RSC Advances



View Article Online

View Journal | View Issue

PAPER



Cite this: RSC Adv., 2016, 6, 11430

Received 1st December 2015 Accepted 19th January 2016

DOI: 10.1039/c5ra25584h

www.rsc.org/advances

1. Introduction

Strength, lightness and flexibility are crucial features of some materials used in everyday life. For certain specialized applications, extreme strength is required, while lightness and flexibility are still desirable. The challenge to combine these properties into one material is not trivial, as very tough materials are usually brittle and/or dense. By analogy to macroscopic woven materials, such as textiles and ropes, we predict that covalent polymers woven at the molecular level will offer the ultimate strength in a lightweight and flexible material. Mechanical failure of common polymers can occur by the disentangling of individual strands as a result of breaking weak intermolecular bonds. In contrast, disrupting a molecularly woven polymer would require the simultaneous breaking of multiple, strong covalent bonds. Although crosslinking is known to increase strength, high crosslink densities cause

Metal-templated synthesis of intertwined, functionalized strands as precursors to molecularly woven materials[†]

Natasha R. Wadhwa, Neil C. Hughes, Jaafar A. Hachem and Gellert Mezei*

Herein we propose a novel approach toward yet to be realized molecularly woven materials (MWMs), based on metal-templated precursors containing intertwined strands with functional ends. Two different potential precursors, based on terminal alkene-functionalized bis-Schiff base ligands (with either 1,2diaminophenylene or 1,2-diaminoethylene cores) coordinated around a Cu(I) ion, have been tested. During this work, four novel organic ligands were prepared, along with the Cu(I) or Ag(I) complexes of three of them, and were characterized by X-ray diffraction and/or NMR spectroscopy. Chemical reactivity and structural studies (by single-crystal X-ray crystallography) of these novel compounds led to the assessment of their viability as precursors for MWMs. The essential requirement that terminal functionalities on the two intertwined ligand strands of the precursor must be far enough from each other so that only inter- and no intra-molecular reactivity is possible, is only met by the precursor with a 1,2-diaminophenylene core. This precursor, however, is less stable than the analogous one with a 1,2diaminoethylene core, as it easily undergoes intramolecular cyclization/aromatization to yield a stable benzimidazole moiety, resulting in breakdown of the strands. The benzimidazole-containing compound offers an interesting example of chiral crystallization (helical arrangement about a four-fold axis) induced by hydrogen bonding of an otherwise achiral molecule. The results of this study outline the challenges involved in the preparation of a MWM using our approach, and will aid in identifying more robust ligand systems that meet the requirements of a MWM precursor set forth here.

> polymers to become rigid and glassy.¹ Ultra-high molecular weight polyethylene has high impact strength, but melts at relatively low temperatures and easily deforms permanently under tensile load.² Graphene³ and carbon nanotubes⁴ have the highest known tensile strengths; however, they are also the stiffest materials known and have poor resistance to bending, torsion and compression. The interlocked (but not cross-linked) strands of a molecularly woven polymer would provide inherent flexibility, lightness and extreme strength at the same time.

> No molecularly woven materials (MWMs) have been reported to date, as no technology is currently available for the weaving of individual polymer strands.⁵ The possibility of creating a "molecular macramé" by molecular weaving was anticipated in 1992 by Daryle H. Busch: a tetranuclear grid complex, with intertwined strands could, in principle, be extended in two dimensions to yield a 2D woven structure (Fig. 1).⁶ Although such tetranuclear precursors have been reported in the meantime,⁷ it is hard to imagine that long, polymeric analogs of the ligands used as strands would lead to the desired, extended woven materials. Instead, if the eight endings of the tetranuclear precursor's strands were appropriately functionalized, polymerization ("molecular sewing") could then yield a polymer with interwoven strands. Metal complexes containing intertwined strands with functional end-groups have indeed been

Department of Chemistry, Western Michigan University, Kalamazoo, MI, 49008, USA. E-mail: gellert.mezei@wmich.edu

[†] Electronic supplementary information (ESI) available: ¹H and ¹³C NMR spectra, CIF files for compounds **4**, **5**, **6** and **12**. CCDC 1439669–1439672. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra25584h



used for the creation of discreet catenanes, rotaxanes, knots, and higher order links.⁸ Other methods that could possibly be extended to molecular fabrics, such as single-stranded DNA weaving⁹ and surface templated synthesis,¹⁰ have been entertained.

Herein we propose a simpler approach to MWMs, based on mononuclear complexes as precursors (Fig. 2), and report

terminal alkene functionalized precursors that could be "sewn" together on the molecular level by alkene metathesis. Alkene metathesis¹¹ has been used successfully for the synthesis of macrocycles,¹² topologically unusual molecules (such as cate-nanes,¹³ rotaxanes¹⁴ and knots¹⁵) and polymeric materials.¹⁶ To avoid the formation of a [2]catenane (Fig. 3a) and to ensure that only inter-molecular reactivity is possible, our MWM precursor







Fig. 3 (a) Alkene functionalities in close proximity react intra-molecularly and lead to a [2]catenane (92% isolated yield);^{13a} (b) distant alkene functionalities cannot react intra-molecularly and are expected to lead to a molecularly woven polymer.

has the alkene functionalities placed close to the intertwined core and far from each other (Fig. 3b). Thus, intra-molecular reactivity is precluded based on geometric constraints.

2. Results and discussion

2.1. Synthesis

To prepare a MWM precursor with intertwined, alkenefunctionalized strands, we first set out to prepare the bis-Schiff base ligand 1,2-phenylene-bis[nitrilo(E)methylidyne(4allyloxyphenyl)] (compound 7 without the NO2-groups in Fig. 4), by the reaction of 1,2-phenylenediamine with 4-allyloxybenzaldehyde. As 1,2-phenylenediamine turned out to be unreactive toward 4-allyloxybenzaldehyde, we activated the aldehyde by attaching a nitro group to the benzene ring. 3-Nitro-4-hydroxybenzaldehyde is indeed much more reactive, so much so that during the reaction with allyl bromide, condensation of the aldehyde group with the acetone solvent also occurred (which was not the case in the absence of the NO₂-group). To formation of the undesired 4-(3-nitro-4avoid the allyloxyphenyl)-3-buten-2-one (1) (Fig. 4), acetonitrile was used instead of acetone as solvent, and 3-nitro-4allyloxybenzaldehyde (2) was obtained in excellent yield. On reacting with 1,2-phenylenediamine (2:1 molar ratio) in methanol, 2 afforded the mono-Schiff base N-[(3-nitro-4allyloxyphenyl)methylene]-1,2-benzenediamine (3), not the expected bis-Schiff base 7. When the same reaction was carried out in ethanol instead of methanol, 2-(3-nitro-4-allyloxyphenyl)benzimidazole (4) was obtained instead of 7. Compound 4, an achiral molecule, was found to crystallize in a chiral space group (see the Crystallographic studies section below), and formed bis[2-(3-nitro-4-allyloxyphenyl)-benzimidazole] silver(1) nitrate (5) upon reaction with $AgNO_3$ in acetonitrile.

In contrast to the metal-free approach to ligand 7, the use of Cu(I) ion as template yielded completely different results. Thus, when 1,2-phenylenediamine was first reacted with [Cu(CH₃CN)₄] PF_6 in methanol before adding 3-nitro-4-allyloxybenzaldehyde (2) in excess, the desired bis-Schiff base 7 was obtained in the form of bis[1,2-phenylenebis{nitrilo(E)methylidyne(3-nitro-4-allyloxyphenyl)}]copper(1) hexafluorophosphate (6). Crystals of 6 were obtained by slow diffusion of diethyl ether vapor into acetone or acetonitrile solutions. However, 6 turns out to be a rather delicate molecule: attempts to crash it out from an acetone solution by pouring into excess diethyl ether led to decomposition and yielded the benzimidazole 4. The same result was obtained upon attempting to prepare the free ligand 7 by demetalating 6 in acetonitrile with aqueous KCN. The cause of the observed reactivity appears to be the higher stability of benzimidazole due to extended aromaticity.

Although metal-free 1,2-diaminophenylene-based bis-Schiff base ligands can undoubtedly be obtained,¹⁷ it appears that the presence of phenyl groups on the methine carbons leads exclusively to the formation of 2-phenylbenzimidazoles and/or 1-benzyl-2-phenylbenzimidazoles.¹⁸ A notable exception is the case of phenyl groups with an *ortho*-OH¹⁹ or NH²⁰ group, which appear to stabilize the free bis-Schiff base ligand. Coordination to Cu(1) ions stabilizes the elusive ligand 7, and provides the only known example of a 1,2-diaminophenylene-based bis-Schiff base (6) without a stabilizing *ortho*-OH or NH group on the methine-bound phenyl groups.

Based on the fact that ligand 7 could not be obtained in the metal-free form, we predict that demetalation of a MWM based on **6** will lead to breakdown of the material, as the more stable benzimidazole moiety forms upon rupture of the strands. Therefore, we next targeted analogous ligands, with 1,2-dia-minoethylene instead of 1,2-diaminophenylene core, by reacting ethylenediamine with 4-allyloxybenzaldehyde (**8**) or its nitro derivative (**2**). Unlike in the case of the 1,2-diaminophenylene core, the corresponding bis-Schiff bases **9** and **10**, which cannot form benzimidazoles, were readily obtained (Fig. 4). Bis-Schiff bases **9** and **10** were then reacted with $[Cu(CH_3CN)_4]BF_4$ in methanol to yield the MWM precursors **11** and **12**. Differences between the structures of **6** and **12**, caused by changing the 1,2-diaminophenylene core, are discussed below in the 'Crystallographic studies' section.

2.2. Crystallographic studies

2.2.1. 2-(3-Nitro-4-allyloxyphenyl)-benzimidazole (4). Compound 4, an achiral molecule (Fig. 5), crystallizes in a Sohncke space group (P43, chiral space group), wherein chirality is generated by the helical arrangement of the molecules (Fig. 6). The apparent chirality of 4 in the crystalline state originates from the position of the allyl group, which can curve either above or below the plane of the molecule (the dihedral angle between the imidazole and 3-nitro-4-allyloxyphenyl moieties is 13.8°). However, 4 is not a rigid molecule, and it is capable of converting into its mirror image through internal degrees of freedom. A survey of the Cambridge Structural Database indicates that molecules without a chiral center strongly prefer crystallization in centrosymmetric space groups.²¹ It has also been documented that statistically, conformationally flexible achiral molecules are less likely to crystallize in chiral space groups than conformationally rigid ones. Nevertheless, possible factors leading to chiral crystallization of achiral molecules, such as intermolecular hydrogen bonding that results in spiral chains, had been pointed out.22 Within the crystal lattice of 4, adjacent molecules are linked together through imidazole NH···N hydrogen bonds (N1···N2: 2.858(3) Å; N1-H1: 0.86 Å; H1…N2: 2.006 Å; N1-H1…N2: 170.4°) into spiral chains, which are connected to each other by π - π stacking interactions between the benzene rings of the imidazole and the 3-nitro-4-allyloxyphenyl moieties (centroidcentroid distance: 4.028(2) Å; dihedral angle between mean planes: $14.03(9)^{\circ}$). It appears that these intermolecular forces, perhaps along with other weak interactions (such as CH…O hydrogen bonds), lead to a preference for molecular packing via 4₃ screw axes rather than inversion centers and glide planes. The identification of molecular features that lead to chiral crystallization of achiral molecules is especially important for crystal structure prediction, crystal engineering and the development of non-linear optical materials, for which noncentrosymmetric space groups are a requirement for secondharmonic generation.23

Paper



Fig. 4 Reaction scheme for the preparation of compounds 1-12.



Fig. 5 Thermal ellipsoid plot (50%) of 4.

2.2.2. Bis[2-(3-nitro-4-allyloxyphenyl)-benzimidazole]silver(1) nitrate (5). In contrast to 4, crystals of the silver complex of 2-(3-nitro-4-allyloxyphenyl)-benzimidazole are not chiral (Fig. 7 and S1†). Thus, two different conformations of two crystallographically unique Ag-complexes (with different orientations of the allyl end-groups) are found within the crystal structure of 5. The Ag and nitrate ions are located on a C₂ axis, which does not bisect the NO₃⁻ ions symmetrically. Therefore, the nitrate ions are disordered over two positions. In the case of the Ag1 complex, two C-atoms of the allyl group are essentially coplanar with the 2-phenylbenzimidazole moiety (dihedral angle between the imidazole and the phenyl mean planes: $7.11(9)^{\circ}$; dihedral angle between the 2-phenylbenzimidazole mean



Fig. 6 Packing diagram of 4, illustrating the helical arrangement of molecules (highlighted in gold) about the crystallographic 4_3 four-fold axis.



Fig. 7 Ball-and-stick representation of the two crystallographically unique Ag-complexes within the crystal structure of 5. Weak Ag···O and Ag···H interactions are shown with gray and green dashed lines, respectively. Only the H-atoms involved in these interactions, and one of the two disordered positions of each nitrate ion are shown for clarity. Color code: Ag – purple; O – red; N – blue; C – black; H – pink (Ag1–N1: 2.132(3) Å, Ag2–N4: 2.105(3) Å).

planes: 53.89(3)°), whereas in the case of the Ag2 complex, only one C-atom of the allyl group is coplanar with the 2-phenylbenzimidazole moiety (dihedral angle between the imidazole and the phenyl mean planes: $8.58(11)^{\circ}$; dihedral angle between the 2-phenylbenzimidazole mean planes: $39.35(4)^{\circ}$) (Fig. 8). Within the crystal lattice of 5, the Ag1 and Ag2 complexes form alternating layers (Fig. 9), in which individual complexes are linked together by H-bonds between imidazole H-atoms and nitrate ions in one direction (for Ag1, N…O: 2.880(3) Å, N–H: 0.859 Å, N–H…O: 2.037 Å, N–H–O: 166.5°; for Ag2, N…O: 2.757(4) Å, N–H: 0.860 Å, N–H…O: 1.932 Å, N–H–O: 160.2°), and



Fig. 8 Schematic representation of the four different conformers found in the crystal structure of **5**, showing the differences in allyl group orientations and in angles between ligand strands.

by weak Ag–nitrate (Ag…O: 2.698(2) and 3.104(5) Å for Ag1, and 2.844(5) and 3.183(3) Å for Ag2) and π – π interactions between benzene rings of neighboring benzimidazole and 3-nitro-4-allyloxyphenyl moieties in the perpendicular direction (for Ag1, centroid…centroid: 3.6363(17) Å, angle between mean planes: 7.13(10)°; for Ag2, centroid…centroid: 3.918(2) Å, angle between mean planes: 8.65(12)°). Worthy to mention are two short Ag…H distances for both Ag1 (C–H…Ag: 2.434 Å; C–H–Ag angle: 142.1°) and Ag2 (Ag…H: 2.493 Å; C–H–Ag angle: 143.2°), recognized as agostic/anagostic²⁴ interactions (Fig. 7).

2.2.3. Bis[1,2-phenylenebis{nitrilo(E)methylidyne(3-nitro-4-allyloxyphenyl)}]copper(1) hexafluorophosphate (6) and bis [1,2-ethylenebis{nitrilo(*E*)methylidyne(3-nitro-4-allyloxy phenyl)}] copper(1) tetrafluoroborate (12). The exchange of the 1,2-diaminophenylene core in 6 (Fig. 10 and S2[†]) to a 1,2-diaminoethylene core in 12 (Fig. 11 and S3[†]) has a significant influence on the structure of the precursor with intertwined strands (Fig. 12). Although the Cu–N distances (average: 2.038(2) Å in 6, 2.065(2) Å in 12), N-Cu-N angles (84.03(7) and 84.62(7)° in 6, 85.61(6) and $85.56(7)^{\circ}$ in 12; N atoms from same strand) and the angle between planes defined by N-Cu-N are virtually identical $(80.97(7)^{\circ}$ in 6 and $81.27(6)^{\circ}$ in 12), the free rotation around the C-C bond of the 1,2-diaminoethylene bridge in 12 leads to a different relative orientation of the two strands within each complex. Thus, the N-C-C-N torsion angle changes drastically from 1.3(3) and 3.0(3)° in 6, to 53.5(2) and 57.6(2)° in 12 (N…N



Fig. 9 View along the alternating planes formed by the crystallographically unique Ag1 and Ag2 complexes in the crystal structure of 5, showing the disordered nitrate ions.



Fig. 10 Ball-and-stick representation of the crystal structure of $6 (PF_6^-$ counterion and H-atoms omitted for clarity).

separations lengthen from 2.734(2) and 2.738(2) Å in **6** to 2.801(2) and 2.809(3) Å in **12**). As a result, the angle between phenolic Oatom, core (1,2-diaminophenylene or 1,2-diaminoethylene) C–C bond centroid and opposite phenolic O-atom increases from 84.3 and 88.7° in **6** to 103.6 and 106.7° in **12**. This change is accompanied by a shift in π - π interactions: while in **6** intermolecular π - π interactions dominate (centroid-centroid: 3.558(2), 3.752(2) and 3.770(2) Å, parallel benzene rings; closest intramolecular centroid–centroid: 4.420(1) Å), an opposite scenario is observed in **12** (intramolecular centroid–centroid: 3.644(1) and 3.802(1) Å, angle between benzene ring mean planes: 11.5 and 11.7°; closest intermolecular centroid–centroid: 4.157(1) Å). Ultimately, the terminal alkene functionalities are much closer to each other in **12** (closest distance between phenolic O-atoms: 6.02(1) Å) than in **6** (closest distance between phenolic O-atoms: 8.45(1) Å), possibly allowing intramolecular reactivity in **12**.

3. Summary

Herein we have set forth a novel approach toward the preparation of hitherto elusive molecularly woven materials, by "sewing" together (polymerizing) precursors with intertwined, functionalized strands. An essential feature of these precursors is the placement of the terminal functionalities so that only inter- and no intra-molecular reactivity is possible. We have prepared precursors based on terminal alkene-functionalized bis-Schiff base ligands (with either a 1,2-diaminophenylene or a 1,2-diaminoethylene core), coordinated around a Cu(I) ion. It first became evident that the bis-Schiff base with the 1,2-diaminophenylene core (7) can easily undergo intramolecular cyclization/aromatization to yield a stable benzimidazole moiety. Therefore, 7 could only be isolated as the tetrahedral Cu(I) complex (6). The analogous bis-Schiff bases with a 1,2diaminoethylene core (9 and 10), in turn, are stable in both metal-free and complex forms. The structure of the two different precursors, derived from X-ray crystallographic studies, reveals another crucial requirement for the MWM precursor. While in 6 the rigid 1,2-diaminophenylene cores do orient the strands so that the terminal alkene functionalities are



Fig. 11 Ball-and-stick representation of the crystal structure of $12 (BF_4^-$ counterion, nitrobenzene solvent molecule and H-atoms omitted for clarity). Both terminal $-CH=CH_2$ groups and one of the nitro groups of the bis-Schiff base ligand shown in orange are disordered (60/40) over two positions (only one position is shown for clarity).

far from each other, in **12** the flexible 1,2-diaminoethylene core allows the functional groups to approach each other close enough for intramolecular reactions to possibly occur. Furthermore, it also becomes evident that although **6** and **12** are perhaps the synthetically most easily accessible and inexpensive candidates, they are inadequate as MWM precursors, as during alkene metathesis, $(PCy_3)_2Cl_2Ru=CHPh$ (Grubbs catalyst) consistently led to breakdown of the bis-Schiff base ligand (to the benzimidazole derivative **4** in the case of **6**, and to the starting material **2** in the case of **12**). We are currently targeting more robust ligand systems that will address all the requirements for a MWM precursor revealed by this work.

4. Experimental section

4.1. General

Acetone was dried with $CaSO_4$, distilled under N_2 and stored over 4 Å molecular sieves. 4-Allyloxybenzaldehyde,²⁵



Fig. 12 Comparative stick diagrams showing the different relative orientation of the two ligand strands in 6 and in 12.

 $[Cu(CH_3CN)_4]BF_4$ and $[Cu(CH_3CN)_4]PF_6$ (ref. 26) were prepared according to the literature. 3-Nitro-4-hydroxybenzaldehyde was obtained by the nitration of 4-hydroxybenzaldehyde using a modified procedure from the literature.²⁷ 1,2-Benzenediamine (*o*-phenylenediamine) was recrystallized from boiling water/ activated charcoal. K₂CO₃ and KI were dried overnight in an oven at 130 °C. All other commercially available reagents were used as received. NMR spectra were recorded on a Jeol JNM-ECP400 spectrometer.

4.2. Synthesis of 3-nitro-4-hydroxybenzaldehyde (1)

As the published procedure²⁷ was found to yield only 15–22% of product, an improved procedure is reported herein. 4-Hydroxybenzaldehyde (12.0 g, 0.0983 mol) was dissolved with stirring in 100 mL glacial acetic acid, and the solution was cooled in an ice bath. Under vigorous stirring, HNO₃ (70%) (35 mL, 35 g pure HNO₃, 0.55 mol) was added dropwise over 15 minutes. After stirring for 20 hours (the ice slowly melted and the solution warmed up to room temperature), the reaction mixture was cooled in an ice bath. The solid was filtered out, washed with two 7 mL portions of ice-cold acetic acid (70% in water) and then with six 25 mL portions of water. After drying in air, the product was kept in high vacuum for 12 hours. Yield: 8.38 g (51%). ¹H NMR (400 MHz, CDCl₃): 11.01 (s, 1H, OH), 9.93 (s, 1H, CH=O), 8.62 (d, 1H, ⁴J = 2.2 Hz), 8.13 (dd, 1H, ³J = 8.8 Hz, ⁴J = 2.2 Hz), 7.31 (d, 1H, ³J = 8.8 Hz).

4.3. Synthesis of 3-nitro-4-allyloxybenzaldehyde (2)

3-Nitro-4-hydroxybenzaldehyde (0.55 g, 3.3 mmol), anhydrous K_2CO_3 (1.40 g, 10.1 mmol), KI (0.133 g, 0.80 mmol) and allyl bromide (0.90 mL, 1.26 g, 10.4 mmol) were refluxed in 50 mL anhydrous acetonitrile under an N_2 atmosphere for 20 hours. After removal of the solvent and excess allyl bromide in vacuum, the residue was dissolved in 100 mL chloroform and the solution was filtered to remove the insoluble inorganic salts.

Evaporation of the solvent in vacuum yielded 0.66 g of 2 as a yellow liquid, which slowly solidified on standing. Yield: 97%. ¹H NMR (400 MHz, CDCl₃): 9.92 (s, 1H, C*H*==O), 8.34 (d, 1H, ⁴*J* = 1.8 Hz), 8.05 (dd, 1H, ³*J* = 8.8 Hz, ⁴*J* = 2.2 Hz), 7.21 (d, 1H, ³*J* = 8.4 Hz), 6.03 (m, 1H), 5.51 (dm, 1H, ³*J* = 17.6 Hz), 5.38 (dm, 1H, ³*J* = 11.7 Hz), 4.79 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): 189.2, 156.0, 139.8, 135.1, 131.0, 129.0, 126.8, 118.8, 115.1, 70.4 ppm.

4.4. Synthesis of *N*-[(3-nitro-4-allyloxyphenyl)methylene]-1,2-benzenediamine (3)

A solution of 1,2-benzenediamine (0.058 g, 0.54 mmol) in 3.3 mL methanol was added dropwise to a solution of 2 (0.330 g, 1.59 mmol) in 1.6 mL methanol, and the mixture was stirred for two days. The yellow precipitate was filtered, washed with methanol and dried in vacuum. Yield: 0.089 g (68%). ¹H NMR (400 MHz, CDCl₃): 8.48 (s, 1H, N=CH), 8.39 (d, 1H, ⁴J = 2.2 Hz), 8.04 (dd, 1H, ³J = 8.8 Hz, ⁴J = 2.2 Hz), 7.14 (d, 1H, ³J = 8.8 Hz), 7.07 (m, 2H), 6.76 (m, 2H), 6.05 (m, 1H), 5.52 (dm, 1H, ³J = 17.2 Hz), 5.37 (dm, 1H, ³J = 10.6 Hz), 4.76 (m, 2H), 4.25 (s, 2H, NH₂) ppm.

4.5. Synthesis of 2-(3-nitro-4-allyloxyphenyl)-benzimidazole(4)

A solution of 1,2-benzenediamine (0.17 g, 1.6 mmol) in 2.5 mL absolute ethanol was stirred overnight with a solution of 2 (0.66 g, 3.2 mmol) in 5 mL absolute ethanol. The yellow precipitate was filtered, washed with a small amount of ethanol and dried in vacuum. Recrystallization from acetone provided 0.32 g (68%) of 4 as light yellow crystals. ¹H NMR (400 MHz, acetone- d_6): 12.06 (s, 1H), 8.65 (d, 1H, ${}^4J = 1.4$ Hz), 8.44 (dd, 1H, ${}^3J = 8.8$ Hz, ${}^4J = 1.5$ Hz), 7.68 (m, 1H), 7.52 (m, 1H), 7.51 (d, 1H, ${}^3J = 8.8$ Hz), 7.22 (m, 2H), 6.11 (m, 1H), 5.53 (dm, 1H, ${}^3J = 17.1$ Hz), 5.32 (dm, 1H, ${}^3J = 10.8$ Hz), 4.87 (m, 2H) ppm. 13 C NMR (101 MHz, acetone- d_6): 152.4, 149.4, 144.4, 140.3, 135.3, 132.3, 131.9, 123.4, 123.1, 123.0, 122.1, 119.4, 117.6, 115.8, 111.2, 70.0 ppm. Paleyellow X-ray quality single-crystals were obtained by slow cooling of a concentrated, hot acetone solution.

4.6. Synthesis of bis[2-(3-nitro-4-allyloxyphenyl)benzimidazole]silver(1) nitrate (5)

A solution of 4 (14 mg, 53 µmol) in 3 mL CH₃CN was layered over a solution of AgNO₃ (2.6 mg, 15 µmol) in 1 mL CH₃CN. After a few days yellow X-ray quality single-crystals of 5 were obtained. ¹H NMR (400 MHz, DMSO-d₆): 13.22 (s, 2H), 8.68 (d, 2H, ⁴*J* = 2.2 Hz), 8.42 (dd, 2H, ³*J* = 8.8 Hz, ⁴*J* = 2.2 Hz), 7.69 (d, 2H, ³*J* = 7.4 Hz), 7.56 (m, 4H), 7.24 (m, 4H), 6.06 (m, 2H), 5.48 (dd, 2H, ²*J* = 1.1 Hz, ³*J* = 17.2 Hz), 5.33 (dd, 2H, ²*J* = 1.1 Hz, ³*J* = 10.6 Hz), 4.87 (d, 4H, ³*J* = 5.1 Hz) ppm. ¹³C NMR (101 MHz, DMSO-d₆): 152.6, 149.9, 140.1, 132.9, 132.8, 123.7, 123.1, 118.7, 118.6, 116.7, 70.3 ppm.

4.7. Synthesis of bis[1,2-phenylenebis{nitrilo(*E*) methylidyne(3-nitro-4-allyloxyphenyl)}]copper(1) hexafluorophosphate (6)

A colorless solution of $[Cu(CH_3CN)_4]PF_6~(0.302~g,~0.810~mmol)$ in 15 mL methanol was added under an N_2 atmosphere to

a solution of 1,2-benzenediamine (0.178 g, 1.65 mmol) in 5 mL methanol. The purple solution obtained was transferred into a solution of 3-nitro-4-allyloxybenzaldehyde (1.000 g, 4.83 mmol) in 10 mL methanol under N₂. A bright red precipitate was obtained, which was stirred for 24 hours, filtered, washed with methanol and dried in vacuum. 0.626 g of 5 was obtained as a red powder. Yield: 65%. ¹H NMR (400 MHz, acetone-d₆): 8.95 (s, 4H, N=CH), 8.30 (d, 4H, ⁴J = 1.8 Hz), 8.02 (dd, 4H, ³J = 8.8 Hz, ⁴J = 1.8 Hz), 7.69 (s, 8H), 6.93 (d, 4H, ³J = 8.8 Hz), 6.01 (m, 4H), 5.43 (dm, 4H, ³J = 17.2 Hz), 5.31 (dm, 4H, ³J = 10.6 Hz), 4.73 (m, 8H) ppm. ¹³C NMR (101 MHz, CDCl₃): 161.5, 154.5, 144.1, 139.3, 135.2, 131.8, 129.9, 126.9, 126.1, 120.2, 117.8, 115.1, 70.2 ppm. Red X-ray quality single-crystals were grown from acetone or acetonitrile solution by slow diethyl ether vapor diffusion.

4.8. Synthesis of 1,2-ethylenebis[nitrilo(*E*)methylidyne(4-allyloxyphenyl)] (9)

A solution of ethylenediamine (0.760 g, 12.6 mmol) in 5 mL absolute ethanol was added dropwise to a solution of 4-allyloxybenzaldehyde (4.010 g, 24.7 mmol) in 35 mL absolute ethanol. A white precipitate started forming soon, which was stirred overnight (~18 h), then filtered out, washed with absolute ethanol and dried in vacuum. Yield: 3.25 g (75%). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: 8.19 (s, 2H, N=CH), 7.61 (d, 4H, ${}^{3}J = 8.8 \text{ Hz})$, 6.90 (d, 4H, ${}^{3}J = 8.8$ Hz), 6.04 (m, 2H), 5.40 (dm, 2H, ${}^{3}J = 17.3$ Hz), 5.29 (dm, 2H, ${}^{3}I = 10.3$ Hz), 4.55 (dm, 4H, ${}^{3}I = 5.4$ Hz), 3.90 (s, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃): 162.0, 160.6, 133.0, 129.7, 129.3, 118.0, 114.8, 68.9, 61.8 ppm. ¹H NMR (400 MHz, acetone- d_6): 8.23 (s, 2H, N=CH), 7.67 (d, 4H, ${}^{3}J = 8.8$ Hz), 6.96 (d, 4H, ${}^{3}J = 8.8$ Hz), 6.06 (m, 2H), 5.41 (dm, 2H, ${}^{3}J = 17.2$ Hz), 5.25 (dm, 2H, ${}^{3}J = 10.6$ Hz), 4.60 (dm, 4H, ${}^{3}J = 5.2$ Hz), 3.83 (s, 4H) ppm. ¹³C NMR (101 MHz, acetone-*d*₆): 160.9, 160.7, 133.6, 129.8, 129.5, 116.8, 114.6, 68.5, 61.7 ppm.

4.9. Synthesis of 1,2-ethylenebis[nitrilo(*E*)methylidyne(3-nitro-4-allyloxyphenyl)] (10)

A solution of ethylenediamine (0.680 g, 11.3 mmol) in 5 mL absolute ethanol was added dropwise to a slightly warmed (30-40 °C) solution of 3-nitro-4-allyloxybenzaldehyde (4.500 g, 21.7 mmol) in 40 mL absolute ethanol. Within an hour a large amount of precipitate formed. After stirring overnight (~18 h), the yellow precipitate was filtered out, washed with absolute ethanol and dried in vacuum. Yield: 3.58 g (75%). ¹H NMR (400 MHz, $CDCl_3$): 8.20 (s, 2H, N=CH), 8.15 (d, 2H, ${}^{4}J = 2.2$ Hz), 7.84 $(dd, 2H, {}^{3}J = 8.4 \text{ Hz}, {}^{4}J = 2.2 \text{ Hz}), 7.06 (d, 2H, {}^{3}J = 8.4 \text{ Hz}), 6.01$ (m, 2H), 5.47 (dm, 2H, ${}^{3}J = 17.2$ Hz), 5.33 (dm, 2H, ${}^{3}J = 10.6$ Hz), 4.70 (dm, 4H, ${}^{3}J = 5.2$ Hz), 3.94 (s, 4H) ppm. ${}^{13}C$ NMR (101 MHz, CDCl₃): 159.6, 153.4, 140.1, 133.2, 131.4, 129.1, 125.3, 118.8, 114.8, 70.2, 61.3. ¹³C NMR (400 MHz, CDCl₃): 159.5, 153.3, 139.9, 133.4, 131.4, 129.1, 125.0, 118.6, 114.8, 70.1, 61.3 ppm. ¹H NMR (400 MHz, acetone-*d*₆): 8.34 (s, 2H, N=*CH*), 8.19 (d, 2H, ⁴*J* = 1.8 Hz), 7.96 (dd, 2H, ${}^{3}J =$ 8.8 Hz, ${}^{4}J =$ 1.8 Hz), 7.37 (d, 2H, ${}^{3}J =$ 8.8 Hz), 6.07 (m, 2H), 5.48 (dm, 2H, ${}^{3}J = 17.6$ Hz), 5.29 (dm, 2H, ${}^{3}J = 10.6$ Hz), 4.82 (dm, 4H, ${}^{3}J = 5.1$ Hz), 3.92 (s, 4H) ppm. ${}^{13}C$

Table 1 Crystallographic details for compounds 4, 5, 6 and 12

Compound	4	5	6	12 C ₆ H ₅ NO ₂
Formula	C16H13N3O3	C32H26AgN7O9	$\mathrm{C}_{52}\mathrm{H}_{44}\mathrm{CuF}_6\mathrm{N}_8\mathrm{O}_{12}\mathrm{P}$	C ₅₀ H ₄₉ BCuF ₄ N ₉ O ₁₄
Formula weight	295.29	760.47	1181.46	1150.33
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic
Space group	P43	P2/c	$P2_1/n$	$P2_1/n$
a/Å	8.7624(1)	26.7698(3)	15.2157(2)	14.5499(2)
b/Å	8.7624(1)	7.3672(1)	14.5593(2)	18.8640(2)
c/Å	18.3758(2)	15.5539(2)	22.9542(3)	19.3788(2)
$\alpha/^{o}$	90	90	90	90
β /°	90	97.758(1)	102.021(1)	105.378(1)
$\gamma/^{\rm o}$	90	90	90	90
$V/\text{\AA}^3$	1410.89(3)	3039.44(7)	4973.5(1)	5128.45(11)
Ζ	4	4	4	4
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.390	1.662	1.578	1.490
Absorption coefficient, μ/mm^{-1}	0.099	0.734	0.569	0.517
Reflections collected/unique	33 826/3510	46 487/6232	94 617/11 859	89 433/10 493
Observed reflections $(I > 2\sigma(I))$	2811	4468	8664	8312
Goodness-of-fit (on F^2)	1.047	1.007	1.027	1.009
$R_1(F); R_w(F) (I > 2\sigma(I))$	0.0437; 0.0908	0.0389; 0.0682	0.0408; 0.0928	0.0359; 0.0779
$R_1(F); R_w(F)$ (all data)	0.0628; 0.0995	0.0718; 0.0778	0.0673; 0.1054	0.0524; 0.0857
Largest diff. peak & hole (e \mathring{A}^{-3})	0.341/-0.232	0.463 / -0.551	0.458 / -0.508	0.403 / -0.393

NMR (101 MHz, acetone-*d*₆): 159.4, 152.8, 140.4, 133.2, 132.3, 129.6, 124.0, 117.5, 115.2, 69.9, 61.1 ppm.

70.2, 61.9 ppm. Single-crystals were grown from a nitrobenzene solution by diethyl ether vapor diffusion.

4.10. Synthesis of bis[1,2-ethylenebis{nitrilo(*E*) methylidyne(4-allyloxyphenyl)}]copper(1) tetrafluoroborate (11)

[Cu(CH₃CN)₄]BF₄ (0.225 g, 0.715 mmol) in 7.5 mL CH₃CN was added to compound **9** (0.500 g, 1.43 mmol) in 30 mL CH₃CN under stirring. The colorless solution immediately turned orange. After stirring for 10 minutes, the solvent was removed in vacuum. Yield: 0.59 g (97%). ¹H NMR (400 MHz, CDCl₃): 8.27 (s, 2H, N=CH), 7.60 (d, 4H, ³J = 8.8 Hz), 6.84 (d, 4H, ³J = 8.8 Hz), 6.02 (m, 2H), 5.40 (dm, 2H, ³J = 17.6 Hz), 5.28 (dm, 2H, ³J = 10.6 Hz), 4.56 (s, 4H), 3.97 (s, 4H) ppm. ¹H NMR (400 MHz, acetone-*D*₆): 8.52 (s, 2H, N=CH), 7.81 (d, 4H, ³J = 8.8 Hz), 7.00 (d, 4H, ³J = 8.8 Hz), 6.04 (m, 2H), 5.40 (dm, 2H, ³J = 17.6 Hz), 5.26 (dm, 2H, ³J = 10.6 Hz), 4.61 (dm, 4H, ³J = 5.1 Hz), 4.14 (s, 4H) ppm. ¹³C NMR (101 MHz, acetone-*D*₆): 164.4, 161.7, 133.3, 130.8, 127.2, 117.1, 114.6, 68.7, 61.4 ppm.

4.11. Synthesis of bis[1,2-ethylenebis{nitrilo(*E*) methylidyne(3-nitro-4-allyloxyphenyl)}]copper(1) tetrafluoroborate (12)

[Cu(CH₃CN)₄]BF₄ (0.180 g, 0.572 mmol) in 4 mL CH₃CN was added to compound **10** (0.500 g, 1.14 mmol) in 19 mL CH₃CN under stirring. The color of the solution turned from yellow to orange. After stirring for 10 minutes, the solvent was removed in vacuum. Yield: 0.55 g (94%). ¹H NMR (400 MHz, acetone-*D*₆): 8.67 (s, 2H, N=CH), 8.20 (d, 2H, ⁴*J* = 2.2 Hz), 7.96 (dd, 2H, ³*J* = 8.8 Hz, ⁴*J* = 1.8 Hz), 7.45 (d, 2H, ³*J* = 8.8 Hz), 6.07 (m, 2H), 5.49 (dm, 2H, ³*J* = 17.2 Hz), 5.33 (dm, 2H, ³*J* = 10.6 Hz), 4.84 (dm, 4H, ³*J* = 5.1 Hz), 4.19 (s, 4H) ppm. ¹³C NMR (101 MHz, acetone-*D*₆): 164.1, 154.0, 139.7, 135.0, 132.1, 126.5, 124.3, 117.8, 115.5,

4.12. X-ray crystallography

X-ray diffraction data were collected at 100 K from a singlecrystal mounted atop a glass fiber under Paratone-N oil, with a Bruker SMART APEX II diffractometer using graphitemonochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. The structures were solved by employing SHELXTL direct methods and refined by full-matrix least squares on F^2 , using the APEX2 v2014.9-0 software package (Bruker AXS Inc.: Madison, WI, 2014).²⁸ All non-H atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined using a riding model. Bondlength and atomic displacement parameter restraints were used for the disordered groups in **12**. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers: CCDC 1439669–1439672). Crystallographic details are summarized in Table 1.

Acknowledgements

This material is based upon work supported by a Faculty Research and Creative Activities Award from Western Michigan University (FRACAA, No. P11-014).

References

- 1 *"Engineering with Rubber"*, ed. A. N. Gent, Carl Hanser Verlag, Munich, 2nd edn, 2001.
- 2 H. L. Stein, "Ultrahigh molecular weight polyethylene (UHMWPE)", in *Engineered Materials Handbook (Vol. 2: Engineering Plastics)*, ed. C. Dostal, ASM International, 1988, pp. 167–171.

- 3 C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385–388.
- 4 (a) P. J. F. Harris, *Carbon Nanotube Science: Synthesis*, *Properties and Applications*, Cambridge University Press, 2009; (b) A. Jorio, G. Dresselhaus and M. S. Dresselhaus, *Carbon Nanotubes: Advanced Topics in the Synthesis*, *Structure*, *Properties and Applications*, Springer, 2008.
- 5 Molecularly woven materials (MWMs) are defined here as covalent molecular strands that are mechanically interlocked by multiple crossings, excluding structures based on strands consisting of smaller units linked together by coordinate bonds, hydrogen bonds, or other weak bonds.
- 6 (a) D. H. Busch, J. Inclusion Phenom. Mol. Recognit. Chem., 1992, 12, 389–395; (b) D. H. Busch, "Ligand design for enhanced molecular organization Selectivity and specific sequencing in multiple receptor ligands, and orderly molecular entanglements", in Transition Metals in Supramolecular Chemistry, ed. L. Fabbrizzi and A. Poggi, Kluwer Academic Publishing, 1994, pp. 55–80; (c) T. J. Hubin, A. G. Kolchinski, A. L. Vance and D. H. Busch, Adv. Supramol. Chem., 1999, 5, 237–357; (d) T. J. Hubin and D. H. Busch, Coord. Chem. Rev., 2000, 200–202, 5–52; (e) D. L. Cockriel, J. M. McClain, K. C. Patel, R. Ullom, T. R. Hasley, S. J. Archibald and T. J. Hubin, Inorg. Chem. Commun., 2008, 11, 1–4.
- 7 (a) J. Hausmann and S. Brooker, Chem. Commun., 2004, 1530–1531; (b) C. S. Campos-Fernández, R. Clérac and K. R. Dunbar, Angew. Chem., Int. Ed., 1999, 38, 3477–3479; (c) T. Bark, M. Düggeli, H. Stoeckli-Evans and A. von Zelewsky, Angew. Chem., Int. Ed., 2001, 40, 2848–2851.
- 8 (a) R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, 111, 5434–5464; (b) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh and R. T. McBurney, *Angew. Chem., Int. Ed.*, 2011, 50, 9260–9327.
- 9 (a) T. Ciengshin, R. Sha and N. C. Seeman, *Angew. Chem., Int. Ed.*, 2011, **50**, 4419–4422; (b) W. Liu, H. Zhong, R. Wang and N. C. Seeman, *Angew. Chem., Int. Ed.*, 2011, **50**, 264–267.
- 10 D. Andrae, New J. Chem., 2006, 30, 873-882.
- 11 (a) R. H. Grubbs, Handbook of Metathesis, Wiley-VCH, Weinheim, 2003; (b) R. H. Grubbs, Tetrahedron, 2004, 60, 7117-7140; (c) R. H. Grubbs and T. M. Trnka, "Rutheniumcatalyzed olefin metathesis", in Ruthenium in Organic Synthesis, ed. S.-I. Murahashi, Wiley-VCH, Verlag GmbH, 2005; (d) D. Astruc, New J. Chem., 2005, 29, 42-56; (e) R. R. Schrock and A. H. Hoveyda, Angew. Chem., Int. Ed., 2003, 42, 4592-4633; (f) T. M. Trnka and R. H. Grubbs, Acc. Chem. Res., 2001, 34, 18-29; (g) G. C. Vougioukalakis and R. H. Grubbs, Chem. Rev., 2010, 110, 1746-1787.
- 12 (a) C. W. Lee and R. H. Grubbs, J. Org. Chem., 2001, 66, 7155–7158; (b) A. V. Chuchuryukin, H. P. Dijkstra, B. M. J. M. Suijkerbuijk, R. J. M. Klein Gebbink, G. P. M. van Klink, A. M. Mills, A. L. Spek and G. van Koten, Angew. Chem., Int. Ed., 2003, 115, 238–240; (c) M. Yu, C. Wang, A. F. Kyle, P. Jakubec, D. J. Dixon, R. R. Schrock and A. H. Hoveyda, Nature, 2011, 479, 88–93;

(*d*) A. Gradillas and J. Pérez-Castells, *Angew. Chem., Int. Ed.*, 2006, **45**, 6086–6101.

- 13 (a) B. Mohr, M. Weck, J.-P. Sauvage and R. H. Grubbs, Angew. Chem., Int. Ed., 1997, 36, 1308–1310; (b) D. A. Leigh, P. J. Lusby, R. T. McBurney, A. Morelli, A. M. Z. Slawin, A. R. Thomson and D. B. Walker, J. Am. Chem. Soc., 2009, 131, 3762–3771; (c) M. Gupta, S. Kang and M. F. Mayer, Tetrahedron Lett., 2008, 49, 2946–2950; (d) E. N. Guidry, S. J. Cantrill, J. F. Stoddart and R. H. Grubbs, Org. Lett., 2005, 7, 2129–2132; (e) H. Iwamoto, K. Itoh, H. Nagamiya and Y. Fukazawa, Tetrahedron Lett., 2003, 44, 5773–5776; (f) F. Arico, P. Mobian, J.-M. Kern and J.-P. Sauvage, Org. Lett., 2003, 5, 1887–1890; (g) M. Weck, B. Mohr, J.-P. Sauvage and R. H. Grubbs, J. Org. Chem., 1999, 64, 5463–5471; (h) D. A. Leigh, R. G. Pritchard and A. J. Stephens, Nat. Chem., 2014, 6, 978–982; (i) L. Wang, M. O. Vysotsky, A. Bogdan, M. Bolte and V. Böhmer, Science, 2004, 304, 1312–1314.
- 14 (a) S. Li, M. Liu, B. Zheng, K. Zhu, F. Wang, N. Li, X.-L. Zhao and F. Huang, Org. Lett., 2009, 11, 3350-3353; (b) S. M. Goldup, D. A. Leigh, P. J. Lusby, R. T. McBurney and A. M. Z. Slawin, Angew. Chem., Int. Ed., 2008, 47, 6999-7003; (c) S. Kang, B. M. Berkshire, Z. Xue, M. Gupta, C. Layode, P. A. May and M. F. Mayer, J. Am. Chem. Soc., 2008, 130, 15246-15247; (d) A. F. M. Kilbinger, S. J. Cantrill, A. W. Waltman, M. W. Day and R. H. Grubbs, Angew. Chem., Int. Ed., 2003, 42, 3281-3285; (e) R. G. E. Coumans, J. A. A. W. Elemans, P. Thordarson, R. J. M. Nolte and A. E. Rowan, Angew. Chem., Int. Ed., 2003, 42, 650-654.
- 15 (a) C. Dietrich-Buchecker, G. Rapenne and J.-P. Sauvage, *Chem. Commun.*, 1997, 2053–2054; (b) J. Guo, P. C. Mayers, G. A. Breault and C. A. Hunter, *Nat. Chem.*, 2010, 2, 218– 222; (c) J.-F. Ayme, G. Gil-Ramírez, D. A. Leigh, J.-F. Lemonnier, A. Markevicius, C. A. Muryn and G. Zhang, *J. Am. Chem. Soc.*, 2014, 136, 13142–13145; (d) C. Dietrich-Buchecker, G. Rapenne and J.-P. Sauvage, *Coord. Chem. Rev.*, 1999, 185–186, 167–176.
- 16 M. R. Buchmeiser, Chem. Rev., 2000, 100, 1565-1604.
- 17 (a) N. M. Glagovich, E. M. Reed, G. Crundwell, J. B. Updegraff III, M. Zeller and A. D. Hunter, Acta Crystallogr., Sect. A: Found. Crystallogr., 2005, E61, 01251-01253; (b)R. Hadjikhani, S. Dehghanpour, A. Mahmoudi and F. Mojahed, Z. Anorg. Allg. Chem., 2006, 632, 723-725; (c) T. W. Bell and F. Guzzo, J. Chem. Soc., Chem. Commun., 1986, 769-771; (d) O. Q. Munro, S. D. Joubert and C. D. Grimmer, Chem.-Eur. J., 2006, 12, 7987-7999; (e) F. Franceschi, G. Guillemot, E. Solari, C. Floriani, N. Re, H. Birkedal and P. Pattison, Chem.-Eur. J., 2001, 7, 1468-1478.
- 18 (a) J. G. Smith and I. Ho, *Tetrahedron Lett.*, 1971, 12, 3541–3544; (b) P. Li, I. J. Scowen, J. E. Davies and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 1998, 3791–3800; (c) Y.-S. Lee, Y.-H. Cho, S.-J. Lee, J.-K. Bin, J.-H. Yang, G.-S. Chae and C.-H. Cheon, *Tetrahedron*, 2015, 71, 532–538.
- 19 Over 70 crystal structures in the CCDC†; for the parent compound, see: N. Bresciani-Pahor, M. Calligaris,

Paper

P. Delise, G. Dodic, G. Nardin and L. Randaccio, J. Chem. Soc., Dalton Trans., 1976, 2478–2483.

- 20 (a) J. Mahía, M. A. Maestro, M. Vázquez, M. R. Bermejo,
 A. M. González and M. Maneiro, Acta Crystallogr., Sect. A: Found. Crystallogr., 2000, C56, 492–493; (b) P. G. Owston,
 R. Peters, E. Ramsammy, P. A. Tasker and J. Trotter, J. Chem. Soc., Chem. Commun., 1980, 1218–1220.
- 21 E. Pidcock, Chem. Commun., 2005, 3457-3459.
- 22 (a) T. Matsuura and H. Koshima, J. Photochem. Photobiol., C, 2005, 6, 7–24; (b) M. Miyata, N. Tohnai, I. Hisaki and T. Sasaki, Symmetry, 2015, 7, 1914–1928.
- 23 L. R. Dalton, L. P. Yu, M. Chen, L. S. Sapochak and C. Xu, *Synth. Met.*, 1993, **54**, 155–160.
- 24 (a) M. Brookhart, M. L. H. Green and G. Parkin, Proc. Natl. Acad. Sci. U. S. A., 2007, 104, 6908-6914; (b) A. Ilie, C. I. Raţ, S. Scheutzow, C. Kiske, K. Lux, T. M. Klapötke, C. Silvestru and K. Karaghiosoff, Inorg. Chem., 2011, 50, 2675-2684.
- 25 N. L'Hermite, J.-F. Peyrat, P. Hildgen, J.-D. Brion and M. Alami, *Synthesis*, 2008, 1049–1060.
- 26 G. J. Kubas, Inorg. Synth., 1979, 19, 90-92.
- 27 P. Ionita, S. Afr. J. Chem., 2008, 61, 123-126.
- 28 *APEX2 v2014.9-0*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.