Homolytic H$_2$ cleavage by a mercury-bridged Ni(I) pincer complex [[[PNP]Ni]$_2$[μ-Hg]]

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Reduction of the pincer nickel(II) complex [(PNP)NiBr] with sodium amalgam (Na/Hg) forms the mercury-bridged dimer [[[PNP]Ni]$_2$[μ-Hg]], which homolytically cleaves dihydrogen to form [(PNP)NiH]. Reversible CO$_2$ insertion into the Ni–H bond is observed for [(PNP)NiH], forming the monodentate $^2$O-formate complex [(PNP)NiOC(O)H].

Pincer ligands have become a highly topical field of chemical research in recent years because of their readily modifiable steric and electronic properties. This, together with the high thermal stability of their metal complexes, makes them highly attractive ligands in small molecule activation and catalysis. Combinations of pincer ligands and environmentally benign 3d-elements have been of particular interest in catalyst development for hydrofunctionalizations, cross-coupling reactions, CH-bond or CO$_2$ activation and dehydrogenation reactions. These precedents were the motivation for our studies on sterically encumbered monoanionic pyrrolyl-based PNP pincer systems and their phosphine-substituted derivatives (1, Chart 1). The phenyl-substituted PNP ligand was introduced independently in 2012 by the groups of Tonzetich,$^9$ Gade$^{10}$ and Mani,$^{11}$ who employed this support in the synthesis of nickel and palladium complexes.

In comparison to the related amine- and diphenylaniline-derived PNP-ligands II$^{12}$ and III,$^{13}$ the pyrrolyl-based system 1 has received less attention (Chart 1). In this contribution we report on the preparation and reactivity of the tBu-(1a)$^{1b}$ and iPr-(1b)$^{14}$ substituted PNP nickel pincer systems (ESI). X-ray structures of 1b and the lithium salt 2a are reported in the ESI.$^\dagger$ The tBu-substituted derivative was employed to stabilize a remarkable Hg-bridged dinickel species exhibiting an interesting electronic structure, which enables this complex to act as a source of the (PNP)Ni fragment. This was illustrated by the homolytic cleavage of H$_2$ to give (PNP)NiH. The insertion chemistry of CO$_2$ into the Ni–H bond is also briefly discussed.

The nickel(II) bromide species [[[PNP]NiBr] (3)] may be synthesised in moderate yields (40–52%) starting either from 1a and [NiBr$_2$(dme)] (dme = 1,2-dimethoxyethane) in the presence of NEt$_3$ or the isolated lithium salts [(RPNP)Li]$_n$ (R = iPr, n = 2, 2a; R = tBu, 2b) and [NiBr$_2$(dme)] (Scheme 1). The lithium salts are best prepared from the reaction of 1 with Li[N(SiMe$_3$)$_2$] in hexane at 0 °C or by addition of nBuLi to a hexane solution of 1 at −78 °C (ESI†).

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The molecular structure of 3b (Fig. 1) features the expected square planar geometry at the nickel atom with an Ni–N distance of 1.8520(18) Å and N–Ni–Br angle of 178.67(6)°.‡

Previous electrochemical studies indicate that [[(POCOP)NiCl], [(PhPNP)NiCl] and [[(POCOP)NiCl] can be reduced below ca. −2 V (vs. Fe/CFe) in THF.‡ However, [[(POCOP)Ni]2]10 is the only example in which the identity of the PNP-Ni(i) species is definitively established.3 Monomeric Ni(i) complexes are radicals and therefore highly reactive species, which makes their isolation challenging. Nevertheless, Ni(i) complexes have been proposed as catalytically competent species in C–S cross-coupling.3b

Despite the dearth of other examples, we attempted to isolate such a Ni(i) complex of 3b using commonly employed reducing reagents such as KC8 and Na/Hg. Although no isolable product was obtained with KC8, reduction with Na/Hg in THF gives an intense dark red solution, from which the diamagnetic, mercury-bridged dimer [[[(POCOP)Ni]2]2(m-Hg)] (4) is isolated (Scheme 1, ESI†).

Complex 4 exhibits good solubility in THF, but is only moderately soluble in aromatic and aliphatic hydrocarbons. The 199Hg NMR spectrum recorded in C6D6 shows a singlet at 76.5 ppm with a strong 199Hg to 31P coupling (JPHg = 333 Hz). Furthermore, 4 is remarkably stable in C6D6 solution, showing no degradation when heated to 80 °C for 4 days. Crystals suitable for X-ray diffraction were grown by slow evaporation of concentrated benzene solutions at ambient temperatures.‡ The solid state structure features a slightly distorted square planar geometry at the nickel atoms with Ni–N distances of 1.9223(3) Å and 1.923(3) Å in two independent molecules. To minimize steric hindrance, the two [[(POCOP)Ni]2] fragments are nearly orthogonal to each other (interplanar angles between the five-membered rings are 89.9°, corresponding to approximate S4 symmetry of the first molecule, and 80.5°) and coordinate the Hg atom in a linear fashion. The Ni1–Hg–Ni2 angles are 178.699(13)° and 175.056(13)°, and the Ni–Hg distances are 2.648(4), 2.6491(4), 2.6322(4), 2.6379(4) Å (Fig. 2).

While transition metal complexes with a bridging M–Hg–M fragment are known,23 the cobalt pincer complex [[[(POCOP)Co]2]2(m-Hg)] (POCOP = C6H5-1,3-[(OP(tBu)]2)16 and the nickel complex [[[(η5-C5H5)Ni(P(tBu)]2]2(m-Hg)]17 exhibit similar structural features to 4. The latter complex was prepared by Hg insertion into the Ni–Ni bond of [[[(η5-C5H5)Ni(P(tBu)]2]2] and shows a linear Ni–Hg–Ni arrangement with an Ni–Hg distance of 2.468(1) Å,17 significantly shorter than in 4. Unfortunately the reactivity of [[[(η5-C5H5)Ni(P(tBu)]2]2(m-Hg)] has not been explored, so the intrinsic reactivity of the Ni2(m-Hg) fragment is unknown. The cobalt pincer complex [[[(POCOP)Co]2]2(m-Hg)] does react with H2 to yield mixtures of [[[(POCOP)Co](η5-H2)] and [[[(POCOP)CoH2(η5-H2)]]] depending on the reaction conditions.16 The question arises whether complex 4 could act as a synthon for two (PNP)Ni(i) fragments and therefore initiate homolytic bond cleavage reactions. A similar reactivity was observed for the well investigated [[[(nacnac)Ni]2(m-Hg)] (nacnac = HC(CMeNC6H3(iPr)2)2)] which readily releases N2 and converts to the corresponding nickel hydride [[[(nacnac)Ni(m-H)]2]18 from frontier orbital considerations, taking into account the interactions between the two square-planar Ni(i) PNP fragments (d9) and Hg(0), one can readily rationalize the diamagnetism of 4 on the basis of a 3c,2e-bond (Fig. 3). This picture is also supported by more elaborate DFT computations at the B97D level of theory, which show that the computed geometry for the singlet ground state is in good agreement with the experimental data (ESI†). The computed singlet-triplet energy separation (ΔE0) is 64.3 kJ mol−1; and thus consistent with the experimentally observed diamagnetic ground state.

To investigate the ability of 4 to act as a suitable synthon for (PNP)Ni(i) fragments, complex 4 was exposed to H2. Gratifyingly, when 4 is treated with H2 (1 atm) metallic Hg precipitates from solution and the nickel(i) hydride [[[(POCOP)NiH]2] (5b) can be isolated (Scheme 1 and ESI†). This reaction proceeds slowly at ambient temperature, but complete homolytic cleavage of H2 can...
be reached in less than 2 hours when heated to 60 °C. Similar to observations with \([^1]^3\text{PNP}[\text{Ni}]\)\(^{3a}\), \(5b\) is thermally stable and no \(H_2\) elimination is observed when heated in \(C_6D_6\) solution. Alternatively, \(5b\) may also be prepared by oxidative addition of \(1b\) to \([\text{cod}]_2[\text{Ni}]\) (cod = \(\eta^4\)-cyclooctadiene). However, this method requires thermostability at 80 °C and 5 bar pressure of \(H_2\) to ensure clean conversion, notably harsher conditions than when the sterically smaller \(1a\) is employed (ESI†). The monohydride complexes \(5a\) and \(5b\) feature a high field-shifted Ni–H resonance in the \(^1\text{H}\) NMR spectrum at \(\delta = -17.59\) and \(-17.65\) ppm, which are split to a triplet with \(J_{\text{HP}} = 59\) and \(56\) Hz, respectively. Furthermore a strong absorption in the IR spectrum of \(5b\) at 1832 cm\(^{-1}\) can readily be prepared and used for the synthesis of \([\text{PNP}][\text{Ni}]\) complexes. Reduction of \([\text{BuPNP}][\text{NiBr}]\) with Na/Hg gives the unique \([\text{BuPNP}][\text{Ni}][\text{Hg}]\) (4), which is diamagnetic because of a 3c,2e-bond formed within the \(\text{NiHg}\) moiety. Upon addition of a suitable substrate, complex 4 can act as a synthon for two \([\text{BuPNP}][\text{Ni}])\) fragments, as illustrated by the homolytic cleavage of \(H_2\) to furnish \([\text{BuPNP}][\text{Ni}]\) (5b). Further investigations with these PNP ligands to stabilize low-valent \(3d\)-metals are ongoing and will be reported in due course.

![Displacement ellipsoid plot (50% probability) of \([\text{BuPNP}][\text{Ni}]\) (5b). Hydrogen atoms, except Ni–H, are omitted for clarity. Selected bond distances (Å) and angles (°): Ni–N 1.8699(9), Ni–P 2.1587(3), Ni–P 2.1611(3), Ni–H 1.8484(11), N–Ni–H 175.22(5), P1–Ni–P2 94.30(3), P1–Ni–H 92.6(7), P2–Ni–H 96.3(7).](attachment://Fig_4.png)

![Displacement ellipsoid plot (50% probability) of \([\text{BuPNP}][\text{NiO(O)}](OH)\) (5a). Hydrogen atoms, except the H-atom attached to C19, are omitted for clarity. Selected bond distances (Å) and angles (°): Ni–N 1.8484(11), Ni–O1 1.8914(10), Ni–P1 2.1213(4), Ni–P2 2.1954(4), O1–C19 1.2754(19), C19–O2 1.2162(2), N–Ni–O1 175.22(5), P1–Ni–P2 167.39(17), N–Ni–P1 84.69(4), N–Ni–P2 84.40(4). Through-space Ni–O2 distance: 2.937(1) Å.](attachment://Fig_5.png)
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