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New heterometallic copper zinc alkoxides: synthesis, structure properties and pyrolysis to Cu/ZnO composites

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Abstract

The copper compound $[(THF)KCu(O^tBu)_3]_\infty$ **1** was obtained by interaction of a 1:1 mixture of $ZnCl_2/CuCl_2$ with KO^tBu. Bi- and trifunctional aminoalcohols were used to synthesize the intramolecularly donor stabilized Cu(II) alkoxides $Cu(OCH(R)CH_2NMe_2)_2$ (**3**: R = Me, **4**: = CH_2NMe_2) where **4** was structurally characterized. Lewis acid–base adduct formation with $(Me_3Si)_3CZnCl$ gave the heterodinuclear compounds $(Me_3Si)_3CZnCl \cdot Cu(OCH(R)CH_2NMe_2)_2$ (**5**: R = Me, **6**: R = CH_2NMe_2), which were characterized by X-ray single-crystal structure analysis. The two metal centers Cu and Zn of **5** and **6** are bridged by two oxygen atoms to form a Cu–O–Zn core. Pyrolysis of compounds **5** and **6** in dry argon or a H_2/N_2 mixture at atmospheric pressure forms metallic copper and zinc oxide, whereas pyrolysis under O_2/Ar forms additionally oxidized copper species. Elemental analysis of the pyrolysis products showed carbon and nitrogen contamination. Scanning electron microscopy and energy dispersive X-ray analysis were performed to get information on the morphology and the chemical composition of the pyrolysis products. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: copper; heterometallic alkoxides; oxides; pyrolysis; zinc

1. Introduction

Mixed-metal oxides represent an important class of materials for advanced applications, including catalysts, structural ceramics, sensors and actuators as well as ferroelectric and dielectric materials for microelectronic data processing devices [1–6]. The investigation and the use of heterometallic alkoxides as single molecule precursors (SMPs) for the synthesis of mixed-metal oxides have continuously increasing over the past decade. This is particularly connected with the elucidation of the complex sol–gel chemistry of oxide materials processing in general [7] as well as with the related precursor chemistry for the growth of metal oxide thin film materials by chemical vapor deposition techniques [1,2,4,8]. However, virtually all of these examples refer to single-phased metal oxide materials. Only recently it was shown, mainly by the work of Veith et al. [9], that SMPs can be designed to produce unusual multiphased composite materials directly in one single step depending on both the metal composition and the particular precursor design. Within the context of heterogeneous catalysis the most noteworthy examples are thin films or powders of nanostructured metals homogeneously dispersed in a metal oxide matrix derived from SMPs. Many catalysts are composed of finely dispersed, i.e. nanoscale metal particles bound to a metal oxide support (metal@metal-oxide) [10]. Tailored SMPs may thus represent an interesting alternative approach for catalyst preparation.

We were attracted by this idea and selected the Cu@ZnO system as a study object. The Cu@ZnO system is of eminent importance in large-scale industrial methanol synthesis (10^7 tonnes per year) from $CO/CO_2/H_2$ [11]. The industrial Cu@ZnO-based catalysts for methanol synthesis are generally prepared by a well developed and empirically optimized coprecipitation technique. An aqueous solution of alkali carbonates is

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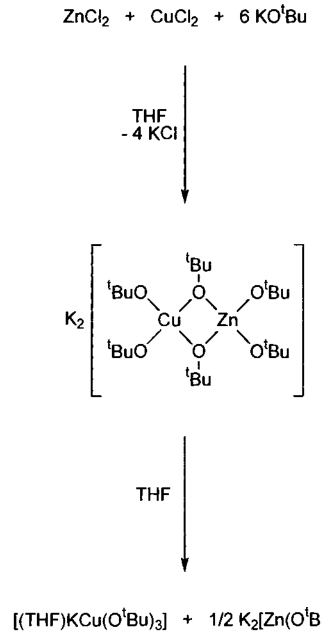
mixed with a solution of copper and zinc salts, such as nitrates, resulting in the formation of precipitates, including malachite $Cu_2(CO_3)(OH)_2$, aurichalcite $(Cu,Zn)_5(CO_3)_2(OH)_6$ or hydrozincite $Zn_5(CO_3)_2(OH)_6$ as well as other related phases with various ratios of zinc and copper ions [12]. Those precursors are then converted into the active Cu@ZnO composite by aging, calcination and reduction. The oxide phases obtained after calcination consist of copper oxide and zinc oxide phases which do not contain multiphased oxides such as a hypothetical $Cu_xZn_yO_z$, but referring to the work of Locmelis and Binnewies [13] there may be a partial dissolution of copper oxide in zinc oxide (2 mol%) and ZnO in CuO (4 mol%). The effects of precursors and preparations on the catalyst activity have been shown to correlate with the copper metal surface area, i.e. with the dispersion of the Cu particles [11,12]. It was suggested, that particular single phased mixed-metal precursors, such as auricalcite $(Cu,Zn)_5(CO)_3(OH)_6$ (with a Cu:Zn ratio of 1:1) containing the Cu and Zn in an atomically pre-mixed state, represent superior precursors [14]. However, these inorganic solid state precursors are neither soluble nor volatile. This limits their application as precursors for the impregnation of highly porous supports based on alumina or silica. We were thus led to investigate the possibility to develop soluble or even volatile Cu/Zn metallo-organic SMPs for the preparation of Cu@ZnO catalyst systems. Herein we wish to give a first account on our results on new heterometallic Cu/Zn alkoxide complexes and their solid state pyrolysis to obtain Cu@ZnO composites.

2. Results and discussion

2.1. Synthesis

A great number of homoleptic Cu- and Zn-alkoxides with simple aliphatic or aromatic alkoxide ligands (e.g. OMe, OEt, O^iPr, O^tBu, $OCEt_3$, $OCH_2CH_2NMe_2$, OCH_2CH_2OMe, OAr) are known [15–23]. The steric demand and the coordinative flexibility of the ligand system has a great influence on aggregation and volatility of the complexes, e.g. $[Zn(O^tBu)_2]_\infty$ [17] is an insoluble polymer, while $[Zn(OCEt_3)_2]_{2.5}$ [15] is a soluble aggregate which could be distilled under drastic conditions. Mixed alkoxides $MM'(OR)_{x+y}$ are often more soluble and volatile than their components $M(OR)_x$ and $M'(OR)_y$. Structurally characterized heterometallic alkoxides of the general type $Cu_xM_y(OR)_z$ and $Zn_xM_y(OR)_z$ (M = Li, Na, Ba, Al, Sn, Zr, Ta, Bi, Nb, Pb, Ge, Ni) represent a well established class of compounds. They are synthesized via salt methathesis, Lewis acid–base adduct formation or protolysis reactions [2,3,8,24–26]. In contrast to this long list of Cu/M and Zn/M′ mixed-metal complexes, only very few examples with a Cu–O–Zn linkage have been reported. Those systems containing aromatic macrocyclic ligands have been synthesized mainly with the intention to study the magnetic exchange interactions between the two different metal centers [27–31]. Homoleptic heterometallic alkoxides, suitable as precursors for materials, such as $M[Al(OR)_4]_2$, $[ClM{-}Zr_2(OiPr)_9]_2$ or $M[Zr_2(OiPr)_9]_2$ (M = Cu, Zn) are available via salt metathesis, e.g. by KCl elimination or reaction of anionic, nucleophilic Al- or Zr-alkoxide complexes with MCl_2 [2,25].

Following these lines we treated a 1:1 mixture of oven dried $ZnCl_2/CuCl_2$ in THF with six equivalents of KO^tBu (dissolved in THF) at room temperature. Immediately a green slightly turbid solution formed. Filtration and recrystallization from hexane afforded well-shaped green orthorhombic crystals of $[(THF)KCu(O^tBu)_3]_\infty$ **1** (45% yield) as the only isolable product (Scheme 1). Varying the reaction conditions (temperature, reaction time, solvent) or using four equivalents of KO^tBu does not change the result. According to the literature the related compound $NaCu(O^tBu)_3$ could independently be synthesized by adding three equivalents of KO^tBu to a suspension of $CuCl_2$ in THF [22]. Attempts to use isolated **1** or $K_2[Zn(O^tBu)_3]_2$ [16] as a synthetic equivalent for a nucleophilic metal alkoxide species to substitute Cl-ligands at Cu or Zn metal atoms to get heterometallic Cu–Zn-alkoxides failed. These reaction conditions favour compounds like **1** and the supposed byproduct dimer $K_2[Zn(O^tBu)_3]_2$ [16] over a homoleptic heterometallic system like $K_2[(O^tBu)_2Cu(\mu^2\text{-}O^tBu)_2Zn(O^tBu)_2]$ which probably exists in solution but could not be isolated. We suppose that in the reaction



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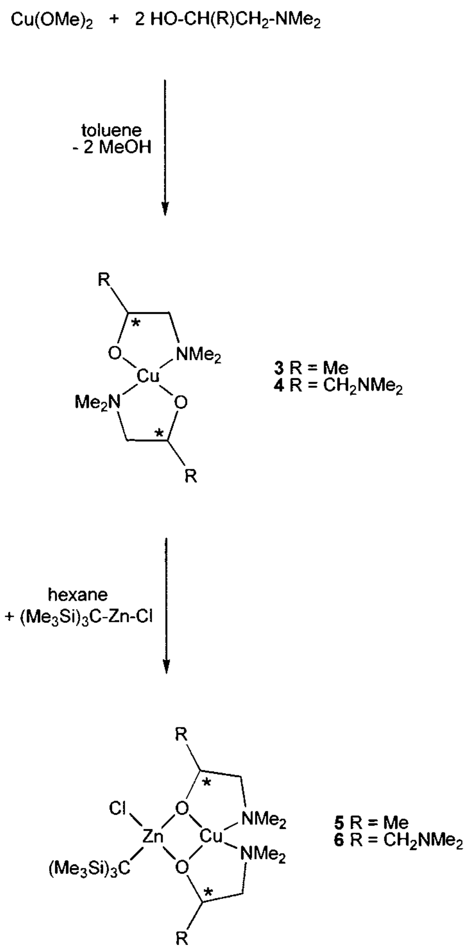
Scheme 1. Synthesis of compound **1**.

system $ZnCl_2/CuCl_2/KO^tBu$ either the coordination of K^+ at an alkoxide ligand or of Cl^- at a metal center predominate over elimination of KCl. This is additionally supported by isolation and structural characterization of $(THF)_4Cu_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_6$ **2** during the reaction of $K_2[Zn(O^tBu)_3]_2$ with $CuCl_2$ in THF.

We conclude that, at least in our hands, products like **1** and the probable other intermediate $K_2[Zn(O^tBu)_3]_2$ dominate the reaction mixture of Scheme 1 and are thermodynamically preferred over hypothetic homoleptic mixed-metal systems like '$Zn[Cu(O^tBu)_3]_2$'. It follows, that the tendency to oligomerize as well as the formation of coordination polymers such as **1** has to be suppressed especially for the copper component.

One successful approach to reduce oligomerization of copper alkoxides and thus improving solubility and volatility has been the use of multidentate alkoxy ligands as in many other related cases $[Cu(OR)_2$, where R = Me, Et, Pr, Bu, are insoluble and non-volatile]. Particularly relevant examples include $Cu(OCH_2CH_2OCH_2CH_2OMe)_2$ [20], which is soluble in a range of organic solvents, while $Cu(OCH_2CH_2OBu)_2$ [32], $Cu(OCH_2CH_2NEt_2)_2$ [32], $Cu(OCHRCH_2NMe_2)_2$ (R = H, Me) [21], and $Cu(OCH_2CH_2NMeCH_2CH_2NMe_2)_2$ [21], represent the most volatile copper(II) alkoxides known, subliming at 60–110 °C at 10^{-4} Torr. Buhro and co-workers also observed that an apparently slight variation in the ligand sphere may cause a quite big change in the pyrolysis properties. They examined the pyrolysis up to 300 °C of two different monometallic copper(II) aminoalkoxides under N_2 at ambient pressure. It was found that $Cu(OCHMeCH_2NMe_2)_2$ forms pure copper metal as the only phase (XRD), while pyrolysis of $Cu(OCH_2CH_2NMe_2)_2$ without the α-substituent leads to the formation of Cu, CuO and Cu_2O under the same conditions [21]. $Cu(OCH_2CH_2NMe_2)_2$ has also been studied as an unusual Cu(II) precursor for MOCVD of pure copper metal at substrate temperatures of 200–210 °C, while higher substrate temperatures (250–270 °C) cause significant oxygen and carbon contamination [33]. For these reasons we selected pure $Cu[OCH(Me)CH_2NMe_2]_2$ **3** and $Cu[OCH(CH_2NMe_2)_2]_2$ **4** as target molecules. The remaining Lewis basic sites (O, NMe_2) were expected to bind coordinative a suitable Lewis acidic zinc fragment. This strategy to obtain mixed-metal precursors is also well established in the recent literature [34].

Following the alcohol exchange procedure established by Mehrotra et al. [19] the intramolecularly stabilized copper complexes **3** (previously reported by Buhro et al. [21]) and **4** could be obtained by reaction of $Cu(OMe)_2$ with the corresponding aminoalcohols 1,3-bis-(dimethylamino)-2-propanol and 1-dimethylamino-2-propanol in toluene at room temperature in nearly quantitave yield. Compounds **3** and **4** are readily soluble in polar and non-polar solvents (e.g. pentane, toluene, THF, CH_2Cl_2) and could be sublimed at 60–80 °C/10^{-2} Torr. Suitable single crystals for X-ray analysis were obtained by slow sublimation. In a first attempt **3** and **4** were combined with diethyl zinc, but immediate reduction and the formation of metallic copper occurred rather than the formation of a stable Lewis acid–base adduct. Finally, the stoichiometric reaction of $(Me_3Si)_3CZnCl$ [35], which is a much less reactive alkyl zinc compound, with the copper(II) alkoxides **3** and **4** in hexane lead to the blue heterobimetallic copper zinc alkoxides **5** and **6** in yields of about 85% after filtration and crystallization from THF at −40 °C. Both complexes are insoluble in non-polar solvents such as hexane and toluene, but soluble in THF or CH_2Cl_2. The mixed-metal compounds are not volatile, i.e. they do not sublime without decomposition (Scheme 2).



Scheme 2. Synthesis of compounds **3**, **4**, **5** and **6**.

2.2. Structural characterization

2.2.1. Copper compounds 1, 2 and 4

The crystal structure of compound $[(THF)KCu(O^tBu)_3]_\infty$ **1** contains a linear polymer chain with alternating (THF)KO^{t}Bu and Cu(O^{t}Bu)$_2$ units connected by bridging μ_2-O^{t}Bu ligands (Fig. 1). The Cu center is coordinated in a trigonal planar fashion (sum of angles 359.2°) by three O^{t}Bu moities. The bond lengths Cu–O(1) and Cu–O(2) with 1.849(4) and 1.810(5) Å, respectively, are normal and lie in the range of typical Cu-μ_2-O^{t}Bu units [Cu–O distances in Li$_4$Cu$_4$(O^{t}Bu)$_8$ [36]: 1.823–1.850 Å; [CuO^{t}Bu]$_4$ [23]: 1.813–1.878 Å]. The bond angles O(1)–Cu–O(1′) and O(1)–Cu–O(2) are different with 133.7(1) and 91.9(2)°, respectively. The potassium center shows a quasi-tetrahedral coordination sphere as seen from the sum of the bond angles at the O$_4$K-unit of 330.4°. The three K–O^{t}Bu bond lengths are nearly equal [2.564(4)–2.612(5) Å] and without any specific feature (K–O distance in [KO^{t}Bu]$_4$: 2.623 Å) [37].

Because **2** is isostructural to a large number of other oxid containig copper(II) chlorides with the general formula [(R)$_4$Cu$_4$(μ_4-O)(μ_2-Cl)$_6$], where R = Me$_2$NH [38], MeCN [39], hexamethylentetramine [40], *N*,*N*-diethylnicotinamide [41], Cl [42–44], OPPh$_3$ [45], *N*-methyl-2-pyrrolidinone [46], 2-methylpyridine [47], nicotine [48], dimethylsulphoxide [49], its structure is not discussed any further.

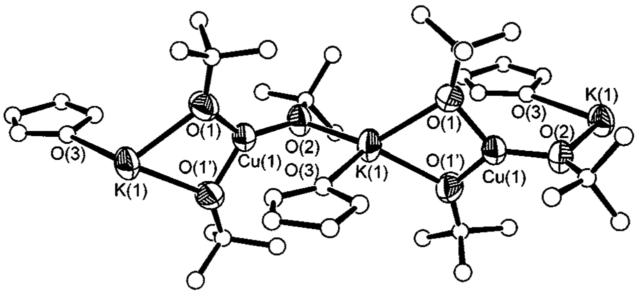


Fig. 1. A part of the polymer structure of **1** in the solid state (ORTEP drawing; hydrogen atoms are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.849(4), Cu(1)–O(2) 1.810(5), K(1)–O(1) 2.564(4), K(1)–O(2) 2.612(5), K(1)–O(3) 2.718(7), Cu(1)···K(1) 3.409(2) and 3.533(2); O(1)–Cu(1)–O(1′) 91.9(2), O(1)–Cu(1)–O(2) 133.7(1), Cu(1)–O(1)–K(1) 99.9(1), O(1)–K(1)–O(1′) 62.4(2), O(1)–K(1)–O(2) 129.7(1), O(1′)–K(1)–O(3) 112.8(2), O(2)–K(1)–O(3) 104.7(2).

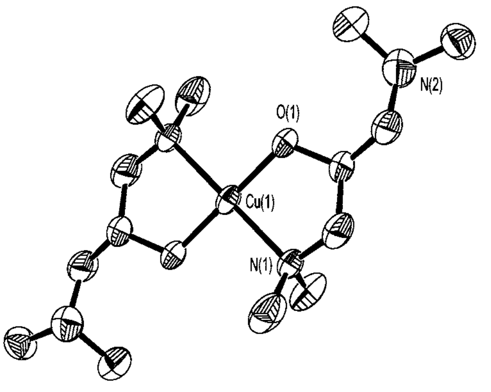


Fig. 2. Molecular structure of **4** in bthe solid state (ORTEP drawing; hydrogen atoms are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.851(4), Cu(1)–N(1) 2.060(4); N(1)–Cu(1)–O(1) 86.7(2), N(1)–Cu(1)–O(1′) 93.4(2).

The square planar structure of **4** is shown in Fig. 2. Although the compound contains two chirality centers in the organic ligand sphere, only the achiral isomer with an inversion center (Cu) in the molecule crystallized from the reaction solution and was crystallographically characterized. The copper center is coordinated by two nitrogen *N*,*N*′ and two oxygen atoms *O*,*O*′ in a *trans* fashion. The two further NMe$_2$ functionalities show no interaction with any other Cu center, i.e. intermolecular contacts are absent. The Cu–N and Cu–O distances [2.060(4), 1.851(4) Å] are comparable with the analogous distances in the related compound Cu(OCHMeCH$_2$NMe$_2$)$_2$ (**3**) [Cu–N: 2.052(3), Cu–O: 1.865(3)] described by Buhro et al. [21]. The bond angles N(1)–Cu–O(1) and O(1)–Cu–N(1′) are with 86.7(2) and 93.4(2)° close to the ideal angle of 90°.

*2.2.2. Copper/zinc compounds **5** and **6***

The molecular structure of the monomeric complexes **5** and **6** are shown in Figs. 3 and 4. Both compounds contain two chiral carbon atoms in the coordinated aminoalkoxide ligands, but only the achiral meso-isomers with approximately C_s symmetry crystallized and were characterized by X-ray analysis. Since **5** and **6** are isostructural and the respective bond lengths and angles differ just a little, only compound **6** will be described and discussed in some detail.

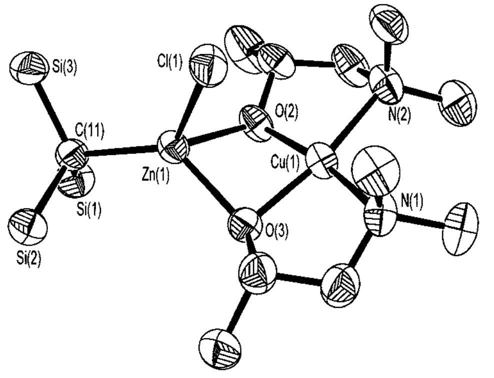


Fig. 3. Molecular structure of **5** in the solid state (ORTEP drawing; hydrogen atoms and THF are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°):Cu(1)–O(2) 1.921(6), Cu(1)–O(3) 1.944(7), Cu(1)–N(1) 2.054(8), Cu(1)–N(2) 2.069(9), Zn(1)–O(2) 2.063(7), Zn(1)–O(3) 2.051(6), Zn(1)–Cl(1) 2.38(3), Zn(1)–C(11) 2.052(9), Cu(1)···Zn(1) 2.869(2); Cu(1)–O(3)–Zn(1) 91.8(3), Cu(1)–O(2)–Zn(1) 92.1(3), O(3)–Cu(1)–O(2) 81.9(3), N(2)–Cu(1)–N(1) 104.3(3), O(3)–Cu(1)–N(2) 168.1(3), O(2)–Cu(1)–N(2) 87.1(3), O(3)–Cu(1)–N(1) 86.7(3), O(2)–Cu(1)–N(1) 168.5(3), O(2)–Zn(1)–O(3) 76.0(3), Cl(1)–Zn(1)–C(11) 120.5(3), O(2)–Zn(1)–Cl(1) 93.7(2), O(3)–Zn(1)–Cl(1) 93.2(2), O(2)–Zn(1)–C(11) 130.7(3), O(3)–Zn(1)–C(11) 129.8(3).

The molecular structure of **6** in the solid state shows a base adduct of the alkylzinc chloride fragment with an intramolecularly donor stabilized Cu center exhibiting the two aminoalkoxide ligands chelating in a *N,N′-cis* fashion. Interestingly, the two additional CH_2NMe_2 donor functions are not coordinating to any metal center. The zinc atom prefers the *O,O′*-coordination mode of the alkoxide groups. The crystal lattice contains one molecule of non-coordinating THF. The two metal centers are bridged by the alkoxide oxygen atoms O(13) and O(23). The Cu(1) atom lies in the plane defined by N(11), N(21), O(13) and O(23), while Zn(1) shows a distored tetrahedral coordination sphere involving the two oxygen atoms, Cl(1) and C(30). Compared to **4** the average Cu(1)–O distance (1.95 Å) in **6** is elongated by 0.1 Å most likely because of the bridging function to the second metal center, and the Cu(1)–N (2.063 Å) distances in **6** are nearly equal to those in **4** (2.060 Å). The heterodinuclear core exhibits a distorted square geometry. The Zn(1)–O distances [Zn(1)–O(13) 2.067(4) Å, Zn(1)–O(23) 2.078(5) Å] and the Cu(1)–O distances [Cu(1)–O(13) 1.945(4) Å, Cu(1)–O(23) 1.955(5) Å] differ by only 0.12 Å. The Zn(1)–O(13)–Cu(1) [93.1(2)°] and Zn(1)–O(23)–Cu(1) [92.5(1)°] angles are nearly equal. A larger deviation exists in the angles of O(13)–Cu(1)–O(23) [81.7(2)°] and O(13)–Zn(1)–O(23) [76.0(2)°], because of the unsymmetrical coordination at the zinc, the high steric demand of the tris(trimethylsilyl)methyl group and the repulsive interaction with the two uncoordinated CH_2NMe_2 groups of the chelating ligand systems. The distances Zn(1)–Cl(1) with 2.377(4) Å and Zn(1)–C(30) with 2.070(6) Å are comparable with those of related systems like $[(Me_3Si)_3C\text{-}Zn]_2(\mu\text{-}Cl)(\mu$-2,5-di(*tert*-butyl)pyrollide) [50] (Zn–Cl 2.410 Å, Zn–C 2.013 Å), $Ph(Me_3Si)CH{-}ZnCl(tmeda)$ [51] (Zn–Cl 2.252 Å, Zn–C 2.011 Å) and dimeric $(PhMe_2Si)_3C{-}ZnCl$ [52] (Zn–Cl 2.303–2.365 Å, Zn–C 1.970–1.984 Å). Interestingly, the Zn center prefers the coordination by the two alkoxide sites rather than the coordination by one amine donor and one alkoxide bridge.

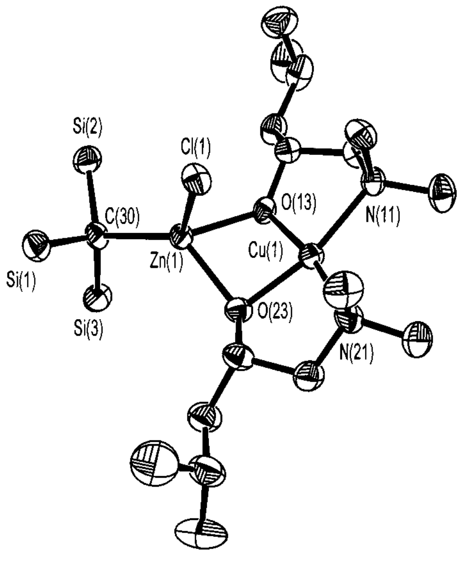


Fig. 4. Molecular structure of **6** in the solid state (ORTEP drawing; hydrogen atoms and THF are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): Cu(1)–O(13) 1.945(4), Cu(1)–O(23) 1.955(5), Cu(1)–N(11) 2.071(5), Cu(1)–N(21) 2.055(5), Zn(1)–O(13) 2.067(4), Zn(1)–O(23) 2.078(5), Zn(1)–Cl(1) 2.377(4), Zn(1)–C(30) 2.070(6), Cu(1)···Zn(1) 2.914(4); Cu(1)–O(13)–Zn(1) 93.1(2), Cu(1)–O(23)–Zn(1) 92.5(1), O(13)–Cu(1)–O(23) 81.7(2), N(21)–Cu(1)–N(11) 102.9(2), N(11)–Cu(1)–O(13) 87.2(2), N(21)–Cu(1)–O(23) 88.0(2), N(11)–Cu(1)–O(23) 166.4(2), N(21)–Cu(1)–O(13) 169.6(2), O(13)–Zn(1)–O(23) 76.0(2), Cl(1)–Zn(1)–C(30) 119.1(2), O(13)–Zn(1)–Cl(1) 92.8(2), O(23)–Zn(1)–C(30) 130.6(2).

2.3. *Thermal analysis and solid state pyrolysis*

The thermal properties of the compounds **5** and **6** were investigated by thermogravimetry (TG) under an argon atmosphere and gave evidence for the onset of decomposition at low temperatures. TG analysis of the copper and zinc educts provides further information of the course of thermal decomposition, and hints for the origin of carbon and nitrogen impurities in the residues may be obtained. The TG curve of $Cu[OCHMeCH_2NMe_2]_2$ **3** shows a small step at 133 °C followed by a substantial weight loss at 180 °C. There is no further weight loss observed above 210 °C and a residue of about 18.1% is left behind in the crucible which fits closely with the calculated value expected for complete decomposition to copper metal (19.6%). A similar experiment has also been carried out by Buhro et al. [21], and they found that copper metal is the only phase detected by X-ray powder diffraction if **3** is pyrolysed in the temperature range of 25–300 °C under N_2 at ambient pressure. The TG pattern of compound **4** shows a single weight loss starting at about 100 °C. This step ends at about 210 °C to leave a residue of 19.5% of the initial mass (17.95% calculated for complete conversion to elemental copper). Compounds **5** and **6** show similar TG curves beginning with weight loss at 125 °C for **5** and 105 °C for **6**. After a multistep decomposition process a residue amounting ca. 30% of the initial compound weight is measured which is close for a Cu@ZnO composite (**5**: 24%, **6**: 21%) containing some C-impurities. Compound **5** shows three stages in weight loss beginning with a big step from 125 to 195 °C. The next step from 200 to 250 °C is directly followed by the last stage ranging from 260 to about 320 °C, resulting in a residue amounting of 30% of the initial compound weight (calc. for Cu@ZnO: 24%). For compound **6** we find as well a three-step weight loss during heating from 30 to 500 °C in an argon atmosphere (Fig. 5), but the temperature ranges differ from those of compound **5**. The first stage ranges from 110

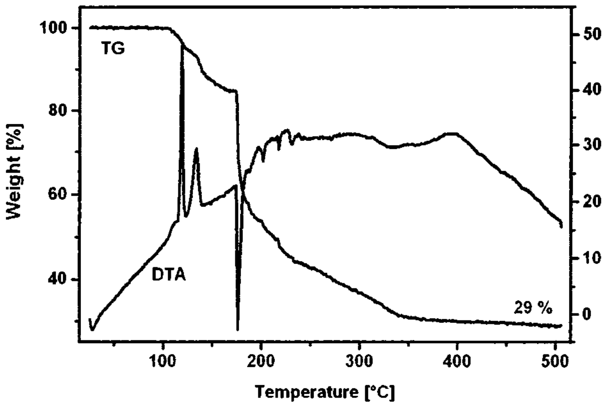


Fig. 5. TG/DTA analysis of **6** under argon atmosphere (heating rate 2 °C min^{-1}).

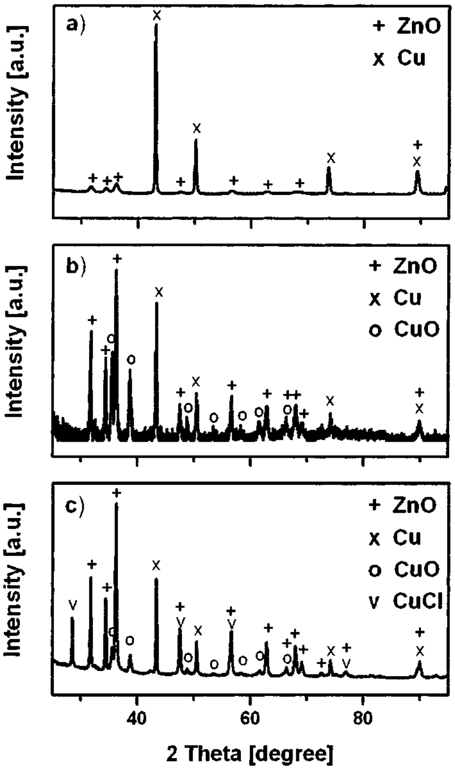


Fig. 6. Powder X-ray diffractograms of the pyrolysis residues obtained using **5** or **6** in argon or $H_2(10)/N_2(90)$ atmosphere (a), **6** in $O_2(5)/Ar(95)$ (b) and **5** in $O_2(5)/Ar(95)$ (c).

to about 130 °C. Another short step can be observed from 135 to 165 °C. This one is followed by the biggest weight loss step from 175 to 340 °C. The total amount of residue was quantified to be 29% (calc. for Cu@ZnO: 21%).

The TGA pattern of $(Me_3Si)_3CZnCl$ shows the first weight loss step at about 50 °C and merges into a significant step at about 250 °C. Two endothermic peaks are observed that belong to sublimation and partial thermal decomposition of the compound. A further exothermic peak was detected at about 400 °C, which is accompanied by a small mass loss to give a final mass of 12.6% of the initial amount. X-ray powder diffractometry proved the existence of zinc metal and zinc chloride in the residue which was obtained by a preparative pyrolysis experiment.

Preparative pyrolysis experiments of compound **5** and **6** were carried out under three different conditions (Ar, $H_2(10)/N_2(90)$ and $O_2(5)/Ar(95)$) using a corundum crucible in a horizontal quartz tube as the precursor reservoir. An inert atmosphere (Ar), as well as a reducing one (H_2/Ar) gave a rather clean decomposition into metallic copper and zinc oxide for **5** and **6**, respectively, as shown by X-ray powder diffraction (Fig. 6a). Oxidative conditions in addition lead to copper(II) oxide for **6** (Fig. 6b), and in the case of compound **5** the formation of copper(I) chloride (Fig. 6c) was observed, too, although both compounds contain nearly the same ligands.

Elemental analysis were obtained from all residues and confirmed the presence of carbon, nitrogen and hydrogen impurities: a carbon content of 13.5% for **5** and of 17.7% for **6** if argon or a mixture of nitrogen and hydrogen ($H_2(10)/N_2(90)$) was used. A somewhat lower carbon content was found in the residue when the compounds were pyrolysed under diluted oxygen atmosphere ($O_2(5)/95\%Ar(95)$): 12% carbon content for **5** and 13.4% for **6**. The nitrogen contents for all pyrolysis products (argon, hydrogen or oxygen atmosphere) of compounds **5** and **6** were determined to be 1.6% **5** and 2.5% **6**. Independently of the gases used, less than 1% of hydrogen impurities were detected for both compounds after pyrolysis.

2.4. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis

The pyrolysis products were analysed by SEM and EDX. Fig. 7 shows the SEM image of the residue of compound **5** under oxidative conditions ($O_2(5)/Ar(95)$). It shows a very uniform polycrystalline morphology. The EDX spectrum proved the presence of copper and zinc as well as impurities of oxygen, chlorine, carbon and silicon.

Pyrolysis of **6** in diluted oxygen atmosphere results in the formation of particles shown in Fig. 8. The material consists to a higher extent of zinc and oxygen, which may be ascribed to zinc oxide, also observed in the corresponding X-ray powder diffractogram (Fig. 6c).

3. Conclusion

We describe here the synthesis and structural characterization of copper alkoxides as well as new heterobimetallic copper zinc alkoxides. While salt elimination reactions in the system $CuCl_2/ZnCl_2/KO^tBu$ yields only the product [(THF)KCu(O^{t}Bu)$_3$]$_\infty$ **1**, adduct formation using the residual Lewis basic sites of intramolecularly donor stabilized copper(II) alkoxides Cu(OCH(R)CH$_2$NMe$_2$)$_2$ (**3**: R = Me [21], **4**: R = CH$_2$NMe$_2$) with the Lewis acid (Me$_3$Si)$_3$CZnCl yields the heterobimetallic compounds of the general type (Me$_3$Si)$_3$CZnCl · Cu(OCH(R)CH$_2$NMe$_2$)$_2$ (**5**: R = Me, **6**: R = CH$_2$NMe$_2$) in good yields. The pyrolysis studies showed, that the general idea of combination a copper precursor moiety with a Zn containing fragment in one organometallic molecule gives a two-phase Cu@ZnO composite material in one single decomposition step, even in the absence of additional reducing agents (hydrogen) and at low temperatures. This is an encouraging result to further develop improved mixed-metal Cu/Zn organometallic precursors. A suitable combina-

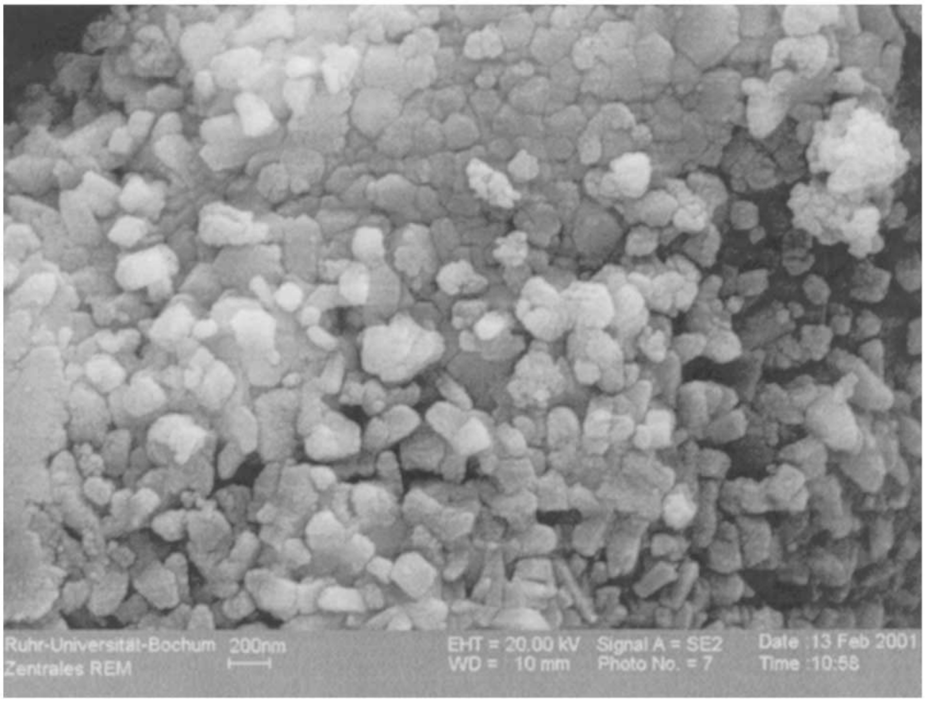


Fig. 7. SEM image of the pyrolysis product of **5** (under O$_2$(5)/Ar(95) atmosphere).

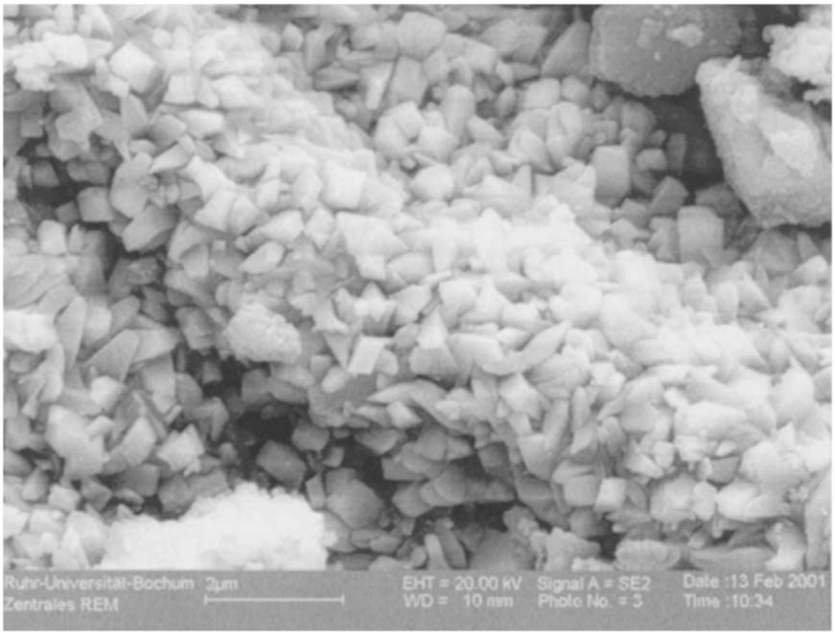


Fig. 8. SEM image of the pyrolysis product of **6** (under O$_2$(5)/Ar(95) atmosphere).

tion of Zn and Cu containing fragments needs to be found, which gives a cleaner decomposition into Cu and ZnO with less carbon and no chlorine impurities. Also the pyrolysis conditions need to be carefully optimized in order to obtain highly dispersed small copper particles, for example by using diluted solutions of **5** and **6** or similar precursors for impregnation/pyrolysis of inert supports of high surface area. Nevertheless the results described here are a first step to reach this goal.

4. Experimental

All manipulations were performed using carefully oven-dried reaction vessels and Schlenk techniques under an inert atmosphere of purified argon or in a glove box. Solvents were dried under argon by standard methods and stored over 4 Å molecular sieves (residual water < 3 ppm, Karl-Fischer). Starting materials not available from commercial sources were synthesized according to the literature, i.e. $Cu(OCH(CH_3)CH_2NMe_2)_2$ (**3**) [21], $Cu(OMe)_2$ [19], $(Me_3Si)_3CZnCl$ [35]. Elemental analysis were provided by the Service Centre of the Faculty of Chemistry at the Ruhr-University of Bochum (AAS: Vario 6 1998; EA: CHNSO Vario EL 1998). X-ray powder diffraction measurements were taken on a D8-Advance Bruker AXS diffractometer with Cu–K_α radiation ($\lambda = 1.5418$ Å) with θ–2θ geometry using a position sensitive detector. UV–vis absorption spectra were obtained by a Perkin–Elmer Lambda 9N-1062 spectrometer. TG measurements were performed on Seiko 6300S11 instrument in a range from 25 to 500 °C. The heating rate was 2 or 10 °C min^{-1} under a constant flow of argon (100 ml min^{-1}, 1 bar). SEM and EDX analysis were performed on a LEO Gemini SEM 1530 apparatus. EI-mass spectra were recorded on a CH 5 Varian MAT (1991) apparatus.

4.1. Synthesis of the new compounds **1**, **4**, **5** and **6**

4.1.1. $[(THF)KCu(O^tBu)_3]_\infty$ (**1**)

A mixture of $CuCl_2$ (500 mg, 3.7 mmol) and $ZnCl_2$ (507 mg, 3.7 mmol) in THF (60 ml) was treated with a solution of KO^{t}Bu (2.491 g, 22.2 mmol) in THF (15 ml). The color changed from orange to green and the solution was stirred for 4 days. After evaporation to dryness the solid material was washed three times with *n*-hexane and the resulting solution was concentrated and cooled to -40 °C to give green single crystals suitable for X-ray structural analysis of **1** (650 mg, 1.65 mmol, 44.6%). $C_{16}H_{35}CuKO_4$: Calc.: C, 48.76; H, 8.95; Cu, 16.12; Anal. Found: C, 47.83; H, 8.83; Cu, 15.87%. Decomposition at 190°C.

According to the literature the related compound $NaCu(O^tBu)_3$ could independently be synthesized by adding three equivalents of KO^{t}Bu to a suspension of $CuCl_2$ in THF [22].

4.1.2. $Cu[OCH(CH_2NMe_2)_2]_2$ (**4**)

$Cu(OMe)_2$ (2.8 g, 22.29 mmol) was suspended in toluene (25 ml) and 1,3-bis-(dimethylamino)-2-propanol (9.78 g, 66.88 mmol) was added. The resulting violet solution was stirred for 2 h. After removing the solvent by vacuum distillation at room temperature, the product was obtained by slow sublimation in vacuo (90 °C, 10^{-3} mbar). Yield: 5.69 g (16.07 mmol, 72%). UV–vis [nm (ε)] (THF): 263 (5400), 479 (90), 596 (40). MS (EI, 70 eV) m/z (rel. int.): 353 $[M^+ - H]$ (0.3), 295 (1), 266 (2.8), 237 (9), 208 (1), 150 (4), 128 (2), 113 (1), 84 (16), 58 (100), 42 (18) 30 (8). $C_{14}H_{34}CuN_4O_2$ (353.99): Calc.: C, 47.50; H, 9.68; N, 15.83; Cu, 17.95; Anal. Found: C, 46.87; H, 9.67; N, 16.24; Cu, 16.6%. M.p. (dec.): 95 °C.

4.1.3. $Cu[OCH(Me)CH_2NMe_2]_2 \cdot (Me_3Si)_3CZnCl$ (**5**)

A solution of $(Me_3Si)_3CZnCl$ (1 g, 3.01 mmol) in *n*-hexane (15 ml) was added to a solution of $Cu[OCH(Me)CH_2NMe_2]_2$ [21] (0.81 g, 3.01 mmol) in *n*-hexane (20 ml). The resulting blue insoluble product was washed three times with *n*-hexane (10 ml) and dried in vacuo to give **5** (1.69 g, 2.82 mmol, 94%). Suitable single crystals for X-ray analysis were obtained by crystallization from tetrahydrofuran. $C_{20}H_{51}ClCuN_2O_2Si_3Zn$: Calc.: C, 40.02; H, 8.56; N, 4.67; Cu, 10.59; Zn, 10.89; Anal. Found: C, 39.54; H, 8.60; N, 4.66; Cu, 10.73; Zn, 9.40. M.p. (dec.): 126 °C. UV–vis [nm (ε)] (THF): 263 (5600), 608 (70).

4.1.4. $Cu[OCH(CH_2NMe_2)_2]_2 \cdot (Me_3Si)_3CZnCl$ (**6**)

A solution of $(Me_3Si)_3CZnCl$ (1 g, 3.01 mmol) in *n*-hexane (15 ml) was added to a solution of $Cu[OCH(CH_2NMe_2)_2]_2$ (1.06 g, 3.01 mmol) in *n*-hexane (20 ml). The resulting blue insoluble product was washed three times with *n*-hexane (10 ml) and dried in vacuo to give **6** (1.75g, 2.55 mmol, 85%). Suitable single crystals for X-ray analysis were obtained by crystallization from tetrahydrofuran. $C_{24}H_{61}ClCuN_4O_2Si_3Zn$: Calc.: C, 42.00; H, 8.96; N, 8.16; Cu, 9.26; Zn, 9.53; Anal. Found: C, 41.75; H, 8.81; N, 8.29; Cu, 9.9; Zn, 8.51%. M.p. (dec.): 118 °C. UV–vis [nm (ε)] (THF): 263 (5300), 615 (70).

4.2. Pyrolysis studies

Preparative pyrolysis experiments of compounds **5** and **6** were carried out under three different conditions (Ar, H_2/N_2 and O_2/Ar) using a corundum crucible in a horizontal quartz tube as the precursor reservoir. All gases were passed through P_2O_5 to avoid hydrolysis of the compounds. Every experiment was performed using about 1 g of the compounds. The obtained black

Table 1
Crystallographic and data collection parameters for **1**, **4**, **5** and **6**

	1	**4**	**5**	**6**
Formula	$C_{16}H_{35}CuKO_4$	$C_{14}H_{34}CuN_4O_2$	$C_{24}H_{58}ClCuN_2O_3Si_3Zn$	$C_{28}H_{69}ClCuN_4O_3Si_3Zn$
Formula mass (g mol^{-1})	394.08	353.99	671.36	758.50
T (K)	293(2)	293(2)	203(2)	203(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, *Pnma*	Monoclinic, $P2_1/c$	Tetragonal, $P4/ncc$	Monoclinic, $P2_1/c$
Unit cell dimensions				
a (Å)	13.139(3)	9.064(2)	21.604(5)	17.05(4)
b (Å)	11.112(2)	8.672(2)	21.604(5)	12.19(2)
c (Å)	15.395(3)	11.848(3)	34.642(1)	20.55(4)
α (°)	90	90	90	90
β (°)	90	93.132(5)	90	105.51(5)
γ (°)	90	90	90	90
V (Å^3)	2247.8(8)	929.9(3)	16168(8)	4114(1)
Z	4	4	16	4
D_{calc} (g cm^{-3})	1.165	1.278	1.164	1.225
μ (mm^{-1})	1.168	1.190	1.300	1.282
F (000)	844	386	6064	1628
Scan range (°)	$2.04 < \theta < 25.12$	$2.25 < \theta < 25.10$	$1.51 < \theta < 22.50$	$1.96 < \theta < 25.07$
Reflections collected	9269	2207	63233	16433
Reflections [$I > 2\sigma(I)$]	1223	1174	3835	4217
Unique data (R_{int})	2112 (0.0912)	1453 (0.0222)	5288 (0.0719)	6858 (0.0932)
Parameters	115	97	340	387
[a]R_1 [$I > 2\sigma(I)$]	0.0722	0.0609	0.0768	0.0559
[b]wR_2 [$I > 2\sigma(I)$]	0.1700	0.1650	0.2199	0.1180
[b]wR_2 (all data)	0.2012	0.1709	0.2868	0.1398
GOF [c] on F^2	0.953	1.071	1.173	0.941
Residual density (e Å^{-3})	1.520/−0.312	1.260/−0.439	1.737/−0.501	0.868/−0.871

[a] $R_1 = \Sigma(\|F_o\| - |F_c\|)/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$.
[c] $\mathrm{GOF} = [\Sigma_w(F_o^2 - F_c^2)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$.

residues were transferred into a glove box (O_2, $H_2O < 1$ ppm) and finely ground for X-ray powder diffractometry and elemental analysis. The temperature for the pyrolysis experiments was as follows: Pyrolysis under argon was started at 100 °C for 2 h, then the temperature was adjusted to 200 °C for 2 h and finally it was held at 500 °C for an additional 3 h. The temperature program for a reducing ($H_2(10)/N_2(90)$) and an oxidizing ($O_2(5)/Ar(95)$) atmosphere was: 1.5 h at 120 °C, 2.5 h at 240 °C, 1 h at 360 °C and 1 h at 480 °C.

4.3. Structure determinations

X-ray single-crystal measurements were performed on a Bruker AXS CCD 1000 diffractometer, equipped with a cryogenic nitrogen cold stream to prevent loss of solvent. Graphite-monochromated Mo–K$_\alpha$ radiation (0.71073 Å) was used. The structures were solved with direct methods and refined anisotropically with the SHELXL-97 program suite. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma(\|F_o\| - |F_c\|)/\Sigma|F_o|$ and $wR_2 = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$. Drawings were produced with the ORTEP program suite (ORTEP-3 for Windows, version 1.0.2, 1998). Table 1 lists the crystallographic data.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159929 for compound **1**, CCDC no. 159932 for compound **2**, CCDC no. 159930 for compound **4**, CCDC no. 159928 for compound **5** and CCDC no. 159931 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] L.G. Hubert-Pfalzgraf, Polyhedron 13 (1994) 1181.
[2] M. Veith, S. Mathur, C. Mathur, Polyhedron 17 (1998) 1005.
[3] K.G. Caulton, L.G. Hubert-Pfalzgraf, Chem. Rev. 90 (1990) 969.

[4] (a) W.A. Herrmann, N.W. Huber, O. Runte, Angew. Chem. 107 (1995) 2371;
(b) W.A. Herrmann, N.W. Huber, O. Runte, Angew. Chem. Int. Ed. Engl. 34 (1995) 2187.
[5] M. Veith, Chem. Rev. 90 (1990) 3.
[6] C.D. Chandler, C. Roger, M.J. Hampden-Smith, Chem. Rev. 93 (1993) 1205.
[7] L.G. Hubert-Pfalzgraf, Coord. Chem. Rev. 180 (1998) 967.
[8] R.C. Mehrotra, A. Singh, S. Sogani, Chem. Rev. 94 (1994) 1643.
[9] M. Veith, S. Faber, R. Hempelmann, S. Janssen, J. Prewo, H. Eckerlebe, J. Mater. Sci. 31 (1996) 2009.
[10] G. Ertl, H. Knözinger, J. Weitkamp, Handbook of Heterogeneous Catalysis, Wiley-VCH, Weinheim, 1997.
[11] A. Cybulski, Catal. Rev. Sci. Eng. 36 (1994) 557.
[12] M.S. Spencer, Catal. Lett. 66 (2000) 255.
[13] S. Locmelis, M. Binnewies, Z. Anorg. Allg. Chem. 625 (1999) 1578.
[14] T. Fujitani, J. Nakamura, Appl. Catal. A. Gen. 191 (2000) 111.
[15] S.C. Goel, M.Y. Chiang, W.E. Buhro, Inorg. Chem. 29 (1990) 4646.
[16] A.P. Purdy, C.F. George, Polyhedron 13 (1994) 709.
[17] R.C. Mehrotra, M. Arora, Z. Anorg. Allg. Chem. 370 (1969) 300.
[18] R.L. Geerts, J.C. Huffman, K.G. Caulton, Inorg. Chem. 25 (1986) 1803.
[19] J.V. Singh, B.P. Baranwal, R.C. Mehrotra, Z. Anorg. Allg. Chem. 477 (1981) 235.
[20] S.C. Goel, K.S. Kramer, P.C. Gibbons, W.E. Buhro, Inorg. Chem. 28 (1989) 3620.
[21] S.C. Goel, K.S. Kramer, M.Y. Chiang, W.E. Buhro, Polyhedron 9 (1990) 611.
[22] A.P. Purdy, C.F. George, J.H. Callahan, Inorg. Chem. 30 (1991) 2812.
[23] T. Greiser, E. Weiss, Chem. Ber. 109 (1976) 3142.
[24] R.C. Mehrotra, A. Singh, Chem. Soc. Rev. 25 (1996) 1.
[25] R.C. Mehrotra, A. Singh, Polyhedron 17 (1998) 689.
[26] D. Weiß, A. Schier, H. Schmidbaur, Z. Naturforsch. Sect. b 53 (1998) 1307.
[27] F. Teixidor, T. Flor, J. Casabo, C. Miravitlles, J. Rius, E. Molins, Inorg. Chim. Acta 122 (1986) 95.
[28] C. Fukuhara, K. Tsuneyoshi, N. Matsumoto, S. Kida, M. Mikuriya, M. Mori, J. Chem. Soc. Dalton Trans. (1990) 3473.
[29] S. Ohtsuka, M. Kodera, K. Motoda, M. Ohba, H. Okawa, J. Chem. Soc. Dalton Trans. (1995) 2599.
[30] K.K. Nanda, S. Mohanta, U. Flörke, S.K. Dutta, K. Nag, J. Chem. Soc. Dalton Trans. (1995) 3831.
[31] M. Yonemura, Y. Matsumura, H. Furutachi, M. Ohba, H. Okawa, D.E. Fenton, Inorg. Chem. 36 (1997) 2711.
[32] H.S. Horowitz, S.J. McLain, A.W. Sleight, J.D. Druliner, P.L. Gai, M.J. VanKavelaar, J.L. Wagner, B.D. Biggs, S.J. Poon, Science 243 (1989) 66.
[33] V.L. Young, D.F. Cox, M.E. Davis, Chem. Mater. 5 (1993) 1701.
[34] A.N. Gleizes, Chem. Vap. Deposition 6 (2000) 155.
[35] M. Westerhausen, B. Rademacher, W. Schwarz, J. Weidlein, J. Organomet. Chem. 469 (1994) 135.
[36] A.P. Purdy, C.F. George, Polyhedron 14 (1995) 761.
[37] M.H. Chisholm, S.R. Drake, A.A. Nahni, W.E. Streib, Polyhedron 10 (1991) 337.
[38] V. Pavlenko, V. Kokozay, O. Babich, Z. Naturforsch. Sect. b 48 (1993) 1321.
[39] W. Hiller, A. Zinn, K. Dehnicke, Z. Naturforsch. Sect. b 45 (1990) 1593.
[40] J. Pickardt, N. Rautenberg, Z. Naturforsch. Teil. b 37 (1982) 1355.
[41] A. El-Toukhy, G.Z. Cai, G. Davies, T.R. Gilbert, K.D. Onan, M. Veidis, J. Am. Chem. Soc. 106 (1984) 4596.
[42] J.A. Bertrand, J.A. Kelley, Inorg. Chem. 8 (1969) 1982.
[43] R. Belford, D.E. Fenton, M.R. Truter, J. Chem. Soc. Dalton Trans. (1972) 2345.
[44] R.L. Harlow, S.H. Simonsen, Acta Crystallogr. Sect. B 33 (1977) 2784.
[45] J.A. Bertrand, Inorg. Chem. 6 (1967) 495.
[46] M.R. Curchill, F.J. Rotella, Inorg. Chem. 18 (1979) 853.
[47] N.S. Gill, M. Sterns, Inorg. Chem. 9 (1970) 1619.
[48] H.M. Haendler, Acta Cystallogr. Sect. C (Cr. Str. Comm.) 46 (1990) 2054.
[49] S. Brownstein, N.F. Han, E. Gabe, F. Lee, Can. J. Chem. 67 (1989) 551.
[50] M. Westerhausen, M. Wieneke, H. Nöth, T. Seifert, A. Pfitzner, W. Schwarz, O. Schwarz, J. Weidlein, Eur. J. Inorg. Chem. (1998) 1175.
[51] M. Westerhausen, M. Wieneke, W. Schwarz, J. Organomet. Chem. 522 (1996) 137.
[52] S.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock, J.D. Smith, K. Tavakkoli, A.D. Webb, J. Organomet. Chem. 462 (1993) 45.