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Synthesis of symmetric and non-symmetric Ni(II) thiophosphinito PECSP (E = S, O) pincer complexes and applications in Kumada coupling under mild conditions

Patrick Hasche,[a] Markus Joksch,[a] Georgia Vlachopoulou,[a] Hemlata Agarwala,[a,b] Anke Spannenberg,[a] and Torsten Beweries*[a]

Abstract: The reaction of 1,3-dimercaptobenzene with $i\mathrm{Pr_2PCl}$ in the presence of the base NaH, furnishes the symmetric ligand $[\mathrm{C_6H_4}\text{-1,3-}(\mathrm{SP}i\mathrm{Pr_2})_2]$ (**1a**). The direct reaction of this ligand as well as of the literature-known non-symmetric ligand $[\mathrm{C_6H_4}\text{-1-}(\mathrm{SP}i\mathrm{Pr_2})\text{-3-}(\mathrm{OP}i\mathrm{Pr_2})]$ (**1b**) with $\mathrm{NiCl_2}$ affords the symmetric bis(thiophosphinito) PSCSP pincer complex $[\{\mathrm{C_6H_3}\text{-2,6-}(\mathrm{SP}i\mathrm{Pr_2})_2\}\mathrm{NiCl}]$ (**2a**) as well as the phosphinito–thiophosphinito POCSP pincer complex $[\{\mathrm{C_6H_3}\text{-2-}(\mathrm{SP}i\mathrm{Pr_2})\text{-6-}(\mathrm{OP}i\mathrm{Pr_2})\}\mathrm{NiCl}]$ (**2b**). Both complexes were fully characterized and their catalytic performance in Kumada coupling of aryl halides and *p*-tolyl magnesium bromide under mild conditions was evaluated.

Introduction

Transition metal pincer complexes represent a group of compounds with very unique and interesting properties, among which their high thermal stability and robustness as well as the readily tunable nature of the tridentate ligand should be the most highlighted.[1] As a consequence, pincer compounds have attracted considerable attention of the chemistry community for a variety of applications, particularly in homogeneous catalysis.[2] Depending on the field of interest, organometallic chemists have developed different types of pincer complexes, containing a wide range of donor/acceptor groups, backbone structures, or side-arm moieties that allow for a rational control of steric and electronic properties of the catalysts.[3] Moreover, enantiomerically pure complexes have been employed in asymmetric catalysis and enantioselective synthesis.[4]
As one of the most notable variations of pincer compounds, Jensen[5] and Brookhart[6] presented bisphosphinite Ir complexes of the type $[(^{R}\mathrm{POCOP}^{R})\mathrm{IrHX}]$ ($^{R}\mathrm{POCOP}^{R} = \kappa^3\text{-1,3-}(\mathrm{OPR_2})_2\text{-}\mathrm{C_6H_3}$; R = *t*Bu; X = H, Cl) that showed by orders of magnitude better performance in cycloctane (COA)/*t*-butyl ethylene (TBE), transfer dehydrogenation reactions than the parent, oxygen free PCP Ir complexes (PCP = $\kappa^3\text{-1,3-}(\mathrm{CH_2PR_2})_2\text{-}\mathrm{C_6H_3}$).[7] As an extension of this concept, later Huang and co-workers reported on the catalytic dehydrogenation of *n*-alkanes and heterocycles using a related PSCOP pincer Ir catalyst $[(^{iPr}\mathrm{POCSP}^{iPr})\mathrm{IrHCl}]$ (Figure 1) under relatively mild conditions.[8] Comparison of catalytic activity with the related $[(^{tBu}\mathrm{POCOP}^{tBu})\mathrm{IrHCl}]$ showed significantly better performance of the POCSP complex, yet it should be noted that direct comparison of these complexes is difficult due to subtle differences in the phosphine donor sites. Later, the same authors presented a thorough study of COA/TBE transfer dehydrogenation using isostructural $^{tBu}\mathrm{POCOP}^{tBu}$ and $^{tBu}\mathrm{POCSP}^{tBu}$ Ir complexes and found lower activity for the latter catalysts.[9] However, hemilability of one of the side arms of the pincer ligands might be of importance in this case as it was discussed before for asymmetric pincer complexes on several occasions.[10] Apart from these Ir complexes, only a handful of other $^{R}\mathrm{POCSP}^{R}$ transition metal complexes are known (Figure 1). Huang *et al.* presented a study of acceptorless COA dehydrogenation using a series of $^{R}\mathrm{POCSP}^{R}$ Ru catalysts[11] and the group of Morales-Morales reported on a $^{Ph}\mathrm{POCSP}^{Ph}$ Pd chlorido complex that was tested for Suzuki-Miyaura cross coupling reaction of bromobenzene and phenylboronic acid. Also in this case the asymmetric complex was found to be a better, faster catalyst than the symmetric $^{Ph}\mathrm{POCOP}^{Ph}$ analogue under identical reaction conditions.[12]

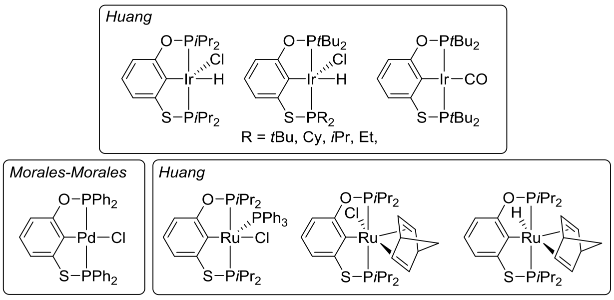

Figure 1. Hitherto known $^{R}\mathrm{POCSP}^{R}$ pincer complexes.

The absence of systematic studies of these asymmetric, potentially hemilabile ligands along with promising catalytic effects reported prompted us to further investigate $^{R}\mathrm{POCSP}^{R}$ complexes of other transition metals. In recent studies, we had reported on the synthesis of isostructural group 10 $^{tBu}\mathrm{POCOP}^{tBu}$ halido complexes.[13] For this study, we decided to focus on a comparison of Ni complexes that possess ligands with no, one, or two S atoms. It should be noted that $^{R}\mathrm{PSCSP}^{R}$ ligands or complexes thereof are unknown to date.

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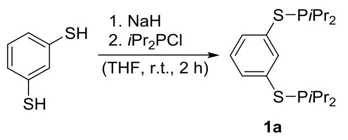
Supporting information for this article is given via a link at the end of the document. CCDC 1584392 and 1584393 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Results and Discussion

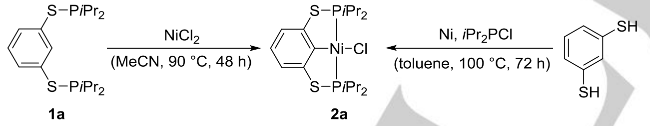
The reaction of 1,3-dimercaptobenzene with two equivalents of $i\text{Pr}_2\text{PCl}$ in the presence of the base NaH in THF affords the ligand $[\text{C}_6\text{H}_4\text{-1,3-(SP}i\text{Pr}_2)_2]$ (**1a**) as a colourless clear viscous oil with yields >90% (Scheme 1).



Scheme 1. Synthesis of ligand **1a**.

Analysis of this ligand by ^{1}H NMR spectroscopy (benzene-d_6) shows the aromatic fragment as well as characteristic signals due to the isopropyl group at 1.03, 1.14, and 1.82 ppm. ^{31}P{^{1}H} NMR spectra in benzene-d_6 show the presence of a sharp singlet at 66.2 ppm. Comparison with the -SPR_2 ^{31}P NMR resonance of Huang's $^{i\text{Pr}}$POCSP$^{i\text{Pr}}$ ligand **1b** (*cf.* 68.7 ppm in CDCl_3) shows that the value for **1a** is in the same range despite the absence of the electron withdrawing -OPR_2 moiety. Based on quantitative ^{31}P NMR spectra, ligand **1a** was found to be pure enough to be directly used in the following metallation step.

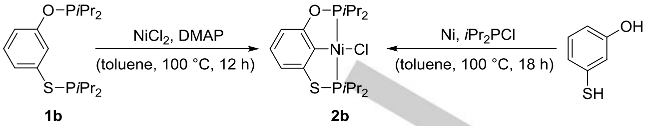
For complexation of ligands **1a** and **1b** to Ni, we have evaluated different protocols that were previously described for the synthesis of related complexes of the type [($^{\text{R}}$POCOP$^{\text{R}}$)NiCl].[14] Reaction of ligand **1a** with anhydrous NiCl_2 in refluxing toluene in the presence of dimethylaminopyridine (DMAP) to assist C-H activation and scavenge the HCl by-product did not give the desired product **2a**. However, when DMAP was omitted and the solvent was changed to MeCN, the symmetric bis(thiophosphinito) complex **2a** was obtained as a yellow, microcrystalline solid in low yields (around 20%) due to its good solubility in non-polar solvents (Scheme 2).



Scheme 2. Synthesis of complex **2a**.

Alternatively, this complex can be accessed in a more atom-efficient and convenient way starting from Ni powder, diisopropylchlorophosphine, and 1,3-dimercaptobenzene, thus avoiding previous synthesis and isolation of ligand **1a** (Scheme 2). The latter one-pot procedure was presented recently by Zargarian and co-workers for related [($^{\text{R}}$POCOP$^{\text{R}}$)NiCl] complexes.[14c]

The synthesis of the related non-symmetric complex [($^{i\text{Pr}}$POCSP$^{i\text{Pr}}$)NiCl] (**2b**) can be performed in yields of up to 40% using the aforementioned protocol that uses DMAP as a base (Scheme 3). However, also in this case, direct reaction of the ligand precursors, diisopropylchlorophosphine and 3-mercaptophenol, with Ni powder affords the desired complex as yellow crystals in similar yields (Scheme 3).



Scheme 3. Synthesis of complex **2b**.

Investigation of these complexes by ^{1}H NMR spectroscopy in toluene-d_8 shows characteristic signals for the aromatic ligand backbone along with CH and CH_3 resonances due to the P$i\text{Pr}_2$ groups. ^{31}P{^{1}H} NMR analysis of both complexes **2a** and **2b** in toluene-d_8 shows that coordination of the ligands to the Ni centre results in a significant downfield shift of the P$i\text{Pr}_2$ resonances (**1a**: 66.2; **2a**: 98.9 ppm and **1b**: SP$i\text{Pr}_2$ 65.2, OP$i\text{Pr}_2$ 148.7; **2b**: SP$i\text{Pr}_2$ 105.0, OP$i\text{Pr}_2$ 179.7 ppm). Compared to the analogous bisphosphinite Ni complex [($^{i\text{Pr}}$POCOP$^{i\text{Pr}}$)NiCl] (**2c**) which was described by Zargarian *et al.*, the value for OP$i\text{Pr}_2$ for **2b** is in the same range (*cf.* **2c**: 185.5 ppm).[15] Notably, the substitution of O for the less electron-withdrawing S in the side arms of the pincer ligands results in a shielding of the P nuclei and thus gives resonances for SP$i\text{Pr}_2$ in the upfield region of the ^{31}P NMR spectra. Mass spectrometric analysis of both complexes **2a** and **2b** using chemical ionisation in positive mode shows the molecular ion peaks along with characteristic signals due to the loss of the chloride ligands.

Single crystals of both complexes suitable for X-ray analysis were obtained from saturated toluene (**2a**) or THF/*n*-hexane (**2b**) solutions at -78 °C. The molecular structures are depicted in Figure 2.

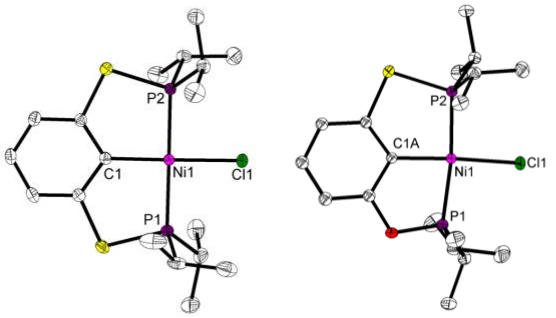


Figure 2. Molecular structures of complexes **2a** and **2b**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms as well as the second position of the disordered ligand (for **2b**) are omitted for clarity.

Both complexes display distorted square planar coordination geometries around the Ni centre.[16] Bond lengths are in the expected range and resemble those found before for complex **2c** (Table 1). Density Functional Theory (DFT) calculations were performed on these complexes (see Experimental Section for details). The bond distances and angles of the optimised structures agree well with the values obtained from X-ray analysis (Table 1 and S2). Interestingly, introduction of the two S atoms results in a significant change in the coordination geometry. For **2c** coordination around the Ni centre is best described as distorted square planar, whereas for **2a** only very minor deviation from that coordination geometry is observed,

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2a**, **2b**, and **2c**.

	2a		**2b**		**2c**	
	X-ray analysis	DFT[a]	X-ray analysis	DFT[a]	X-ray analysis[c,d]	DFT[a]
Ni-C	1.9190(15)	1.927	[b]	1.907	1.879(2) 1.875(2)	1.887
Ni-Cl	2.2134(4)	2.255	2.1945(4)	2.239	2.1944(6) 2.1887(6)	2.225
Ni-P1	2.1671(4)	2.177	2.1395(4)	2.145	2.1582(6) 2.1533(6)	2.158
Ni-P2	2.1589(4)	2.175	2.1686(4)	2.185	2.1603(6) 2.1379(6)	2.157
C-Ni-P1	89.82(6)	90.30	[b]	83.68	82.20(6) 82.80(6)	82.50
P1-Ni-Cl	90.73(2)	89.48	93.00(2)	92.82	97.70(2) 98.94(2)	97.66
Cl-Ni-P2	89.65(2)	90.01	93.83(2)	93.59	97.88(2) 96.16(2)	97.30
P2-Ni-C	89.80(5)	90.21	[b]	89.91	82.33(6) 82.12(6)	82.54

[a] M06/6-31G*(for C,H,O,S,P,Cl)/LanL2DZ(for Ni)/vacuum. [b] Values are not given due to strongly disordered POCSP ligand. [c] Data from Ref. 15. [d] Two molecules are present in the asymmetric unit.

most likely due to the larger size of S that releases ring strain in the five-membered metallacyclic units formed by each of the side arms of the pincer ligand (Table 1). As a consequence, for complex **2a**, P donor atoms are located above (0.34 Å) and below (-0.33 Å) the plane formed by the Ni centre, S and the C atoms of the aryl backbone.[17]

For an initial evaluation of the catalytic performance of complexes **2a** and **2b** compared to the known **2c**, we tested these as pre-catalysts for Kumada coupling reaction between different aryl halides and *p*-tolyl magnesium bromide. Since the pioneering work in the 1970s by Kumada and Curriu[18], group 10 metal catalysed C–C coupling between aryl halides and Grignard reagents were extensively investigated in the past and widely used in modern synthetic organic chemistry. Exploration of catalytic systems for activation of unactivated electrophilic substrates such as aryl chlorides is still of significant interest.[19] A number of different types of nickel complexes have been reported to catalyse the Aryl-Alkyl and Alkyl-Alkyl Kumada coupling effectively.[20,21] Each of the complexes **2a**-**2c** was capable of catalysing the cross coupling reactions in THF at room temperature within 24 hours to yield the desired biaryl **3** along with considerable amounts of the Grignard homocoupling product **4** (Table 2) and protio-quenched material (*i.e.* toluene).

Among the catalysts tested, the Ni bis(phosphinito) POCOP pincer complex **2c** showed relatively low catalytic activity and only very low conversion of the starting materials (Table 2, entries 1-3), while **2b** (Table 2, entries 4-6), and especially **2a** showed moderate to good conversion after 24 hours at room temperature and promising catalytic activity with respect to formation of the coupling product **3** (Table 2, entries 7-9). For example, in the reaction of *p*-Me-C_6H_4MgBr and PhCl, formation of **3** was observed in 62% yield. Formation of the homocoupling product **4** was however a problem in all experiments. In general, formation of these side products is often observed at higher reaction temperatures. It is interesting to note, however, that the selectivity towards the heterocoupled product **3** is higher with **2c** than **2a** or **2b**, as can be seen from the ratio of **3**/**4** (Table 2). Unfortunately, when reactions were performed at 0 °C, formation of the product of homocoupling **4** could not be suppressed. However, especially complex **2a** still shows promising activity and good conversion of most aryl halide starting materials (Table 2, entries 10-12). In contrast to reactions at 25 °C, where the yield was mainly only determined by the used catalyst, reactions at 0 °C also revealed PhI as the most useful aryl halide. In previous studies[21d], independent reactions of the catalyst with both coupling partners were performed to evaluate the possibility of a radical pathway that includes single electron transfer between coupling partners and subsequent reduction of the Ni(II) centre. Therefore, we investigated the reaction of Ni complexes **2a**, **2b**, and **2c** with 2 equivalents of *p*-Me-C_6H_4MgBr in THF at room temperature and the ^{31}P NMR spectra showed significant differences with slow formation of the corresponding aryl complex for **2b** and **2c**. In case of **2b**, this species slowly converts into an unknown species. For **2a**, we did not observe the aryl complex, instead rapid formation of the aforementioned unknown species takes place. No reaction occurs between PhI and any of the catalyst complexes. As we see significant reactivity of the Ni catalysts with the Grignard component, we believe that in our case interaction of the Ni(II) halide with the substrate is a key step as it was reported before.[22]

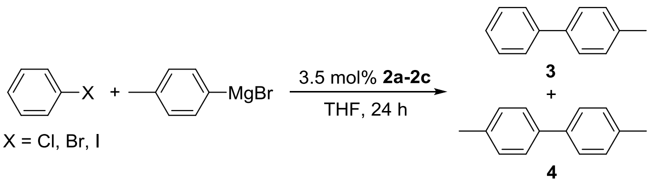


Table 2. Catalytic coupling of p-Me-C_6H_4MgBr and aryl halides by complexes **2a**-**2c**.[a]

entry	aryl halide	catalyst	T [°C]	conversion **3** [%]	yield **3** [%]	yield **4** [%]	ratio **3**/**4**
1	PhCl	**2c**	25	13	14	1	14.00
2	PhBr	**2c**	25	6	6	1	6.00
3	PhI	**2c**	25	7	8	1	8.00
4	PhCl	**2b**	25	18	19	2	9.50
5	PhBr	**2b**	25	41	51	23	2.22
6	PhI	**2b**	25	32	41	21	1.95
7	PhCl	**2a**	25	56	62	7	8.86
8	PhBr	**2a**	25	48	58	18	3.22
9	PhI	**2a**	25	57	69	17	4.06
10	PhCl	**2a**	0	35	28	4	7.00
11	PhBr	**2a**	0	35	30	9	3.33
12	PhI	**2a**	0	78	60	11	5.45

[a] Reaction conditions: 3.5 mol% catalyst, 0.6 mmol Grignard reagent, 0.5 mmol aryl halide, THF, 24 h. 50 µL of n-dodecane were used as an internal standard. Yields were determined with GC.

Analysis of the DFT calculated molecular orbitals (MOs) for complexes **2a**, **2b**, and **2c** reveals substantial differences that might explain the differences in reactivity. Looking into the contribution of different molecular fragments in each of the complexes, to the molecular orbitals (Tables S3-S5), it can be noted that for complex **2c**, Ni gives the largest contribution (44%) to the HOMO (Table S5). On the contrary, in the case of **2a** (Table S3) and **2b** (Table S4), the most significant portion of the HOMO is made up by the S atoms in the side arm of the pincer ligands (MO contribution from S: 23% (**2a**, averaged); 37% (**2b**)). However, the higher contributions of Ni to the HOMO−n (n=1-5) orbitals in **2a** and **2b** should be kept in mind. As it has been reported in the previous studies on Ni(II) pincer halide catalysed Kumada coupling reactions, oxidation of the Ni centre is often discussed to be an important step of the catalytic cycle.[20] Therefore, as is apparent from the MO contributions, the Ni(II) centre in **2c** is most likely to undergo oxidation compared to the other probable sites in the catalyst, during the catalytic cycle. Alternatively, if the coupling proceeds via reduction of the precatalyst, it can be predicted from the fragment contributions (Tables S3-S5) to the LUMO, that all the three complexes would show similar reactivity towards reduction, which would principally be on the Ni center (Ni: 28/29%, P (averaged): 12-16%, C_{ipso}: 10-11%; Tables S3-S5). However, from preliminary experiments it is observed that the aryl group of the Grignard reagent binds to Ni, with considerably varying rates of reactivity for the three complexes **2a**-**c**. Hence, it is not just the electronic situation of the Ni centre which affects the kinetics of the catalysis, but some other factors seem to be operating. A detailed explanation of the mechanistic aspects of the catalysis involved herein as well as of the further potential of complexes **2a** and **2b** needs additional investigation, which is currently being undergone in our lab, and will be revealed in the upcoming future.

Conclusions

In summary, we have presented the synthesis and characterisation of two Ni(II) chloride complexes that display bis(thiophosphinito) PSCSP (**2a**) and phosphinito–thiophosphinito POCSP (**2b**) pincer ligands. Both complexes were tested in Kumada cross coupling reactions of aryl halides and p-tolyl magnesium bromide under mild conditions and showed significantly better activity than the known bis(phosphinito) POCOP complex **2c**.

Acknowledgements

We thank our technical and analytical staff, in particular Benjamin Andres, for assistance. Support by LIKAT is gratefully acknowledged.

Keywords: nickel • pincer complexes • homogeneous catalysis • coupling reactions • X-ray analysis

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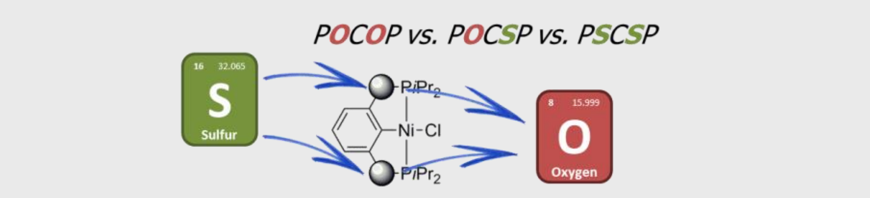

Nickel POCSP and PSCSP pincer complexes have been prepared for the first time using two different protocols: metalation of the pincer ligand precursor, as well as direct one-pot synthesis starting from Ni powder and the arene and phosphine components. Both complexes were studied in an Aryl-Aryl Kumada coupling, showing better activity than a similar POCOP complex.

Pincer Complexes

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Synthesis of symmetric and non-symmetric Ni(II) thiophosphinito PECSP (E = S, O) pincer complexes and applications in Kumada coupling under mild conditions