SUPPORTING INFORMATION

Tetrahedral Nickel Nitrosyl Complexes with Tripodal [N_3] and [Se_3] Donor Ancillary Ligands: Structural and Computational Evidence that a Linear Nitrosyl is a Trivalent Ligand

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Received xxxx xx, 2006.

EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of dry glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.[1] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker Avance 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H; 7.26 for $CDCl_3$; 1.94 for CHD_2CN).[2] Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a JMS-HX110/110 Double Focusing mass spectrometer using fast atom bombardment (FAB). $Ni(PPh_3)_2(NO)Br$,[3] $[Tp^{Me_2}]K$[4] and $[Tse^{Mes}]K$[5] were obtained by the literature methods.

X-ray structure determinations

X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.10).[6]

Computational Details

All calculations were carried out using DFT as implemented in the Jaguar 6.5 suite of *ab initio* quantum chemistry programs.[7] Geometry optimizations were performed with the B3LYP density functional[8] and the 6-31G** (C, H, N, B, P, and O), LAV3P (Se) and LACVP (Ni)[9] basis sets. Cartesian coordinates for geometry optimized structures are listed in Table 2. Molecular orbital analyses were performed with the aid of Jimp 2,[10] which employs Fenske-Hall calculations[11] and visualization using MOPLOT.[12]

Synthesis of $[Tp^{Me2}]$NiNO

A solution of $[Tp^{Me2}]K$ (10 mg, 0.030 mmol) in CD_3CN (0.7 mL) was added to $Ni(PPh_3)_2(NO)Br$ (21 mg, 0.030 mmol) resulting in the immediate formation of a bright blue precipitate which was isolated by filtration. The precipitate was extracted into C_6H_6 and the volatile components removed by lyophilization to give $[Tp^{Me2}]$NiNO as a blue powder, which was washed with pentane (1.5 mL) and dried *in vacuo* (8 mg, 70% yield). ^{1}H NMR ($CDCl_3$): 2.15 [s, 9H of 3Me], 2.63 [s, 9H of $3C\underline{H}_3$], 5.91 [s, 3H of $3C\underline{H}$]. ^{1}H NMR (C_6D_6): 1.98 [s, 9H of $3C\underline{H}_3$], 2.59 [s, 9H of $3C\underline{H}_3$], 5.75 [s, 3H of $3C\underline{H}$]. Anal. Calcd. for $C_{15}H_{22}BN_7NiO$: C, 46.7 %; H, 5.8 %; N, 25.4 %. Found: C, 46.4 %; H, 5.6 %; N, 25.2 %. Mass spectrum: $m/z = 355.2$ $\{M - NO\}^+$. IR Data (KBr pellet, cm^{-1}): $\nu_{NO} = 1786$ cm^{-1}. X-ray quality crystals were obtained from C_6H_6.

Synthesis of $[Tse^{Mes}]$NiNO

A solution of $[Tse^{Mes}]K$ (20 mg, 0.024 mmol) in CH_3CN (1 mL) was added dropwise to a solution of $Ni(PPh_3)_2(NO)Br$ (16 mg, 0.023 mmol) in CH_3CN (1 mL) giving a dark brown solution. The mixture was stirred at room temperature for 2 hours, thereby resulting in the formation of a blue-green precipitate. The precipitate was isolated and dissolved in THF (*ca.* 1 mL). The solution was allowed to evaporate slowly, depositing $[Tse^{Mes}]$NiNO as a blue-green microcrystalline material, which was isolated and washed with CH_3CN (1 mL) and pentane (1 mL), and dried *in vacuo* (8 mg, 39% yield). ^{1}H NMR (C_6D_6): 1.98 [s, 9H of 3Me], 2.10 [s, 9H of $3C\underline{H}_3$], 2.58 [s, 9H of 3Me], 6.06 [d, $J_{H\text{-}H} = 2$ Hz, 3H of imidazole], 6.58 [d, $J_{H\text{-}H} = 2$ Hz, 3H of imidazole], 6.70 [s, 3H of aryl], 6.77 [s, 3H of aryl]. Anal. Calcd. for $C_{36}H_{40}BN_7NiOSe_3{\bullet}(THF)$: C, 49.8 %; H, 5.0 %; N, 10.2 %. Found: C, 49.4 %; H, 4.1 %; N, 10.1 %. Mass spectrum: $m/z = 862.2$ $\{M - NO - 1\}^+$. IR Data (KBr pellet, cm^{-1}): $\nu_{NO} = 1763, 1752$ cm^{-1}. Crystals of the composition $[Tse^{Mes}]NiNO{\bullet}0.5PPh_3$ were obtained from the corresponding reaction of $Ni(PPh_3)_2(NO)Cl$, followed by crystallization of the reaction precipitate from benzene rather than THF.

Table 1. Crystal, intensity collection and refinement data.

	[Tp^{Me2}]NiNO	**[Tse^{Mes}]NiNO·0.5(PPh$_3$)**
Lattice	Orthorhombic	Rhombohedral
Formula	$C_{15}H_{22}BN_7NiO$	$C_{45}H_{47.5}BN_7NiOP_{0.5}Se_3$
formula weight	385.92	1024.29
space group	*Pmc2$_1$*	*R-3c*
a/Å	13.1151(8)	14.5179(5)
b/Å	8.0075(5)	14.5179(5)
c/Å	17.4989(11)	73.730(5)
α/°	90	90
β/°	90	90
γ/°	90	120
V/Å^3	1837.7(2)	13458.0(12)
Z	4	12
temperature (K)	243	243
Radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.395	1.517
μ (Mo Kα), mm^{-1}	1.074	2.927
θ max, deg.	28.30	28.31
no. of data	3957	3489
no. of parameters	266	197
R_1	0.0371	0.0315
wR_2	0.0821	0.0609
GOF	1.005	1.083

Table 2. Cartesian Coordinates for Geometry Optimized Structures.

[Tp^{Me_2}]NiNO			
Atom	x-coordinate	y-coordinate	z-coordinate
Ni	0.000000000	0.000000000	1.441119655
N	0.000000000	0.000000000	3.074821985
O	0.000000000	0.000000000	4.243916617
N	-1.665658123	0.000000000	0.259650870
N	0.832829062	1.442502249	0.259650870
N	0.832829062	-1.442502249	0.259650870
B	0.000000000	0.000000000	-1.623979244
H	0.000000000	0.000000000	-2.819981617
N	-1.456548042	0.000000000	-1.087438202
N	0.728274021	1.261407606	-1.087438202
N	0.728274021	-1.261407606	-1.087438202
C	1.787170690	3.095470437	1.847110175
C	1.824668815	3.160419095	-0.773595688
C	1.493921828	2.587548508	0.469084083
C	-2.649458859	0.000000000	-1.737073454
C	-2.776648216	0.000000000	-3.228984817
C	-3.574341380	0.000000000	1.847110175
C	1.388324108	2.404647892	-3.228984817
C	1.324729430	2.294498678	-1.737073454
C	-3.649337631	0.000000000	-0.773595688
C	-2.987843655	0.000000000	0.469084083
C	1.787170690	-3.095470437	1.847110175
C	1.824668815	-3.160419095	-0.773595688

C	1.493921828	-2.587548508	0.469084083
C	1.388324108	-2.404647892	-3.228984817
C	1.324729430	-2.294498678	-1.737073454
H	1.392200322	2.411361692	2.602076871
H	2.866147839	3.198113523	2.010384687
H	1.336573635	4.081213601	2.010384687
H	2.357867595	4.083946472	-0.948844811
H	-3.833702430	0.000000000	-3.506525706
H	-2.308107371	0.882012119	-3.678373051
H	-2.308107371	-0.882012119	-3.678373051
H	-2.784400644	0.000000000	2.602076871
H	-4.202721474	0.883100078	2.010384687
H	-4.202721474	-0.883100078	2.010384687
H	1.916851215	3.320083695	-3.506525706
H	1.917898587	1.557873558	-3.678373051
H	0.390208784	2.439885677	-3.678373051
H	-4.715735190	0.000000000	-0.948844811
H	1.392200322	-2.411361692	2.602076871
H	1.336573635	-4.081213601	2.010384687
H	2.866147839	-3.198113523	2.010384687
H	2.357867595	-4.083946472	-0.948844811
H	1.916851215	-3.320083695	-3.506525706
H	0.390208784	-2.439885677	-3.678373051
H	1.917898587	-1.557873558	-3.678373051

[Tse^{Me}]NiNO			
Atom	x-coordinate	y-coordinate	z-coordinate
Ni	0.000000000	0.000000000	-1.717817984
N	0.000000000	0.000000000	-3.368904290
O	0.000000000	0.000000000	-4.535763988
Se	2.272876625	-0.047986594	-0.598646605
Se	-1.094880703	1.992362194	-0.598646605
Se	-1.177995922	-1.944375600	-0.598646605
B	0.000000000	0.000000000	2.275927839
H	0.000000000	0.000000000	3.483466831
N	1.010998230	-1.111998228	1.862183174
N	2.480038524	-2.454443599	0.952296489
N	0.457519599	1.431549264	1.862183174
N	0.885591247	3.374998163	0.952296489
N	-1.468517829	-0.319551036	1.862183174
N	-3.36562977	-0.920554565	0.952296489
C	1.876930666	-1.240612247	0.823702089
C	3.451429978	-3.012354780	0.021138660
C	1.085869444	-2.261979692	2.636652560
C	1.991567969	-3.098971225	2.076563130
C	0.135936389	2.245775761	0.823702089
C	0.883060776	4.49520343	0.021138660
C	1.415997154	2.07138037	2.636652560
C	1.688003822	3.274234067	2.076563130
C	-2.012867055	-1.005163514	0.823702089
C	-4.334490753	-1.482848650	0.021138660

C	-2.501866598	0.190599322	2.636652560
C	-3.679571791	-0.175262842	2.076563130
H	0.481687344	-2.378851131	3.521280875
H	2.335245048	-4.077684326	2.370209956
H	1.81930184	1.606579042	3.521280875
H	2.363755691	4.061223699	2.370209956
H	-2.300989183	0.772272089	3.521280875
H	-4.699000739	0.016460627	2.370209956
H	-4.353868149	-2.573335521	0.091344556
H	-5.318830820	-1.081168819	0.268214777
H	-4.061608407	-1.205770803	-0.998624878
H	4.405508008	-2.483892661	0.091344556
H	3.595735073	-4.065658199	0.268214777
H	3.075032350	-2.914570659	-0.998624878
H	-0.051639859	5.057228183	0.091344556
H	1.723095747	5.146827018	0.268214777
H	0.986576057	4.120341462	-0.998624878

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