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Taming Copper(I) Cyanate and Selenocyanate with N-Heterocyclic Carbenes

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Taming Copper(I) Cyanate and Selenocyanate with N-Heterocyclic Carbenes

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This manuscript is dedicated to Dr John Reglinski and Dr Mark D. Spicer.

Abstract: The synthesis of N-heterocyclic carbene (NHC) adducts of copper(I) cyanate and copper(I) selenocyanate has been successfully achieved via the reaction of [Cu(NHC)Cl] with silver(I) cyanate and potassium selenocyanate respectively. Three copper(I) cyanate complexes [Cu(IXy)(NCO)] (**1**), [Cu(IPr)(NCO)] (**2**) and [Cu(SIPr)(NCO)] (**3**) [IXy = 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] have been prepared and fully characterised. The X-ray crystal structures reveal the three complexes to be monomeric species in which the cyanate ligand is end-on, N-bound. These complexes, represent the first examples of monomeric copper(I) cyanate complexes. In addition, the copper(I) selenocyanate species [Cu(IPr)(NCSe)]₂ (**4**) was prepared and fully characterised. The X-ray crystal structure reveals that a centrosymmetric dimer is formed with bridging selenocyanate ligands bound through both N and Se. This is in contrast to the monomeric structure observed in the previously reported and related complex [Cu(IPr)(NCS)]. Complex **4** represents a rare example of a stable dimeric adduct of copper(I) selenocyanate.

Introduction

Since the first reported synthesis of copper(I) cyanate in 1957^[1] there has only been one structurally characterized adduct of copper(I) cyanate reported in the literature. This is quite remarkable given the diverse range of copper(I) pseudohalide complexes that are known.^[2] The sole structurally characterized example in the literature is a polymeric pyrazine (pyz) adduct, [Cu(pyz)(μ-1,1-NCO)]_n, reported by Goher et al.^[3] This air stable species was prepared via the reaction of copper(I) cyanate with pyrazine in the presence of a concentrated solution of either sodium or potassium cyanate. The copper(I) centres exist in a distorted tetrahedral environment with the coordination sphere composed of two nitrogen atoms from the pyrazine ligands and two nitrogen atoms from the cyanate ligands. The cyanate ligands bridge μ-1,1-NCO (see scheme 1) between neighbouring copper(I) atoms. This report was followed up with a study on copper(I) dimethyldipicolinate (dmdp) complexes, in which a copper(I) dmdp complex containing a cyanate ligand was synthesised. While no conclusive evidence was provided as to the identity of the product, it was inferred from the IR data that the cyanate ligand was N-bound to the copper(I) centre.^[4] It is a similar story with copper(I) selenocyanate, the preparation of which, was first reported in 1974.^[5] The majority of copper(I) selenocyanate species reported exist as polymeric anions, a pertinent example being [WS₄(CuNCSe)₄]²⁻, which contains a

only discrete molecular copper(I) selenocyanate species to have been structurally characterized.^[7] Within the reported structures, the selenocyanate ligand, is commonly observed to coordinate in a bridging μ-1,3-NCSe mode (see scheme 1) between the copper(I) centres. More recently, copper(I) selenocyanate has been shown to have potential as a p-type semiconductor, therefore raising the profile of this species and related adducts.^[8]

Our own interest in this area focused initially on copper(I) thiocyanate and specifically on the synthesis of N-heterocyclic carbene (NHC) adducts.^[9] We successfully reported the synthesis and structural characterization of copper(I) thiocyanate adducts with three different NHC ligands (scheme 2). It was found that the steric bulk of the NHC ligand influenced the

Scheme 1. Possible coordination modes for cyanate and selenocyanate ligands.

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centrosymmetric double-bridged Cu₂(NCSe)₂ unit.^[5] The mixed valent cation [Cu^{II}Cu^I(phen)₃(CN){(Se,S)CN}]⁺ represents the

structural motif observed. A dimeric solid state structure was obtained when IMes and IXy were used while the bulkier IPr ligand resulted in a monomeric solid state structure being obtained. In the dimeric structures the thiocyanate ligands bridge end-to-end (μ -1,3-NCS) between the copper(I) atoms while in the monomeric structure the thiocyanate ligand is coordinated in terminal mode (-NCS) to the copper(I) atom. Related to our studies, Nolan et al have also illustrated, that, starting from [Cu(IPr)OH], a number of interesting compounds can be prepared, including the cyanide containing species [Cu(IPr)CN].^[10] We decided to explore if copper(I) cyanate and copper(I) selenocyanate could be stabilized by NHC ligands by utilizing the same synthetic strategy as that employed during the synthesis of NHC complexes of copper(I) thiocyanate.

Scheme 2. Previously reported copper(I) thiocyanate complexes.

Herein we report the successful synthesis and structural characterization of three NHC copper(I) cyanate complexes and one NHC copper(I) selenocyanate complex. During the study four different NHC ligands were used namely 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene (IXy), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), and 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (SIPr).

Results and Discussion

The synthesis of [Cu(IXy)(NCO)] (**1**), [Cu(IPr)(NCO)] (**2**) and [Cu(SIPr)(NCO)] (**3**) proceeded via the reaction of the corresponding [Cu(NHC)Cl] complex with a small excess of silver(I) cyanate in dichloromethane at ambient temperature (scheme 3). Near quantitative yields could be obtained after allowing the reaction mixture to stir overnight followed by a

Scheme 3. Synthetic routes to copper(I)-NHC cyanate (top) and copper(I)-NHC selenocyanate (bottom) complexes.

simple work-up. The initial success of the reactions could be determined by FT-IR, with the presence of a $\nu_a(\text{NCO})$ band indicating that a cyanate group was coordinated to the copper(I) centre. However, in contrast to the related thiocyanate ligand, it is difficult to assign the coordination mode (N-bound, O-bound, bridging) of the cyanate ligand from the FT-IR spectrum. The FT-IR spectra for **1-3** were similar with all three displaying a strong IR band attributable to $\nu_a(\text{NCO})$ at 2228 (complex **1**), 2233 (complex **2**) and 2224 cm^{-1} (complex **3**). These values are in good agreement with other reported M-NCO species.^[11] In addition all three displayed a weaker shoulder in the range 2170–2176 cm^{-1} . Further evidence for the preparation of cyanate complexes was provided by NMR spectroscopy, with ^1H and ^{13}C NMR providing evidence that only one species was present in solution. Furthermore ^{13}C NMR spectroscopy confirmed the presence of a cyanate group, with the observation of a broad resonance that can be attributed to NCO at 125.7 (complex **1**), 125.9 (complex **2**) and 125.8 ppm (complex **3**). The chemical shift values compare well with other reported cyanate complexes.^[12] Definitive evidence as to the identity of the products was provided by single-crystal X-ray diffraction (SXD). Crystals were readily grown via the vapour diffusion of n-hexane into a chloroform solution of the product.

The structure of **1** (Figure 1) was revealed to be monomeric, in which the copper(I) centre is 2-coordinate with linear geometry ($\text{C}_{\text{carbene}}\text{-Cu-N} = 179.79(15)^\circ$). Each molecule of **1** has crystallographically imposed mirror symmetry ($Z' = 0.5$) with the mirror plane passing through the Cu centre, the carbene C and the anion. The $\text{C}_{\text{carbene}}\text{-Cu}$ bond length is 1.867(4) Å, which is shorter than the chloride precursor (1.887(2) Å) but comparable (1.866(4) Å) to the related thiocyanate species [Cu(IPr)(NCS)].^[9] The Cu-N bond length is 1.810(4) Å which, as expected, is significantly shorter than the corresponding bond in the previously reported [Cu(pyz)(μ -1,1-NCO)]_n (Cu-N = 2.035(3)/2.101(3) Å).^[3] To the best of our knowledge there are no examples reported in the crystallographic database of end-on, N-bonded copper(I) cyanate adducts. The cyanate ligand is only slightly distorted from linear geometry as evidenced by the N-C-O bond angle of 178.0(7)°. Additionally the cyanate ligand deviates only slightly from a linear orientation with respect to the copper-carbon bond with a $\text{Cu-N}_{\text{cyanate}}\text{-C}_{\text{cyanate}}$ bond angle of 176.2(4)°. Important bond lengths and angles for complexes **1-3** are shown in table 1.

Figure 1. Ortep plot of [Cu(IXy)(NCO)] (**1**). Ellipsoids are represented at 30% probability levels. Hydrogen atoms are omitted for clarity.

The molecular structure of **2** is also monomeric with a 2-coordinate copper(I) centre. There is a small but experimentally significant distortion from ideal linear geometry in **2** when compared with **1**, as evidenced by the $C_{\text{carbene}}\text{-Cu-N}$ bond angle, which measures $178.08(13)^\circ$. The $C_{\text{carbene}}\text{-Cu}$ bond length is $1.880(2)$ Å which is slightly longer than both **1** and the related complexes [Cu(IPr)(NCS)]^[9] and [Cu(IPr)(CN)]^[10]. The Cu-N bond length is $1.817(2)$ Å, which compares well to the equivalent

Figure 2. Ortep plot of [Cu(SIPr)(NCO)] (**3**). Ellipsoids are represented at 30% probability levels. Hydrogen atoms are omitted for clarity.

distance reported for **1**. The N-C-O bond angle is comparable with **1** at $178.9(4)^\circ$ while the $C_{\text{cyanate}}\text{-N}_{\text{cyanate}}\text{-Cu}$ angle is $175.3(2)^\circ$.

The molecular structure of saturated **3** (Figure 2) is, as would be expected, broadly analogous to that of unsaturated **2**. The $C_{\text{carbene}}\text{-Cu}$ bond length is $1.890(2)$ Å and the Cu-N bond length is $1.818(2)$ Å, both of which compare well to the equivalent values in **1** and **2**. Furthermore the $C_{\text{carbene}}\text{-Cu-N}$ bond angle is $176.63(14)^\circ$ which although more distorted from ideal linear geometry than **2**, still compares well. As with **1**, the structure of **3** has crystallographic mirror symmetry, $Z' = 0.5$. A more noticeable difference is the $C_{\text{cyanate}}\text{-N}_{\text{cyanate}}\text{-Cu}$ bond angle which measures $162.1(3)^\circ$ and is significantly less linear than the corresponding angles in complexes **1** and **2**. Figure 3 illustrates this difference. This difference may be as a consequence of the packing interactions that occur between neighbouring molecules. Both **1** and **2** feature short O contacts with the C-H bonds of the carbene backbone. These contacts form the basis of essentially linear extended structural motifs as illustrated in Figure 4. However, **3** forms a different extended structure based on four short C-H...O interactions that occur between the oxygen of the cyanate ligand and the hydrogen atoms of methyl and methylene groups of two neighbouring molecules. These combine to give a 2-dimensional network that does not contain the simple linear arrangements seen in **1** and **2** (Figure 5).

The three complexes reported are the first examples of NHC complexes of copper(I) cyanate and more importantly they represent the first examples of stable monomeric adducts of copper(I) cyanate.

Figure 3. View through the heterocycle plane illustrating the difference in $C_{\text{cyanate}}\text{-N}_{\text{cyanate}}\text{-Cu}$ bond angles between complexes **2** and **3**.

Figure 4. Illustration of the linear extended structural motif observed in **1**.

Figure 5. Illustration of the 2-dimensional network observed in complex **3**.

Having established that copper(I) cyanate could be stabilized by NHC ligands via a straightforward benchtop synthesis it was decided to investigate the possibility that the same methodology could be deployed for the synthesis of NHC adducts of copper(I) selenocyanate. The synthesis of [Cu(IPr)(NCSe)]₂ (**4**) proved possible through the room temperature reaction of [Cu(IPr)Cl] with potassium selenocyanate in dichloromethane (scheme 3). It would appear that an appreciable amount of degradation occurs

during the reaction as evidenced by the red solid (elemental selenium) that forms during this reaction. Switching to inert atmosphere techniques did not appear to remedy the situation and as such, complex **4** could only be produced in moderate yield. As was the case with both the cyanate and thiocyanate reactions the initial success of the reaction could be determined by FT-IR with the CN stretching frequency indicating the presence of the selenocyanate ligand. In the case of **4** a strong stretching band was observed at 2119 cm^{-1} with a weaker shoulder also present at 2084 cm^{-1} . The ^{13}C NMR spectrum displayed a broad resonance at 122.31 ppm which could be attributed to SeCN and this compared well to literature values for N-bound selenocyanate ligands.^[12] An SXD study revealed the solid state structure of **4** to be a dimer with crystallographically imposed centrosymmetry ($Z' = 0.5$). The two central copper(I) atoms are bridged by two selenocyanate ligands with one IPr ligand capping each copper(I) atom (Figure 6). The copper(I) atoms display distorted trigonal planar geometry with $\text{C}_{\text{carbene}}\text{-Cu-N}$, $\text{C}_{\text{carbene}}\text{-Cu-Se}$ and Se-Cu-N bond angles of $129.67(9)^\circ$, $126.77(7)^\circ$ and $103.37(6)^\circ$ respectively. The $\text{C}_{\text{carbene}}\text{-Cu}$ bond

Figure 6. Ortep plot of $[\text{Cu}(\text{IPr})(\text{NCSSe})]_2$ (**4**). Ellipsoids are represented at 30% probability levels. Hydrogen atoms are omitted for clarity.

length is $1.904(2)\text{ \AA}$ which compares well to the equivalent bond in the related thiocyanate complex $[\text{Cu}(\text{IMes})(\text{NCS})]_2$ which displayed a $\text{C}_{\text{carbene}}\text{-Cu}$ bond length of $1.902(2)\text{ \AA}$. The Cu-N and Cu-Se bond lengths are $1.939(2)\text{ \AA}$ and $2.399(4)\text{ \AA}$ respectively. The Cu-N bond lengths are approximately $0.12\text{ \AA}$ longer than in the monomeric NCO complexes **1** to **3**, but compare well to the distances reported in both $[\text{WS}_4(\text{CuNCS})_4]^{2-}$ ^[7] ($1.944\text{--}2.030\text{ \AA}$) and $[\text{Cu}(\text{CN})(\text{SeCN})]_2^{2-}$ ^[13] ($2.026\text{--}2.033\text{ \AA}$). The Cu-Se bond distances are shorter for complex **4** especially when compared to $[\text{Cu}(\text{CN})(\text{SeCN})]_2^{2-}$ ($2.613\text{--}2.649\text{ \AA}$). The selenocyanate ligand is close to linear with a N-C-Se bond angle of $178.3(2)^\circ$. Perhaps of greater interest, is the difference observed in the solid state structures between **4** and the previously reported IPr adduct of copper(I) thiocyanate. Looking at relevant sulfur analogues, the complex $[\text{Cu}(\text{IPr})(\text{NCS})]$ and the previously unreported $[\text{Cu}(\text{SiPr})(\text{NCS})]$ (**5**) are monomeric in comparison to the IMes, IXy and previously unreported SIMes (**6**) adducts which display dimeric structures, similar to that of **4**. This difference in solid state structure was previously attributed to differences in the steric bulk of the NHC ligands used, with the bulkier IPr and SiPr ligands precluding the formation of a dimer.^[9] The structure of complex **4** was therefore expected to

display a monomeric structure in keeping with these previous observations. The reasons for this difference in the solid state structure of the thiocyanate system versus the selenocyanate system are still unclear. Efforts to answer this question have firstly centered around the synthesis of further NHC complexes of copper(I) selenocyanate. However attempts at generating both the IXy and IMes analogues have so far proven unsuccessful with NMR spectroscopic data suggesting the presence of two species in solution. FT-IR data does however indicate the presence of a CN stretching band with comparable values to those observed for complex **4**. Important bond lengths and angles for complex **4** are shown in Table 1.

Conclusions

Sixty years on from the original report on the synthesis of copper(I) cyanate the first examples of SXD structures of simple monomeric adducts have been reported. Three NHC copper(I) cyanate complexes have been synthesised via the reaction of $[\text{Cu}(\text{IXy})\text{Cl}]$, $[\text{Cu}(\text{IPr})\text{Cl}]$ and $[\text{Cu}(\text{SiPr})\text{Cl}]$ with equimolar quantities of silver cyanate. For all three reactions, complexes with the general formula $[\text{Cu}(\text{NHC})(\text{NCO})]$ were isolated, in which the copper(I) centre exists in a linear coordination environment with the cyanate ligand coordinating end-on and N-bound. In addition, the first NHC adduct of copper(I) selenocyanate has also been reported, with the reaction of $[\text{Cu}(\text{IPr})\text{Cl}]$ and potassium selenocyanate resulting in the isolation of the dimeric species $[\text{Cu}(\text{IPr})(\text{NCS})]_2$. Within the centrosymmetric dimer the copper(I) atoms display distorted trigonal planar geometry with the selenocyanate ligands bridging ($\mu\text{-}1,3\text{-NCSe}$ mode) between the copper(I) centres. The dimeric structure observed with selenocyanate is in contrast to the monomeric structure observed with thiocyanate, in the previously reported $[\text{Cu}(\text{IPr})(\text{NCS})]$. The complexes generated, aside from being rare examples of adducts of copper(I) cyanate and selenocyanate, also serve to expand the library of known mononuclear^[10, 14] and dinuclear^[14, 15] copper(I) NHC complexes. Current efforts are directed towards the preparation of selenocyanate complexes with other NHC ligands, which to date, we have been unable to isolate.

Experimental Section

General Information: Imine,^[16] amine,^[17] imidazolium chloride,^[16] imidazolium chloride^[18] and $[\text{Cu}(\text{NHC})\text{Cl}]$ ^[19] precursors were prepared according to published literature methods. All other chemicals were obtained commercially and used without further purification.

Spectroscopic Methods: ^1H and ^{13}C spectra were obtained with a Bruker 400 MHz spectrometer. CDCl_3 was passed through basic alumina to remove traces of HCl prior to use. FT-IR spectra were recorded on an Agilent 5500 series spectrometer or a Perkin Elmer Spectrum One spectrometer. Elemental analyses were carried out at the University of Strathclyde and University of Glasgow.

X-ray Crystallography: Crystallographic measurements for complexes **1-3**, **5** and **6** used Oxford Diffraction instruments and monochromated radiation. Crystallographic measurements for complex **4** were performed by the UK National Crystallography Service using a Rigaku AFC12 rotating anode source.^[20] All structures were refined to convergence

against F^2 using all unique reflections and the program SHELXL-2014.^[21] Hydrogen atoms were placed in geometric positions and refined in riding modes. One propyl group in the structure of **2** was modelled as disordered over two sites. Appropriate restraints were applied to the bond length and displacement parameters of this disordered group. Selected crystallographic data and refinement parameters for **1** to **4** are given in Table 2 and parameters for **5** and **6** are given in the ESI.

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1911070 to 1911075 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

[Cu(IXy)(NCO)] (1): [Cu(IXy)Cl] (252 mg, 0.67 mmol) was dissolved in dichloromethane (7 mL). To this was added silver cyanate (103 mg, 0.69 mmol) and the mixture was stirred for 24 h. The colourless solution was filtered by gravity through glass wool/Celite to remove silver chloride and any unreacted silver cyanate. The filtrate was reduced to dryness using a rotary evaporator, yielding an off-white powder. Yield 224 mg, 88% (based on [Cu(IXy)Cl]). Crystals suitable for X-ray diffraction were grown by dissolving 30 mg of the product in chloroform (0.8 mL) and vapour diffusing with n-hexane. **¹H NMR** (400.1 MHz, CDCl₃): δ = 2.15 (s, 12 H, CH₃), 7.10 (s, 2 H, C=CH), 7.22 (d, 4 H, *meta*-CH, $^3J_{\text{HH}}$ = 7.7 Hz), 7.33 (t, 2 H, *para*-CH, $^3J_{\text{HH}}$ = 7 Hz). **¹³C {¹H} NMR** (100.6 MHz, CDCl₃): δ = 17.76 (CH₃), 122.29 (NC=CN), 125.73 (NCO), 128.84 (Ar-C_{3,5}), 129.68 (Ar-C₄), 134.81 (Ar-C_{2,6}), 137.38 (Ar-C₁), 178.54 (NCN). C₂₀H₂₀N₃OCu: calcd. C 62.92; H 5.24; N 11.01%; found. C 62.73; H 5.11; N 10.99%. **ATR FT-IR:** 2228, 2171 (NCO) cm⁻¹.

[Cu(IPr)(NCO)] (2): [Cu(IPr)Cl] (250 mg, 0.51 mmol) was dissolved in dichloromethane (4 mL). To this was added silver cyanate (80 mg, 0.53 mmol) and the mixture was stirred for 24 h. The colourless solution was filtered by gravity through glass wool/Celite to remove silver chloride and any unreacted silver cyanate. The filter cake was washed with an additional aliquot of dichloromethane (1 mL). The filtrate was reduced to dryness using a rotary evaporator, yielding an off-white powder. Yield: 245 mg, 97% (based on [Cu(IPr)Cl]). Crystals suitable for X-ray diffraction were grown by dissolving 37 mg of product in CDCl₃ (0.7 mL) and vapour diffusing with n-hexane. **¹H NMR** (400.1 MHz, CDCl₃): δ = 1.22 (d, 12 H, CH₃, $^3J_{\text{HH}}$ = 6.8 Hz), 1.27 (d, 12 H, CH₃, $^3J_{\text{HH}}$ = 6.8 Hz), 2.53 (sept, 4 H, CH(CH₃)₂, $^3J_{\text{HH}}$ = 6.8 Hz), 7.13 (s, 2 H, C=CH), 7.30 (d, 4 H, *meta*-CH, $^3J_{\text{HH}}$ = 8 Hz), 7.51 (t, 2 H, *para*-CH, $^3J_{\text{HH}}$ = 8 Hz). **¹³C {¹H} NMR** (100.6 MHz, CDCl₃): δ = 23.97 (CH₃), 24.83 (CH₃), 28.83 (CH(CH₃)₂), 123.34 (Ar-C₄), 124.32 (Ar-C_{3,5}), 125.91 (NCO), 130.72 (NC=CN), 134.41 (Ar-C₁), 145.65 (Ar-C_{2,6}), 180.57 (NCN). C₂₈H₃₈N₃OCu: calcd. C 68.10; H 7.29; N 8.51%; found. C 67.71; H 7.20; N 8.50%. **FT-IR (KBr disk):** 2233, 2176 (NCO) cm⁻¹.

[Cu(SIPr)(NCO)] (3): [Cu(SIPr)Cl] (90 mg, 0.18 mmol) was dissolved in dichloromethane (3 mL). To this was added silver cyanate (40 mg, 0.27 mmol) and the mixture was stirred for 24 h. The colourless solution was filtered by gravity through glass wool/Celite to remove silver chloride and unreacted silver cyanate. The filter cake was washed with an additional aliquot of dichloromethane (1 mL). The filtrate was taken to dryness using a rotary evaporator, yielding an off-white powder. Yield 85 mg, 95% (based on [Cu(SIPr)Cl]). Crystals suitable for X-ray diffraction were grown by dissolving 39 mg of product in CDCl₃ (0.7 mL) and vapour diffusing with n-hexane. **¹H NMR** (400.1 MHz, CDCl₃): δ = 1.34 (d, 12 H, CH₃, $^3J_{\text{HH}}$ = 6.8 Hz), 1.35 (d, 12 H, CH₃, $^3J_{\text{HH}}$ = 6.8 Hz), 3.04 (sept, 4 H, CH(CH₃)₂, $^3J_{\text{HH}}$ = 6.8 Hz), 4.02 (s, 4 H, H₂C-CH₂), 7.26 (d, 4 H, *meta*-CH, $^3J_{\text{HH}}$ = 7.2 Hz), 7.43 (t, 2 H, *para*-CH, $^3J_{\text{HH}}$ = 7.6 Hz). **¹³C {¹H} NMR** (100.6 MHz, CDCl₃): δ = 23.99 (CH₃), 25.48 (CH₃), 29.00 (CH(CH₃)₂), 53.82 (NC-CN), 124.66 (Ar-C_{3,5}), 125.82 (NCO), 130.02 (Ar-C₄), 134.39 (Ar-C₁), 146.72 (Ar-C_{2,6}), 203.33 (NCN). C₂₈H₃₈N₃OCu: calcd. C 67.82; H

7.66; N 8.47%; found. C 67.44; H 7.41; N 8.45%. **FT-IR (KBr disk):** 2224, 2170 (NCO) cm⁻¹.

[Cu(IPr)(NCSe)]₂ (4): [Cu(IPr)Cl] (181 mg, 0.37 mmol) was dissolved in dichloromethane (4 mL). To this was added potassium selenocyanate (58 mg, 0.4 mmol) and the mixture was stirred for 19 h. After this time the initially colourless mixture had turned red with the formation of a red precipitate. The mixture was filtered by gravity through glass wool/Celite to remove all insoluble material, resulting in the isolation of a faint peach coloured filtrate. The filtrate was taken to dryness using a rotary evaporator, yielding an off-white powder. Yield 135 mg, 66% (based on [Cu(IPr)Cl]). Crystals suitable for X-ray diffraction were grown by dissolving the product in chloroform and vapour diffusing with n-hexane. **¹H NMR** (400.1 MHz, CDCl₃): δ = 1.18 (d, 12 H, CH₃, $^3J_{\text{HH}}$ = 7.2 Hz), 1.23 (d, 12 H, CH₃, $^3J_{\text{HH}}$ = 6.8 Hz), 2.49 (sept, 4 H, CH(CH₃)₂, $^3J_{\text{HH}}$ = 6.8 Hz), 7.09 (s, 2 H, C=CH), 7.27 (d, 4 H, *meta*-CH, $^3J_{\text{HH}}$ = 7.6 Hz), 7.48 (t, 2 H, *para*-CH, $^3J_{\text{HH}}$ = 7.6 Hz). **¹³C {¹H} NMR** (100.6 MHz, CDCl₃): δ = 24.15 (CH₃), 24.66 (CH₃), 28.79 (CH(CH₃)₂), 122.31 (NCSe), 123.20 (NC=CN), 124.29 (Ar-C_{3,5}), 130.64 (Ar-C₄), 134.54 (Ar-C₁), 145.59 (Ar-C_{2,6}), 181.52 (NCN). C₅₆H₇₂N₆Se₂Cu₂: calcd. C 60.40; H 6.47; N 7.55%; found. C 60.72; H 6.53; N 6.50%. **FT-IR (KBr disk):** 2119, 2084 (NCSe) cm⁻¹.

Supporting Information: FT-IR, ¹H and ¹³C {¹H} NMR data for complexes **1** to **4** are given. In addition the X-ray diffraction data for complexes **5** and **6** is also available.

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Keywords: Copper • Carbene ligands • N, O ligands • X-ray diffraction • NMR spectroscopy

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Table 1. Selected bond lengths (Å) and angles (°) in complexes **1-4**.

Complex	C-Cu	Cu-N	Cu-Se	C-Cu-N	C-Cu-Se	N-C-	Cu-N-C
1	1.867(4)	1.810(4)	n/a	179.79(15)	n/a	178.0(7)	176.2(4)
2	1.880(2)	1.817(2)	n/a	178.9(4)	n/a	178.9(4)	175.3(2)
3	1.890(2)	1.818(3)	n/a	176.63(14)	n/a	178.3(4)	162.1(3)
4	1.902(2)	1.939(2)	2.399(4)	129.67(9)	126.77(7)	178.3(2)	162.19(19)

Table 2. Crystallographic data for complexes **1-4**.

	1	2	3	4
Formula	C ₂₀ H ₂₀ CuN ₃ O	C ₂₈ H ₃₆ CuN ₃ O	C ₂₈ H ₃₈ CuN ₃ O	C ₅₆ H ₇₂ Cu ₂ N ₆ Se ₂
M	381.93	494.14	496.15	1114.19
Crystal system	monoclinic	orthorhombic	orthorhombic	triclinic
Space group (no.)	P2 ₁ /m	P2 ₁ 2 ₁ 2 ₁	Pnma	P-1
<i>a</i> / Å	6.0066(6)	10.5093(3)	17.2285(7)	9.3895(4)
<i>b</i> / Å	15.5194(12)	10.9319(3)	20.6200(9)	10.9745(4)
<i>c</i> / Å	9.7426(10)	23.6245(6)	7.8086(3)	14.0542(5)
α / °	90	90	90	101.181(3)
β / °	91.913(10)	90	90	90.311(3)
γ / °	90	90	90	105.620(4)
<i>U</i> / Å ³	907.69(15)	2714.14(13)	2774.0(2)	1365.71(10)
<i>Z</i>	2	4	4	1
Temp. / K	293(2)	123(2)	123(2)	100(2)
λ / Å	0.71073	1.5418	1.5418	0.71073
μ / mm ⁻¹	1.215	1.302	1.274	2.152
<i>F</i> (000)	396	1048	1056	576
θ_{max} / °	27.49	73.04	70.98	27.48
Total number reflections	4169	8899	12088	27022

R_{int}	0.0395	0.0235	0.0346	0.0991
Unique reflections	2063	5206	2761	6245
Observed reflections	1498	5000	2361	5069
No. of params.	123	318	161	306
$R_1, wR_2 [I > 2\sigma(I)]$	0.0477, 0.1084	0.0315, 0.0838	0.0399, 0.1013	0.0426, 0.0977
R_1, wR_2 (all data)	0.0717, 0.1273	0.0330, 0.0851	0.0483, 0.1093	0.0562, 0.1024
GOF	1.037	1.039	1.029	1.076

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