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Synthesis and characterisation of new $PC_{sp3}P$-supported nickel complexes

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ABSTRACT

The coordination behaviour of the aliphatic pincer ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl) cyclohexane with $NiCl_2$ and $NiBr_2$ was studied. Reflux in toluene afforded cyclometalated, tridentate $PC_{sp3}P$ pincer complexes, that were characterised by elemental analysis and NMR spectroscopy; the solid state structures were determined by X-ray diffraction showing an unusually long Ni—Br bond in the bromo complex. A preliminary account of their reactivity is reported and they were found to be unreactive towards base and hydride sources and to be poor catalysts in Kumada coupling reactions.

1. Introduction

Over the last 30 years, pincer metal complexes have earned recognition as potent and versatile compounds in homogeneous catalysis [1]. However, replacement of precious metals with cheaper and more abundant first row transition metal alternatives remains one of the great challenges for the field [2]. One problem in this aspect might be the reluctance of 3d metals to undergo 2-electron oxidative addition and reductive elimination reactions. In combination with the weaker M—C bonds of the 3d metals this usually makes C—H activation and cyclometalation reactions more difficult. On the other hand, in the case of nickel complexes, 1-electron processes are more frequently occurring, opening up for catalytic pathways that may not be accessible for heavier analogues [3]. Recent advances of nickel pincer complexes in the literature involve various cross-coupling reactions [3,4], direct alkylations [5] alkene hydrogenations [6], hydroaminations [7], hydrosilylations [8] and reduction of carbon dioxide to methanol [9].

Amongst the published work on PCP pincer complexes, pincer ligands with aromatic backbones are in vast majority and this is also true for nickel complexes, although a number of aliphatic nickel pincer complexes have been reported [10,11]. In general, there are several known examples where the nature of the coordinating carbon alters the reactivity of a pincer complex, illustrating how a strongly σ-donating C_{sp3}-hybridised ligand can be a useful tool for electrochemical tuning [12], and this has opened up N—H oxidative addition pathways unavailable with traditional aromatic pincer ligands [13]. We have previously reported on the synthesis of the cyclohexyl-based $PC_{sp3}P$ ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane (**1**), and we and others have shown its ability to cyclometalate with second and third row transition metals, such as palladium [14], platinum [15], rhodium [16] and iridium [17]. Here we report on the first complexation of this ligand with nickel, together with some reactivity data of these $PC_{sp3}P$-coordinated complexes.

2. Experimental section

2.1. General considerations

All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except where noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane (**1**) was synthesized according to previously reported procedures [14]. All other chemicals where purchased from Acros, Alfa Aesar or Sigma Aldrich and used as received. ^{1}H, ^{13}C and ^{31}P NMR spectroscopy experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at

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499.76 MHz (^{1}H). Chemical shifts are given in ppm downfield from TMS, using residual solvent peaks (^{1}H and ^{13}C) or H_3PO_4 (^{31}P) as reference. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (v) virtual. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. XRD-quality crystals of **2a** and **2b** were obtained through recrystallisation from pentane. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using ω-scans and Mo Kα ($\lambda = 0.71073$ Å) radiation [18]. The data were extracted and integrated using Crysalis RED [19]. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL5.1 [20]. Molecular graphics were generated using CrystalMaker 8.3.5 [21]. All crystallographic data are available in CIF format (CCDC reference numbers 978220-21).

2.2. Preparation of trans-[NiCl{cis-1,3-bis-((di-tert-butylphosphino)methyl)}cyclo-hexane] (*2a*)

DMAP (15.2 mg, 0.125 mmol) was added to a stirred mixture of the *cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane ligand (50.0 mg, 0.125 mmol) and anhydrous $NiCl_2$ (48.5 mg, 0.374 mmol) in toluene (5 mL). The reaction mixture was heated to reflux for 24 h under a nitrogen atmosphere. The cooled suspension was concentrated *in vacuo*, dispersed in ethyl acetate and filtered in air through a pad of silica. Removal of the solvent afforded **2a** as a yellow crystalline powder. Yield: 36.9 mg (69% based on **1**). ^{1}H NMR (C_6D_6): δ 1.82–1.77 (m, Cy, 2H), 1.74–1.70 (m, Cy, 1H), 1.69–1.63 (m, PCH_2CH, 2H), 1.55–1.45 (m, Cy, 2H), 1.48 (vt, $J = 13.0$ Hz, ^{t}Bu, 18H), 1.45 (vt, $J = 13.0$ Hz, ^{t}Bu, 18H), 1.27 (t, $J_{PH} = 11.0$ Hz, HC–Ni), 1.29–1.24 (m, Cy, 1H), 1.11–1.03 (m, PCH_2CH, 2H), 0.82–0.74 (m, Cy, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 53.3 (t, $^2J_{PC} = 11$ Hz, HC–Ni), 49.5 (vt, $J_{PC} = 21$ Hz, CH), 35.7 (vt, $J_{PC} = 19$ Hz, $CHCH_2CH_2$), 35.2 (vt, $J_{PC} = 11$ Hz, $C(CH_3)_3$), 34.6 (vt, $J_{PC} = 14$ Hz, $C(CH_3)_3$), 32.3 (vt, $J_{PC} = 18$ Hz, P–CH_2), 30.4 (vt, $J_{PC} = 5.0$ Hz, $C(CH_3)_3$), 29.6 (vt, $J_{PC} = 4.0$ Hz, $C(CH_3)_3$), 27.2 (s, $CH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.79 (s). Anal. Calcd for $C_{24}H_{49}ClNiP_2$ (493.74): C, 58.38; H, 10.00. Found: C, 58.24; H, 10.12.

2.3. Preparation of trans-[NiBr{cis-1,3-bis-((di-tert-butylphosphino)methyl)}-cyclohexane] (*2b*)

The compound was synthesized according to the same procedure and in the same scale as the corresponding chloride complex (**2a**). Yield: 42.9 mg (71% based on **1**). ^{1}H NMR (C_6D_6): δ 1.83–1.79 (m, Cy, 2H), 1.73–1.67 (m, Cy, 1H and m, PCH_2CH, 2H), 1.55–1.50 (m, Cy, 2H), 1.49 (vt, $J = 12.5$ Hz, ^{t}Bu, 18H), 1.46 (vt, $J = 12.0$ Hz, ^{t}Bu, 18H), 1.30–1.22 (m, Cy, 1H), 1.27 (t, $J_{PH} = 11.0$ Hz, HC–Ni), 1.11–1.05 (m, PCH_2CH, 2H), 0.81–0.73 (m, Cy, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 56.3 (t, $^2J_{PC} = 11$ Hz, HC–Ni), 49.3 (vt, $J_{PC} = 26$ Hz, CH), 35.7 (vt, $J_{PC} = 19$ Hz, $CHCH_2CH_2$), 35.5 (vt, $J_{PC} = 11$ Hz, $C(CH_3)_3$), 35.1 (vt, $J_{PC} = 14$ Hz, $C(CH_3)_3$), 32.8 (vt, $J_{PC} = 18$ Hz, P–CH_2), 30.7 (vt, $J_{PC} = 4.7$ Hz, $C(CH_3)_3$), 29.7 (vt, $J_{PC} = 4.5$ Hz, $C(CH_3)_3$), 27.2 (s, $CH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.47 (s). Anal. Calcd for $C_{24}H_{49}BrNiP_2$ (493.74): C, 53.56; H, 9.18. Found: C, 53.44; H, 9.11.

2.4. General procedure for attempted Kumada coupling

RMgCl (0.27 mmol, 3 M THF solution) was added to a solution of RX (0.26 mmol) and the catalyst (3 mol%) in THF (0.5 mL). The mixture was heated to 120 °C for the desired time. A sample of the reaction was then withdrawn, quenched with 0.5 M HCl and diluted with THF. The organic phase was dried over $MgSO_4$ and filtered, and the resultant solution was analyzed by GC.

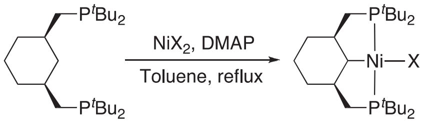
3. Results and discussion

The straightforward synthesis of pincer complexes **2a** and **2b** is illustrated in Scheme 1, following the synthetic protocol of Zargarian and coworkers for the non-cyclic 1,5-bis(phosphinito) pentane ligand [10b], but increasing the amount of NiX_2 from 2 to 3 equivalents.

The products were isolated in moderate to good yields, and no phosphorus containing species apart from the products could be observed in the crude reaction mixture by means of ^{31}P NMR spectroscopy. Thus, there is no indication that byproducts such as previously reported binuclear 16-atom ring chelate complexes or mononuclear complexes with *cis*-coordination to the P atoms are formed [22]. This however does not rule out the formation of such 16-atom cyclic dimers, since these compounds are known to be highly fluxional and sometimes low-soluble which makes them hard to detect by NMR spectroscopy. The somewhat limited yields could also be accounted for by formation of phosphorus containing nickel salts, but the solid residues formed during the reactions are highly insoluble and probably NMR silent, and any attempted characterization has been unsuccessful. The group of Zargarian has reported that nickelation of the 1,5-bis(phosphino)pentane ligand gives a byproduct with low solubility identified as a zwitterionic complex with an anionic tetrahedral nickel centre and a mono-coordinated pincer ligand with one protonated non-coordinated phosphine. The protonation is suggested to take place by *in situ* generated HX, which supports their and our observation that addition of DMAP or other bases improves the yield for the complexation reaction [10a].

The $^{31}P\{^1H\}$ NMR spectra of **2a** and **2b** display a sharp singlet resonance that confirms the equivalence of the phosphorus nuclei in agreement with an expected *trans* geometry; this is also consistent with the appearance of the ^{t}Bu protons as virtual triplets in ^{1}H NMR spectra. The characteristic pattern of virtual triplets is also observed in the $^{13}C\{^1H\}$ NMR spectra, where all nuclei except the most remote methylene carbons of the cyclohexyl ring display coupling to phosphorus.

To confirm the cyclometalated structures, crystals of both complexes were subjected to an X-ray diffraction experiment. The details of the crystal structure solution and refinement are given in Table 1. The molecular structures, including selected bond distances and angles, of compound **2a** and **2b** are shown in Figs. 1 and 2, respectively. As expected from the NMR spectroscopy results, the *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane ligand is coordinated meridionally with the P atoms positioned *trans* to each other. The Ni atom adopts a distorted square planar geometry, with P(1)–Ni–P(2) angles around 170°. The cyclohexyl ring has a chair conformation and the three coordinated positions are all equatorially oriented in agreement with previous observations [14,15]. The Ni–Cl bond in **2a** is longer than in the analogous aromatic compounds [23], and very close to the reported bond length for a similar non-cyclic $^{tBu}PC_{sp3}P$ nickel complex [10a], underpinning the greater trans-influence from a sp^3-hybridized coordinated carbon compared to its sp^2-hybridized aromatic counterpart. However, the Ni–Br bond in **2b** (2.4303(4) Å) is significantly longer than Ni–Br



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X = Cl (**2a**)
X = Br (**2b**)

Scheme 1. Synthesis of **2a** and **2b**.

Table 1
Crystal data and collection and refinement details for compounds **2a** and **2b**.

	2a	**2b**
Formula	$C_{24}H_{49}ClNiP_2$	$C_{24}H_{49}BrNiP_2$
Fw	493.71	538.16
Space group	$Pna2_1$	$P2_1/c$
a/Å	22.9163(5)	11.4024(2)
b/Å	8.4324(3)	15.8824(3)
c/Å	14.4279(4)	15.6999(4)
α/deg	90	90
β/deg	90	98.245(2)
γ/deg	90	90
V/Å^3	2788.04	2813.83
Z	4	4
D_{calcd}/g cm^{-3}	1.176	1.270
μ/mm^{-1}	0.915	2.231
θ/range/deg	2.57–28.88	2.44–28.97
No. reflns collected	46,663	61,313
No. of unique reflns	6821	6895
$R(F)$ $(I > 2\sigma(I))$[a]	0.0563	0.0450
$wR2(F^2)$ (all data)[b]	0.1242	0.1005
S[c]	1.095	1.254
R_{int}	0.0975	0.0665

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

[b] $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.

[c] $S = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.

bonds in both aromatic (2.3290–2.3601 Å) [10d,24,25] and aliphatic (2.3712–2.3866 Å) [10a,10d] PCP nickel bromide complexes in literature. It approaches the bond length for the aromatic NCN nickel bromide complexes reported by van Koten and co-workers (NCN = C_6H_3-2,6-{$CH_2N(^iPr)Me$}$_2$ and C_6H_3-2,6-{$CH_2N(^tBu)Me$}$_2$, Ni–Br = 2.437(2) Å and 2.4459(30) Å) [26], and thus is one of the longest Ni(II)–Br distances reported to this date. The reason for this deviation is not obvious to us especially since the trans influence of the cyclohexyl ring in **2a** is no different from other sp^3-hybridized ligands. It can be noted that the position of the bromide deviates slightly from the coordination plane and it is also possible that the Ni–Cl distance is underestimated by the crystal structure due to libration [27].

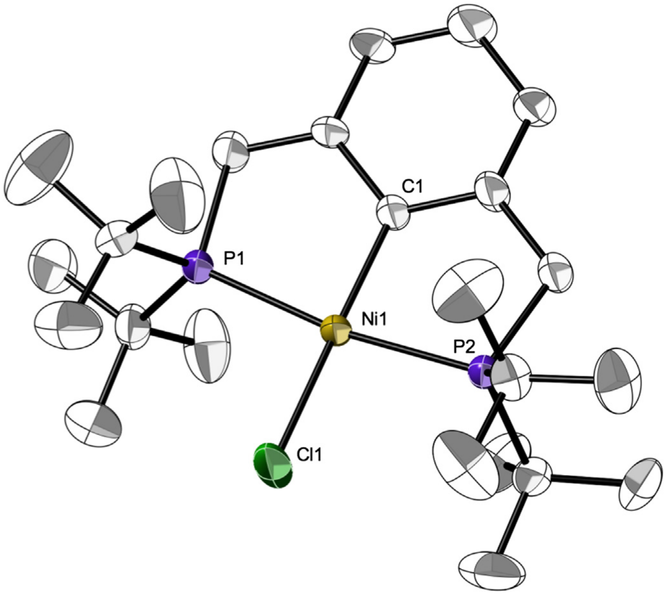

Fig. 1. Molecular structure of **2a** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.990(4), Ni1–P1 = 2.2346(11), Ni1–P2 = 2.2251(11), Ni1–Cl1 = 2.2497(14), C1–Ni1–Cl1 = 178.81(18), P1–Ni1–P2 = 170.83(5), P1–Ni1–C1 = 85.97(13), P2–Ni1–C1 = 85.06(13), P1–Ni1–Cl1 = 94.70(5), P2–Ni1–Cl1 = 94.46(5).

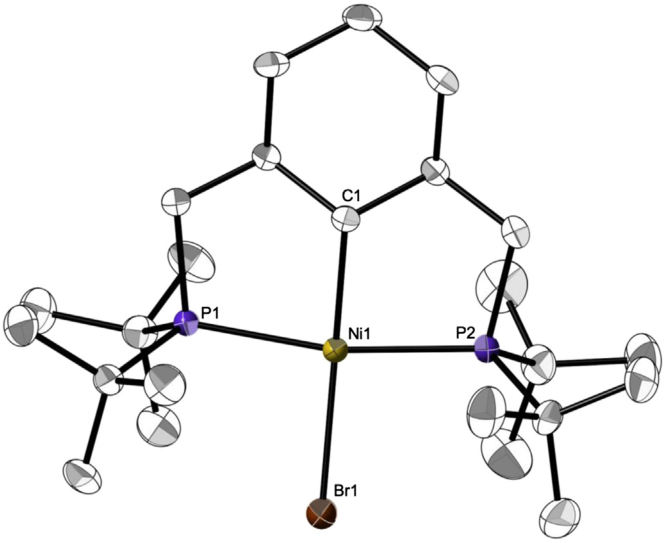

Fig. 2. Molecular structure of **2b** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.998(2), Ni1–P1 = 2.2402(7), Ni1–P2 = 2.2325(7), Ni1–Br1 = 2.4303(4), C1–Ni1–Br1 = 169.48(7), P1–Ni1–P2 = 168.42(3), P1–Ni1–C1 = 85.09(7), P2–Ni1–C1 = 85.15(7), P1–Ni1–Br1 = 95.476(19), P2–Ni1–Br1 = 95.26(2).

The complexes showed no sign of decomposition upon exposure to air in solution, and could be stored under air as solids at room temperature or in pentane solution at −30 °C for several weeks. Initial studies confirm a low reactivity of these complexes; refluxing **2a** in toluene/ethanol (1:1) with $NaBH_4$ did not result in any conversion to the corresponding hydride, as is reported for the analogous aromatic nickel pincer complex [28], nor did treatment with $LiAlH_4$ in toluene that has been used for the synthesis of similar phosphinite pincer hydride complexes [9b]. Piers and co-workers have reported on the conversion of a $PC_{sp3}P$ nickel bromide complex to a rare nickel carbene complex through dehydrobromination with $KN(SiMe_3)_2$ [29], but under the same reaction conditions **2b** did not display any such reactivity. This rather unexpected lack of reactivity towards the strongly donating hydride and amide is more likely attributed to the bulky ^{t}Bu-substituents than to the electronic environment at the metal centre. **2a** and **2b** have also been tested as catalysts for Kumada coupling of alkyl and aryl halides with alkyl Grignard reagents, but the best GC yields were around 15%, for the coupling of EtMgCl and PhBr. Zargarian et al. have shown that the steric bulk of the phosphorus substituents strongly influences the reactivity in such reactions [10d], and a replacement of the ^{t}Bu-groups for less sterically demanding ^{i}Pr-groups is a topic for future investigations.

4. Conclusion

The complexation behaviour of the cyclohexyl-based $PC_{sp3}P$ ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane towards $NiCl_2$ and $NiBr_2$ has been studied, giving two new $PC_{sp3}P$-supported nickel complexes. The bond distances found in the molecular structures indicate a high reactivity but they were found to be more or less unreactive in a number of standard reactions for these types of complexes.

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References

[1] (a) M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759;
(b) M. Albrecht, M.M. Lindner, Dalton Trans. 40 (2011) 8733;
(c) J. Choi, A.H.R. MacArthur, M. Brookhart, A.S. Goldman, Chem. Rev. 111 (2011) 1761;
(d) N. Selander, K.J. Szabo, Chem. Rev. 111 (2011) 2048.

[2] R.M. Bullock (Ed.), Catalysis without Precious Metals, Wiley-VCH, Hoboken, NJ, 2010.

[3] X.L. Hu, Chem. Sci. 2 (2011) 1867.

[4] (a) O. Vechorkin, X.L. Hu, Angew. Chem. Int. Ed. 48 (2009) 2937;
(b) O. Vechorkin, V. Proust, X.L. Hu, J. Am. Chem. Soc. 131 (2009) 9756;
(c) O. Vechorkin, D. Barmaz, V. Proust, X.L. Hu, J. Am. Chem. Soc. 131 (2009) 12078;
(d) O. Vechorkin, R. Scopelliti, X.L. Hu, Angew. Chem. Int. Ed. 50 (2011) 11777.

[5] O. Vechorkin, V. Proust, X.L. Hu, Angew. Chem. Int. Ed. 49 (2010) 3061.

[6] K.V. Vasudevan, B.L. Scott, S.K. Hanson, Eur. J. Inorg. Chem. (2012) 4898.

[7] A. Castonguay, D.M. Spasyuk, N. Madern, A.L. Beauchamp, D. Zargarian, Organometallics 28 (2009) 2134.

[8] S. Chakraborty, J.A. Krause, H. Guan, Organometallics 28 (2009) 582.

[9] (a) S. Chakraborty, J. Zhang, J.A. Krause, H.R. Guan, J. Am. Chem. Soc. 132 (2010) 8872;
(b) S. Chakraborty, Y.J. Patel, J.A. Krause, H.R. Guan, Polyhedron 32 (2012) 30.

[10] For synthesis and characterization of aliphatic nickel pincer complexes, see: (a) A. Castonguay, C. Sui-Seng, D. Zargarian, A.L. Beauchamp, Organometallics 25 (2006) 602;
(b) V. Pandarus, D. Zargarian, Organometallics 26 (2007) 4321;
(c) V. Pandarus, D. Zargarian, Chem. Commun. (2007) 978;
(d) A. Castonguay, A.L. Beauchamp, D. Zargarian, Organometallics 27 (2008) 5723.

[11] For a thorough kinetic and mechanistic study on the nickelation of aromatic versus aliphatic PCP and POCOP ligands, see: B. Vabre, M.L. Lambert, A. Petit, D.H. Ess, D. Zargarian Organometallics 31 (2012) 6041.

[12] (a) W. Leis, H.A. Mayer, W.C. Kaska, Coord. Chem. Rev. 252 (2008) 1787;
(b) D. Gelman, S. Musa, ACS Catal. 2 (2012) 2456.

[13] J. Zhao, A.S. Goldman, J.F. Hartwig, Science 307 (2005) 1080.

[14] S. Sjovall, O.F. Wendt, C. Andersson, J. Chem. Soc. Dalton (2002) 1396.

[15] D. Olsson, A. Arunachalampillai, O.F. Wendt, Dalton Trans. (2007) 5427.

[16] V.F. Kuznetsov, A.J. Lough, D.G. Gusev, Inorg. Chim. Acta 359 (2006) 2806.

[17] A. Arunachalampillai, D. Olsson, O.F. Wendt, Dalton Trans. (2009) 8626.

[18] Crysalis CCD, Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, 2005.

[19] Crysalis RED, Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, 2005.

[20] G.M. Sheldrick, SHELXTL5.1, Program for Structure Solution and Least Squares Refinement, University of Göttingen, Göttingen, Germany, 1998.

[21] CrystalMaker® Software, Begbroke Science Park, Sandy Lane, Yarnton, Oxfordshire, OX5 1PF, United Kingdom, 2010.

[22] (a) V. Pandarus, A. Castonguay, D. Zargarian, Dalton Trans. (2008) 4756;
(b) M.T. Johnson, O.F. Wendt, Inorg. Chim. Acta 367 (2011) 222.

[23] B.J. Boro, D.A. Dickie, K.I. Goldberg, R.A. Kemp, Acta Crystallogr. E64 (2008) m1304.

[24] A.R. Kennedy, R.J. Cross, K.W. Muir, Inorg. Chim. Acta 231 (1995) 195.

[25] F. Bachechi, Struct. Chem. 14 (2003) 263.

[26] J.A.M. Vanbeek, G. van Koten, M.J. Ramp, N.C. Coenjaarts, D.M. Grove, K. Goubitz, M.C. Zoutberg, C.H. Stam, W.J.J. Smeets, A.L. Spek, Inorg. Chem. 30 (1991) 3059.

[27] J.P. Clusker, M. Lewis, M. Rossi, Crystal Structure Analysis for Chemists and Biologists, Wiley-VCH, 1994.

[28] C.J. Moulton, B.L. Shaw, J. Chem. Soc. Dalton (1976) 1020.

[29] D.V. Gutsulyak, W.E. Piers, J. Borau-Garcia, M. Parvez, J. Am. Chem. Soc. 135 (2013) 11776.