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ARTICLE

Synthesis and Coordination Behaviour of a Novel Tridentate P,N,O-Ketiminate Ligand

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Dedicated to Professor Dr. Peter Klüfers on the Occasion of his 70th Birthday

Treatment of *o*-(diphenylphosphino)aniline with 3-formylacetylacetone led to the formation of the ketimine type Schiff base 3-((*o*-diphenylphosphino-phenylamino)-methylene)-pentane-2,4-dione ($o\text{–}PPh_2\text{–}C_6H_4\text{–}NH\text{–}CH{=}C(COCH_3)_2$, HL). Complexes [$ML_2$] (M = Fe, Co, Ni, Cu) were obtained from the reaction of HL with the corresponding metal acetate or acetylacetonate derivatives. The [ML_2] complexes (M = Fe, Co, Ni) exhibit a distorted octahedral coordination from two tridentate P,N,O ketiminate ligands L^-. The arrangement of the ligands is meridional in the case of [FeL_2] and [NiL_2]. The cobalt complex [CoL_2] displays a facial coordination. In the case of the nearly square planar copper complex [CuL_2], only the ketiminate functionalities of the ligands are involved in coordination and the participation of the PPh_2 groups is neglectable.

Introduction

3-Formylacetylacetone is a versatile starting material for the generation of hybrid ligands containing a 2,4-pentanedionate functionality in combination with other potentially coordinating donor groups. Typically, the derivatization of 3-formylacetylacetone comprises the reaction of the formyl group with a primary amine to give a Schiff base condensation product. This principle has been applied the first time by the group of E. Jäger in order to synthesize salen-type ligands.[1] Recently, this kind of ligands has moved into focus by the research of B. Weber et al. on spin cross-over complexes.[2] In previous work we have shown that treatment of 3-formylacetylacetone with α-aminoacids leads to tridentate Schiff base ligands with N,O,O donor sets.[3] Starting from natural occurring L-aminoacids this procedure provided an easy access to chiral ligands. In extension of this work we were now interested in the synthesis of analogous ligands with P,N,O donor sets. Tridentate P,N,O ligands are of growing interest in literature, particularly due to their promising application in catalysis, e.g. polymerization[4] and hydrogenation reactions.[5] Typical tridentate P,N,O ligands are accessible as Schiff base condensation products from *o*-(diphenylphosphino)aniline and *o*-salicylaldehyde derivatives[6] or 2,4-pentanedione.[7] Alternatively *o*-diphenylphosphino benzaldehyde can be reacted with *o*-aminophenols.[6] For subsequent complex formation the Schiff bases are usually deprotonated at the phenolic OH group. However, neutral tridentate P,N,O ligands bearing OH or OR groups were also used for complex formation.[8] Some recent developments in the field of tridentate ligands comprise phosphine functionalized 8-hydroxychinoline derivatives.[9] Tridentate P,N,O ligands with ionizable NH groups are much less studied.[10] Here we report on the synthesis and coordination properties of such a type of ligand, which is easily available by the condensation reaction of 3-formylacetylacetone with *o*-(diphenylphosphino)aniline.

Results and discussion

Treatment of 3-formylacetylacetone (**1**) with *o*-(diphenylphosphino)aniline in THF as solvent led to the formation of the Schiff base HL (**2**) according to Scheme 1. After the removal of the solvent, the oily residue was treated with *n*-hexane to precipitate compound **2** as colourless microcrystalline powder in yields around 85 %. The Schiff base is soluble in polar solvents like THF and ethanol and less soluble in aliphatic hydrocarbons like *n*-hexane. The ^1H NMR spectrum of **2** in $CDCl_3$ indicates the presence of the tautomeric enamine form. The singlet signals of the methyl groups are observed at $\delta = 2.51$ and 2.26 ppm. The NH signal appears at $\delta = 13.13$ pm and the signal of the CH group is located at $\delta = 8.04$ ppm. Additional signals in the range from 7.47 to 7.00 pm originate from the phenyl groups and the *o*-phenylene unit. The ^{31}P NMR spectrum consists of a singlet signal with a chemical shift of $\delta = -19.6$ ppm. This is close to the value observed for the parent *o*-(diphenylphosphino)aniline (−20.5 ppm).[11]

Treatment of [$Fe(acac)_2(TMEDA)$] with the Schiff base (**2**) in boiling THF led to the formation of the iron(II)complex [FeL_2] (**3**) along with the liberation of acetylacetone and TMEDA (Scheme 2). A similar procedure was used for the synthesis of the cobalt(II) complex [CoL_2] (**4**) and the copper(II) derivative [CuL_2] (**6**) starting from the metal acetylacetonates [$M(acac)_2$] and HL (**2**). In both cases the reactions were carried out in refluxing *o*-xylene at 140 °C. In the case of the nickel(II)complex

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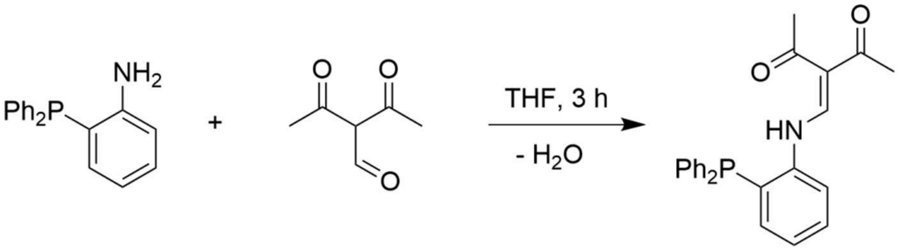
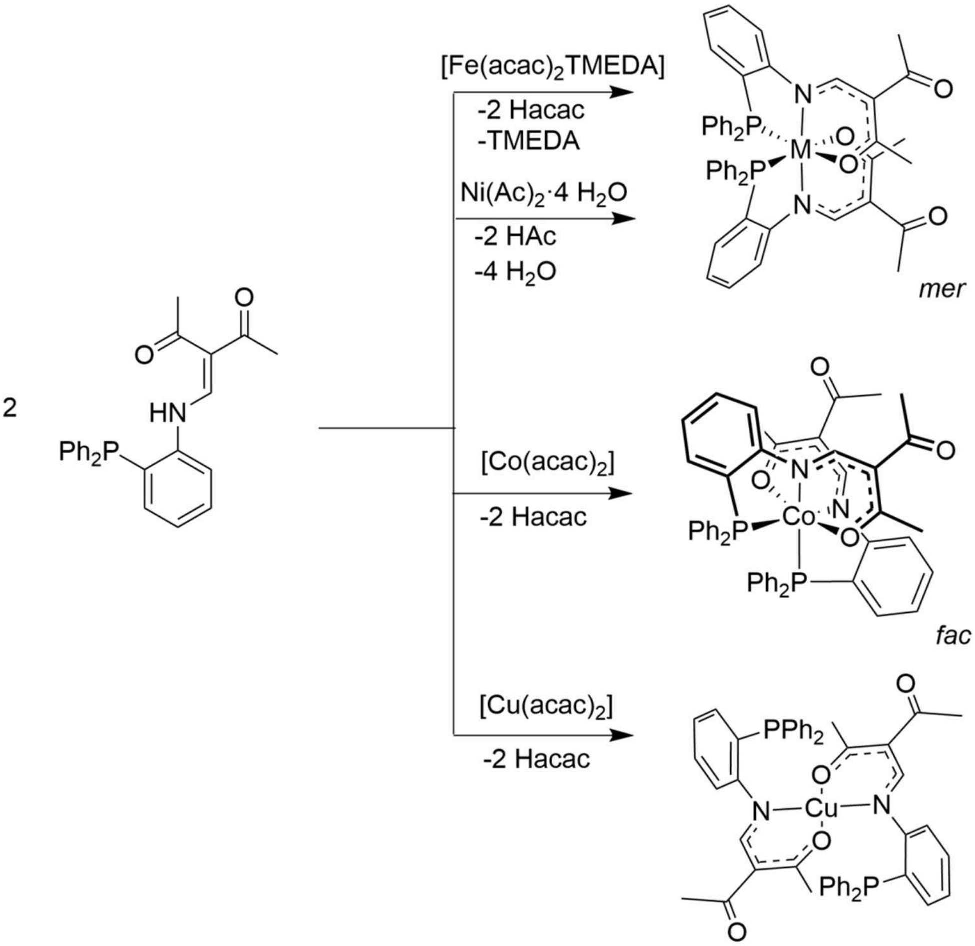


Scheme 1. Preparation of the Schiff base HL (**2**).



Scheme 2. Preparation of complexes ML_2, M = Fe (**3**), Co (**4**), Ni (**5**), Cu (**6**).

[NiL_2] (**5**), nickel(II) acetate was used and the reaction was carried out in ethanol. Complexes **3**–**6** were obtained in yields of 70–85 %. Recrystallization from THF/*n*-heptane afforded red brown, violet brown and green crystals of complexes [FeL_2], [CoL_2] and [CuL_2], resp. Green single crystals of the nickel(II) compound [NiL_2] were obtained from an ethanol/*n*-heptane mixture. The complexes are soluble in polar solvents like THF, methanol, toluene, and chloroform and less soluble in *n*-hexane. On contact with air, the solid complexes **3**–**5** decompose slowly. However, the copper complex **6** instantly oxidizes in air. Moreover, the copper(II) derivative displays the lowest thermal stability in this series and decomposes at 130 °C. Complexes **3**–**5** are melting without decomposition at 246, 262 and 250 °C, resp.

Regarding the magnetism, it is worth mentioning that the iron(II) complex **2** exhibits diamagnetic low spin behaviour at room temperature. This is in contrast to iron(II) complexes with related Schiff bases (e.g. 3-[{(pyridin-2-yl)methylamino}methylene]pentan-2,4-dione), which are in the high spin state in temperature ranges from 50–300 K.[12]

Crystal structures

The molecular structures of compounds **1**–**6** were determined by single crystal X-ray diffraction. Details of the data collection and the crystal structure refinement are collected in Table 1.

3-Formylacetylacetone (1)

3-Formylacetone is known since its first synthesis from acetylacetone and triethylorthoformate reported by L. R. Claisen in 1893.[13] Usually, 3-formylacetone is obtained as a colorless crystalline solid, which slowly decomposes on contact with air to give a yellowish viscous oil. Single crystals of 3-formylacetylacetone (**1**) were grown from the melt which was stored at −25 °C under an inert atmosphere of argon to prevent decomposition. **1** forms crystals in the triclinic space group $P\bar{1}$, with two formula units per unit cell. The molecular structure (Figure 1) clearly reveals that 3-formylacetylacetone exists in its enolic form in the solid state. Due to the proximity of the acetyl O atom to the enol OH group a strong intramolecular O···H–O hydrogen bond with an O···O separation of 241.3(2) pm is formed. The hydrogen bridge is asymmetric with different O–H (115(2) pm) and O···H (131.4(2) pm) distances. The six membered ring O1–C2–C3–C4–O2–H2 is nearly planar. In agreement with the enolic character of compound **1** the C–OH distance (128.7(2) pm) is larger than the C=O distance (126.6(1) pm) and the formal double bond C3–C2 (140.6(2) pm) is shorter than the formal single bond C3–C4 (143.1(2) pm). The presence of such intramolecular O···H–O hydrogen bridges is quite characteristic for enol tautomers of β-dicarbonyl compounds and similar structures have been observed in various cases, e.g. 1,3-diphenyl-1,3-propanedione[14] or 3-hydroxy-1,3-bis(pyridin-3-yl)prop-2-en-1-one.[15]

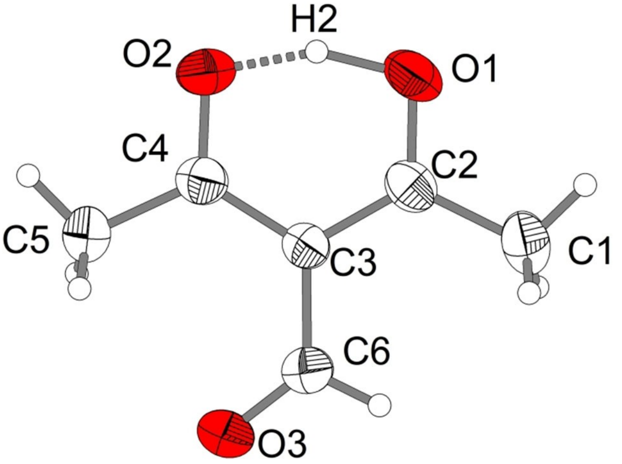


Figure 1. Molecular structure of 3-formylacetylacetone (**1**) in the crystal. Thermal ellipsoids at the 50 % probability level. Selected bond lengths (pm) and angles (°): O1–C2 129.0(1), O2–C4 126.9(1), O3–C6 121.5(1), C1–C2 149.5(1), C2–C3 141.2(1), C3–C4 143.5(1), C4–C5 148.4(1), C3–C6 145.2(1), O1–C2–C3 120.7(1), O2–C4–C3 119.9(1), O3–C6–C3 127.1(1).

Schiff base HL (2)

Compound **2** (Figure 2) displays a nearly co-planar arrangement of the aminomethylene pentane-2,4-dione (C1–C6 O1, O2, N) fragment and the *o*-phenylene-PPh$_2$ unit (C7–C12) attached to the nitrogen atom. The Schiff base exists in its enamine tautomeric form with a formal double bond between the carbon atoms C3 and C6 (C–C: 145.2(1) pm). Similar enamine motifs have been observed in the related compounds

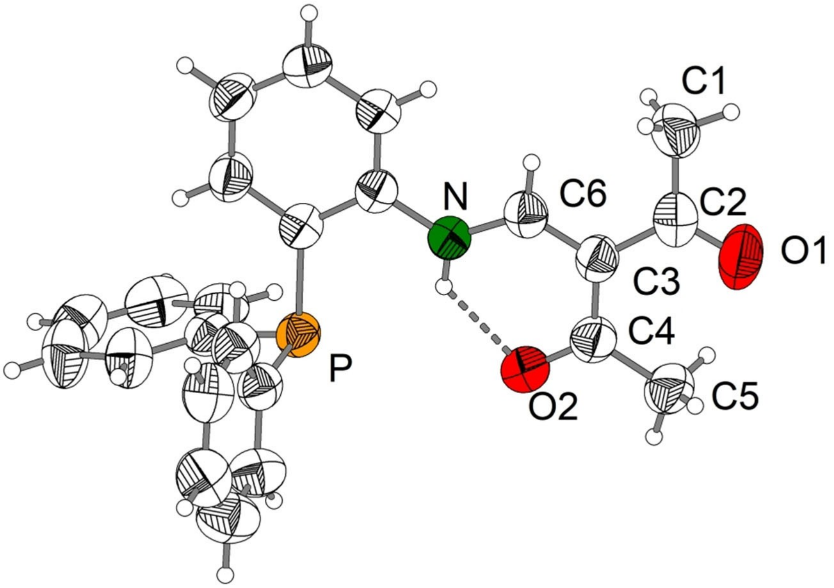


Figure 2. Molecular structure of HL (**2**) in the crystal. Thermal ellipsoids at the 50 % probability level.

Table 1. Crystallographic data for compounds 1–6.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Molecular formula	$C_6H_8O_3$	$C_{24}H_{22}NO_2P$	$C_{56}H_{58}FeN_2O_6P_2$	$C_{48}H_{42}CoN_2O_4P_2$	$C_{48}H_{42}N_2NiO_4P_2$	$C_{52}H_{50}CuN_2O_5P_2$
Formula weight/g mol^{-1}	256.25	387.39	972.83	831.70	831.48	908.42
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	*Pbca*	*C*2/*c*	*P*2/*n*	$P\bar{1}$	*C*2/*c*
a/pm	459.65(3)	880.1(1)	2411.1(1)	1162.8(1)	1020.8(2)	2228.5(1)
b/pm	827.72(5)	1831.2(3)	1300.9(1)	1267.3(1)	1139.5(2)	1441.6(1)
c/pm	924.01(6)	2556.8(8)	1965.0(1)	1389.1(1)	2019.1(6)	1537.6(1)
α/°	113.274(5)	90	90	90	91.79(2)	90
β/°	91.390(5)	90	128.916(3)	94.133(4)	99.86(2)	111.999(4)
γ/°	101.536(5)	90	90	90	114.01(1)	90
Cell volume/nm^3	0.31433(4)	4.121(2)	4.7953(4)	2.0416(2)	2.1003(9)	4.5803(4)
Molecules per cell *Z*	2	8	4	2	2	4
Calc. density ρ/g cm^{-3}	1.365	1.249	1.348	1.353	1.315	1.317
μ (Mo-K_α)/mm^{-1}	0.109	0.152	0.436	0.546	0.584	0.597
Crystal size/mm	0.31 × 0.22 × 0.17	0.55 × 0.14 × 0.08	0.39 × 0.34 × 0.22	0.20 × 0.16 × 0.05	0.39 × 0.20 × 0.09	0.28 × 0.20 × 0.14
Diffractometer	STOE IPDS 2	STOE IPDS 2	STOE IPDS 2T	STOE IPDS 2T	STOE IPDS 2	STOE IPDS 2T
T/K	213(2)	213(2)	200(2)	200(2)	213(2)	200(2)
θ range/°	2.415–29.143	1.593–24.993	1.905–29.225	2.178–24.997	1.969–25.999	2.462–24.999
Absorption correction	none	none	none	numerical	none	none
Reflections collected	6505	14885	16070	13493	29747	9946
Reflections unique	1676	3633	6447	3567	8263	4008
Reflections with $F_o > 4\sigma(F_o)$	1450	2556	4546	2291	7063	2357
Completeness of dataset/%	99.0	99.9	99.8	99.0	99.9	99.1
R_{int}	0.0289	0.0518	0.0591	0.0713	0.0473	0.0825
Parameters	88	255	305	260	518	306
R_1 ($I > 2\sigma(I)$)	0.0402	0.0389	0.0368	0.0385	0.0372	0.0521
wR_2 (all data)	0.1195	0.1155	0.1063	0.0897	0.0946	0.1500
GooF	1.046	1.030	1.010	0.912	1.057	1.031
Software programs used	OLEX2,[21] SHELX,[22] PLATON,[23] Diamond[24]					

3-(aminomethylene)pentane-2,4-dione,[16] 3-(methylaminomethylene)pentane-2,4-dione,[17] and the Schiff base condensation products of 3-formylacetylacetone and α-aminoacids.[3] The hydrogen atom H22 attached to the nitrogen atom acts as donor in an intramolecular N–H···O hydrogen bridge with $S^1_1(6)$ topology. The N···O2 distance of 259.3(2) pm fits well to the observations into the above mentioned Schiff base derivatives.[3]

Complexes 3–6

The complexes **3**–**6** are composed of divalent metal cations M^{2+} and deprotonated Schiff bases L^-. Upon deprotonation HL is formally transformed into a N,O-ketiminate type ligand which is suitable for the formation of six-membered $M–NC_3O$ chelate rings. Additionally, the auxiliary PPh_2 group may be involved in coordination. In the case of the copper complex **6** the coordination is nearly exclusively based on the ketiminate units (*vide infra*) while the other derivatives **3**–**5** clearly reveal the participation of the PPh_2 donor groups. Thus, complexes **3**–**5** exhibit metal atoms in a distorted octahedral $P_2N_2O_2$ environment provided by two tridentate P,N,O-ketiminate ligands L^-. The presence of two tridentate ligands allows for the formation of *mer*- and *fac*-isomers. $[FeL_2]$ (**3**) and $[NiL_2]$ (**5**) (Figure 3) are *mer* isomers with the ketiminate N atoms in *trans* positions and the PPh_2 groups along with the O acetyl atoms in mutual *cis* arrangement. The cobalt complex **4** (Figure 4) displays a *facial* arrangement of the ligands with the acetyl O atoms in mutual *trans*-arrangement. The PPh_2 groups and the ketiminate N atoms are in *cis* positions.

Generally, the octahedral complexes **3**–**5** exhibit M–N, M–O and M–P distances within the expected range (Table 3). In the case of the iron complex **3**, the Fe–N, Fe–O and Fe–P distances are 195.4(1) pm, 197.2(1) pm and 219.82(4) pm, resp. Currently, the CSD database comprises only one octahedral iron(II) complex with a $P_2N_2O_2$ donor set of the type $[Fe(II)L_2]^{2+}$) L = *o*-(diphenylphosphino)benzaldehyde benzoylhydrazone)[18] with

Table 2. Selected bond lengths [pm], bond and torsion angles [°] in compounds **2**–**6**.

	HL (**2**)	$[Fe(L)_2]$ (**3**)	$[Co(L)_2]$ (**4**)	$[Ni(L)_2]$ (**5**)	$[Cu(L)_2]$ (**6**)
O2–C4	124.1(2)	126.2(2)	125.5(3)	125.5(2), 126.5(3)*	127.1(4)
C3–C4	145.8(3)	142.9(2)	142.9(4)	144.7(3), 143.3(3)	141.4(5)
C2–C3	147.6(3)	146.5(2)	143.9(4)	147.2(3), 147.7(3)	147.7(5)
O1–C2	121.6(3)	121.4(2)	122.6(3)	123.3(3), 121.7(3)	121.0(4)
C3–C6	137.3(3)	141.5(2)	142.6(4)	142.2(3), 141.3(3)	140.9(5)
N–C6	133.4(2)	131.0(2)	129.6(3)	131.9(3), 130.5(3)	131.8(5)
N–C7	141.4(2)	142.6(2)	143.6(3)	142.1(3), 142.1(3)	143.0(4)
C3–C4–O2	119.9(2)	123.5(2)	123.0(3)	122.1(2), 124.2(2)	122.9(3)
N–C6–C3	126.4(2)	128.6(2)	127.0(2)	127.4(2), 126.8(2)	127.6(3)
C6–N–C7	126.1(2)	117.1(1)	118.7(2)	119.3(2), 118.6(2)	116.7(3)
O2–C4–C3–C6	–2.6(3)	8.8(2)	7.7(4)	19.4(3), 13.4(3)	−8.4(6)
C12–C7–N–C6	0.6(3)	−29.2(2)	27.4(4)	33.6(3), 45.1(3)	70.5(4)

* corresponding parameters for the second ligand.

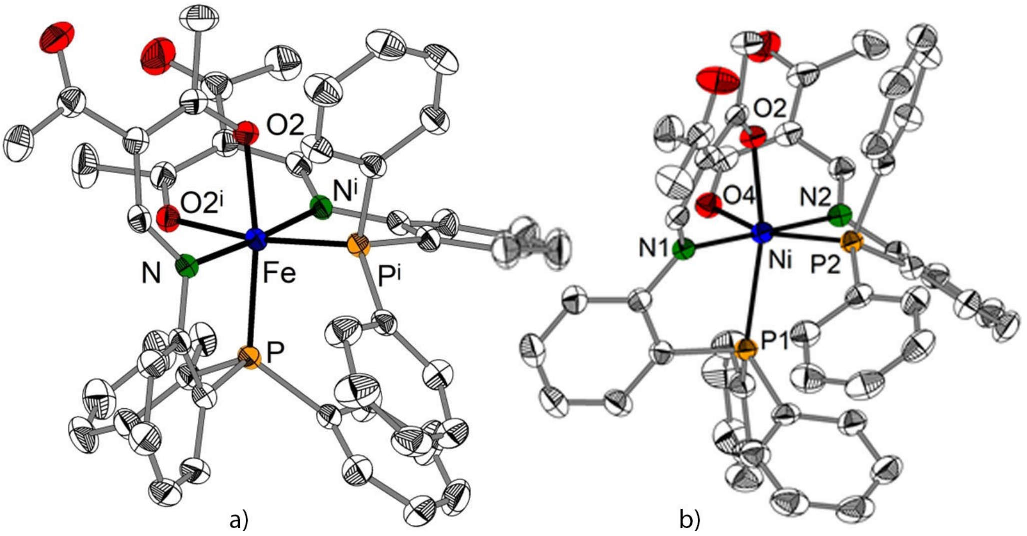


Figure 3. a) Molecular structures of FeL_2 (**3**) and b) NiL_2 (**5**) in the crystal. Thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity.

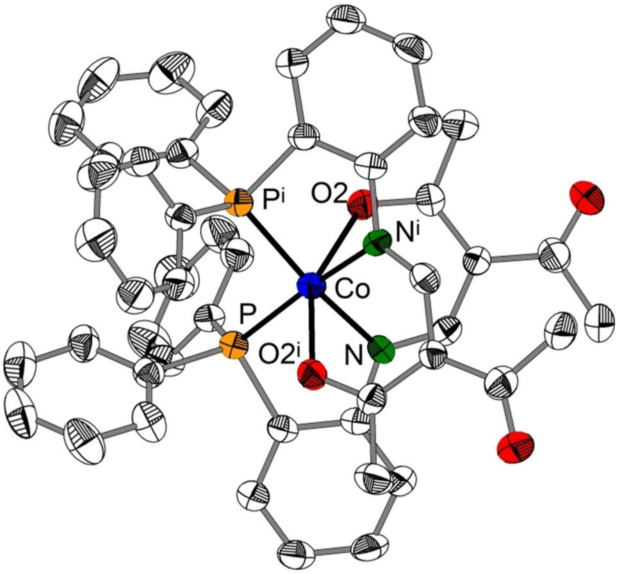


Figure 4. Molecular structure of [CoL$_2$] (**4**) in the crystal. Thermal ellipsoids at the 50 % probability level. H atoms are omitted for clarity.

Fe–N, Fe–O and Fe–P distances (188–190, 197–198 and 223.2 and 224.9 pm resp.) close to the observations in complex **3**.

Changing to the cobalt complex **4**, a slight reduction of the metal phosphorus distance to 218.4(1) pm and a more pronounced increase of the metal nitrogen and metal oxygen separations to 201.5(2) and 220.8(2) pm, resp. is observed. Currently, there are only three Co(II) complexes with $P_2N_2O_2$ donor sets reported in the CSD database. Among these complexes the Co–P distances are ranging from 220.5(1) pm in a complex with a tridentate salicylaldimido ligand[19] to 225.3(1) pm in a bis(ketopyrrolyl)/trimethylphosphine complex.[20] The Co–N distances are in a relatively narrow range between 192.1(3)–193.4(4) pm and thus around 8 pm shorter than in compound **4**. Regarding the Co–O distances, a larger variation is observed. The maximum Co–O distances are found in two bis (ketopyrrolyl)/trimethylphosphine complexes (232.0(3) pm and 238.5(2) pm[20]). In the case of the tridentate salicylaldimido derivative the Co–O distances is shortened to 191.4(3) pm.

The nickel complex **5** displays some similarities with the iron derivate **3** concerning the meridional arrangement of the tridentate P, N, O ligands. Compared with compound **3** the metal oxygen (204.1(2)–206.4(2) pm) and metal nitrogen (201.3(2)–202.4(2) pm) distances are moderately enlarged by around 7 pm. However, regarding the metal phosphorus distances of 246.4(1) and 247.6(1) pm, the increase is more pronounced and amounts to 27 pm. The occurrence of relatively large Ni–P distances is quite characteristic for octahedral Ni(II) phosphine complexes with additional chelating O,O or N,O donor ligands. [Ni(acac)$_2$(PMe$_2$Ph)$_2$] (Ni–P: 244.1 pm)[25] and [Ni(acac)$_2$(PMePh$_2$)$_2$] (Ni–P: 250.0 pm)[26] may serve as representative references. Obviously, as indicated by the large Ni–P distances the nickel phosphine interaction is rather low in these compounds. This is in accordance with the observation that [Ni(acac)$_2$(PMe$_2$Ph)$_2$] is only stable at lower temperatures and readily decomposes on dissolution in organic solvents. In compound **5** this dissociation process is preserved by the presence of a rigid *o*-phenylene bridge connecting the P and the N donor site of the tridentate ligand.

In the case of the copper complex **6** (Figure 5) the coordination mode of the ligands is essentially bidentate. The central Cu^{2+} ion is surrounded by two N,O-ketiminate groups in a distorted square planar arrangement with the N atoms in *trans* positions to each other. The Cu–O (190.6(2) pm) and the Cu–N distances (195.4(3) pm) are in the expected range. Comparable values were found for copper(II) ketiminates such as bis[4-(benzylamino)-1,1,1-trifluorobut-3-en-2-one]-copper(II) (Cu–O 191.3(3), Cu–N 199.4(4) pm)[27] or [Cu(salen)] (Cu–O 192–196, Cu–N 195–199 pm).[28] Formally, the PPh$_2$ groups are completing the coordination square to yield a strongly distorted octahedron with facial arrangement of the ligands. However, regarding the large Cu–P distances (322.3(1) pm), the interaction of the PPh$_2$ groups may be considered as marginal. This clearly reflects the preference of Cu^{2+} for "hard" donors along with the tendency to form square planar complexes with optional presence of weakly bound axial ligands.

Cu^{2+} complexes with two P, N, O donor sets are rare in literature. The only structurally characterized example is a dinuclear Cu(II)/Cr(0) complex containing a (μ_2-1,1-bis (diphenylphosphino)-6-(dimethylamino)-3-azahexane-P,P′,N,N′) ligand. In this case the diphenylphosphino groups are solely linked to the Cr(CO)$_4$ fragment. Cu^{2+} is coordinated by two O

Table 3. Selected metal ligand bond lengths [pm] and angles [°] for complexes **3**–**6**.

	[Fe(L)$_2$] (**3**)	[Co(L)$_2$] (**4**)	[Ni(L)$_2$] (**5**)	[Cu(L)$_2$] (**6**)
M–O2	197.2(1)	220.8(2)	204.1(2), 206.4(2)*	190.6(2)
M–N	195.4(1)	201.5(2)	202.4(2), 201.3(2)	195.4(3)
M–P	219.82(4)	218.4(1)	246.4(1), 247.6(1)	322.3(1)
O2–M–N	90.57(5)	80.6(1)	85.85(6), 93.80(6)**/ 85.05(6), 94.74(6)	89.9(1)
O2–M–P	171.40(3)	107.6(1)	166.13(4), 87.71(5)/ 161.60(4), 91.54(5)	98.1(1)
N1–M–P	84.62(4)	82.0(1)	81.11(5), 101.46(5)/ 78.70(5), 99.22(5)	63.5(1)
O–M–O′	82.71(6)	153.9(1)	84.80(6)	180.0(2)
N–M–N′	176.49(7)	100.0(1)	179.61(6)	180
P–M–P′	97.89(2)	98.0(1)	99.47(3)	180

* corresponding parameters for the second ligand. ** angle between different ligand units.

atoms (Cu–O: 198.2(4)–203.2(5) pm) and two N atoms (Cu–N: 203.1(4)–203.4(4) ppm).[29]

A comparison of the geometric parameters of the Schiff base HL (**2**) and the L^- ligand in complexes **3**–**6** reveals some characteristic structural changes that occur upon deprotonation and coordination (Table 2): In particular this concerns the ketiminate unit with a pronounced elongation of the bond C(3)–C(6) from 137.3(3) pm to 141.2(5)–142.7(4) pm and a moderate shortening of the bond C6–N from 133.4(2) to 131.9(3)–129.8(3) pm. Additionally, the distance C(3)–C(4) is decreased by 1.1–3.4 pm and the bond C(4)–O(2) is elongated by 1.4–2.4 pm. Moreover, there is a certain influence on some of the bond angles, i.e. the C6–N–C7 angle decreases upon coordination while the C3–C4–O2 and N–C6–C3 angles display the opposite trend. Concerning the conformation of the ligand, the co-planarity of the aminomethylene pentane-2,4-dione fragment and the *o*-phenylene-PPh_2 part is lost upon coordination and the C12–C7–N–C6 torsion angle is increased to approx. 30° for the Fe, Ni and Co complex. In the particular case of the copper complex, the torsion angle is 70.2°.

Conclusion

A new tridentate P, N, O-ligand derived from 3-formylacetylacetone was prepared and its coordination properties were investigated systematically with four different M^{2+} ions (M = Fe, Co, Ni, Cu). The synthesis of the complexes $[ML_2]$ is easily done by the reaction of the Schiff base HL with the metal acetates or acetylacetonates. Depending on M^{2+}, the deprotonated Schiff base L^- adopts different coordination modes. In the case of M = Fe, Co and Ni the coordination is essentially tridentate leading to nearly octahedral complexes with meridional (Fe, Ni) or facial (Co) arrangement of the ligands. In the copper(II) complex the coordination mode changes to N,O bidentate and Cu^{2+} exhibits a distorted square-planar coordination from two N,O-ketiminate ligands. The axially arranged PPh_2 groups are not or only marginally involved in coordination. Future investigations are devoted to use this potentially coordinating PPh_2 groups for the linkage of the $[CuL_2]$ units with other metal centers in order to synthesize heterobimetallic complexes and coordination polymers. Furthermore, the redox chemistry of the Fe(II), Co(II) and Cu(II) derivatives will be studied.

Experimental Section

All reactions were performed under argon atmosphere using Schlenk techniques. The compounds 3-formylacetylacetone,[13] *o*-(diphenylphosphino)aniline,[30] $[Fe(acac)_2(TMEDA)]$[31] and $[Co(acac)_2]$[32] were prepared according to literature methods. IR spectra were measured with a Bruker Tensor 27 spectrometer equipped with a diamond ATR unit. ^1H, ^{13}C and ^{31}P NMR-spectra were recorded on an INOVA 500-sprectrometer (500 MHz for ^1H). Magnetic susceptibilities were determined at room temperature with a Johnson-Matthey Evans balance. Elemental analysis was

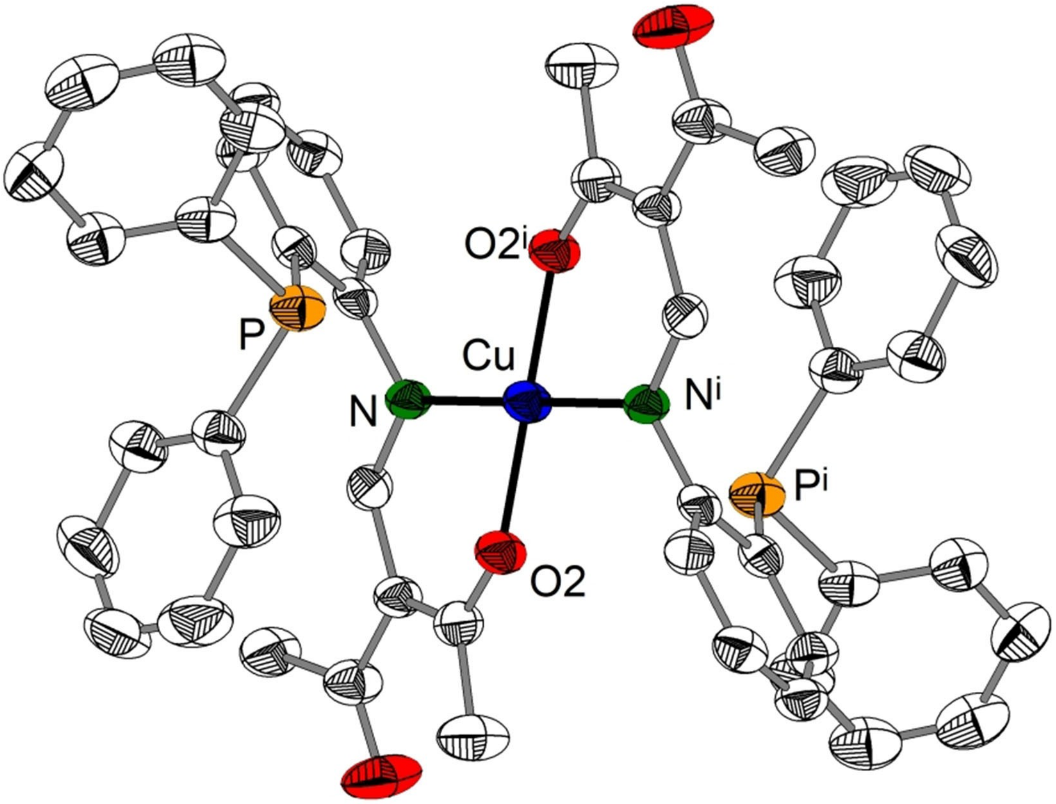


Figure 5. Molecular structure of $[CuL_2]$ (**6**) in the crystal. Thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity.

carried out on a vario EL system. An Agilent Technologies Cary 60 UV/Vis spectrometer was used to measure UV/Vis spectra and for photometry. Metal contents were determined by appropriate photometric methods. Iron and cobalt were determined as thiocyanato complexes,[33] nickel as oxidized dimethylglyoximato complex[34] and copper as ammine complex.[35]

The crystal structures were solved by direct methods (SHELXS) and refined with the SHELXL program.[21] OLEX2 was used as graphical user interface.[22] The hydrogen atoms of the NH, CH and CH_3 groups were positioned geometrically using a riding model. All reflections with error/e.s.d. >7 were omitted, with error/e.s.d. = $(wD^2/<wD^2>)^{0.5}$ and $D = F_o^2 - F_c^2$. Due to a highly disordered ethanol molecule the refinement of the crystal structure of compound **5** required the application of the SQUEEZE routine.[23] Compound **6** contains a disordered THF molecule residing on a center of inversion. The split positions were generated with the FragmentDB molecular database.[36] The crystal structure drawings were generated with DIAMOND.[24]

CCDC 2046478-2046483 contain the supplementary crystallographic data for compounds **1**–**6** in this paper (**1**: 2046478, **2**: 2046479, **3**·2THF: 2046480, **4**: 2046481, **5**: 2046482, **6**·THF: 2046483). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of HL (2): 3-formylacetylacetone (2.5 g, 19,5 mmol) and *o*-(diphenylphosphino)aniline (5.0 g, 18,0 mmol) were dissolved in THF (20 ml) and stirred for three hours. Half the solvent was removed in vacuo and *n*-hexane was added. The resulting colourless solid was filtered off and subsequently washed with *n*-hexane. Yield: 6.12 g (87 %). m.p. 97 °C. $C_{24}H_{22}NO_2P$ (387.39 g/mol): C 73.11 (calc. 74.42); H 5.53 (5.68); N 3.47 (3.62)%. **MS:** (ESI, positive): m/z (%) 388.2 (100) $[M+H]^+$, 410.1 (52) $[M+Na]^+$, 426.1 (61) $[M+K]^+$, 346.3 (31) $[M–CH_2=C=O]^+$. **^{1}H NMR:** (500 MHz, $CDCl_3$) $\delta = 13.13$ (d, $J = 11.9$ Hz, 1H, N*H*), 8.04 (d, $J = 12.3$, 1H, NH=C*H*), 7.47–7.00 (m, 14H, $CH_{aromatic}$), 2.51 (s, 3H, CH_3), 2.26 (s, 3H, CH_3). **^{13}C{^{1}H} NMR:** 200.6, 194.9, 152.7 (d, $J = 1.9$ Hz), 143.1 (d, $J = 21.0$ Hz), 134.6, 134.6 (d, $J = 8.6$ Hz), 134.0 (d, $J = 19.9$ Hz), 130.5, 129.6 (d, $J = 15.8$ Hz), 129.3, 128.7 (d, $J = 7.4$ Hz), 126.1, 117.8 (d, $J = 2.5$ Hz), 113.8, 31.8, 27.2. **^{31}P{^{1}H} NMR:** −19.6 ppm. **IR:** $\tilde{\nu} = 3342$ (w), 3054 (w), 2966 (w), 1627 (m), 1599 (m), 1573 (m), 1477 (m), 1436 (m), 1394 (w), 1354 (m), 1312 (m), 1262 (m), 1201 (m), 1160 (m), 1092 (m), 1071 (w), 1027 (w), 985 (w), 931 (w), 802 (m), 743 (s), 696 (s), 632 (m), 579 (m), 544 (m), 494 (m), 476 (m), 399 (m), 285 (m), 259 (m) cm^{-1}.

Preparation of [Fe(L)$_2$] (3): [Fe(acac)$_2$(TMEDA)] (0.45 g, 1.22 mmol) and HL (1.00, 2.58 mmol) were dissolved in THF (20 ml) and stirred for three hours under reflux. The resulting solution was treated with *n*-heptane to afford red brown crystals of **2**·THF suitable for single crystal structure analysis. Yield: 0.94 g (80 %), m.p. 246–247 °C. $C_{48}H_{42}FeN_2O_4P_2$ (828.62 g/mol): Fe 6.97 (calc. 6.74)%. **MS:** (ESI, positive): m/z (%) 828.1 (100) $[M]^+$, 829.1 (67) $[M+H]^+$, 851.3 (4) $[M+Na]^+$. **^{1}H NMR:** (500 MHz, THF-d_8) δ 7.82 (pd, J = 8.2 Hz, 2H, N–C*H*), 7.63 (pt, J = 7.3 Hz, 2H, $CH_{aromatic}$), 7.50 (pd, J = 7.3 Hz, 2H), 7.24–6.62 (m, 22H, $CH_{aromatic}$), 2.25 (s, 6H, CH_3), 1.57 (s, 6H, CH_3). **^{31}P{^{1}H} NMR:** 26.8 ppm. **IR:** $\tilde{\nu} =$ 3057 (w), 2964 (w), 2862 (w), 1635 (m), 1587 (m), 1572 (m), 1559 (s), 1467 (m), 1435 (m), 1382 (s), 1349 (m), 1292 (m), 1263 (s), 1199 (m), 1180 (m), 1165 (w), 1136 (m), 1091 (m), 1062 (m), 1026 (w), 990 (w), 935 (m), 872 (w), 797 (m), 753 (m), 738 (m), 695 (s), 658 (w), 646 (w), 629 (w), 597 (m), 544 (m), 521 (s), 503 (s), 491 (s), 416 (w), 387 (w), 298 (w), 258 (w), 222 (w) cm^{-1}. **UV/VIS:** 262, 348, 430 nm.

Preparation of [Co(L)$_2$] (4): [Co(acac)$_2$] (0.30 g, 1.17 mmol) and HL (1.00 g, 2.58 mmol) were dissolved in *o*-xylene (20 ml) and stirred under reflux for one hour. After removal of the volatiles in vacuo, the residue was dissolved in THF (10 ml). Addition of *n*-heptane afforded dark violet brown crystals suitable for single crystal structure analysis. Yield: 0.83 g (85 %). m.p. 262–263 °C. $C_{48}H_{42}CoN_2O_4P_2$ (831.74) Co 6.87 (calc. 7.08)%. $\mu_{eff} = 3.72$ B.M.. **MS:** (ESI, positive): m/z (%) 831.2 (100) $[M]^+$, **IR:** $\tilde{\nu} = 3052$ (w), 2922 (w), 2853 (w), 1627 (w), 1592 (m), 1561 (s), 1484 (m), 1466 (m), 1437 (s), 1377 (m), 1349 (m), 1336 (m), 1299 (m), 1263 (m), 1198 (m), 1161 (w), 1097 (m), 1046 (w), 1027 (w), 976 (m), 930 (s), 857 (w), 752 (s), 694 (m), 638 (m), 599 (m) 588 (w), 574 (m), 540 (m), 502 (s), 490 (s), 451 (w), 421 (w), 378 (w), 349 (m), 222 (m) cm^{-1}. **UV/VIS:** 239, 334, 503 nm.

Preparation of [Ni(L)$_2$] (5): Nickel(II)acetate tetrahydrate (0.30 g, 1.21 mmol) and HL (1.00 g; 2.58 mmol) were dissolved in ethanol (20 ml). On stirring for three hours **5** precipitated as green solid which was filtered off. The remaining filtrate was treated with *n*-heptane to obtain crystals suitable for single crystal structure analysis. Yield: 0.75 g (74 %). m.p. 250 °C. $C_{48}H_{42}N_2NiO_4P_2$ Ni 6.96 (calc. 7.06)%. **MS:** (ESI, positive): m/z (%) 831.0 (100) $[M+H]^+$, 853.1 (26) $[M+Na]^+$, 426.2 (28) $[L+K]^+$, 461.8 (25) $[NiL(H_2O)]^+$, 475.9 (74) $[NiL(MeOH)]^+$. **IR:** $\tilde{\nu} = 3052$ (b), 1638 (m), 1584 (s), 1569 (s), 1560 (s), 1482 (m), 1461 (s), 1435 (m), 1379 (s), 1348 (m), 1291 (m), 1262 (m), 1209 (m), 1158 (m), 1127 (w), 1101 (w), 1047 (w), 1027 (w), 983 (m), 956 (w), 935 (w), 855 (w), 759 (s), 743 (s), 695 (m), 641 (m), 612 (m), 586 (m), 548 (m), 511 (m), 499 (m), 486 (s), 446 (w), 425 (m), 332 (w), 253 (m), 233 (s) cm^{-1}. **UV/VIS:** 283, 366 nm.

Preparation of [Cu(L)$_2$] (6): [Cu(acac)$_2$] (0.30 g, 1.15 mmol) and HL (1.00 g, 2.58 mmol) were dissolved in *o*-xylene (20 ml) and stirred for an hour under reflux. After removal of the volatiles in vacuo, the residue was dissolved in THF (10 ml). Upon addition of *n*-heptane the product was precipitated as green crystalline solid. Yield: 0.69 g (70 % for copper(II)acetylacetonate). m.p. (dec.) 131–132 °C. $C_{48}H_{42}CuN_2O_4P_2$ (836.32 g/mol): Cu 7.38 (calc. 7.60)%. **MS:** (ESI, positive): m/z (%) 836.9 (5), $[M+H]^+$, 723.8 (100) $[M–C_6H_8O_2+H]^+$, 851.9 (10) $[M+O+H]^+$, 867.9 (1) $[M+2O+H]^+$, 448.8 (20) $[M–L+H]^+$, 480.9 (40) $[M–L+MeOH+H]^+$ **IR:** $\tilde{\nu} = 3053$ (w), 2971 (w), 2859 (w), 1626 (s), 1596 (m), 1573 (s), 1476 (m), 1434 (m), 1390 (m), 1352 (m), 1311 (m), 1262 (m), 1246 (m), 1199 (w), 1092 (m), 1065 (m), 1024 (w), 993 (w), 930 (m), 801 (w), 783 (s), 742 (s), 694 (w), 652 (w), 630 (m), 612 (w), 587 (w), 577 (w), 540 (w), 514 (m), 493 (m), 475 (m), 454 (m), 430 (w), 412 (w), 288 (w), 215 (m) cm^{-1}.

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Keywords: Schiff Base · Ketiminate Ligand · Crystal Structure · X-ray

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