

Supporting Information for

Variable Nitric Oxide Reactivity of Tropocoronand Cobalt(III) Nitrite Complexes as a Function of Polymethylene Linker Chain Length

Julia Kozhukh and Stephen J. Lippard

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139

Email: lippard@mit.edu

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Table S1. Summary of bond lengths (Å) and angles (deg) of interest for $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-4,4})]$.^a

Co(1)–N(2)	1.861(3)	N(2A)–Co(1)–N(2)	96.31(17)
Co(1)–N(1)	1.904(3)	N(2A)–Co(1)–N(1)	82.17(12)
Co(1)–O(1)	2.019(3)	N(2)–Co(1)–N(1)	94.60(12)
		N(1)–Co(1)–N(1A)	175.18(18)
		N(2A)–Co(1)–O(1)	162.65(11)
		N(2)–Co(1)–O(1)	101.00(11)
		N(1)–Co(1)–O(1)	95.22(11)
		N(1A)–Co(1)–O(1)	88.92(11)
		O(1)–Co(1)–O(1A)	61.73(14)

^aThe atom-labeling scheme is shown in Figure 1, *left*. The numbers in parentheses correspond to the estimated standard deviation of the last significant figures.

Table S2. Summary of bond lengths (Å) and angles (deg) of interest for $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-5,5})]$.^a

Co(1)–N(2)	1.8728(19)	N(2A)–Co(1)–N(2)	92.22(12)
Co(1)–N(1)	1.9107(18)	N(2)–Co(1)–N(1A)	97.19(8)
Co(1)–O(1)	2.0237(17)	N(1A)–Co(1)–N(1)	179.05(12)
		N(2)–Co(1)–N(1)	82.14(8)
		N(2)–Co(1)–O(1A)	102.89(8)
		N(1)–Co(1)–O(1)	94.63(7)
		N(2)–Co(1)–O(1)	164.84(8)
		N(1)–Co(1)–O(1A)	86.19(7)
		O(1A)–Co(1)–O(1)	62.03(10)

^aThe atom-labeling scheme is shown in Figure 1, *middle*. The numbers in parentheses correspond to the estimated standard deviation of the last significant figures.

Table S3. Summary of bond lengths (Å) and angles (deg) of interest for [Co(η^2 -NO₂)(TC-6,6)], listed for both crystallographically independent molecules.^a

Co(1)–N(4)	1.880(3)	N(4)–Co(1)–N(2)	91.83(14)	N(6)–Co(2)–N(8)	92.79(14)
Co(1)–N(2)	1.888(3)	N(4)–Co(1)–N(1)	97.08(14)	N(6)–Co(2)–N(9)	97.53(15)
Co(1)–N(1)	1.914(3)	N(2)–Co(1)–N(1)	81.60(14)	N(8)–Co(2)–N(9)	82.09(14)
Co(1)–N(3)	1.917(3)	N(4)–Co(1)–N(3)	81.67(14)	N(6)–Co(2)–N(7)	81.93(15)
Co(1)–O(2)	1.995(3)	N(2)–Co(1)–N(3)	96.87(14)	N(8)–Co(2)–N(7)	98.17(15)
Co(1)–O(1)	2.017(3)	N(1)–Co(1)–N(3)	178.01(14)	N(9)–Co(2)–N(7)	179.42(16)
		N(4)–Co(1)–O(2)	102.29(13)	N(6)–Co(2)–O(3)	102.33(14)
		N(2)–Co(1)–O(2)	165.69(13)	N(8)–Co(2)–O(3)	164.72(14)
		N(1)–Co(1)–O(2)	94.23(13)	N(9)–Co(2)–O(3)	93.60(13)
Co(2)–N(6)	1.888(3)	N(3)–Co(1)–O(2)	87.55(13)	N(7)–Co(2)–O(3)	86.29(13)
Co(2)–N(8)	1.899(3)	N(4)–Co(1)–O(1)	164.84(13)	N(6)–Co(2)–O(4)	164.33(14)
Co(2)–N(9)	1.908(3)	N(2)–Co(1)–O(1)	103.31(13)	N(8)–Co(2)–O(4)	102.71(14)
Co(2)–N(7)	1.920(3)	N(1)–Co(1)–O(1)	85.99(13)	N(9)–Co(2)–O(4)	86.96(13)
Co(2)–O(3)	2.010(3)	N(3)–Co(1)–O(1)	95.62(13)	N(7)–Co(2)–O(4)	93.49(14)
Co(2)–O(4)	2.014(3)	O(2)–Co(1)–O(1)	62.61(12)	O(3)–Co(2)–O(4)	62.29(13)
		N(4)–Co(1)–N(5)	133.70(14)	N(6)–Co(2)–N(10)	133.20(15)
		N(2)–Co(1)–N(5)	134.42(14)	N(8)–Co(2)–N(10)	134.01(15)
		N(1)–Co(1)–N(5)	89.53(13)	N(9)–Co(2)–N(10)	90.57(13)
		N(3)–Co(1)–N(5)	92.46(13)	N(7)–Co(2)–N(10)	89.62(14)
		O(2)–Co(1)–N(5)	31.41(11)	O(3)–Co(2)–N(10)	30.95(12)
		O(1)–Co(1)–N(5)	31.21(11)	O(4)–Co(2)–N(10)	31.35(13)

^aThe atom-labeling scheme is shown in Figure 1, *right*. The numbers in parentheses correspond to the estimated standard deviation of the last significant figures.

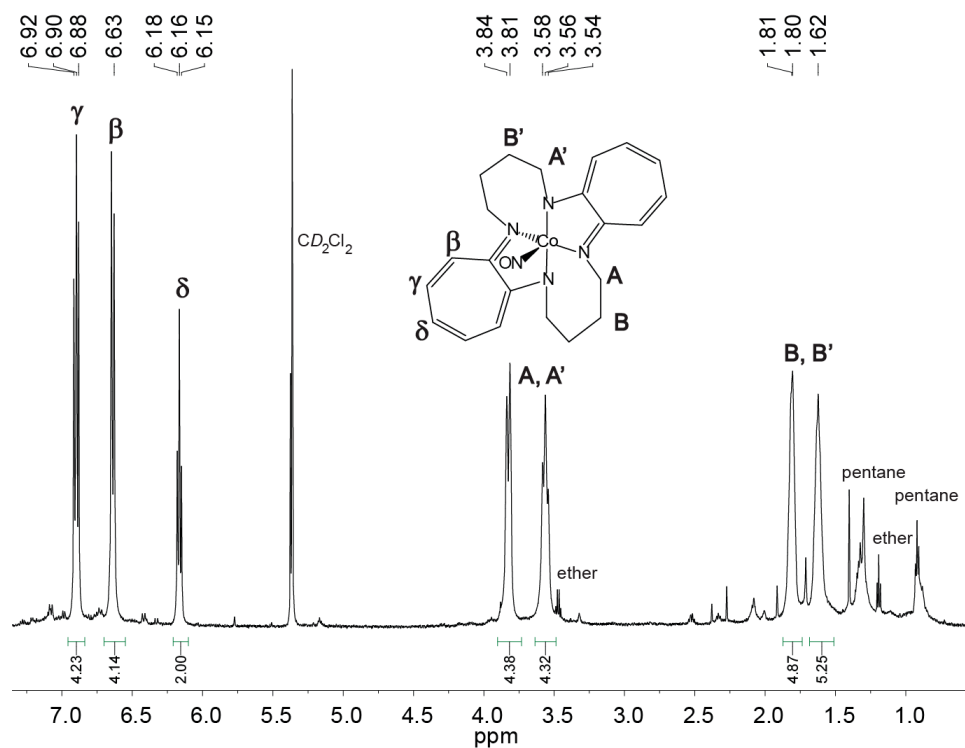


Figure S1. ^1H NMR spectrum of the reaction products of $[\text{Co}(\eta^2\text{-NO}_2)(\text{TC-4,4})]$ with NO (g).

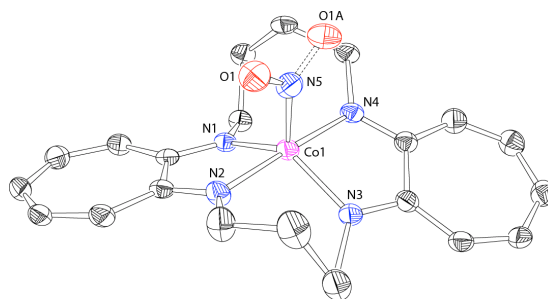


Figure S2. Thermal ellipsoid plot of $[\text{Co}(\text{NO})(\text{TC-4,4})]$, crystallized from the $[\text{Co}(\text{NO}_2)(\text{TC-4,4})]/\text{NO}$ reaction mixture. Ellipsoids are depicted at 50% probability. Hydrogen atoms are omitted for clarity. The oxygen atom of the nitrosyl is disordered over two positions.

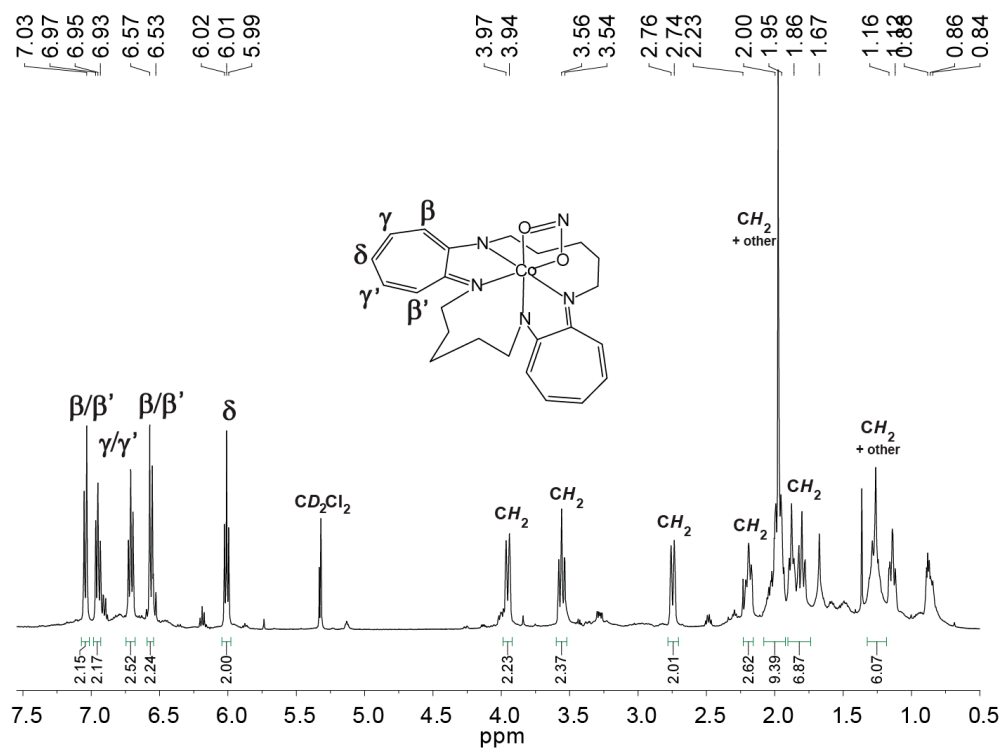


Figure S3. 1H NMR spectrum of the reaction products of $[Co(\eta^2-NO_2)(TC-5,5)]$ with NO (g).

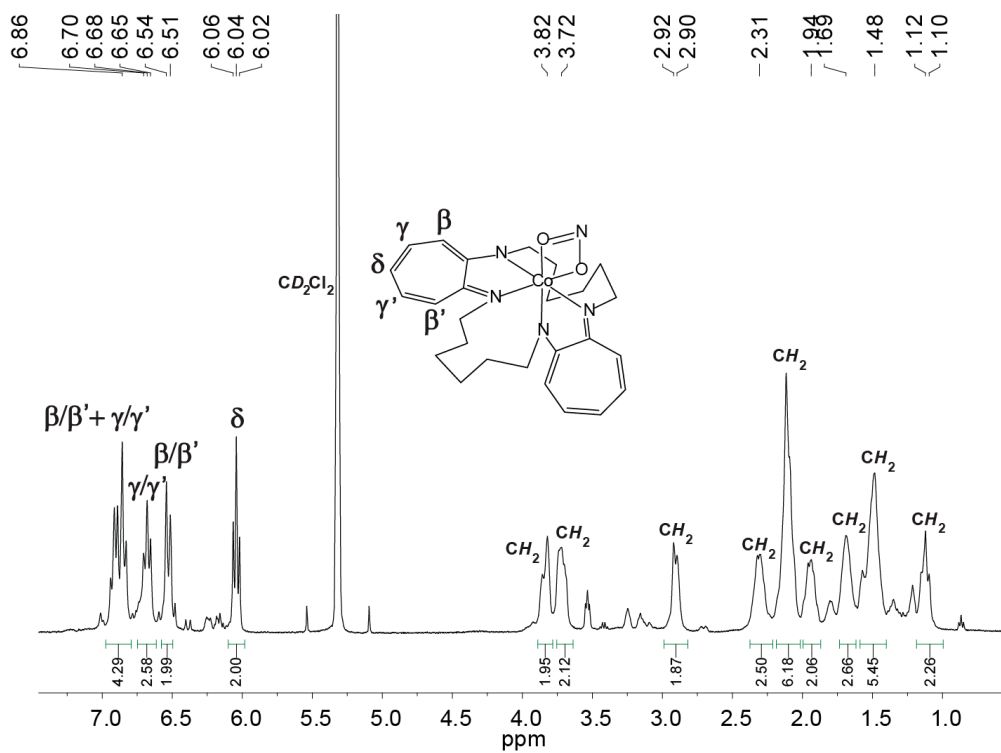


Figure S4. 1H NMR spectrum of the reaction products of $[Co(\eta^2-NO_2)(TC-6,6)]$ with NO (g).