Synthesis and characterization of side-bound aryldiazo and end-bound nitrosyl complexes of nickel†‡

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Structural characterization of a nickel aryldiazo complex supported by the bulky 1,2-bis(di-*tert*-butylphosphino)ethane ligand reveals square-planar Ni geometry and an unusual side-on coordination mode for the N_2R moiety, while the related nitrosyl complex displays trigonal-planar geometry at Ni and end-on coordination of the NO ligand.

Transition metal aryldiazo complexes have been of general interest since the first example was reported by Parshall in 1965.[1] This interest has been motivated by the ligand's relevance to N_2-fixation intermediates, as well as by its varied structural and reactivity properties.[1,2] The coordination modes of N_2R ligands are well established and are illustrated in Fig. 1. End-on coordination with the M–N_2R fragment adopting linear (a), singly-bent (b), and doubly-bent (c) conformations gives rise to the most common forms (including bridging examples), with isomers (b) and (c) corresponding to the well-known linear and bent geometries, respectively, observed for isolobal nitrosyl ligands. Side-on bound aryldiazo ligands (d) are quite rare, but have been reported in monomeric $(C_5H_5)TiCl_2(\eta^2\text{-}N_2Ph)$ and dimeric $Co_2(CO)_4(Ph_2PCH_2PPh_2)(\eta^2,\mu^2\text{-}N_2Tol)$.[3] In contrast, η^2-nitrosyl ligands have only been observed at a copper site in the enzyme nitrite reductase,[4] and several excited-state transition-metal complexes.[5]

As part of our ongoing studies of the interactions of diazo substrates with low-valent Ni,[6] we have investigated the reactivity of the Ni(0) benzene complex $[(dtbpe)Ni]_2(C_6H_6)$ (**1**;[7] dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) with diazonium salts. Cold diethyl ether solutions of **1** react cleanly with *p*-methoxyphenyldiazonium hexafluorophosphate to effect benzene displacement with formation of the diazonium complex $[(dtbpe)Ni(\eta^2\text{-}N_2C_6H_4\text{-}p\text{-}OMe)][PF_6]$ (**2**), isolated as red blocks in 80% yield (eqn. 1).

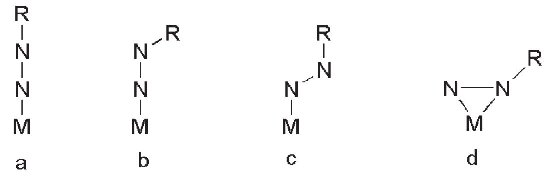
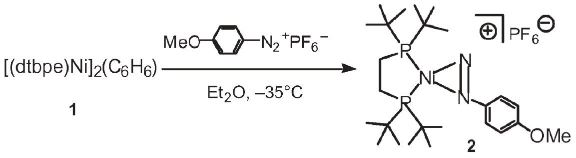


Fig. 1 Coordination modes of diazenido ligands (R = H, alkyl, aryl, silyl).

Complex **2** was characterized by infrared, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The NMR data indicate square-planar Ni with inequivalent phosphorus nuclei, consistent with a side-bound aryldiazo ligand. The infrared spectrum of **2** exhibits a low value for *ν*(NN) at 1602 cm^{-1}, which can be compared to the corresponding value of 1550 cm^{-1} found in $(C_5H_5)TiCl_2(\eta^2\text{-}N_2Ph)$.[3]



(1)

To confirm the unusual side-on coordination of the aryldiazo ligand, a crystallographic study of **2** was carried out.§ The salt has well-separated cations and anions, and features planar Ni with the aryldiazo ligand bound in an η^2 fashion (Fig. 2). The N(1)–N(2) bond length (1.224(3) Å) is typical of a N–N double bond, and the N(2)–N(1)–C(71) angle is bent (126.4(2)°) with trigonal-planar geometry at N(1). Although not crystallographically required, the heavy atoms of the phenylmethoxy substituent lie in the Ni coordination plane.

Adducts of Ni with η^2-diazoalkane ligands are known (*e.g.*, $(dtbpe)Ni(\eta^2\text{-}N_2CPh_2)$ and $(t\text{-}BuNC)_2Ni(\eta^2\text{-}NNC_{13}H_8)$),[6,8] but to our knowledge **2** is the first example of a Ni aryldiazo complex.

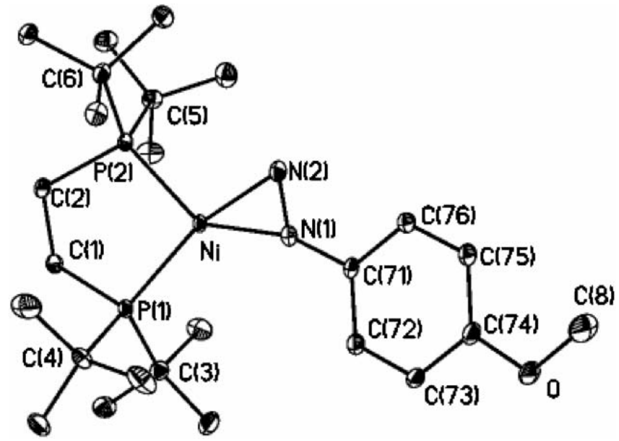


Fig. 2 ORTEP view of the complex cation of **2** (35% probability thermal ellipsoids; H-atoms omitted for clarity). Selected metrical parameters: Ni–P(1) = 2.211(7), Ni–P(2) = 2.185(6), Ni–N(1) = 1.861(2), Ni–N(2) = 1.863(2), N(1)–N(2) = 1.224(3), N(1)–C(71) = 1.428(3) Å; P(1)–Ni–P(2) = 92.4(2), P(2)–Ni–N(2) = 103.6(6), P(1)–Ni–N(1) = 125.5(6), N(1)–Ni–N(2) = 38.4(8), Ni–N(2)–N(1) = 70.72(13), Ni–N(1)–N(2) = 70.90(12), Ni–N(1)–C(71) = 162.2(2), N(2)–N(1)–C(71) = 126.4(2)°.

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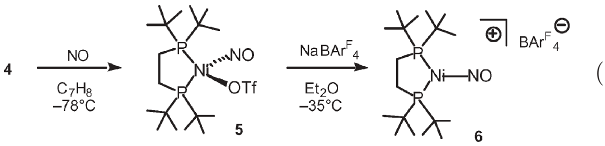
‡ This paper is dedicated to Professor Ian Rothwell, in memoriam.

Several Pt examples have been reported, *i.e.* *trans*-PtCl($N_2C_6H_4$-*p*-F)(PEt_3)$_2$,[1] having a doubly-bent aryldiazo ligand (Fig. 1c), and [Pt(N_2Ph)(PPh_3)$_3$][BF_4].[9] A complex salt of the empirical formula "[Pt(N_2Ph)(PPh_3)$_2$][BF_4]" that exhibits unusual reactivity has been reported; its structure is uncertain, but it has been postulated to be dimeric with bridging aryldiazo ligands.[10]

In the light of these results, we were intrigued by the possibility of preparing an isolobal η^2-nitrosyl complex of the type "[(dtbpe)Ni(NO)][X]". Reaction of **1** with nitrosonium hexafluorophosphate gave a mixture of products, likely complicated by oxidation of **1** by NO^+, so we sought to install the nitrosyl ligand by addition of nitric oxide to a Ni(I) complex containing a labile anionic ligand. Addition of a THF solution of thallium(I) triflate to a light-orange solution of [(dtbpe)NiCl]$_2$ (**3**)[11] affords the triflato complex (dtbpe)Ni(OTf) (**4**; OTf = SO_3CF_3) as paramagnetic (μ_{eff} = 1.98 BM, CD_2Cl_2), golden brown crystals in good yield (eqn. 2). Addition of nitric oxide to a cold (−78 °C) toluene solution of **4** followed by slow warming to room temperature results in a color change to dark blue with formation of the Ni(0) nitrosyl complex (dtbpe)Ni(NO)(OTf) (**5**; eqn. 3). The infrared spectrum of **5** exhibits ν(NO) at 1764 cm^{-1}, which can be compared to that found in the chloride analogue (dtbpe)Ni(NO)Cl (ν(NO) = 1734 cm^{-1}).[11] Complex **5** exhibits a broadened singlet at δ 92 in its ^{31}P NMR spectrum (*cf.*, δ 93 in (dtbpe)Ni(NO)Cl) consistent with pseudotetrahedral geometry at Ni.

$$\underset{\mathbf{3}}{[(\mathrm{dtbpe})\mathrm{NiCl}]_2} \xrightarrow[\mathrm{THF},\ -35^\circ\mathrm{C}]{\mathrm{TlOSO_2CF_3}} \underset{\mathbf{4}}{(\mathrm{dtbpe})\mathrm{Ni(OTf)}} \qquad (2)$$



(3)

Metathesis of **5** with $NaBAr^F_4$ (BAr^F_4 = tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate) in ether results in elimination of NaOTf with formation of the jade-green salt [(dtbpe)Ni(NO)][BAr^F_4] (**6**). Consistent with a change from a neutral to a cationic metal center, ν(NO) for **6** (1836 cm^{-1}) is shifted 72 cm^{-1} to higher energy than in **5**. In contrast with **2**, the ^{1}H and ^{31}P NMR spectra of **6** indicate equivalent *t*-Bu groups and phosphorus nuclei (^{31}P singlet, δ 78) suggestive of a linear, end-on bound nitrosyl ligand.

The solid-state structure of **6** confirms trigonal-planar geometry at Ni with NO coordinated in a linear fashion.¶ The anions and cations are well separated for one of the two independent molecules in the unit cell (Fig. 3, with Ni(1)–N(1) = 1.649(5) Å, N(1)–O(1) = 1.141(8) Å, and Ni(1)–N(1)–O(1) = 177.4(7)°). These values are similar to those recently reported by Puiu and Warren for a neutral, β-diketiminate-supported 3-coordinate Ni nitrosyl complex, [$Me_2C_3H(NMes)_2$]Ni(NO), where Ni–N = 1.610(3) Å, N–O = 1.170(3) Å, and Ni–N–O =171.0(3)°.[12] There are close BAr^F_4 fluorine–nitrosyl oxygen contacts in the second molecule in the unit cell of **6** (3 O···F contacts ~ 2.6–2.8 Å) that result in a slight distortion of the nitrosyl ligand in that unit (Ni(2)–N(2)–O(2) = 168.5(6)°). Thus, while a side-bound nitrosyl proved elusive in this system, complexes **2** and **6** comprise an unusual pair of aryldiazo/nitrosyl analogues with notably different bonding motifs.

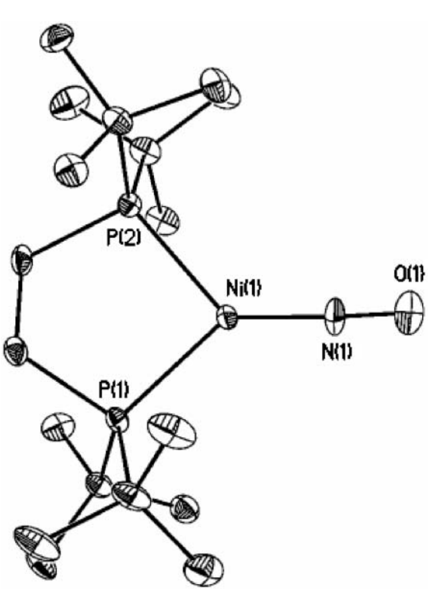


Fig. 3 ORTEP view of one complex cation of **6** (35% probability thermal ellipsoids; H-atoms omitted for clarity). Selected metrical parameters: Ni(1)–P(1) = 2.273(2), Ni(1)–P(2) = 2.258(2), Ni(1)–N(1) = 1.649(5), N(1)–O(1) = 1.141(8) Å; P(1)–Ni(1)–P(2) = 92.13(6), P(1)–Ni(1)–N(1) = 137.4(2), P(2)–Ni(1)–N(1) = 130.5(2), Ni(1)–N(1)–O(1) = 177.4(7)°.

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Notes and references

§ Crystal data: For **2·½(C_4H_8O)**: $C_{27}H_{47}F_6N_2NiO_{1.5}P_3$, M = 693.33, triclinic, $P\bar{1}$, a = 10.6973(9), b = 12.4144(10), c = 13.2900(11) Å, α = 88.4960(10), β = 75.1410(10), γ = 79.4050(10)°, Z = 2, V = 1676.4(2) Å^3, T = 100 K, μ(Mo-Kα) = 0.780 mm^{-1}. A red block of **2** (0.10 × 0.08 × 0.05 mm) grown from THF/n-pentane at −35 °C was mounted in inert oil and transferred to the 100 K gas stream of the diffractometer. Of 10764 total reflections (2.00 < θ < 28.28°), 7554 were independent and 6423 (R_{int} = 4.36%) were observed with $I > 2\sigma(I)$. The structure was solved using direct methods and refined by full-matrix least squares on F^2. No anomalous bond lengths or thermal parameters were observed except for the tetrahydrofuran of solvation which resides at the inversion center with the oxygen atom disordered over two sites. No hydrogen atoms were assigned for this solvent molecule. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically and fit to idealized positions. $R(F)$ = 4.68% and $R(wF)$ = 13.39%. CCDC 279076. See http://dx.doi.org/10.1039/b510131j for crystallographic data in CIF or other electronic format.

¶ For **6·½(C_6H_5Cl)**: $C_{106}H_{109}F_{48}B_2ClNi_2P_4N_2O_2$, M = 2653.32, monoclinic, $P2_1/n$, a = 17.386(16), b = 35.42(3), c = 18.986(17) Å, α = 90, β = 93.651(18), γ = 90°, Z = 4, V = 11668.18 Å^3, T = 100 K, μ(Mo-Kα) = 0.52 mm^{-1}. A green block crystal of **6** (0.10 × 0.25 × 0.25 mm) was grown from C_6H_5Cl/petroleum ether at −35 °C, mounted in inert oil and transferred to the 100 K gas stream of the diffractometer. Of 83543 total reflections (1.15 < θ < 25.00°), 20594 were independent and 17074 (R_{int} = 8.65%) were observed with $I > 2\sigma(I)$. The structure was solved using direct methods and refined by full-matrix least squares on F^2. Several F atoms on the anion were disordered over two sites and no action was taken to resolve them. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically and fit to idealized positions. $R(F)$ = 9.42% and $R(wF)$ = 21.45%. CCDC 279077. See http://dx.doi.org/10.1039/b510131j for crystallographic data in CIF or other electronic format.

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