Synthesis, Structure and Reactivity of the Compound [Cu(C₇H₇NH₂)Cl]₄ derived from CuCl and Benzylamine (C₇H₇NH₂)

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Abstract. The facile synthesis, molecular structure, and reactivity of $[Cu(C_7H_7NH_2)Cl]_4$ (1) towards dioxygen and derivatives is reported. The compound could easily be prepared in good yields by mixing CuCl and benzylamine under inert conditions in dichloromethane. Surprisingly this copper(I) compound, a copper(I) tetramer with Cu^I···Cu^I interactions of 2.89 Å, was formed instead of an expected cubane clus-

diates, however 1 did not show any catalytic activity in the activation of CH bonds. In contrast it turned out that 1 was quite stable towards oxidation. Analogous reactions with CuBr or CuI were different and neither cluster units or polynuclear copper(I) complexes were obtained.

ter. Oxidation reactions led to formation of µ-oxido-species as interme-

Introduction

Copper(I) cubane clusters of the type $[Cu_4OX_6L_4]$ (X = Cl, Br, I, see Figure 1) are well known and have been investigated intensively in the past mainly because of their interesting optical properties.^[1] In most cases synthesis is facile and preparation is accomplished through self-assembly of the cubane cores.^[2] Therefore, simply mixing a copper(I) halide with an according ligand usually leads to a cubane cluster. Especially Davies and El-Saved previously investigated copper(I) cubane systems in regard to their reactivity towards dioxygen.^[2a-2c,3] In this context they also reported the formation of the μ_4 -oxido copper(II) cluster $[Cu_4OCl_6L_4]$ (L = N,N-dimethylaminomethylferrocene) from the reaction of the cubane cluster [Cu₄Cl₄L₄] with dioxygen.^[2a] This is another well known structural motif of a copper cluster; here a copper(II) system, that had been already reported in the 1960s.^[4]

In our efforts to better understand the role of CuCl as well as CuCl₂ in organic syntheses, especially oxidation reactions, we previously investigated complexes derived from the reaction of CuCl₂ with benzylamine.^[5] The reaction behavior of this system turned out to be quite complex. Thus we observed the formation of compound $[CuL^1Cl]_3$ (2), which is in a chemical equilibrium with the μ_4 -oxido-copper cluster $[Cu_4OCl_6L_4^1]_2[CuL_2Cl_2]$ (cluster I, L^1 = benzylamine) and

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Figure 1. Schematic representation of the structural motif of a copper(I) cubane core (left) and a μ_4 -oxido copper(II) cluster (right).

the copper(II) cubane cluster $[Cu_4(O-L)_4Cl_4]$ (L = C₁₁NH₁₄) (cluster II).^[5]

The role of compound 2 in this equilibrium was not clarified. Now we report the synthesis and reactivity of $[CuL^1Cl]_4$ (1). Besides the crystallization behavior (trimer or tetramer in the asymmetric units) compound 1 and 2 are chemically identical. Therefore our conclusions derived for 1 should be valid for 2 as well. In order to gain more information about the reactivity of these copper(I) complexes towards dioxygen in general and thus the role of compound 1/2 in the described chemical equilibrium we investigated this system using UV/ Vis spectroscopy. Furthermore its ability in catalytic oxygenation reactions was tested. Herein we now describe the synthesis, structure, and reactivity of $[Cu(C_7H_7NH_2)Cl]_4$ (1).

Results and Discussion

When mixing CuCl and benzylamine the formation of a copper(I) cubane cluster was expected due to previous reports in the literature on related systems. However, mixing CuCl with benzylamine under inert conditions led to the formation

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of an unexpected copper(I)-tetramer (1). Stoichiometric variations led to the same result. The molecular structure of the colorless compound obtained is shown in Figure 2.

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Figure 2. Molecular structure of 1. Ellipsoids are drawn at the 50% probability level.

The asymmetric unit of the elemental cell shows half of the tetramer with copper-copper distances of 2.89 Å. Cu^I···Cu^I interactions are well known in literature.^[6] So far reasons for these interactions are not quite clear, especially if there is no ligand environment, which enforces the copper(I) ions in such an arrangement. It is known that due to the small bandgap between the 3d and 4s band electrons can transfer from the occupied 3d band into the empty 4s band und thus covalent Cu-Cu bonds are possible. However, the reason for this extraordinary small bandgap is not understood yet. As already described above, the formation of 1 was unexpected. Only the crystal structure revealed the linear character of the formed tetramer instead of the expected cubane structure. Standard spectroscopy (e.g. IR spectroscopy, cryoscopy, elemental analysis) would not have allowed here to distinguish between l and the cluster. In our case most likely only crystal structures can provide clear evidence for a cubane core. So in our opinion previously proposed cubane clusters, without a molecular structure reported, should therefore be considered with care. An attempt to distinguish between both structural units could be fluorescence analysis. Copper(I) cubane cores often show fluorescence. In contrast to these observations 1 does not show any emission properties. At the moment we do not know if that is a unique feature of compound 1 or if this is a general phenomenon of these structure types. To confirm this assumption more investigations on derivatives of 1 have to be carried out in the future.

In addition we investigated the reactivity of 1 towards dioxygen and derivatives. For this purpose a large number of experiments were performed. Bubbling dioxygen through a solution of compound 1 in dichloromethane led to a color change from colorless to green. However, even at room temperature this reaction was very slow. Figure 3 shows the time resolved UV/Vis spectra of this reaction over a time range of 20 min.



Figure 3. UV/Vis spectra of the reaction of compound 1 towards O₂ (solvent: dcm, T = 25 °C, $c = 2 \times 10^{-5}$ mol·L⁻¹, t = 20 min). $\lambda_{\text{max}} = 259$ nm, 746 nm, 829 nm, shoulder at 357 nm.

The spectra show the development of absorption bands at 259, 746, and 824 nm. Additionally a shoulder at ca. 357 nm was formed. In contrast the absorption band at 570 nm decreased. The formed species was stable for days at room temperature before it decomposed. It is difficult to relate the absorption maxima to certain Cu/O2 species, because only little is known about dioxygen activation with tetranuclear copper compounds. The formation of these "oxygen adduct" complexes follow a more complex mechanism, since the 4e⁻ provided by the tetranuclear clusters do not correlate with the 2ereduction of O₂ to peroxide.^[7] Reim et al. reported a tetranuclear µ₄-peroxido complex and provided UV/Vis data of this compound.^[8] However these data do not correlate with the data presented herein. In addition there are no reports of dioxygen activation with compounds that exhibit Cu^I...Cu^I interactions. However we do not have clear evidence that there is only the tetramer 1 in solution. We already observed formation of trimer 2 and the formation of other compounds is possible. Hence it is not possible to exclude that 1 does not dissociate in solution leading to mononuclear complexes [CuL¹Cl]. Spectroscopic features have to be compared to those of mononuclear and polynuclear Cu/O2 species. However, the UV/Vis features reported herein closely resemble UV/Vis data reported by Churchill et al. previously.^[2c] They observed maxima at 235, 255, 770, and 850 nm for the reaction of the cubane cluster $[Cu_4Cl_4(denc)_4]$ (denc = *N*,*N*-diethylnicotineamide) with dioxygen.^[2c] Assigning these findings with the spectroscopic features of 1 the formation of a µ-oxido intermediate ("Cu₂O") is suggested. These species are well known in literature^[9] and µ-oxido intermediates are currently discussed to play an important role in the enzymatic hydroxylation of methane (copper based methane monooxygenase).^[10] Thus µ-oxido species could gain more importance in the search for suitable model systems for enzymatic CH activation.^[11] Despite of the proposed catalytic activity of µ-oxido species, the system investigated by *Churchill* et al. did not show any catalytic activity.^[2c] Davies et al. reported the reaction of the cubane cluster

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[Cu₄Cl₄(pyridine)₄] with dioxygen. However, this system showed similar UV/Vis features in the range of 700–900 nm as the denc system and as 1 (Figure 4). The formation of two complexes was proposed: a μ_4 -oxido species with one oxygen coordinated in the center of the cubane core and a μ -oxido species, a cubane, where each of the two oxygen ions bridges two copper ions. The appearance of two maxima was assigned to these two species. It was furthermore reported that the μ_4 oxido species was active in oxygenation reactions (see below).^[2b,12]



Figure 4. Infrared and near-infrared part of the UV/Vis spectra of the reaction of compound 1 towards O₂ (solvent: dcm, T = 25 °C, $c = 1 \times 10^{-4}$ mol·L⁻¹). $\lambda_{\text{max}} = 746$ and 829 nm.

However, most of these assignments came from spectroscopic studies and only a small number of the proposed cluster structures actually could be experimentally confirmed by crystal structures (e.g. only the crystal structure of $[Cu_4I_4(denc)_4]$ is reported, not of $[Cu_4Cl_4(denc)_4]$). As discussed above the formation of a linear tetramer such as **1** instead of a cubane cluster is possible as well.

This could explain the observed similarities in the UV/Vis spectra. Attempts to obtain crystals of the intermediate species formed during the oxidation were not successful and actually resulted in recrystallization of compound **1**. This emphasized the extraordinary stability of compound **1** towards dioxygen. However, after partial decomposition of the "Cu/O₂" species crystals could be obtained from the green solution. The molecular structure of this final product, the simple copper(II) complex [CuL¹₂Cl₂] (**3**) is shown in Figure 5.

The molecular structure of **3** had been reported previously.^[5,13] The UV/Vis spectrum of pure **1** was compared with those of the "oxygen adduct", compound **3**, and cluster I. As described above the μ_4 -oxido cluster "cluster I" is in a chemical equilibrium with compound **2**/**1**. In addition *Davies* et al. also observed the formation of a μ_4 -oxido copper(II) cluster [Cu₄OCl₆L₄] (L = *N*,*N*-dimethylaminomethylferrocene) after the reaction of the cubane cluster [Cu₄Cl₄L₄] with dioxygen.^[2a] Thus the comparison of the UV/Vis data of the "oxygen adduct" compound with cluster I is essential. The



Figure 5. Molecular structure of $[CuL_2^1Cl_2]$ (3). Ellipsoids are drawn at the 50% probability level.

comparison is shown in Figure 6. Compound 3 exhibits an intense absorption maximum at 285 nm and a shoulder at 350 nm. The absorption maxima at 285 nm is assigned to $\pi \rightarrow \pi^*$ of the coordinated benzylamine group. The shoulder at 350 nm is identified as a LMCT band. Weaker dd or ligand field transitions are observed at 660 nm. The comparison of the UV/Vis spectra of the Cu/O₂ species and cluster I shows strong similarities. For cluster I absorption maxima at 286, 754, and 834 nm and a shoulder at 360 nm are observed. These similarities suggest that 1 reacted with dioxygen to form cluster I as an intermediate. This finding goes along with the equilibrium between cluster I and 1/2. However, analysis of the UV/Vis data is complicated due to the structural similarities between the "oxygen intermediate" complexes proposed by *Davies* et al. and cluster I (both contain a μ_4 -oxido motif). Thus it is currently not possible to explain the UV/Vis features completely. However, we suggest the simultaneous formation of a μ -oxido species and a μ_4 -oxido species (cluster I). This is consistent with two absorption maxima in the range of 700-900 nm as previously proposed by Davies et al. and Endres et al.^[2b,12]



Figure 6. UV/Vis spectra of compound **1**, **3**, the "oxygen adduct" and cluster I (solvent: dcm, T = 25 °C, $c(1) = 2 \times 10^{-5}$ mol·L⁻¹, c(3, cluster I) = 1×10^{-4} mol·L⁻¹).

As mentioned above the oxygen intermediate described by Davies et al. and Endres et al. was active as a catalyst for polymerization of phenols.^[2b,12] Since compound 1 showed similar UV/Vis data for the reaction with dioxygen and µ-oxido species are proposed to be catalytically active, it was obvious to test its ability to catalyze oxidation reactions for reactions that had been investigated previously with cluster I. As already described above 2/1 was isolated for the first time from a redox equilibrium of cluster I with other copper(I) and copper(II) species. This equilibrium caused the oxidation and hydroxylation of solvent molecules and additives. We already assumed that a copper(I) compound is the active species in these oxidation reactions.^[5] In order to find out if 1 was the active species we now tested the ability of 1 to oxygenate aliphatic and/or aromatic CH bonds instead of repeating the reactions, which were performed by *Davies* et al. Thus compound 1 was dissolved either in dichloromethane or acetonitrile, cyclohexane was added, and dioxygen was bubbled through the solution. However, no oxygenation product was observed. So H₂O₂ was added instead of O2 to the solution. But again no oxygenation occurred. In another attempt H₂O₂ was substituted with the urea adduct $(H_2N)_2CO \cdot H_2O_2$ in order to avoid the presence of water as much as possible. But again no oxygenation reaction could be observed. Furthermore, the substrate was changed from aliphatic cyclohexane to aromatic benzene. Still, compound 1 proved to be unreactive as an oxygenation catalvst.

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Previously we had observed that cluster I was converted to a different copper(II) cubane cluster (cluster II) when stored in denaturated ethanol (here 2-butanone is added to the ethanol to avoid drinking it).^[5] Scheme 1 shows the proposed mechanism for the formation of the new ligand.



Scheme 1. Proposed reaction for the formation of 3-benzylimino-butan-2-olate.^[5]

The ligand benzylamine reacts with 2-butanone present in solution to form an imine. Intramolecular hydroxylation of this Schiff base leads to the ligand 3-benzylimino-butane-2-olate and finally to cluster II. Therefore, it seemed to be interesting to test if compound 1 actually was responsible for this conversion. However, adding 1 to a solution of 2-butanone and bubbling dioxygen through this solution did not cause formation of cluster II and thus 1 seems not to be involved in this reaction. In conclusion and quite surprising 1 is extraordinary stable concerning reactivity towards dioxygen or derivatives. Generally solutions of 1 were stable at room temperature and under atmospheric conditions for hours before they turned green. Crystals of 1 were even more stable and quite often the pure copper(I) complex was obtained again after treating a solution of it with dioxygen as discussed above. So far we do not understand this extraordinary stability towards oxidation.

Having observed previously that also copper(II) cluster complexes were obtained using $CuBr_2$ instead of $CuCl_2^{[5]}$ we

investigated the reactivity of CuBr and CuI towards benzylamine as well. Interestingly neither CuBr nor CuI reacted with benzylamine under inert conditions. So the syntheses were repeated under atmospheric conditions. Due to the large stability of both copper salts, syntheses of cubane clusters are sometimes carried out under atmospheric conditions as well.^[1b,2d] However, formation of a cubane cluster or a tetramer was neither observed in dichloromethane nor methanol.

The reaction of CuBr with benzylamine led to dark green solutions and colorless crystals were obtained from the methanol solution. However no copper complex was isolated but the carbamate of benzylamine (HL¹)(C_7H_7NHCOO) was obtained, that has been described previously (its molecular structure is reported in the Supporting Inofrmation).^[15] Most likely benzylamine reacted with carbon dioxide present in air to give this carbamate. In contrast when reacting CuI with benzylamine in dichloromethane the solution turned purple, but no product could be isolated. When reacting CuI and benzylamine in methanol the solution turned blue and green crystals were obtained from this solution that turned out to be $[CuL_2^1(OMe)]_2[Cu_{3,5}I_6](HL^1)_{0.5}\cdot nH_2O\cdot nMeOH$ (4). The molecular structure of the cation of 4 is shown in Figure 7.



Figure 7. Molecular structure of $[L_2^1(OMe)Cu^{II}]_2^{2+}$, the cation of **4**. Ellipsoids are drawn at the 50% probability level.

For clarity the anion $[Cu_{3,5}I_6]HL_{0,5}^{1}e^{-1}$ is not shown. The structure of the cation shows the copper(II) complex $[L_2^1(OMe)Cu^{II}]_2^{2+}$. Here the copper(II) ions have a square-planar arrangement. They coordinate two benzylamine groups per ion and are bridged via methoxy groups derived from the solvent methanol.

Methanolate bridged copper compounds are well known. Only some examples for such compounds with monodentate N-donor ligands are listed in the references.^[14] The question of the origin of the copper(II) ions is not easy to answer. It is not very likely that the copper(I) ions disproportionated because the precipitation of elemental copper was not observed. Probably a part of the dissolved copper(I) ions were oxidized by atmospheric oxygen to give copper(II) ions. In addition an acid-base-reaction must have occurred between methanol and benzylamine allowing the formation of the methoxy bridged complex and the benzylammonium ions. The larger part of CuI probably did not react with either benzylamine or atmospheric dioxygen and did not form long polymeric chains. The voids of these chains were filled with solvent molecules, methanol and water.

In summary for both CuBr as well as CuI syntheses of a cubane cluster or an analogue to 1 were not successful.

Conclusions

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Reacting CuCl with benzylamine under inert conditions led to the linear compound $[CuL^1Cl]_4$ (1) instead of an expected cubane cluster. 1 showed unsupported Cu^I...Cu^I interactions. The nature of these interactions is not completely clarified yet. In contrast formation of either cluster compounds or polynuclear copper(I) complexes was not observed when CuBr or CuI was used instead of CuCl. Spectroscopically it could be shown that μ -oxido complexes and a μ_4 -oxido species formed when 1 was oxidized with dioxygen. Despite the fact that μ -oxido species are proposed to play an important role in catalytic hydroxylation reactions of CH bonds, 1 turned out to have an extraordinary stability towards dioxygen/peroxides and proved to be inreactive in oxidation reactions. Probably the Cu^I···Cu^I interactions might somehow be the reason for the stability towards oxidation. From these findings we can conclude that polynuclear copper(I) complexes such as 1 or 2 do not seem to be directly involved in catalytic oxidation reactions observed previously using cluster I as a catalyst. Furthermore, it turned out that formation of cubane cluster units derived from copper(I) halogenides is not always as facile as expected and alternative reaction products are possible. Distinguishing these different reaction products only spectroscopically is complicated due to their spectral similarities. Therefore, copper cubane cluster complexes reported in the literature without a crystal structure should be considered with care.

Experimental Section

All chemicals used were of p.a. quality and were purchased from Acros, Aldrich, Fluka, or Merck, if not mentioned otherwise. Dry solvents for air sensitive reactions were redistilled in an argon atmosphere. Analytical data (elemental analyses, IR spectra, and crystallographic data^[16]) are summarized in the Supporting Information.

Preparation of 1: The synthesis was performed under inert conditions in a glove box. CuCl (165 mg, 1.67 mmol) was dissolved in absolute dichloromethane (ca. 10 mL) and benzylamine (358 mg, 3.33 mmol) was added dropwise to the solution whilst stirring. The mixture was stirred until CuCl was dissolved completely and crystallization occurred. The resulting colorless crystals were filtered off and dried to give compound **1** (260 mg, 0.31 mmol, 79%).

Preparation of Compound 4: CuI (170 mg, 0.892 mmol) was dissolved in methanol (ca. 20 mL) and benzylamine (96 mg, 0.89 mmol) was added to the stirred solution. The solution was allowed to stand until crystallization occurred.

Preparation of (HL¹)(C₇H₇NHCOO): CuBr (128 mg, 0.892 mmol) was dissolved in methanol (ca. 20 mL) and benzylamine (96 mg,

0.89 mmol) was added to the stirred solution. The solution was allowed to stand until crystallization occurred.

Attempted Oxygenation of Cyclohexane:

With O_2 : Compound 1 (10 mg, 13 µmol) was dissolved in acetonitrile (ca. 3 mL) and cyclohexane (840 mg, 10 mmol) was added. Afterwards dry O_2 was bubbled through the solution for 20 min. The solution was analyzed by GC-MS. The reaction was also performed in dichloromethane.

With H_2O_2 : Compound 1 (21 mg, 25 µmol) was dissolved in acetonitrile (ca. 10 mL) and cyclohexane (840 mg, 10 mmol) was added. Afterwards H_2O_2 (aqueous 30%, 2.0 mL, 20 mmol) was added to the stirred solution. The solution was stirred for ca. 6 h and then analyzed by GC-MS. The reaction was also performed in dichloromethane.

With $(NH_2)_2CO \cdot H_2O_2$: Compound 1 (21 mg, 25 µmol) was dissolved in dichloromethane (ca. 10 mL) and cyclohexane (840 mg, 10 mmol) was added. Afterwards $(NH_2)_2CO \cdot H_2O_2$ (1.9 g, 20 mmol) was added to the stirred solution. The solution was stirred for ca. 6 h and then analyzed by GC-MS.

Attempted Hydroxylation of Benzene: Compound 1 (10 mg, 13 μ mol) was dissolved in absolute benzene (ca. 3 mL) and dry O₂ was bubbled through the solution for 20 min. The solution was separated into three parts. The first was analyzed by GC-MS. A small part of H₂O was added to the second part and a small part of HCl to the third part. All samples were analyzed by GC-MS.

Attempted Hydroxylation of 2-Butanone: The reaction was performed under inert conditions in a glove box. Compound 1 (8 mg, 10 μ mol) was dissolved in absolute dichloromethane (ca. 20 mL) and 2-butanone (ca. 3 mL) was added. The solution was heated to ca. 30 °C for ca. 15 min and then dry O₂ was bubbled into the solution for 20 min. The solution was analyzed by GC-MS. The reaction was also performed in absolute methanol.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-982979 (for 1) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Spectroscopic data, photographs, and crystallographic data.

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References

 a) F. De Angelis, S. Fantacci, A. Sgamellotti, E. Cariati, R. Ugo, P. C. Ford, *Inorg. Chem.* **2006**, *45*, 10576–10584; b) A. Kobayashi, K. Komatsu, H. Ohara, W. Kamada, Y. Chishina, K. Tsuge, H.-C. Chang, M. Kato, *Inorg. Chem.* **2013**, *52*, 13188–98; c) K. R. Kyle, W. E. Palke, P. C. Ford, *Coord. Chem. Rev.* **1990**, *97*, 35– 46; d) C. K. Ryu, K. R. Kyle, P. C. Ford, *Inorg. Chem.* **1991**, *30*, 3982–3986; e) P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* **1999**, *99*, 3625–3648. [2] a) A. Ali, G. Davies, S. Larsen, J. Zubieta, *Inorg. Chim. Acta* 1992, 194, 139–149; b) G. Davies, M. A. El-Sayed, *Inorg. Chem.* 1983, 22, 1257–1266; c) M. R. Churchill, I. G. Davies, M. A. El-Sayed, J. P. Hutchinson, M. W. Rupichic, *Inorg. Chem.* 1982, 21, 995–1001; d) E. Sugahara, M. Paula, I. Vencato, C. Franco, *J. Coord. Chem.* 1996, 39, 59–70; e) T. H. Kim, G. Park, Y. W. Shin, K.-M. Park, M. Y. Choi, J. Kim, *Bull. Korean Chem. Soc.* 2008, 29, 499–502; f) J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, C. L. Raston, A. H. White, *J. Chem. Soc., Dalton Trans.* 1985, 831–838.

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Zeitschrift für anorganische und allgemeine Chemie

- [3] a) M. A. El-Sayed, A. Abu-Raqabah, G. Davies, A. El-Thouky, Inorg. Chem. 1989, 28, 1909–1914; b) A. Abu-Raqabah, G. Davies, M. A. El-Sayed, Inorg. Chim. Acta 1992, 192, 31–42; c) G. Davies, M. A. El-Sayed, R. E. Fasano, Inorg. Chim. Acta 1983, 71, 95–99; d) G. Davies, A. El-Toukhy, K. D. Onan, M. Veidis, Inorg. Chim. Acta 1984, 84, 41–50; e) A. El-Toukhy, G.-Z. Cai, G. Davies, T. R. Gilbert, K. D. Onan, M. Veidis, J. Am. Chem. Soc. 1984, 106, 4596–4605; f) K. Z. Ismail, M. A. El-Sayed, A.-M. Al-Kouraty, G. Davies, Inorg. Chim. Acta 1994, 217, 85–92; g) K. D. Onan, M. Veidis, G. Davies, M. A. El-Sayed, A. El-Thoukhy, Inorg. Chim. Acta 1984, 81, 7–13.
- [4] a) J. A. Bertrand, J. A. Kelley, *Inorg. Chem.* 1966, *5*, 4746–4747;
 b) H. tom Dieck, H.-P. Brehm, *Chem. Ber.* 1969, *102*, 3577–3583;
 c) H. Bock, H. tom Dieck, H. Pyttlik, M. Schnöller, Z. Anorg. Allg. Chem. 1968, 357, 54–61; d) J. A. Bertrand, J. A. Kelley, *Inorg. Chim. Acta* 1970, *4*, 526–528; e) H. tom Dieck, *Inorg. Chim. Acta* 1973, *7*, 397–403; f) B. T. Kilbourn, J. D. Dunitz, *Inorg. Chim. Acta* 1967, *1*, 209–216; g) J. A. Bertrand, *Inorg. Chem.* 1967, *6*, 495–498; h) J. J. de Boer, D. Bright, J. N. Helle, *Acta Crystallogr, Sect. B* 1972, *28*, 3436–3437; i) N. S. Gill, M. Sterns, *Inorg. Chem.* 1970, *9*, 1619–1625; j) J. A. Bertrand, J. A. Kelly, C. E. Kirkwood, *Chem. Commun. (London)* 1968, 1329–1330.
- [5] S. Löw, J. Becker, C. Würtele, A. Miska, C. Kleeberg, U. Behrens, O. Walter, S. Schindler, *Chem. Eur. J.* 2013, *19*, 5342– 5351.

- [6] a) S. H. Oakeley, M. P. Coles, P. B. Hitchcock, *Inorg. Chem.*2004, 43, 5168–5172; b) S.-L. Zheng, M. Messerschmidt, P. Coppens, *Angew. Chem. Int. Ed.* 2005, 44, 4614–4617; c) M. Angels Carvajal, S. Alvarez, J. J. Novoa, *Chem. Eur. J.* 2004, 10, 2117–2132; d) G. M. Chiarella, D. Y. Melgarejo, A. Rozanski, P. Hempte, L. M. Perez, C. Reber, J. P. J. Fackler, *Chem. Commun.* 2010, 46, 136–138; e) G. Margraf, J. W. Bats, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Commun.* 2003, 8, 956–957.
- [7] L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* 2004, 104, 1013–1045.
- [8] a) J. Reim, B. Krebs, Angew. Chem. Int. Ed. Engl. 1994, 33, 1969–1971; b) J. Reim, R. Werner, W. Haase, B. Krebs, Chem. Eur. J. 1998, 4, 289–298.
- [9] P. Haack, C. Limberg, Angew. Chem. 2014, 126, 4368–80; Angew. Chem. Int. Ed. 2014, 53, 4282–93.
- [10] E. I. Solomon, J. W. Ginsbach, D. E. Heppner, M. T. Kieber-Emmons, C. H. Kjaergaard, P. J. Smeets, L. Tian, J. S. Woertink, *Far-aday Discuss.* 2011, 148, 11.
- [11] A. E. Shilov, A. A. Shteinman, Russ. Chem. Rev. 2012, 81, 291.
- [12] G. F. Endres, A. S. Hay, J. W. Eustance, J. Org. Chem. 1962, 27, 1300–1305.
- [13] G. Zi, L. Xiang, Y. Zhang, Q. Wang, Z. Zhang, Appl. Organomet. Chem. 2007, 21, 177–182.
- [14] a) R. Wang, W.-P. Su, R. Cao, Y.-J. Zhao, M.-C. Hong, *Chin. J. Struct. Chem.* 2001, 20, 37; b) H.-L. Zhu, C.-X. Ren, X.-M. Chen, J. Coord. Chem. 2002, 55, 667–673; c) G. a. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Polyhedron* 2004, 23, 993–998; d) A. S. Komaei, G. A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Polyhedron* 1999, 18, 1991–1997; e) M. F. Haddow, H. Kara, G. R. Owen, *Inorg. Chim. Acta* 2009, 362, 3502–3506.
- [15] a) I. Tiritiris, W. Kantlehner, Z. Naturforsch. 2011, 66b, 104; b) M. M. Olmstead, J. U. Franco, D. Pham, Private Communication 2008, CCDC-No: 698121.
- [16] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112–122.

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