Synthesis and reactivity of BINEPINE-based chiral Fe(II) PNP pincer complexes

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Abstract A new asymmetric chiral PNP ligand based on the 2,6-diaminopyridine scaffold featuring a R-BINEPINE moiety was prepared. Treatment of anhydrous FeX₂ (X = Cl, Br) with 1 equiv of PNP-iPr,BIN at room temperature afforded the coordinatively unsaturated paramagnetic complexes [Fe(PNP-iPr,BIN)X₂]. The structure of [Fe(PNP-iPr,BIN)Cl₂] is described. Both complexes react readily with the strong π-acceptor ligand CO in solution to afford selectively the diamagnetic complexes trans-[Fe(PNP-iPr,BIN)(CO)X₂] in quantitative yield. Due to the lability of the CO ligand, these complexes are only stable under a CO atmosphere and isolation in pure form was not possible. The preparation of the carbonyl hydride complex [Fe(PNP-iPr,BIN)(H)(CO)Br] was achieved albeit in low yields via a one pot procedure by treatment of [Fe(PNP-iPr,BINEP)Br₂] with CO and subsequent reaction with Na[HBEt₃]. This complex was obtained as an inseparable mixture of two diastereomers in a ca. 1:1 ratio and was tested as catalyst for the hydrogenation of ketones. The catalyst showed acceptable activity under mild conditions (5 bar H₂, room temperature) with yields up to >99 % within 18 h.

Keywords Iron · Pincer ligands · Chiral phosphines · Carbon monoxide

Introduction

In view of concerns regarding economy, environment, and sustainable energy, there is a constant need for the discovery of new catalytic reactions. A process we are interested in is the catalytic hydrogenation of polar multiple bonds via molecular hydrogen. This plays a significant role in modern synthetic organic chemistry and is excellently performed by many transition metal hydride complexes containing noble metals such as ruthenium, rhodium, or iridium [1–5]. The limited availability of precious metals, their high price, and their toxicity lowers the attractiveness of these metals in the future and more economical and environmentally friendly alternatives have to be found which are in line with green chemistry guidelines. In this respect, the preparation of well-defined iron-based hydride catalysts of comparable or even higher activity is desirable [6–12]. Iron is the most abundant transition metal in the earth crust, and ubiquitously...
available. Accordingly, it is not surprising that the field of iron catalyzed hydrogenations of polar multiple bonds is rapidly evolving as shown by several recent examples [13–27].

We are currently focusing on the synthesis and reactivity of iron complexes containing PNP pincer ligands based on the 2,6-diaminopyridine scaffold [28–38]. In these ligands the aromatic pyridine ring and the phosphine moieties are connected via NH, N-alkyl, or N-aryl linkers. Complexes of the type [Fe(PNP-iPr)(H)(CO)(L)]n with labile ligands (L = Br−, CH3CN, BH4−) and NH spacers were found to be efficient catalysts for the hydrogenation of both ketones and aldehydes to alcohols under mild conditions (Scheme 1) [35].

Herein we report on the synthesis, characterization, and preliminary catalytic activity of asymmetric chiral iron pincer complexes where PiPr2 and BINEPINE moieties are connected to the pyridine ring of the PNP ligand via NH spacers. The iPr substituents were chosen to prevent the coordination of two PNP ligands as found recently for sterically little demanding PNP systems [34, 36].

Results and discussion

Treatment of the mono-phosphinated ligand PNNH2-iPr (1) with 1 equiv of BIN-PCI (2) (in the R-form) in the presence of NEt3 afforded the new asymmetric chiral PNP ligand PNP-iPr,BIN (3) in 64% isolated yield (Scheme 2). The optically pure ligand was isolated as air stable solid and was characterized by elemental analysis, 1H, 13C{1H}, and 31P{1H} NMR spectroscopy.

Treatment of anhydrous FeCl2 with 1 equiv of the PNP ligand PNP-iPr,BIN (3) in THF at room temperature afforded the coordinatively unsaturated complex [Fe(PNP-iPr,BIN)Cl2] (4a) in 79% isolated yields (Scheme 3). The analogous bromide complex [Fe(PNP-iPr,BIN)Br2] (4b) was obtained in similar fashion by straightforward complexation of the respective free PNP ligand with anhydrous ferrous dibromide (84% yield). All complexes are thermally robust pale yellow solids that are air sensitive in the solid state and particularly in solution. They display large paramagnetic shifted 1H and 13C{1H} NMR solution spectra with broad and featureless signals which, due to the complexity of the PNP ligands, were not assignable and thus not informative. These complexes were characterized by elemental analysis. In addition the molecular structure of 4d was determined by X-ray crystallography. In this case, the racemic BIN-PCI (2) was used, since all attempts to grow crystals suitable for X-ray diffraction studies failed for the chiral compounds. A structural view of 4a is depicted in Fig. 1 with selected bond distances and angles given in the caption. The coordination geometry of the iron center is distorted square pyramidal. Bond distances and angles are in good accord with the solid state structures of similar complexes of the type [Fe(κ3P,N,P-PNP)Cl2] [29]. Particularly characteristic for all these complexes are the comparatively long Fe–N and Fe–P bonds which clearly...
indicate that they are in high-spin state; low-spin Fe–PNP complexes have Fe–N and Fe–P bonds by ca. 0.2 Å shorter.

In order to obtain iron-based hydrogenation catalysts it appears to be important to have diamagnetic complexes. Accordingly, virtually all iron complexes that are active catalysts feature the strong field CO and hydride ligands, which seem to maintain a low spin configuration throughout the catalytic cycle. Complexes 4a and 4b react readily with the strong \( \pi \)-acceptor ligand CO in solution to afford selectively the diamagnetic, octahedral complexes 5a and 5b which exhibit a single low-intensity triplet resonance at 220.7 ppm (t, \( \text{\text{^1}H} \)) and 223.1 ppm (t, \( \text{\text{^1}H} \)), respectively. The \( \text{\text{^31}P} \)\( \text{\text{^1}H} \) NMR spectra afford rise to two doublets centered at 143.6/125.3 ppm and 143.9/125.1 ppm, respectively, with large \( \text{\text{JPP}} \) coupling constants of 190 and 177 Hz which are consistent with a \( \text{\text{trans-P,P}} \) configuration.

The preparation of carbonyl hydride complexes was attempted via a one pot procedure by treatment of \([\text{Fe(PNP-iPr,BIN)Br}_2]\) (4b) with CO and subsequent reaction with 1.1 equivs of Na[HBEt_3] (Scheme 4). Complex \([\text{Fe(PNP-iPr,BIN)}(\text{H})(\text{CO})\text{Br}]\) (6) was obtained as an inseparable mixture of two diastereomers in a ca. 1:1 ratio. Together with 6, a considerable amount of free PNP-iPr-BIN ligand was detected in the \( \text{\text{^31}P} \)\( \text{\text{^1}H} \) NMR spectrum, and the yield was low (ca 50 %). In good agreement with the experimental findings, also DFT/B3LYP calculations showed that the energy difference between the two isomers (denoted as 6A and 6B) is merely 10.5 kJ/mol (Fig. 2). In both isomers, the hydride ligands are located \text{\text{trans}} to the bromide ligand. Complex 6 turned out to be unstable in solution and slow decomposition took place. Accordingly, complete purification and characterization was unsuccessful. The products were identified by \( \text{\text{^1}H} \) NMR where the hydride signals of the two isomers 6A and 6B gave rise to triplet resonances at \(-22.15 \text{ ppm (t, } \text{\text{\text{JPH}} = 61.6 Hz}) \) and \(-22.36 \text{ ppm (t, } \text{\text{\text{JPH}} = 31.1 Hz}) \), respectively (Fig. 3). The assignments are based on DFT calculations.

Despite these facts, complex 6 (as mixture of two diastereomers), prepared in situ, was tested as catalyst for the hydrogenation of some ketones. Since the catalyst could not be isolated in pure form, only preliminary tests were performed with five substrates. These results are depicted in Table 1. The catalyst showed acceptable activity under mild conditions (5 bar \( \text{H_2} \), room temperature) with yields up to \( >99 \% \) within 18 h indicating that in
further experiments the catalyst loadings and possibly reaction times can be reduced significantly.

In conclusion, we describe here the synthesis of a new asymmetric chiral PNP ligand based on the 2,6-diaminopyridine scaffold featuring an R-BINEPINE moiety. This ligand reacts with anhydrous FeX2 (X = Cl, Br) to afford the coordinatively unsaturated paramagnetic complexes [Fe(PNP-iPr,BIN)X2]. Both complexes react...
Table 1 Hydrogenation of ketones catalyzed by [Fe(PNP-iPr,BIN)(H)(CO)Br] (6)

| Entry | Substrate | Product | Yield%* |
|-------|-----------|---------|---------|
| 1     |           |         | 89      |
| 2     |           |         | 96      |
| 3     |           |         | >99     |
| 4     |           |         | >99     |

* Yields were determined by 1H NMR
b R = naphtyl

readily with the strong π-acceptor ligand CO in solution to afford selectively and quantitatively trans-[Fe(PNP-iPr,BIN)(CO)(CO)Br] was achieved albeit in low yields via a one pot synthesis. This complex was obtained as an inseparable mixture of two diastereomers and was successfully tested as catalyst for the hydrogenation of ketones.

Experimental

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in an MBraun inert-gas glovebox. The solvents were purified according to standard procedures [39]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. The ligands N2-(diisopropylphosphanyl)pyridine-2,6-diamine (PNP-iPr,BIN) (1) and (1R)-4-chloro-4,5-dihydro-3H-dinaphtho[2,1-c:1’,2’-e]phosphepin (BIN-PCI) (2) were prepared according to the literature [37, 40]. 1H, 13C{1H}, and 31P{1H} NMR spectra were recorded on Bruker AVANCE-250, AVANCE-300 DPX, and AVANCE-400 spectrometers. 1H and 13C{1H} NMR spectra were referenced internally to residual protio-solvent, and solvent resonances, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). 31P{1H} NMR spectra were referenced externally to H3PO4 (85%) (δ = 0 ppm).

(1R)-N2-(3,5-Dihydro-4H-dinaphtho[2,1-c:1’,2’-e]phosphepin-4-yl)-N6-(diisopropylphosphanyl)pyridine-2,6-diamine (PNP-iPr,BIN)(3, C33H35N3P2)

1 (1.00 eq, 6.55 mmol, 1.47 g) was dissolved in 100 cm3 toluene and 1.4 cm3 Et3N (1.50 eq, 9.83 mmol) was added. After cooling to 0°C, 2.50 g 2 (1.10 eq, 7.21 mmol) in 50 cm3 toluene was added and the reaction was stirred at 80°C for 12 h. The suspension was filtered over a small pad of Celite® and the solvent was removed under reduced pressure. The crude product was purified via flash chromatography using silica gel (conditioned with 5 vol % NEt3) and 1:1 MC/EE as eluent. Yield: 2.25 g (64%), 1H NMR (CDCl3, 20°C): δ = 7.89–7.79 (m, 4H, naph), 7.47 (dd, 3JHH = 8.3 Hz, 1H, naph), 7.38–7.32 (m, 2H, naph), 7.31 (dd, 3JHH = 8.3 Hz, 1H, naph), 7.23 (m, 5H, py4, naph), 6.43 (dd, 3JHH = 8.0 Hz, 3JHH = 1.9 Hz, 1H, py5), 6.22 (dd, 3JHH = 8.4 Hz, 1H, py5), 4.31 (dd, 2JHH = 10.9 Hz, 1H, NHNPh), 4.08 (dd, 2JHH = 10.7 Hz, 1H, NHNPh), 3.03 (dd, 2JHH = 17.0 Hz, 1JCP = 11.9 Hz, 1H, CH2), 2.70 (dd, 2JHH = 14.3 Hz, 1JCP = 12.8 Hz, 1H, CH2), 2.50 (dd, 2JHH = 18.2 Hz, 2JHH = 14.3 Hz, 1H, CH2), 2.29 (dd, 2JHH = 11.9 Hz, 1H, CH2), 1.68 (m, 2H, CH(CH3)2), 1.04–0.95 ppm. 31P{1H} NMR (CDCl3, 20°C): δ = 159.92 (d, 2JCP = 20.0 Hz, py5), 157.01 (d, 2JCP = 17.4 Hz, py5), 139.25 (s, py5), 133.79 (d, JCP = 4.1 Hz, naph), 133.43 (s, naph), 133.08 (s, naph), 132.82 (d, JCP = 1.5 Hz, naph), 132.72 (s, naph), 132.38 (s, naph), 132.28 (d, JCP = 1.8 Hz, naph), 132.15 (s, naph), 128.24 (s, naph), 127.58 (s, naph), 127.23 (d, JCP = 2.1 Hz, naph), 126.69 (d, JCP = 10.8 Hz, naph), 126.06 (d, JCP = 11.5 Hz, naph), 125.09 (d, JCP = 11.9 Hz, naph), 98.90 (d, JCP = 18.4 Hz, py5), 98.73 (d, 2JCP = 15.7 Hz, py5), 36.04 (d, 1JCP = 15.0 Hz, CH2), 34.90 (d, 1JCP = 24.2 Hz, CH2), 26.43 (d, 1JCP = 11.5 Hz, CH(CH3)2), 16.34 (d, 1JCP = 11.0 Hz, CH(CH3)2), 17.82 (d, 2JCP = 19.8 Hz, CH(CH3)2), 17.22 (d, 2JCP = 10.6 Hz, CH(CH3)2), 17.14 (d, 2JCP = 10.4 Hz, CH(CH3)2) ppm; 31P{1H} NMR (CDCl3, 20°C): δ = 48.6 (s, iPr), 48.1 (s, BIN) ppm.

[(Dichloro)(1R)-N2-(3,5-dihydro-4H-dinaphtho[2,1-c:1’,2’-e]phosphepin-4-yl)-N6-(diisopropylphosphanyl)pyridine-2,6-diamine]iron(II)] ((Fe(PNP-iPr,BIN)Cl2) (4a, C33H35Cl2FeN3P2)

A suspension of 71 mg anhydrous FeCl2 (0.56 mmol) and 300 mg 3 (0.56 mmol) was stirred in 15 cm3 of THF at
CO was bubbled through a solution of 30 mg 4a in 0.6 cm³ of CD₂Cl₂ for 2 min, whereupon the colour changed to dark violet. ¹H NMR (CD₂Cl₂, 20 °C): δ = 8.01–7.90 (m, 4H, naph), 7.80 (d, 3JHH = 7.9 Hz, 1H, naph), 7.54 (d, 3JHH = 7.5 Hz, 1H, naph), 7.41–7.36 (m, 3H, naph), 7.30 (d, 3JHH = 8.4 Hz, 1H, naph), 7.25–7.03 (m, 3H, naph, py 5), 6.50 (bs, 1H, py 5), 6.32 (d, 2JPP = 5.9 Hz, 1H, NH(Pr)), 5.83 (bs, 1H, py 5), 5.50 (d, 2JPP = 6.0 Hz, 1H, NH(BIN)), 4.67 (dd, 2JHH = 12.5 Hz, 2JPP = 3.9 Hz, 1H, CH₂), 3.94 (dd, 2JHH = 15.1 Hz, 2JPP = 8.8 Hz, 1H, CH₂), 3.10 (m, 3H, CH₂, CH(CH₃)₂), 2.73 (dd, 2JHH = 17.3 Hz, 2JPP = 13.3 Hz, 1H, CH₂), 1.49 (dd, 3JHH = 5.8 Hz, 2JPP = 12.1 Hz, 3H, CH(CH₃)₂), 1.45 (dd, 3JHH = 6.8 Hz, 2JPP = 15.3 Hz, 3H, CH(CH₃)₂), 1.41 (dd, 3JHH = 7.2 Hz, 2JPP = 16.9 Hz, 3H, CH(CH₃)₂), 1.32 (dd, 3JHH = 7.2 Hz, 2JPP = 16.6 Hz, 3H, CH(CH₃)₂) ppm; ¹³C{¹H} NMR (CD₂Cl₂, 20 °C): δ = 223.05 (t, 2JCP = 21.9 Hz, CO), 161.97 (dd, 2JCP = 12.6 Hz, 3JCP = 5.3 Hz, py 6), 160.60 (dd, 2JCP = 13.3 Hz, 3JCP = 5.1 Hz, py 5), 140.11 (s, py 5), 134.65 (s, naph), 134.12 (d, JCP = 5.0 Hz, naph), 133.67 (d, JCP = 10.9 Hz, naph), 133.18 (d, JCP = 2.6 Hz, naph), 132.92 (d, JCP = 1.3 Hz, naph), 132.44 (s, naph), 132.18 (d, JCP = 2.4 Hz, naph), 131.61 (d, JCP = 2.9 Hz, naph), 129.08 (s, naph), 128.80 (d, JCP = 2.2 Hz, naph), 128.39 (d, JCP = 6.2 Hz, naph), 128.22 (d, JCP = 3.5 Hz, naph), 127.63 (d, JCP = 1.6 Hz, naph), 126.92 (d, JCP = 13.8 Hz, naph), 126.41 (s, naph), 126.10 (s, naph), 125.61 (d, JCP = 13.5 Hz, naph), 100.17 (d, 3JCP = 7.0 Hz, py 5), 99.67 (d, 3JCP = 7.2 Hz, py 5), 36.23 (d, 4JCP = 23.3 Hz, CH₂), 31.39 (d, 4JCP = 27.9 Hz, CH₂), 28.48 (d, 4JCP = 22.6 Hz, CH(CH₃)₂), 28.01 (d, 4JCP = 23.3 Hz, CH(CH₃)₂), 18.97 (d, 4JCP = 4.5 Hz, CH(CH₃)₂), 18.52 (m, CH(CH₃)₂) ppm; ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): δ = 143.9 (d, 2JPP = 176.6 Hz, BIN), 125.1 (d, 2JPP = 176.5 Hz, iPr) ppm.

Reformation of [Fe(PNP-iPr,BIN)Br₂] (4b) with CO and Na[HBEt₃]. Formation of [(bromo)(hydrido)(carbonyl)(1R)-N₂-(3,5-dihydro-4H-dinaphtho[2,1-c:1',2'-e]phosphepin-4-yl)-N₆-(disopropylphosphanyl)pyridine-2,6-diamine)iron(II)] (trans-[Fe(PNP-iPr,BIN)(CO)Br₂]) (5b, C₃₃H₃₅Br₂FeN₆OP₂)

A solution of 300 mg 4b (0.40 mmol) in 15 cm³ THF was purged with CO for 3 min, whereupon the colour changed to deep blue. The reaction mixture was then cooled to 0 °C and...
Calculations were performed using the Gaussian 09 software package [46], and the B3LYP functional [47–49] without symmetry constraints. This functional was shown to perform well in mechanistic studies of spin forbidden reactions in closely related Fe system. The optimized geometries were obtained with the Stuttgart/Dresden ECP (SDD) basis set [50–52] to describe the electrons of the iron atom. For all other atoms a standard 6-31G** basis set was employed [53–58]. Frequency calculations were performed to confirm the nature of the stationary points yielding no imaginary frequency for the minima.

X-ray structure determination

X-ray diffraction data of 4a-xTHF-(2-x)Et2O (CCDC number 1445976) were collected at $T = 100$ K in a dry stream of nitrogen on a Bruker Kappa APEX II diffractometer system using graphite-monochromatized MoKα radiation (λ = 0.71073 Å) and fine sliced φ- and ω-scans. Data were reduced to intensity values with SAINT and an absorption correction was applied with the multi-scan approach implemented in SADABS [41]. The structures were solved by charge flipping using SUPERFLIP [42] and refined against F with JANA2006 [43]. The electron density in distinct voids of the structure could be attributed to two solvent positions. On one was located an Et2O molecule and the other was substitutionally disordered by Et2O and THF molecules. Since no refinement with reasonable ADPs of the solvent molecules could be obtained, contributions of the solvent molecules to the diffraction data were removed using the SQUEEZE procedure of PLATON [44]. The non-hydrogen atoms were refined anisotropically.

The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. H atoms connected to N located in difference Fourier maps. Since the point group 4/m of the crystal is a merohedry twinning via twofold rotation about [110] was included in the model. Such models did not result in improved residuals and twinning was ultimately dropped from the refinement. Molecular graphics were generated with the program MERCURY [45]. Crystal data are given in Table S1.

Computational details

References

1. Noyori R, Ohkuma T (2001) Angew Chem Int Ed 40:40
2. Noyori R (2013) Angew Chem Int Ed 52:79
3. de Vries JG, Elsevier CJ (eds) (2007) Handbook of homogeneous hydrogenation. Wiley, Weinheim
4. Johnson NB, Lennon IC, Moran PH, Ransdams JA (2007) Acc Chem Res 40:1291
5. Dub PA, Ikariya T (2012) ACS Catal 2:1718
6. Morris RH (2009) Chem Soc Rev 38:2282
7. Enthaler S, Junge K, Beller M (2008) Angew Chem Int Ed 47:3317
8. Gaillard S, Renaud J-L (2008) ChemSusChem 1:505
9. Bauer I, Kno¨ lker H-J (2015) Chem Rev 115:3170
10. Sues PE, Demmans Z, Morris RH (2014) Dalton Trans 43:7650
11. Bullock RM (2013) Science 342:1054
12. Langer R, Diskin-Posner Y, Leitus G, Ben-David Y, Milstein D (2011) J Am Chem Soc 133:5816
13. Casey CP, Guan H (2009) J Am Chem Soc 131:2499
14. Zell T, Ben-David Y, Milstein D (2013) Chem Eur J 19:8068
15. Langer R, Leitus G, Ben-David Y, Milstein D (2011) Angew Chem Int Ed 50:2120
16. Zell T, Ben-David Y, Milstein D (2014) Angew Chem Int Ed 53:4685
17. Zell T, Ben-David Y, Milstein D (2015) Catal Sci Technol 5:822
18. Berkessel A, Reichau S, von der Höh A, Leconte N, Neudörfl J-M (2011) Organometallics 30:3880
19. Sui-Seng C, Freutel F, Lough AJ, Morris RH (2008) Angew Chem Int Ed 47:940
20. Sui-Seng C, Haque FN, Hadzovic A, Pütz A-M, Reuss V, Meyer N, Lough AJ, Zimmer-De Iuliis M, Morris RH (2009) Inorg Chem 48:735
21. Lagaditis PO, Sues PE, Sonnenberg JF, Wan KY, Lough AJ, Morris RH (2014) J Am Chem Soc 136:1367
22. Zillo W, Tauer S, Prokopchuk DE, Morris RH (2014) Organometallics 33:5791
23. Tili A, Schranck J, Neumann H, Beller M (2012) Chem Eur J 18:15935
27. Fleischer S, Zhou S, Junge K, Beller M (2013) Angew Chem Int Ed 52:5120
28. Benito-Garagorri D, Becker E, Wiedermann J, Lackner W, Pollak M, Mereiter K, Kisala J, Kirchner K (2006) Organometallics 25:1900
29. Benito-Garagorri D, Wiedermann J, Pollak M, Mereiter K, Kirchner K (2007) Organometallics 26:217
30. Benito-Garagorri D, Puchberger M, Mereiter K, Kirchner K (2008) Angew Chem Int Ed 47:9142
31. Benito-Garagorri D, Alves LG, Puchberger M, Mereiter K, Veiros LF, Calhorda MJ, Ferreira LP, Godinho M, Kirchner K (2009) Organometallics 28:6902
32. Benito-Garagorri D, Alves LG, Veiros LF, Standfest-Hauser CM, Tanaka S, Mereiter K, Kirchner K (2010) Organometallics 29:4923
33. Bichler B, Holzhacker C, Stöger B, Puchberger M, Veiros LF, Kirchner K (2013) Organometallics 32:4114
34. Bichler B, Glatz M, Stöger B, Mereiter K, Veiros LF, Kirchner K (2014) Dalton Trans 43:14517
35. Gorgas N, Stöger B, Pittenauer E, Allmaier G, Veiros LF, Kirchner K (2014) Organometallics 33:6905
36. Glatz M, Bichler B, Mastalir M, Stöger B, Mereiter K, Weil M, Pittenauer E, Allmaier G, Veiros LF, Kirchner K (2015) Dalton Trans 44:281
37. Holzhacker C, Stöger B, Carvalho MD, Ferreira LP, Pittenauer E, Allmaier G, Veiros LF, Kirchner K (2015) Dalton Trans 44:13071
38. Glätz M, Holzhacker C, Bichler B, Mastalir M, Stöger B, Mereiter K, Weil M, Veiros LF, Kirschner K, Rüegsegger (2015) Eur J Inorg Chem 5053
39. Perrin DD, Armarego WLF (1988) Purification of laboratory chemicals, 3rd edn. Pergamon Press, New York
40. Junge K, Oehme G, Monsees A, Riermeier T, Dingerdissen U, Beller M (2003) J Organomet Chem 675:91
41. Bruker Computer Programs (2012) APEX2, SAINT, and SADABS. Bruker AXS Inc., Madison, WI
42. Palatinus L, Chapuis G (2007) J Appl Cryst 40:786
43. Petříček V, Dušek M, Palatinus L (2006) JANA2006, the crystallographic computing system. Institute of Physics, Praha, Czech Republic
44. Spek AL (2009) Acta Cryst D65:148
45. Macrae CF, Edgington PR, McCabe P, Pidcock E, Shields GP, Taylor R, Towler M, van de Streek J (2006) J Appl Cryst 39:453
46. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman Jr, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision A.02. Gaussian Inc., Wallingford
47. Becke AD (1993) J Chem Phys 98:5648
48. Miehlich B, Savin A, Stoll H, Preuss H (1989) Chem Phys Lett 157:200
49. Lee C, Yang W, Parr G (1988) Phys Rev B 37:785
50. Haeusermann U, Dolg M, Stoll H, Preuss H (1993) Mol Phys 78:1211
51. Kuechle W, Dolg M, Stoll H, Preuss H (1994) J Chem Phys 100:7535
52. Leininger T, Nicklass A, Stoll H, Dolg M, Schwerdtfeger P (1996) J Chem Phys 105:1052
53. McLean AD, Chandler GS (1980) J Chem Phys 72:5639
54. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72:6560
55. Hay PJ (1977) J Chem Phys 66:4377
56. Raghavachari K, Trucks GW (1989) J Chem Phys 91:1062
57. Binning RC, Curtiss LA (1995) J Comput Chem 16:6104
58. McGrath MP, Radom L (1991) J Chem Phys 94:511