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Highly efficient [Ni{*i*PrHNC(S)NP(S)(O*i*Pr)$_2$-1,3-*N*,*S*′}$_2$]/PR$_3$ (R$_3$ = Me$_3$, Me$_2$Ph) complexes for the generation of Ni^0 for catalysis†

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We have developed new complexes of the type [Ni{*i*Pr-HNC(S)NP(S)(O*i*Pr)$_2$-1,3-*N*,*S*′}$_2$]/PR$_3$ (R$_3$ = Me$_3$, Me$_2$Ph) for the generation of Ni^0 catalysts which can be used for the catalytic addition of Ph$_2$S$_2$ to 1-, 2- and 3-hexynes. A detailed study of the catalytic reaction mechanism suggests two possible pathways for the *in situ* formation of Ni^0 species, depending on the presence or absence of water.

During the last few decades there has been an increasing interest in the palladium catalyzed stereoselective addition of alkyl$_2$S(Se)$_2$ and aryl$_2$S(Se)$_2$ substrates to various alkynes.[1] Phosphane ligands have been extensively used as additional ligands to generate catalytically active Pd^0 species. However, due to the increasing cost of Pd, cheaper and more readily accessible catalysts are desirable. Recently, it was established that some Ni^{II} salts and complexes in combination with phosphane ligands are also capable to catalyze the stereoselective addition of alkyl$_2$S(Se)$_2$ and aryl$_2$S(Se)$_2$ to alkynes.[1h,2] The presence of a phosphane seems to be a necessary condition to generate the Ni^0 species. Thus, the synthesis of new easily accessible and easy to handle Ni^{II} precatalytic systems is a formidable challenge and of importance.

The synthesis and complexation properties of *N*-(thio)-phosphorylated thioamides and thioureas RC(S)NHP(X)(OR′)$_2$ (X = O, S) (**NTT**) towards various metal cations has been studied.[3] We have undertaken extensive studies into the synthesis of Ni^{II} complexes with **NTT** (X = O) ligands and found, that the square-planar complexes **[Ni(NTT)$_2$]** exhibit either a 1,3-*N*,*S*- or a 1,5-*O*,*S* coordination mode (Chart 1, **A** and **B**). It was established, that intramolecular hydrogen bonds N–H···O=P are a necessary condition for the formation of 1,3-*N*,*S*-isomers for R = PhHN, *p*-MeOC$_6$H$_4$HN, *p*-BrC$_6$H$_4$HN, *i*PrHN, *t*BuHN, *cyclo*-C$_6$H$_{11}$HN, 1-AdHN, (4′-benzo-15-crown-5)HN,[4] while 1,5-*O*,*S* coordination takes place when H-bonding in the coordinated anionic ligands is not possible (R = Et$_2$N, morpholine-*N*-yl).[5] Moreover, *N*-phosphorylated thioamides RC(S)NHP(O)(O*i*Pr)$_2$ (R = *p*-BrC$_6$H$_4$, Ph)[6] form distorted octahedral complexes with Ni^{II}, where two deprotonated ligands are coordinated through the sulfur and oxygen atoms of the C=S and P=O groups, respectively, and two neutral forms of the ligands are bonded through the oxygen atoms of the P=O groups (Chart 1, **C**). Furthermore, the 1,3-*N*,*S*-coordination of the **NTT** (X = O) ligands towards Ni^{II} allows the synthesis of octahedral complexes by reaction with additional donor ligands such as 2,2′-bipyridine (**bpy**) and 1,10-phenanthroline (**phen**).[4e] It is important to note, that the **NTT** coordination to Ni^{II} is further complicated by the possibility that tetrahedrally configured complexes can be obtained as was recently shown for the complexes [Ni{R$_2$NC(S)NP(S)(O*i*Pr)$_2$}$_2$] (R = Me, H), which in polar solvents exhibit spectral features for a tetrahedral complex (colour, paramagnetism), while in unpolar solvents and in solid form complexes with a *trans* square-planar geometry exist (Chart 1, **B**). Both configurations exhibit clearly a 1,5-*S*,*S*′-coordination.[6]

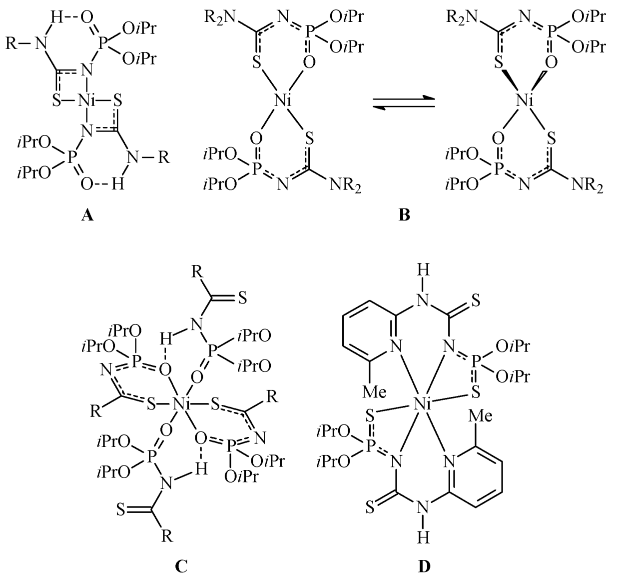

Chart 1

Recently we reported the first example of 1,5,7-*N*,*N*′,*S*-coordination of the deprotonated chelate ligand in the square-planar Ni^{II} complex [Ni{2-Py(6-Me)NHC(S)NP(S)(O*i*Pr)$_2$}$_2$]. The molecular structure of this complex has not been determined so far, but from spectroscopic results it is obvious, that the

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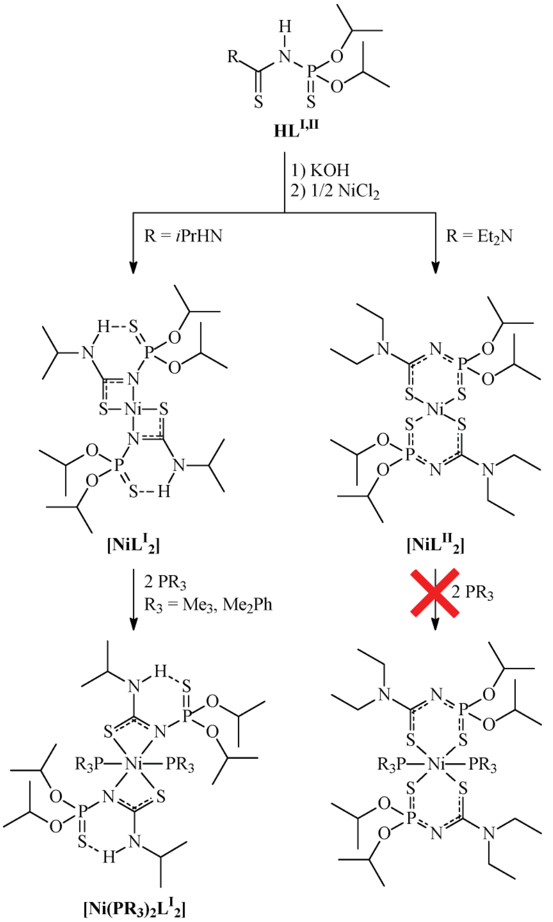
2-pyridyl donors of the ligand are also coordinated in an overall octahedral complex (Chart 1, **D**).[7] As a preliminary result we have also reported the formation of the 1,3-*N*,*S*-coordination mode in the *trans* square-planar Ni^{II} complex with the dithio-substituted **NTT** ligands.[8]

In this study we have investigated the formation of octahedral Ni^{II} complexes formed by the addition of a number of phosphanes to the square-planar complexes [Ni{*i*PrHNC(S)NP(S)(O*i*Pr)$_2$-1,3-*N*,*S*′}$_2$] (**[NiL$^{I}_2$]**) and [Ni{Et$_2$NC(S)NP(S)(O*i*Pr)$_2$-1,5-*S*,*S*′}$_2$] (**[NiL$^{II}_2$]**). The complexes of type **[Ni(PR$_3$)$_2$L$^{I}_2$]** (R = Me$_3$, Me$_2$Ph) have been used to generate Ni^0 species used in the catalytic addition of Ph$_2$S$_2$ to 1-, 2- and 3-hexynes.

Complexes **[NiL$^{I,II}_2$]** were prepared by following a similar procedure in each case. First, the ligand selected was deprotonated *in situ* using KOH, followed by reaction with NiCl$_2$ (Scheme 1, see also ESI†). The IR and NMR spectra confirm the formation of the complexes **[NiL$^{I,II}_2$]** (see ESI for additional information†).



Scheme 1 Preparation of the Ni^{II} complexes.

Complexes **[NiL$^{I,II}_2$]** were obtained as dark violet microcrystals. Dissolving the crystals of **[NiL$^{I}_2$]** in CH$_2$Cl$_2$ leads to a greenish-blue solution, while the DMF solution of **[NiL$^{I}_2$]**, and CH$_2$Cl$_2$ and DMF solutions of **[NiL$^{II}_2$]** are dark green. The spectrum of **[NiL$^{I}_2$]** in CH$_2$Cl$_2$ contains two intense bands in the UV region, one lying at 264 nm, the other one at 331 nm (see ESI†). Absorption bands for the free and protonated **NTT** ligands are rather high in energy ($\lambda_{\max}^{\mathrm{abs}} < 250$ nm) while the absorption bands of **KL^{I,II}** were observed at 298 and 301 nm (ε = 187–190 M^{-1} cm^{-1}), respectively. These absorptions have been assigned to intraligand transitions.[9] Thus, the UV absorptions of the complex **[NiL$^{I}_2$]** in CH$_2$Cl$_2$ can be assigned to corresponding intraligand transitions (π–π* or n-π* type). In the visible region essentially two absorption bands were observed, one at 532 nm and another being rather invariant at 649 nm. From the rather low intensities (164–171 M^{-1} cm^{-1}) of the two long-wavelength these bands were assigned to ligand field (d–d) transitions. The UV-Vis absorption spectra of **[NiL$^{I}_2$]** in DMF and **[NiL$^{II}_2$]** in CH$_2$Cl$_2$ and DMF are very similar. For a CH$_2$Cl$_2$ solution of **[NiL$^{II}_2$]** the spectrum showed an intense band at 246–270 nm with an intense shoulder at 265–281 nm in the UV region, as well as two bands at 531–535 nm and 644–662 nm accompanied by a shoulder at 438 nm. This spectrum is very similar to the UV-Vis absorption spectrum of the complex [Ni{H$_2$NC(S)NP(S)(O*i*Pr)$_2$}$_2$] in CH$_2$Cl$_2$.[6] Thus, the behavior of **[NiL$^{I}_2$]** in DMF and **[NiL$^{II}_2$]** in CH$_2$Cl$_2$ and DMF indicate that the deprotonated ligand **L^{I,II}** is coordinated exclusively in the 1,5-*S*,*S*′-mode, at least in the solvent studies.

The different behavior of the complex **[NiL$^{I}_2$]** in CH$_2$Cl$_2$ might be explained by the simultaneous presence of the 1,3-*N*,*S*- and 1,5-*S*,*S*′-isomers (as indicated by NMR measurements). It is noteworthy, that bands in the range of 700–800 nm, which are inherent features of tetrahedral or pseudo-tetrahedral complexes of Ni^{II},[10] were not observed in the electronic spectra of the complexes **[NiL$^{I,II}_2$]**, indicating a negligible contribution for pseudo-tetrahedral isomers in solution.

Crystals of **[NiL$^{I,II}_2$]** were obtained by slow evaporation of the solvent from CH$_2$Cl$_2$–*n*-hexane solution (see ESI†). The molecular structures of the complexes are shown in Fig. 1 and S1,† while selected bond lengths and angles are given in Table S1 (see ESI†).

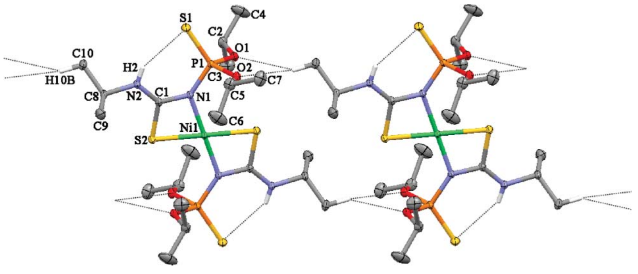


Fig. 1 Thermal ellipsoid (30%) plot of the complex **[NiL$^{I}_2$]**. H-atoms, not involved in hydrogen bonding and short contacts, have been omitted for clarity.

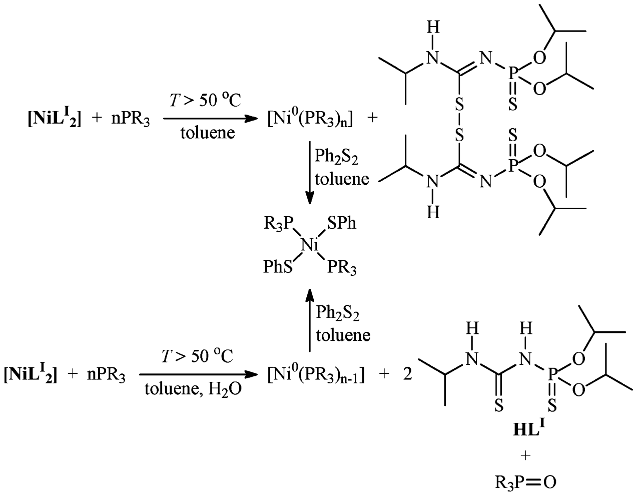
Complexes **[NiL$^{I,II}_2$]** crystallize in the triclinic space group $P\bar{1}$ and show centrosymmetric structures. The Ni^{II} ion is coordinated in a square-planar fashion with the donor atoms of the ligands arranged in a *trans*-configuration (Fig. 1 and S1 in ESI†). The four-membered Ni–S–C–N metallocycles are planar in **[NiL$^{I}_2$]**. The six-membered Ni–S–C–N–P–S metallocycles in the complex **[NiL$^{II}_2$]** adopt an asymmetric boat form. The values of the intracyclic S–Ni–N angles in the four-membered rings of **[NiL$^{I}_2$]** fall in the range of 74–75°, while the intracyclic S–Ni–S angle in **[NiL$^{II}_2$]** measures about 99°. Inspection of the C–S and P–N bond lengths of **[NiL$^{I}_2$]** indicates, that these bonds are best described as single bonds, while the P═S distances indicate the presence of a double bond (Fig. 1).[3] A lengthening of the C═S and shortening of the

C–N bonds has been observed upon formation of the complex **[NiL$^{II}_2$]** in comparison to the free **NTT** ligand.[3] The same change, but to a smaller degree, has been observed for the P–N and P=S bonds. The alkyl NH protons in **[NiL$^{I}_2$]** are involved in intramolecular hydrogen bonds of the N–H···S=P type (Fig. 1). Due to the formation of these hydrogen bonds, flat *syn*,*syn*-conformation of the N–C–N–P–S unit is favored. Furthermore, there are intermolecular hydrogen contacts of the C–H···O–P and C–H···S=C types in the complexes **[NiL$^{I,II}_2$]**, respectively (Fig. 1 and S1 in ESI†). These short contacts lead to the formation of polymeric chains in the crystal.

We studied the coordination of a number of phosphane ligands PR_3 (R_3 = Me_3, Me_2Et, $MeEt_2$, Me_2Ph, $MePh_2$, Et_3, Et_2Ph, $EtPh_2$, $(n\text{Pr})_3$, $(n\text{Pr})_2\text{Ph}$, $(n\text{Pr})\text{Ph}_2$, $(i\text{Pr})_3$, $(i\text{Pr})_2\text{Ph}$, $(i\text{Pr})\text{Ph}_2$, Cy_3, Cy_2Ph, $CyPh_2$, PPh_3) to the complexes **[NiL$^{I,II}_2$]**. According to the NMR and UV-Vis data it is evident that the complex **[NiL$^{II}_2$]** does not form any mixed-ligand compounds. It was also found, that the complex **[NiL$^{I}_2$]** forms the mixed-ligand structures exclusively with two equivalents of the PMe_3 and PMe_2Ph phosphanes (see ESI†). Furthermore, according to the NMR and UV-Vis data the reaction of **[NiL$^{I}_2$]** with one equivalent of PMe_3 or PMe_2Ph leads to the mixture of the starting complex and **[Ni(PR$_3$)$_2$L$^{I}_2$]** (R_3 = Me_3, Me_2Ph) with no evidence for the formation of pentacoordinated derivatives.[11] Such a behavior of the complex **[NiL$^{I}_2$]** might be due to the coordinatively unsaturated Ni^{II} atom in the N_2S_2 environment together with small S–Ni–N bite angles (Fig. 1) compared to the S_4 coordination environment and considerably bigger S–Ni–S angles in the complex **[NiL$^{II}_2$]** (Fig. S1 in ESI†). Complex **[NiL$^{I}_2$]** does not form mixed-ligand adducts with another phosphanes, probably, due to the bulky *i*PrO substituents (Fig. 1). It should be noted, that the 1,3-*N*,*S*-coordination mode of the deprotonated **NTT** ligands in the Ni^{II} complexes is conserved in the mixed-ligand complexes with additional donor ligands **bpy** and **phen**.[4e] Moreover, the introduction of the **bpy** or **phen** ligands into the coordination sphere of the metal cation of the complexes $[Zn\{RC(S)NP(O)(OiPr)_2\text{-}1,5\text{-}O,S\}_2]$ (R = H_2N, PhHN) leads to a change from 1,5-*O*,*S*- to 1,3-*N*,*S*-coordination of the anionic ligands.[12] Dissolving of the complexes **[Ni(PR$_3$)$_2$L$^{I}_2$]** in acetone, DMSO or DMF leads to the formation of a mixture of the starting complex **[NiL$^{I}_2$]** and free phosphanes. Only traces of the mixed-ligand complexes are observed in this case.

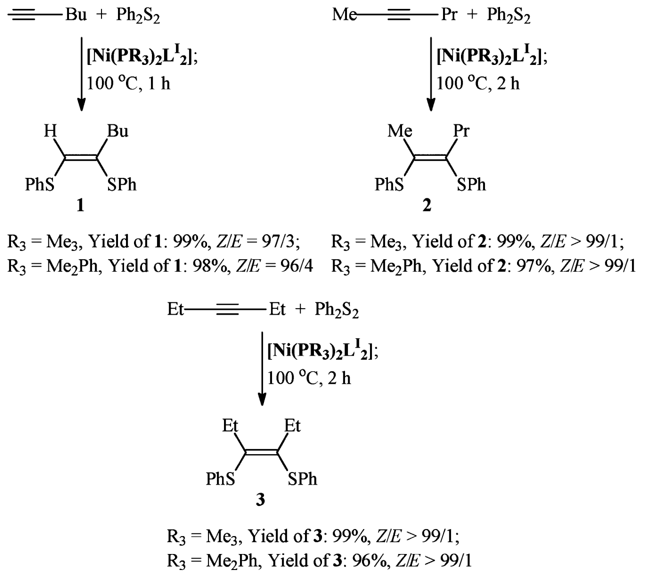
The NMR and IR data of the complexes **[Ni(PR$_3$)$_2$L$^{I}_2$]** are very similar and are in accordance with the proposed structures (see ESI†). A CH_2Cl_2 solution of **[Ni(PR$_3$)$_2$L$^{I}_2$]** shows an orange color and the UV-Vis spectra are characterized by an intense band in the UV region at 281–285 nm assigned to an intraligand transition in addition to several weak bands in the range 400–800 nm (see ESI†). A closer inspection reveals four absorption maxima with the wavelength band at about 785 nm (ε 15–17 M^{-1} cm^{-1}). The number of bands and the extremely low intensity is a strong indication for octahedral Ni^{II} species, while the d–d bands of complexes with tetrahedral geometry usually have ε values in the range 100–300 M^{-1} cm^{-1}.[13]

We have also noticed that increasing the temperature of the toluene solutions containing **[Ni(PR$_3$)L$^{I}_2$]** to values above 50 °C leads to a number of species. To identify the possible formation of Ni^0 we used Ph_2S_2, according to the described procedure,[2f] to trap the Ni^0 species by an oxidative addition reaction. The formation of the stable **[Ni(PR$_3$)$_2$(SPh)$_2$]** (R_3 = Me_3, Me_2Ph) complexes was observed. The same **[Ni(PR$_3$)$_2$(SPh)$_2$]** (R_3 = Me_3, Me_2Ph) complexes were formed using the reaction of **[Ni(COD)$_2$]/PR$_3$** with Ph_2S_2. We have also examined the decomposition mechanism of the complexes **[Ni(PR$_3$)$_2$L$^{I}_2$]** in dry and aqueous toluene. According to the $^{31}P\{^1H\}$ and ^1H NMR spectroscopy data the complexes decompose until formation of the disulfide $(i\text{PrO})_2\text{P(S)–N=C(NH}i\text{Pr)–S–S–C(NH}i\text{Pr)=N–P(S)(O}i\text{Pr)}_2$ was observed (Scheme 2). A related formation of similar disulfides with the generation of Hg^0 and Pd^0 species was found earlier.[14] Using aqueous toluene in the decomposition of **[Ni(PR$_3$)$_2$L$^{I}_2$]** leads to the formation of the **HL^{I}** ligand (see ESI†) and the corresponding phosphane oxide R_3P=O (R_3 = Me_3, Me_2Ph) (Scheme 2).



Scheme 2 Generation of **[Ni^0(PR$_3$)$_n$]** (R_3 = Me_3, Me_2Ph).

We have studied the catalytic reaction of Ph_2S_2 with 1-, 2- and 3-hexynes (Scheme 3) using the mixed-ligand complex systems



R_3 = Me_3, Yield of **1**: 99%, *Z*/*E* = 97/3;
R_3 = Me_2Ph, Yield of **1**: 98%, *Z*/*E* = 96/4

R_3 = Me_3, Yield of **2**: 99%, *Z*/*E* > 99/1;
R_3 = Me_2Ph, Yield of **2**: 97%, *Z*/*E* > 99/1

R_3 = Me_3, Yield of **3**: 99%, *Z*/*E* > 99/1;
R_3 = Me_2Ph, Yield of **3**: 96%, *Z*/*E* > 99/1

Scheme 3 Catalytic addition of Ph_2S_2 to 1-, 2- and 3-hexynes in toluene (1 mL) at 100 °C (*t* = 10–12 h; C(**[NiL$^{I}_2$]**) = 0.01 mmol, C(PR_3) = 0.1 mmol, C(hexyne) = 0.75 mmol).

[Ni(PR$_3$)$_2$L^I$_2$] as precatalysts (see ESI†). It is known, that this type of reaction is catalyzed by Ni^0 species.[2]

It was found that the products of the catalytic reaction **1–3** are formed in high yields (96–99%) and with efficient selectivity from 96/4 to > 99/1 (Scheme 3). However, the addition of Ph$_2$S$_2$ to 1-hexyne has shown the worst selectivity among the studied alkynes. This might be explained by the higher lability of 1-hexyne. Furthermore, the isolated yields of **1–3** were 91–95%. These results are compared with the data for the **[Ni^{II}(acac)$_2$]** and **[Ni^0(COD)$_2$]** complexes as precatalysts.[2f] Using the latter compounds together with PMePh$_2$ in the catalytic addition of Ph$_2$S$_2$ to 3-hexyne also leads to the formation of **3** in high yield (99%) and a selectivity of > 99/1. However, this reaction requires 3 h. Furthermore, handling of **[Ni(COD)$_2$]** is rather complicated and requires an inert atmosphere. In contrast to this situation, the complexes **[Ni(PR$_3$)$_2$L^I$_2$]** (R = Me$_3$, Me$_2$Ph) are easily synthesized and can be isolated with no precautions necessary. They can be kept in air at least for several months without any signs of decomposition, while the complex **[Ni(PMe$_2$Ph)$_2$(acac)]** was isolated at −17 °C and is only stable at low temperature.[2f] Thus, the Ni^{II} complex **[NiL^I$_2$]** in combination with phosphanes PR$_3$ (R$_3$ = Me$_3$, Me$_2$Ph) yields a highly efficient mixture for the generation of Ni^0 species *in situ*, which subsequently show a high catalytic activity in the addition of Ph$_2$S$_2$ to 1-, 2- and 3-hexynes.

We have synthesized the Ni^{II} complexes [Ni{*i*PrHNC(S)NP(S)(O*i*Pr)$_2$-1,3-*N*,*S*}$_2$] **[NiL^I$_2$]** and [Ni{Et$_2$NC(S)NP(S)(O*i*Pr)$_2$-1,5-*S*,*S*′}$_2$] **[NiL^{II}$_2$]**. The former complex is the first example for a Ni^{II} complex containing an asymmetric **NTT** ligand featuring an alkyl-NH substituent at the thiocarbonyl group and coordinating to the metal in the 1,3-*N*,*S*-fashion in the solid state. It was established that the complex **[NiL^I$_2$]** forms stable mixed-ligand octahedral complexes with phosphanes PR$_3$ (R$_3$ = Me$_3$, Me$_2$Ph). These mixed-ligand complexes are efficient precatalysts for the *in situ* generation of Ni^0 species which were successfully used to catalyze the addition of Ph$_2$S$_2$ to 1-, 2- and 3-hexynes.

Acknowledgements

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