Simplified and versatile access to low valent Ni complexes by metal-free reduction of Ni II precursors

Emile Moser, Erwann Jeanneau, Nicolas Mézailles, Hélène Olivier-Bourbigou, Pierre-Alain Breuil

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Simplified and Versatile access to low valent Ni complexes by Metal-free reduction of Ni[II] precursors.†

E. Moser[a], E. Jeanneau[b], N. Mézailles[c]*, H. Olivier-Bourbigou[a], Pierre-Alain R. Breuil[a]*

The reduction of [Ni(DME)Cl₂] with 2 equiv. of bis(trimethylsilyl)-1,4-tetramethyldihydropyrazine in presence of a ligand L and an excess of olefin cleanly leads to [Ni(L)(alkene)₂] complexes. When reduction is done in presence of 1,5-cyclooctadiene (COD), [Ni(COD)₂] is obtained. Such approach also allows access to the Ni[I] dimer [Ni(bis(dicyclohexylphosphino)propane)Cl]₂.

Low valent, ligand stabilized (phosphines, N-heterocyclic carbenes = NHC) Ni(0) complexes are important species, being catalytically relevant in many transformations, such as cross coupling processes.[1] Among the known Ni(0) complexes, stable [Ni(L)(alkene)₂] or [Ni(L)(bis-alkene)] species (L=phosphines, NHC) are rare because of a lack of efficient, versatile synthetic route or availability of the appropriate precursors.[2] Indeed, [Ni(phosphine)(C₂H₄)₂] have been reported by displacement of the poly-ene ligand from the extremely sensitive [Ni(CDT)] precursor (CDT = 1,5,9-cyclododecatriene), whereas other [Ni(L)(bis-alkene)] species have been prepared from air, light and heat sensitive [Ni(COD)₂].[3-8] In turn, both Ni(0) complexes [Ni(CDT)] and [Ni(COD)₂] require the use of pyrophoric alkylaluminium derivatives to be synthesized. It is thus desirable to devise a rational, experimentally simpler, versatile method to access families of Ni(0) species.

Recently, bis(trimethylsilyl)-1,4-tetramethyl-dihydropyrazine **1** has been shown to behave as a one or two-electron reducing agent for numerous transition metal complexes.[9,10,11] It was also used to reduce several late transition metal halide precursors to the corresponding metallic nanoparticles in the absence of stabilizing ligand.[12] In the case of Ni, nanoparticles active in carbon-carbon cross coupling process were obtained. We have hypothesized that if the *in situ* generated reduced Ni center could be efficiently trapped by ligands the aforementioned desirable Ni(0) complexes would be readily accessible. In the present work, we show that from the simple, commercially available, [Ni(DME)Cl₂] precursor (DME = dimethoxy-ethane), several Ni(0) complexes could be synthesized in one pot. We also report that with strongly donating bis-phosphine ligands, the reaction leads to Ni(I) complexes instead.

Our work started with the synthesis of the emblematic and sensitive [Ni(COD)₂] complex. To date it is synthesized by reduction of Ni(acac)₂ with alkylaluminum compounds such as triethylaluminium or DIBAL-H in presence of COD and butadiene at low temperature, followed by low temperature crystallization and filtration to eliminate aluminium side products.[13] The room temperature reduction of [Ni(DME)Cl₂] with two equivalents of **1** was carried out in a first stage in THF with the presence of a large excess (20 equiv. of COD). Formation of black precipitate (likely Ni metal) pointed to a fast reduction compared to coordination by COD. The low temperature reduction (-78°C) was attempted to prevent Ni(0) precipitate formation, but the reaction does not proceed at this temperature within a day. The optimized reduction temperature was found to be at -20°C. In this case, we were able to synthesize [Ni(COD)₂] as crystalline material in 54% isolated yield, fully characterized by ¹H and ¹³C NMR (Scheme 1). The moderate yield can be explained by the remaining formation of nickel black particles during the reduction, which can nevertheless be readily eliminated by filtration prior to crystallization of [Ni(COD)2] from cold toluene.
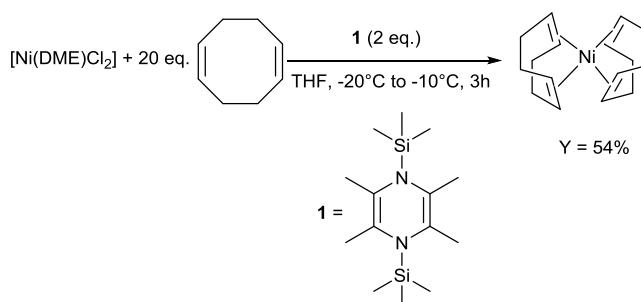
Scheme 1 Synthesis of [Ni(COD)₂] by organic reduction of Ni(II) halide

Beyond the synthesis of [Ni(COD)₂] itself, the reaction proved our hypothesis right, clearly indicating that monometallic Ni(0) can be

a. IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France
b. Centre de Diffractométrie Henri Longchambon, Site CLEA - Bât. ISA, 3ème étage, 5 rue de La Doua; 69100 Villeurbanne, France
c. Laboratoire Hétérochimie Fondamentale et Appliquée UMR 5069 CNRS, Université Paul Sabatier 118 Route de Narbonne ; 31062 Toulouse, France

trapped. The next level of complexity concerns the selective stabilization by two different types of ligands. Indeed, in order to be able to generate efficient catalytic species, it is crucial for the metal to bear strongly bound ligands as well as weakly bound ligands that will be displaced during the transformation. For example, Lappert et al. studied the coordination of 1,3-divinyltetramethyldisiloxane (dvtms) to Ni(0) centers in order to synthesize hydrosilylation catalysts.[6,8] For that purpose, they synthesized [Ni(PR$_3$)(dvtms)] (R=Ph, Cy and *p*-Tol) complexes from [Ni$_2$(dvtms)$_3$] or [Ni(COD)$_2$]. We therefore turned our attention to the synthesis of Ni(0) complexes stabilized by phosphine and alkene ligands. Pleasingly, the reduction of [Ni(DME)Cl$_2$] in THF with two equiv. of **1**, in presence of two equiv. of dvtms and one equiv. of phosphine ligand appeared remarkably selective. Indeed, in each case, a single complex is formed as shown by ^{31}P NMR spectroscopy. The isolated yields (not optimized) are between 24 and 77%, because of their high solubility (Scheme 2).

PR$_3$ = PCy$_3$ (Y = 77%) (**2a**)
PPh$_3$ (Y = 43%) (**2b**)
P^{i}Pr$_3$ (Y = 43%) (**2c**)
P^{t}Bu^{i}Pr$_2$ (Y = 24%) (**2d**)
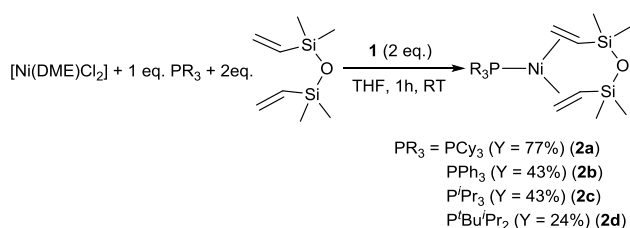
Scheme 2 Synthesis of [Ni(PR$_3$)(dvtms)] complexes (**2a**-**2d**)

Complexes **2a-d** were characterized by ^{1}H, ^{13}C and ^{31}P NMR in accordance with literature.[8] The structure of complex **2d** was not known and is presented here (Figure 1). The local geometry at the three-coordinate nickel atom is planar and the angles P-Ni-L^1 and P-Ni-L^2 (with L^1 and L^2 the centers of the coordinated double bounds) of 116.9° and 113.7° confirm the slightly distorted trigonal structure. The six-membered ring (Ni-C13-Si-O-Si-C18) adopts a chair structure.[6] The CC bond lengths of the olefins ligands measured at 1.40 Å (average) attest here the back donation from the nickel center into the π* orbitals of the coordinated olefins.
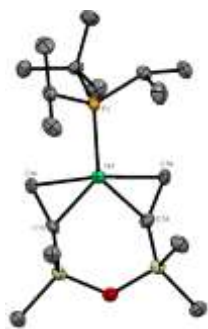
Figure 1 ORTEP drawings of **2d**, Hydrogen atoms were omitted for clarity. Bond distances [Å] and angles [°] : Ni-P 2.2284(10), Ni-C14 2.010(3), Ni-C13 2.018(3) Ni-C19 2.008(3), Ni-C18 2.030(3), C13-C14 1.402(4), C18-C19 1.404(4), P-Ni-C13 133.98(9) , P-Ni-C14 93.36(9), P-Ni-C19 96.585(10), P-Ni-C18 137.27(9).

With this very encouraging result, we targeted more challenging [Ni(L)(C$_2$H$_4$)$_2$] complexes. Indeed, examples of these are very scarce. The synthesis of [Ni(PCy$_3$)(C$_2$H$_4$)$_2$] was only reported via the substitution of CDT from the highly sensitive complex [Ni(CDT)] in 1971.[5] Following our strategy, the same complex [Ni(PCy$_3$)(C$_2$H$_4$)$_2$], **3**, was formed exclusively (100% ^{31}P NMR) at room temperature after 45 minutes (Scheme 3).
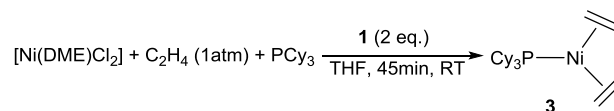
Scheme 3 Synthesis of a Ni(0)-phosphine bis-ethylene complex

Complex **3** is thermally sensitive and decomposes almost instantly at room temperature. Crystallization of the bulk solution at -34°C yielded crystals that were analyzed by XRD.[3] The measurement of the P-Ni-Centroid 116.3° and 116.7° (with Centroid being the centers of the two ethylene ligands) confirms the slightly distorted trigonal planar structure. The CC bond lengths of the ethylene ligands measured at 1.39 Å (average) attest here also the back donation from the nickel center into the π* orbitals of ethylene.

Figure 2 ORTEP drawings of **3**, hydrogen atoms were omitted for clarity. Bond distances [Å] and angles [°] : Ni-P 2.1873(10), Ni-C22 2.000(4), Ni-C21 1.987(4), Ni-C23 1.985(4), Ni-C24 1.988(4), C22-C21 1.392(6), C23-C24 1.389(6), P-Ni-C22 95.89(12), P-Ni-C21 136.69(13), P-Ni-C23 137.14(15), P-Ni-C24 96.26(13), C21-Ni-C23 86.01(19).

Having shown on several examples the efficiency of the reduction method for the synthesis of phosphine stabilized Ni(0) complexes, we then turned our attention to the related NHC complexes. We chose the known complex **4** as a representative example. Complex **4** has been obtained by COD substitution in [Ni(COD)$_2$] by NHC^{IPr} (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in the presence of styrene with a 90% yield.[7] Our one pot synthesis from [Ni(DME)Cl$_2$] (Scheme 4) allowed the isolation of complex **4** in 44% yield.
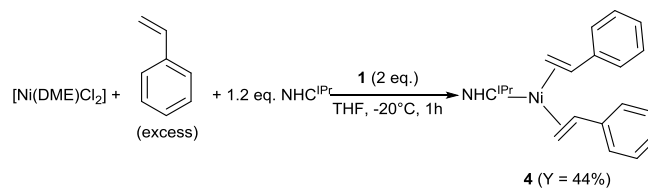
Scheme 4 Synthesis of a Ni(0) NHC-stabilized complex

These examples show the versatility of the reduction method, employing monodentate phosphines or NHC in conjunction with alkenes or dienes. In all cases, the reaction was highly selective in the formation of the desired [Ni(L)(alkene)$_2$] or [Ni(L)(diene)] complexes.

Mechanistically, the reaction sequence can be proposed to involve either reduction of the Ni(II) salt to unsaturated Ni(0) species to which the ligands bind with very fast kinetics, or coordination of the ligand(s) to the Ni(II) precursor prior to reduction followed again by coordination of other ligands to complete the coordination sphere. In addition, the intermediacy of Ni(I) species remains an open question. In order to provide preliminary information on the mechanism, we investigated the influence of the Ni precursor on the nature of the reduced Ni complexes. When the complex [Ni(PCy$_3$)$_2$Cl$_2$] was reduced with 2 equiv. of **1** in presence of ethylene, the known complex [Ni(PCy$_3$)(C$_2$H$_4$)$_2$] **3** was observed together with liberation of one equiv. of PCy$_3$. This experiment showed that the redox potential of species **1** is low enough to reduce electron-rich Ni(II) into Ni(0). Interestingly in this case, despite the presence of two PCy$_3$ in the medium, no trace of the [Ni(PCy$_3$)$_2$(C$_2$H$_4$)] complex was detected. In order to favor the formation of such type of complex, we turned to more strongly bound bidentate diphosphine ligands. Unexpectedly, the reduction of complex [Ni(dcpp)Cl$_2$] with 2 equiv. of **1** in presence of ethylene did not lead to the expected Ni(0) complex [Ni(dcpp)(C$_2$H$_4$)] as no signal was observed in the ^{31}P NMR spectrum of the crude mixture. An EPR spectrum revealed an intense signal for a Ni(I) species. From this mixture, the known paramagnetic Ni(I) dimer **5** [Ni(dcpp)Cl]$_2$ was isolated with a 70% yield (Scheme 5).[14]
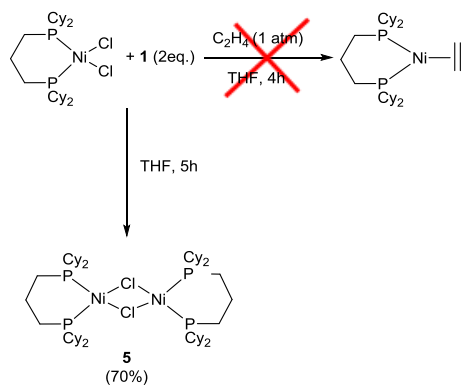
Scheme 5 Isolation of Ni(I)dccp dimer

This observation raised further mechanistic questions. Mashima and coworkers have investigated the reduction process using species **1** with several metal centers. They have shown that despite the fact that **1** is a potential 2-electron reducing agent, an excess (2 equiv.) of **1** was needed to reduce efficiently Ni(II) into Ni(0) nanoparticles and only half of reductant **1** was converted.[12] They

have moreover proposed that coordination of the reducing agent is needed for the electron transfer and TMSCl elimination.[9]

It was therefore of interest to investigate the mechanism of the reduction of a Ni(II) complex, using both NMR and EPR spectroscopies. We chose to study the reduction of [Ni(DME)Cl$_2$] in presence of one equiv. of PCy$_3$ and two equiv. of dvtms into complex [Ni(PCy$_3$)(dvtms)] **2a**. Most interestingly, with one equiv. of species **1**, complex **2a** is formed with a *ca* 50% yield (^{31}P NMR) within 5 minutes at room temperature, along with *ca* 50% of free PCy$_3$. Interestingly, at this point already, the ^{1}H NMR spectrum is very poorly resolved, which prevented quantification of reagent **1** consumption, and points to the formation of paramagnetic species. After 30 min the intensity of the signal had drastically decreased to a very poorly defined ^{31}P NMR spectrum (ESI). A well-defined EPR spectrum was observed, consistent with the formation of Ni(I) species. Indeed, the room temperature X-band EPR solution is triplet with hyperfine coupling to two equivalent phosphorus nuclei. Simulation of this spectrum gives a g value of 2.143 and a coupling constant with P of 73 G. This data is fully consistent with literature precedence for [(bidentate phosphine)NiCl] species.[15] Formation of [Ni(PCy$_3$)$_2$Cl] either as a monomer or dimer is therefore evidenced during the process, following a comproportionation mechanism between generated Ni(0) and Ni(II) precursor.[16] Nonetheless, when a second equiv. of **1** was added, the quantitative formation of complex **2a** was observed by ^{31}P NMR spectroscopy together with the loss of the EPR signal. These experimental observations are only consistent with the mechanism presented in Scheme 6. It involves a fast reduction of half of the [Ni(DME)Cl$_2$] into the [Ni(PCy$_3$)(dvtms)] complex **2a** via a two electron transfer and coordination of the ligands followed by comproportionation to form a Ni(I) species. This intermediate can be reduced to Ni(0) efficiently by the addition of a second equiv. of **1**. Overall, our experiments confirm that two equivalents of the reducing agent are essential for an efficient reduction, despite the fact that only one equivalent is consumed.
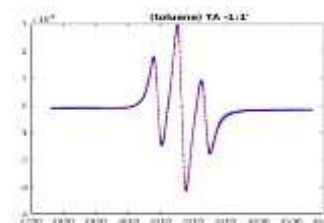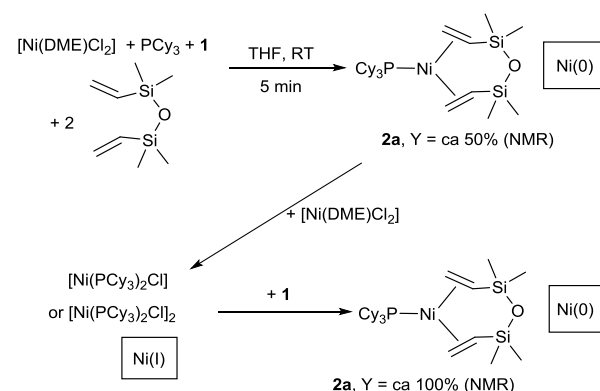
Scheme 6 Proposed reduction mechanism

A major difference can be seen between the complexes featuring mono and bidentate ligands. Indeed, starting from [Ni(dcpp)Cl$_2$], a stable Ni(I) dimer is formed. The four-coordinate Ni center adopts a square planar geometry and it is likely that the bulkiness of the ligand prevents coordination of the reducing agent necessary to allow further electron transfer.

In summary we have demonstrated the potential of organic reducing agent **1** to synthesize stabilized Ni(0) complexes from Ni(II) halides. We have shown the versatility of this method toward diversified ligands such as alkenes, tertiary phosphines and NHCs. Mechanistically, a two electron reduction of the Ni(II) precursor to Ni(0) followed by comproportionation to Ni(I) species is involved. When a monodentate trialkyl phosphine ligand is used, further reduction to Ni(0) is possible, while with the strongly donating bidentate ligand dcpp, the reaction stops at the Ni(I) stage. Preliminary experiments showed promising results in the use of this method to access active species in various catalytic transformations.

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