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Stoichiometric sensitivity and structural diversity in click-active copper(I) N,S-heterocyclic carbene complexes†

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A series of novel Cu(I) N,S-heterocyclic carbene (NSHC) complexes $[Cu(\mu\text{-}Br)(NSHC)]_2$, $[Cu(\mu\text{-}X)(NSHC)]_4$ (X = Br or I), $[(NSHC)_2Cu(\mu\text{-}Br)_2Cu(NSHC)]$, and $[(NSHC)_2CuBr]$ have been isolated from *in situ* generated CuO^{t}Bu and N-substituted benzothiazolium halides and characterized by X-ray crystallography. Five structural motifs were observed, *viz.* M_xL_y where $x : y$ = 2 : 2, 4 : 4, 2 : 3, 1 : 2 and 2 : 4, with Cu···Cu separation traversing over a wide range of 2.5626(7) to 3.4725(7) Å distances. A preliminary investigation of the catalytic activity of these compounds indicated that the unusual mononuclear complex **6** $[(NSHC)_2CuBr]$ is an active catalyst for the Huisgen 1,3-dipolar cycloaddition of azide and alkynes while complexes **1–5** and **7** were marginally less active.

Introduction

Copper N-heterocyclic carbene (NHC) complexes are an efficient and economical class of catalysts for a range of important C–C, C–H and C–N bond forming reactions of unsaturated substrates.[1–4] Investigations have concentrated on copper N,N-heterocyclic carbene (NNHC) catalysts, while copper N,S-heterocyclic carbenes (NSHC) have received little attention, and there are relatively few published X-ray crystal structures. We previously prepared[5] NSHC complexes of Ni, Cu, Au, Ru, Pd and Pt and demonstrated subtle differences in reactivity of Pd(II)-NHSC catalyzed Suzuki coupling reactions.[6] This difference may reflect the stronger metal–carbene bond that results from a decreased carbenoid carbon stabilizing ability of S relative to N and therefore increased π back donation from capable metals. This delicate electronic influence is manifest in the formation of a Pt(II)-NSHC complex of stereochemistry opposite to that of a comparable Pt(II)-NNHC complex.[7]

We have previously reported the isolation of an unusual bridging complex of Cu(I) with a close Cu···Cu contact.[8] This finding suggested a hitherto unknown intramolecular migration of NHC across neighboring metal centers. The passage of the ligand presumably requires an expandable and reversible coordination state. As an extension of that study and of our previous metal-NSHC work, we herein report a series of Cu(I)-NSHC complexes that exhibit a remarkable range of stoichiometry dependent coordination geometries, as determined by X-ray crystallography. Preliminary studies indicate that these complexes are promising catalysts for the Huisgen 1,3-dipolar cycloaddition of azides to alkenes.

Experimental

General procedures

All experiments were performed under an inert Ar atmosphere using a Labmate glove box or by Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled over benzophenone sodium-ketyl and kept under Ar. Acetone and dichloromethane were distilled over molecular sieves and $CaCl_2$ respectively and stored under Ar. Benzothiazole was purchased from Sigma-Aldrich and distilled prior to use. Allyl bromide, propyl bromide, crotyl bromide, iodomethane and allyl iodide, NaO^{t}Bu and CuCl were purchased from Sigma-Aldrich and used as received. Phenylacetylene was purchased from Acros and used as received. CuO^{t}Bu was prepared according to literature methods.[9] ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AMX 500 spectrometers using Me_4Si as an internal

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† Electronic supplementary information (ESI) available: Table S1 Selected bond lengths (Å) for **1–7**. Table S2 Selected crystal data, data collection and refinement parameters of compounds **1–7**. CCDC 952963–952971. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52059e

standard. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

Synthesis of complexes 1–7

Preparation of [Cu(μ-Br)(NSCH)]$_2$ (NSHC = *N*-allylbenzothiazolin-2-ylidene) (1). A solution of NaO^{t}Bu (49 mg, 0.5 mmol) in THF (2 mL) was added to a suspension of CuCl (50 mg, 0.5 mmol) in THF (5 mL). The mixture was stirred for 1 h. After filtration, a bright orange solution was obtained. A suspension of *N*-allylbenzothiazolium bromide (128 mg, 0.5 mmol) in THF (5 mL) was added to the CuO^{t}Bu solution to stir for 4 h. Filtration through celite and concentration under vacuum, followed by cooling of the THF solution to −20 °C provided crystals suitable for X-ray diffraction (Fig. 1). Yield: 114 mg (0.179 mmol, 72%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.11 (d, 2H, J = 8.2 Hz, Aryl-H), 7.98 (d, 2H, J = 8.2 Hz, Aryl-H), 7.62 (t, 2H, J = 7.6 Hz, Aryl-H), 7.55 (t, 2H, J = 7.6 Hz, Aryl-H), 6.11 (m, 2H, CH═CH$_2$), 5.47 (d, J = 5.6 Hz, 4H, CH═CH$_2$), 5.28 (s, 2H, CH$_2$), 5.25 (d, J = 5.7 Hz, 2H, CH$_2$). ^{13}C-NMR (^{1}H): δ 215.1 (NCS), 143.3 (s, Aryl-C), 134.3 (s, Aryl-C), 132.4 (s, CH═CH$_2$), 127.7 (s, Aryl-C), 125.9 (s, Aryl-C), 123.5 (s, Aryl-C), 119.6 (s, CH═CH$_2$), 116.0 (s, Aryl-C), 56.7 (s, CH$_2$). Anal. calcd for **1**, $C_{20}H_{18}Br_2Cu_2N_2S_2$: C, 37.69; H, 2.85; N, 4.32. Found: C, 37.73; H, 2.91; N, 4.32.

Preparation of [Cu(μ-Br)(NSCH)]$_2$ (NSHC = *N*-propylbenzothiazolin-2-ylidene) (2a). Compound **2a** was prepared and purified using a method similar to that for **1**. Yield: 125 mg (0.1 mmol, 78%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.11 (m, 8H, Aryl-H), 7.64 (m, 4H, Aryl-H), 7.55(m, 4H, Aryl-H), 4.81 (m, 8H, CH$_2$), 1.94 (m, 8H, CH$_2$CH$_3$), 0.94 (m, 12H, CH$_3$). ^{13}C-NMR (^{1}H): δ 215.9 (NCS), 143.5 (s, Aryl-C), 134.3 (s, Aryl-C), 127.6 (s, Aryl-C), 125.7 (s, Aryl-C), 123.5 (s, Aryl-C), 115.7 (s, Aryl-C), 55.8 (s, CH$_2$), 23.2 (s, CH$_2$CH$_3$), 11.5 (s, CH$_3$). Anal. calcd for **2a**, $C_{40}H_{44}Br_4Cu_4N_4S_4$: C, 37.45; H, 3.46; N, 4.37. Found: C, 37.76; H, 3.54; N, 4.27.

Preparation of [Cu(μ-Br)(NSCH)]$_4$ (NSHC = *N*-crotylbenzothiazolin-2-ylidene) (2b). Compound **2b** was prepared and purified using a method similar to that for **1**. Yield: 134.6 mg (0.101 mmol, 81%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 7.98 (d, 4H, J = 8.2 Hz, Aryl-H), 7.94 (d, 4H, J = 8.2 Hz, Aryl-H), 7.59 (t, 4H, J = 8.2 Hz, Aryl-H), 7.50 (t, 4H, J = 7.6 Hz, Aryl-H), 6.00 (m, 4H, CH═CH), 5.83 (m, 4H, CH═CH), 5.38 (d, J = 6.3 Hz, 8H, CH$_2$), 1.72 (t, 12H, J = 6.3 Hz, CH$_3$). ^{13}C-NMR (^{1}H): δ 212.4 (NCS), 144.0 (s, Aryl-C), 135.5 (s, Aryl-C), 133.3 (s, CH═CH), 127.8 (s, Aryl-C), 126.1 (s, Aryl-C), 125.3 (s, Aryl-C), 123.5 (s, CH═CH), 116.0 (s, Aryl-C), 57.1 (s, CH$_2$), 17.9 (s, CH$_3$). Anal. calcd for **2b**, $C_{44}H_{44}Br_4Cu_4N_4S_4$: C, 39.71; H, 3.33; N, 4.21. Found: C, 39.53; H, 2.84; N, 4.20.

Preparation of [Cu(μ-I)(NSCH)]$_4$ (NSHC = *N*-methylbenzothiazolin-2-ylidene) (3). A suspension of *N*-methylbenzothiazolium iodide (138 mg, 0.5 mmol) in THF (8 mL) was added to a solution of CuO^{t}Bu (68 mg, 0.5 mmol) in THF (2 mL). After a few minutes, the mixture turned clear, and a yellow precipitate appeared. After stirring for an additional one hour, the yellow precipitate was collected and washed with diethyl ether to obtain complex **3**. X-ray diffraction quality crystals were obtained from a DCM solution at −20 °C (Fig. 1). Yield: 161 mg (0.186 mmol, 74%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.06 (d, 4H, J = 8.2 Hz, Aryl-H), 7.94 (d, 4H, J = 8.2 Hz, Aryl-H), 7.62 (m, 4H, Aryl-H), 7.52 (m, 4H, Aryl-H), 4.34

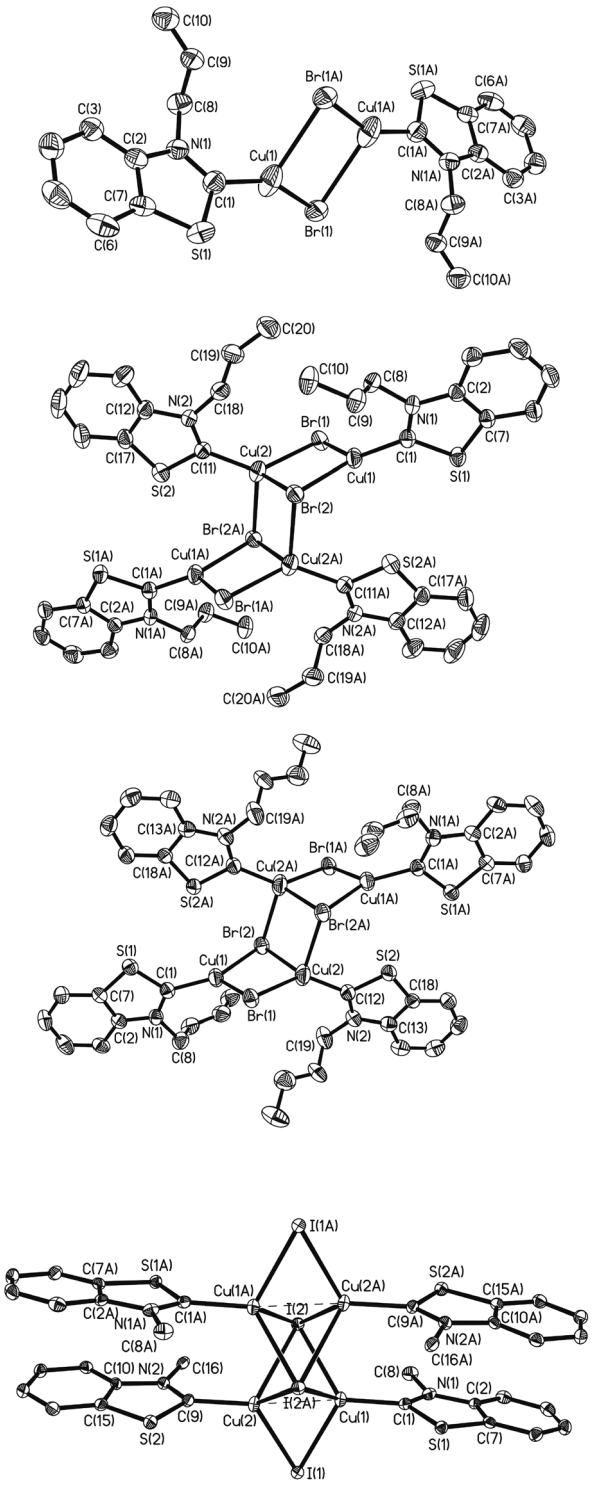


Fig. 1 ORTEP view of complexes (**1**), (**2a**), (**2b**) and (**3**) with 40% thermal ellipsoids.

(s, 12H, CH_3), 3.58 (m, THF), 1.75 (m, THF). ^{13}C-NMR (^{1}H): δ 216.4 (NCS), 144.4 (s, Aryl-C), 134.0 (s, Aryl-C), 127.5 (s, Aryl-C), 125.7 (s, Aryl-C), 123.2 (s, Aryl-C), 115.6 (s, Aryl-C), 67.4 (s, THF), 42.0 (s, CH_3), 25.6 (s, THF). Anal. calcd for **3**·0.5THF, $C_{34}H_{32}I_4Cu_4O_{0.5}N_4S_4$: C, 29.28; H, 2.31; N, 4.02. Found: C, 29.21; H, 2.32; N, 3.94.

Preparation of [(NSCH)Cu(μ-Br)(μ-O^{t}Bu)Cu(NSCH)] (NSHC = *N*-crotylbenzothiazolin-2-ylidene) (4). Compound **4** was prepared and purified using a method similar to that for **1** using *N*-crotylbenzothiazolium bromide (135 mg, 0.5 mmol) and CuO^{t}Bu (102 mg, 0.75 mmol) as starting materials. Yield: 129.9 mg (0.195 mmol, 78%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.13 (d, 2H, J = 7.6 Hz, Aryl-H), 8.05 (d, 2H, J = 8.2 Hz, Aryl-H), 7.66 (m, 2H, Aryl-H), 7.57 (m, 2H, Aryl-H), 5.92 (m, 2H, CH═CH), 5.79 (m, 2H, CH═CH), 5.40 (d, 4H, J = 6.3 Hz, CH_2), 3.58 (m, THF), 1.75 (m, THF), 1.65 (d, 6H, J = 6.3 Hz, CH_3), 1.34 (s, 9H, $C(CH_3)_3$). ^{13}C-NMR (^{1}H): δ 210.3 (NCS), 143.1 (s, Aryl-C), 134.2 (s, Aryl-C), 131.8 (s, CH═CH), 127.9 (s, Aryl-C), 126.1 (s, Aryl-C), 125.2 (s, Aryl-C), 123.6 (s, CH═CH), 116.0 (s, Aryl-C), 67.4 (s, THF), 56.5 (s, CH_2), 36.0 (s, $C(CH_3)_3$), 25.6 (s, THF), 18.0 (s, CH_3), 14.0 (s, $C(CH_3)_3$). Anal. calcd for **4**·0.1THF, $C_{26.4}H_{31.8}Cu_2BrO_{1.1}N_2S_2$: C, 47.62; H, 4.81, N, 4.21. Found: C, 48.01; H, 4.34; N, 4.44.

Preparation of [(NSCH)Cu(μ-Br)$_2$(NSCH)$_2$] (NSHC = *N*-allylbenzothiazolin-2-ylidene) (5a). A suspension of *N*-allylbenzothiazolium bromide (64 mg, 0.25 mmol) in THF (5 mL) was added to a solution of **1** (159 mg, 0.25 mmol) in THF (5 mL), and then NaO^{t}Bu (24 mg, 0.25 mmol) in THF (1 mL) was added. The mixture was stirred for 1 h. Filtration through celite and concentration under vacuum, followed by cooling of the THF solution to −20 °C provided crystals suitable for X-ray diffraction. Yield: 166 mg (0.21 mmol, 82%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.13 (d, 3H, J = 8.2 Hz, Aryl-H), 7.98 (d, 3H, J = 8.2 Hz, Aryl-H), 7.63 (m, 3H, Aryl-H), 7.54 (m, 3H, Aryl-H), 6.15 (m, 3H, CH═CH_2), 5.53 (d, 6H, J = 5.6 Hz, CH═CH_2), 5.29 (m, 6H, CH_2), 3.58 (m, THF), 1.75 (m, THF). ^{13}C-NMR (^{1}H): δ 219.2 (NCS), 143.6 (s, Aryl-C), 134.4 (s, Aryl-C), 132.7 (s, CH═CH_2), 127.5 (s, Aryl-C), 125.7 (s, Aryl-C), 123.4 (s, Aryl-C), 119.5 (s, CH═CH_2), 115.8 (s, Aryl-C), 67.4 (s, THF), 56.2 (s, CH_2), 25.6 (s, THF). Anal. calcd for **5a**·0.5THF, $C_{32}H_{31}Cu_2Br_2O_{0.5}N_3S_3$: C, 45.29; H, 3.68; N, 4.95. Found: C, 45.34; H, 3.22; N, 5.29.

Preparation of [(NSCH)Cu(μ-Br)$_2$Cu(NSCH)$_2$] (NSHC = *N*-crotylbenzothiazolin-2-ylidene) (5b). Compound **5b** was prepared and purified using a method similar to that for **5a**. Yield: 168 mg (0.20 mmol, 80%). ^{1}H-NMR (500 MHz, THF-d_8): δ 7.92 (d, 3H, J = 8.2 Hz, Aryl-H), 7.87 (d, 3H, J = 8.2 Hz, Aryl-H), 7.52 (m, 3H, Aryl-H), 7.43 (m, 3H, Aryl-H), 5.99 (m, 3H, CH═CH), 5.88 (m, 3H, CH═CH), 5.52 (m, 3H, CH_2), 3.57 (m, THF), 1.72 (m, THF), 1.68 (d, 9H, J = 6.2 Hz, CH_3). ^{13}C-NMR (^{1}H): δ 131.0 (s, CH═CH_2), 126.3 (s, Aryl-C), 125.3 (s, Aryl-C), 124.6 (s, Aryl-C), 122.3 (s, CH═CH_2), 114.8 (s, Aryl-C), 67.2 (s, THF) 55.5 (s, CH_2), 25.1 (s, THF), 17.0 (s, CH_3). Anal. calcd for **5b**·0.5THF, $C_{35}H_{37}Cu_2Br_2O_{0.5}N_3S_3$: C, 47.19; H, 4.19; N, 4.95. Found: C, 47.42, H, 4.29; N, 4.45.

Preparation of [CuBr(NSCH)$_2$] (NSHC = *N*-crotylbenzothiazolin-2-ylidene) (6). A suspension of *N*-crotylbenzothiazolium bromide (270 mg, 1 mmol) in THF (8 mL) was added to CuO^{t}Bu (68 mg, 0.5 mmol) and NaO^{t}Bu (48 mg, 0.5 mmol) in THF (4 mL). Filtration through celite and concentration under vacuum, followed by cooling of the THF solution to −20 °C provided crystals suitable for X-ray diffraction. Yield: 142 mg (0.27 mmol, 54%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.12 (d, 2H, J = 7.6 Hz, Aryl-H), 8.02 (d, 2H, J = 8.2 Hz, Aryl-H), 7.62 (m, 2H, Aryl-H), 7.53 (m, 2H, Aryl-H), 5.90 (m, 2H, CH═CH), 5.80 (m, 2H, CH═CH), 5.44 (d, 4H, J = 4.4 Hz, CH_2), 3.58 (m, THF), 1.75 (m, THF), 1.61 (d, 6H, J = 5.0 Hz, CH_3). ^{13}C-NMR (^{1}H): δ 219.0 (NCS), 143.6 (s, Aryl-C), 134.5 (s, Aryl-C), 131.2 (s, CH═CH), 127.5 (s, Aryl-C), 125.6 (s, Aryl-C), 125.5 (s, Aryl-C), 123.4 (s, CH═CH), 115.8 (s, Aryl-C), 67.4 (s, THF), 55.6 (s, CH_2), 25.6 (s, THF), 18.0 (s, CH_3). Anal. calcd for **6**, $C_{22}H_{22}CuBrN_2S_2$: C, 50.62; H, 4.25; N, 5.37. Found: C, 50.42; H, 4.21; N, 5.19.

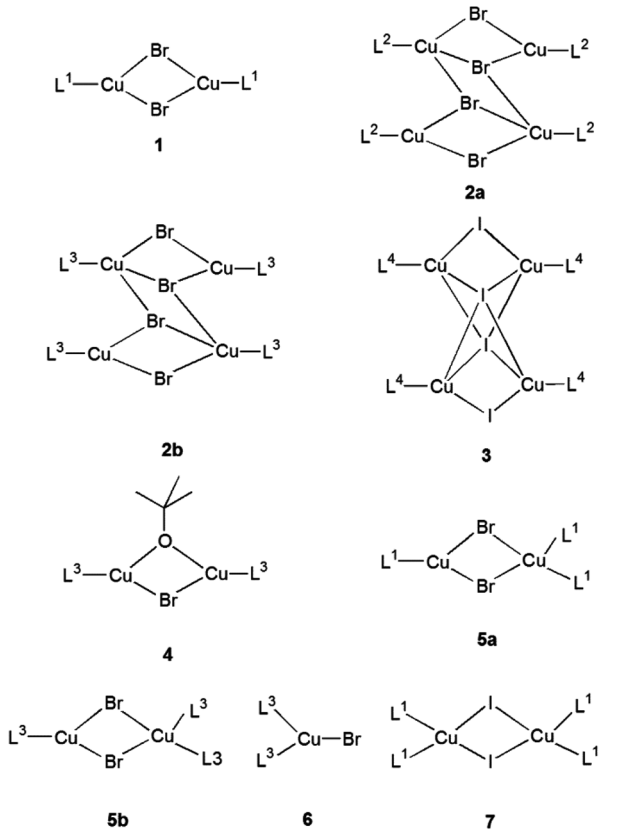
Preparation of [Cu(μ-I)(NSCH)$_2$]$_2$ (NSHC = *N*-allylbenzothiazolin-2-ylidene) (7). Compound **7** was prepared and purified using a method similar to that for **3** with *N*-allylbenzothiazolium iodide (303 mg, 1 mmol), CuO^{t}Bu (68 mg, 0.5 mmol) and NaO^{t}Bu (48 mg, 0.5 mmol). Yield: 175.8 mg (0.162 mmol, 65%). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.15 (d, J = 8.2 Hz, 4H, Aryl-H), 8.06 (d, J = 8.2 Hz, 4H, Aryl-H), 7.66 (m, 4H, Aryl-H), 7.57 (m, 4H, Aryl-H), 5.92 (m, 4H, CH═CH_2), 5.81 (m, 8H, CH═CH_2), 5.39 (d, 8H, CH_2). ^{13}C-NMR (^{1}H): δ 143.4 (s, Aryl-C), 134.5 (s, Aryl-C), 131.9 (s, CH═CH_2), 127.7 (s, Aryl-C), 125.9 (s, Aryl-C), 125.3 (s, Aryl-C), 123.5 (s, CH═CH_2), 116.0 (s, Aryl-C), 56.0 (s, CH_2). Anal. calcd for **7**, $C_{40}H_{36}Cu_2I_2N_4S_4$: C, 44.41; H, 3.35; N, 5.18. Found: C, 43.92; H, 3.75; N, 5.14.

Results and discussion

Copper(I)-NSHC complex [Cu(μ-Br)L^1]$_2$ (L^1 = *N*-allylbenzothiazolin-2-ylidene) (**1**) (Scheme 1) was synthesized from the reaction of *N*-allylbenzothiazolium bromide with CuO^{t}Bu, generated *in situ* from CuCl and NaO^{t}Bu. Completion of this room temperature reaction (typically within 2 h) was monitored by the disappearance of the N–C*H*–S proton in the ^{1}H-NMR spectrum.

Although Pd(II) and Ni(II) NSHC complexes are usually prepared from direct reaction of the benzothiazolium salt with a basic metal precursor, such as $PdCl_2$, $Pd(OAc)_2$, $NiCl_2$ or $Ni(OAc)_2$,[5d,6,7] this methodology failed to yield the desired product from CuCl, CuOAc or Cu_2O[10,11] in THF at room temperature or at 60 °C. The alternative use of free carbene as the substrate, which is also common[12] for the preparation of NHC complexes, was similarly unsuccessful. Thiazolinylidene copper(I) complexes have previously been prepared in a comparable, albeit less convenient, procedure employing ^{n}BuLi at low temperatures.[13]

Reaction of *N*-propyl- and *N*-crotyl-benzothiazolium bromides with CuO^{t}Bu gave the tetranuclear copper complexes [Cu(μ-Br)(L^2)]$_4$ (L^2 = *N*-proylbenzothiazolin-2-ylidene) (**2a**) and [Cu(μ-Br)(L^3)]$_4$ (L^3 = *N*-crotylbenzothiazolin-2-ylidene) (**2b**) respectively, as determined by X-ray crystallography. The



L^1 = N-allylbenzothiazolin-2-ylidene, L^2 = N-proylbenzothiazolin-2-ylidene, L^3 = N-crotylbenzothiazolin-2-ylidene, L^4 = N-methylbenzothiazolin-2-ylidene

Scheme 1

aromatic ^{1}H and ^{13}C NMR signals of **2a** and **2b** in DMSO-d_6 were very similar to each other and were almost indistinguishable from monomeric **1**. It is difficult, therefore, to establish whether the solid-state structures of **2a** and **2b** are replicated in solution. It is possible that complexes **2a** and **2b** dissociate to dinuclear or even mononuclear copper species in this highly coordinating solvent. *N*-methylbenzothiazolium iodide as the substrate provided $[Cu(\mu\text{-}I)(L^4)]_4$ (L^4 = *N*-methylbenzothiazolin-2-ylidene) (**3**) in the solid state with unusual μ_4 capping iodides in place of μ_3 bridging bromides. The aromatic ^{1}H and ^{13}C NMR signals for this complex were significantly different from the corresponding signals in the preceding three complexes with, for example, a >0.5 ppm downfield shift in the carbene ^{13}C signal, reflecting a decrease in the Lewis acidity of the metal by virtue of the increase in the σ-donor ability of the iodide ligands.[14]

[(NHC)CuO^{t}Bu]-type complexes generated from [(NHC)-CuCl] and NaO^{t}Bu or KO^{t}Bu are known to be active catalysts for a range of reactions involving carbonyl and alkene substrates, including with the control of absolute stereochemistry.[15] We therefore prepared $[Cu_2(\mu\text{-}Br)(\mu\text{-}O^tBu)(L^3)_2]$ (**4**) from the reaction of *N*-crotylbenzothiazolium bromide with 1.5 equivalents of CuO^{t}Bu. The product of this reaction was a unique dinuclear carbene complex with mixed bromide and butoxide bridges. The 5 ppm upfield shift in the carbene ^{13}C NMR signal is commensurate with the more electronegative, bridging ancillary oxygen ligand.[14a]

The dinuclear 1 : 1 Cu : NSHC complex **1** reacted with an equimolar equivalent of *N*-allylbenzothiazolium bromide in the presence of NaO^{t}Bu to yield the unsymmetrical tricarbene complex, $[Cu_2(\mu\text{-}Br)_2(L^1)_3]$ (**5a**), in the solid state. Complex **2b** is the dimeric form of **1** (albeit with different *N*-alkyl groups) and reacted with two equivalents of *N*-crotylbenzothiazolium bromide and NaO^{t}Bu to yield the analogous $[Cu_2(\mu\text{-}Br)_2(L^3)_3]$ **5b**. While the NMR spectra of **5a** and **5b** are quite distinct from those of the parent complexes **1** and **2b**, there is no evidence of two ligand environments in the NMR spectra for either complex. This suggests that either the unsymmetrical solid-state structures are not replicated in solution, or that a rapid, dynamic process is occurring in solution. However, cooling a d_2-DCM solution of **5b** to 193 K failed to resolve any extra signals.

Using an excess of *N*-crotylbenzothiazolium bromide in a 1 : 2 : 1 substrate ratio of CuO^{t}Bu : L^3HBr : NaO^{t}Bu provided $[CuBr(L^3)_2]$ (**6**). This was the only mononuclear Cu(I) carbene observed in this series and it is unusual to see a terminal bromide in the solid-state despite its basicity and donor potential to a neighbouring Cu(I). The isolation of this complex possibly suggests a low energy barrier between a mono- and dinuclear form and that dissociation of these Cu(I) carbene complexes can be anticipated in solution. Anions such as BF_4^- and PF_6^- are known to support cationic complexes of type $[Cu(carbene)_2]Z$.[16,17]

The reaction of *N*-allylbenzothiazolium iodide with CuO^{t}Bu and NaO^{t}Bu in a ratio of 2 : 1 : 1 provided $[Cu(\mu\text{-}I)(L^1)_2]_2$, **7** in the solid-state. The larger halide of **7** presumably makes it easier for two copper spheres to come into bonding contact. Its formation validates our earlier DFT based prediction that a fourth carbene could be added to the $[Cu_2I_2(L^1)_3]$ complex.[8]

In general, **1**, **2a**, **2b**, **4**, **5b** and **6** are more soluble in THF than **3**, **5a** and **7**. All are however soluble in CH_2Cl_2 and DMSO. They are stable in air for a few hours and can be stored under argon at low temperature for several months. As discussed above, their NMR spectra (^{1}H and ^{13}C) carry little stoichiometric information and nuclearity may change on dissolution or, indeed, vary in different solvents. X-ray single-crystal diffraction analysis of complexes **1–7**, however, revealed remarkable structural diversity in the solid state depending on the reagent stoichiometry and inorganic ligand (bridging halide or alkoxide). These compounds can be classified into five motifs, *viz.* M_xL_y where $x : y$ = 2 : 2 (**1**) (**4**), 4 : 4 (**2**) (**3**), 2 : 3 (**5**), 1 : 2 (**6**) and 2 : 4 (**7**). The Cu(I) geometry is either trigonal planar or tetrahedral with the metal carrying one or two carbene ligands. The final structure is determined by the preferred coordination mode of the inorganic ligand, *viz.* from terminal and unidentate (**6**) to doubly bridging μ_2 (**1**, **2**, **3**, **4**, **5**, **7**) and triply μ_3 bromide bridging (**2**) to quadruply μ_4 iodide capping (**3**). Despite this diversity, the Cu–C carbene bond lengths cover a fairly narrow range (1.852(5)–1.932(4) Å, Table S1†) and compare well with those of other copper NHC complexes.[16]

Complex **1** is dinuclear with two trigonal planar Cu(I) atoms, each of which carries a carbene ligand (Fig. 1). Association of the two Cu(I) spheres is unsymmetrical with two significantly uneven Cu–Br bonds (2.3037(8) and 2.772(1) Å respectively), thus also pointing to possible dissociation in solution. Its monomeric form has not been isolated, except for **6** in which an additional carbene provides the needed stabilization. The two NSHC planes are parallel to each other and twisted by 122.5° from the $[Cu_2Br_2]$ coordination plane. This structure is similar to the previously reported $[Cu(\mu\text{-}Cl)L]_2$ (L = *N*-methyl-4,5-dimethylthiazolin-2-ylidene) complex which also exhibits two unequal Cu–Cl bonds (1.888(6) and 2.122(2) Å).[13]

Complex **2a** is tetranuclear in the solid state with the $[Cu_4Br_4]$ assembled in a step fashion. The two internal Cu(I) are tetrahedral whereas the two external Cu(I) are trigonal planar and each metal atom bears a carbene ligand. This complex can be viewed as the dimeric form of **1** with two triply bridging bromides linking the subunits. The Cu–C bond at the three-coordinated Cu(I) [Cu(1)–C(1) 1.900(2) Å] is only marginally shorter than the corresponding bond of the four-coordinated Cu(I) [Cu(2)–C(11) 1.910(3) Å)], but both are slightly longer than their counterparts in **1** (1.887(4) Å) and those in the literature.[16] The structure of **2b** is similar to that of **2a**. However, Cu(2)–Br(2A) and Cu(2A)–Br(2) in **2b** (2.7138(9) and 2.7139(9) Å respectively) are significantly longer than other Cu–Br bonds (2.4396(7), 2.4155(8), 2.4263(8), 2.6435(8) Å respectively) and their counterparts in **2a** (2.5828(5) and 2.5827(5) Å), indicating weaker secondary, bridging interactions between the two monomeric subunits.

Complex **3** is also tetranuclear but the four Cu(I) atoms are planar (the dihedral angle between the planes of Cu(1)Cu(2)-Cu(1A) and Cu(2)Cu(1A)Cu(2A) is 0°) and capped above and below by quadruply capping iodides and two additional edge-bridging iodides. This is the only complex in this series with tetrahedral-only Cu(I) centers, each of which carries one carbene ligand. The quadruply bridging iodides I(2) and I(2A) bring the two non-bonding Cu···Cu (2.5626(7) Å) into close proximity. This distance is significantly shorter than all other Cu···Cu lengths in this series. The methyl N-substituents on the parallel NSHC planes across Cu(1)–Cu(2A) are oriented opposite to one another to avoid steric interaction.

Complex **4**, like **1**, has purely trigonal planar Cu(I) centers (Fig. 2). The contrast in the size and electronegativity of the bridging atoms imparts a sharp distortion to the central $[Cu_2BrO]$ ring with strong Cu–O (Cu(1)–O(1) = 1.874(3) Å and Cu(2)–O(1) = 1.907(3) Å) bonds and longer Cu–Br bonds (2.7460(9) Å) that draw the two copper atoms closer in **4** (2.9964(8) Å) than in **1** (3.400 Å). This mixed-ligand formulation with a butoxide bridge appears to give a more acidic Cu(I) leading to the strongest Cu–C carbene bonds (1.869(5) and 1.852(5) Å) in this series.

Two independent molecules co-crystallized in the unit cell of **5a**. Their structures are similar to that of $[L^1Cu(\mu\text{-}I)_2CuL^1{}_2]$ previously reported.[8] There are two copper geometries, *viz.* trigonal planar with one carbene (16 electron) and tetrahedral with two carbenes (18 electron) connected by the two

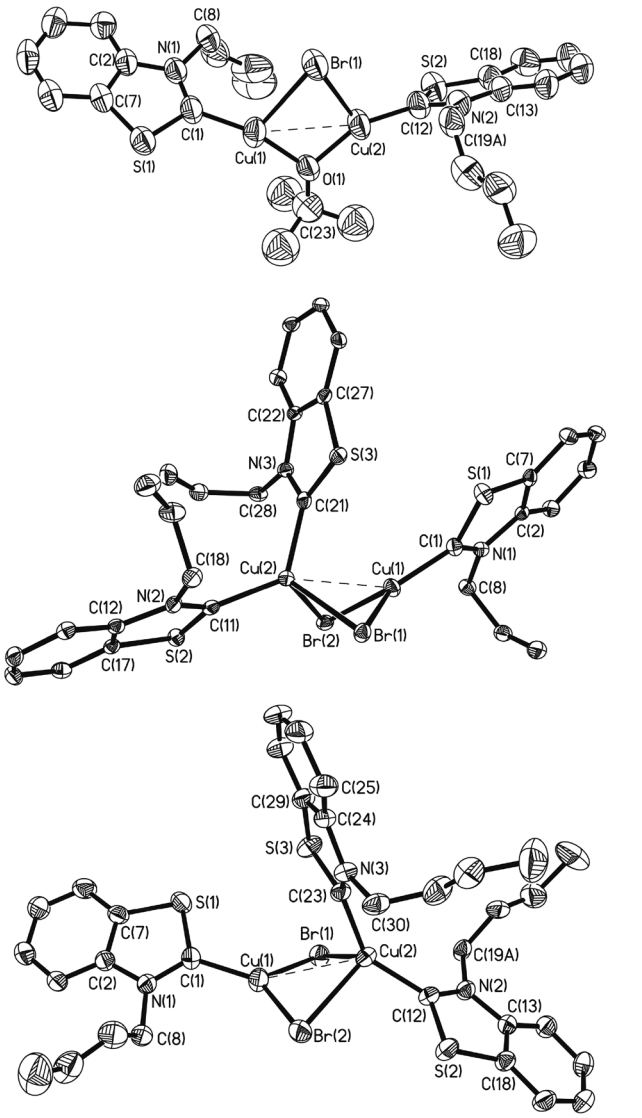


Fig. 2 ORTEP view of complexes (**4**), (**5a**) and (**5b**) with 40% thermal ellipsoids.

bromides. The Cu–C(carbene) bond is understandably stronger in the copper monocarbene moiety (Cu(1)–C(1) 1.899(3) Å) than in the copper dicarbene moiety (Cu(2)–C(11) 1.914(3) Å and Cu(2)–C(21) 1.931(3) Å). Similarly, the Cu–Br bonds on the copper dicarbene are significantly weaker (Cu(1)–Br(1) 2.4343(5) Å and Cu(1)–Br(2) 2.4538(5) Å) on Cu(1) compared to 2.5794(5) and 2.7097 (5) Å for Cu(2)). The NSHC ring with the longest Cu–C carbene bond (Cu(2)–C(21) 1.931(3) Å) is almost perpendicular to the other two NSHC rings, the Cu(1)Br(1)-Cu(2) and Cu(1)Br(2)Cu(2) planes (dihedral angles of 111.4°, 102.1°, 98.6° and 83.4°, respectively), consistent with an adduct-like addition of free NSHC ligand to electron deficient complex **1**.

It is unusual, although not unprecedented, to obtain a mononuclear dicarbene Cu(I) complex with a terminal halide (complex **6**).[16,17] The trigonal planar geometry of Cu(I) in **6** is distorted with a large C(1)–Cu(1)–C(12) angle of 142.8(1)°

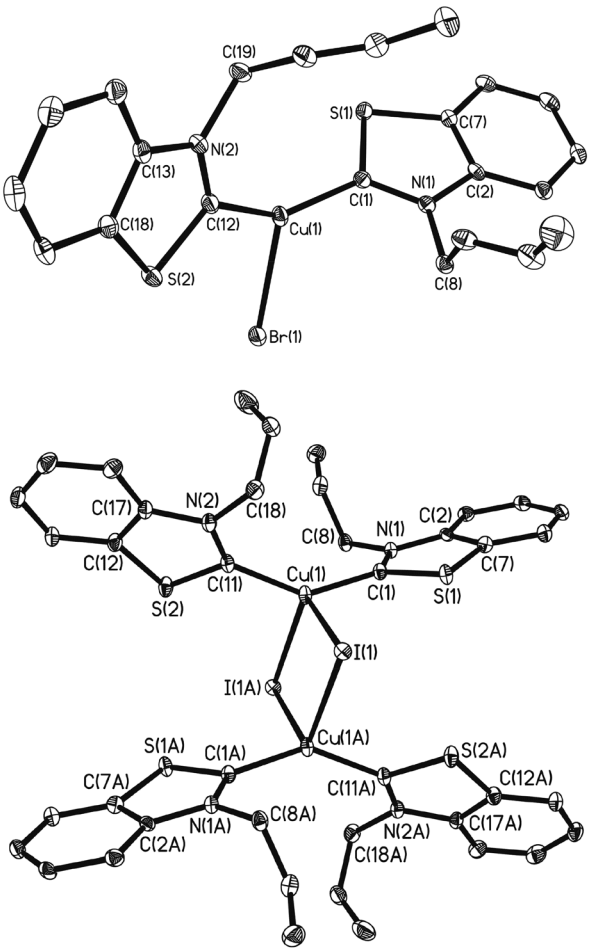


Fig. 3 ORTEP view of complexes 6 and 7 with 40% thermal ellipsoids.

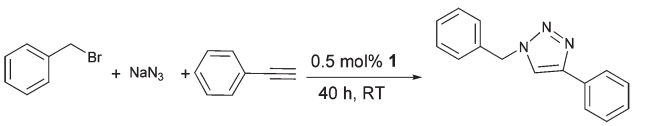
(Fig. 3). The shorter of the Cu–C(carbene) bonds (1.904(3) Å and 1.924(3) Å) are significantly shorter than their counterparts in the corresponding NHC analogue (1.930(3) Å).[16] The two NSHC planes are nearly perpendicular to each other with the dihedral angle of 111.5°. This twist allows the two carbene moieties to draw closer to the coordination sphere enabling a stronger Cu–C contact but without invoking undesirable inter-ligand repulsions.

Complex **7** can be viewed as the dimeric form of **6**. Such associations tend to produce a more electron rich Cu(I) and weaken the Cu–C carbene link ((1.923(3) & 1.925(3) Å in **7** relative to 1.904(3) & 1.924(3) Å in **6**). The four Cu–I bonds fall in a narrow range of 2.8330(5)–2.8594(5) Å, and are significantly longer than the Cu–I bonds in the corresponding $[CuI(NHC)_2]$ complex (2.7623(7) Å).[16] The dihedral angles of the Cu(1)I(1)-Cu(1A)I(1A) to C(1)N(1)S(1) and C(11)N(2)S(2) planes are 69.3° and 103.8° respectively, which support minimum inter-ligand interaction. The C(1)N(1)S(1) and C(11)N(2)S(2) planes are twisted by 62.8° to avoid non-bonding contacts. The Cu···Cu separation (3.473 Å) is, unsurprisingly, the longest in this series. However, as discussed above, only one set of signals was observed in the NMR spectra of these complexes, indicating that the observed solid structures might not be significant in solution or a fast shuttle of the ligands between the metals could be operating. Discrepancy between solid-state and solution structures for NHC complexes has been reported previously.[18]

CuX(NHC) (X = Cl and Br)[19,20] and $[Cu(NHC)_2]Z$ (Z = PF_6 and BF_4)[1e,21] are very efficient catalysts for the Huisgen 1,3-dipolar cycloaddition of azides to alkynes (including internal alkynes), particularly in aqueous solvents and under solvent free conditions. We therefore conducted some preliminary screening of our compounds in this respect. Complex **1** was chosen as a model catalyst in the "click reaction" of benzyl azide and phenylacetylene to optimize conditions (Table 1). Yields were highest in aqueous CH_3CN and DMF (entries 2 & 3). Surprisingly, solvent-free conditions or reactions in water, aqueous EtOH or aqueous THF were significantly lower yielding (entries 1, 4 & 7). These results are at odds with the performance of CuX(NHC) and $[Cu(NHC)_2]Z$ under solvent-free conditions and/or in water or in a variety of aqueous solvents.[19,20] We suggest that these more strongly Cu(I)-coordinating solvents DMF and CH_3CN may be needed to promote dissociation of **1** into catalytically active [CuBr(NSHC)] and this proposition is supported by a comparison of different catalysts below (Table 2).

Aqueous acetonitrile (in the ratio of 1 : 1) was chosen as the solvent system for preliminary screening of our different copper NSHC complexes. Not surprisingly, given the solvent dependence study above, the marginally more efficient catalyst proved to be mononuclear complex **6**. While the solution structures of some complexes are not known precisely, one interpretation of these results is that cuprophilic coordinating solvents result in dissociation to give mononuclear [CuX(NSHC)] or $[Cu(NSHC)_2]^+$ species which then react rapidly with phenyl acetylene to provide intermediate [Cu(NSHC)(CCPh)].[1e] This hypothesis implies that the yields displayed in Table 2 may reflect the rate of dissociation and portends the use of these dinuclear and tetranuclear complexes as slow-release catalysts for a range of applications. Quantitative yield was achieved by raising the loading of precatalyst **1** to 1% (Table 2, entry 1).

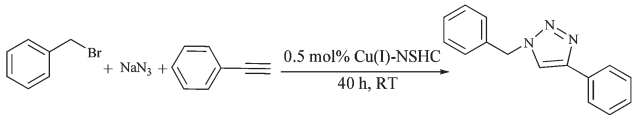
Table 1 Influence of solvent on yield



Entry	Solvent[a]	Yield[b]/%
1	EtOH–H_2O	43
2	CH_3CN–H_2O	95
3	DMF–H_2O	97
4	THF–H_2O	23
5	CH_3CN	19
6	H_2O	60
7	Nil	13

[a] Mixed solvent in the ratio of 1 : 1. [b] Isolated yields.

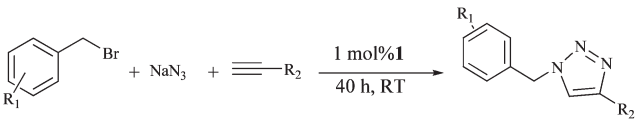
Table 2 Comparison of different Cu(I)-NSHC complexes



Entry	Cat.	Yield[a]/%
1	$[CuBr(NSHC)]_2$ (**1**)	95, 100[b]
2	$[CuBr(NSHC)]_4$ (**2a**)	81
3	$[CuBr(NSHC)]_4$ (**2b**)	75
4	$[CuI(NSHC)]_4$ (**3**)	40
5	$[Cu_2Br(O^tBu)(NSHC)_2]$ (**4**)	40
6	$[Cu_2Br_2(NSHC)_3]$(**5a**)	25
7	$[Cu_2Br_2(NSHC)_3]$ (**5b**)	69
8	$[CuBr(NSHC)_2]$ (**6**)	98
9	$[CuI(NSHC)_2]_2$ (**7**)	36

[a] Isolated yields. [b] 1 mol% Cu, 14 h.

Table 3 Comparison of different alkyne and aryl bromide substrates



Entry	R_1	R_2	Yield[a]/%
1	H	Ph	>99
2	H	4-MeOPh	>99
3	H	4-pip-CH_2	77
4	4-NO_2	Ph	98
5	4-NO_2	4-MeOPh	98
6	4-CN	Ph	87
7	4-CN	4-MeOPh	75
8	4-CN	$SiMe_3$	29
9	4-CN	AcO	78
10	4-^{t}Bu	Ph	>99
11	4-^{t}Bu	AcO	85
12	4-^{t}Bu	$SiMe_3$	45
13	H	AcO	70
14	H	$SiMe_3$	92
15	2-F	Ph	44

[a] Isolated yields.

A one-pot CuAAC protocol with precatalyst **1** (1 mol% in aqueous CH_3CN) generally provided good yields for a wide range of substrates (Table 3). Reactions of ethynyltrimethylsilane were less reliable, presumably due to steric hindrance of the bulky Me_3Si group.

Conclusions

A remarkable array of Cu(I) NSHC complexes have been prepared by variation in the nitrogen substituent of the heterocycle and the stoichiometry of reagents. The solid-state structures of these complexes highlight the geometrical and electronic flexibility of Cu(I), facile aggregation through bridging and capping halides and, importantly, the ability to accommodate more than one carbene ligand on each metal. It is notable that a linear $[Cu(NHSC)_2]^+$ moiety was not observed; however, the formation of mononuclear dicarbene **6** with a coordinating halide ligand was obtained for the first time. The Cu···Cu separation over a wide range of 2.5626(7) to 3.4725(7) Å distances points to the propensity for Cu(I) carbene dissociation and aggregation. This presents an ideal model for us to explore the metal–metal cooperativity and its response to migratory ligands and creation of vacant sites for substrate entry in a typical catalytic pathway. We are currently exploring the applications of this potentially useful property of bridged Cu(I) carbenes.

Notes and references

1 (*a*) T. Ohishi, L. Zhang, M. Nishiura and Z. Hou, *Angew. Chem., Int. Ed.*, 2011, **50**, 8114–8117; (*b*) H. Jang, A. R. Zhugralin, Y. Lee and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2011, **133**, 7859–7871; (*c*) L. Ackermann, *Angew. Chem., Int. Ed.*, 2011, **50**, 3842–3844; (*d*) G. C. Fortman, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2010, **29**, 3966–3972; (*e*) S. Díez-González and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2008, **47**, 8881–8884.

2 (*a*) M. R. L. Furst and C. S. J. Cazin, *Chem. Commun.*, 2010, **46**, 6924–6925; (*b*) M. Yoshida, H. Ohmiya and M. Sawamura, *J. Am. Chem. Soc.*, 2012, **134**, 11896–11899.

3 S. Gaillard, C. S. J. Cazin and S. P. Nolan, *Acc. Chem. Res.*, 2012, **45**, 778–787.

4 R. Y. Tan, F. S. N. Chiu, A. Hadzovic and D. T. Song, *Organometallics*, 2012, **31**, 2184–2192.

5 (*a*) S. K. Yen, L. L. Koh, H. V. Huynh and T. S. A. Hor, *Dalton Trans.*, 2007, 3952–3958; (*b*) N. Ding and T. S. A. Hor, *Dalton Trans.*, 2010, **39**, 10179–10185; (*c*) X. Han, L. L. Koh, Z. Weng and T. S. A. Hor, *Dalton Trans.*, 2009, 7248–7252; (*d*) N. Ding, J. Zhang and T. S. A. Hor, *Dalton Trans.*, 2009, 1853–1858; (*e*) S. K. Yen, L. L. Koh, H. V. Huynh and T. S. A. Hor, *Chem.–Asian J.*, 2008, **3**, 1649–1656.

6 S. K. Yen, L. L. Koh, H. V. Huynh and T. S. A. Hor, *Aust. J. Chem.*, 2009, **62**, 1047–1053.

7 S. K. Yen, D. J. Young, H. V. Huynh, L. L. Koh and T. S. A. Hor, *Chem. Commun.*, 2009, 6831–6833.

8 X. Han, L. L. Koh, Z.–P. Liu, Z. Weng and T. S. A. Hor, *Organometallics*, 2010, **29**, 2403–2405.

9 (*a*) T. H. Lemmen, G. V. Goeden, J. C. Huffman, R. L. Geerts and K. G. Caulton, *Inorg. Chem.*, 1990, **29**, 3680–3685; (*b*) T. Tsuda, T. Hashimoto and T. Saegusa, *J. Am. Chem. Soc.*, 1972, **94**, 658–659.

10 (*a*) J. Chun, H. S. Lee, G. Jung, S. W. Lee, H. J. Kim and S. U. Son, *Organometallics*, 2010, **29**, 1518–1521; (*b*) M. R. L. Furst and C. S. J. Cazin, *Chem. Commun.*, 2010, **46**, 6924–6925.

11 A. A. D. Tulloch, A. A. Danopoulos, S. Kleinhenz, M. E. Light, M. B. Hursthouse and G. Eastham, *Organometallics*, 2001, **20**, 2027–2031.

12 N. P. Mankad, T. G. Gray, D. S. Laitar and J. P. Sadighi, *Organometallics*, 2004, **23**, 1191–1193.
13 H. G. Raubenheimer, S. Cronje, P. H. van Rooyen, P. J. Olivier and J. G. Toerien, *Angew. Chem., Int. Ed. Engl.*, 1994, **106**, 687–688.
14 (*a*) M. V. Baker, P. J. Barnard, S. K. Brayshaw, J. L. Hickey, B. W. Skelton and A. H. White, *Dalton Trans.*, 2005, 37–43; (*b*) W. A. Herrmann, O. Runte and G. Artus, *J. Organomet. Chem.*, 1995, **501**, Cl–C4; (*c*) Y. Han, H. V. Huynh and G. K. Tan, *Organometallics*, 2007, **26**, 6447–6452.
15 (*a*) S. Díez-González and S. P. Nolan, *Acc. Chem. Res.*, 2008, **41**, 349–358; (*b*) K. Takatsu, R. Shintani and T. Hayashi, *Angew. Chem., Int. Ed.*, 2011, **50**, 5548–5552; (*c*) R. Shintani, K. Takatsu and T. Hayashi, *Chem. Commun.*, 2010, **46**, 6822–6824.
16 G. Venkatachalam, M. Heckenroth, A. Neels and M. Albrecht, *Helv. Chim. Acta*, 2009, **92**, 1034–1045.
17 (*a*) S. Díez-González, E. D. Stevens, N. M. Scott, J. L. Petersen and S. P. Nolan, *Chem.–Eur. J.*, 2008, **14**, 158–168; (*b*) S. Díez-González, N. M. Scott and S. P. Nolan, *Organometallics*, 2006, **25**, 2355–2358.
18 S. Díez-González, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 7595–7606.
19 S. Díez-González, E. D. Stevens and S. P. Nolan, *Chem. Commun.*, 2008, 4747–4749.
20 S. Díez-González, A. Correa, L. Cavallo and S. P. Nolan, *Chem.–Eur. J.*, 2006, **12**, 7558–7564.
21 F. Lazreg, A. M. Z. Slawin and C. S. J. Cazin, *Organometallics*, 2012, **31**, 7969–7975.