Inorganica Chimica Acta 374 (2011) 373-384

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Copper complexes of tripodal $\kappa^6 N$ -donor ligands: A structural, EPR spectroscopic and electrochemical study

Ina Trapp, Matthias Löble, Jens Meyer, Frank Breher*

Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 15, 76131 Karlsruhe, Germany

ARTICLE INFO

Article history: Available online 16 March 2011

Dedicated to Prof. Dr. W. Kaim on occasion of his 60th birthday.

Keywords: N-donor ligands Multifunctional ligands Copper complexes EPR spectroscopy Cyclic voltammetry

ABSTRACT

A new tris(pyridylhydrazonyl)methane ligand, HC[N(Me)N=C(H)Py]₃ (L2) (Py = pyridyl), has been synthesized. The latter is accessible from triethyl orthoformate and 2-(2-methylhydrazono)methylpyridine in 63% isolated yield. We have investigated its coordination chemistry towards copper ions and compared the results with those obtained for the recently developed multifunctional ligand, (S)P[N(Me)N=C(H)Py]₃ (L1). The copper(II) complexes [Cu(L1)](OTf)₂ (3) and [Cu(L2)](OTf)₂ (4) (OTf = triflate, (O₃SCF₃)⁻) are mononuclear with the cations coordinated by three imino and three pyridine nitrogen atoms. Almost axial symmetric EPR spectra have been obtained in frozen solutions at X-band. The spectra show resolved hyperfine couplings to the copper nuclei on one of the three g values. X-ray structural analyses revealed in each case a *cis* bond distortion and a trigonal twist due to Jahn–Teller effects. The Cu^{II}/Cu¹ reduction potentials of **3** and **4** were shown to be remarkably low ($E_{1/2}^0 = -0.11$ V for **3**; $E_{1/2}^0 = -0.34$ V for **4**), especially for **3** consisting of the phosphorus supported ligand L1. The corresponding copper(I) complexes [Cu(L1)](OTf) (**5**) and [Cu(L2)](OTf) (**6**) are accessible by reduction using decamethyl ferrocene. Both copper(I) complexes have been characterized in detail including X-ray structure analyses.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The synthesis of tailor-made, multidentate ligand systems that offer specific properties for the generation of transition metal complexes regarding nuclearity, coordination number or geometry is still of high interest. Especially fac-coordinating N-donor ligands with podand topology provide intrinsically well-defined coordination geometries [1]. In particular Trofimenko's tris(pyrazolyl)hydroborate (Tp^R) ligands, which are also known as scorpionates, are among the most important and particularly versatile ligands, comprising applications in coordination-, bio-inorganic and organometallic chemistry [2-7]. More recently, Reger et al. introduced an improved access to the neutral carbon analogs, i.e. the tris(pyrazolyl)methanes (^RTpm), which also show a very rich coordination chemistry [8]. The development of the latter, and the synthesis and reactions of their complexes, have been recorded through many reviews [9–12]. This ligand family has been extended to the anionic tris(pyrazolyl)methanide [13–21] and –silanide [22.23] systems. which are isoelectronic with the hydroborate system, but feature ambidentate characteristics and two possible binding sites, namely the anionic carbon and silicon or the pyrazolyl ring nitrogens. Another possibility for increasing the number of donor atoms in Tp- or Tpm-related scaffolds is to attach further donor-containing substituents in the 3-position of the pyrazolyl entities. In particular, multinucleating ligands based on pyrazolyl-pyridine chelating units merit attention in this context [24]. Our group became interested in non-heterocyclic, tripodal ligands, which are topologically related to the pyrazolyl-pyridine systems. We have focused our attention on the new tris(pyridylhydrazonyl)methane derivative, HC[N(Me)N=C(H)Py]₃ (L2) (Py = pyridyl), which is related to the recently developed multisite coordination ligand, (S)P[N(Me)N=C(H)Py]₃ (L1) [25-26]. In both cases, the ligand features three pyridylhydrazonyl donor units, which are connected by a CH or PS backbone as non-coordinating structural support. Related phosphorus supported N-donor ligands of this kind are known from the literature [27-33]. We present here the synthesis and characterization of L2. In order to compare the coordination chemistry of L2 with those of its phosphorus analog (L1), we have investigated their coordination chemistry towards copper ions. Alongside X-ray structural, EPR spectroscopic and electrochemical investigations on mononuclear Cu^{II} complexes of L1 and L2, we will also present their corresponding Cu^I complexes.

2. Experimental

2.1. Materials and general techniques

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Air sensitive compounds were



^{*} Corresponding author. Tel.: +49 721 608 448 55; fax: +49 721 608 470 21. *E-mail address*: breher@kit.edu (F. Breher).

^{0020-1693/\$ -} see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.02.045

stored and weighed in glove boxes (Braun MB150 G-I and Unilab system). Toluene, hexane and THF were freshly distilled under argon from sodium/benzophenone, diethyl ether from sodium-potassium alloy/benzophenone and acetonitrile from CaH₂ prior to use. CD₃CN was vacuum transferred from CaH₂ into thoroughly dried glassware equipped with Young teflon valves. FeCp*₂ was synthesized according to a literature procedure [34]. All other chemicals were purchased from Aldrich or ABCR and used as received.

2.2. Instrumentation

Elemental analyses and mass spectrometric investigations were carried out in the institutional technical laboratories. IR spectra were recorded on a Bruker Vertex 70 spectrometer in the range from 4000 to 400 cm⁻¹ using a KBr beam splitter. Samples were prepared by using the ATR technique (attenuated total reflection) on bulk material, and the data are quoted in wavenumbers (cm⁻¹). The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong) and br (broad). Solution NMR spectra were recorded with Bruker Avance instruments operating at ¹H Larmor frequencies of 300 and 400 MHz and are referenced according to IUPAC recommendations [35]. Chemical shifts are given relative to TMS for ¹³C and ¹H, CFCl₃ for ¹⁹F and H₃PO₄ for ³¹P. Coupling constants, *J*, are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, or m for singlets, doublets or multiplets, respectively. Broad ¹H NMR resonances (br) of paramagnetic samples are listed only with one digit. Cyclic voltammetry measurements were performed with an EG&G potentiostate (PAR-model 263A) and an electrochemical cell for sensitive compounds [36–38]. We used a freshly polished Pt disk working electrode, a Pt wire as counter electrode, and a Ag wire as (pseudo) reference electrode ([*n*Bu₄N][PF₆] (0.1 M) as electrolyte). Potentials were calibrated against the Fc/Fc⁺ couple [39], which has a potential of $E_{1/2}^0$ = 0.35 V versus Ag/AgCl. Continuous wave (CW) electron paramagnetic resonance spectroscopy was performed at X-band on a Bruker EMXplus spectrometer (microwave frequency 9.43 GHz) equipped with a liquid nitrogen cryostat. The samples were measured with a modulation amplitude of 10 G and a modulation

Table 1	
Crystallographic	data.

frequency of 100 kHz, and the field was calibrated by using 2, 2-diphenyl-1-picrylhydrazyl (DPPH) with a g value of 2.0036. CW EPR simulations were calculated using the Bruker XSOPHE program package (version 1.1.4) [40].

2.3. X-ray crystal structure determination

Crystals of 3, 4, 5 and 6 suitable for X-ray diffraction were obtained from acetonitrile/diethyl ether. In order to avoid quality loss, crystals were removed from the reaction flask under a stream of argon gas and immediately covered with a layer of perfluoropolvalkylether oil. A suitable crystal was selected, attached to a glass fiber and immediately placed in the low temperature nitrogen stream using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using a STOE STADI 4 diffractometer equipped with a CCD detector and graphite-monochromated Mo Ka (0.71073 Å) radiation. All calculations were performed using SHELXTL (ver. 6.12) program suite [41,42]. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks. Crystal data collection and processing parameters are given in Table 1.

2.4. Synthesis of $HC[N(Me)N=C(H)Py]_3$ (L2)

2-Pyridinealdehyde (21.4 g, 0.20 mol) was cooled to -78 °C and *N*-methylhydrazine (9.2 g, 0.20 mol) was carefully added. The cooling bath was removed and the mixture was slowly heated to 80 °C and stirred at that temperature for 3 h. 2-(2-Methylhydrazon-o)methylpyridine was received as a yellowish, oily liquid by fractional distillation in vacuum (23.0 g, 0.17 mol, 85%). Triethyl orthoformate (5.9 g, 0.04 mol) and 2-(2-methylhydrazono)methylpyridine (16.2 g, 0.12 mol) were heated in 150 mL toluene to 100 °C in a Schlenk flask connected to a short distillation adapter. Ethanol that formed during the reaction was distilled off constantly. After 20 days the mixture had turned dark brown. The sol-

Compound	3 ·CH ₃ CN	4 ·CH ₃ CN	5	6 ·2(CH ₃ CN)
Empirical formula	C ₂₃ H ₂₄ CuF ₆ N ₉ O ₆ PS ₃ ·C ₂ H ₃ N	$C_{24}H_{25}CuF_6N_9O_6S_2\cdot C_2H_3N$	$C_{22}H_{24}CuF_3N_9O_3PS_2$	$C_{23}H_{25}CuF_3N_9O_3S\cdot 2(C_2H_3N)$
Μ	868.26	818.27	678.13	710.23
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group[70]	$P2_1/n$	$P2_1/c$	$P2_1/c$	PĪ
a (Å)	1153.1(2)	2725.2(5)	1060.9(2)	1175.3(2)
b (Å)	2286.9(5)	2510.1(5)	2052.6(4)	1192.5(2)
c (Å)	1275.4(3)	1489.5(3)	1322.0(3)	1257.8(3)
α (°)				78.14(3)
β(°)	91.78(3)	103.15(3)	106.03(3)	70.75(3)
γ (°)				75.67(3)
$V(\times 10^6 \text{ Å}^3)$	3362(1)	9922(3)	2766.6(9)	1597.7(6)
$\mu (\mathrm{mm}^{-1})$	0.975	0.878	1.063	0.815
$ ho_{ m calcd} ({ m g}{ m cm}^{-3})$	1.716	1.643	1.628	1.476
Ζ	4	12	4	2
T (K)	200(2)	200(2)	200(2)	200(2)
$2\theta_{\max}$ (°)	50.00	50.00	50.00	52.00
Reflections measured	22 949	67 951	18 191	11 908
Reflections unique	5898	17 366	4842	6172
Parameters/restrainer	473/0	1390/0	373/0	420/0
R1 (I $\ge 2\sigma(I)$)	0.0532	0.0794	0.0511	0.0472
wR2 (all data)	0.1430	0.2163	0.1506	0.1351
Maximum/minimum residue electron density $(e \times 10^{-6} \text{ Å}^{-3})$	1.340/-1.365	0.903/-1.020	0.783/-0.806	0.466/-0.609

vent was removed in vacuum and the product was received as fine beige needles by recrystallization of the residue from THF/hexane.

Yield: 10.5 g, (63%); m.p.: 152 °C. Elemental *Anal.* Calc. for $C_{22}H_{25}N_9$: C, 63.60; H, 6.06; N, 30.34. Found: C, 63.52; H, 6.08; N, 30.34%. ¹H NMR (300 MHz, 298 K, CD₃CN): δ = 3.11 (s, 9H, -CH₃), 6.11 (s, 1H, -CH), 7.13 (dd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 4.9 Hz3H, H_{Ar}), 7.48 (s, 3H, -N=C-H) 7.55 (dd, ³J_{HH} = 8.1 Hz, ³J_{HH} = 7.5 Hz, 3H, H_{Ar}), 7.73 (d, ³J_{HH} = 8.1 Hz, 3H, H_{Ar}), 8.48 ppm (d, ³J_{HH} = 4.9 Hz, 3H, H_{Ar}); ¹³C{¹H} NMR (75 MHz, 298 K, CD₃CN): δ = 34.2 (s, -CH₃) 98.0 (s, -CH), 118.2 (s, 3H, C_{Ar}), 121.7 (s, C_{Ar}), 131.4 (s, -C=N), 136.0 (s, C_{Ar}), 149.0 (s, C_{Ar}), 156.2 ppm (s, C_{ipso}). EI-MS: *m*/*z* (%): 78.9 (83) [Py]⁺, 92.0 (95) [CH-Py]⁺, 106.0 (65) [N=CH-Py]⁺, 281.1 (98) [N^{Me}NCHPy]⁺; FT-IR (solid, ATR): *v*(cm⁻¹) = 1573(s), 1459 (m), 1431 (m), 1345 (m), 1237 (m), 1190 (m), 1021 (vs), 986 (s), 865 (m), 775 (s), 741 (s), 623 (m), 566 (m), 525 (m), 403 (s).

2.5. Synthesis of $[Cu(L1)](OTf)_2(3)$

To a stirred solution of Cu(OTf)₂ (181 mg, 0.5 mmol) in 10 mL THF a solution of $(S)P[N(Me)N=C(H)Py]_3$ (L1, 233 mg, 0.5 mmol) in 10 mL THF was added dropwise at room temperature. A green precipitate formed immediately. After stirring over night the precipitate turned red brown, the reaction mixture was filtered and the red brown precipitate was washed with 20 mL THF. The precipitate was then redissolved in 5 mL acetonitrile and the solution layered with diethyl ether. An initially formed grass green precipitate was filtered and the solution was further layered with diethyl ether until the formation of small needles was observed. After a few days the paramagnetic product was obtained as dark red blocks. Yield: 335 mg (81%). m.p.: 295 °C. Elemental Anal. Calc. for C₂₃H₂₄CuF₆₋ N₉O₆PS₃: C, 33.44, H, 2.81, N, 15.26. Found: C, 33.28, H, 2.97, N, 15.23%. ¹H NMR (400 MHz, 298 K, CD₃CN): δ = 5.8 (s, br, $W_{1/2}$ \approx 120 Hz, 9H, -CH₃), 13.3 (s, br, $W_{1/2} \approx$ 70 Hz, 3H, N=C-H), 31.8 (s, br, $W_{1/2} \approx 1200$ Hz, 3H, H_{Ar}), 36.7 ppm (s, br, $W_{1/2} \approx 1500$ Hz, 3H, H_{Ar}); ¹⁹F NMR (377 MHz, 298 K, CD₃CN): $\delta = -79.21$ ppm (s); ESI-MS: m/z (%): 677 (60) $[M-(SO_3CF_3)]^+$, 1505 (100) [2 M- (SO_3CF_3)]⁺; FT-IR (solid, ATR): $v(cm^{-1}) = 1610$ (m), 1561 (w), 1484 (w), 1465 (w), 1445 (w), 1417 (vw), 1376 (vw), 1249 (s), 1221 (m), 1147 (s), 1059 (s), 971 (s), 911 (m), 801 (s), 764 (s), 707 (w), 634 (vs), 572 (m), 533 (m), 515 (s), 467 (m), 416 (m).

2.6. Synthesis of [Cu(L2)](OTf)₂ (4)

To a stirred solution of Cu(OTf)₂ (181 mg, 0.5 mmol) in 10 mL THF a solution of $HC[N(Me)N=C(H)Py]_3$ (L2, 208 mg, 0.5 mmol) in 10 mL THF was added dropwise at room temperature. A dark green precipitate formed immediately. After stirring over night the reaction mixture was filtered and the precipitate was washed with 20 mL THF. It was then re-dissolved in 5 mL acetonitrile and the green brown solution layered with diethyl ether. An initially formed grass green precipitate was filtered and the solution was further layered with diethyl ether until the formation of small needles was observed. After a few days, the paramagnetic product was obtained as dark green blocks. Yield: 320 mg (82%). m.p.: 178 °C. Elemental Anal. Calc. for C24H25CuF6N9O6S2: C, 37.09, H, 3.24, N, 16.22. Found: C, 36.99, H, 3.26, N, 16.31%. ¹H NMR (400 MHz, 298 K, CD₃CN): δ = -8.3 (s, br, $W_{1/2} \approx$ 400 Hz, 1H, -CH), 5.7 (s, br, $W_{1/2} \approx 100$ Hz, 9H, -CH₃), 12.4 (s, br, $W_{1/2} \approx 50$ Hz, 3H, N=C-H), 30.4 (s, br, $W_{1/2} \approx 560$ Hz, 3H, H_{Ar}), 35.6 ppm (s, br, $W_{1/2}$ $_{2} \approx 760$ Hz, 3H, H_{Ar}); ¹⁹F NMR (282 MHz, 298 K, CD₃CN): $\delta = -79.24 \text{ ppm}$ (s); ESI-MS: m/z (%): 627 (40) $[M-(SO_3CF_3)]^+, 1406$ (100) $[2 \text{ M}-(\text{SO}_3\text{CF}_3)]^+$; FT-IR (solid, ATR): $v(\text{cm}^{-1}) = 1610$ (m), 1561 (w), 1484 (w), 1465 (w), 1445 (w), 1417 (vw), 1376 (vw), 1249 (s), 1221 (m), 1147 (s), 1059 (s), 971 (s), 911 (m), 801 (s), 764 (s), 707 (w), 634 (vs), 572 (m), 533 (m), 515 (s), 467 (m), 416 (m).

2.7. Synthesis of [Cu(L1)](OTf) (5)

A solution of [Cu(L1)](OTf)₂(87 mg, 0.1 mmol) in 5 mL acetonitrile was stirred with FeCp^{*}₂ (50 mg, 0.15 mmol) at room temperature overnight. The green brown solution was filtered and then layered with 10 mL diethyl ether. An initially formed beige precipitate was filtered and the solution was layered with additional 40 mL diethyl ether to give dark green block like crystals. Yield: 29 mg (43%). m.p.: 241 °C. Elemental Anal. Calc. for C₂₂H₂₄CuF₃₋ N₉O₃PS₂: C, 39.91, H, 3.79, N, 18.21. Found: C, 40.21, H, 3.81, N 18.15%. ¹H NMR (300 MHz, 298 K, CD₃CN): δ = 3.44 (d, ${}^{3}J_{\text{HP}}$ = 10.1 Hz, 9H, –CH₃), 7.47 (dd, ${}^{3}J_{\text{HH}}$ = 7.7 Hz, ${}^{3}J_{\text{HH}}$ = 5.0 Hz, 3H, H_{Ar}), 7.62 (d, ${}^{3}J_{HH} = 8.0 \text{ Hz}$, 3H, H_{Ar}), 7.91 (dd, ${}^{3}J_{HH} = 8.0 \text{ Hz}$, 3 $J_{HH} = 7.7 \text{ Hz}$, 3H, H_{Ar}), 7.93 (s, 3H, N=C-H), 8.60 ppm (d, ${}^{3}J_{HH} = 5.0 \text{ Hz}$, 3H, H_{Ar}); ${}^{13}C{}^{1}H{}$ NMR (75 MHz, 298 K, CD₃CN); δ = 33.4 (d, ${}^{2}J_{CP} = 11.1$ Hz, $-CH_{3}$), 123.7 (s, C_{Ar}), 125.3 (s, C_{Ar}), 137.8 (s, C_{Ar}), 138.7 (d, ${}^{3}J_{PC} = 12.9$ Hz, C=N), 148.7 (s, C_{Ar}), 151.3 ppm (s, C_{ipso}); ${}^{31}P{}^{1}H$ NMR (130 MHz, 298 K, CD₃CN): δ = 68.2 ppm (s). ${}^{19}F$ NMR (280 MHz, 298 K, CD₃CN): $\delta = -79.34 \text{ ppm}$ (s); ESI-MS: m/z (%): 528.4 (100) [M-(SO₃CF₃)]⁺; FT-IR (solid, ATR): $v(cm^{-1}) = 1601$ (w), 1475 (m), 1263 (vs), 1219 (m), 1138 (s), 1229 (s), 1029 (s), 952 (vs), 906 (m), 776 (s), 759 (s), 693 (m), 632 (vs), 596 (m), 572 (m), 517 (m).

2.8. Synthesis of [Cu(L2)](OTf) (6)

A solution of [Cu(L2)](OTf)₂ (84 mg, 0.1 mmol) in 5 mL acetonitrile was stirred with FeCp^{*}₂ (50 mg, 0.15 mmol) at room temperature overnight. The brown solution was filtered and then layered with 10 mL diethyl ether. An initially formed beige precipitate was filtered off and the solution was layered with additional 40 mL diethyl ether to give small red crystals. Yield: 36 mg (57%); m.p.: 189 °C. Elemental Anal. Calc. for C23H25CuF3N9O3S: C, 43.98, H, 4.01, N, 20.07. Found: C, 44.18, H, 3.90, N, 19.81%. ¹H NMR (400 MHz, 298 K, CD₃CN): δ = 3.19 (s, 9H, -CH₃), 5.79 (s, 1H, -CH), 7.39-7.42 (m, 6H, 2H_{Ar}), 7.56 (s, 3H, N=C-H), 7.84 (dd, ${}^{3}J_{\text{HH}}$ = 8.8 Hz, ${}^{3}J_{\text{HH}}$ = 7.5 Hz, 3H, H_{Ar}), 8.67 ppm (d, ${}^{3}J_{\text{HH}}$ = 3.8 Hz, 3H, H_{Ar}); ¹³C{¹H} NMR (100 MHz, 298 K, CD₃CN): δ = 37.8 (s, -CH₃), 93.3 (s, -CH) 123.2 (s, C_{Ar}), 124.0 (s, C_{Ar}), 130.1 (s, C=N), 137.7 (s, C_{Ar}), 148,3 (s, C_{Ar}), 152.4 ppm (s, C_{ipso}); ¹⁹F NMR (280 MHz, 298 K, CD₃CN): $\delta = -79.36$ ppm (s) ESI-MS: m/z (%): 479 (100) $[M-(SO_3CF_3)]^+$; FT-IR (solid, ATR): $v(cm^{-1}) = 1596$ (m), 1551 (w), 1466 (m), 1281 (m), 1255 (vs), 1221 (s), 1148 (vs), 1103 (w), 1030 (vs), 912 (w), 856 (w), 773 (m), 746 (w), 678 (vw), 636 (vs), 571 (m), 516 (m).

3. Results and discussion

3.1. Syntheses and spectroscopic studies

For the successful synthesis of the new ligand HC[N(Me)N=C(H) Py]₃ (**L2**) we had to develop a new synthetic protocol. To this end, we have tried to use triethyl orthoformate as suitable source for the apical CH group. Note that the same starting material has been used before as C1 building block for the synthesis of cyclic imidazolinium chlorides [43]. Following a slightly modified procedure, the reaction of triethyl orthoformate with three equivalents of the pyridine derivative 2-(2-methylhydrazono)methylpyridine in toluene furnished the tripodal ligand HC[N(Me)N=C(H)Py]₃ (**L2**, Scheme 1) after recrystallization from a THF/hexane mixture. The reaction needs elevated temperatures of 100 °C and reasonable yields (63%) are only achieved after 2–3 weeks, even if the formed ethanol is constantly removed by distillation during the reaction. However, recrystallization of the crude product from THF and hexane affords analytically pure **L2**.



Scheme 1. Synthesis of L2.



Scheme 2. Syntheses of 3 and 4.

L2 is stable in air over a long period of time and is soluble in a wide range of organic solvents. The ¹H NMR of **L2** shows four multiplets for the pyridyl protons as well as one singlet for the imine proton in the aromatic region, one singlet for the *N*-methyl groups at δ = 3.11 ppm and one for the apical proton at δ = 6.11 ppm.

The multidentate ligands **L1** and **L2** consist in each case of six nitrogen donor atoms for possible metal coordination, that is one pyridine and one imino nitrogen atom for each chelating entity. In case all six nitrogen donors are $\kappa^6 N$ coordinated to a metal atom, the podand ligand topology pre-determines a (possibly distorted) trigonal prismatic environment within the ligands cavity. To obtain the mononuclear copper complexes of **L1** and **L2** we used commercially available copper(II)triflate (Cu(OTf)₂; OTf = triflate, (O₃SCF₃)⁻) as metal source. The formation of the dicationic copper complexes [Cu(**L1**)](OTf)₂ (**3**) and [Cu(**L2**)](OTf)₂ (**4**) proceeds under mild conditions at room temperature in THF (Scheme 2).

The title compounds were obtained as red-brown and greenbrown precipitates. Recrystallization from an acetonitrile/diethylether mixture afforded the analytically pure samples as block-like crystals (81% (**3**); 82% (**4**)). The ESI mass spectra showed characteristic ion envelopes and isotope distributions for $[M-(OTf)]^+$ as well as $[2M-(OTf)]^+$. For both compounds, paramagnetic ¹H NMR studies revealed only two of the four pyridine protons, which were observed as very broad signals with chemical shifts between 30 and 37 ppm ($W_{1/2}$ = 1200 and 1500 Hz for **3** and 560 and 760 Hz for **4**). The *N*methyl groups and the imino protons appear in the diamagnetic region of the spectra and the apical proton of **4** at δ = -8.29 ppm.

3.2. Molecular structures of 3 and 4

Complex **3** crystallizes in the monoclinic space group $P_{2_1/n}$ with four molecules and four lattice solvent molecules in the unit cell.

The molecular structure is depicted in Fig. 1. Selected bond lengths and angles are listed in Table 2.

The molecular structure of **3** verified the formation of a mononuclear Cu(II) complex with the copper cation coordinated by six nitrogen atoms of the ligand to create an overall distorted trigonal prismatic coordination environment. The triflate counter anions are not in spatial contact with the copper cation. For two of the three hydrazonyl entities, the copper nitrogen distances of 2.022–2.110 Å are in accord with the expected values for nondistorted copper nitrogen bonds in trigonal prismatic as well as in octahedral complexes [44,45]. However, it is remarkable, that the nitrogen atoms of the third arm show an unexpected large distance from the metal (*cf.* Cu1–N8 = 2.384 Å; Cu1–N9 = 2.264 Å). It is clear from these structural parameters that the copper cation is not centered within the cavity of the multifunctional ligand, but dislocated to one square face of the trigonal prism, furnishing to two elongated *cis* Cu–N bonds (Fig. 2).

Similar *cis* bond length distortions have been observed for trigonal prismatic complexes of Cu^{II} cations before [46–51]. Recently, Echeverría et al. reported that Cu^{II} complexes with a trigonal prismatic coordination sphere show an elongation of two bonds in *cis* position due to a Jahn–Teller effect (unlike the more common octahedral Cu^{II} compounds, which usually undergo a *trans* distortion) [52]. The benefit of this *cis* distortion mainly arises from the splitting of the e'' orbitals (idealized D_{3h} symmetry), possessing significant Cu–N antibonding character. The structural distortion towards C_{2v} symmetry leads to an energetically stabilized b_2 orbital (Fig. 3).

According to calculations performed by Echeverría et al. [52], trigonal prismatic Cu^{II} complexes show tendencies to undergo a rotation in direction of the more favored octahedral conformation, which is a result of the second order Jahn–Teller effect. This



Fig. 1. Molecular structure of compound 3 (left) and top view along the PS bond (right). Thermal ellipsoids are shown at the 30% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

Table 2Selected bond lengths (Å) and angles (°) for 3.

Bond		Angle	
Cu1-N2	2.087(3)	N2-Cu1-N3	77.5(1)
Cu1-N3	2.110(3)	N5-Cu1-N6	79.5(1)
Cu1-N5	2.028(3)	N8-Cu1-N9	69.5(1)
Cu1-N6	2.022(3)	N1-P1-N4	104.5(2)
Cu1-N8	2.384(3)	N4-P1-N7	105.8(2)
Cu1-N9	2.264(3)	N7-P1-N1	104.5(2)
P1-N1	1.677(3)	P1-N1-N2-Cu1	19.6(4)
P1-N4	1.677(3)	P1-N4-N5-Cu1	38.7(4)
P1-N7	1.666(3)	P1-N7-N8-Cu1	33.3(3)



Fig. 2. Visualization of the distorted trigonal prismatic coordination environment around Cu^{II} in 3 and the *cis* bond lengths distortion.

distortion overweighs the *cis* bond length distortion unless the ligand architecture prevents this Bailar trigonal twist [53]. Accordingly, a *trans* distorted octahedral geometry is expected for flexible ligands, where the donor atoms can liberally rotate, whereas the *cis* distortion predominates for inflexible ligands with constrained donor atoms.

In case of complex **3**, the trigonal prismatic structure, which is pre-determined by the tripodal ligand, is only slightly distorted towards an octahedron. It appears that the pyridylhydrazonyl entities are somewhat flexible and enable the complex to twist along the Bailar path towards the octahedral coordination environment. This trend can easily be observed in the P–N–N–Cu torsion angels, which are in a range from 19.6° to 38.7°. Therefore, in accord with the Jahn–Teller theorem [54,55], both distortions, a *cis* as well as a *trans* distortion are observed in the structure. The *a priori* less obvious *trans* distortion is manifested in two elongated bonds, i.e. Cu1– N3 (2.110 Å) and Cu1–N8 (2.384 Å).

Complex **4** crystallizes in the monoclinic space group $P_{2_1/n}$ with 12 title molecules and 12 acetonitrile lattice solvent molecules in the unit cell. The molecular structure consists of three complexes in the asymmetric unit. They do not differ substantially in the bond lengths of the ligands but in the positions of the copper cation in the ligands cavity. The molecular structure of one complex molecule is shown in Fig. 4. Selected bond lengths and angles are listed in Table 3.



Fig. 3. Splitting of the e" state of the trigonal prism by a *cis* distortion $(D_{3h} \rightarrow C_{2v})$. See Ref. [52] for more details.



Fig. 4. Molecular structure of **4**. Only one complex molecule is shown (Cu1). Thermal ellipsoids are shown at the 30% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

The complexes containing Cu1 and Cu3 exhibit substantial *cis* bond lengths distortions of the trigonal prismatic nitrogen environment, which are even stronger than the distortion in compound **3**. The third molecule in the asymmetric unit comprising Cu2 also shows a clear *cis* distortion in the bond lengths, but much less substantial as compared to the other two. The complexes with Cu1 and

Table 3 Selected bond lengths (Å) and angles (°) for 4.

Bond		Angle	
Cu1-N2	2.017(6)	N2-Cu1-N3	80.1(2)
Cu1-N3	1.985(5)	N5-Cu1-N6	66.6(2)
Cu1-N5	2.416(5)	N8-Cu1-N9	79.4(2)
Cu1-N6	2.428(5)	N1-C1-N4	111.8(5)
Cu1-N8	2.000(5)	N4-C1-N7	114.6(6)
Cu1-N9	2.062(5)	N7-C1-N1	110.7(6)
C1-N1	1.459(9)	C1-N1-N2-Cu1	34.6(7)
C1-N4	1.432(9)	C1-N4-N5-Cu1	20.9(7)
C1-N7	1.426(9)	C1-N7-N8-Cu1	-1.4(8)
Cu2-N11	2.170(5)	N11-Cu2-N12	76.2(2)
Cu2-N12	2.061(5)	N14-Cu2-N15	72.9(2)
Cu2-N14	2.170(5)	N17-Cu2-N18	80.0(2)
Cu2-N15	2.298(5)	N10-C23-N13	111.7(5)
Cu2-N17	1.989(5)	N13-C23-N16	113.3(5)
Cu2-N18	2.059(5)	N16-C23-N10	111.8(5)
C23-N10	1.465(8)	C23-N10-N11-Cu2	27.3(6)
C23-N13	1.448(8)	C23-N13-N14-Cu2	-26.5(7)
C23-N16	1.461(8)	C23-N16-N17-Cu2	-25.0(6)
Cu3-N20	2.003(5)	N20-Cu3-N21	80.4(2)
Cu3-N21	2.026(5)	N23-Cu3-N24	79.9(2)
Cu3-N23	2.026(5)	N26-Cu3-N27	63.6(2)
Cu3-N24	2.035(5)	N19-C45-N22	110.8(5)
Cu3-N26	2.506(5)	N22-C45-N25	115.4(5)
Cu3-N27	2.547(5)	N25-C45-N19	112.9(5)
C45-N19	1.447(7)	C45-N19-N20-Cu3	15.1(7)
C45-N22	1.460(8)	C45-N22-N23-Cu3	19.7(7)
C45-N25	1.442(7)	C45-N25-N26-Cu3	2.7(7)

Cu3 only show a minor twist of the pyridylhydrazonyl entities, whereas the latter is distinctively twisted towards an octahedron in case of Cu2. The average value for the C–N–N–Cu torsion angle is 26.3° (Fig. 5). This fact is also reflected in a pronounced *trans* distortion, which is directly observed for the elongated (~0.1 Å) Cu2–N11 (2.170 Å) and Cu2–N15 (2.298 Å) bonds. Within the Cu3 containing complex, the two trigonal faces are almost congruent and the elongated Cu–N distances in *cis* position exceed 2.5 Å. A conceivable *trans* distortion is almost not observable. The observation of distorted and non-distorted (but twisted) complexes in one crystal structure is quite unusual. Based on these data it appears that both the *cis* Jahn–Teller distortion and the twist along the Bailar path result in structurally different though energetically very similar complexes.

In order to shed more light on the differences in the solid-state structures of **3** and **4**, we performed a closer analysis of the structural parameters. The size of the bridging CH and PS entity strongly influences the ligand cavity: The N-P-N angles of complex 3 with an average value of 104.9° differ significantly from the corresponding N-C-N angles of 4 (112.6°). Furthermore, the C-N bonds (1.449 Å) are much shorter than the P-N bonds (1.673 Å). Both effects lead to longer N...N distances between the imino N-donor atoms (2.848 Å) in **3** as compared to **4** (2.763 Å). The more obtuse N-C-N angle in 4 leads in turn to longer N...N distances of the lower pyridine *N*-donor atoms (**3**: = 3.100 Å; **4**: = 3.141 Å). Table 4 summarizes and compares relevant distances between the donor atoms in the complexes 3 and 4. As expected, 3 consists of a narrower trigonal prismatic cavity, showing similar areas of the imino and pyridine nitrogen triangular faces, while the coordination cavity of **4** can be described as a truncated trigonal pyramid.

3.3. Electron paramagnetic resonance spectroscopy

Fig. 6 shows the experimental X-band EPR spectra of **3** and **4** recorded in a frozen acetonitrile solution at 100 K along with the simulation, obtained for a system with S = 1/2 and hyperfine



Fig. 5. Details of the trigonal prismatic cavities of the three different complexes in the crystal structure of 4.

Table 4 Distances between the pyridine and imino nitrogen atoms in 3 and 4 (Å).

Imino-N		Pyridine-N	
3			
N2-N5	2.890	N3-N6	3.098
N5-N8	2.864	N6-N9	3.116
N8-N2	2.790	N9-N3	3.085
4			
Cu1: N2-N5	2.706	N3-N6	3.113
N5-N8	2.710	N6-N9	3.103
N8-N2	2.849	N9-N3	3.142
Cu2: N11-N14	2.770	N12-N15	3.156
N14-N17	2.759	N15-N18	3.170
N17-N11	2.744	N18-N12	3.084
Cu3: N20-N23	2.822	N21-N24	3.180
N23-N26	2.783	N24-N27	3.165
N26-N20	2.721	N27-N21	3.158

couplings to ⁶³Cu and ⁶⁵Cu with I = 3/2, a natural abundance of 69.17% and 30.83% and a magnetogyric ratio for the free atom of 7.1113 and 7.6043, respectively. Both experimental spectra look very similar with no resolved nitrogen hyperfine couplings. In each case we detected EPR signals of almost axial symmetry. However, the simulations have been performed using rhombic *g* tensors. The spectra of the two compounds show resolved hyperfine couplings (hfcs) to the copper nuclei on one of the three *g* values of

484 and 518 MHz for **3** and 528 and 565 MHz for **4**, respectively. Due to the large line width, the copper hfcs are only poorly resolved. Relevant data are compiled in Table 5.

The EPR spectra of **3** and **4** are comparable with those observed for distorted octahedral copper complexes known in the literature. For example, the axially compressed complex $[Cu(terpyR8)_2](ClO_4)_2$ (with terpyR8 = 4'-octoxy-2,2':6',2"-terpyridine) exhibits a spectrum with two smaller g values without resolved hyperfine coupling and one g value of 2.26 and a hyperfine splitting of 474 MHz [56]. Sánchez-Piso et al. presented the distorted octahedral complex $[CuL(phen)_2]$ with L being N,N-bis[(4-methylphenyl)sulfonyl]ethylenediamine. This compound also shows similar g values and copper hfcs [57]. The spectrum of the six-coordinate copper complex $[Cu(pepica)_2](ClO_4)_2$ (pepica = 2-(2-pyridylethyl)picolylamine) by Huang et al. is also comparable to the observed spectra [58]. As mentioned before, trigonal prismatic Cu^{II} complexes are relatively rare in the literature. The copper(II)bis(1,4,7-triazacyclononane) complex reported by Haidar et al. shows a nearly axial spectrum with $g_{||}$ = 2.225, g_{\perp} = 2.045 and $A_{||}$ = 510 MHz ($A_{\perp} \approx 0$). A rhombic distor-

Table 5

EPR spectroscopic data for 3 and 4. Hyperfine couplings are given in MHz.

Compound	g_1	g_2	g_3	A_1	A2	A ₃
3	2.0635	2.0868	2.2486	≼60	≤100	484(⁶³ Cu)/518(⁶⁵ Cu)
4	2.0680	2.0905	2.2460	≼60	≤100	528(⁶³ Cu)/565(⁶⁵ Cu)



Fig. 6. Experimental (exp.) and simulated (sim.) CW EPR spectra of 3 (left) and 4 (right) recorded in a frozen acetonitrile solution at 100 K at X-band.



Fig. 7. Cyclic voltammograms of **3** (left) and **4** (right) in acetonitrile at room temperature vs. Fc/Fc^* . Scan rate 100 mV s⁻¹, $Pt/[nBu_4N][PF_6]/Ag$. Both redox waves show completely the same behavior in a second CV cycle; only one is shown here for clarity.

tion can only be estimated because of the slightly broadened lines [51].

3.4. Electrochemistry

The electronic properties of **3** and **4** were examined by cyclic voltammetry in acetonitrile at room temperature (Fig. 7). All potentials (including those known from the literature) are given against the ferrocene/ferrocenium couple (Fc/Fc^+) [39].

The voltammogram of **3** shows a quasi-reversible one electron reduction process centered at $E_{1/2}^0 = -0.11$ V, with a peak-to-peak separation of 82 mV and $i_{\rm pa}/i_{\rm pc} \approx 1$. We assigned this wave to the Cu^{II}/Cu^I redox couple. Compared with other Cu^{II}/Cu^I redox couples known from the literature, the potential is a considerably anodically shifted (usually around -0.5 V) [57,59,60]. More positive potentials have only been observed for complexes with highly constrained ligands strongly favoring a coordination to Cu¹ ions in order to minimize adverse steric interactions [61-64]. The cyclic voltammogram of **4** also shows a quasi-reversible Cu^{II}/Cu^I reduction event, but at a more cathodically shifted potential of $E_{1/2}^0$ = -0.34 V ($\Delta \phi$ = 80 mV; $i_{\rm pa}/i_{\rm pc} \approx 1$). Knight et al. introduced a bipyridine based hexadentate, tripodal ligand, which also has a strong preference for trigonal prismatic coordination geometries [45]. A tremendous Jahn–Teller *cis* distortion was observed for the Cu^{II} complex with one of the elongated Cu-N bonds exceeding 2.8 Å. They also found the reduction process to be centered at $E_{1/2}^0 = -0.523$ V.

In general, several parameters can influence the redox properties of transition metal complexes. As can be seen from the selected values discussed for copper(II) complexes, more cathodically shifted Cu^{II}/Cu^I reduction potentials are expected for Jahn–Teller distorted complexes – either *trans* distorted octahedral complexes or *cis* bond length distorted and trigonal twisted structures. The more effective the Jahn–Teller distortion, the more negative Cu^{II}/ Cu^I reduction potentials are observed (in the first approximation and excluding other effects).¹ The experimentally observed $E_{1/2}^0$ values for **3** and **4** clearly show that both ligands are not perfectly suited to stabilizing copper(II) ions (anodically shifted potentials). In addition to this, the steric or geometric differences of the ligands L**1** and L**2**,² which are governed by the inherent properties of the PS and CH anchoring units, also result in sizably differing reduction potentials for **3** and **4** ($\Delta E_{1/2}^0 = 0.23$ V). Based on the electrochemical data it appears that **L1** is less flexible in stabilizing copper(II) ions as compared to **L2**. This would also be in accord with the molecular structures of **3** and **4** showing a less pronounced distortion, i.e. less effective Jahn–Teller stabilization for **3**. Although the true reason remains the subject of speculations, this may, for instance, be a result of steric repulsions between the *N*-methyl groups and the PS entity, which would in turn lead to a less effective *cis* bond length distortion or trigonal twisting along the Bailar path of the ligand cavity.

In addition to the quasi-reversible redox processes discussed so far, we detected further redox processes at more negative potentials. It seems likely that the electrochemically irreversible reduction events below -0.6 V(3) and -1.0 V(4) lead to decomposition of the complexes and deposition of metallic copper on the electrode. The observation of sharp anodic peaks in the return sweeps in both voltammograms (for **3**: $E_{pa}^0 = -0.72 V$; for **4**: $E_{pa}^0 = -0.68 V$) is characteristic for the so-called "anodic stripping" process, i.e. a re-dissolution of Cu⁰ from the electrode surface [61,65,66]. The high current intensity associated with these peaks is due to the fast re-oxidation of metallic copper. As expected, the "stripping" potential is independent from the nature of the ligand, further supporting this assumption. We also detected some additional, not well-resolved redox waves, which cannot be assigned to any specific process yet.

3.5. Syntheses and spectroscopic studies of 5 and 6

We were also interested in isolating the corresponding copper(I) complexes and therefore performed some additional preparative studies. Considering the anodically shifted reduction potentials, we treated both compounds with one equivalent of decamethyl ferrocene, FeCp*₂, in acetonitrile $(E_{1/2}^0(\text{FeCp}*_2) = -0.48 \text{ V} \text{ in this solvent})$. The anticipated products, [Cu(L1)](OTf) (**5**) and [Cu(L2)](OTf) (**6**), are formed in moderate isolated yields of 43% and 57% and were obtained as analytically pure dark green and red crystals from an acetonitrile/diethyl ether mixture, respectively (Scheme 3).

The NMR spectra of **5** and **6** indicated the formation of mononuclear, diamagnetic Cu¹ complexes. The ³¹P{¹H} NMR spectrum of **5** exhibits a singlet at δ = 68.2 ppm, which is shifted by 5 ppm to lower frequencies as compared to the free ligand. A shift to higher frequencies was observed for the *N*-methyl protons in the ¹H NMR spectra of both compounds. The aromatic region of the¹H NMR spectra is displayed in Fig. 8. Upon coordination of the Cu¹ cations,

¹ This can also be explained by qualitative MO arguments. A more pronounced *cis* bond length distortion leads to an energetically more destabilized acceptor orbital (a_2 , Fig. 3). ² Electronic effects exerted by the different bridging PS and CH entities should also

² Electronic effects exerted by the different bridging PS and CH entities should also not be neglected.



Scheme 3. Syntheses of 5 and 6.



Fig. 8. ¹H NMR spectra of the free ligands L1 (1) and L2 (2) as compared to their copper(1) complexes 5 (5) and 6 (6). Only the aromatic regions of the spectra are shown.



Fig. 9. Molecular structure of 5 (left) and view from the top along the P-S-bond (right). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

the imino protons of the free ligands **L1** and **L2** (*cf.* δ = 7.81 ppm for L1 and 7.48 ppm for L2) are shifted to higher frequencies and appear as singlets at 7.93 ppm and 7.56 ppm. The doublets of the pyridine protons in the 3-position are observed at lower frequencies, whereas the remaining signals of aromatic protons are shifted to higher frequencies. Especially the protons in para position to the pyridine nitrogen atoms are strongly influenced ($\Delta \delta$ = 0.3 ppm for **6** and 0.5 ppm for **5**). The apical proton of the ligand **L2** is shifted by 0.3 ppm to lower frequencies upon coordination.

3.6. Molecular structures of 5 and 6

The dark green and red crystals of 5 and 6 were suitable for Xray diffraction studies. The molecular structures of 5 and 6 are shown in Figs. 9 and 10. Selected bond lengths and angles are listed in Tables 6 and 7. 5 crystallizes in the monoclinic space group $P2_1/c$ with four complex molecules in the unit cell, while **6** crystallizes in the triclinic space group $P\overline{1}$ with two complex molecules and four solvent molecules in the unit cell.

The structural parameters of **5** and **6** are quite similar. Both still show a distorted trigonal prismatic coordination environment

Ta	ab	le	6		
~					

able b			
Selected bond	lengths (Å) and	angles (°) for 5

Bond		Angle	
Cu1–N2	2.595(3)	N2-Cu1-N3	69.7(1)
Cu1-N3	2.068(3)	N5-Cu1-N6	71.5(1)
Cu1-N5	2.480(3)	N8-Cu1-N9	74.0(1)
Cu1-N6	2.063(3)	N1-P1-N4	106.8(1)
Cu1-N8	2.391(3)	N4-P1-N7	106.9(1)
Cu1-N9	2.080(3)	N7-P1-N1	105.3(1)
P1-N1	1.674(3)	P1-N1-N2-Cu1	31.2
P1-N4	1.669(3)	P1-N4-N5-Cu1	25.8
P1-N7	1.667(3)	P1-N7-N8-Cu1	37.4
Distances betw	veen the imino (lefi	t) and pyridine (right) nitro	gen atoms
N2…N5	2.928	N3…N6	3.289
N5…N8	2.970	N6…N9	3.333
N8…N2	2.890	N9…N3	3.208

Table 7								
Selected	bond	lengths	(Å)	and	angles	(°)	for	6.

Bond		Angle	
Cu1-N2	2.543(2)	N2-Cu1-N3	70.84(8)
Cu1-N3	2.096(2)	N5-Cu1-N6	72.69(8)
Cu1-N5	2.440(2)	N8-Cu1-N9	71.54(8)
Cu1-N6	2.102(2)	N1-C1-N4	112.8(2)
Cu1-N8	2.487(2)	N4-C1-N7	113.5(2)
Cu1-N9	2.089(2)	N7-C1-N1	112.5(2)
C1-N1	1.452(4)	C1-N1-N2-Cu1	14.02
C1-N4	1.445(4)	C1-N4-N5-Cu1	16.62
C1-N7	1.446(3)	C1-N7-N8-Cu1	20.25
Distances bet	ween the imino (lej	ft) and pyridine (right) nitro	ogen atoms
N2-N5	2.805	N3-N6	3.288
N5-N8	2.860	N6-N9	3.398
N8-N2	2.839	N9-N3	3.351

around the copper(I) cations. The views along the (idealized) C_3 axes from the top of the molecules show a minor twist of the ligands towards octahedral coordination spheres. This can also be quantitatively deduced from the P–N–N–Cu and C–N–N–Cu torsion angles listed in Tables 6 and 7. Overall, complex 5 is slightly more twisted as compared to 6, but the twist is in both cases by far not as large as in the corresponding Cu^{II} complexes. The copper(I) cations in **5** and **6** are in each case slightly dislocated towards the trigonal face formed by the three pyridine nitrogen atoms. The pyridine copper distances fall within expected ranges (d(Cu-N(py)) =



Fig. 10. Molecular structure of 6 (left) and view from the top along the C1-Cu1-axis (right). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

2.07 Å for **5** and 2.09 Å for **6**) [67–69]. However, the imino nitrogen atoms show, with an average of 2.49 Å for both complexes, a comparatively long distance from the copper(I) cations. Both ligands are somewhat dilated, which becomes apparent from the N...N distances between the pyridine nitrogen atoms and the imino nitrogen atoms listed in Tables 6 and 7. The larger separation of the nitrogen atoms within the pyridine triangle, as compared to the triangle spanned by the imino nitrogen atoms, clearly shows that the ligand cavities in both complexes resemble a truncated trigonal pyramid rather than a perfect trigonal prism.

4. Conclusions

We have described the synthesis and detailed characterization of the new tripodal, multidentate $\kappa^6 N$ -donor ligand HC[N(Me) $N=C(H)Py_{3}$ (L2) and its coordination behavior towards copper. We also synthesized analogous complexes of the phosphorus supported ligand (S)P[N(Me)N=C(H)Py]₃ (L1) for comparison. Both the copper(II) and copper(I) complexes are mononuclear with the cations coordinated by three imino and three pyridine nitrogen atoms. The solid-state structures of the copper(II) species [Cu (L1)](OTf)₂(3) and [Cu(L2)](OTf)₂(4) show a *cis* bond length distortion and a trigonal twist due to Jahn-Teller effects. Electrochemical studies revealed the Cu^{II}/Cu^I reduction potentials to be anodically shifted as compared to other redox couples known from the literature, especially for the copper(II) complex 3 consisting of the phosphorus supported ligand L1. It appears that the latter is less flexible in stabilizing copper(II) ions as compared to L2. The corresponding copper(I) complexes **5** and **6** are accessible by reduction with decamethyl ferrocene. X-ray structures clearly show that the ligand cavities in both complexes resemble a truncated trigonal pyramid rather than a perfect trigonal prism.

Acknowledgment

Financial support by the Federal Ministry of Education and Research is gratefully acknowledged (BMBF Project 02NUK012B).

Appendix A. Supplementary material

CCDC 810586-810589 contain 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.045.

References

- [1] I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster, F. Breher, Dalton Trans. (2008) 5836.
- [2] S. Trofimenko, Chem. Rev. 93 (1993) 943.
- [3] S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999.
- [4] G. Parkin, Adv. Inorg. Chem. 42 (1995) 291.
- [5] D.L. Reger, Coord. Chem. Rev. 147 (1996) 571.
- [6] M. Etienne, Coord. Chem. Rev. 156 (1997) 201.
- C. Janiak, Coord. Chem. Rev. 163 (1996) 107.
- [8] D.L. Reger, T.C. Grattan, K.J. Brown, C.A. Little, J.J.S. Lamba, A.L. Rheingold, R.D. Sommer, J. Organomet. Chem. 607 (2000) 120.
- [9] D.L. Reger, Comm. Inorg. Chem. 21 (1999) 1.
- [10] H.R. Bigmore, S.C. Lawrence, P. Mountford, C.S. Tredget, Dalton Trans. (2005) 635.
- [11] C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 525.
- [12] A. Otero, J. Fernandez-Baeza, A. Antinolo, J. Tejeda, Á. Lara-Sánchez, Dalton Trans. (2004) 1499.
- [13] P.K. Byers, N. Carr, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1990) 3701.
- [14] P.K. Byers, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1991) 93.
- [15] S.C. Lawrence, M.E.G. Skinner, J.C. Green, P. Mountford, Chem. Commun. (2001) 705.

- [16] F. Breher, J. Grunenberg, S.C. Lawrence, P. Mountford, H. Rüegger, Angew. Chem. 116 (2004) 2575
- [17] H.R. Bigmore, S.R. Dubberley, M. Kranenburg, S.C. Lawrence, A.J. Sealey, J.D. Selby, M.A. Zuideveld, A.R. Cowley, P. Mountford, Chem. Commun. (2006) 436
- [18] I. Krummenacher, H. Rüegger, F. Breher, Dalton Trans. (2006) 1073.
- [19] H.R. Bigmore, J. Meyer, I. Krummenacher, H. Rüegger, E. Clot, P. Mountford, F. Breher, Chem. Eur. J. 14 (2008) 5918.
- [20] I. Kuzu, I. Krummenacher, I.J. Hewitt, Y. Lan, V. Mereacre, A.K. Powell, P. Höfer, J. Harmer, F. Breher, Chem. Eur. J. 15 (2009) 4350.
- [21] M.G. Cushion, J. Meyer, A. Heath, A.D. Schwarz, I. Fernández, F. Breher, P. Mountford, Organometallics 29 (2010) 1174.
- F. Armbruster, I. Fernández, F. Breher, Dalton Trans. (2009) 5612.
- [23] I. Fernández, P. Oña-Burgos, F. Armbruster, I. Krummenacher, F. Breher, Chem. Commun. (2009) 2586.
- [24] M.D. Ward, J.A. McCleverty, J.C. Jeffery, Coord. Chem. Rev. 222 (2001) 251.
- [25] M. Löble, T. Vitova, I. Fernández, P. Oña-Burgos, P. Lindqvist-Reis, M. Neumaier, A. Geist, M.A. Denecke, F. Breher, in preparation.
- [26] T. Vitova, B. Brendebach, K. Dardenne, M.A. Denecke, A. Lebid, M. Löble, J. Rothe, O.N. Batuk, J. Hormes, D. Liu, F. Breher, H. Geckeis, IOP Conf. Ser.: Mat. Sci. Eng. 9 (2010) 012053.
- [27] S. Fischer, J. Hoyano, L.K. Peterson, Can. J. Chem. 54 (1976) 2710.
- [28] D. Colombo-Khater, Z. He, A.-M. Caminade, F. Dahan, R. Krämer, J.-P. Majoral, Synthesis (1993) 1145.
- [29] J.S. Fleming, E. Psillakis, J.C. Jeffery, K.L.V. Mann, J.A. McCleverty, M.D. Ward, Polyhedron 17 (1998) 1705
- [30] V. Chandrasekhar, R. Azhakar, G.T.S. Andavan, V. Krishnan, S. Zacchini, J.F. Bickley, A. Steiner, R.J. Butcher, P. Kögerler, Inorg. Chem. 42 (2003) 5989.
- [31] For structurally related tripodal ligands see for instance: Y. Sunatsuki, T. Kobayashi, K. Harada, T. Yamaguchi, M. Nonoyama, M. Kojima, Bull. Chem. Soc. Jpn 81 (2008) 716.
- [32] S. Liu, E. Wong, V. Karunaratne, S.J. Rettig, C. Orvig, Inorg. Chem. 32 (1993) 1756.
- [33] T. Yamaguchi, J.-P. Costes, Y. Kishima, M. Kojima, Y. Sunatsuki, N. Bréfuel, J.-P. Tuchagues, L. Vendier, W. Wernsdorfer, Inorg. Chem. 49 (2010) 9125.
- [34] J.L. Robbins, N. Edelstein, B. Spencer, J.C. Smart, J. Am. Chem. Soc. 104 (1982) 1882
- [35] R.K. Harris, E.D. Becker, S.M. Cabral de Menezes, P. Granger, R.E. Hoffman, K.W. Zilm, Pure Appl. Chem. 80 (2008) 59.
- [36] K. Hinkelmann, J. Heinze, H.-T. Schacht, J.S. Field, H. Vahrenkamp, J. Am. Chem. Soc. 111 (1989) 5078.
- [37] C.H. Hamann, W. Vielstich, Elektrochemie, Wiley-VCH, Weinheim, 2005.
- [38] J. Heinze, Angew. Chem., Int. Ed. 23 (1984) 831.
- [39] N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.
- [40] G.R. Hanson, K.E. Gates, C.J. Noble, M. Griffin, A. Mitchell, S. Benson, J. Inorg. Biochem. 98 (2004) 903.
- [41] SHELXTL v6.12, Bruker AXS Inst. Inc., Madison, WI, USA, 2000.
- [42] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
 [43] A.J. Arduengo, R. Krafczyk, R. Schmutzler, H.A. Craig, J.R. Goerlich, W.J. Marshall, M. Unverzagt, Tetrahedron 55 (1999) 14523.
- [44] O.P. Anderson, J. Chem. Soc., Dalton Trans. (1972) 2597.
- [45] J.C. Knight, S. Alvarez, A.J. Amoroso, P.G. Edwards, N. Singh, Dalton Trans. 39 (2010) 3870.
- [46] See for example: X.-H. Bu, X.-C. Cao, W.-Q. Zhang, R.-H. Zhang, T. Clifford, Transition Met. Chem. (London) 22 (1997) 513.
- [47] W. Han, L. Li, W. Gu, Z.-Q. Liu, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang, P. Cheng, J. Coord. Chem. 57 (2004) 41.
- [48] K. Wieghardt, U. Bossek, P. Chaudhuri, W. Herrmann, B.C. Menke, J. Weiss, Inorg. Chem. 21 (1982) 4308.
- [49] X.-M. Feng, Z. Zhang, Y.-Z. Li, N.-S. Bian, Z.-L. Wang, Trans. Met. Chem. (London) 32 (2007) 95.
- [50] A.A. Watson, A.C. Willis, D.P. Fairlie, Inorg. Chem. 36 (1997) 752.
- [51] R. Haidar, M. Ipek, B. DasGupta, M. Yousaf, L.J. Zompa, Inorg. Chem. 36 (1997)
- 3125. [52] J. Echeverría, E. Cremades, A.J. Amoroso, S. Alvarez, Chem. Commun. (2009) 4242
- [53] J.C. Bailar Jr., J. Inorg. Nucl. Chem. 8 (1958) 165.
- [54] H.A. Jahn, E. Teller, R. Soc. London Ser. A 161 (1937) 220.
- [55] R.J. Deeth, M.A. Hitchman, Inorg. Chem. 25 (1986) 1225.
- [56] P. Nielsen, H. Toftlund, J.F. Boas, J.R. Pilbrow, B. Moubaraki, K.S. Murray, S.M. Neville, Inorg. Chim. Acta 361 (2008) 3453.
 - J. Sánchez-Piso, J.A. García-Vázquez, J. Romero, M.L. Durán, A. Sousa-Pedrares, [57] E. Labisbal, O.R. Nascimento, Inorg. Chim. Acta 328 (2002) 111.
 - [58] G.-S. Huang, J.-K. Lai, C.-H. Ueng, C.-C. Su, Trans. Met. Chem. 25 (2000) 84.
 - [59] T.N. Sorell, D.L. Jameson, Inorg. Chem. 21 (1982) 1014.
 - [60] G.S. Patterson, R.H. Holm, Bioinorg. Chem 4 (1975) 257.
 - [61] A.J. Bard, M. Stratmann, F. Scholz, C.J. Pickett, Encyclopedia of Electrochemistry, Inorganic Chemistry, vol. 7b, Wiley-VCH, Weinheim, 2006.
 - [62] N. Wei, N.N. Murthy, Z. Tyeklár, K.D. Karlin, Inorg. Chem. 33 (1994) 1177.
 - [63] S. Chen, J.F. Richardson, R.M. Buchanan, Inorg. Chem. 33 (1994) 2376.
 - [64] P. Comba, H. Jakob, Helv. Chim. Acta 80 (1997) 1983.
 - [65] B. Keita, E. Abdeljalil, L. Nadjo, B. Avisse, R. Contant, J. Canny, M. Richet, Electrochem. Commun. 2 (2000) 145.
 - A.P. Neves, K.C.B. Maia, M.D. Vargas, L.C. Visentin, A. Casellato, M.A. Novak, A.S. [66] Mangrich, Polyhedron 29 (2010) 2884.

- [67] See for example: A. Boudebous, E.C. Constable, C.E. Housecroft, M. Neuburger, S. Schaffner, A. Listorti, C. Sabatini, F. Barigelletti, Inorg. Chim. Acta 362 (2009) 1825.
 [60] M. Gurra in M. Tanani and A. Sabatini, F. Barigelletti, Inorg. Chim. Acta 362 (2009)
- [68] M. Gennari, M. Tegoni, M. Lanfranchi, M.A. Pellinghelli, M. Giannetto, L. Marchiò, Inorg. Chem. 47 (2008) 2223.
- [69] L. Yang, R.P. Houser, Inorg. Chem. 45 (2006) 9416.
 [70] T. Hahn, International Tables for Crystallography, vol. A, fifth ed., Kluwer Academic, Dordrecht, 2002.