Inorganic Chemistry Communications 38 (2013) 131–134

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Exploring the coordination chemistry of 1-benzoyl-4,5-dihydro-3,5-bis(trifluoromethyl)-1*H*-pyrazol-5-ol to copper

Chika I. Someya [a], Shigeyoshi Inoue [b], Stephan Enthaler [a,*]

[a] *Technische Universität Berlin, Department of Chemistry, Cluster of Excellence "Unifying Concepts in Catalysis", Straße des 17. Juni 115/C2, 10623 Berlin, Germany*
[b] *Institute of Chemistry, Metalorganics and Inorganic Materials, Technische Universität Berlin, Straße des 17. Juni 135/C2, D-10623 Berlin, Germany*

ARTICLE INFO

Article history:
Received 26 August 2013
Accepted 11 October 2013
Available online 24 October 2013

Keywords:
Copper
N,O-ligand
Phosphane ligands
DFT calculations
Catalysis

ABSTRACT

The coordination chemistry of the ligand 1-benzoyl-4,5-dihydro-3,5-bis(trifluoromethyl)-1*H*-pyrazol-5-ol (**1a**) has been recently investigated. In dependency of the metal (e.g., nickel, zinc, molybdenum) and the added co-ligand (phosphanes, pyridines, amines) different coordination modes were feasible (e.g., *O,N,O′*, *O,N*, *O,O′*). Herein we present the reaction of **1a** with $Cu(OAc)_2$ and triphenylphosphane as co-ligand to form the copper complex **2** [Cu(**1a**-H)$(PPh_3)_2$]. The complex was characterized and investigated by various techniques, pointing out a new bidentate coordination mode of the ligand. In more detail, X-ray crystallography determined a *N,O*-coordination in which the ligand is planar and the other coordination sites on the copper centre are occupied by two PPh_3 creating a tetrahedral coordination geometry. Moreover, the complex has been applied as precatalyst in the copper-catalyzed amination of aliphatic C–H bonds.

Catalysis is one key technology for the development of sustainable, efficient, and selective synthesis. Furthermore, high atom efficiency, reduced amounts of waste as well as energy, and in consequence advantageous economics can be realized [1]. In this regard, metal catalysis turned out to be an excellent methodology illustrated by countless applications in organic chemistry [2]. In more detail, the properties of the catalyst is strongly influenced and finetuned by ligands [3]. Hence, the choice of ligands coordinated to the transition metal should be considered from chemical and economical points of view, taking into account inexpensiveness, great availability, easy synthesis, high tunability, high flexibility and stability. Based on that, the design of new ligands and the study of their coordination chemistry is an important research aim [4]. With respect to these requirements an interesting motif can be the ligand class **1**, which is easily accessible starting from commercially available chemicals (Fig. 1). Recently, the coordination chemistry of ligand class **1** was investigated. Interestingly, different coordination modes were observed, depending on the metal and the added co-ligands (e.g., *O,N,O′*, *O,N*, *O,O′*). For instance, the reaction of ligand class **1** with $Ni(OAc)_2$•$4H_2O$ and 4-dimethylaminopyridine resulted after double deprotonation in the formation of an octahedral complex with a *O,N,O′*-coordination (Fig. 1, **A**), while in the presence of phosphane co-ligands a square planar geometry was observed [5]. Interestingly, various applications as precatalysts have been reported, e.g., C–C cross-coupling reactions, hydrodehalogenations, hydrodecyanations [6]. On the other hand reacting **1** with $ZnMe_2$ revealed a *O,O′*-coordination after deprotonation (Fig. 1, **B**) [7]. Interestingly, addition of a base (TMEDA) to the complex allowed the second deprotonation and created a seven-membered ring system (Fig. 1, **C**). Furthermore, the reaction of $Mo_2(O^tBu)_6$ with ligand class **1** showed *O,O′*-coordination and was a useful precatalyst for the reduction of organic amides to amines (Fig. 1, **D**) [8]. Based on our ongoing interest in the coordination chemistry of 5-hydroxypyrazoline ligands we report herein on the synthesis and characterization of a 5-hydroxypyrazoline copper complex revealing a new coordination mode and the application as precatalyst in the copper-catalyzed amination of C-H bonds.

The ligand **1a** was synthesized in accordance with methods reported in the literature [9]. In more detail, benzohydrazide was refluxed with hexafluoroacetyl acetone in ethanol obtaining ligand **1a** after work-up as crystalline compound. Next, to investigate the coordination abilities of **1a** with copper a mixture of **1a**, $Cu(OAc)_2$ and an excess of triphenylphosphane (3.0 equiv.) was stirred at room temperature for 16 h (Scheme 1). Afterwards all volatiles were removed in vacuum and the residue was extracted with methanol. The filtrate was concentrated to result in the formation of a yellow powder in 43% yield. Crystals suitable for X-ray diffraction analysis were attained from a toluene solution by slow evaporation of the solvent. The solid-state structure of complex **2** has been characterized by single-crystal X-ray diffraction analysis [10]. The thermal ellipsoid plots, selected bond lengths and angles are shown in Fig. 2. In contrast to other row 4 metals (e.g., Ni, Fe or Zn) a *N,O′*-coordination was observed. In more detail, a planar five-membered ring is created by the coordination of the benzoyl oxygen O1 and the N1 to the copper. In addition, two triphenylphosphanes are coordinated to the copper center creating a tetrahedral geometry. Interestingly, the oxygen O2 is not coordinated to the metal. However, with the obtained data it was not possible to accurately describe the bond situation in complex **2**, since different isomers (**2–1**, **2–2**, **2–3**, **3–4**) and a disorder of the non-coordinated

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* Corresponding author. Tel.: +49 30314 22039; fax: +49 30314 29732.
E-mail address: stephan.enthaler@tu-berlin.de (S. Enthaler).

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http://dx.doi.org/10.1016/j.inoche.2013.10.016

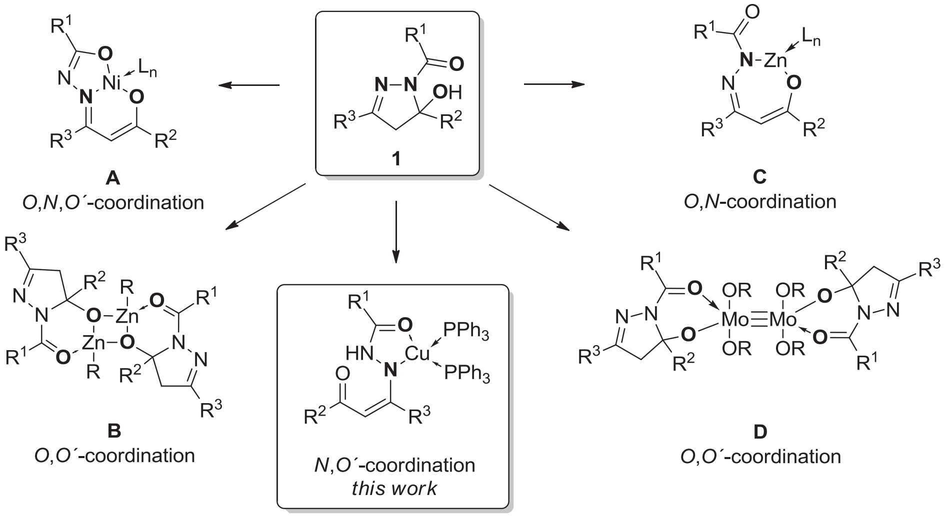
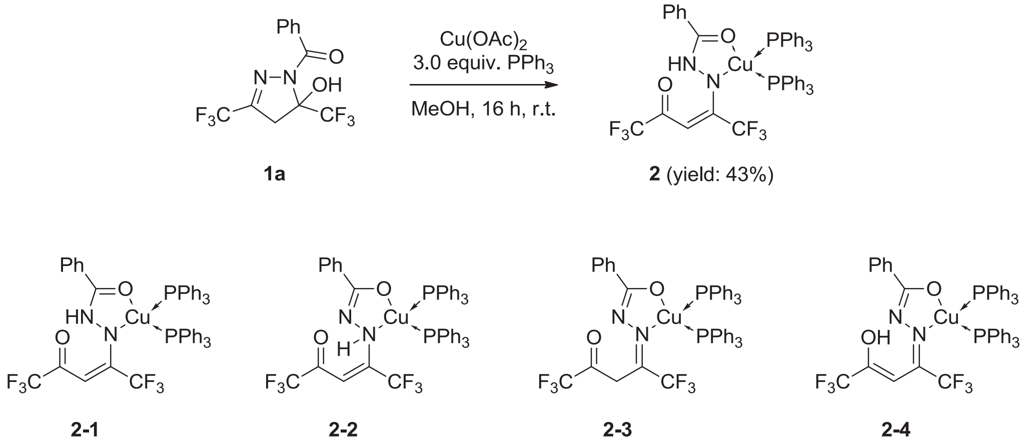


Fig. 1. Coordination modes of ligand class **1**.



Scheme 1. Synthesis of the copper complex **2** and its possible isomers.

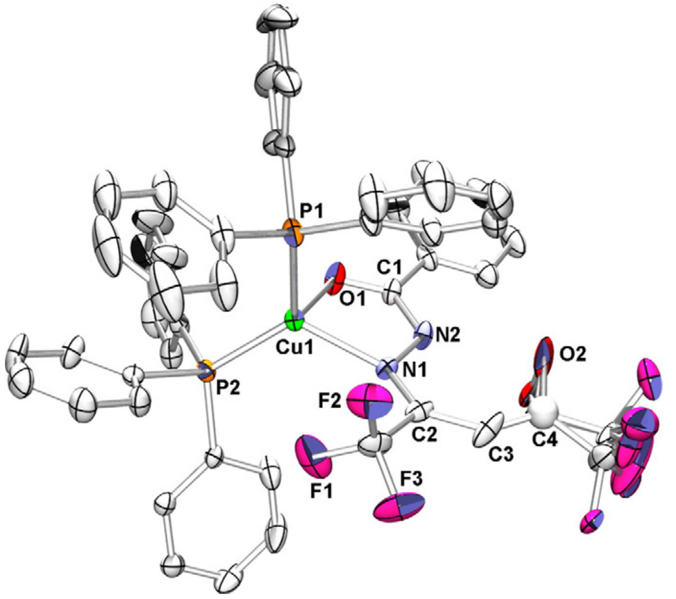


Fig. 2. Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarify. Selected bond lengths (Å) and angle (°) Cu-O1: 2.0937(19); Cu-N1: 2.121(2); Cu-P1: 2.2566(8); Cu-P2: 2.2482(8); O1-C1: 1.239(3); C1-N2: 1.354(3); N1-N2: 1.393(3); N1-C2: 1.311(3); C2-C3: 1.435 (5); O1-Cu1-N1: 77.29(8); P1-Cu1-P2: 124.30(3).

$C(O)CF_3$ are feasible (Scheme 1). Moreover, to clarify the oxidation state of the copper Electron Paramagnetic Resonance (EPR) measurements have been carried out. However, no signals for unpaired electrons were detected excluding the presence of a Cu(II)-d^9, and a Cu(I)-d^{10} centre with no unpaired electrons is assumed. Based on that, during the complex formation a reduction process of Cu(II) to Cu(I) takes place, probably with portions of the ligand **1a** or the solvent methanol as sacrificial reagents [11]. The analysis of the filtrate revealed the formation of triphenylphosphane oxide and numerous unknown fluorine containing compounds, which originated from the ligand **1a**. The properties of the diamagnetic complex **2** were investigated by NMR techniques in solution. A signal was found at $\delta = 5.79$ ppm assigned to the C3–H proton. This was further proven by the absence of any signal of the former CH_2 group in the ligand. In addition, a broad signal at $\delta = 17.17$ ppm could be attributed to N–H or O–H protons. Interestingly, the addition of methanol-d4 showed a fast exchange of the N–H or O–H proton. Noteworthy, a ratio of 1:1 of the C3–H proton and the N–H or O–H proton was found. Based on that, the isomer **2–3** with a CH_2 group can be excluded (Scheme 1). Moreover, the tetrahedral structure was confirmed by the occurrence of a single signal at $\delta = -0.66$ ppm in the $^{31}P\{^1H\}$ NMR for the triphenylphosphane ligands, which furthermore proves the coordination to the copper (free PPh_3 $\delta = -4.75$ ppm). In order to distinguish between the isomers **2–1**, **2–2** and **2–4** DFT calculations have been performed [12]. The optimized structures and energies are shown in Fig. 3. As the most stable isomer **2–1** was observed, while for **2–2** and **2–4** an energy difference of 85–95 kJ/mol

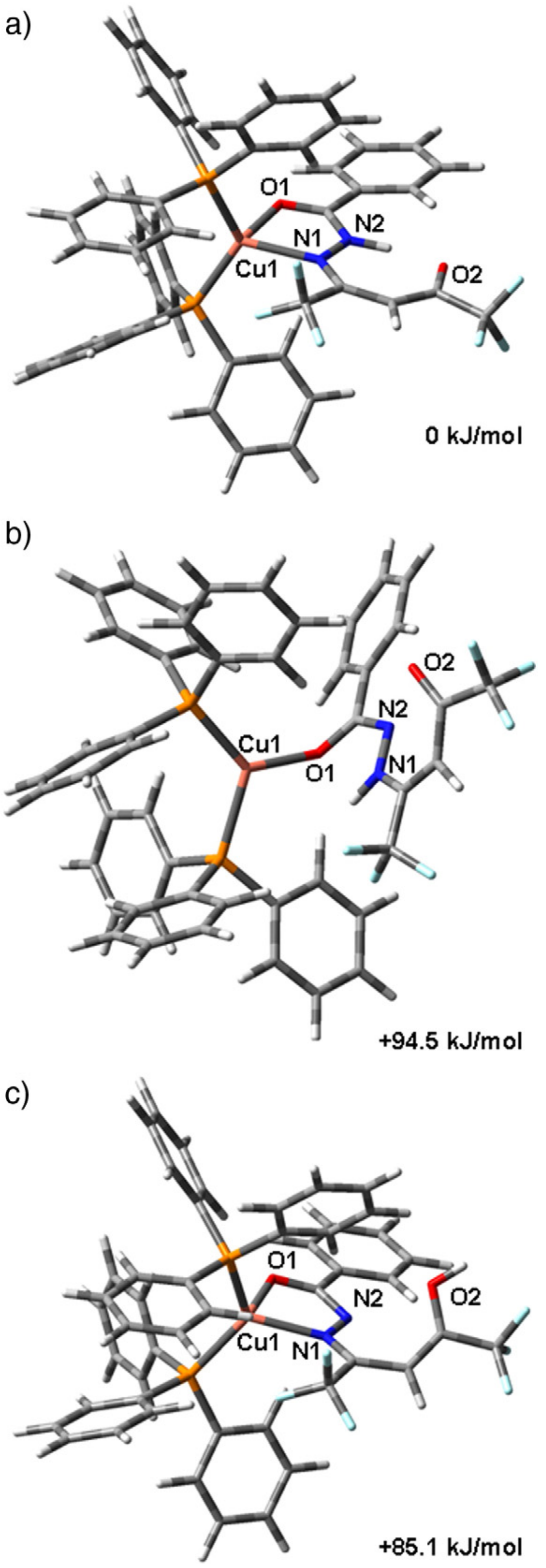


Fig. 3. Optimized structures and energies of the isomers **2–1** (a), **2–2** (b) and **2–4** (c): B3LYP level 6-31G(d) basis set for N, C, O, F, P and H atoms and LANL2DZ for the Cu atom.

was calculated. To understand the electronic nature of complex **2** a molecular orbital analysis was performed. Fig. 4 represents the frontier molecular orbitals. The highest occupied molecular orbital (HOMO) is mainly delocalized over the ligand and also slightly on the d-orbital of the metal (−4.99 eV). On the other hand, the lowest unoccupied molecular orbital (LUMO) is mainly delocalized over the ligand as well as the aromatic substituent of the ligand (−1.45 eV). The energy gap of the HOMO and LUMO was 3.54 eV, which is comparable to the work of Dharmaraj et al. applying a similar ligand motif [11a]. In recent years the application of copper complexes as precatalysts in the amination of C-H bonds to form C-N bonds have been reported [13]. Hence, the catalytic abilities of complex **2** were investigated in the copper-catalyzed amination of aliphatic C-H bonds. In more detail, an excess of cyclohexane (**3**) was reacted with benzamide (**4**) in the presence of 10 mol% **2** applying di-*tert*-butyl peroxide as the oxidant (Scheme 2). After 24 hours at 100 °C a yield of 87% of product **5** and a turnover number of 8.7 were realized, demonstrating the potential of complex **2** in the amination of aliphatic C-H bonds. In summary we have investigated the coordination chemistry of the ligand 1-benzoyl-4,5-dihydro-3,5-bis(trifluoromethyl)-1*H*-pyrazol-5-ol (**1a**) with $Cu(OAc)_2$ and triphenylphosphane as co-ligand to form the copper complex **2** [Cu(**1a**-H)$(PPh_3)_2$]. The complex was characterized and investigated by various techniques, showing a new bidentate coordination mode and the copper center in the oxidation state +1. In more detail, X-ray crystallography revealed a *N,O′*-coordination in which the ligand is

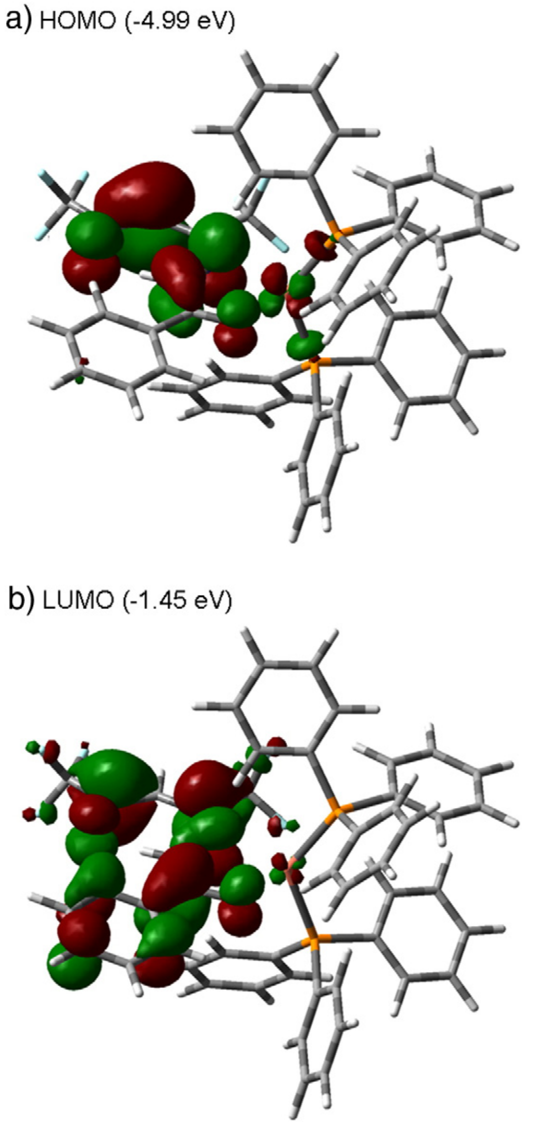
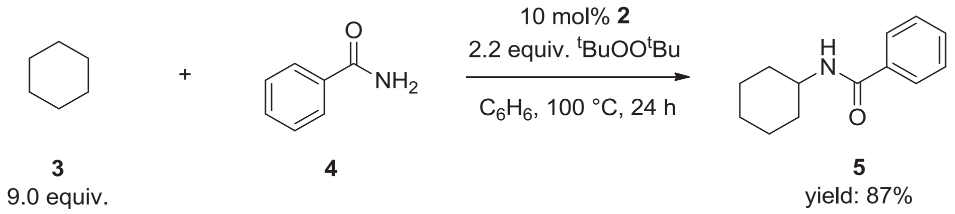


Fig. 4. Molecular orbitals of complex **2**. B3LYP level 6-31G(d): basis set for N, C, O, F, P and H atoms and LANL2DZ for the Cu atom.



Scheme 2. Catalytic abilities of complex **2** in the amidation of aliphatic C-H bonds.

planar and the other coordination sites on the copper centre are occupied by two PPh_3 creating a tetrahedral coordination geometry. Moreover, the complex has been successfully applied as precatalyst in the copper-catalyzed amination of aliphatic C-H bonds. In ongoing studies the scope and limitations and the reaction mechanism of the amination reaction will be investigated in more detail.

Acknowledgement

Financial support from the Cluster of Excellence "Unifying Concepts in Catalysis" (EXC 314/1; www.unicat.tu-berlin.de; funded by the Deutsche Forschungsgemeinschaft and administered by the Technische Universität Berlin) is gratefully acknowledged. Chika I. Someya thanks the Berlin International Graduate School of Natural Sciences and Engineering (BIG NSE) for ideational support. Moreover, Dr. Eckhard Bill (Max Planck Institute for Chemical Energy Conversion) is thanked for EPR measurements and Dr. Ba Tran (University of California, Berkeley) is thanked for supporting this work.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.10.016.

References

[1] a) P.T. Anastas, M.M. Kirchhoff, Acc. Chem. Res. 35 (2002) 686–694;
b) P.T. Anastas, M.M. Kirchhoff, T.C. Williamson, Appl. Catal. A 221 (2001) 3–13;
c) P.T. Anastas, ChemSusChem 2 (2009) 391–392.
[2] a) B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, 1996.;
b) M. Beller, C. Bolm, Transition Metals for Organic Synthesis, Wiley-VCH, Weinheim, 2004.;
c) B. Cornils, W.A. Herrmann, I.T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, Multiphase Homogenous Catalysis, Wiley-VCH, Weinheim, 2005.;
d) A. Behr, Angewandte homogene Katalyse, Wiley-VCH, Weinheim, 2008.
[3] a) A. Börner, Phosphorus Ligands in Asymmetric Catalysis, Wiley-VCH, Weinheim, 2008.;
b) Q.-L. Zhou, Privileged Chiral Ligands and Catalysts, Wiley-VCH, Weinheim, 2011.
[4] a) A selection:R.D. Hancock, A.E. Martell, Chem. Rev. 89 (1989) 1875–1914;
b) A.L. Gavrilova, B. Bosnich, Chem. Rev. 104 (2004) 349–383;
c) M. Miura, Angew. Chem. 116 (2004) 2251–2253;
Angew. Chem. Int. Ed. 43 (2004) 2201–2203;
d) P.J. Steel, Acc. Chem. Res. 38 (2005) 243–250;
e) A.S. Borovik, Acc. Chem. Res. 38 (2005) 54–61.
[5] a) C.I. Someya, S. Inoue, S. Krackl, E. Irran, S. Enthaler, Eur. J. Inorg. Chem. (2012) 1269–1277;
b) C.I. Someya, E. Irran, S. Enthaler, Asian J. Org. Chem. 1 (2012) 322–326.
[6] a) M. Weidauer, E. Irran, C.I. Someya, M. Haberberger, S. Enthaler, J. Organomet. Chem. 729 (2013) 53–59;
b) M. Weidauer, E. Irran, C.I. Someya, S. Enthaler, Asian J. Org. Chem. 2 (2012) 150–156.
[7] C.I. Someya, S. Inoue, E. Irran, S. Krackl, S. Enthaler, Eur. J. Inorg. Chem. (2011) 2691–2697.
[8] S. Krackl, C.I. Someya, S. Enthaler, Chem. Eur. J. 18 (2012) 15267–15271.
[9] a) L. Sacconi, Z. Anorg. Allg. Chem. 275 (1954) 249–256;
b) L. Sacconi, P. Paoletti, F. Maggio, J. Am. Chem. Soc. 79 (1957) 4067–4069;
c) K.N. Zelenin, A.R. Tugusheva, S.I. Yakimovich, V.V. Alekssev, E.V. Zerova, Chem. Heterocycl. Compd. 38 (2002) 668–676.
[10] CCDC-939571 (for **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Space group: P-1; unit cell dimensions: a = 11.6984(6) Å, b = 12.9220(7) Å, c = 14.7020(6) Å, $\alpha = 82.872(4)°$, $\beta = 77.676(4)°$, $\gamma = 77.661(4)°$; Volume: 2113.90(18) $Å^3$; GOF: 0.915; $R_1 = 0.0621$; $wR_2 = 0.133$
[11] a) P. Krishnamoorthy, P. Sathyadevi, K. Senthilkumar, P.T. Muthiah, R. Ramesh, N. Dharmaraj, Inorg. Chem. Commun. 14 (2011) 1318–1322;
b) D. Ramakrishna, B.R. Bhat, Inorg. Chem. Commun. 14 (2011) 690–693;
c) C. Gökçe, R. Gup, Appl. Organomet. Chem. 27 (2013) 263–268;
d) A. Mukhopadhyay, S. Pal, Eur. J. Inorg. Chem. (2009) 4141–4148.
[12] a) M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.;
b) A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652;
c) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789;
d) B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200–206.
[13] a) see for instance and references therein:R.T. Gephart III, T.H. Warren, Organometallics 31 (2012) 7728–7752;
b) G. Pelletier, D.A. Powell, Org. Lett. 8 (2006) 6031–6034;
c) D.A. Powell, H. Fan, J. Org. Chem. 75 (2010) 2726–2729;
d) N. Borduas, D.A. Powell, J. Org. Chem. 73 (2008) 7822–7825;
e) R.T. Gephart III, C.L. McMullin, N.G. Sapiezynski, E.S. Jang, M.J.B. Aguila, T.R. Cundari, T.H. Warren, J. Am. Chem. Soc. 134 (2012) 17350–17353;
f) S. Wiese, Y.M. Badiei, R.T. Gephart, S. Mossin, M.S. Varonka, M.M. Melzer, K. Meyer, T.R. Cundari, T.H. Warren, Angew. Chem. Int. Ed. 49 (2010) 8850–8855;
g) E. Shirakawa, N. Uchiyama, T. Hayashi, J. Org. Chem. 76 (2011) 25–34;
h) S. Sueki, Y. Kuninobu, Org. Lett. 15 (2013) 1544–1547;
i) Q. Xia, W. Chen, H. Qiu, J. Org. Chem. 76 (2011) 7577–7582;
j) H. Yang, P. Sun, Y. Zhu, H. Yan, L. Lu, X. Qu, T. Li, J. Mao, Chem. Commun. 48 (2012) 7847–7849.