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P,C-bond cleavage in the ligand sphere of a nickel(II) complex†

Simon P. Walg,[a] Alexandra D. Schmidt,[a] Marcus Schmitz,[a] Saeid Farsadpour,[a] Johannes Lang,[a] Mark Niebergall,[a] Yu Sun,[a] Peter W. Roesky,[b] Gereon Niedner-Schatteburg[a] and Werner R. Thiel*[a]

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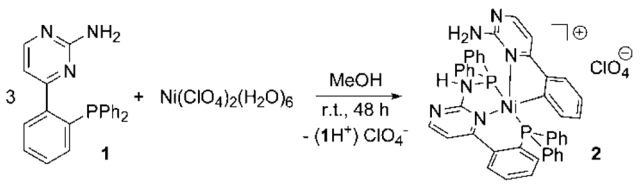
Reacting nickel(II)perchlorate with a bidentate P,N-ligand in methanol leads to P,C-bond cleavage and gives a five-coordinate nickel complex wherein the nickel(II) site is coordinated by a tridentate P,N,P-ligand and a bidentate N,C-ligand. The carbanion of the latter is the result of the P,C-bond cleaving process. The diamagnetic nickel(II) complex was characterized by means of elemental analysis, NMR spectroscopy, cyclic voltammetry and X-ray structure analysis.

Introduction

Nickel(II) complexes have been established for a long time as catalysts for a series of catalytic transformations such as Kumada-[1] and Negishi-type[2] cross-coupling or olefin polymerization reactions.[3] The broad catalytic applications in combination with the rich variety of catalytically active nickel(II) systems led us to focus on the coordination chemistry of [(2-aminopyrimidin-4-yl)aryl]phosphanes with this metal. In the last few years we have investigated chelating ligands containing 2-aminopyrimidin-4-yl fragments bound to either a second N-donor or a phosphine moiety. In the case of tertiary amino groups being located at the 2-position of the pyrimidine ring, such ligands easily undergo a so-called roll-over metallation[4] leading to C–H activation in the 5-position of the pyrimidine ring.[5] The resulting metal complexes which are coordinated by a carbanion show good activities in transfer hydrogenation (Ru) and Suzuki–Miyaura coupling reactions (Pd). This inspired us to extend the investigation of this class of ligand to other late transition metals.

Herein we report on an unusual P–C bond cleavage performed in the ligand backbone of a nickel(II) complex leading to a stable, diamagnetic, five-coordinate nickel(II) complex. Interestingly this P,C-cleavage occurs at the P,N-ligand [(2-aminopyrimidin-4-yl)aryl]phosphane (**1**) containing a primary amine (Scheme 1), which is the most unreactive member in the series of primary, secondary and tertiary [(2-aminopyrimidin-4-yl)aryl]phosphanes we had investigated so far.



Scheme 1 Synthesis of the nickel(II) complex **2**.

P,C-cleaving reactions have frequently been described in the literature. There are even some bacteria being able to perform this reaction in the case of alkyl phosphorous species.[6] The cleavage of aryl and alkyl phosphorous bonds can be performed at clusters[7] or mono- to trinuclear metal complexes[8] leading to bridging phosphido ligands. These conversions are mainly following oxidative addition processes at the metal site. According to these findings Hartwig, Bergman and Andersen suggested that the P,C-cleavage occurring at a ruthenium(II) complex also includes an oxidative addition step.[9] The most prominent example for a reductive P,C-cleavage is the reaction of PPh_3 with lithium to provide Ph_2PLi and PhLi,[10] which is also reported for other phosphines with different reducing reagents.[11] To the best of our knowledge, there is one example, wherein an electrophile (H^+) attacks a non-coordinating phosphorous atom in the periphery of a transition metal complex (here: Zr), resulting in a P,C-bond cleavage.[12] On the other hand, the attack of a nucleophile to a metal-coordinated phosphorous atom or a phosphorous site possessing good leaving group properties can also lead to P,C-bond cleavage and generate a carbanion, which is further stabilized by coordination to the metal site or by protonation.[13]

[a]*Technische Universität Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Straße 54, D-67663 Kaiserslautern, Germany. E-mail: thiel@chemie.uni-kl.de*
[b]*Karlsruher Institut für Technologie (KIT), Institut für Anorganische Chemie, Engesserstraße 15, D-76131 Karlsruhe, Germany*

†Electronic supplementary information (ESI) available: Spectroscopic data, additional structure plots. CCDC-1014112. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt02158d

Results and discussion

Ligand **1** is accessible in a few steps starting from diphenyl(trimethylsilyl)phosphane and 1-(2-fluorophenyl)-3-*N*,*N*-dimethylaminoprop-2-en-1-one.[14] Reacting $Ni(ClO_4)_2(H_2O)_6$ with **1** in a 1 : 3 ratio in methanol gives the red-colored, five-coordinate nickel(II) complex **2** in high yields (Scheme 1).

Single crystals of **2** suitable for an X-ray structure determination were grown from a concentrated solution in methanol. The nickel(II) complex **2** crystallizes in the triclinic space group $P\bar{1}$ with two molecules of methanol in the asymmetric unit. One methanol molecule is distorted over two positions, the perchlorate counter anion is distorted as well. Fig. 1 shows the molecular structure of the cation. Characteristic bond parameters are listed in the caption.

The determination of the molecular structure of the nickel(II) complex **2** proves that a PPh_2 moiety has been split from one of the [(2-aminopyrimidin-4-yl)aryl]phosphanes and has been attached to the NH_2 group of the second ligand. The nickel(II) ion is now coordinated in a distorted square-pyramidal manner by two phosphorous atoms, two nitrogen atoms and one carbon atom. Pentacoordinate nickel complexes are not uncommon. However, they are mainly observed in a trigonal-bipyramidal geometry with nitrogen and sulphur donors.[15] Since the angle P1–Ni1–P2 is close to 140° and the angles P1–Ni1–N4 and P2–Ni1–N4 are larger than 100°, the compound adopts a geometry, which is in between a square-pyramidal and a trigonal-bipyramidal coordination mode. This coordination mode is caused by the bending in the six-membered ring (N1–C–C–C–P1–Ni1) which prevents the donor atoms of the tridentate P,N,P-ligand from being located in one plane with the nickel(II) site. The Ni–P bond lengths differ only slightly. In contrast, there is a big difference in the Ni–N bond lengths: Ni–N1 (1.978 Å) is about 15 pm shorter than Ni1–N4 (2.135 Å), although the nitrogen atom N1 is located in the *trans*-position to the carbanion site C44, exhibiting a strong *trans*-influence. This observation is frequently made for rigid tridentate ligands: due to steric restrictions, the M–L distance to the inner donor site is generally found to be considerably shortened compared to the outer ones.[16] The reason why C44 is found in the *trans*-position to N1 is probably an intramolecular hydrogen bond that exists between H6A and N1 (2.51 Å). As expected, the Ni–C44 (1.903 Å) bond is the shortest of all M–L bonds, thus approx. 23 pm shorter than the Ni–N4 bond, reflecting the anionic nature of this carbon atom and the resulting very strong Ni–C bond. The ligand backbone of compound **2** contains several sites that can act as proton donors or acceptors in intermolecular hydrogen bonds, resulting in the formation of a zig-zag chain (see the ESI†) generated by linkages between H3N and N2 as well as H6B and N5. The perchlorate anion interacts *via* a hydrogen bond with H6A. The Ni–C-bond is neither hydrolysed by the protic amino group of the molecule nor by the protic solvent methanol as a result of the almost perfect shielding by the two diphenylphosphino moieties. These are located in the *trans*-positions of the distorted square pyramidal coordination environment (see the ESI†).

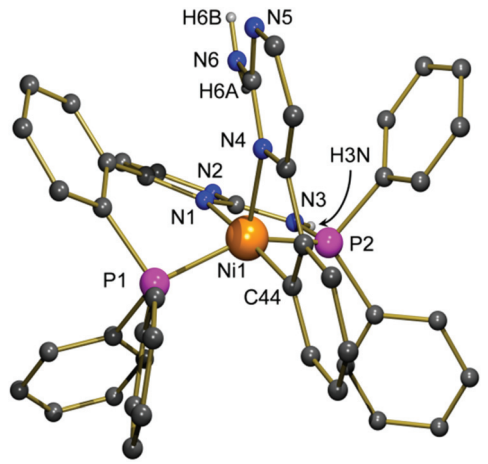


Fig. 1 Molecular structure of the cation of compound **2** in the solid state; carbon bound hydrogen atoms, the perchlorate anion and both co-crystallizing methanol molecules are omitted for clarity. Characteristic bond lengths [Å], bond angles [°], and hydrogen bond parameters: Ni1–P1 2.1968(9), Ni1–P2 2.1367(9), Ni1–N1 1.978(3), Ni1–N4 2.135(3), Ni1–C44 1.903(3), P1–Ni1–P2 149.25(4), P1–Ni1–N1 89.12(8), P1–Ni1–N4 106.20(7), P1–Ni1–C44 90.58(9), P2–Ni1–N1 86.71(8), P2–Ni1–N4 104.42(7), P2–Ni1–C44 90.53(10), N1–Ni1–N4 102.94(10), N1–Ni1–C44 174.06(12), N4–Ni1–C44 82.84(12); hydrogen bonds (O1 from perchlorate): N3–H3N 0.86(3), H3N···N2 2.07(3), N3···N2 2.929(5), N3–H3N···N2 179(4), N6–H6A 0.87(3), H6A···O1 2.58(4), N6···O1 3.129(5), N6–H6A···O1 122(3), N6–H6A 0.87(3), H6A···N1 2.51(3), N6···N1 3.150(4), N6–H6A···N1 131(3), N6–H6B 0.87(3), H6B···N5 2.14(3), N6···N5 3.013(4), N6–H6B···N5 179(5).

The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two sharp resonances for the phosphorous atoms P1 (13.9 ppm) and P2 (47.2 ppm) with a $^2J_{PP}$ coupling of 231.6 Hz. The large coupling is consistent with two different phosphorous sites being located in the *trans*-position to each other. Since there is no structurally related nickel(II) complex in the literature, we took diamagnetic, four-coordinate complexes as makeshifts to assign the ^{31}P resonance of compound **2**. The ^{31}P resonance of *trans*-$(PPh_3)_2Ni(Ph)Cl$ is reported to appear at approx. 21 ppm.[17] Kirchner *et al.* investigated a square-planar nickel(II) pincer complex with two *trans*-orientated arylamino(diphenyl)-phosphine units and found a ^{31}P resonance at 77.8 ppm.[18] These values allow to assign the resonance at 13.9 ppm to the triaryl-substituted phosphorous atom and the resonance at 47.2 to the diphenylphosphine site carrying one amino group. The general shift of the ^{31}P resonances of **2** (18 VE system) to lower field compared to the model systems (16 VE systems) is due to the increased electron density. Hey-Hawkins *et al.* found the homoleptic nickel(0) complex $Ni(Ph_2P\text{-}NHPh)_2$ with a ^{31}P signal at 16.6 ppm.[19] Due to the completely asymmetric structure of **2**, resulting in four different phenyl groups, and the multiple P,H-couplings, the complete interpretation of the ^1H NMR spectrum is difficult. Nevertheless by means of a H,H-COSY experiment, the two sets of AB spin systems (8.54/7.12 ppm, $^2J_{HH}$ = 5.05 Hz; 8.19/7.33 ppm, $^2J_{HH}$ = 5.38 Hz) being affiliated to the two pyrimidine rings can easily be identified.

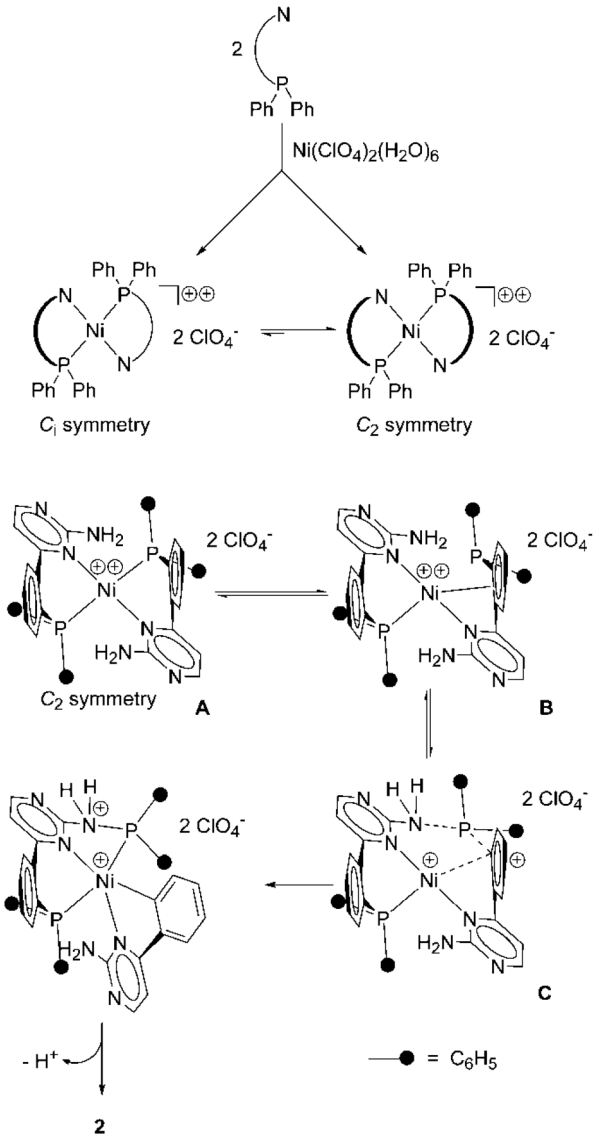
Since the resonance at 8.54 ppm shows a second coupling of 1.20 Hz (either to the NH-group or the N–P phosphorous atom), it can be assigned to the pyrimidine proton next to the ring nitrogen atom in the tridentate P,N,P-ligand. Furthermore there are the signals of two ABCD spin systems (7.84/7.65/7.58/7.50 and 7.62/6.75/6.35/6.26 ppm) standing for the two *ortho*-substituted phenylene rings. The latter one is considerably deshielded and can therefore be assigned to the bidentate ligand with the Ni–C bond. Examination of the course of the generation of **2** by ^{31}P NMR spectroscopy failed due to the formation of insoluble ($HL^{+}ClO_4^{-}$). However, no intermediate could be detected even at the beginning of the reaction either due to a very rapid transformation of this intermediate into **2** or due to a paramagnetic nature of the intermediate.

ESI-MS measurements further confirm the molecular composition of the cation of **2** (m/z = 767 amu with respect to ^{58}Ni, see the ESI†). In the infrared spectrum of **2**, one would expect to generally find the bands of three N–H stretching vibrations, one for the NH–PPh_2 unit and the symmetric and the asymmetric vibration of the NH_2 group. In fact, there are two bands, one at 3437 and a slightly stronger band at 3354 cm^{-1}. We assign the latter one to the overlapped bands of the N–H stretching vibration[10] and the symmetric NH_2 stretching vibration.[20]

Cyclic voltammetry was carried out to get an insight into the redox behaviour of compound **2**. The nickel(II) complex is irreversibly oxidized at a peak potential of 0.77 V in acetonitrile solution with respect to the SCE (for a graphic see the ESI†). No reduction could be observed up to a potential of −1.50 V. Electron rich square planar PCP-type pincer complexes of nickel(II) show similar oxidation potentials depending on the nature of the C-donor site,[21] while *e.g.* for less electron rich complexes such as $(PPh_3)_2Ni(NCS)_2$ no oxidation was found, but irreversible reduction processes.[22] This shows the electron-rich nature of the five-coordinate nickel(II) complex **2**.

We suggest an intramolecular mechanism for the P,C-bond cleavage and the P,N-bond formation. The nucleophilic character of the amino group of aminopyrimidines is not very strong. In the nucleophilic solvent methanol the formation of methoxy(diphenyl)phosphine as the main product should occur in an intermolecular reaction. We propose, that in the first step, the formation of the dicationic nickel(II) complex **A** takes place (Scheme 2, top). In **A** the two P,N-donors are coordinated in a square planar mode. This compound might undergo loose interaction with the perchlorate anions (not drawn). Provided that the P,N bond formation takes place in an intramolecular way, the two nitrogen resp. and the two phosphorous sites have to be oriented *trans* to each other, a situation which would also prevent steric hindrance of the two diphenylphosphino units.

We know from a X-ray structure analysis of the palladium(II) complex (**1**)$PdCl_2$,[5] wherein the palladium centre is *cis*-coordinated by the phosphorous and the nitrogen atom, that the six-membered ring including P, Pd, and N is severely bent. Due to the bending of the P,N units, compound **A** might exist in two isomeric forms (Scheme 2, top), wherein the bridging



Scheme 2 Generation of the nickel(II) complex **2** by P,C-bond cleavage and subsequent P,N-bond formation.

phenylene units either point in opposite directions (C_i symmetry) or in the same direction (C_2 symmetry). According to preliminary quantum chemical calculations on the mechanism, the C_2 symmetric isomer is about 9 kcal mol^{-1} lower in energy than the C_i symmetric one. After Ni–P cleavage has occurred in the first step of the mechanism, the detached phosphorous atom has to move towards the NH_2 group of the second ligand. This is, in our opinion, strongly favoured for the C_2 symmetric isomer (Scheme 2, bottom), since the nickel site can only in this case undergo an interaction with the bridging phenylene unit, that will lead to an electrophilic attack at the phosphorous substituted carbon atom (**B**). This allows a neighboring amino group to perform a nucleophilic attack at the phosphorous atom which cleaves the P,C-bond and forms the P,N-bond (**C**). Finally a third equivalent of ligand **1**, which is necessary to obtain high yields of the product, takes over the

proton from the nitrogen atom and the aminophosphine coordinates to the nickel centre resulting in the formation of compound (**2**).

This kind of P,C-bond cleavage reaction is up to now limited to nickel(II) and ligand **1**. We have carried out the same reaction with manganese(II), iron(II), cobalt(II), copper(II) and zinc(II) perchlorates which do not show any reaction with the ligand. The same was observed for other triphenylphosphine functionalized tertiary aminopyrimidines and pyrazoles, which we frequently use in our group. In none of these cases, P,C-bond cleavage could be found. Instead, expected coordination compounds with intact ligand structures have been observed. The behaviour of these ligands might be explained by steric and electronic considerations: pyrazoles are poor nucleophiles since the N-σ orbital is occupied for the N–H bond, while the N-π orbital is conjugated in the 6-electron ring structure. For [(2-aminopyrimidin-4-yl)aryl]phosphanes carrying a tertiary amino group $-NR_2$, steric hindrance of the groups R will prevent the attack of the phosphorous atom at the amino group.

Experimental

General remarks

All reaction steps were carried out under an argon atmosphere using Schlenk techniques. Nickel(II) perchlorate hexahydrate was purchased from Sigma Aldrich and used without further purification. Ligand **1** was synthesized according to a published procedure.[5] All solvents were degassed according to standard techniques before use. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Spectrospin Avance 400 device, ESI mass spectra were recorded on a Bruker Esquire 6000 equipment.

Synthesis of the nickel(II) complex 2

Nickel(II) perchlorate hexahydrate (373 mg, 1.02 mmol) was dissolved in methanol (20 ml) and **1** (1.11 g; 3.11 mmol) was added to the green solution. The resulting green suspension was stirred for 48 h at room temperature whereby its colour changed to red. The solvent was removed in vacuum and dichloromethane (20 ml) was added, leading to a red solution and a white precipitate, which was filtered off. After evaporation of the solvent from the filtrate, the remaining reddish-brown solid was stirred with toluene (15 ml) at room temperature for 16 h to dissolve residues of the free ligand **1**, then filtered off and dried under vacuum. To obtain crystals suitable for an X-ray structure analysis, the compound was recrystallized from a minimum amount of methanol. Yield: 778 mg (896 μmol; 88%) of a reddish-brown solid. Elemental analysis for $C_{44}H_{35}ClN_6NiO_4P_2$ (867.91): calcd C 60.89%, H 4.06%, N 9.68%; found C 61.19%, H 4.24%, N 9.48%.

Cyclic voltammetry

Electrochemical experiments were performed at room temperature in 0.2 M solution of NBu_4ClO_4 in acetonitrile using a potentiostat/galvanostat 273 A of Princeton Applied Research, a platinum foil as the working electrode, a platinum net as the counter electrode and a saturated calomel electrode as the reference electrode. The scan rate was 100 mV s^{-1}. The ferrocene/ferrocenium redox couple served as the internal reference (+0.42 V *vs.* SCE).

Table 1 Crystallographic data, data collection and refinement

	2
Empirical formula	$C_{46}H_{43}ClN_6NiO_6P_2$
Formula weight	931.96
Crystal size [mm]	0.16 × 0.10 × 0.06
T [K]	150(2)
λ [Å]	1.54184
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	11.6115(7)
b [Å]	13.4918(9)
c [Å]	14.9171(10)
α [°]	87.203(5)
β [°]	75.689(6)
γ [°]	70.567(6)
V [Å^3]	2134.0(2)
Z	2
$\rho_{calcd.}$ [g cm^{-3}]	1.450
μ [mm^{-1}]	2.417
θ-range [°]	3.48–62.85
Refl. coll.	14 868
Indep. refl.	6800 [R_{int} = 0.0275]
Data/restr./param.	6800/122/612
Final R indices [$I > 2\sigma(I)$][a]	0.0525, 0.1340
R indices (all data)	0.0610, 0.1419
GooF[b]	1.027
$\Delta\rho_{max/min}$ (e Å^{-3})	1.307/−1.224

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $\omega R_2 = [\sum\omega(F_o^2 - F_c^2)^2/\sum\omega F_o^2]^{1/2}$. [b] GooF = $[\sum\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$.

X-ray structure analysis of 2

Crystal data and refinement parameters for compound **2** are collected in Table 1. The structure was solved using a direct method (SIR92[23]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[24] A semi-empirical absorption correction from equivalents (Multiscan) was carried out.[25] The molecule was found co-crystallized with two equivalents of methanol, one of which being disordered. The hydrogen atoms bound to the nitrogen atoms N3 and N6 were located in the difference Fourier synthesis and were refined semi-freely with the help of a distance restraint, while constraining their U-values to 1.2 times the $U_{(eq)}$ values of the corresponding nitrogen atoms. All the other hydrogen atoms were placed in calculated positions and refined using a riding model. CCDC-1014112 contains the supplementary crystallographic data for this paper.

Conclusions

The reaction of [(2-aminopyrimidin-4-yl)aryl]phosphane with nickel(II)perchlorate hexahydrate leads to a novel five-coordinate nickel(II) complex in high yield wherein the nickel(II) site

is coordinated by a tridentate P,N,P′-ligand and a bidentate, carbanionic N,C-ligand. Both ligand systems are formed from the bidentate[(2-aminopyrimidin-4-yl)aryl]phosphane which undergoes a P,C-bond cleavage. The pyridinyl amino group acts as a nucleophile and takes over a PPh_2 unit in an intramolecular process from the neighbouring ligand moiety.

Acknowledgements

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Notes and references

1 K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, 1972, **94**, 4374; R. J. P. Corriu and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 1972, 144; J. Terao, H. Watanabe, A. Ikumi, H. Kuniyasu and N. Kambe, *J. Am. Chem. Soc.*, 2002, **124**, 4222; J. Terao, A. Ikumi, H. Kuniyasu and N. Kambe, *J. Am. Chem. Soc.*, 2003, **125**, 5646; L.-C. Liang, P.-S. Chien, J.-M. Lin, M.-H. Huang, Y.-L. Huang and J.-H. Liao, *Organometallics*, 2006, **25**, 1399; O. Vechorkin and X. Hu, *Angew. Chem., Int. Ed.*, 2009, **48**, 2937; O. Vechorkin, Z. Csok, R. Scopelliti and X. Hu, *Chem. – Eur. J.*, 2009, **15**, 3889; S. Gu and W. Chen, *Organometallics*, 2009, **28**, 909.

2 A. Devasagayaraj, T. Stüdemann and P. Knochel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2723; R. Giovannini and P. Knochel, *J. Am. Chem. Soc.*, 1998, **120**, 11186; A. E. Jensen, W. Dohle and P. Knochel, *Tetrahedron*, 2000, **56**, 4197; C. E. Tucker and J. G. de Vries, *Top. Catal.*, 2002, **19**, 111; J. Zhou and G. C. Fu, *J. Am. Chem. Soc.*, 2003, **125**, 12527; J. Zhou and G. C. Fu, *J. Am. Chem. Soc.*, 2003, **125**, 14726; A. Gavryushin, C. Kofink, G. Manolikakes and P. Knochel, *Org. Lett.*, 2005, **7**, 4871; A. Gavryushin, C. Kofink, G. Manolikakes and P. Knochel, *Tetrahedron*, 2006, **62**, 7521; E. Negishi, *Angew. Chem., Int. Ed.*, 2011, **50**, 6738.

3 W. Keim, B. Hoffmann, R. Lodewick, M. Peuckert and G. Schmitt, *J. Mol. Catal.*, 1979, **6**, 79; M. Peuckert and W. Keim, *Organometallics*, 1983, **2**, 594; A. Behr, V. Falbe, U. Freudenberg and W. Keim, *Isr. J. Chem.*, 1986, **27**, 277; G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 185; N. A. Kolhatkar, A. M. Monfette, S. Lin and M. J. Miri, *J. Polym. Sci.*, 2002, **50**, 986; J. N. L. Dennett, A. L. Gillon, K. Heslop, D. J. Hyett, J. S. Fleming, C. E. Lloyd-Jones, A. G. Orpen, P. G. Pringle, D. F. Wass, J. N. Scutt and R. H. Weatherhead, *Organometallics*, 2004, **23**, 6077; G. Noël, J. C. Röder, S. Dechert, H. Pritzkow, L. Bolk, S. Mecking and F. Meyer, *Adv. Synth. Catal.*, 2006, **348**, 887; F.-S. Liu, H.-B. Hu, Y. Xu, L.-H. Guo, S.-B. Zai, K.-M. Song, H.-Y. Gao, L. Zhang, F.-M. Zhu and Q. Wu, *Macromolecules*, 2009, **42**, 7789.

4 G. Nord, A. C. Hazell, R. G. Hazell and O. Farver, *Inorg. Chem.*, 1983, **22**, 3429; P. J. Spellane, R. J. Watts and C. J. Curtis, *Inorg. Chem.*, 1983, **22**, 4060; P. S. Braterman, G. H. Heat, A. J. Mackenzie, B. C. Noble, R. D. Peacock and L. J. Yellowlees, *Inorg. Chem.*, 1984, **23**, 3425; E. C. Tyo, A. W. Castleman Jr., D. Schröder, P. Milko, J. Roithova, J. M. Ortega, M. A. Cinellu, F. Cocco and G. Minghetti, *J. Am. Chem. Soc.*, 2009, **131**, 13009; G. Minghetti, S. Stoccoro, M. A. Cinellu, G. L. Petretto and A. Zucca, *Organometallics*, 2008, **27**, 3415.

5 S. Farsadpour, L. Taghizadeh Ghoochany, Y. Sun and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2011, 4603; S. Farsadpour, L. Taghizadeh Ghoochany, S. Shylesh, G. Dörr, A. Seifert, S. Ernst and W. R. Thiel, *ChemCatChem*, 2012, **4**, 395; L. Taghizadeh Ghoochany, C. Kerner, S. Farsadpour, Y. Sun, F. Menges, G. Niedner-Schatteburg and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2013, 4305.

6 C. M. Chen, Q. Z. Ye, Z. M. Zhu, B. L. Wanner and C. T. Walsh, *J. Biol. Chem.*, 1990, **265**, 4461; J. W. McGrath, G. B. Wisdom, G. McMullan, M. J. Larkin and J. P. Quinn, *Eur. J. Biochem.*, 1995, **234**, 225; A. Inoue, H. Shinokubo and K. Oshima, *J. Am. Chem. Soc.*, 2003, **125**, 1484.

7 M. Randles, A. C. Willis, M. P. Cifuentes and M. G. Humphrey, *J. Organomet. Chem.*, 2007, **692**, 4467; W. H. Watson, G. Wu and M. G. Richmond, *Organometallics*, 2006, **25**, 930; S. M. Waterman, V.-A. Tolhurst, M. G. Humphrey, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1996, **515**, 89; A. J. Deeming, M. K. Shinhmar, A. J. Arce and Y. De Sanctis, *J. Chem. Soc., Dalton Trans.*, 1999, 1153.

8 N. M. Doherty, G. Hogarth, S. A. R. Knox, K. A. Macpherson, F. Melchior, D. A. V. Morton and A. G. Orpen, *Inorg. Chim. Acta*, 1992, **198–200**, 257; W.-D. Wang and R. Eisenberg, *J. Am. Chem. Soc.*, 1990, **112**, 1833; H. Wachtler, W. Schuh, K.-H. Ongania, K. Wurst and P. Peringer, *Organometallics*, 1998, **17**, 5640; P. E. Garrou, *Chem. Rev.*, 1985, **85**, 171.

9 J. F. Hartwig, R. G. Bergman and R. A. Andersen, *J. Organomet. Chem.*, 1990, **394**, 417.

10 P. H. M. Budzelaar, J. A. van Doorn and N. Meijboom, *Recl. Trav. Chim. Pays-Bas*, 1991, **110**, 420–432.

11 M. F. Cain, S. C. Reynolds, B. J. Anderson, D. S. Glueck, J. A. Golen, C. E. Moore and A. L. Rheingold, *Inorg. Chim. Acta*, 2011, **369**, 55; S. A. Reiter, S. D. Nogai and H. Schmidbaur, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2595.

12 Y. El Harouch, V. Cadierno, A. Igau, B. Donnadieu and J.-P. Majoral, *J. Organomet. Chem.*, 2004, **689**, 953.

13 A. Caballero, F. A. Jalón, B. R. Manzano, G. Espino, M. Pérez-Manrique, A. Mucientes, F. J. Poblete and M. Maestro, *Organometallics*, 2004, **23**, 5694; A. Inoue, H. Shinokubo and K. Oshima, *J. Am. Chem. Soc.*, 2003, **125**, 1484; T. J. Geldbach and P. S. Pregosin, *Eur. J. Inorg. Chem.*, 2002, 1907; S.-C. Tsai, Y.-S. Fu, J.-H. Liao and S. J. Yu, *Helv. Chim. Acta*, 2006, **89**, 3007.

14 A. Reis, D. Dehe, S. Farsadpour, I. Munstein, Y. Sun and W. R. Thiel, *New J. Chem.*, 2011, **35**, 2488; D. Dehe, I. Munstein, A. Reis and W. R. Thiel, *J. Org. Chem.*, 2011, **76**, 1151.

15 J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1084; J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1090; P. S. Shetty and Q. Fernando, *J. Am. Chem. Soc.*, 1970, **92**, 3964; T. E. Kokina, L. A. Glinskaya, R. F. Klevtsova and S. V. Larionov, *J. Struct. Chem.*, 2002, **43**, 312; S. V. Larionov, T. E. Kokina, L. A. Glinskaya and R. F. Klevtsova, *Russ. J. Coord. Chem.*, 2002, **28**, 560.

16 (*a*) F. Bachechi, *Struct. Chem.*, 2003, **14**, 263.H. Glas, K. Köhler, P. Maas, E. Herdtweck, M. Spiegler and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2001, **4**, 2075.

17 A. Zeller, E. Herdtweck and T. Strassner, *Eur. J. Inorg. Chem.*, 2003, 1802; H. A. Bronstein and C. K. Luscombe, *J. Am. Chem. Soc.*, 2009, **131**, 12894.

18 D. Benito-Garagorri, V. Bocokić, K. Mereiter and K. Kirchner, *Organometallics*, 2006, **25**, 3817.

19 O. Kühl, P. C. Junk and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1591.

20 (*a*) L. Varga, T. Nagy, I. Kövesdi, J. Benet-Buchholz, G. Dormán, L. Ürge and F. Darvas, *Tetrahedron*, 2003, **59**, 655.A. Alberola, C. Andrés, A. González Ortega, R. Pedrosa and M. Vicente, *Synth. Commun.*, 1987, **17**, 1309; X.-Y. Yu, P.-G. Yi, D.-H. Ji, B.-R. Zeng, X.-F. Li and X. Xu, *Dalton Trans.*, 2012, **41**, 3684.

21 A. Castonguay, A. L. Beauchamp and D. Zargarian, *Organometallics*, 2008, **27**, 5723.

22 K. Ramalingam, R. Thiruneelakandan, G. Bocelli and L. Righi, *Transition Met. Chem.*, 2012, **37**, 265.

23 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

24 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.

25 *CrysAlisPro*, Agilent Technologies, Version 1.171.36.24, 2012.