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N-Atom transfer *via* thermal or photolytic activation of a Co-azido complex with a PNP pincer ligand†

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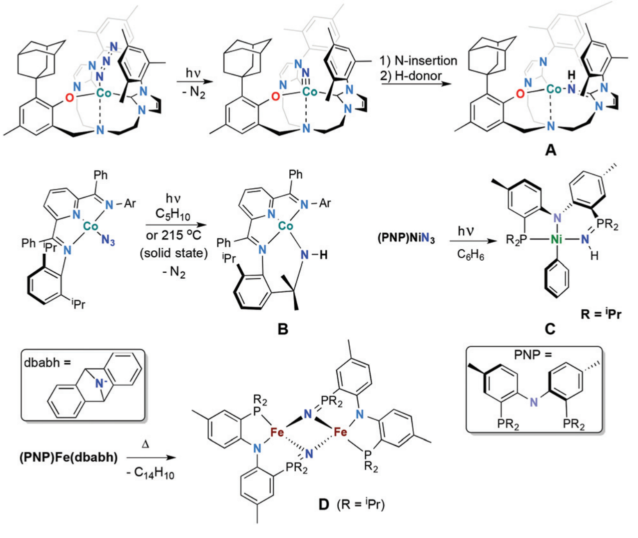
Thermal or photolytic activation of well-defined mononuclear [Co(N$_3$)(PNP)] (PNP = 2,2′-bis(diisopropylphosphino)-4,4′-ditolylamido) results in the structurally characterized dinuclear species [Co(μ-N;κ^3-*P*,*N*,*N*-PN^{P}N)]$_2$ (3), with two N-bridging phosphiniminato bridgeheads. Density Functional Theory (DFT) calculations indicate the intermediacy of a mononuclear cobalt–nitrido complex, followed by N-migratory insertion into a Co–P bond. Reaction of 3 with two equiv. HCl leads to rupture of the dimer with formation of mononuclear [CoCl(PN^{P}N^H)] (4) by protonation of the N-bridges.

Transition metal complexes featuring multiple bonded terminal nitrido (M≡N) ligands are attracting interest, as these species are proposed to play important roles in N$_2$ splitting, N-atom transfer reactions and in biochemical processes.[1] Terminal nitrido complexes with metals up to Group 8 are well-known but bona fide M≡N complexes with metals from Group 9 onwards are still rare due to a mismatch between the strongly π-donating nitrido (N^{3-}) ligand and the electron-rich metal centers, leading to increasingly filled antibonding π-orbitals and overall destabilization of the M–N bond.[2]

Typically, azido complexes are used as precursors to generate the nitrido species *via* either thermolysis, chemical oxidation or photolysis. For Group 9 metals, this has resulted in isolable terminal Ir–nitrido compounds,[3,4] but terminal nitrido- or nitridyl[5] complexes with Rh proved too reactive for isolation and only species arising from follow-up reactivity have been structurally characterized to date.[6–9] A Co(IV)–nitrido complex stabilized by a bis(NHC)(aryloxido)-amine ligand scaffold was detected by EPR spectroscopy at 10 K. At higher temperatures, migratory insertion of the N-atom into a metal–carbene bond and subsequent H-atom abstraction (from a sacrificial H-atom donor) resulted in a cobalt-bound imidazolin-2-imine fragment (Scheme 1, **A**).[10] Similar intramolecular reactivity was previously observed upon photolysis or thermolysis of bis(imino)pyridine cobalt azide complexes, leading to N-insertion into a ligand C–H bond to form **B**, with a putative transient Co-nitrido proposed as intermediate.[11]

We recently described the photolysis of [Ni(N$_3$)(PNP)] (PNP = 2,2′-bis(diisopropylphosphino)-4,4′-ditolylamido) in a benzene solution, resulting in clean transformation to complex **C**, [Ni(Ph)(PN^{P}N^H)].[12] DFT-studies resulted in the proposal of a mechanism involving a transient terminal Ni–nitrido complex, with N-migratory insertion into a Ni–P bond and intermolecular C–H activation of benzene solvent to provide the final product. Mindiola and coworkers reported the thermolysis of [Fe(dbabh)(PNP)] (dbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene), generating anthracene and



Scheme 1 N-Insertion products from activation of first-row metal nitrido precursors.

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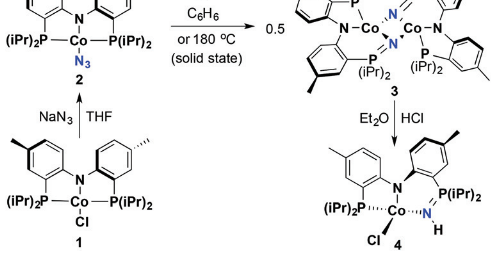
dimer **D** after N-insertion into the Fe–P bond. The formation of a transient Fe≡N species was proposed as a possible intermediate in this reaction.[13] We herein report the formation of [Co(N_3)(PNP)] complex **2** from Cl-precursor **1** and the fate of this azido-complex upon thermolysis and photolysis, seeking to answer the following questions: (i) how do activation of **2** and the resulting reactivity compare to the Ni analogue and other Group 9 examples and (ii) are intermediates or products of the azide activation interesting targets for follow-up chemistry.

Following a modified literature procedure,[14] dark blue [CoCl(PNP)] complex **1** was prepared in high yield by the addition of $CoCl_2$ to *in situ* prepared (PNP)Li (Scheme 2). Subsequent efficient salt metathesis between **1** and NaN_3 led to the desired dark green [Co(N_3)(PNP)] species (**2**) in 95% yield. Solution IR spectroscopy of **2** showed absorption bands (ν_{N_3} = 2052 and 2025 cm^{-1}) and a shoulder (ν_{N_3} = 2043 cm^{-1}) in the expected region for metal-azido species (Fig. S2†).[15] The UV-vis spectrum of **2** (Fig. S3†) contains a strong absorption at 302 nm (ε = 12 100 M^{-1} cm^{-1}) and a shoulder at 338 nm (ε = 6800 M^{-1} cm^{-1}). The IR spectrum of **2-^{15}N** shows the expected shifts of the azide bands (ν_{N_3} = 2043 and 2036 cm^{-1} and a shoulder at 2010 cm^{-1}). The paramagnetic ^{1}H NMR spectrum ranges from 44 ppm to −25 ppm. At room temperature the μ_{eff} is 1.77μ_B (using Evans' method),[16] suggestive of an S = 1/2 spin ground state. X-band EPR spectroscopy reveals a slightly rhombic, almost axial spectrum (Fig. S4†), with the following g-values based on spectral simulation g_{11} = 3.000 (A^{Co} 270 MHz), g_{22} = 2.008 (A^{Co} NR) and g_{33} = 1.950 (A^{Co} NR). The combined results confirm the formation of a low-spin square planar Co^{II} species. A preliminary X-ray crystallographic connectivity plot for the molecular structure of this species supports this assignment (see ESI†). No azide activation of **2** was observed under electrochemical conditions, as a reversible one-electron oxidation was found by cyclic voltammetry (Fig. S5†), with the redox-active ligand being the suggested locus for this event.[17,18] Using TGA-DSC, we established that **2** undergoes an exothermic event around 169 °C, associated with a mass loss of −3.1%, indicative of decomposition of the azido group.[19] Large scale thermolysis led to formation of a dark red pentane-soluble and air-sensitive complex **3** with no apparent azide stretch in the IR spectrum.



Scheme 2 Synthetic scheme for complexes **2–4**, starting from [CoCl(PNP)] **1**.

We succeeded to obtain single crystals, suitable for X-ray structure determination, from a cold pentane solution. The molecular structure of the *centro*-symmetric dimeric Co^{II}_2-species is depicted in Fig. 1. The nitrogen atoms of two monoanionic phosphiniminato units act as bridging donors to two tetrahedral Co^{II} centers, similar as in the aforementioned iron analogue, providing [Co(μ-PN^P*N*)]$_2$ (**3**).[13,20] Photolysis in benzene led to selective formation of the same dinuclear complex, with no sign of intermolecular C–H activation as observed for the Ni-analogue.[12] The phosphiniminato unit is proposed to originate from thermal activation of the inorganic azide fragment and subsequent insertion of a transient nitrido N-atom into a Co–P bond, resulting in formation of the asymmetric dianionic PN^P*N* ligand. Two of the backbone phenyl rings are directed away from the diamonoid Co_2N_2 center. The other phenyl rings are nearly co-planar (centroid–centroid distance 4.485 Å) and almost perpendicular to the Co_2N_2 center.

The ^{1}H NMR spectrum of complex **3** ranges from 25 to −5.5 ppm and shows relatively sharp signals that allow for integration and also some degree of (nuclear spin) multiplicity determination (see ESI†). All CH_x groups of the ligand framework are inequivalent, signifying overall asymmetry in the binding motif of the PN^{P}N skeleton. The ^{1}H NMR chemical shifts for all signals are temperature dependent, showing uncomplicated Curie-like behavior indicative of a single contributing spin state in the temperature range of −60 °C to 80 °C (see ESI†). The effective magnetic moment of **3** in toluene at 20 °C of μ_{eff} = 2.75μ_B (Evans' method), is consistent with an S = 1 ground state of the dinuclear complex.

A plausible reaction mechanism for the azide activation and N-insertion was investigated using DFT calculations. Both the doublet and the quartet spin states were considered using the BP86 DFT functional (Fig. 2).[21] In accord with the experimental data, starting material **2** is clearly most stable in the S = 1/2 state.

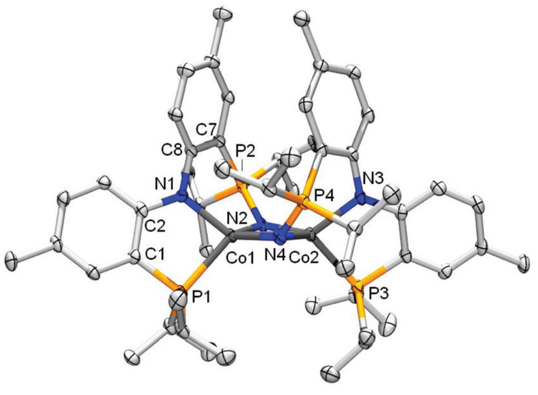


Fig. 1 Displacement ellipsoid plots (50% probability level) of one of the two crystallographically independent molecules of **3**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co1–Co2 2.5679(8); Co1–N1 1.965(3); Co1–N2 1.982(3); Co1–N4 1.927(3); Co2–N2 1.938(3); Co2–N3 1.976(3); Co2–N4 1.989(3); Co1–P1 2.3148(11); Co2–P3 2.3313(11); P2–N2 1.580(3); P4–N4 1.582(3); Co1–N2–Co2 48.34(9); N2–Co1–N4 97.97(12).

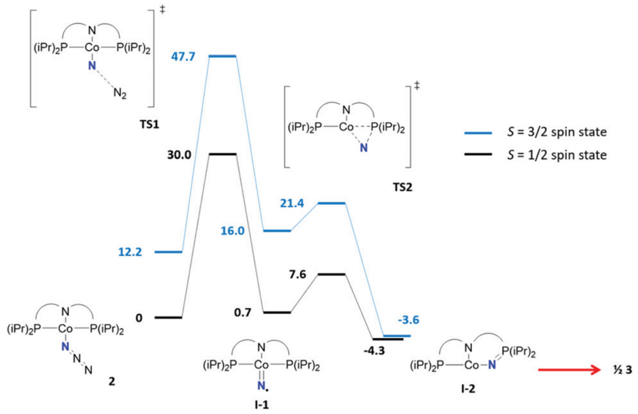


Fig. 2 Proposed pathway for formation of **3** from **2** based on DFT calculations (BP86-D3, def2-TZVP). Energies in kcal mol^{-1} relative to S = 1/2 spin state of **2**. Dimerization of **I-2** to form **3** is likely a low-barrier step, but this step was not calculated.

Activation of the azide leading to N_2 release proceeds *via* transition state **TS1**, which is high in energy (30.0 kcal mol^{-1}) but much lower than the activation barrier calculated for the previously reported $[Ni(N_3)(PNP)]$ species (46.2 kcal mol^{-1})[12] and in line with an accessible thermal activation pathway. Expulsion of N_2 results in nitrido structure **I-1**, which also is most stable in the doublet spin state. The spin density in **I-1** is distributed over the Co center (0.58) and the nitrido N atom (0.39) (Fig. 3), giving the latter significant nitridyl character. The Wiberg and Mayer bond orders for the cobalt–nitrido fragment were calculated to be 1.777 and 1.949, respectively (see ESI†).

Insertion of the nitrido N into the Co–P bond *via* transition state **TS2**, with a relatively low barrier of +6.9 kcal mol^{-1} for S = 1/2, leads to species **I-2**. This T-shaped intermediate is equally stable in the doublet and quartet spin state, with at least one vacant coordination site to reach a square planar geometry. Dimerization of two species **I-2** to form final product **3** is therefore a likely process. Indeed, the energy of **3** with S = 1 was calculated to be −38.0 kcal mol^{-1}.[22] The transition state from **I-2** to **3** was not calculated, but it is likely a low-barrier process considering the coordinatively unsaturated nature of **I-2**.

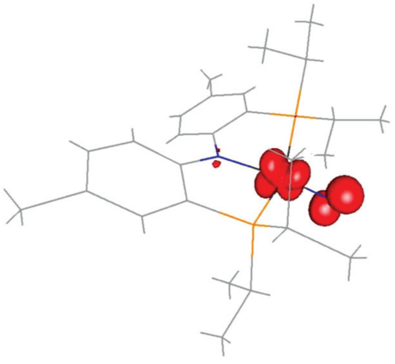


Fig. 3 Spin density plot for **I-1** (S = 1/2) (BP86-D3, def2-TZVP).

To the best of our knowledge, the potential of a metal-bound phosphiniminato to act as proton-responsive ligand has hardly been addressed to date.[23] To assess if the sterically congested Co–(μ-N) bond can interact with acidic H–E fragments, **3** was reacted with an equimolar amount of HCl (2 M in Et_2O). This generates paramagnetic brown solid **4** in 56% yield after work-up (as well as some blue $CoCl_2$ precipitate), which is characterized by an IR absorption band at ν = 3375 cm^{-1} (Fig. S8†) that is assigned to an P═*N–H* stretch.[12] X-ray diffraction studies of single red crystals confirmed the structure of **4** as mononuclear $[CoCl(PN^{P}N^{H})]$ (Fig. 4), with cobalt in a distorted tetrahedral geometry (∠N1–Co1–Cl1 132.53(10)°); (N2–Co1–P1 122.18(10)°). The preparative route to obtain the protonated iminophosphorane fragment and the metal geometry are different from the Ni analogue recently reported by us (involving C–H activation of benzene and a square planar Ni^{II}).[12] The dimeric nature of **3** does not impede reactivity of the Co–($^{P═}$*N*) bond with HCl in a heterolytic manner. Complex **3** can be viewed as containing two masked mononuclear coordinatively unsaturated Co^{II} species, with the anionic phosphiniminato moiety potentially available as internal base for metal–ligand bifunctional activation of polar substrates.[24]

In summary, the activation of $[Co(N_3)(PNP)]$ (**2**) and subsequent reactivity of the proposed transient cobalt nitrido is subtly but significantly different than for the nickel congener. Both thermal and photolytical pathways are accessible with **2**. Loss of N_2 results in insertion of the α-N_{azide} atom into a Co–P bond to create an anionic phosphiniminato fragment and dimeric structure **3**, featuring a diamonoid Co_2N_2 core with bridging N-donors. No evidence for C–H activation of arene solvent is observed for Co. DFT calculations support the energetic accessibility of a cobalt nitrido intermediate (with substantial nitridyl character), with facile follow-up trapping by the ligand.

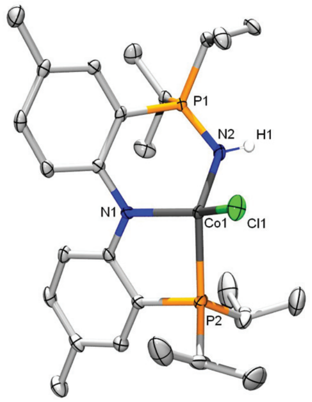


Fig. 4 Displacement ellipsoid plot (50% probability level) of **4**. Hydrogen atoms omitted for clarity, except for H1 on N2. Selected bond lengths (Å) and angles (°): Co1–Cl1 2.2549(11); Co1–N1 1.959(3); Co1–N2 1.960(3); N2–P1 1.597(3); Co1–P2 2.3271(11); N1–Co1–P2 85.20(9); N2–Co1–P2 122.18(10); N1–Co1–Cl1 132.53(10); N1–Co1–N2 95.65(13); Co1–N2–P1 117.23(18).

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