

$Ni(acac)_2/Phosphine as an Excellent Precursor of Nickel(0) for Catalytic Systems^{\dagger}$

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Received April 30, 2010

The coordination of phosphine ligands to nickel acetylacetonate was studied in toluene solution, and the first X-ray structure of the unstable complex *trans*-[Ni(acac)₂(PMe₂Ph)₂] has been reported. A convenient procedure was developed to generate Ni(0) species in situ in solution from a Ni(acac)₂ precursor, and their application in catalysis was demonstrated. A study of the reaction mechanism has suggested that water may play an important role in the formation of zerovalent nickel species. The nature of the Ni(0) species was confirmed by trapping with Ph₂S₂, and the structure of the resulting complexes *trans*-[Ni(SPh)₂L₂] was established by X-ray analysis for $L = PMe_2Ph$, PMePh₂, PBu₃.

1. Introduction

The development of Pd-catalyzed reactions has shown outstanding growth, and the synthetic methods created have attained widespread application in modern organic chemistry.¹ The easy generation of Pd(0) species—an active form of the catalyst—by in situ reduction of PdX₂ salts is of great importance for the practical application of the catalytic reactions to synthetic procedures. In fact, Pd(II) catalyst precursors usually were reduced to Pd(0) by 1 equiv of phosphine ligand and allowed controlled generation of coordination unsaturated (n= 1–3) and saturated (n= 4) PdL_n species, depending on the overall amount of the phosphine ligand L added to the reaction (Scheme 1).

This simple in situ procedure in many cases avoided the synthesis of air-sensitive PdL_4 complexes and, especially,

rather complicated procedures for the preparation of highly unstable unsaturated species PdL_n (n = 1-3). Not surprisingly, a PdX_2/L combination is now routinely utilized in various catalytic reactions.² The mechanism of this transformation has been thoroughly discussed and involves coordination of the phospine ligand to Pd followed by reduction of the metal center.³

The increasing cost of Pd has stimulated a search for reliable Ni alternatives for catalysis; moreover, in some cases it was reported that Ni catalysts were more active than the Pd analogues.^{1,4} In this regard, direct involvement of a readily accessible and easy to handle Ni(II) precursor in the catalytic reactions is a topic of much practical importance.⁵

In contrast to palladium, a similar procedure for in situ generation of Ni(0) species from convenient Ni(II) precursors has not been routinely applied. Although utilization of a NiX₂/L combination in catalytic reactions was reported, it was accompanied by addition of special reducing agents (diisobutylaluminium hydride (DIBAL), AlR₃, NaBH₄, Zn, LiAlH₄, etc.). Usage of such reducing agents to form soluble metal complexes requires fine control of the reaction conditions, since this may also lead to the formation of Ni nanoparticles⁶ and may result in changing the nature of the

[†] Part of the Dietmar Seyferth Festschrift.

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catalytic system.⁷ Another drawback of this methodology can considerably limit the scope of the catalytic system: as a typical example, the reagents for catalyst activation listed above readily react with functional groups in the substrates (carbonyl groups, etc.). In spite of the great practical importance of in situ generation of Ni(0) species for homogeneous catalysis applications, a mechanistic picture has not been addressed so far.⁸

Recently we have found that Ni(acac)₂ is an excellent catalyst precursor for the catalytic reactions of carbon–heteroatom bond formation.^{4,9} An active form of the catalyst was generated directly in a catalytic system containing phosphine ligands without addition of any dedicated reagents. Interestingly, Ni(acac)₂ was found to be a better catalyst precursor compared to NiCl₂ or Ni(OAc)₂.¹⁰

These results are unusual, since reduction of the metal center with phosphines requires coordination of the phosphine ligand as the first necessary step. At the moment no structures for the $[Ni(acac)_2(PR_3)_n]$ complexes have been reported, in sharp contrast with the case for other NiX₂ salts, where numerous $[NiX_2(PR_3)_2]$ derivatives have been prepared and characterized.¹¹ It was even assumed that Ni(acac)₂ does not coordinate phosphines and only in a few studies was coordination proposed on the basis of spectral and electrochemical measurements.¹²

In the present study we have addressed the questions of whether Ni(acac)₂ can be reduced by phosphine ligands to generate Ni(0) species and what is the pathway of this transformation. The metal complexes were detected in solution by NMR, the key species were isolated, and their structures were determined by X-ray analysis. Finally, the performances of directly added Ni⁰(COD)₂ catalyst and Ni(0) species generated in situ from Ni^{II}(acac)₂ were compared in selected catalytic reactions.

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Scheme 2. Formation of Ni^0L_n Species and Trapping with Diphenyl Disulfide



2. Results and Discussion

First, we explored the possibility of coordination of phosphine ligands with nickel acetylacetonate. After several attempts under different reaction conditions we have found that phosphine ligands coordinate to the nickel center (Scheme 2). A complex with 2 equiv of the PMe₂Ph ligand was isolated at -17 °C, and the structure of *trans*-[Ni(acac)₂-(PMe₂Ph)₂] (**1a**) was determined by X-ray analysis (Figure 1).¹³ Complex 1a possessed an elongated-octahedral coordination geometry with the metal-phosphorus bond length Ni-P =2.440 Å. The Ni-O distances between the metal and acac ligands, 2.028 and 2.045 Å, were slightly longer as compared to oxygen coordination in the bis(acetylacetonato)nickel diethanol complex Ni(acac)₂(EtOH)₂, 1.997 and 2.026 Å.¹⁴ In complex 1a the Ni-P distance was shorter and the Ni-O distances were longer compared to those in the trans-[Ni(1-C₆H₅-3-CF₃ $acac)_2(PPh_3)_2$ complex, where Ni-P = 2.552 Å and Ni-O = 2.011 and 2.013 Å.^{f2c}

The complex was stable in the solid state at low temperature, while an attempt to increase the temperature to roomtemperature conditions or to dissolve the complex in organic solvents afforded quick decomposition. Poor stability in solution and in the solid state is the likely reason, which precluded isolation of the complex in previous studies.

We have studied the decomposition pathways of complex **1a** and have found that it either underwent a back-reaction to a mixture of Ni(acac)₂ and PMe₂Ph or afforded formation of new metal species, according to ³¹P NMR. The formation of new species provided some evidence for possible generation of Ni(0). However, rather broad signals observed in the ³¹P NMR spectrum did not allow unambiguous identification of the products. In agreement with earlier studies, the NMR data for M^0L_n compounds in solution may not be characteristic, due to the dynamic nature of the system caused by ligand dissociation and the formation of series of species.¹⁵

A better way to identify Ni(0) species in solution is to trap them with an oxidative addition reaction and detect the formation of a well-defined metal complex, which gives an unambiguous NMR spectrum. In our case we proposed trapping with diphenyl disulfide in order to form a stable Ni(SPh)₂L₂ complex.¹⁶ To examine the reliability of the Ph₂S₂ trapping, first we

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⁽¹⁶⁾ Diphenyl disulfide was much more efficient for trapping Ni(0) species in comparison to the dialkyl disulfide ${}^{n}Bu_{2}S_{2}$. Single crystals of **1a** were obtained from the solution containing ${}^{n}Bu_{2}S_{2}$, which was not coordinated to the metal center.



Figure 1. X-ray molecular structures of *trans*-[Ni(acac)₂(PMe₂Ph)₂] (1a), *trans*-[Ni(SPh)₂(PMe₂Ph)₂] (2a), *trans*-[Ni(SPh)₂(PMePh₂)₂] (2b), and *trans*-[Ni(SPh)₂(PBu₃)₂] (2c).

studied the reaction with a well-known zerovalent nickel complex—bis(cyclooctadiene)nickel (Scheme 2). A clean reaction was observed in toluene at 40 °C; a yellow solution of Ni(COD)₂ immediately turned brown upon addition of the phosphine ligand and Ph₂S₂. The oxidative addition reaction was carried out with three different phosphine ligands— PMe₂Ph, PMePh₂, and PBu₃—and formation of a single complex was identified in the ³¹P NMR in each case with > 80% yield. Complexes **2a**-**c** were isolated from the toluene solution as crystalline products, and the structures were determined by X-ray analysis (Figure 1). A typical square-planar geometry was adopted in the complexes with a trans arrangement of the ligands and the distances Ni-P = 2.203–2.215 Å and Ni-S = 2.217–2.233 Å.¹³ In complexes **2a**, **c** the phenyl rings of the SPh groups possessed an anti orientation around the plane containing the metal and heteroatoms; the bond angles $P-Ni-P = 180.0^{\circ}$ and $S-Ni-S = 180.0^{\circ}$ were observed in both complexes. Complex **2b** crystallized with a syn orientation of the phenyl rings around the plane containing the metal and heteroatoms; the bond angles P-Ni-P = 169.3° and $S-Ni-S = 175.5^{\circ}$ were observed in the complex. The $\pi-\pi$ stacking interaction between the phenyl rings was present in the crystal of **2b**, and this was the likely reason for the change of the SPh group alignment.

This trapping procedure was applied to Ni(0) species generated from Ni(acac)₂ in toluene solution (Scheme 2). The formation of complexes 2a-c was observed in the studied reactions as detected with NMR. Identical ³¹P and ¹H spectra were recorded for the complexes 2a-cobtained from Ni(COD)₂ and Ni(acac)₂, thus confirming the generation of zerovalent nickel species from nickel acetylacetonate.



Scheme 4. Catalytic Stereoselective Addition of Diphenyl Disulfide to 3-Hexyne



[Ni] = Ni(COD)₂, PMePh₂: 99%, *Z/E* > 99/1 [Ni] = Ni(acac)₂, PMePh₂: 99%, *Z/E* > 99/1

It is interesting to consider the mechanistic pathway of in situ generation of Ni(0) species. Carrying out the reaction with a Ni(acac)₂·H₂O salt and PMe₂Ph ligand under ¹H NMR monitoring revealed the release of acacH.¹⁷ The formation of O=PMe₂Ph (3) was detected by ³¹P NMR and was proven by X-ray analysis.¹⁸ In the presence of water the reduction of Ni(II) to Ni(0) was accompanied by the oxidation of the phosphine ligand and transfer of the hydrogen atoms from water to the acac ligand (Scheme 3).

The same outcome was observed on carrying out the reaction with Ni(acac)₂ in the dried solvent—complexes **2a**-**c** were formed after reaction with Ph₂S₂. However, the release of free acacH was not observed in ¹H NMR. The presence of **3** was detected by ³¹P NMR, indicating that oxygen abstraction from the acac ligand took place. Since no ¹H NMR signals of acac residues or products of their transformation were resolved, we can propose that in the absence of water reduction of Ni(acac)₂ was accompanied by decomposition of the acetylacetonate ligand. The result is quite comparable with the reported reaction on reduction of Pd(OAc)₂ with phosphine ligands (PR₃), which led to the formation of O=PR₃ (via oxygen abstraction) and Ac₂O.³ In the case of acetylacetone dimerization of the residues should be considered unlikely.

Therefore, depending on the presence of water, two different pathways may operate in the system when reduction of Ni(II) to Ni(0) occurs in solution. In either case generation of zerovalent nickel species took place smoothly and formation of product 2 was observed. This preliminary evidence on the involvement of water could be of great importance in considering catalytic reactions. In a typical catalytic reaction a small amount of the metal complex is utilized in comparison to the other reagents and reduction of Ni(II) may be assisted by traces of water.

To reveal the efficiency of in situ generated zerovalent nickel species in catalysis, we have studied the catalytic addition of Ph_2S_2 to the triple bond of alkynes. The catalytic reaction is known to proceed with involvement of Ni(0) species and takes place with high stereoselectivity, producing only the Z isomer.¹⁹ Under the same conditions the reaction was carried out using two catalytic systems based on Ni-(COD)₂ and Ni(acac)₂ (Scheme 4). In both catalytic systems the product was formed in excellent yield (99%) with exceptional selectivity (>99/1). The isolated yield of **4** after purification with rapid flash chromatography was 85-87%.

Generation of zerovalent nickel species in situ resulted in a high-performance catalytic procedure as good as that involving bis(cyclooctadiene)nickel. As already outlined, Ni(acac)₂ is much cheaper and easier to handle (all manipulations were carried out in air), while Ni(COD)₂ is extremely air sensitive and requires a glovebox.

In conclusion, we have shown that a phosphine ligand can coordinate with nickel acetylacetonate and Ni(0) species can be smoothly generated in situ in solution. The nature of the Ni(0) species was confirmed by trapping experiments, and the structures of the resulting nickel complexes were established. It is important to generate Ni(0) for homogeneous catalysis by utilizing an additional amount of the phosphine ligand without using other reducing agents, which may alter the properties of the catalytic system. The replacement of Ni(0) with a readily available and stable catalyst precursor also has important practical advantages for developing costefficient synthetic procedures.

3. Experimental Section

3.1. General Procedures. All manipulations with Ni(COD)₂ were carried out in a glovebox under an argon atmosphere; manipulations with Ni(acac)₂ were carried out by the usual technique in air. Unless otherwise noted, Ni(acac)₂ was dried under vacuum (0.1–0.05 Torr, 60 °C, 30 min) before use. Solvents were purified according to published methods. The reactions were carried out in PTFE screw-capped tubes or flasks. NMR measurements were performed using Bruker AVANCE 500 and 600 MHz spectrometers. The spectra were processed on a Linux workstation using the TOPSPIN software package.

3.2. Synthesis of *trans*-[Ni(acac)₂(PMe₂Ph)₂] (1a). Ni(acac)₂ $(2.0 \times 10^{-4} \text{ mol}, 51.4 \text{ mg}), 0.75 \text{ mL}$ of toluene, and PMe₂Ph $(6.0 \times 10^{-4} \text{ mol}, 82.9 \text{ mg})$ were stirred until a homogeneous brown solution was formed (ca. 1–3 min).²⁰ A 3 mL portion of hexane was added to the mixture, which was then cooled to -17 °C. Blue crystals precipitated from the mixture over 5 h (50% yield).

3.3. Synthesis of *trans*-[Ni(SPh)₂(L)₂] (2a-c). Ni(COD)₂ $(2.0 \times 10^{-4} \text{ mol}, 53.4 \text{ mg})$ and 0.6 mL of toluene were stirred until a light yellow solution was obtained. The phosphine ligand $(6.0 \times 10^{-4} \text{ mol})$ was added to the solution, and the mixture was stirred for 1 min. Ph₂S₂ $(2.0 \times 10^{-4} \text{ mol}, 43.7 \text{ mg})$ was added to the mixture, which was then heated to 40 °C for 1 h. The mixture turned dark brown. The solvent was slowly evaporated at room temperature for a few days, and dark crystals were obtained (ca. 60% yield).

trans-[Ni(SPh)₂(PMe₂Ph)₂] (2a). ¹H NMR (C₆D₆; δ , ppm): 1.37 (12H, s), 6.97 (6H, m), 7.30 (m, 6H), 7.58 (4H, m), 7.80 (4H, m). ³¹P{¹H} NMR (C₆D₆; δ , ppm): -7.9. Anal. Calcd for C₂₈H₃₂NiP₂S₂: C, 60.78; H, 5.83; Ni, 10.61; S, 11.59. Found: C, 60.50; H, 6.01; Ni, 10.72; S, 11.33.

trans-[Ni(SPh)₂(PMePh₂)₂] (2b). ¹H NMR (C₆D₆; δ , ppm): 1.60 (6H, s), 6.91 (10H, m), 7.30 (5H, m), 7.62 (5H, m). ³¹P{¹H} NMR (C₆D₆; δ , ppm): -26.4. Anal. Calcd for C₃₈H₃₆NiP₂S₂: C, 67.37; H, 5.36; Ni, 8.66; S, 9.47. Found: C, 67.59; H, 5.62; Ni, 8.40; S, 9.16.

trans-[Ni(SPh)₂(PBu₃)₂] (2c). ¹H NMR (C_6D_6 ; δ , ppm; J, Hz): 0.86 (18H, t, J = 7.5), 1.27 (12H, m), 1.62 (12H, br m), 1.70 (12H, br m), 6.95 (2H, t, J = 7.4) 7.10 (4H, t, J = 7.3), 8.30 (4H,

⁽¹⁷⁾ The observed signals were compared with the spectrum of an authentic sample.

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⁽²⁰⁾ As an experiment to demonstrate the trapping inefficiency of dibutyl disulfide, ${}^{n}Bu_{2}S_{2}$ (2.0 × 10⁻⁴ mol, 35.7 mg) was added to the solution at this stage and the mixture stirred for 10 min. Single crystals of **1a** were obtained in the presence of ${}^{n}Bu_{2}S_{2}$ in the same yield.

d, J = 7.3). ³¹P{¹H} NMR (C₆D₆; δ , ppm): -1.4. Anal. Calcd for C₃₆H₆₄NiP₂S₂: C, 63.43; H, 9.46; Ni, 8.61; S, 9.41. Found: C, 63.65; H, 9.70; Ni, 8.31; S, 9.19.

3.4. NMR Monitoring of Formation of 2a-c. Ni $(acac)_2(1.0 \times 10^{-4} \text{ mol}, 25.7 \text{ mg})$ and 0.5 mL of toluene- d_8 were transferred to the NMR tube, followed by addition of the phosphine ligand $(3.0 \times 10^{-4} \text{ mol})$ and Ph₂S₂ $(1.0 \times 10^{-4} \text{ mol}, 21.8 \text{ mg})$. The mixture was heated to 40 °C for 1 h and shaken. The solution turned to dark brown. The ¹H and ³¹P NMR spectra were recorded directly for the mixture.

3.5. Catalytic Procedure for the Stereoselective Addition of Diphenyl Disulfide to 3-Hexyne.¹⁹ 3.5.1. Reaction with Nickel Acetylacetonate Catalyst Precursor. Ni(acac)₂ (3.0×10^{-5} mol, 7.7 mg), Ph₂S₂ (1.0×10^{-3} mol, 218.3 mg), PMePh₂ (3.0×10^{-4} mol, 60.0 mg), and toluene (0.5 mL) were placed in a reaction vessel and stirred at room temperature until a homogeneous brown solution was formed (ca. 1–3 min). 3-Hexyne (1.5×10^{-3} mol, 123.2 mg) was added to the solution, and the reaction was carried out at 100 °C for 8 h with stirring. An excess of the phosphine ligand was utilized to maintain homogeneous reaction conditions. After completion of the reaction the products were purified by dry column flash chromatography on silica (hexanes/toluene).²¹ After drying under vacuum the pure products were obtained. Compound **4** was identified by ¹H and ¹³C NMR according to the published data, and the elemental analysis was carried out to confirm purity (agreed within 0.1% with previously published data).¹⁹

3.5.2. Reaction with Bis(Cyclooctadiene) Nickel Catalyst. The procedure was the same as that above using $Ni(COD)_2$ instead of $Ni(acac)_2$.

3.6. Description of the X-ray Study. Single-crystal X-ray diffraction experiments were carried out with a Bruker APEX2 1000 CCD area detector at 100 K (**2b**) and 150 K (**2b**) and with a

Bruker SMART 1000 CCD area detector at 120 K (**1a**, **2c**), using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Experimental data have been corrected for absorption effects with the SADABS program.²²

The structures were solved by direct methods and refined by the full-matrix least squares method against F^2 in the anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were placed in geometrically calculated positions and refined in the isotropic approximation in the riding model. All calculations were performed using the SHELXTL software.²³

Crystallographic data and refinement parameters for compounds 1a and 2a-c, crystal packing and geometric parameters for the complexes, and details of the X-ray study of compound 3 are provided in the Supporting Information. Molecular structures for compounds 1a and 2a-c are shown in Figure 1.

Crystallographic data for the structures reported in this study have been deposited with the Cambridge Crystallographic Data Centre as supplementary CCDC files 775145 (1a), 775146 (2a), 775147 (2b), 775148 (2c), and 775149 (3).

Acknowledgment. The research work was supported by the Russian Foundation for Basic Research (Project No. 10-03-00370), Research Grant MD-4831.2009.3, and Program No. 1 of the Division of Chemistry and Material Sciences of the RAS.

Supporting Information Available: Tables, figures, and CIF files giving details of the X-ray structure analysis of compounds **1a**, **2a**–**c**, and **3** and geometric parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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