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Methanetrisamidines in coordination chemistry – syntheses, structures and CH–NH tautomerism†

Benjamin Gutschank, Stephan Schulz,* Dieter Bläser and Christoph Wölper

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Methanetrisamidines $\{HC[C(NR)NHR]_3\}$ (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 $\{[C(C(NH\text{-}i\text{-}Pr)_2)_3]^{2+}[NiCl_4]^{2-}\}$ **2**, whereas the reaction with CuCl gave $[C(C(N(i\text{-}Pr)CuCl)NH\text{i-}Pr)_2(C(NH\text{i-}Pr)_2)]$ **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 ligand 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. Hydridotris(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 intensively 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).

We recently reported on the synthesis of two C_3-symmetric methanetrisamidines 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.

Temperature dependent ^1H NMR spectroscopic studies of solutions of **1a–c** in different solvents (C_6D_6, CD_3CN) 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 of 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 $\{CH[C(N\text{i-Pr})_2AlR_2]_3\}$ (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 $\{C[C(N(\eta^3\text{-Ph}))N(Ph)ZnMe]_2\text{-}[C(N(Ph)MMe_2)_2]\}$ (M = Al, Ga).[10] Herein we report on our studies on the formation of coordination complexes utilizing the multiple coordinative imino sites of neutral methanetrisamidines.

Results and discussion

The reaction of **1a** with $NiCl_2(H_2O)_6$ in CH_3CN at 80 °C led to the formation of the dicationic trisamidinium salt $\{[C(C(NH\text{-}i\text{-}Pr)_2)_3]^{2+}[NiCl_4]^{2-}\}$ **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 trisamidine **1a**.

2 is insoluble in THF-d_8, acetonitrile-d_3 and even D_2O, hence preventing **2** from being characterised by NMR-spectroscopy. However, its structure was proven by X-ray

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University of Duisburg-Essen, Universitätsstr. 5–7, S07 S03 C30, 45117 Essen, Germany. E-mail: stephan.schulz@uni-due.de; Fax: Int (+)201 1833830; Tel: Int (+)201 1834635

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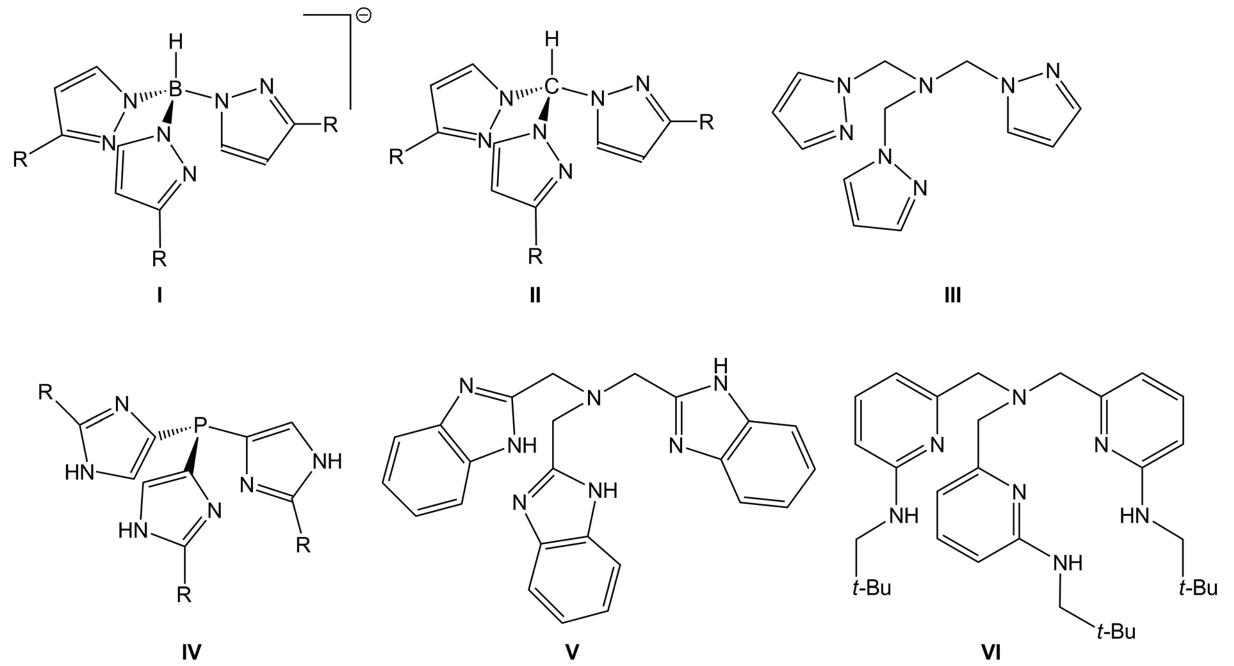
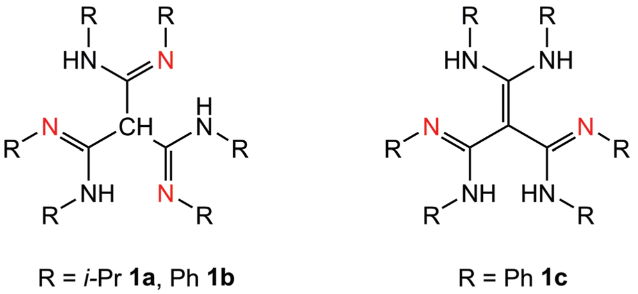


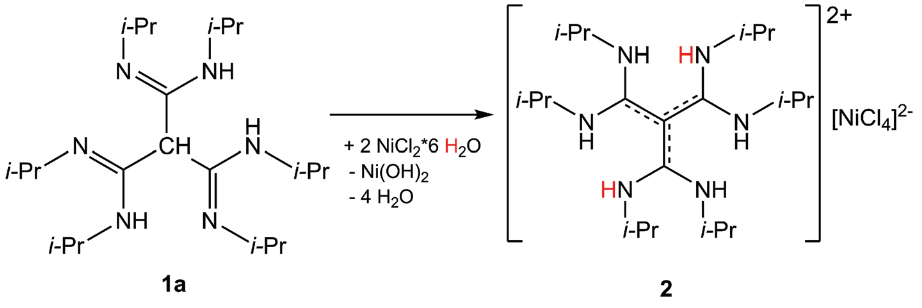
Scheme 1 Structures of C_3-symmetric tripodal ligands typically used in coordination chemistry.



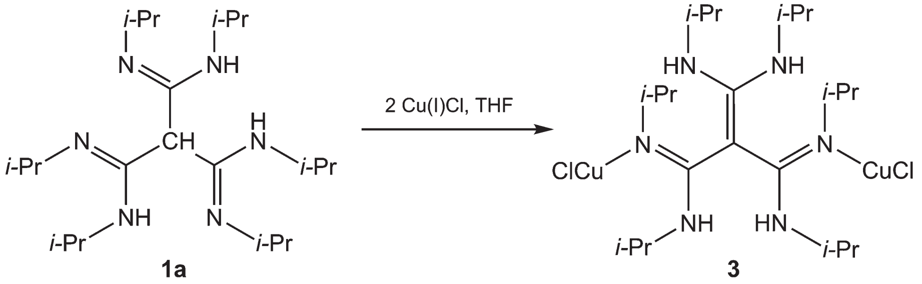
Scheme 2 *N*,*C*-Tautomeric methanetrisamidines; potentially basic coordinative imino sites are depicted in red.

crystallography. Single crystals of **3** were obtained upon storage of a solution of **2** in CH_3CN 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.

The structure of the dication $[C(C(NHi\text{-}Pr)_2)_3]^{2+}$ in **2** is similar to that of the $\{[C(C(NHPh)_2)_3]^{2+}$ dication, which 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 $CH[(CNHi\text{-}Pr)Ni\text{-}Pr]_3$ **1a** has obviously migrated to an imine centre, yielding the corresponding N–H tautomeric form. While the formation of the CH- and the NH-tautomers has previously been 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 hybridisation 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



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



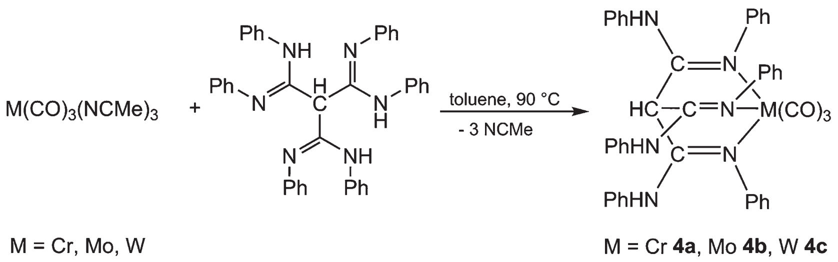
Scheme 4 Formation of **3** with formal tautomerization of **1a**.

observed in the dication in **2** is thus expected to be energetically favoured compared to a hypothetical sp^3-hybridised 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]

In order to suppress the strong tendency of the Lewis basic methanetrisamidine **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). ^{1}H and ^{13}C 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, the resonance due to the presence of the C–H moiety did not appear in the ^{1}H NMR spectrum of **3**.

Single crystals of **3** suitable for X-ray crystal analysis were obtained upon storage of a solution of **3** in THF at −30 °C. **3** crystallizes 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$_2$O)$_6$, 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 to 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-tautomeric form due to the migration of the C–H proton to an imino group. The central sp^2-hybridised carbon atom C1 in **3** binds to two amidine carbon atoms (C2, C3) and a methylendiamine moiety (C4). The C–C bond lengths in **3** are in between the typical values for C–C single and C═C double bonds, indicating a delocalised π-electron 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 lengths (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(l-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(hppSiMe$_3$) (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(PPh$_3$)$_2$Br(μ-3,5-Ph$_2$pz)-CuCl (Cu–N 1.86(3) Å, N–Cu–Cl 177.0(8)°),[14] and Cp(PPh$_3$)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.

The reactions of **1a** with NiCl$_2$(H$_2$O)$_6$ 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$_2$AlH, 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)$_3$CH-(C(NHPh)NPh)$_3$] (M = Cr **4a**, Mo **4b**, W **4c**; Scheme 5). The CH tautomeric form of **1b** is preserved and **1b** acts as a tripodal N,N,N-donor to a single metal centre. ^{1}H 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



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

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).

Orange crystals of **4a** suitable for a single-crystal X-ray analysis were obtained from a solution in THF upon storage at −30 °C for 5 days. **4a** crystallizes in the orthorhombic space group $Pna2_1$ 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 of 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 ν(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.* $[LCr(CO)_3][PF_6]$-dmf (Cr–C 1.817(4) Å, Cr–N 2.182(4) Å, C–O 1.172(5) Å),[20] $\{HC(CN(2\text{-i-Pr-Ph})Me)_3\}Cr(CO)_3$ (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]

Conclusions

Reactions of two methanetrisamidines **1a** and **1b** with different metal complexes were investigated. **1a** reacts with $NiCl_2(H_2O)_6$ with protonation of the Lewis-basic imine centres and with CuCl with formation of $[C(C(N(i\text{-}Pr)CuCl)NHi\text{-}Pr)_2\text{-}(C(NHi\text{-}Pr)_2)]$ **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 $[M(NCMe)_3(CO)_3]$ (M = Cr, Mo, W) resulted in the formation of *fac*-$[M(CO)_3CH(C(NHPh)\text{-}NPh)_3]$ (M = Cr **4a**, Mo **4b**, W **4c**) containing the central metal centres in an octahedral coordination mode. The methanetrisamidine ligand **1b** serves as a 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**[1] and $M(NCMe)_3(CO)_3$[27] were prepared according to literature methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal THF-d_8 (^{1}H: δ = 3.58; ^{13}C: δ = 67.4) and acetone-d_6 (^{1}H: δ = 2.04; ^{13}C: δ = 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.

$\{[C(C(NHi\text{-}Pr)_2)_3]^{2+}[NiCl_4]^{2-}\}$ 2

0.25 g (0.6 mmol) **1a** and 0.30 g (1.3 mmol) $NiCl_2(H_2O)_6$ 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 12 h upon storage at −10 °C. Yield: 0.21 g (55%). Mp.: >250 °C. Elemental analysis calculated (%) for $C_{22}H_{48}N_6Cl_4Ni$ (M = 597.16 g mol^{-1}): 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}.

{[C(C(HN*i*-Pr)$_2$)(C[N(CuCl)*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 °C. Filtration of the reaction mixture gave a yellowish solution, from which yellow crystals of **3** were formed within 5 days upon storage at −30 °C. Yield: 0.27 g (74%). Mp.: 117 °C (dec.). Elemental analysis calc. (%) for $C_{22}H_{46}N_6Cl_2Cu_2$ (M = 592.64 g mol^{-1}): H 7.82, C 44.59, N 14.18; found: H 7.63, C 44.83, N 13.89. ^{1}H-NMR (300 MHz, THF-d$_8$, 25 °C): δ 1.21 (m (broad), CH-(C*H*$_3$)$_2$), 5.02 (m (broad), C*H*(CH$_3$)$_2$). ^{13}C-NMR (75.5 MHz, THF-d$_8$, 25 °C): δ 19–23 (CH(*C*H$_3$)$_2$), 45 (*C*H(CH$_3$)$_2$), 85 (*C*(CN$_2$)$_3$), 159 (N*C*N). 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}.

{HC[C(NPh)NHPh]$_3$M(CO)$_3$} 4a–c

0.15 g **1c** (0.8 mmol) and 0.8 mmol M(NCMe)$_3$(CO)$_3$ were suspended in 15 mL of toluene. The reaction mixture was then heated to 90 °C for 4 h, upon which the reaction darkened and the products **4a–c** precipitated. After cooling, the reaction mixture was filtered off 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 °C for 5 days.

4a: yield: 0.14 g (76.1%). Mp.: >250 °C (dec.). Elemental analysis calc. (%) for $C_{43}H_{34}CrN_6O_3$ (M = 734.76 g mol^{-1}): H 4.66, C 70.29, N 11.44; found: H 4.57, C 69.80, N 11.25. ^{1}H-NMR (300 MHz, THF-d$_8$, 25 °C): δ 5.16 (s, 1H, *H*C(CN$_2$)$_3$), 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, N*H*). ^{13}C-NMR (75.5 MHz, THF-d$_8$, 25 °C): δ 43.9 (*C*H), 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}.

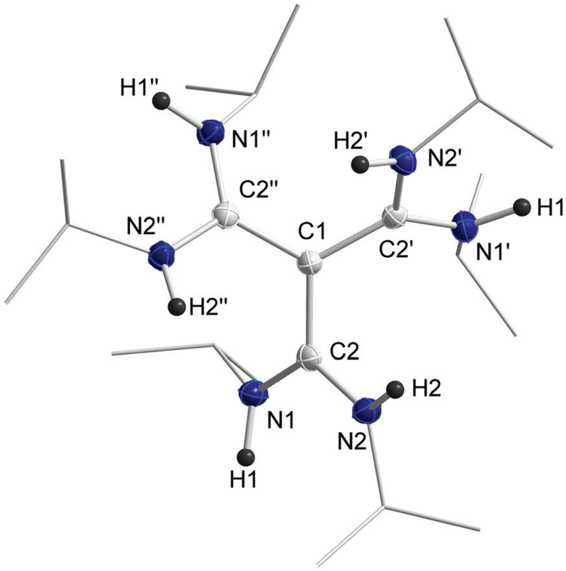


Fig. 1 Molecular structure of **2** (thermal ellipsoids at 50% probability levels, hydrogen atoms at arbitrary radii; *i*-Pr groups reduced to bonds and H atoms and the anion omitted for clarity).

4b: yield: 0.16 g (82.0%). Mp.: >250 °C (dec.). Elemental analysis calc. (%) for $C_{43}H_{34}MoN_6O_3$ (M = 778.73 g mol^{-1}): H 4.40, C 66.32, N 10.79; found: H 4.36, C 66.10, N 10.65. ^{1}H-NMR (300 MHz, THF-d$_8$, 25 °C): δ 5.01 (s, 1H, *H*C(CN$_2$)$_3$), 6.78 (m, 6H, Ar), 6.89 (m, 3H, Ar), 6.95 (m, 6H, Ar), 7.09

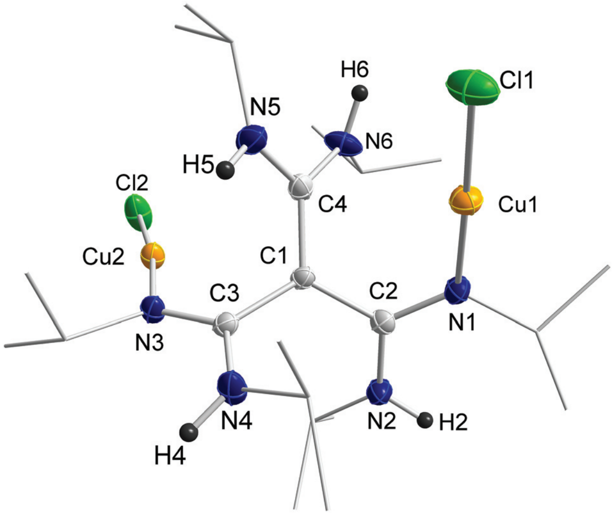


Fig. 2 Molecular structure of **3** (thermal ellipsoids at 50% probability levels, hydrogen atoms at arbitrary radii; *i*-Pr groups reduced to bonds and H atoms omitted for clarity).

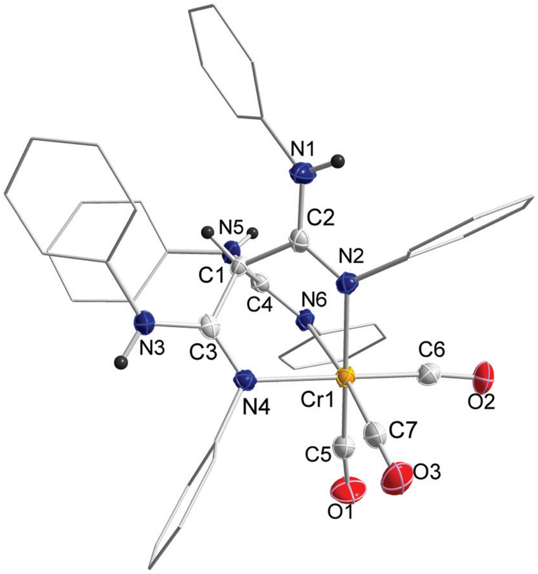


Fig. 3 Molecular structure of **4a** (thermal ellipsoids at 50% probability levels, hydrogen atoms at arbitrary radii; phenyl groups reduced to bonds and H atoms omitted for clarity).

Table 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 $-z + 1, x - 1/2, -y + 1/2$.

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(17)
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)

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

Complex[f]	ν(CO)/cm^{-1}	Ref.
$(Et_4N)[(HB(3,5\text{-}Me_2pz)_3Cr(CO)_3]$	1891, 1748[a]	17
$\{HC(pz)_3\}Cr(CO)_3$	1898, 1758[b]	18
$\{MeSi(3,5\text{-}Me_2pz)_3\}Cr(CO)_3$	1898, 1755[c]	19
$LCr(CO)_3$	1903, 1762[a]	20
$\{HC(CN(2\text{-i-Pr-Ph})Me)_3\}Cr(CO)_3$	1893, 1796, 1775[d]	21
$\{HC(C(NPh)NHPh)_3\}Cr(CO)_3$ **4a**	1881, 1757[e]	This work
$(NCP)[HB(pz)_3Mo(CO)_3]$	1882, 1736[c]	22
$\{HC(3,5\text{-}Me_2pz)_3\}Mo(CO)_3$	1900, 1760[b]	23
$\{MeSi(3,5\text{-}Me_2pz)_3\}Mo(CO)_3$	1896, 1755[c]	19
$LMo(CO)_3$	1907, 1768[a]	20
$\{HC(CN(2\text{-i-Pr-Ph})Me)_3\}Mo(CO)_3$	1897, 1787, 1776[d]	21
$\{HC(C(NPh)NHPh)_3\}Mo(CO)_3$ **4b**	1881, 1751[e]	This work
$\{MeSi(3,5\text{-}Me_2pz)_3\}W(CO)_3$	1887, 1747[c]	19
$LW(CO)_3$	1897, 1757[a]	20
$\{HC(CN(2\text{-i-Pr-Ph})Me)_3\}W(CO)_3$	1898, 1785, 1775[d]	21
$\{HC(C(NPh)NHPh)_3\}W(CO)_3$ **4c**	1869, 1756[e]	This work

[a] Acetonitrile solution. [b] Nujol. [c] KBr pellets. [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*-$NCC_5H_4NMe^+$.

(m, 3H, Ar), 7.21 (m, 6H, Ar), 7.33 (m, 6H, Ar), 7.62 (s, 3H, N*H*). ^{13}C-NMR (75.5 MHz, THF-d$_8$, 25 °C): δ 46.6 (*C*H), 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 °C (dec.). Elemental analysis calc. (%) for $C_{43}H_{34}WN_6O_3$ (M = 866.61 g mol^{-1}): H 3.95, C 59.60, N 9.70; found: H 3.88, C 59.55, N 9.61. ^{1}H-NMR (300 MHz, acetone-d$_6$, 25 °C): δ 5.33 (s, 1H, *H*C(CN$_2$)$_3$), 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, N*H*). ^{13}C-NMR (75.5 MHz, acetone-d$_6$, 25 °C): δ 46.8 (*C*H), 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 (MoKα radiation, λ = 0.71073 Å) at 150(1) K (**2**, **3**) and 141(2) K (**4a**), are summarized in Table 5. The solid-state structures of **2**, **3** and **4a** are shown in Fig. 1–3, bond lengths and angles of **2**, **3** and **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 the 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** were refined isotropically. The solvent molecule in **3** was only partially occupied.

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‡ The crystallographic data of **2**, **3** and **4a** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-971997 (**2**), CCDC-886453 (**3**) and CCDC-971998 (**4a**).

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)				

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

	2	**3**	**4a**
Empirical formula	$C_{22}H_{48}Cl_4N_6Ni$	$C_{25.42}H_{52.88}Cl_2Cu_2N_6O_{0.86}$	$C_{47}H_{42}CrN_6O_4$
M	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
T [K]	100(1)	100(1)	180(1)
Crystal system	Cubic	Monoclinic	Orthorhombic
Space group	$Pa\bar{3}$	$P2_1/n$	$Pna2_1$
a [Å]	18.5823(18)	9.8688(3)	24.6646(14)
b [Å]	18.5823(18)	25.3571(7)	14.2926(7)
c [Å]	18.5823(18)	14.0716(4)	11.5541(7)
α [°]	90	90	90
β [°]	90	94.1590(10)	90
γ [°]	90	90	90
V [Å^3]	6416.5(11)	3512.06(18)	4073.1(4)
Z	8	4	4
D_{calc} [g cm^{-1}]	1.236	1.257	1.316
μ(MoK$_\alpha$ [mm^{-1}])	0.958	1.389	0.333
Transmissions	0.75/0.64	0.75/0.60	0.75/0.66
F(000)	2544	1385	1688
Index ranges	$-25 \le h \le 25$	$-13 \le h \le 13$	$-31 \le h \le 31$
	$-25 \le k \le 24$	$0 \le k \le 34$	$-18 \le k \le 12$
	$-22 \le l \le 17$	$0 \le l \le 18$	$-14 \le l \le 14$
θ_{max} [°]	29.48	28.73	27.169
Reflections collected	40 041	52 732	32 293
Independent reflections	2961	8907	8839
R_{int}	0.0506	0.0312	0.0607
Refined parameters	100	310	522
R_1 [$I > 2\sigma(I)$]	0.0296	0.0497	0.0443
wR_2 [all data]	0.0813	0.1560	0.0961
x(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

Notes and references

1 S. Trofimenko, *J. Am. Chem. Soc.*, 1966, **88**, 1842–1844.

2 J. C. Calabrese, S. Trofimenko and J. S. Thompson, *J. Chem. Soc., Chem. Commun.*, 1986, 1122–1123; S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1987, **26**, 1507–1514.

3 H. R. Bigmore, S. C. Lawrence, P. Mountford and C. S. Tredget, *Dalton Trans.*, 2005, 635–651.

4 G. J. van Driel, W. L. Driessen and J. Reedijk, *Inorg. Chem.*, 1985, **24**, 2919–2925.

5 P. C. Kunz and W. Kläui, *Collect. Czech. Chem. Commun.*, 2007, **72**, 492–502.

6 A. G. Blackman, *Polyhedron*, 2005, **24**, 1–39.

7 J. C. Mareque-Rivas, R. Prabaharan and S. Parsons, *Dalton Trans.*, 2004, 1648–1655.

8 B. Gutschank, S. Schulz, M. Marcinkowski, G. Jansen, H. Bandmann, D. Bläser and C. Wölper, *Angew. Chem.*,

2012, **124**, 11051–11055, (*Angew. Chem. Int. Ed.*, 2012, **51**, 10893–10897).

9 (*a*) M. Münch, U. Flörke, M. Bolte, S. Schulz and D. Gudat, *Angew. Chem.*, 2008, **120**, 1535–1537, (*Angew. Chem. Int. Ed.*, 2008, **47**, 1512–1514); (*b*) S. Schmidt, S. Gondzik, S. Schulz, D. Bläser and R. Boese, *Organometallics*, 2009, **28**, 4371–4376; (*c*) S. Schmidt, B. Gutschank, S. Schulz, D. Bläser, R. Boese and C. Wölper, *Eur. J. Inorg. Chem.*, 2011, **28**, 4464–4470.

10 B. Gutschank, M. Bayram, S. Schulz, D. Bläser and C. Wölper, *Eur. J. Inorg. Chem.*, 2013, 5495–5502.

11 *Cambridge Structural Database, Version 5.34*, see also; F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380–388. Bonds were set to "any" type. The search yielded 38 hits with 53 bonds. The mean Cu–N bond length was found to be 1.909(61) Å (min 1.803 Å, max 2.102 Å).

12 J. M. Goodwin, P.-C. Chiang, M. Brynda, K. Penkina, M. M. Olmstead and T. E. Patten, *Dalton Trans.*, 2007, 3086–3092.

13 S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2004, **43**, 5168–5170.

14 J. P. Fackler Jr., R. G. Raptis and H. H. Murray, *Inorg. Chim. Acta*, 1992, **193**, 173–183.

15 V. Comte and H. Vahrenkamp, *J. Organomet. Chem.*, 2001, **627**, 153–158.

16 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313–348.

17 S. Trofimenko, *J. Am. Chem. Soc.*, 1969, **91**, 588–595.

18 S. Trofimenko, *J. Am. Chem. Soc.*, 1970, **92**, 5118–5126.

19 E. E. Pullen, D. Rabinovich, C. D. Incarvito, T. E. Concolino and A. L. Rheingold, *Inorg. Chem.*, 2000, **39**, 1561–1567.

20 T. Beissel, B. S. P. C. Della Vedova, K. Wieghardt and R. Boese, *Inorg. Chem.*, 1990, **29**, 1736–1741.

21 D. Barnes, G. L. Brown, M. Brownhill, I. German, C. J. Herbert, A. Jolleys, A. R. Kennedy, B. Liu, K. McBride, F. S. Mair, R. G. Pritchard, A. Sanders and J. E. Warren, *Eur. J. Inorg. Chem.*, 2009, 1219–1233.

22 T. M. Bockman and J. K. Kochi, *New J. Chem.*, 1992, **16**, 39–49.

23 I. K. Dhawan, M. A. Bruck, B. Schilling, C. Grittini and J. H. Enemark, *Inorg. Chem.*, 1995, **34**, 3801–3808.

24 H. Brunner, A. Winter and B. Nuber, *J. Organomet. Chem.*, 1998, **558**, 213–218.

25 F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851–1854.

26 *Cambridge Structural Database, Version 5.34*, see also; F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380–388. A search for a CrNNN fragment with "any" bonds and coordination number of Cr equal to 6 yielded 998 hits with 26 670 Cr–N bonds. Mean 2.055(66) Å, min 1.544 Å, max 2.67 Å.

27 (*a*) D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433–434; (*b*) H. Werner, K. Deckelmann and U. Schönenberger, *Helv. Chim. Acta*, 1970, **53**, 2002–2009.

28 SHELXS-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 467–473.

29 G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, Universität Göttingen, 1997. See also; G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.

30 PLATON/SQUEEZE: P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 194–201.