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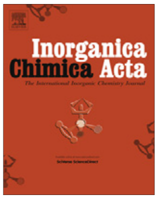

Structural and spectroscopic characteristics of [Ni{(Ph$_2$P)$_2$N-*S*-CHMePh-*P*,*P′*}X$_2$], X = Cl, Br: Catalytic activity and selectivity in Kumada and Suzuki–Miyaura coupling reactions

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ABSTRACT

The [Ni{(Ph$_2$P)$_2$N-*S*-CHMePh-*P*,*P′*}Br$_2$] complex was prepared by a ligand-exchange reaction between [Ni(dme)Br$_2$] (dme is 1,2-dimethoxyethane) and the P–N–P ligand (Ph$_2$P)$_2$N(*S*-CHMePh). X-ray crystallography revealed a square planar NiP$_2$Br$_2$ coordination sphere, i.e., the presence of a four-membered Ni–P–N–P ring. The same structural features with nearly equal values of the X–Ni–X, P–Ni–P and P–N–P angles have been earlier revealed for the isomorphous [M{(Ph$_2$P)$_2$N-*S*-CHMePh-*P*,*P′*}Cl$_2$], M = Ni, Pd, complexes. The structure of the above complexes significantly differs from that of [Ni(dppp)Cl$_2$] (dppp is 1,3-bis{diphenylphosphine}propane). This NiP$_2$Cl$_2$-type complex comprises a six-membered Ni–P–C–C–C–P ring, with significantly larger P–Ni–P and much smaller Cl–Ni–Cl angles. The ^{1}H and ^{31}P NMR properties of [Ni{(Ph$_2$P)$_2$N-*S*-CHMePh-*P*,*P′*}Br$_2$] are consistent with its crystal structure. The [Ni{(Ph$_2$P)$_2$N-*S*-CHMePh-*P*,*P′*}X$_2$] complexes were tested as catalysts in Kumada and Suzuki–Miyaura coupling reactions, and their reactivity was compared with that of [Ni(dppp)Cl$_2$]. The differences observed in their catalytic efficiency are discussed with regards to their structural characteristics.

1. Introduction

During the last four decades, various cross-coupling reactions have been thoroughly investigated [1–6], which has yielded well established preparative methods of major importance for chemical synthesis. A steady development of coupling reactions afforded methods for the formation of C–C bonds under very mild conditions and with excellent tolerance to many functional groups. Many transition metal ions, such as Cr(III), Fe(III), Co(II), Mn(II), Ru(0, I, II, III), Ni(II) and Pd(II) were shown to form complexes that are catalytically active in cross-coupling reactions [7,8]. The most widely used catalysts are based on complexes of Pd(II) with ligands such as mono- or multi-dentate phosphines and *N*-heterocyclic carbenes [9–11]. Among the most promising alternative to those Pd(II) complexes are similar complexes of Ni(II) [12], the cost of which is significantly lower. However, these complexes are usually less active than their Pd(II) counterparts, with only a few exceptions [13,14]. Therefore, the development of novel Ni(II) catalysts with increased catalytic efficiency in various types of reactions is of interest to academic as well as industrial researchers.

The catalytic activity in the vinyl type polymerization of norbornene has been recently investigated for two [Ni(P,P)Cl$_2$] type of complexes, namely [Ni{(Ph$_2$P)$_2$N(*p*-C$_6$H$_4$OMe)-*P*,*P′*}Cl$_2$] [15] and [Ni{(Ph$_2$P)$_2$N-*S*-CHMePh-*P*,*P′*}Cl$_2$] [16] bearing P–N–P chelating ligands [17]. In addition, analogous [Ni(P,P)Br$_2$] complexes with various groups linked to the nitrogen atom of the P–N–P ligand backbone have been employed as catalysts for the polymerization [18] and oligomerization [19] of ethene. However, complexes of this type have not yet been examined as catalysts in other types of reactions, and, therefore, additional investigations are highly desirable. Towards this aim, herein, we report on the catalytic activity of [Ni{(Ph$_2$P)$_2$N-*S*-CHMePh-*P*,*P′*}X$_2$], X = Cl, Br, in Kumada and Suzuki–Miyaura coupling reactions. The former reaction has been recently employed by some of us for the synthesis of polymeric materials [20,21]. The new dibromo-containing complex was spectroscopically and crystallographically characterized and found to have a square planar NiP$_2$Br$_2$ coordination sphere and a four-membered Ni–P–N–P ring. The recently described analogous dichloro complex exhibits a similar metal-ligand ring and an NiP$_2$Cl$_2$ coordination sphere [16]. In parallel, in this work we report

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Table 1
Crystallographic data for [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2].

	[Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2]·CH_2Cl_2
Formula	$C_{33}H_{31}Br_2Cl_2NNiP_2$
Fw	792.96
Space group	$P2_12_12_1$
a (Å)	8.7343(1)
b (Å)	18.1316(3)
c (Å)	20.7322(3)
V (Å^3)	3283.29(8)
Z	4
T (°C)	−93
Radiation	Cu Kα
ρ_{calcd} (g cm^{-3})	1.604
μ (mm^{-1})	6.306
R_1[a]	0.0397[b]
wR_2[a]	0.1043[b]
CCDC	849058

[a] $w = 1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP]$ and $P = ((\max F_o^2, 0) + 2F_c^2)/3$, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[b] For 5258 reflections with $I > 2\sigma(I)$.

on the activity of [Ni(dppp)Cl_2] (dppp is 1,3-bis{diphenylphosphine}propane), which also contains a square planar NiP_2Cl_2 coordination sphere, but a six membered Ni–P–C–C–C–P ring [22]. The results obtained point to the importance of the chelate ring size for the catalytic activity of these complexes.

2. Experimental

2.1. Materials and methods

All syntheses were performed under an argon atmosphere. The solvents used were dried and distilled according to literature procedures [23]. The $(Ph_2P)_2$N(*S*-CHMePh) ligand [24a] as well as the [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Cl_2] [16] and [Ni(dppp)Cl_2] [22] complexes were synthesized using procedures described in the literature. The chemical reagents needed for the synthesis of the above compounds as well as [Ni(dme)Br_2] (dme is 1,2-dimethoxyethane) and catalyst PEPPSI™-IPr [10] were purchased from Aldrich. FTIR spectra were recorded on a Shimadzu IR Affinity-1 instrument using KBr pellets. NMR spectra were recorded on a Varian V 300 MHz spectrometer at 25 °C. Kumada as well as Suzuki–Miyaura coupling reactions were carried out under an argon atmosphere using Schlenk techniques; reaction conditions are listed in Table 4. The resulting reaction mixtures were analyzed by the GC-FID method (Shimadzu 6000) to obtain yields of products and side products of catalytic reactions. Mesitylen was used as an internal standard. The calibration standards were obtained by the chromatographic (silicagel/hexane) purification of the products of reactions introduced as entries Std in Table 4 (Kumada coupling induced with [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2]) and Table 5 (Suzuki–Miyaura coupling induced with PEPPSI™-IPr).

2.2. Synthesis of [Ni{$(Ph_2P)_2$N-S-CHMePh-P,P′}Br_2]

A mixture of $(Ph_2P)_2$N(*S*-CHMePh) (100 mg, 0.20 mmol) and [Ni(dme)Br_2] (63 mg, 0.20 mmol) was stirred overnight in CH_2Cl_2 (10 mL) under Ar atmosphere at room temperature. The red solution formed was filtered in order to remove a non-reacted [Ni(dme)Br_2] and the volume of the reaction mixture was reduce to ~3 mL. Addition of hexane (~15 mL) resulted in a precipitation of a red solid that was isolated by filtration and dried under vacuum (isolated yield: 134 mg, 93%). Selected IR bands (KBr, cm^{-1}): 1434, 1096, 870, 749, 693, 507. ^{1}H NMR (300.0 MHz, $CDCl_3$): δ = 8.1–6.6 (m, 25H, aryl protons), 5.30 (s, 2H, C**H$_2$**Cl$_2$), 4.32 (m, 1H, C**H**-*S*-CHMePh), 1.01 (d, $^3J_{HH}$ = 7.0 Hz, 3H, C**H$_3$**-*S*-CHMePh). A signal at 1.54 ppm due to the residual water [25,26] was also observed. ^{31}P-{^{1}H} NMR (121.4 MHz, $CDCl_3$, ref to ext. 85% H_3PO_4): δ 53.3 (s). ^{13}C-{^{1}H} NMR (75.0 MHz, $CDCl_3$): δ = 127.5–139.1 (Ar); 61.7 (**C**H-*S*-CHMePh); 21.5 (**C**H$_3$-*S*-CHMePh).

Table 2
Selected bond lengths (Å) and angles (°) for [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2].

Bond lengths			
Ni–P(1)	2.1283(12)	Ni–P(2)	2.1362(12)
Ni–Br(1)	2.3318(7)	Ni–Br(2)	2.3495(7)
P(1)–N(31)	1.707(3)	P(2)–N(31)	1.701(3)
N(31)–C(31)	1.501(6)	C(31)–C(32)	1.517(6)
Angles			
P(1)–Ni–P(2)	73.45(4)	Br(1)–Ni–Br(2)	98.17(3)
P(1)–Ni–Br(2)	94.51(3)	P(2)–Ni–Br(1)	94.12(4)
Ni–P(1)–N(31)	94.89(12)	Ni–P(2)–N(31)	94.79(12)
P(1)–N(31)–C(31)	129.0(3)	P(2)–N(31)–C(31)	134.1(3)
N(31)–C(31)–C(32)	112.8(4)	P(1)–N(31)–P(2)	96.86(18)

2.3. X-ray crystal structure determination

A red crystal of [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2] (0.13 × 0.48 × 0.63 mm) was taken from a mother liquor and immediately cooled to −93 °C. Diffraction measurement was made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated Cu Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and empirical absorption correction) was performed using the CRYSTALCLEAR program package [27]. The structure was solved by direct methods using SHELXS-97 [28] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [29]. Important crystallographic and refinement data are listed in Table 1. Further crystallographic details for [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2]: $2\theta_{max}$ = 130°; reflections collected/unique/used, 36731/5332 [R_{int} = 0.0528]/5332; 463 parameters refined; $(\Delta/\sigma)_{max}$ = 0.002; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.987/−0.595 e/Å^3; R/R_w (for all data) 0.0415/0.1048. Hydrogen atoms were located by the difference maps and refined isotropically or they were introduced to calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically.

3. Results and discussion

3.1. Synthesis

The complex [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2] was obtained in a high yield by the ligand-exchange reaction:

$$[\mathrm{Ni(dme)Br_2}] + (\mathrm{Ph_2P})_2\mathrm{N}(S\text{-CHMePh}) \\ \rightarrow [\mathrm{Ni}\{(\mathrm{Ph_2P})_2\mathrm{N}\text{-}S\text{-CHMePh-}P,P'\}\mathrm{Br_2}] + \mathrm{dme}$$

Suitable rod-like crystals of [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2] were obtained by a CH_2Cl_2/ hexane (1:3 by vol.) solvent mixture.

3.2. Description of the structure of [Ni{$(Ph_2P)_2$N-S-CHMePh-P,P′}Br_2]

Selected bond lengths and angles in the structure of [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2] are listed in Table 2. The first coordination sphere of the complex (Fig. 1) contains a distorted square planar NiP_2Br_2 core in which the Ni(II) ion is coordinated by one (*P*,*P*) chelate forming together a four-membered Ni–P–N–P ring; in addition, two bromide ions are coordinated to the Ni(II) ion. The four-membered ring is nearly planar (the largest deviation from the plane defined by the Ni1, P1, N31, and P2 atoms is 0.013 Å for N31). The crystal of [Ni{$(Ph_2P)_2$N-*S*-CHMePh-*P*,*P*′}Br_2] is isomorphous to the earlier reported analogous crystals of [M{$(Ph_2P)_2$N-S-CHMePh-*P*,*P*′}Cl_2], M = Ni [16] or Pd [24a].