Nickel nitrosyl complexes in a sulfur-rich environment: The first poly(mercaptoimidazolyl)borate derivatives

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Abstract

The diamagnetic nickel mononitrosyl complexes $(Tm^R)Ni(NO)$ ($R = Bu^t$, p-Tol) and $(Bm^R)Ni(PPh_3)(NO)$ ($R = Me$, Bu^t) have been readily prepared from $Ni(PPh_3)_2(NO)Br$ and the appropriate $Na(Tm^R)$ or $Na(Bm^R)$ reagents, respectively. These species constitute the first nickel nitrosyl complexes supported by these ligand systems. An X-ray diffraction study of $(Tm^{p\text{-}Tol})Ni(NO)$ confirmed its pseudo-tetrahedral geometry and the presence of a nearly linear nitrosyl ligand. In contrast, $(Bm^{Me})Ni(PPh_3)(NO)$ can be best described as having a trigonal pyramidal geometry, a spatial arrangement unprecedented in nickel nitrosyl chemistry, which is facilitated by the disposition of the Bm^{Me} ligand and the presence of a weak intramolecular $Ni\cdots H–B$ interaction opposite to the apical triphenylphosphine ligand.

1. Introduction

One of the most fascinating aspects of the chemistry of nitric oxide (NO) pertains the wide range of roles that this simple yet versatile molecule plays in biological processes, including neurotransmission, tumor growth inhibition, hepatic metabolism, cell differentiation, and blood pressure regulation [1–3]. This biochemical and physiological promiscuity, completely unforeseen 20 years ago, is unmistakably responsible for the renewed interest in the coordination chemistry of NO observed during the past two decades [4–8]. Thousands of transition metal nitrosyl complexes are now known and more than 2200 compounds having terminal NO ligands have been structurally charac-

terized, nearly 90% of which belong to groups 6 through 8 of the periodic table [9].[1]

Nickel nitrosyl complexes, while significantly less common than those of other transition metals, include well-known species such as the bis(phosphine) compounds $Ni(PR_3)_2(NO)X$ [10–13] and cyclopentadienyl derivatives like $CpNi(NO)$ [14,15] and $Cp^*Ni(NO)$ [16,17]. Many cationic C_3-symmetric complexes of general formula $[L_3Ni(NO)]^+$, which contain three monodentate isonitriles [18], phosphines [19–22] or phosphites [23,24], or a single triphosphine [25,26], have also been prepared, and the neutral tris(diphenylphosphino)borate derivative $\{PhB(CH_2PPh_2)_3\}Ni(NO)$ was isolated recently by Peters and

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[1] The distribution of structurally characterized terminal nitrosyl complexes of the transition metals (total: 2227) is as follows: V (16), Nb (4), Ta (5), Cr (120), Mo (386), W (237), Mn (67), Tc (12), Re (367), Fe (416), Ru (326), Os (69), Co (94), Rh (26), Ir (38), Ni (34), Pd (3), Pt (6) and Cu (1).

coworkers [27]. Nickel nitrosyl compounds containing sulfur-donor ligands, examples of which include tetrahedral xanthate derivatives $(Ph_3P)Ni(S_2COR)(NO)$ [28,29] and the heterodinuclear complexes $(Cp'V)_2(\mu-S)_4\{Ni(NO)\}_2$ [30] and $(ON)Ni\{(\mu-SCH_2CH_2)_2S\}Fe(NO)_2$ [31], are less common. A compound particularly relevant to our work is the tris(thioether)borate derivative $\{PhB(CH_2SBu^t)_3\}$-Ni(NO), reported almost a decade ago [32], which was until now the only mononuclear nickel nitrosyl complex supported by an $[S_3]$ donor set.

Seeking to further explore the synthesis of nickel nitrosyl complexes in a sulfur-rich environment, we turned our attention to the tris(mercaptoimidazolyl)borate (Tm^R) [33] and bis(mercaptoimidazolyl)borate (Bm^R) [34] ligand systems, which we have previously used to model certain structural elements of the nickel center in [NiFe] hydrogenases [35,36]. We describe in this paper the preparation and characterization of the first nickel nitrosyl complexes containing poly(mercaptoimidazolyl)borate ligands, namely $(Tm^R)Ni(NO)$ and $(Bm^R)Ni(PPh_3)(NO)$ [37,38]. These species, together with Parkin's recently reported tris(pyrazolyl)borate and tris(selenoimidazolyl)borate complexes $(Tp^{Me2})Ni(NO)$ and $(Tse^{Mes})Ni(NO)$ that feature $[N_3]$ and $[Se_3]$ donor groups [39], expand the pool of nickel mononitrosyl complexes now available for the comparative study of their molecular structures and spectroscopic properties.

2. Results and discussion

2.1. Syntheses of nickel nitrosyl complexes

The tris(mercaptoimidazolyl)borate complexes (Tm^R)-Ni(NO) $(R = Bu^t, p\text{-Tol})$ were readily prepared by reacting equimolar amounts of the purple triphenylphosphine complex $Ni(PPh_3)_2(NO)Br$ [10] and the corresponding $Na(Tm^R)$ reagents (Scheme 1), and the turquoise $(R = Bu^t)$ or greenish blue $(R = p\text{-Tol})$ products were isolated in ca. 40–50% yield after the appropriate work-up. The bis(mercaptoimidazolyl)borate derivatives $(Bm^R)Ni$-$(PPh_3)(NO)$ $(R = Me, Bu^t)$, which are the first transition metal nitrosyl complexes containing Bm^R ligands to be synthesized, were similarly obtained as slate green $(R = Me)$ or indigo $(R = Bu^t)$ microcrystalline solids in ca. 65–80% yield. All the new complexes are air-stable in the solid state and dissolve in a variety of organic solvents, including acetone, acetonitrile, benzene, dichloromethane, tetrahydrofuran (THF), and toluene, to give solutions that are markedly more sensitive to oxygen.

The four new complexes, all of which have a $\{Ni(NO)\}^{10}$ configuration in the Enemark–Feltham notation [40], were characterized by a combination of analytical and spectroscopic techniques, including elemental analyses (CHN) and IR and NMR spectroscopies. The observation of sharp resonances in their ^1H and ^{13}C NMR spectra and the
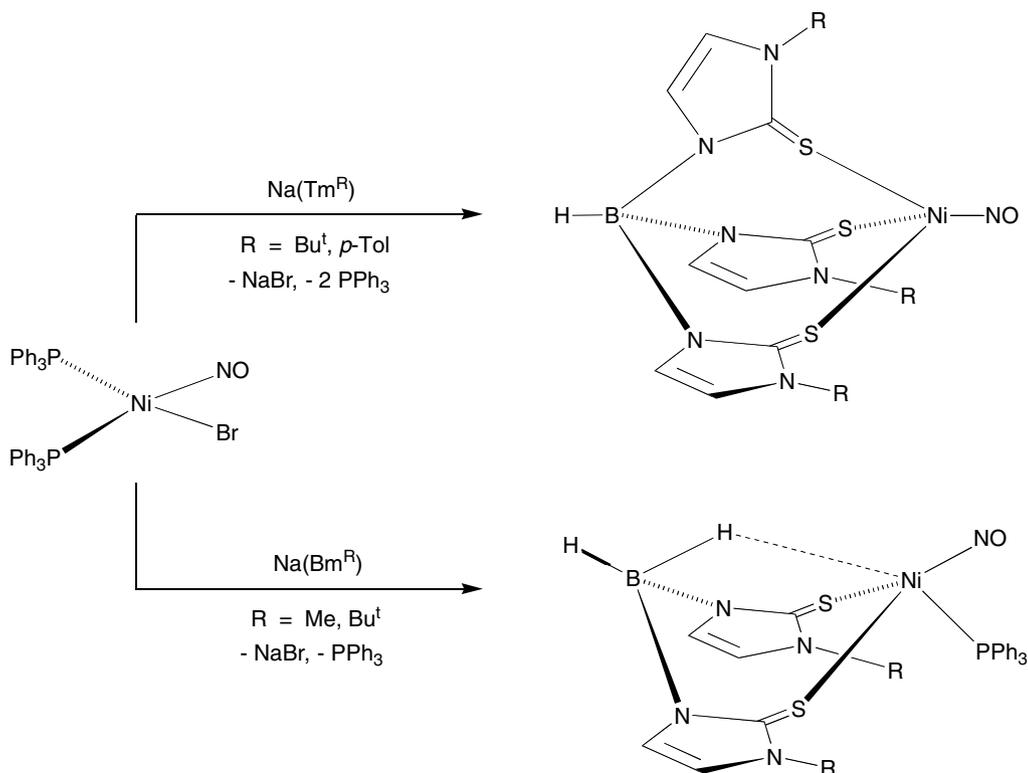
Scheme 1.

Table 1
IR data (v_{NO}/cm^{-1}) for selected nickel mononitrosyl complexes

Complex	v_{NO}/ cm^{-1}	Medium	Ref.
[{MeC(CH$_2$O)$_3$P}$_3$Ni(NO)]BF$_4$	1867	Nujol	[23]
CpNi(NO)	1839	Ar, 20 K	[14]
[(Bu^{t}NC)$_3$Ni(NO)]NO$_3$	1828	Nujol	[18]
[(PPh$_3$)$_3$Ni(NO)]PF$_6$	1790	Nujol	[19]
Cp*Ni(NO)	1787	Nujol	[16]
(Tp^{Me2})Ni(NO)	1786	KBr	[39]
{PhB(CH$_2$SBu^t)$_3$}Ni(NO)	1785	CH$_2$Cl$_2$	[32]
[(PTA)$_3$Ni(NO)]NO$_3$	1778	KBr	[20]
[{MeC(CH$_2$PEt$_2$)$_3$}Ni(NO)]BPh$_4$	1760	Nujol	[25]
[{N(CH$_2$CH$_2$PPh$_2$)$_3$}Ni(NO)]BPh$_4$	1755	Nujol	[26]
(Tm$^{p\text{-}Tol}$)Ni(NO)	1752	KBr	this work
[(PH$_2$Mes)$_3$Ni(NO)]BF$_4$	1751	KBr	[21]
[(PEt$_3$)$_3$Ni(NO)]PF$_6$	1745	KBr or Nujol	[22]
(Tm^{tBu})Ni(NO)	1741	KBr	this work
{PhB(CH$_2$PPh$_2$)$_3$}Ni(NO)	1737	C$_6$H$_6$	[27]

magnetic equivalency of the mercaptoimidazolyl groups in the NMR time scale are consistent with the presence in each case of diamagnetic, pseudo-tetrahedral metal complexes in solution. FT-IR spectroscopy was conveniently used to evaluate the electronic nature of the complexes *via* the v(NO) stretching frequencies of the nitrosyl groups. More specifically, the v(NO) frequencies of (Tm$^{p\text{-}Tol}$)-Ni(NO) (1752 cm^{-1}) and (Tm^{tBu})Ni(NO) (1741 cm^{-1}) reflect a considerable degree of backbonding to the NO π^* orbitals and are among the lowest observed for nickel mononitrosyl complexes (Table 1). Thus, there is mounting evidence suggesting that the Tm^R ligands are more electron releasing than their hard nitrogen-donor counterparts, the ubiquitous tris(pyrazolyl)borates (Tp$^{RR'}$) [41–43], and that they are electronically comparable to other soft ligands such as the tris(phosphino)borates [27] and the tris(seleno-imidazolyl)borates [39].

The v(NO) frequencies of the (Bm^R)Ni(PPh$_3$)(NO) complexes (1688 and 1728 cm^{-1} for R = Me and Bu^t, respectively) are even lower than those found for the (Tm^R)Ni(NO) derivatives described above. Even though

the correlation between v(NO) frequencies and the extent of bending in the M–N–O moieties of metal nitrosyl complexes is notoriously unreliable [4], this situation suggests that some deviation from linearity in the NiNO units of the (Bm^R)Ni(PPh$_3$)(NO) compounds may be taking place nevertheless (vide infra). In this regard, a Ni–N–O angle of 152.7° was found in the nickel azide complex Ni(PPh$_3$)$_2$(NO)(N$_3$), which displays a v(NO) frequency of 1710 cm^{-1} [44]. It is also worth noting that DFT calculations on the closely related bis(selenoimidazolyl)borate complex (Bse^{Me})Ni(PPh$_3$)(NO) suggest that the nitrosyl ligand bends in order to stabilize the occupied M–N σ^* antibonding orbital [45].

2.2. Molecular structures of (Tm$^{p\text{-}Tol}$)Ni(NO) and (Bm^{Me})Ni(PPh$_3$)(NO)

The molecular structure of (Tm$^{p\text{-}Tol}$)Ni(NO) (Fig. 1) was determined using a single crystal obtained at room temperature by slow diffusion of pentane into a THF solution of the complex, and selected bond lengths and angles are given in Table 2. It is a rare example of a structurally characterized mononuclear nickel nitrosyl complex having a [NiS$_3$N] core, second only to Riordan's {PhB(CH$_2$SBu^t)$_3$}-Ni(NO) [32]. As expected, (Tm$^{p\text{-}Tol}$)Ni(NO) presents a slightly distorted tetrahedral geometry, with the three mercaptoimidazolyl groups of the Tm$^{p\text{-}Tol}$ ligand in a propeller-like arrangement around the metal center, canted relative to the pseudo-C_3 axis that contains the boron atom and the fairly linear NO moiety [Ni–N–O = 173.9(4)°]. The average S–Ni–S and S–Ni–N angles (101.5° and 116.6°, respectively) deviate only slightly from the ideal tetrahedral value.

The Ni–S bond distances in (Tm$^{p\text{-}Tol}$)Ni(NO), between 2.319 and 2.350 Å, are longer than those found in a variety of four-coordinate nickel complexes containing thioureas or heterocyclic thiones, which are in the approximate range 2.14–2.30 Å [9]. However, they are shorter than those in Ni(Tm^{Me})$_2$ [2.440(1)–2.483(1) Å] [46], a disparity likely to arise from the higher coordination number of the nickel center in the latter. Despite these differences, the Ni–N

Fig. 1. Molecular structure of (Tm$^{p\text{-}Tol}$)Ni(NO).

Table 2
Selected bond lengths (Å) and bond angles (°) for (Tm$^{p\text{-}Tol}$)Ni(NO)

Bond lengths	
Ni–S(1)	2.3432(11)
Ni–S(2)	2.3503(11)
Ni–S(3)	2.3190(10)
Ni–N(1)	1.665(3)
N(1)–O	1.131(4)
Bond angles	
S(1)–Ni–S(2)	101.34(4)
S(1)–Ni–S(3)	103.87(4)
S(2)–Ni–S(3)	99.30(4)
S(1)–Ni–N(1)	114.47(10)
S(2)–Ni–N(1)	121.34(11)
S(3)–Ni–N(1)	114.01(11)
Ni–N(1)–O	173.9(4)
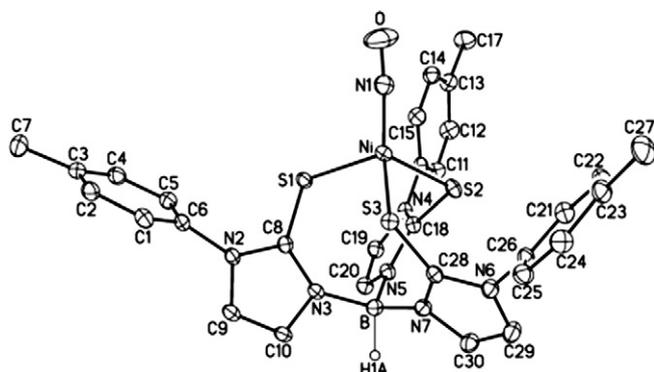
and N–O bond lengths [1.665(3) and 1.131(4) Å, respectively] are within the corresponding ranges of values observed for such bonds in four-coordinate nickel nitrosyl complexes (1.58–1.69 and 1.12–1.19 Å, respectively) [9]. It is also worth noting that compelling structural and computational evidence implying that the M–N interactions in linear nitrosyl complexes have actually multiple bond character has recently been provided [39]. More specifically, a combination of X-ray crystallography and DFT calculations performed on $(Tp^{Me2})Ni(NO)$ and $(Tse^{Mes})Ni(NO)$ indicate that a multiply bonded resonance form such as $Ni\equiv N^{+}–O^{-}$ is a dominant contributor to the bonding scheme in this type of compounds, which exhibit quite short Ni–N bond distances [39].

The molecular structure of $(Bm^{Me})Ni(PPh_3)(NO)$ (Fig. 2) was also determined using a single crystal obtained at room temperature by slow diffusion of pentane into a THF solution of the complex, and selected bond lengths
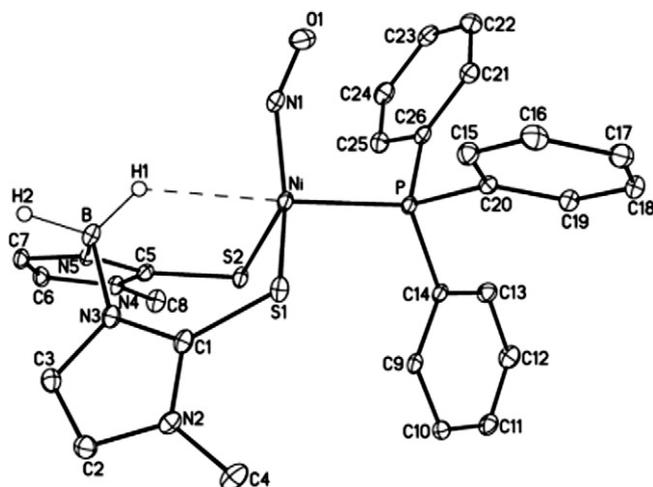
Fig. 2. Molecular structure of $(Bm^{Me})Ni(PPh_3)(NO)$.

Table 3
Selected bond lengths (Å) and bond angles (°) for $(Bm^{Me})Ni(PPh_3)(NO)$

Bond lengths	
Ni–P	2.2260(6)
Ni–S(1)	2.3225(7)
Ni–S(2)	2.3145(7)
Ni···H(1)	2.51(3)
Ni–N(1)	1.6892(19)
N(1)–O(1)	1.170(3)
Bond angles	
S(1)–Ni–S(2)	102.87(2)
N(1)–Ni–S(1)	125.38(7)
N(1)–Ni–S(2)	124.16(7)
S(1)–Ni–P	103.87(2)
S(2)–Ni–P	96.54(3)
N(1)–Ni–P	97.21(6)
S(1)–Ni···H(1)	78.1(6)
S(2)–Ni···H(1)	85.2(6)
P–Ni···H(1)	177.0(6)
N(1)–Ni···H(1)	79.7(6)
Ni–N(1)–O(1)	149.64(17)

and angles are listed in Table 3. It is the first structurally characterized transition metal nitrosyl complex bearing a Bm^R ligand and only the second having a $[NiS_2PN]$ core, following the cyclopentylxanthate derivative $(PPh_3)Ni(S_2-COC_5H_9)(NO)$ [29]. The geometry of the complex can be best described as trigonal pyramidal, with the two thione sulfurs of the Bm^{Me} ligand and a bent NO group [Ni–N–O = 149.6(2)°] that is tilted towards the phosphine making up the base of the pyramid. This spatial arrangement, unprecedented in nickel nitrosyl chemistry, is facilitated by the unique spatial disposition of the Bm^{Me} ligand, which forms an eight-membered ring in an "extended boat" conformation, and the presence of a weak intramolecular Ni···H–B interaction trans to the apical triphenylphosphine ligand. Although $(Bm^{Me})Ni(PPh_3)(NO)$ could be alternatively regarded as a five-coordinate complex displaying a trigonal bipyramidal geometry, we tend to favor the preceding description given the electronic saturation of the metal center (i.e., an 18-electron count) and the ensuing weakness of the Ni···H–B interaction. In this regard, the latter is characterized by a Ni···H separation [2.51(3) Å] that is considerably longer than those previously observed for such interactions, in the range 1.47–2.15 Å [35,36,47–56].

A number of metrical parameters suggest that the trigonal pyramidal structure of $(Bm^{Me})Ni(PPh_3)(NO)$ is slightly distorted towards a tetrahedral geometry. This include the observation of moderately obtuse P–Ni–X angles (average = 99.2°) and a sum of angles around the nickel center in the basal plane (352.4°) that is less than a full circle. In the same vein, the nickel atom is located ca. 0.5 Å above the plane defined by S(1), S(2) and N(1), and the calculated four-coordinate geometry index τ_4 recently introduced by Houser [57] (0.78) is somewhat lower than the value corresponding to a perfect trigonal pyramid (0.85). The Ni–S bond distances in $(Bm^{Me})Ni(PPh_3)(NO)$, 2.315(1) and 2.323(1) Å, are virtually identical to those in (Tm^{p-Tol})-Ni(NO) and the Ni–N and N–O bond lengths [1.689(2) and 1.170(3) Å, respectively] are marginally longer but still within the ranges mentioned above for such bonds in four-coordinate nickel nitrosyl complexes.

3. Conclusions

The first bis- and tris(mercaptoimidazolyl)borate nickel nitrosyl complexes have been readily prepared and fully characterized. The observation of fairly low $v(NO)$ stretching frequencies in their IR spectra provides evidence that the Bm^R and Tm^R ligands are strongly electron-donating tripodal $[S_3]$ ligands. Whereas $(Tm^{p-Tol})Ni(NO)$ displays the expected slightly distorted tetrahedral geometry and features a linear nitrosyl ligand, $(Bm^{Me})Ni(PPh_3)(NO)$ constitutes the first trigonal pyramidal nickel nitrosyl complex to be structurally characterized. The reactivity of these complexes towards thiols and thiolates, aimed at the generation of S-nitrosothiols [58,59], will be investigated in due course.

4. Experimental

4.1. General considerations

All reactions were performed under aerobic conditions unless otherwise noted, solvents were purified and degassed by standard procedures, and all commercially available reagents were used as received. Whereas $Na(Bm^R)$ ($R = Me$, Bu^t) [60] and $Na(Tm^R)$ ($R = Bu^t$, *p*-Tol) [61,62] were prepared as reported, the nickel nitrosyl complex $Ni(PPh_3)_2(NO)Br$ was synthesized by a combination of literature procedures [10,63], as described below. ^{1}H and ^{13}C NMR spectra were obtained on Varian Gemini (300 MHz) or JEOL ECA-500 (500 MHz) FT spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$ ppm) and were referenced internally with respect to the solvent resonances ([1]H: δ 2.49 for DMSO-d_5, 7.15 for C_6D_5H, 7.24 for CHCl$_3$; [13]C: δ 39.5 for DMSO-d_6, 77.0 for CDCl$_3$, 128.0 for C_6D_6); coupling constants are given in hertz (Hz). IR spectra were recorded from KBr pellets on a Thermo Mattson Satellite 3000 FT-IR spectrophotometer and are reported in cm^{-1}; relative intensities of the absorptions are indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

4.2. Synthesis of $Ni(PPh_3)_2(NO)Br$

Tetrahydrofuran (20 mL) was added to a 100-mL round-bottom flask containing $Ni(PPh_3)_2Br_2$ (1.00 g, 1.346 mmol), triphenylphosphine (0.36 g, 1.373 mmol), and NaNO$_2$ (1.60 g, 23.188 mmol), and the resulting purple suspension was stirred and refluxed under argon for 35 min. The suspension was allowed to cool to room temperature, filtered, and the solvent was removed under reduced pressure from the filtrate to give a purple solid, which was washed with methanol (15 mL) and dried *in vacuo* for 18 h (0.676 g, 73%). IR data: 1733 (vs) [ν_{NO}].

4.3. Synthesis of $(Bm^{Me})Ni(PPh_3)(NO)$

Methanol (5 mL) was added to a 4-dram glass vial containing a mixture of $Ni(PPh_3)_2(NO)Br$ (1.092 g, 1.575 mmol) and $Na(Bm^{Me})$ (0.417 g, 1.591 mmol), resulting in the formation of a purple suspension and, within minutes, a slate green solid suspended in a grey-green solution. After stirring the suspension for 3 h, the product was isolated by filtration and dried *in vacuo* for 18 h (0.740 g, 80%). Mp = 147–149 °C (dec.). NMR data (in C_6D_6): [1]H δ 2.79 (s, 6H, CH_3), 4.60 (br s, 2H, BH_2), 5.63 (d, $^3J_{H-H}$ = 2.0, 2H, imidazole H), 6.49 (d, $^3J_{H-H}$ = 2.0, 2H, imidazole H), 7.03 (m, 9H, C_6H_5), 7.56 (m, 6H, C_6H_5); [13]C δ 34.3 (q, $^1J_{C-H}$ = 140, 2C, CH$_3$), 118.7 (dd, $^1J_{C-H}$ = 195, $^2J_{C-H}$ = 13, 2C, imidazole C), 122.1 (d, $^1J_{C-H}$ = 194, 2C, imidazole C), 128.7 (dd, $^1J_{C-H}$ = 163, $^3J_{P-C}$ = 8, 6C, C_m in C_6H_5), 129.4 (d, $^1J_{C-H}$ = 163, 3C, C_p in C_6H_5), 134.4 (dd, $^1J_{C-H}$ = 160, $^2J_{P-C}$ = 16, 6C, C_o in C_6H_5), 160.4 (s,

2C, C=S), C_{ipso} not observed. IR data: 2918 (w), 2849 (w), 2475 (m), 2396 (m), 2359 (m), 1688 (vs) [ν_{NO}], 1558 (s), 1479 (w), 1456 (m), 1434 (m), 1413 (m), 1381 (s), 1186 (m), 1164 (w), 1123 (m), 1095 (m), 747 (w), 725 (m), 696 (s), 520 (m), 508 (w). *Anal.* Calc. for $C_{26}H_{27}BN_5$-NiOPS$_2$: C, 52.9; H, 4.6; N, 11.9. Found: C, 53.3; H, 4.7; N, 10.9%.

4.4. Synthesis of $(Bm^{tBu})Ni(PPh_3)(NO)$

Under a nitrogen atmosphere, tetrahydrofuran (5 mL) was added to a 4-dram glass vial containing a mixture of $Ni(PPh_3)_2(NO)Br$ (0.202 g, 0.291 mmol) and $Na(Bm^{tBu})$ (0.100 g, 0.291 mmol), resulting in the formation of a purple suspension and, within minutes, a deep blue solution. After stirring for 3 h, the solution was concentrated to ca. 1 mL and addition of pentane (ca. 3 mL) lead to the separation of the product as a dark indigo solid, which was isolated by decantation and dried *in vacuo* for 16 h (0.125 g, 64%). Mp = 121–123 °C (dec.). NMR data (in CDCl$_3$): [1]H δ 1.64 [s, 18H, C(CH_3)$_3$], 6.59 (s, 2H, imidazole H), 6.71 (s, 2H, imidazole H), 6.90–7.40 (m, 15H, C_6H_5); [13]C δ 28.9 (q, $^1J_{C-H}$ = 126, 6C, C(CH_3)$_3$], 58.9 [s, 2C, C(CH$_3$)$_3$], 117.1 (dd, $^1J_{C-H}$ = 194, $^2J_{C-H}$ = 14, 2C, imidazole C), 121.2 (d, $^1J_{C-H}$ = 193, 2C, imidazole C), 128.7 (d, $^1J_{C-H}$ = 160, 6C, C_m in PPh$_3$), 130.2 (d, $^1J_{C-H}$ = 154, 3C, C_p in PPh$_3$), 132.4 (s, 3C, C_{ipso} in PPh$_3$), 134.3 (d, $^1J_{C-H}$ = 159, 6C, C_o in PPh$_3$), 158.7 (s, 2C, C=S). IR data: 2974 (m), 2918 (m), 1728 (vs) [ν_{NO}], 1567 (m), 1480 (s), 1434 (s), 1366 (s), 1314 (m), 1237 (m), 1095 (s), 745 (s), 694 (vs), 521 (s). *Anal*. Calc. for $C_{32}H_{39}BN_5NiOPS_2$: C, 57.0; H, 5.8; N, 10.4. Found: C, 58.1; H, 5.9; N, 7.9%. Repeated attempts to obtain a better elemental analysis for this compound have not been successful.

4.5. Synthesis of $(Tm^{tBu})Ni(NO)$

In a Schlenk tube under an atmosphere of argon, a purple stirred suspension of $Ni(PPh_3)_2(NO)Br$ (0.399 g, 0.575 mmol) in methanol (15 mL) was treated dropwise with a solution of $Na(Tm^{tBu})$ (0.288 g, 0.575 mmol) in the same solvent (25 mL), resulting in the formation of a turquoise microcrystalline solid suspended in a blue solution. After stirring for 30 min, the suspension was concentrated under reduced pressure to ca. 5 mL and the product was isolated by filtration and dried *in vacuo* for 1 h (0.156 g, 48%). Mp = 78–79 °C (dec.). ^{1}H NMR data (in DMSO-d_6): δ 1.92 [s, 27H, C(CH_3)$_3$], 6.61 (s, 3H, imidazole H), 7.11 (s, 3H, imidazole H), BH not observed; ^{13}C NMR data (in CDCl$_3$): δ 29.1 [q, $^1J_{C-H}$ = 127, 9C, C(CH_3)$_3$], 59.2 [s, 3C, C(CH$_3$)$_3$], 115.3 [dd, $^1J_{C-H}$ = 194, $^2J_{C-H}$ = 12, 3C, imidazole C], 122.3 [dd, $^1J_{C-H}$ = 194, $^2J_{C-H}$ = 6, 3C, imidazole C], 159.2 (s, 3C, C=S). IR data: 3206 (w), 3135 (w), 2965 (m), 2916 (w), 2387 (w), 2297 (w), 2233 (w), 1741 (vs) [ν_{NO}], 1565 (m), 1483 (w), 1418 (m), 1398 (m), 1361 (vs), 1302 (m), 1260 (w), 1228 (m), 1198 (s), 1176 (s), 1132 (w), 1071 (w), 1030 (w), 928 (w), 823 (w), 760

(m), 727 (m), 687 (m), 591 (w), 553 (w), 497 (w), 462 (w). *Anal.* Calc. for $C_{21}H_{34}BN_7NiOS_3$: C, 44.5; H, 6.1; N, 17.3. Found: C, 44.4; H, 6.2; N, 17.1%.

4.6. Synthesis of $(Tm^{p\text{-}Tol})Ni(NO)$

In a Schlenk tube under an atmosphere of argon, a purple stirred suspension of $(PPh_3)_2Ni(NO)Br$ (0.300 g, 0.433 mmol) in methanol (20 mL) was treated dropwise with a solution of $Na(Tm^{p\text{-}Tol})$ (0.261 g, 0.433 mmol) in the same solvent (20 mL), resulting in the formation of a greenish-blue microcrystalline solid suspended in a dark blue solution. After stirring for 30 min, the suspension was concentrated under reduced pressure to ca. 5 mL and the spectroscopically pure product was isolated by filtration and dried *in vacuo* for 1 h (0.115 g, 40%). Mp = 70–71 °C (dec.). NMR data (in DMSO-d_6): ^1H δ 2.39 (s, 9H, CH_3), 6.97 (s, 3H, imidazole H), 7.35 (s, 3H, imidazole H), 7.37 (d, $^3J_{H-H} = 8.1$, 6H, H_o or H_m), 7.57 (d, $^3J_{H-H} = 8.1$, 6H, H_o or H_m), BH not observed; ^{13}C δ 20.7 (q, $^1J_{C-H} = 125$, 3C, CH_3), 120.6 (d, $^1J_{C-H} = 199$, 3C, imidazole C), 124.4 (d, $^1J_{C-H} = 199$, 3C, imidazole C), 126.5 (d, $^1J_{C-H} = 162$, 6C, C_o or C_m), 129.4 (d, $^1J_{C-H} = 159$, 6C, C_o or C_m), 135.4 (s, 3C, C_{ipso} or C_p), 138.0 (s, 3C, C_{ipso} or C_p), 158.7 (s, 3C, C=S). IR data: 2919 (w), 2850 (w), 2413 (w), 2368 (w), 2343 (w), 1752 (vs) [ν_{NO}], 1513 (m), 1476 (w), 1428 (m), 1362 (s), 1271 (m), 1192 (s), 1093 (w), 1022 (w), 821 (m), 742 (m), 695 (m). *Anal.* Calc. for $C_{30}H_{28}BN_7NiOS_3$: C, 53.9; H, 4.2; N, 14.7. Found: C, 52.9; H, 4.4; N, 12.8%.

4.7. X-ray structure determinations

X-ray diffraction data were collected on a Bruker-AXS APEX CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). A summary of crystal data collection and refinement parameters for $(Bm^{Me})Ni(PPh_3)(NO)$ and $(Tm^{p\text{-}Tol})Ni(NO)$ is presented in Table 4. Crystals were selected and mounted on glass fibers or plastic loops with viscous oil and cooled to the data collection temperature. All data sets were treated with SADABS absorption corrections. Unit cell parameters were determined by sampling three different sections of the Ewald sphere. No symmetry higher than triclinic was observed in the diffraction data and structural solution in the centrosymmetric space group option, $P\bar{1}$, yielded chemically reasonable and computationally stable results of refinement for (Bm^{Me})-$Ni(PPh_3)(NO)$. The systematic absences in the diffraction data were uniquely consistent for the reported space group $P2_1/c$ for $(Tm^{p\text{-}Tol})Ni(NO)$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the boron atoms were located from the difference map and refined with isotropic parameters constrained as $0.20U_{eq}$ of the boron atom. All other hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL (version 6.12) program library [64].

Table 4
Crystallographic data for $(Tm^{p\text{-}Tol})Ni(NO)$ and $(Bm^{Me})Ni(PPh_3)(NO)$

	$(Tm^{p\text{-}Tol})Ni(NO)$	$(Bm^{Me})Ni(PPh_3)(NO)$
Formula	$C_{30}H_{28}BN_7NiOS_3$	$C_{26}H_{27}BN_5NiOPS_2$
Formula weight	668.29	590.14
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Temperature (K)	120(2)	120(2)
Unit cell dimensions		
a (Å)	19.196(9)	9.747(2)
b (Å)	10.047(5)	11.399(3)
c (Å)	17.976(8)	13.015(3)
α (°)	90	85.365(3)
β (°)	115.262(6)	89.817(3)
γ (°)	90	67.581(3)
V (Å^3)	3135(2)	1331.8(5)
Z	4	2
ρ_{calc} (g cm^{-3})	1.416	1.472
μ(Mo Kα) (mm^{-1})	0.855	0.976
θ_{max} (°)	28.20	28.05
Number of data	7171	5738
Number of parameters	394	342
R_1 ($I > 2\sigma(I)$)[a]	0.0502	0.0368
wR_2 ($I > 2\sigma(I)$)[a]	0.1233	0.0966

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \left\{ \sum\left[w(F_o^2 - F_c^2)^2\right] \Big/ \sum[w(F_o^2)^2] \right\}^{1/2}$.

5. Supplementary material

CCDC 640731 and 640732 contain the supplementary crystallographic data (excluding structure factors) for $(Bm^{Me})Ni(PPh_3)(NO)$ and $(Tm^{p\text{-}Tol})Ni(NO)$. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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