}\text{H}_{12}\text{N}_4\text{F}_{15}\text{O}$: C, 35.10; H, 1.41; N, 6.55. Found: C, 35.25; H, 1.29; N, 6.50.

$[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]\text{ReH}_2$ (5**)**. Methylolithium was added to 100 mg of **2** (0.101 mmol) under dihydrogen (1 atm) and the reaction was stirred for 12 hours before workup; yield 43 mg dark red crystals (52%): ^1H NMR (CD_3CN) δ - 0.68 (s, H_2), 3.10 (t, 6, $^3J = 5.7$), 3.79 (t, 6, $^3J = 5.7$); ^1H NMR (CD_2Cl_2) δ - 0.89 (s, H_2), 3.07 (t, 6, $^3J = 6.3$), 3.80 (t, 6, $^3J = 5.4$); ^{19}F NMR (CD_3CN) δ -152.2 (m), -166.4 (t, $^3J = 21$), -167.1 (m); ^{19}F NMR (CD_2Cl_2) δ -152.0 (m), -165.8 (t, $^3J = 22$), -166.6 (m); ^{13}C NMR (CD_3CN) δ 57.6 (CH_2), 64.3 (CH_2), 136.7, 137.5, 139.8, 142.6, 144.3, 145.8 (all C_{aryl}). Calcd for $\text{ReC}_{24}\text{H}_{14}\text{N}_4\text{F}_{15}$ C, 34.75; H, 1.70; N, 6.75. Found: C, 34.49; H, 1.86; N, 7.14.

$[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]\text{Re}(\text{H})(\text{D})$ (5-d₁**)**. The synthesis was essentially the same as for **5** itself from 157 mg **2** (0.159 mmol) in the presence of HD gas at 1 atm for 48 hours. Workup yielded 50 mg of dark red crystals (38%): ^1H NMR (CD_3CN) δ - 0.74 (t, H, $^2J_{\text{HD}} = 15$); ^2H NMR (CH_2Cl_2) δ - 0.98 (d, D, $^2J_{\text{HD}} = 17$). The remaining portions of the spectra were the same as for **5** itself.

$(\text{F}_5\text{C}_6\text{NCH}_2\text{CH}_2)_3\text{N}]\text{ReD}_2$ (5-d₂**)**. The synthesis was essentially the same as for **5** itself from 100 mg **2** (0.101 mmol) in the presence of D_2 gas at 1 atm for 12 hours. Workup yielded 40 mg of dark red crystals (48%): ^2H NMR (THF) δ -0.43 (s, 2 D). The remaining portions of the spectra were the same as for **4** itself. Calcd for $\text{ReC}_{24}\text{H}_{12}\text{D}_2\text{N}_4\text{F}_{15}$: C, 34.66; H(D), 1.45; N, 6.74. Found: C, 34.32; H(D), 1.65; N, 6.91.

$(\text{F}_5\text{C}_6\text{NCH}_2\text{CH}_2)_3\text{N}]\text{Re}(\text{C}_2\text{H}_4)$ (6**)**. Methylolithium (0.344 mmol) was added to 162 mg **2** (0.162 mmol) under an atmosphere of ethylene. After 16 hours workup gave 58 mg of product as dark green needles (0.068 mmol, 42%). An analogous reaction with ethylene- $^{13}\text{C}_2$ gave the product in 52% yield: ^1H NMR (THF- d_8) δ 2.61 (br s, 4), 3.27 (t, 6, $^3J = 5.7$), 3.87 (t, 6, $^3J = 5.7$);

^{19}F NMR (THF- d_8) δ -150.9 (m), -164.3 (t, $^3J = 21$), -166.6 (m); ^1H NMR (CD_2Cl_2) δ 2.57 (br s, 4), 3.12 (t, 6, $^3J = 5.7$), 3.79 (t, 6, $^3J = 5.7$); ^{19}F NMR (CD_2Cl_2) δ -151.1 (m), -163.2 (t, $^3J = 21$), -165.7 (m). Calcd for $\text{ReC}_{26}\text{H}_{16}\text{N}_4\text{F}_{15}$: C, 36.50; H, 1.88; N, 6.55. Found: C, 36.70; H, 1.81; N, 6.88.

The analogous compound prepared from doubly ^{13}C labelled ethylene showed a non-first-order multiplet in THF- d_8 at δ 54.7.

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