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Methanetrissamidines in Coordination Chemistry - Syntheses, Structures and CH-NH Tautomerism

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Methanetrissamidines $\{HC[C(NR)NHR]_3\}$ (R = *i*-Pr **1a**; Ph **1b**) were reacted with different metal complexes. Reaction of **1a** with $NiCl_2(H_2O)_6$ occurred with protonation of **1a** and formation of $\{[C(C(NH*i*-Pr)_2)_3]^{2+}[NiCl_4]^{2-}\}$ **2**, whereas the reaction with CuCl gave $[C(C(N(*i*-Pr)CuCl)NH*i*-Pr)_2(C(NH*i*-Pr)_2)]$ **3**. The formation of **2** and **3**, which contain the N-H tautomeric form of **1a**, occurred with H-migration from carbon to nitrogen. In contrast, reactions of **1b** with $[M(NCMe)_3(CO)_3]$ (M = Cr, Mo, W) yielded octahedral complexes *fac*- $[M(CO)_3CH(C(NHPh)NPh)_3]$ (M = Cr **4a**, Mo **4b**, W **4c**), in which the C-H tautomeric form is preserved. **1b** is a rather strong σ -donor as was shown by IR spectroscopy. The structures of **2**, **3** and **4a** were determined by single crystal X-ray diffraction.

Introduction

C_3 -symmetric tripodal ligands have a long standing history in coordination chemistry. Hydrotris(pyrazolyl)borates (R = H, **I**), which have been initially prepared by Trofimenko in 1966,^[1] as well as their sterically more demanding "organic" derivatives (R = alkyl)^[2] have been intensely used in coordination chemistry including bioinorganic chemistry, in which they were used as supporting ligands for the modelling of various zinc enzymes. Moreover, other types of tripodal ligands such as tris(pyrazolyl)methane (**II**),^[3] tris(pyrazolylmethyl)amine (**III**),^[4] tris(2-phenylimidazol-4-yl)phosphine (**IV**),^[5] tris(benzimidazolylmethyl)amine (**V**)^[6] as well as tris(5-amino-1-pyridylmethyl)amine **VI**^[7] have been investigated in detail (scheme 1).

Scheme 1. Structures of C_3 -symmetric tripodal ligands typically used in coordination chemistry.

We recently reported on the synthesis of two C_3 -symmetric methanetrissamidines of the general type $\{HC[C(NR)NHR]_3\}$ (R = *i*-Pr **1a**; Ph **1b**),^[8] which were formed by hydrolysis of tetranuclear zinc amidinate complexes $\{C[C(NR)_2ZnMe]_4\}$ (R = *i*-Pr; Ph).^[9] In addition, the NH-tautomeric form of the Ph-substituted derivative, $\{C[C(NPh)N(Ph)H]_2[C(HNPh)_2]\}$ **1c** (scheme 2), was isolated and structurally characterized, whereas the corresponding *i*-Pr-substituted derivative was not observed.

Scheme 2. N,C-tautomeric methanetrissamidines; potentially basic coordinative imino sites are depicted in red.

Temperature dependent ¹H NMR spectroscopic studies of solutions of **1a-c** in different solvents (C₆D₆, CD₃CN) revealed the presence of a dynamic equilibrium between the two tautomeric forms **1b** and **1c**, which can be controlled to some extent by temperature and the solvent polarity. In contrast, no

indication for an analogous tautomeric equilibrium was found for **1a**. The capability of the C_3 -symmetric ligands **1a** and **1b** as well as that of **1c** to react with metal alkyl complexes MR_n and alkyl metal hydrides HMR_n with alkane or hydrogen elimination was demonstrated and several homometallic tri- and tetranuclear complexes such as $\{CH[C(N*i*-Pr)_2AlR_2]_3\}$ (R = Me, *i*-Bu) were structurally characterized.^[9] In addition, **1c** was found to undergo stepwise deprotonation reactions with two different metal alkyl complexes at different reaction temperatures, which was successfully used for the synthesis of heterometallic tetranuclear complexes $\{C[C(N(\eta^3-Ph)N(Ph)ZnMe)_2[C(N(Ph)MMe_2)_2]\}$ (M = Al, Ga).^[10] Herein we report on our studies concerning the formation of coordination complexes utilizing the multiple coordinative imino sites of the neutral methanetrissamidines.

Results and discussion

The reaction of **1a** with $NiCl_2(H_2O)_6$ in CH₃CN at 80 °C led to the formation of the dicationic trissamidinium salt $\{[C(C(NH*i*-Pr)_2)_3]^{2+}[NiCl_4]^{2-}\}$ **2** (scheme 3). Obviously, the H-atoms of water molecules of the nickel chloride hydrate are acidic enough to protonate the rather strong Lewis-basic trissamidine **1a**.

Scheme 3. Formation of dicationic trissamidinium salt **2** with formal tautomerization of **1a**.

2 is insoluble in THF-d₈, acetonitrile-d₃ and even D₂O, hence preventing **2** from characterization by NMR-spectroscopy. However, its structure was proven by X-ray crystallography. Single crystals of **3** were obtained upon storage of a solution of **2** in CH₃CN at -30 °C for 12 h. **2** crystallizes in the cubic space group *Pa* $\bar{3}$ with the anion and the cation placed on a three-fold axis.

Fig. 1. Molecular structure of **2** (thermal ellipsoids at 50% probability levels, hydrogen atoms at arbitrary radii; *i*-Pr groups reduced to bonds and H atoms omitted for clarity).

The structure of the dication $\{[C(C(NHi-Pr)_2)_3]^{2+}$ in **2** is similar to that of the $\{[C(C(NHPh)_2)_3]^{2+}$ dication, that was recently observed in $\{[C(C(NHPh)_2)_3]^{2+}[Ac^-]_2\}$.^[8] Both dications contain a central sp^2 -hybridized carbon atom (C1) similar to the NH-tautomeric form of the free amidine **1c**. In contrast to **1c**, all nitrogen atoms in **2** carry protons, resulting in the presence of six NH groups. This result is quite surprising since the proton originally bound to the central carbon atom (C1) of the C-H tautomer $CH[(C(NHi-Pr)Ni-Pr)_3]$ **1a** was obviously migrated to an imine centre, yielding the corresponding N-H tautomeric form. While the formation of the CH- and the NH-tautomers were previously reported for the Ph-substituted trisamidine (**1b** and **1c**), we have never observed the formation of the NH-tautomer of **1a** before. The resulting change of hybridization state at the central carbon atom from formally sp^3 to sp^2 allows the resonance stabilization of the twofold positive charge over the whole C_4 -moiety. The N-H tautomeric form as observed in the dication in **2** is thus expected to be energetically favoured compared to a hypothetical sp^3 -hybridized dication (C-H tautomer). The C-C bond lengths within the trigonal-planar C_4 -moiety of **2** are identical (C1-C2 1.4508(14) Å) due to the C_3 symmetry of the ion and in between the typical values of C-C single and double bonds. The same is true for the C-N bond lengths (mean value: 1.3417(25) Å). Additionally the C2'-C1-C2 bond angle of 119.893(12)° is in accordance with the sp^2 geometry. The structural findings suggest an ideal delocalisation of the twofold positive charge over the planar C_4 -moiety as was observed for the dication $[C(C(NHPh)_2)_3]^{2+}$ in $\{[C(C(NHPh)_2)_3]^{2+}[Ac^-]_2\}$.^[8]

Table 1. Bond lengths (Å) and angles (°) of **2**.

In order to suppress the strong tendency of the Lewis basic methanetrissamidine **1a** to undergo protonation reactions, further experiments were conducted with hydrate free metal salts. The reaction of **1a** with two equivalents of copper(I)chloride in THF led to the formation of $[C(C(N(i-Pr)CuCl)NH(i-Pr)_2(C(NHi-Pr)_2)]$ **3** (scheme 4). ¹H and ¹³C NMR spectroscopic analysis of **3** in THF-*d*₈ showed highly broadened resonances of the *i*-Pr groups, indicating a dynamic exchange between CuCl moieties and amino protons of the ligand in solution. In addition, a resonance due to the presence of the C-H moiety did not appear in the ¹H NMR spectrum of **3**.

Scheme 4. Formation of **3** with formal tautomerization of **1a**.

Single crystals of **3** suitable for an X-ray crystal analysis were obtained upon storage of a solution of **3** in THF at -30 °C. **3** crystallize in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit and an additional disordered THF molecule. As was observed in the protonation reaction of **1a** with $NiCl_2(H_2O)_6$, the proton of the central CH-moiety in **1a** migrated to one imino group in **3**, yielding the corresponding N-H tautomeric form. The remaining two imino sites each coordinate one Cu(I)Cl molecule. These findings prove that both the protonation of the imino group as well as the coordination of the imino group to a metal centre such as Cu(I) favours the formation of the NH-tautomer form due to the migration of the C-

H proton to an imino group. The central sp^2 -hybridized carbon atom C1 in **3** binds to two amidine carbon atoms (C2, C3) and a methylenediamine moiety (C4). The C-C bond lengths in **3** are in between typical values for C-C single and C=C double bonds, indicating a delocalised π -system within the planar C_4 -moiety. The C1-C4 bond is slightly shortened, which can be attributed to the higher double bond character (C1-C4 1.424(4) Å, C1-C3 1.473(3) Å, C1-C2 1.468(3) Å). The C-N bond lengths of the imino groups within the amidine moieties are slightly elongated (C3-N3 1.314(3) Å, C2-N1 1.317(3) Å) due to the coordination to the Cu(I)Cl fragment, which results in an increased coordination number and the loss of electron density at the nitrogen atoms. CuCl adopts a η^1 -coordination mode. The N-Cu-Cl bond angles slightly differ from linearity (N1-Cu1-Cl1 175.94(8)°, N3-Cu2-Cl2 171.97(7)°) and the Cu-N bond length (N1-Cu1 1.893(2) Å, N3-Cu2 1.880(2) Å) are close to the mean value found for Cl-Cu-N fragments in the CSD.^[11] Comparable values were reported for Cu(I-PETAEA)CuCl (PETAEA = bis-(2-(2-pyridyl)ethyl)-2-(*N*-toluenesulfonylamino)ethylamine) (N-Cu 1.9054(15) Å, N-Cu-Cl 174.18(5)°),^[12] CuCl(hppSiMe₃) (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine) (Cu-N 1.877(2) Å, N-Cu-Cl 176.43(7)°),^[13] Pt(PPh₃)₂Br(μ -3,5-Ph₂pz)CuCl (Cu-N 1.86(3) Å, N-Cu-Cl 177.0(8)°),^[14] and Cp(PPh₃)Ru-CN-CuCl (Cu-N 1.810(4) Å, N-Cu-Cl 178.7(1)°),^[15] respectively. A packing analysis did not show any stabilizing interactions between copper and other donor atoms.

Fig. 2. Molecular structure of **3** (thermal ellipsoids at 50% probability levels, hydrogen atoms at arbitrary radii; *i*-Pr groups reduced to bonds and H atoms omitted for clarity).

Table 2. Bond lengths (Å) and angles (°) of **3**.

The reactions of **1a** with $NiCl_2(H_2O)_6$ as well as CuCl both occurred with migration of the proton from the carbon to the nitrogen atom (CH – NH tautomerism). These findings are in remarkable contrast to those recently observed in reactions of **1a** with trialkylalanes AlR_3 and dialkylalanes R_2AlH , which were found to proceed with threefold alkane/hydrogen elimination and preservation of the C-H tautomeric form.^[8] In contrast, analogous reactions of **1b** with AlR_3 occurred with fourfold alkane elimination due to the initial formation of the N-H tautomeric form.^[8] We therefore became interested in reactions of **1b** with transition metal complexes and reacted **1b** with group 6 metal complexes of the general type $[M(NCMe)_3(CO)_3]$ (M = Cr, Mo, W). Reactions of **1b** with $[M(NCMe)_3(CO)_3]$ (M = Cr, Mo, W) in toluene at 90 °C yielded octahedral complexes *fac*- $[M(CO)_3CH(C(NHPh)NPh)_3]$ (M = Cr **4a**, Mo **4b**, W **4c**). The CH tautomeric form of **1b** is preserved and **1b** acts as a tripodal *N,N,N*-donor to a single metal centre. ¹H NMR spectra in THF-*d*₈ (**4a**, **4b**) and acetone-*d*₆ (**4c**) each show the characteristic singlet resonance of the backbone CH moiety (**4a**: 5.16, **4b**: 5.01, **4c**: 5.33 ppm), which was confirmed by additional DEPT experiments (**4a**: 43.9, **4b**: 46.6, **4c**: 46.8 ppm). The equivalent NH groups result in one sharp singlet resonance (**4a**: 7.60, **4b**: 7.62, **4c**: 8.11). The carbonyl resonances of **4a-c** show weak signals at about 230 ppm (**4a**: 235, **4b**: 230.2, **4c**: 226.8 ppm) in

the ^{13}C NMR spectra, indicating a terminal coordination of the carbonyl ligands to the metal centre.^[16] This coordination mode was also proven by solid-state IR spectroscopy, showing the absorption bands in **4a-c** due to the carbonyl groups (ν_{CO} : 1881, 1757 (**4a**), 1881, 1751 (**4b**), 1869, 1756 cm^{-1} (**4c**)) at rather low frequency numbers. According to these studies, the σ -donor capacity of methanetrisamidine **1b** toward group 6 metal carbonyl complexes is comparable to that of typical *N,N,N*-tripodal donor ligands such as trispyrazolylborates, triazacyclononanes or methyltrispyrazolylsilanes (table 3).

Table 3. IR-data for several group 6 metal carbonyl complexes with different *N,N,N*-tripodal ligands.

Scheme 5. Formation of tripodal complexes **4a-c**.

Table 4. Bond lengths (Å) and angles ($^{\circ}$) of **4a**.

Orange crystals of **4a** suitable for a single-crystal X-ray analysis were obtained from a solution in THF upon storage at $-30\text{ }^{\circ}\text{C}$ for 5 days. **4a** crystallizes in the orthorhombic space group *Pna*2₁ with one molecule and one additional, partially disordered THF molecule in the asymmetric unit. The central sp^3 hybridized carbon atom C1 is bonded to three amidine carbon atoms and one hydrogen atom. The C-C bond lengths are in the typical range of C-C single bonds (C1-C2 1.517(5), C1-C3 1.520(5), C1-C4 1.523(5) Å) and the C-C1-C angles are roughly 110° . The C-N bond lengths within the amidine moieties are typical for single and double bonds. The central atom Cr1 is coordinated by three imino nitrogen atoms of the trisamidine ligand (Cr1-N2 2.138(3), Cr1-N4 2.133(3), Cr1-N6 2.146(3) Å) and three carbonyl ligands (Cr1-C5 1.819(5), C5-O1 1.171(5); Cr1-C6 1.809(4), C6-O2 1.184(5); Cr1-C7 1.823(4), C7-O3 1.168(5) Å), resulting in an octahedral coordination mode as was deduced by infrared analysis, exhibiting two $\nu(\text{CO})$ stretching vibrations (A1 and E), *vide supra*. Each set of three identical ligands occupies one face of the octahedron surrounding the metal atom. The bond lengths in **4a** are in good agreement with the structural data of similar tripodal complexes, e. g. [LCr(CO)₃][PF₆]-dmf (Cr-C 1.817(4) Å, Cr-N 2.182(4) Å, C-O 1.172(5) Å),^[20] {HC(CN(2-*i*-Pr-Ph)Me)₃}Cr(CO)₃ (Cr-C 1.8336(12) Å, Cr-N 2.1218(19) Å, C-O 1.1673(15) Å),^[21] *cis*-(diethylenediaminechromium)tricarbonyl (Cr-C 1.816 Å, Cr-N 2.185 Å, C-O 1.173 Å)^[24] and tricarbonyl{*N,N',N''*-tris[(S)-1'-phenylethyl]hexahydro-1,3,5-triazine}chromium (Cr-C 1.799 Å, C-N 2.209 Å, C-O 1.174 Å).^[25,26]

Fig. 3. Molecular structure of **4a** (thermal ellipsoids at 50% probability levels, hydrogen atoms at arbitrary radii; Phenyl groups reduced to bonds and H atoms omitted for clarity).

Table 5. Crystallographic data of **2**, **3**, **4a**.

Conclusions

Reactions of two methanetrisamidines **1a** and **1b** with different metal complexes were investigated. **1a** reacts with $\text{NiCl}_2(\text{H}_2\text{O})_6$ with protonation of the Lewis-basic imine centres and with CuCl with formation of $[\text{C}(\text{C}(\text{N}(\textit{i}$ -Pr)CuCl)NH*i*-Pr)₂(C(NH*i*-Pr)₂)] **3**, containing two coordinated CuCl moieties. Both reactions occurred with migration of the proton from the central carbon atom to an imine centre (CH – NH tautomerism). In contrast, the reaction of **1b** with $[\text{M}(\text{NCMe})_3(\text{CO})_3]$ (M = Cr, Mo, W) resulted in the formation of *fac*- $[\text{M}(\text{CO})_3\text{CH}(\text{C}(\text{NHPh})\text{NPh})_3]$ (M = Cr **4a**, Mo **4b**, W **4c**) containing the central metal centres in a octahedral coordination mode. The methanetrisamidine ligand **1b** serves as tripodal chelating *N,N,N*-donor ligand, in which the C-H tautomeric form is preserved.

Experimental

All manipulations were performed in a glovebox under an Ar atmosphere or using standard Schlenk techniques. Solvents were carefully dried over Na/K and degassed prior to use. **1a-c**^[11] and $\text{M}(\text{NCMe})_3(\text{CO})_3$ ^[27] were prepared according to literature methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal THF-*d*₈ (^1H : $\delta = 3.58$; ^{13}C : $\delta = 67.4$) and acetone-*d*₆ (^1H : $\delta = 2.04$; ^{13}C : $\delta = 29.8$). IR spectra were recorded on an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor*, University of Essen.

$[\{\text{C}(\text{C}(\text{NH*i*-Pr})_2)_3\}^{2+}[\text{NiCl}_4]^{2-}]$ **2**.

0.25 g (0.6 mmol) **1a** and 0.30 g (1.3 mmol) $\text{NiCl}_2(\text{H}_2\text{O})_6$ were suspended in 20 ml of acetonitrile and heated under reflux for 2 h. Filtration of the reaction mixture gave a blue coloured filtrate, from which pale blue crystals of **2** were formed within 12h upon storage at $-10\text{ }^{\circ}\text{C}$. Yield: 0.21 g (55%). Mp.: $>250\text{ }^{\circ}\text{C}$. Elemental analysis calculated (%) for $\text{C}_{22}\text{H}_{48}\text{N}_6\text{Cl}_4\text{Ni}$ (M = 597.16 g/mol): H 8.10, C 44.25, N 14.07; found: H 7.96, C 44.49, N 13.89. Crystalline **2** is completely insoluble in common organic solvents; hence solution NMR data could not be obtained. ATR-IR: ν 3302, 3252, 2966, 2931, 2872, 1642, 1574, 1551, 1521, 1459, 1386, 1386, 1365, 1306, 1259, 1121, 1091, 1009, 979, 870, 797, 674, 618, 559 cm^{-1} .

$[\{\text{C}(\text{C}(\text{HN*i*-Pr})_2)(\text{C}[\text{N}(\text{CuCl})\textit{i}$ -Pr)NH*i*-Pr)₂}] **3**.

0.25 g **1a** (0.6 mmol) and 0.12 g (1.3 mmol) CuCl were suspended in 20 mL of THF and stirred for 1 h at $60\text{ }^{\circ}\text{C}$. Filtration of the reaction mixture gave a yellowish solution, from which yellow crystals of **3** were formed within 5 d upon storage at $-30\text{ }^{\circ}\text{C}$. Yield: 0.27 g (74%). Mp.: $117\text{ }^{\circ}\text{C}$ (dec.). Elemental analysis calc. (%) for $\text{C}_{22}\text{H}_{46}\text{N}_6\text{Cl}_2\text{Cu}_2$ (M = 592.64 g/mol): H 7.82, C 44.59, N 14.18; found: H 7.63, C 44.83, N 13.89. ^1H -NMR (300 MHz, THF-*d*₈, $25\text{ }^{\circ}\text{C}$): δ 1.21 (m (broad), $\text{CH}(\text{CH}_3)_2$), 5.02 (m (broad), $\text{CH}(\text{CH}_3)_2$). ^{13}C -NMR (75.5 MHz, THF-*d*₈, $25\text{ }^{\circ}\text{C}$): δ 19-23 ($\text{CH}(\text{CH}_3)_2$), 45 ($\text{CH}(\text{CH}_3)_2$), 85 ($\text{C}(\text{CN}_2)_3$), 159 (NCN). ATR-IR: ν 3447, 3371, 3328, 3302, 2957, 2922, 2866, 1630, 1562, 1459, 1418, 1383, 1362, 1309, 1297, 1221, 1165, 1124, 1068, 971, 926, 877, 767, 735, 667, 617, 570 cm^{-1} .

$\{\text{HC}[\text{C}(\text{NPh})\text{NPh}]_3\text{M}(\text{CO})_3\}$ **4a-c**.

0.15 g **1c** (0.8 mmol) and 0.8 mmol $\text{M}(\text{NCMe})_3(\text{CO})_3$ were suspended in 15 mL of toluene. The reaction mixture was then heated to $90\text{ }^{\circ}\text{C}$ for 4 h, upon which the reaction darkening and

the products **4a-c** precipitated. After cooling, the reaction mixture was filtrated and crude **4a-c** were isolated as yellow to red solids. The crude products were washed with 10 mL of *n*-hexane, yielding analytically pure **4a-c**. Suitable crystals of **4a** for single-crystal diffraction were obtained from a solution in THF upon storage at $-30\text{ }^{\circ}\text{C}$ for 5 days.

4a: Yield: 0.14 g (76.1%). Mp.: $> 250\text{ }^{\circ}\text{C}$ (dec.). Elemental analysis calc. (%) for $\text{C}_{43}\text{H}_{34}\text{CrN}_6\text{O}_3$ ($M = 734.76\text{ g/mol}$): H 4.66, C 70.29, N 11.44; found: H 4.57, C 69.80, N 11.25. $^1\text{H-NMR}$ (300 MHz, THF- d_8 , $25\text{ }^{\circ}\text{C}$): δ 5.16 (s, 1H, HC(CN) $_2$), 6.79 (m, 9H, Ar), 6.91 (m, 6H, Ar), 7.09 (m, 3H, Ar), 7.19 (m, 6H, Ar), 7.36 (m, 6H, Ar), 7.60 (s, 3H, NH). $^{13}\text{C-NMR}$ (75.5 MHz, THF- d_8 , $25\text{ }^{\circ}\text{C}$): δ 43.9 (CH), 123.6 (Ar), 123.8 (Ar), 125.3 (Ar), 125.4 (Ar), 129.8 (Ar), 130.0 (Ar), 139.4 (Ar), 151.1 (Ar), 158.4 (N=C=N), 235 (C=O). IR: ν 3358, 3078, 3049, 3019, 1881, 1757, 1624, 1589, 1498, 1483, 1368, 1233, 1203, 1174, 1068, 1024, 909, 750, 712, 694, 641, 527, 506, 471 cm^{-1} .

4b: Yield: 0.16 g (82.0%). Mp.: $> 250\text{ }^{\circ}\text{C}$ (dec.). Elemental analysis calc. (%) for $\text{C}_{43}\text{H}_{34}\text{MoN}_6\text{O}_3$ ($M = 778.73\text{ g/mol}$): H 4.40, C 66.32, N 10.79; found: H 4.36, C 66.10, N 10.65. $^1\text{H-NMR}$ (300 MHz, THF- d_8 , $25\text{ }^{\circ}\text{C}$): δ 5.01 (s, 1H, HC(CN) $_2$), 6.78 (m, 6H, Ar), 6.89 (m, 3H, Ar), 6.95 (m, 6H, Ar), 7.09 (m, 3H, Ar), 7.21 (m, 6H, Ar), 7.33 (m, 6H, Ar), 7.62 (s, 3H, NH). $^{13}\text{C-NMR}$ (75.5 MHz, THF- d_8 , $25\text{ }^{\circ}\text{C}$): δ 46.6 (CH), 123.6 (Ar), 124.9 (Ar), 125.6 (Ar), 126.1 (Ar), 130.0 (Ar), 139.4 (Ar), 151.1 (Ar), 158.0 (N=C=N), 230.2 (C=O). IR: ν 3352, 3079, 3052, 3022, 1881, 1751, 1727, 1621, 1589, 1500, 1483, 1365, 1233, 1203, 1177, 1068, 1024, 909, 750, 712, 694, 656, 553, 550, 503, 474 cm^{-1} .

4c: Yield: 0.15 g (69.1%). Mp. $> 250\text{ }^{\circ}\text{C}$ (dec.). Elemental analysis calc. (%) for $\text{C}_{43}\text{H}_{34}\text{WN}_6\text{O}_3$ ($M = 866.61\text{ g/mol}$): H 3.95, C 59.60, N 9.70; found: H 3.88, C 59.55, N 9.61. $^1\text{H-NMR}$ (300 MHz, acetone- d_6 , $25\text{ }^{\circ}\text{C}$): δ 5.33 (s, 1H, HC(CN) $_2$), 6.94 (m, 9H, Ar), 6.99 (m, 6H, Ar), 7.09 (m, 3H, Ar), 7.25 (m, 6H, Ar), 7.36 (m, 6H, Ar), 8.11 (s, 3H, NH). $^{13}\text{C-NMR}$ (75.5 MHz, acetone- d_6 , $25\text{ }^{\circ}\text{C}$): δ 46.8 (CH), 123.8 (Ar), 124.3 (Ar), 125.9 (Ar), 126.0 (Ar), 129.9 (Ar), 130.2 (Ar), 138.6 (Ar), 138.7 (Ar), 150.4 (Ar), 158.4 (N=C=N), 226.8 (C=O). IR: ν 3349, 3079, 3049, 3022, 1869, 1756, 1741, 1719, 1616, 1586, 1497, 1483, 1368, 1315, 1233, 1201, 1177, 1068, 1024, 912, 768, 750, 714, 697, 635, 615, 553, 541, 506, 476, 414 cm^{-1} .

Single crystal X-ray diffraction.

Crystallographic data of **2**, **3** and **4a**, which were collected on a Bruker AXS APEX2 diffractometer (MoK α radiation, $\lambda = 0.71073\text{ \AA}$) at 150(1) K (**2**), 150(1) K (**3**) and 141(2) K (**4a**), are summarized in Table 5. The solid-state structures of **2**, **3** and **4a** are shown in Figures 1 - 3, bond lengths and angles of **2**, **3**, **4a** are summarized in tables 1, 2 and 4. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97).^[28,29] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. **3** was refined against data produced by PLATON/SQUEEZE^[30]. The complete solvent molecule in **3** and the disordered part of it in **4a** was refined isotropically.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: Crystallographic data of **2**, **3** and **4a**. See DOI: 10.1039/b000000x/
- ‡ The crystallographic data of **2**, **3** and **4a** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (Christoph) as supplementary publication nos. CCDC-971997 (**2**), CCDC-886453 (**3**) and CCDC-971998 (**4a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).
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ARTICLE TYPE

Table 1. Bond lengths (Å) and angles (°) of **2**

Ni(1)-Cl(1)	2.2345(8)	Cl(1)-Ni(1)-Cl(2)#1	110.194(14)	N(2)-C(2)-N(1)	119.42(13)
Ni(1)-Cl(2)#1	2.2696(5)	Cl(2)#1-Ni(1)-Cl(2)#2	108.739(14)	N(2)-C(2)-C(1)	118.68(13)
N(1)-C(2)	1.3449(19)	C(2)-N(1)-C(3)	125.26(12)	N(1)-C(2)-C(1)	121.89(13)
N(2)-C(2)	1.3386(18)	C(2)-N(2)-C(6)	125.75(13)		
C(1)-C(2)	1.4508(14)	C(2)-C(1)-C(2)#1	119.892(12)		

#1 y+1/2,-z+1/2,-x+1 #2 -z+1,x-1/2,-y+1/2

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Table 2. Bond lengths (Å) and angles (°) of **3**

Cu(1)-N(1)	1.893(2)	C(1)-C(4)	1.424(4)	C(3)-N(3)-C(11)	119.8(2)
Cu(1)-Cl(1)	2.0983(8)	C(1)-C(2)	1.468(3)	C(3)-N(3)-Cu(2)	122.90(18)
Cu(2)-N(3)	1.880(2)	C(1)-C(3)	1.473(3)	C(11)-N(3)-Cu(2)	117.31(13)
Cu(2)-Cl(2)	2.1020(8)			C(3)-N(4)-C(14)	127.4(2)
N(1)-C(2)	1.317(3)	N(1)-Cu(1)-Cl(1)	175.94(8)	C(4)-N(5)-C(17)	127.4(3)
N(2)-C(2)	1.351(3)	N(3)-Cu(2)-Cl(2)	171.97(7)	C(4)-N(6)-C(20)	126.0(3)
N(3)-C(3)	1.314(3)	C(2)-N(1)-C(5)	120.1(2)	C(4)-C(1)-C(2)	119.8(2)
N(4)-C(3)	1.350(3)	C(2)-N(1)-Cu(1)	119.89(17)	C(4)-C(1)-C(3)	117.2(2)
N(5)-C(4)	1.360(4)	C(5)-N(1)-Cu(1)	118.39(17)	C(2)-C(1)-C(3)	121.4(2)
N(6)-C(4)	1.338(3)	C(2)-N(2)-C(8)	128.1(2)		

Table 3. IR-data for several group 6 metal carbonyl complexes with different *N,N,N*-tripodal ligands.

Complex ^f	$\nu(\text{CO})/\text{cm}^{-1}$	Ref.
(Et ₄ N)[(HB(3,5-Me ₂ pz) ₃ Cr(CO) ₃]	1891, 1748 ^a	17
{HC(pz) ₃ }Cr(CO) ₃	1898, 1758 ^b	18
{MeSi(3,5-Me ₂ pz) ₃ }Cr(CO) ₃	1898, 1755 ^c	19
LCr(CO) ₃	1903, 1762 ^a	20
{HC(CN(2- <i>i</i> -Pr-Ph)Me) ₃ }Cr(CO) ₃	1893, 1796, 1775 ^d	21
{HC(C(NPh)NHP) ₃ }Cr(CO) ₃ 4a	1881, 1757 ^e	this work
(NCP)[HB(pz) ₃ Mo(CO) ₃]	1882, 1736 ^c	22
{HC(3,5-Me ₂ pz) ₃ }Mo(CO) ₃	1900, 1760 ^b	23
{MeSi(3,5-Me ₂ pz) ₃ }Mo(CO) ₃	1896, 1755 ^c	19
LMo(CO) ₃	1907, 1768 ^a	20
{HC(CN(2- <i>i</i> -Pr-Ph)Me) ₃ }Mo(CO) ₃	1897, 1787, 1776 ^d	21
{HC(C(NPh)NHP) ₃ }Mo(CO) ₃ 4b	1881, 1751 ^e	this work
{MeSi(3,5-Me ₂ pz) ₃ }W(CO) ₃	1887, 1747 ^c	19
LW(CO) ₃	1897, 1757 ^a	20
{HC(CN(2- <i>i</i> -Pr-Ph)Me) ₃ }W(CO) ₃	1898, 1785, 1775 ^d	21
{HC(C(NPh)NHP) ₃ }W(CO) ₃ 4c	1869, 1756 ^e	this work

^a Acetonitrile solution. ^b Nujol. ^c KBr pellet. ^d Presence of *i*-Pr groups destroys planes of symmetry, hence splitting the E band into a doublet. ^e ATR technique. ^f Ligand abbreviations: pz = pyrazolyl, L = 1,4,7-tribenzyl-1,4,7-triazacyclononane, NCP = *N*-methyl-4-cyanopyridinium, *p*-NCC₅H₄NMe⁺.

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Table 4. Bond lengths (Å) and angles (°) of **4a**

Cr(1)-C(6)	1.809(4)	C(6)-Cr(1)-C(5)	83.69(19)	C(2)-N(1)-C(11)	131.9(4)
Cr(1)-C(5)	1.819(5)	C(6)-Cr(1)-C(7)	85.72(19)	C(2)-N(2)-C(21)	115.4(3)
Cr(1)-C(7)	1.823(5)	C(5)-Cr(1)-C(7)	85.63(19)	C(2)-N(2)-Cr(1)	121.2(3)
Cr(1)-N(4)	2.133(3)	C(6)-Cr(1)-N(4)	176.68(16)	C(21)-N(2)-Cr(1)	122.8(2)
Cr(1)-N(2)	2.138(3)	C(5)-Cr(1)-N(4)	98.30(16)	C(3)-N(3)-C(31)	126.2(3)
Cr(1)-N(6)	2.146(3)	C(7)-Cr(1)-N(4)	91.77(15)	C(3)-N(4)-C(41)	117.3(3)
N(1)-C(2)	1.366(5)	C(6)-Cr(1)-N(2)	95.21(16)	C(3)-N(4)-Cr(1)	121.7(3)
N(2)-C(2)	1.294(5)	C(5)-Cr(1)-N(2)	175.10(16)	C(41)-N(4)-Cr(1)	120.2(2)
N(3)-C(3)	1.358(5)	C(7)-Cr(1)-N(2)	99.06(16)	C(4)-N(5)-C(51)	121.1(3)
N(4)-C(3)	1.289(5)	N(4)-Cr(1)-N(2)	83.03(12)	C(4)-N(6)-C(61)	118.3(3)
N(5)-C(4)	1.368(5)	C(6)-Cr(1)-N(6)	99.97(15)	C(4)-N(6)-Cr(1)	120.5(3)
N(6)-C(4)	1.290(5)	C(5)-Cr(1)-N(6)	93.01(17)	C(61)-N(6)-Cr(1)	120.0(2)
O(1)-C(5)	1.171(5)	C(7)-Cr(1)-N(6)	173.98(17)	C(2)-C(1)-C(3)	110.6(3)
O(2)-C(6)	1.184(5)	N(4)-Cr(1)-N(6)	82.62(12)	C(2)-C(1)-C(4)	108.9(3)
O(3)-C(7)	1.168(5)	N(2)-Cr(1)-N(6)	82.47(13)	C(3)-C(1)-C(4)	110.3(3)
C(1)-C(2)	1.517(5)				
C(1)-C(3)	1.520(5)				
C(1)-C(4)	1.523(5)				

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Table 5. Crystallographic data of **2**, **3**, **4a**

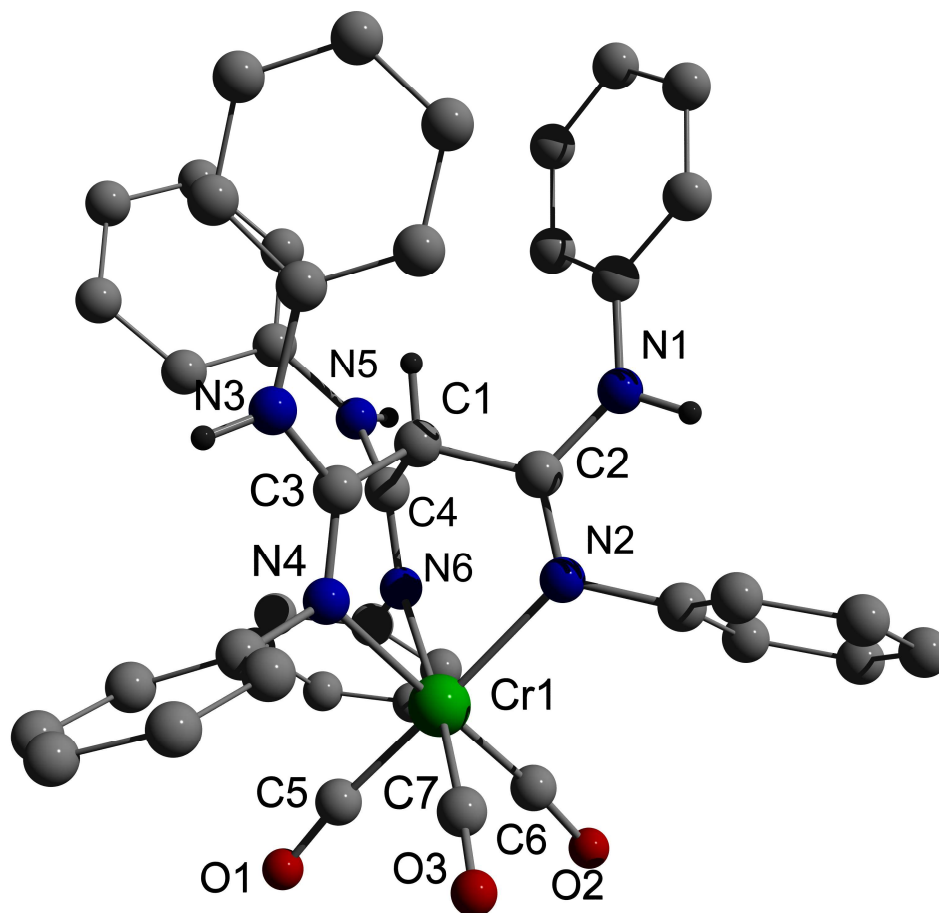
	2	3	4a
Empirical formula	C ₂₂ H ₄₈ Cl ₄ N ₆ Ni	C _{25.42} H _{52.88} Cl ₂ Cu ₂ N ₆ O _{0.86}	C ₄₇ H ₄₂ CrN ₆ O ₄
<i>M</i>	597.17	664.73	806.86
Crystal size [mm]	0.18 × 0.16 × 0.12	0.32 × 0.23 × 0.17	0.150 × 0.120 × 0.030
<i>T</i> [K]	100(1)	100(1)	180(1)
Crystal system	cubic	monoclinic	orthorhombic
Space group	<i>Pa</i> -3	<i>P2</i> ₁ / <i>n</i>	<i>Pna</i> 2 ₁
<i>a</i> [Å]	18.5823(18)	9.8688(3)	24.6646(14)
<i>b</i> [Å]	18.5823(18)	25.3571(7)	14.2926(7)
<i>c</i> [Å]	18.5823(18)	14.0716(4)	11.5541(7)
α [°]	90	90	90
β [°]	90	94.1590(10)	90
γ [°]	90	90	90
<i>V</i> [Å ³]	6416.5(11)	3512.06(18)	4073.1(4)
<i>Z</i>	8	4	4
<i>D</i> _{calc} [g · cm ⁻³]	1.236	1.257	1.316
μ (MoK α) [mm ⁻¹]	0.958	1.389	0.333
Transmissions	0.75/0.64	0.75/0.60	0.75/0.66
<i>F</i> (000)	2544	1385	1688
Index ranges	-25 ≤ <i>h</i> ≤ 25 -25 ≤ <i>k</i> ≤ 24 -22 ≤ <i>l</i> ≤ 17	-13 ≤ <i>h</i> ≤ 13 0 ≤ <i>k</i> ≤ 34 0 ≤ <i>l</i> ≤ 18	-31 ≤ <i>h</i> ≤ 31 -18 ≤ <i>k</i> ≤ 12 -14 ≤ <i>l</i> ≤ 14
θ _{max} [°]	29.48	28.73	27.169
Reflections collected	40041	52732	32293
Independent reflections	2961	8907	8839
<i>R</i> _{int}	0.0506	0.0312	0.0607
Refined parameter	100	310	522
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0296	0.0497	0.0443
<i>wR</i> ₂ [all data]	0.0813	0.1560	0.0961
χ (Flack)			0.016(12)
GooF	1.137	1.082	1.010
$\Delta\rho$ _{final} (max/min) [e · Å ⁻³]	0.387/-0.255	1.513/-0.809	0.311/-0.353

10

Graphical and textual abstract

C-H tautomeric methanetrissamidine **1a** either serves as tripodal *N,N,N*-chelating ligand or undergoes H-migration and formation of the N-H tautomeric form.

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