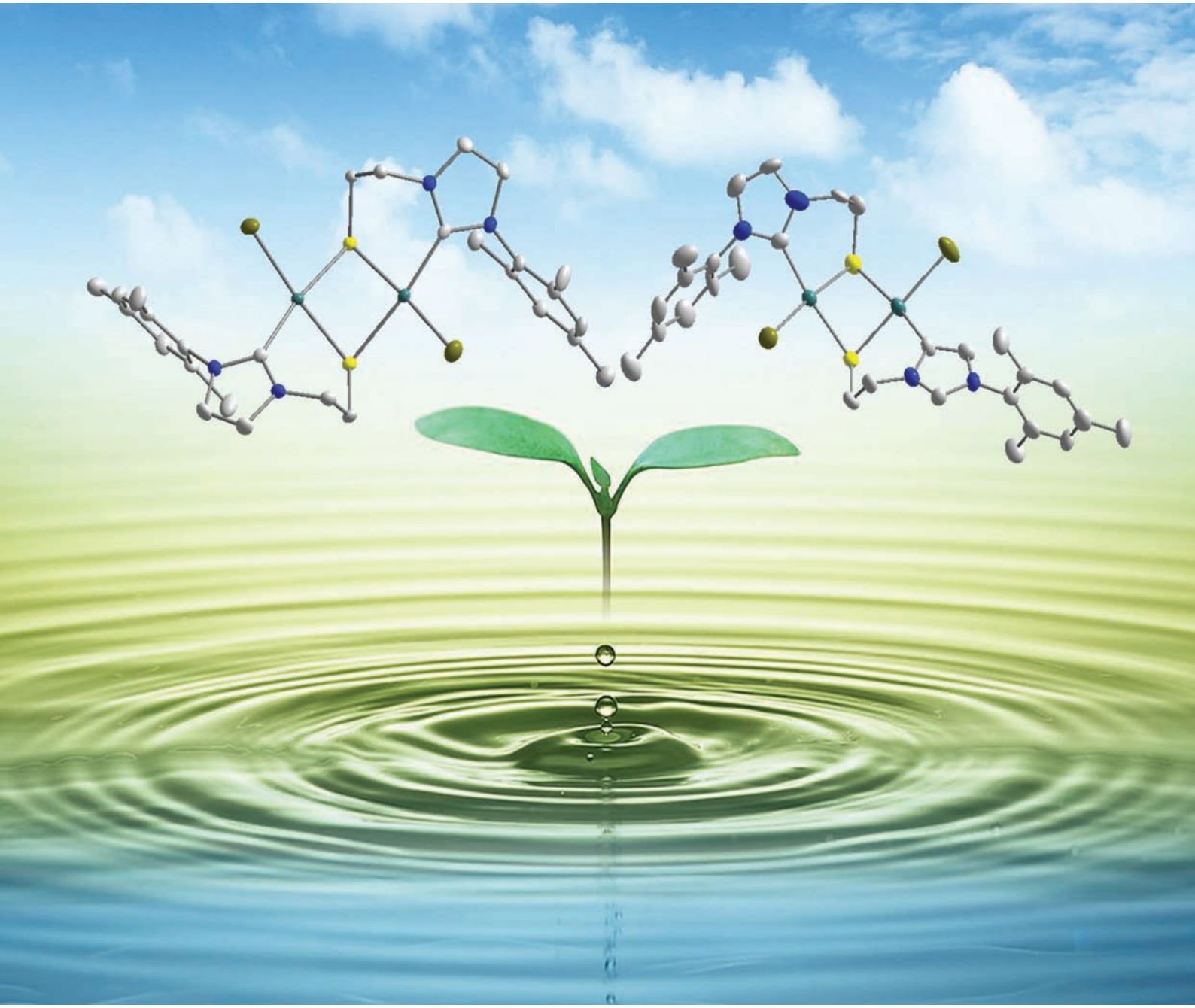
Dalton Transactions

Celebrating 40 years

An international journal of inorganic chemistry

www.rsc.org/dalton

Volume 40 | Number 44 | 28 November 2011 | Pages 11645–11984



ISSN 1477-9226

COVER ARTICLE

Yuan and Huynh

Syntheses and characterizations of thiolato-functionalized N-heterocyclic carbene Pd(II) complexes with normal and mesoionic binding modes

International Year of CHEMISTRY 2011

1477-9226(2011)40:44;1-O

RSC Publishing

Dalton Transactions

Dynamic Article Links

Cite this: *Dalton Trans.*, 2011, **40**, 11698

www.rsc.org/dalton

PAPER

Syntheses and characterizations of thiolato-functionalized N-heterocyclic carbene Pd(II) complexes with normal and mesoionic binding modes†

Dan Yuan and Han Vinh Huynh*

Received 29th April 2011, Accepted 13th June 2011
DOI: 10.1039/c1dt10789e

The thiolato-bridged dimeric Pd(II) NHC complex **1** has been synthesized from the reaction of thioester-functionalized imidazolium salt **B** and $Pd(OAc)_2$. The isolation of its interesting constitutional isomer **2** bearing both classical C(2)-bound and mesoionic C(4)-bound ligands coordinating to two different metal centers in the same complex allowed for a direct comparison of these isomeric carbenes. Reactivity studies of **1** with $NaSCH(CH_3)_2$ and $NaBF_4$ afforded the tetranuclear compound **3** with a $[Pd_4S_4]$ macrocycle. All complexes have been fully characterized by multinuclei NMR spectroscopies, ESI mass spectrometry and X-ray diffraction analysis.

Introduction

N-heterocyclic carbenes (NHCs) have been investigated with great intensity due to their unique properties[1] and the ease of their preparation as well as modification. In particular, donor functions can be introduced at the nitrogen atom of the heterocycle in a simple manner, and various complexes of donor-functionalized NHCs and their use in catalysis have been explored and recently reviewed.[2] Functionalization with *N*-, *O*- and *P*-donor groups have been frequently reported, whereas NHCs bearing *S*-donors,[3] including thiolato-NHCs,[4] thioether-NHCs[5] and thiophene-NHCs,[6] are still less studied. Among these sulfur functionalized NHCs, we are particularly interested in thiolato-NHCs due to the versatile and diverse coordination chemistry of the soft, electron rich and anionic thiolato ligands in general.[7] Previously we reported a straightforward one-pot synthesis of a thiolato-bridged $[Pd_2S_2]$ benzimidazolin-2-ylidene complex from an easily available thioester-functionalized benzimidazolium salt *via in situ* hydrolysis,[4a] which removes the necessity of handling air-sensitive precursors in comparison with other reported procedures.[4b–d] Besides the thiolato-bridged Pd(II) benzimidazolin-2-ylidene complex mentioned above, and to the best of our knowledge, all other reported examples are based on saturated 5- or 6-membered N-heterocycles. Thiolato-NHCs based on imidazole remain unexplored, which is particularly surprising, since the majority of NHCs are derived from imidazoles.

In addition, recent studies have revealed that imidazole-based NHCs can also bind to the metal center through the C(4) carbon (imidazolin-4-ylidene), instead of the usual C(2) carbon.[8] Imidazolin-4-ylidenes, as an important type of mesoionic (abnormal) carbenes,[9] have been a focus of recent academic research due to their interesting nature and unusual bonding situation.[10] Comparative studies on the donor strengths of various ligands[11] show that imidazolin-4-ylidenes are generally stronger donors than their normal counterparts (imidazolin-2-ylidenes). It has also been reported that the increased donicity has led to a better catalytic performance of their complexes in comparison to imidazolin-2-ylidene analogues.[8b]

As an extension of our previously reported methodology, we herein report on the synthesis and structural characterization of a thiolato-bridged $[Pd_2S_2]$ imidazolin-2-ylidene complex (**1**) from a thioester-functionalized imidazolium salt (**B**) *via in situ* hydrolysis. Besides the expected dimeric complex obtained as the major product, an interesting dinuclear hetero-bis(carbene) isomer (**2**) was isolated that contains both normal and mesoionic carbene ligands allowing for a direct comparison of these two isomeric ligands and their influence on the metal center in the same complex. The reaction of the dimeric major isomer (**1**) with sodium isopropyl thiolate led to a rearrangement to a new tetranuclear $[Pd_4S_4]$ molecular rectangle (**3**) supported by carbene ligands and two different μ-thiolato bridges.

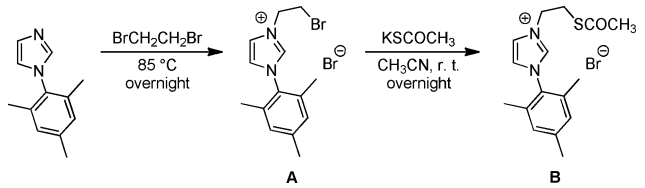
Results and discussion

Thioester-functionalized imidazolium salt

The ligand precursor **B** with a thioester function can be synthesized from 1-mesitylimidazole in a 2-step sequence. Nucleophilic substitution of bromoethyl-substituted **A**[5i] with 1.2 equiv of $KSCOCH_3$ in CH_3CN afforded the thioester-functionalized imidazolium salt **B** as a brown oil (Scheme 1). A base peak in the ESI mass spectrum at $m/z = 289$ for the $[M - Br]^+$ cation indicates the formation of **B**. Compared to its precursor **A**, an upfield shift of the signal for the α-methylene protons from 4.08 ppm to 3.48 ppm

Department of Chemistry, 3 Science Drive 3, National University of Singapore, Singapore, 117543. E-mail: chmhhv@nus.edu.sg; Fax: +65 67791691; Tel: +65 65162670

† Electronic supplementary information (ESI) available. CCDC reference numbers 824213–824215. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/c1dt10789e

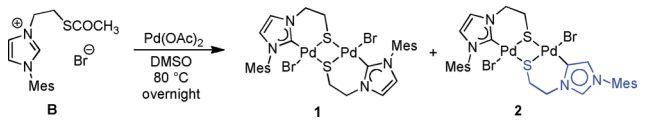


Scheme 1 Synthesis of imidazolium bromides **A** and **B**.

was observed, which further supports the successful replacement of the bromide with the less electronegative thioester function.

Thiolato-bridged Pd(II) carbene complexes

Palladation by treating salt **B** with one equiv of $Pd(OAc)_2$ in DMSO at 80 °C overnight afforded a mixture of thiolato-bridged dinuclear $[Pd_2S_2]$ carbene complexes in an overall yield >72% (Scheme 2). The formation of the thiolato-donor occurs through *in situ* hydrolysis of the methyl-thioester-function by acetic acid liberated from the imidazolium deprotonation step and the water present in the wet DMSO solvent.[4a] Subsequent coordination to two Pd(II) centers further stabilizes the highly nucleophilic sulfur function leading to the formation of thiolato-bridged dinuclear Pd(II) complexes.



Scheme 2 Synthesis of dinuclear Pd_2S_2 complexes **1** and **2**.

The expected dimeric complex **1** was obtained in a yield of 44% after purification by column chromatography as a yellow powder, soluble in CH_2Cl_2, $CHCl_3$, acetone, DMSO, and DMF, but insoluble in less polar solvents such as hexane and diethyl ether. Its formation was confirmed by ^{1}H NMR, which shows the absence of the NCHN and the thioester protons. Upon complex formation, the protons of the methylene group adjacent to the nitrogen become diastereotopic with chemical shifts of 4.44 and 4.32 ppm. Likewise, the methylene protons of the bridge adjacent to the sulfur also give rise to two diastereotopic signals at 3.66 and 1.93 ppm. The carbene carbon resonates at 163.8 ppm in the ^{13}C NMR spectrum, which is as expected more highfield than that of similar compounds bearing saturated[4c] or benzannulated NHCs.[4a] A peak in the ESI mass spectrum at $m/z = 782$ for the mono-cation $[M - Br]^+$ also supports the formation of **1**.

Besides the expected product **1**, its interesting constitutional isomer **2** bearing one imidazolin-2-ylidene and one mesoionic imidazolin-4-ylidene ligand was isolated in a yield of 28% (Scheme 2). Compared to **1**, the two NHCs in **2** adopt different coordination modes: one is bound to the Pd center *via* C(2) (normal bonding mode), while the other one coordinates *via* C(4) (*mesoionic* or *abnormal* bonding mode). The formation of the mesoionic carbene by competing deprotonation at C(4) probably helps to reduce the steric congestion caused by the bulky mesityl substituent. As direct isomers, complexes **1** and **2** cannot be differentiated by mass spectrometry. On the other hand, the formation of **2** is evidenced by NMR spectroscopy, which reveals distinct differences to complex **1**. Due to the unsymmetrical nature of compound **2** as a result of two different carbene ligands, its ^{1}H and ^{13}C NMR spectra are more complicated and exhibit twice the number of signals compared to those of its isomer **1**. More importantly, a sharp signal for the NCHN proton of the mesoionic carbene is still observed downfield at 8.90 ppm in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, two downfield signals are observed for the two inequivalent carbene donor atoms.[8b] The more downfield resonance at 162.9 ppm is attributed to the normal C(2) carbene carbon, while that at 139.8 ppm is assigned to the mesoionic C(4) carbene carbon. Attempts to interconvert **1** into **2** by heating and addition of excess base were met with no success and only led to intractable decomposition products.[8b] A theoretically possible third isomer bearing two mesoionic carbenes was not observed.

Single crystals of $\mathbf{1}\cdot C_3H_6O$ and $\mathbf{2}\cdot 2CH_2Cl_2$ were grown from concentrated acetone and CH_2Cl_2 solutions, respectively, and their molecular structures are depicted in Fig. 1 and 2. In complex **1**, each of the two Pd(II) centers is bound to one carbene, one bromido and two μ-thiolato ligands in a square planar fashion. The dihedral angles between the two $[PdCS_2Br]$ coordination planes and the carbene ring planes amount to 54.1(1)° and 57.8(1)°, respectively, which are substantially smaller than the ideal 90° expected for a monodentate NHC ligand due to the chelation through the thiolato function. The Pd1–S2 [2.3691(12) Å] and Pd2–S1 [2.3642(13) Å] bonds *trans* to the carbene are significantly longer than the Pd1–S1 [2.2887(12) Å] and Pd2–S2 [2.2944(12) Å] bonds *trans* to the bromido ligand due to the strong *trans* influence of the NHC. As observed for the benzimidazolin-2-ylidene analogue,[4a] the $[Pd_2S_2]$ core of **1** is significantly bent with a hinge angle of *ca.* 120.10(4)°.

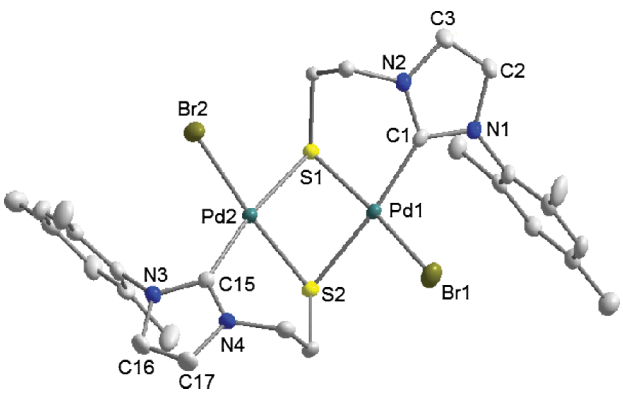


Fig. 1 Molecular structure of $\mathbf{1}\cdot C_3H_6O$ showing 50% probability ellipsoids; hydrogen atoms and the acetone molecule are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Pd1–C1 1.980(5), Pd1–S1 2.2887(12), Pd1–S2 2.3691(12), Pd1–Br1 2.4472(7), Pd2–C15 1.973(5), Pd2–S2 2.2944(12), Pd2–S1 2.3642(13), Pd2–Br2 2.4340(7); C1–Pd1–S1 89.17(13), S1–Pd1–S2 81.05(4), S2–Pd1–Br1 97.36(3), Br1–Pd1–C1 92.49(13), C1–Pd1–S2 170.15(13), S1–Pd1–Br1 172.10(4), C15–Pd2–S2 89.72(13), S2–Pd2–S1 81.04(4), S1–Pd2–Br2 96.58(4), Br2–Pd2–C15 92.95(13), C15–Pd2–S1 170.37(13), S2–Pd2–Br2 171.50(4), Pd1–S1–Pd2 82.52(4), Pd1–S2–Pd2 82.29(4).

The molecular structure of $\mathbf{2}\cdot 2CH_2Cl_2$ shown in Fig. 2 unambiguously confirmed the structure suggested by NMR spectra, which shows that one carbene ligand is bound to the palladium *via* the C(2) carbon while the other ligand is bound through the C(4) carbon. To the best of our knowledge, complex **2** is the first example of a dinuclear complex, in which a normal NHC and its mesoionic isomer are coordinating two different metal centers

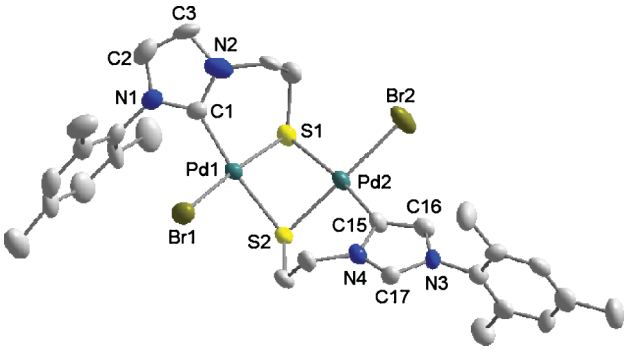
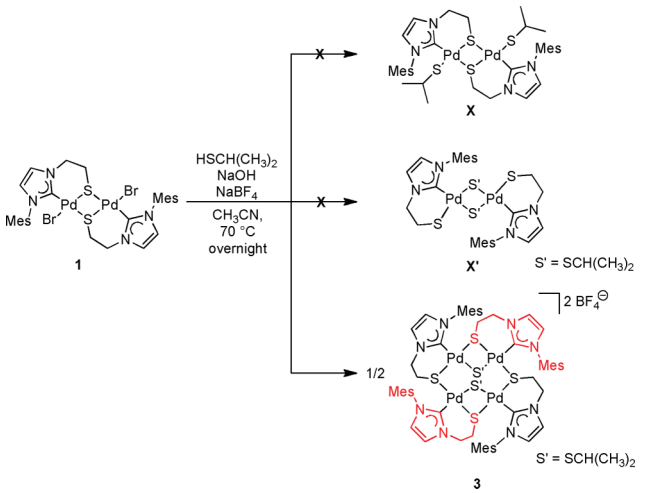


Fig. 2 Molecular structure of **2**·2CH_2Cl_2 showing 50% probability ellipsoids; hydrogen atoms and the CH_2Cl_2 molecules are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Pd1–C1 1.990(11), Pd1–S1 2.297(3), Pd1–S2 2.351(3), Pd1–Br1 2.4466(14), Pd2–C15 1.992(11), Pd2–S2 2.266(3), Pd2–S1 2.378(3), Pd2–Br2 2.4490(15); C1–Pd1–S1 90.7(3), S1–Pd1–S2 79.67(10), S2–Pd1–Br1 95.98(8), Br1–Pd1–C1 93.6(3), C1–Pd1–S2 170.4(3), S1–Pd1–Br1 174.40(9), C15–Pd2–S2 93.5(3), S2–Pd2–S1 79.73(10), S1–Pd2–Br2 95.80(8), Br2–Pd2–C15 91.5(3), C15–Pd2–S1 170.9(3), S2–Pd2–Br2 172.82(9), Pd1–S1–Pd2 82.19(9), Pd1–S2–Pd2 83.47(10).

within the same complex. In principle, this allows for a direct comparison of the two isomeric binding modes and their impact on bond parameters around each metal center.

The two Pd–$C_{carbene}$ distances are essentially the same [1.990(11) and 1.992(11) Å]. As expected, and as a result of the strong NHC *trans* influences, the Pd1–S2 [2.351(3) Å] and Pd2–S1 [2.378(3) Å] bonds *trans* to the carbenes are significantly longer than the Pd1–S1 [2.297(3) Å] and Pd2–S2 [2.266(3) Å] bonds *trans* to the bromido ligands. Notably, the Pd2–S1 bond [2.378(3) Å] *trans* to the mesoionic carbene is longer than the Pd1–S2 bond [2.351(3) Å] *trans* to the normal carbene, suggesting a stronger *trans* influence of C(4)-bound carbenes.[12] In addition, the Pd2–S2 bond [2.266(3) Å] *cis* to the mesoionic carbene is shorter than the Pd1–S1 bond [2.297(3) Å] *cis* to the normal one. On the other hand, the Pd–Br bond lengths [2.4490(15) Å and 2.4466(14) Å] are essentially the same. The dihedral angles between the two [$PdCS_2Br$] coordination planes and the two carbene ring planes are also significantly different. Due to the reduced steric crowding around the mesoionic carbene, this angle has decreased to 31.3(3)°, whereas that of the classical isomer amounts to 50.7(3)°. The hinge angle of the [Pd_2S_2] core in **2**, similar to that of **1** (*vide supra*), is *ca.* 119.0(1)°.

With the aim to study the reactivity of such dimers toward external thiolato ligands, the major dimeric isomer **1** was treated with two equiv sodium isopropyl thiolate. Initially, a simple bromido–thiolato ligand exchange was expected that should give rise to the dimers **X** or **X′**. Although the bromido ligands were indeed abstracted, a tetra-palladium species was formed instead (Scheme 3). Reaction optimization *via* counteranion exchange using $NaBF_4$ resulted in the isolation of the tetranuclear [Pd_4S_4] macrocyclic compound **3**, which was obtained as a yellow powder soluble in CH_2Cl_2, $CHCl_3$, acetone, CH_3CN, but insoluble in diethyl ether, toluene or hexane. In its ESI spectrum, a dicationic base peak at $m/z = 779$ was assigned to the $[M - 2BF_4]^{2+}$ fragment. Moreover, a smaller signal at $m/z = 1644$ assignable to the $[M - BF_4]^+$ monocation was observed as well. The ^{1}H NMR spectrum shows two sets of signal in the aromatic region, suggesting



Scheme 3 Synthesis of the tetranuclear macrocycle **3**.

two inequivalent groups of NHC ligands in this complex. The splitting patterns of the methylene groups and their assignment are complicated not only due to diastereotopicity, but also accidental overlap with signals arising from methyl groups. As expected, two carbene signals are observed at 169.1 and 166.5 ppm, respectively, in the ^{13}C NMR spectrum.

The molecular structure of **3** was finally confirmed by X-ray analysis on single crystals obtained from a concentrated mixed acetone/toluene solution (Fig. 3). Each of the four Pd(II) centers is coordinated by one carbene and three μ-thiolato donors in a square-planar fashion.

Apparently, the bromido ligand in **1** was first replaced with one isopropyl thiolato ligand accompanied by the precipitation of NaBr. The new highly nucleophilic thiolato ligand replaces a second bromido ligand of another Pd(II) center leading to a rearrangement of one Pd–S bond and subsequent dimerization to yield tetranuclear **3**. Similar to a previously reported benzimidazolin-2-ylidene Pd_4 species,[4a] there is an eight-membered [Pd_4S_4] macrocycle with almost the same dimensions of [4.6421(24) Å × 4.6617(24) Å]. The two bridging isopropyl thiolato ligands are found at opposite sides of this macrocycle, which in turn results in two different sets of carbene donors *trans* to these isopropyl thiolato ligands (Fig. 3, lower depiction). As expected, the Pd–S bonds *trans* to the carbenes are longer than those in *cis* positions due to the strong *trans* influence of the carbenes. The formal replacement of two terminal bromido ligands by one bridging thiolato ligand with concurrent rearrangement to a species of higher nuclearity is an interesting reaction that can be exploited as an entry to metallo-based supramolecular chemistry.

Conclusions

In summary, we have presented the first synthesis of *cis*-chelating thiolato/imidazolin-2-ylidene complexes *via* a simple *in situ* hydrolysis and palladation protocol of a thioester-functionalized imidazolium bromide salt **B**. In addition to the desired dimeric Pd(II) complex **1** containing two normal carbenes, its interesting isomer **2** bearing both normal and mesoionic carbenes has been isolated as well. The formation of the latter resulted from competing deprotonation at C(4) instead of C(2) probably due

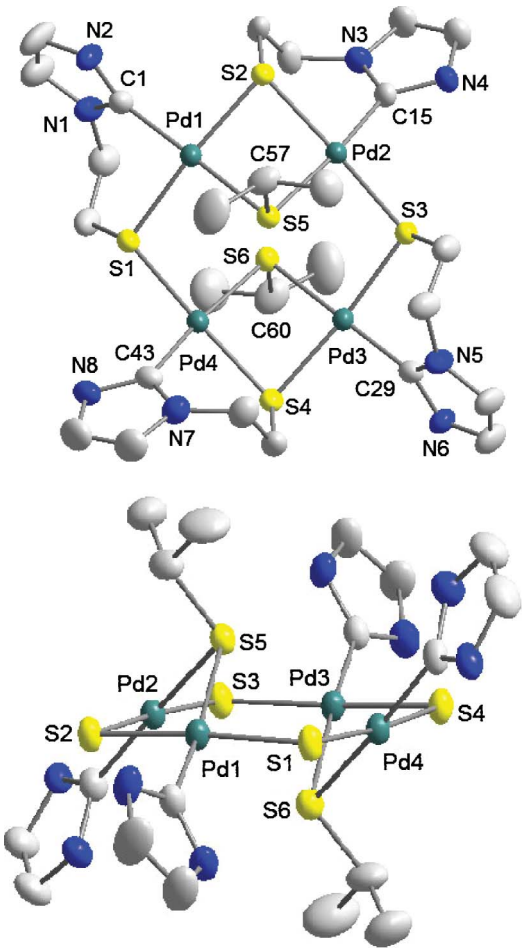


Fig. 3 Molecular structure of compound **3**·2C_7H_8 (upper: top view; lower: side view) showing 50% probability ellipsoids; hydrogen atoms, the toluene molecules, BF_4^- counteranions, and mesityl groups are omitted for clarity. Both *N*-substituents are omitted in the lower depiction. Selected bond lengths [Å] and bond angles [°]: Pd1–C1 1.988(7), Pd1–S2 2.3314(18), Pd1–S5 2.3917(18), Pd1–S1 2.3207(18), Pd2–S2 2.3336(18), Pd2–C15 1.991(7), Pd2–S3 2.3333(18), Pd2–S5 2.3656(17), Pd3–S6 2.3939(18), Pd3–S3 2.3249(18), Pd3–C29 1.994(7), Pd3–S4 2.3267(18), Pd4–S1 2.3335(18), Pd4–S6 2.3703(18), Pd4–S4 2.3315(18), Pd4–C43 1.989(7), S5–C57 1.851(8), S6–C60 1.849(8); C1–Pd1–S2 96.0(2), S2–Pd1–S5 84.24(6), S5–Pd1–S1 93.86(6), S1–Pd1–C1 87.1(2), S2–Pd2–S5 84.24(6), S2–Pd2–C15 90.5(2), C15–Pd2–S3 89.3(2), S3–Pd2–S5 95.20(6), S6–Pd3–S4 83.85(6), S6–Pd3–S3 93.45(6), S3–Pd3–C29 87.5(2), C29–Pd3–S4 95.9(2), S1–Pd4–C43 88.6(2), S1–Pd4–S6 96.14(6), S6–Pd4–S4 84.27(6), S4–Pd4–C43 90.6(2), Pd1–S2–Pd2 83.42(6), Pd1–S5–Pd2 81.45(6), Pd1–S1–Pd4 105.39(7), Pd2–S3–Pd3 105.09(7), Pd4–S6–Pd3 81.28(6), Pd4–S4–Pd3 83.54(6).

to steric reasons. The observed differences in bond parameters around the two inequivalent Pd centers in a single complex is in line with the view that mesoionic C(4)-bound carbenes are stronger electron donors of greater *trans* influence than their direct C(2)-bound classical analogues.

Metathesis reaction of the major isomer **1** with $NaSCH(CH_3)_2$ and $NaBF_4$ led to rearrangement and dimerization to the tetranuclear species **3** with a $[Pd_4S_4]$ macrocycle. All complexes have been fully characterized and their molecular structures determined by X-ray diffraction analyses. Research in our lab is currently on-going to extend the straightforward and promising synthesis of thiolato-functionalized NHC complexes to different transition metals. Furthermore, work is underway to exploit the bromido/thiolato ligand exchange reaction for the controlled synthesis of higher metallo-aggregates.

Experimental section

General considerations

Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received. Compound **A** was synthesized according to a reported procedure.[5i] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C). ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

Syntheses

Thioester imidazolium salt (B). A mixture of salt **A** (374 mg, 1 mmol) and $KSCOCH_3$ (137 mg, 1.2 mmol) in CH_3CN (10 ml) was stirred at ambient temperature overnight. The resulting suspension was filtered and the solvent of the filtrate was removed to yield the product as brown oil quantitatively (369 mg, 1 mmol). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.06 (s, 1 H, NCHN), 8.01 (s, 1 H, NC*H*CHN), 7.16 (t, 1 H, NCHC*H*N), 6.94 (s, 2 H, Ar–H), 4.88 (t, ^3J(H,H) = 6.1 Hz, 2 H, NCH_2), 3.48 (t, ^3J(H,H) = 6.1 Hz, 2 H, CH_2S), 2.27 (s, 3 H, $COCH_3$), 2.28 (s, 3 H, *p*-CH_3), 2.02 (s, 6 H, 2 × *o*-CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d_6): 195.0 (s, CO), 141.5 (s, NCHN), 138.3, 134.5, 131.0, 130.1, 124.4, 123.3 (s, Ar–C), 49.8 (s, NCH_2), 30.9 (s, CH_3), 30.1 (s, CH_2S), 21.4 (s, *p*-CH_3), 17.9 (s, *o*-CH_3). MS (ESI): m/z = 289 [M − Br]$^+$.

Dinuclear thiolato-bridged NHC complexes (1 & 2). A mixture of salt **B** (506 mg, 1.37 mmol) and $Pd(OAc)_2$ (307 mg, 1.37 mmol) in DMSO (5 ml) was stirred at 80 °C overnight. The resulting mixture was filtered and the solvent of the filtrate was removed by vacuum distillation. The resulting residue was washed with H_2O (3 × 20 ml) and diethyl ether (3 × 20 ml). The product was purified by chromatography on silica using ethyl acetate : hexane (0.8 : 1) (**1**, 261 mg, 0.303 mmol, 44%; **2**, 167 mg, 0.194 mmol, 28%). Complex **1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, ^3J(H,H) = 1.9 Hz, 2 H, 2 × NC*H*CHN), 6.98 (s, 2 H, Ar–H), 6.95 (s, 2 H, Ar–H), 6.80 (d, ^3J(H,H) = 1.9 Hz, 2 H, 2 × NCHC*H*N), 4.44 (ps-t, 2 H, 2 × NC*H*H), 4.32 (ps-d, 2 H, 2 × NCH*H*), 3.66 (ps-d, 2 H, 2 × C*H*HS), 2.33 (s, 6 H, 2 × *p*-CH_3), 2.23 (s, 6 H, 2 × *o*-CH_3), 2.22 (s, 6 H, 2 × *o*-CH_3), 1.93 (ps-t, 2 H, 2 × CH*H*S). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): 163.8 (s, NCN), 138.7, 135.8, 135.6, 134.9, 129.2, 129.0, 123.5, 120.9 (s, Ar–H), 56.0 (s, NCH_2), 25.6 (s, CH_2S), 21.2 (s, *p*-CH_3), 19.3 (s, *o*-CH_3), 19.1 (s, *o*-CH_3). Anal. Calc. for $C_{28}H_{34}Br_2N_4Pd_2S_2$: C, 38.95; H, 3.97; N, 6.49. Found: C, 39.06; H, 3.84; N, 6.13%. MS (ESI): m/z = 782 [M − Br]$^+$. Complex **2**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.90 (d, ^4J(H,H) = 1.9 Hz, 1 H, NCHN), 7.63 (d, ^4J(H,H) = 1.9 Hz, 1 H, NCHCN), 7.34 (d, ^3J(H,H) = 1.9 Hz, 1 H, NC*H*CHN), 7.09 (s, 2 H, Ar–H), 7.02 (s, 1 H, Ar–H), 6.97 (s, 1 H, Ar–H), 6.85 (d, ^3J(H,H) = 1.9 Hz, 1 H,

Table 1 Selected X-ray crystallographic data for complexes **1**·C_3H_6O, **2**·$2CH_2Cl_2$ and **3**·$2C_7H_8$

	1·C_3H_6O	**2**·$2CH_2Cl_2$	**3**·$2C_7H_8$
Formula	$C_{28}H_{34}Br_2N_4Pd_2S_2·C_3H_6O$	$C_{28}H_{34}Br_2N_4Pd_2S_2·2CH_2Cl_2$	$C_{62}H_{82}B_2F_8N_8Pd_4S_6·2C_7H_8$
Formula weight	921.41	1033.18	1915.20
Color, habit	Yellow, plate	Yellow, plate	Yellow, block
Cryst size/mm	0.32 × 0.16 × 0.08	0.14 × 0.12 × 0.06	0.26 × 0.26 × 0.20
T/K	100(2)	223(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	17.718(2)	16.9381(14)	15.3906(4)
b/Å	12.4490(18)	8.9830(7)	24.2174(6)
c/Å	15.964(2)	24.9425(19)	24.4807(7)
α (°)	90	90	90
β (°)	103.858(3)	91.468(2)	90.7140(10)
γ (°)	90	90	90
V/Å^3	3418.7(8)	3793.9(5)	9123.7(4)
Z	4	4	4
D_c/g cm^{-3}	1.790	1.809	1.394
Radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ/mm^{-1}	3.542	3.473	0.971
θ range/°	1.18–27.50	1.44–25.00	1.55–25.00
Reflections collected	23 754	20 763	53 165
Independent reflections	7836	6686	16 052
R(int)	0.0483	0.1048	0.0546
Max., min. transmission	0.7648, 0.3969	0.8187, 0.6420	0.8295, 0.7864
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0445$, w$R_2 = 0.1082$	$R_1 = 0.0776$, w$R_2 = 0.1432$	$R_1 = 0.0651$, w$R_2 = 0.1743$
R indices (all data)	$R_1 = 0.0596$, w$R_2 = 0.1159$	$R_1 = 0.1321$, w$R_2 = 0.1591$	$R_1 = 0.0859$, w$R_2 = 0.1873$
Goodness-of-fit on F^2	1.038	1.079	1.047
Peak/hole/e Å^{-3}	1.395/−1.757	1.011/−1.009	1.386/−0.892

NCHC*H*N), 4.70 (ps-d, 1 H, NC*H*H), 4.60 (ps-d, 1 H, NCH*H*), 4.19 (ps-t, 1 H, NC*H*H), 3.96 (ps-t, 1 H, NCH*H*), 3.46 (ps-d, 1 H, C*H*HS), 3.19 (ps-d, 1 H, CH*H*S), 2.32 (s, 6 H, 2 × *p*-CH_3), 2.17 (s, 3 H, *o*-CH_3), 2.15 (s, 3 H, *o*-CH_3), 2.01 (s, 5 H, *o*-CH_3 + CH_2S), 1.98 (s, 3 H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (125.77 MHz, DMSO-d_6): 162.9 (s, NCN), 139.8 (s, N*C*CHN), 138.1, 136.3, 135.9, 135.7, 135.2, 134.9, 134.8, 134.6, 132.4, 129.5, 129.2, 129.1, 127.3, 124.4, 122.7 (s, Ar–H), 55.4 (s, NCH_2), 54.8 (s, NCH_2), 26.9 (s, CH_2S), 23.3 (s, CH_2S), 21.1 (s, *p*-CH_3), 21.0 (s, *p*-CH_3), 19.3 (s, *o*-CH_3), 19.1 (s, *o*-CH_3), 17.3 (s, *o*-CH_3). Anal. Calc. for $C_{28}H_{34}Br_2N_4Pd_2S_2$: C, 38.95; H, 3.97; N, 6.49. Found: C, 39.04; H, 4.03; N, 5.82%. MS (ESI): m/z = 782 $[M - Br]^+$.

Tetranuclear macrocyclic compound (3). A mixture of 2-propanethiol (9.2 µl, 0.1 mmol) and NaOH aqueous solution (16.0 µl, 0.1 mmol, 6.25 mol l^{-1}) was stirred in degassed CH_3CN for 0.5 h. Complex **1** (43 mg, 0.05 mmol) and $NaBF_4$ (5 mg, 0.05 mmol) were added to the mixture. After heating at 70 °C overnight, the mixture was filtered over Celite. The solvent of the filtrate was removed under vacuum to give a yellow solid. The compound was recrystallized by slow evaporation of an acetone/toluene solution (20 mg, 0.012 mmol, 46%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 (s, 2 H, Ar–H), 7.31 (s, 2 H, Ar–H), 6.99 (s, 2 H, Ar–H), 6.97 (s, 2 H, Ar–H), 6.91 (s, 2 H, Ar–H), 6.89 (s, 2 H, Ar–H), 6.84 (s, 2 H, Ar–H), 6.74 (s, 2 H, Ar–H), 4.91–4.84 (m, 4 H, 2 × NCH_2), 4.76 (m, 2 H, 2 × NC*H*H), 4.49 (m, 2 H, 2 × NCH*H*), 2.49 (m, 2 H, 2 × SCH), 2.33 (s, 12 H, 4 × Me), 2.16 (m, 16 H, 4 × Me + 2 × CH_2S), 2.02 (s, 6 H, 2 × Me), 1.98 (s, 6 H, 2 × Me), 1.28 (m, 8 H, 2 × Me + CH_2S), 1.16 (m, 6 H, 2 × Me), 0.93 (m, 2 H, CH_2S). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): 169.1 (s, NCN), 166.5 (s, NCN), 140.4, 139.9, 136.1, 136.0, 135.96, 135.5, 135.2, 134.8, 130.2, 130.1, 130.0, 129.9, 124.2, 123.9, 122.8, 122.4 (s, Ar-C), 55.9, 55.4, 39.5, 34.8, 32.6, 31.7, 30.2, 29.1, 23.4, 21.8, 21.7, 19.8, 19.7, 19.1, 19.0, 14.8 (s, Ali-C). MS (ESI): m/z = 779 $[M - 2BF_4]^{2+}$, 1644 $[M - BF_4]^+$.

X-Ray diffraction studies

X-Ray data for **1**·C_3H_6O, **2**·$2CH_2Cl_2$ and **3**·$2C_7H_8$ were collected with a Bruker AXS SMART APEX diffractometer, using Mo-Kα radiation at 100(2)K (for **1**·C_3H_6O) or at 223(2)K (for **2**·$2CH_2Cl_2$ and **3**·$2C_7H_8$) with the SMART suite of Programs.[13] Data were processed and corrected for Lorentz and polarisation effects with SAINT,[14] and for absorption effects with SADABS.[15] Structural solution and refinement were carried out with the SHELXTL suite of programs.[16] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table 1.

Acknowledgements

The authors thank the National University of Singapore for financial support (WBS R-143-000-407-112). Technical support from staff at the CMMAC of our department is appreciated. In particular, we thank Ms Geok Kheng Tan, Ms Hong Yimian and Prof. Lip Lin Koh for determining the X-ray molecular structures.

Notes and references

1 For a recent review, see: F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122.
2 For a recent review, see: A. T. Normand and K. J. Cavell, *Eur. J. Inorg. Chem.*, 2008, 2781.
3 For a recent review, see: M. Bierenstiel and E. D. Cross, *Coord. Chem. Rev.*, 2011, **255**, 574.

4 (*a*) D. Yuan and H. V. Huynh, *Organometallics*, 2010, **29**, 6020; (*b*) D. Sellmann, F. Geipel and F. W. Heinemann, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1034; (*c*) J. A. Cabeza, I. del Rio, M. G. Sánchez-Vega and M. Suárez, *Organometallics*, 2006, **25**, 1831; (*d*) F. Iwasaki, M. Yasui, S. Yoshida, H. Nishiyama, S. Shimamoto and N. Matsumura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2759.
5 (*a*) H. Seo, H.-J. Park, B. Y. Kim, J. H. Lee, S. U. Son and Y. K. Chung, *Organometallics*, 2003, **22**, 618; (*b*) J. Wolf, A. Labande, J.-C. Daran and R. Poli, *Eur. J. Inorg. Chem.*, 2007, 5069; (*c*) S. J. Roseblade, A. Ros, D. Monge, M. Alcarazo, E. Álvarez, J. M. Lassaletta and R. Fernández, *Organometallics*, 2007, **26**, 2570; (*d*) H. V. Huynh, C. H. Yeo and G. K. Tan, *Chem. Commun.*, 2006, 3833; (*e*) H. V. Huynh, C. H. Yeo and Y. X. Chew, *Organometallics*, 2010, **29**, 1479; (*f*) H. V. Huynh, D. Yuan and Y. Han, *Dalton Trans.*, 2009, 7262; (*g*) A. Ros, D. Monge, M. Alcarazo, E. Álvarez, J. M. Lassaletta and R. Fernández, *Organometallics*, 2006, **25**, 6039; (*h*) C. Fliedel, G. Schnee and P. Braunstein, *Dalton Trans.*, 2009, 2474; (*i*) D. Yuan, H. Tang, L. Xiao and H. V. Huynh, *Dalton Trans.*, 2011, DOI: 10.1039/c1dt10269a.
6 (*a*) D. J. Nielsen, K. J. Cavell, M. S. Viciu, S. P. Nolan, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 2005, **690**, 6133; (*b*) D. S. McGuinness, J. A. Suttil, M. G. Gardiner and N. W. Davies, *Organometallics*, 2008, **27**, 4238; (*c*) H. V. Huynh and Y. X. Chew, *Inorg. Chim. Acta*, 2010, **363**, 1979.
7 B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 769.
8 (*a*) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *J. Am. Chem. Soc.*, 2002, **124**, 10473; (*b*) H. Lebel, M. K. Janes, A. B. Charette and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5046; (*c*) D. Bacciu, K. J. Cavell, I. A. Fallis and L. Ooi, *Angew. Chem., Int. Ed.*, 2005, **44**, 5282.
9 (*a*) G. Guisado-Barrios, J. Bouffard, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 4759; (*b*) Y. Han, H. V. Huynh and G. K. Tan, *Organometallics*, 2007, **26**, 6581; (*c*) R. Jothibasu and H. V. Huynh, *Organometallics*, 2009, **28**, 2505; (*d*) M. Iglesias and M. Albrecht, *Dalton Trans.*, 2010, **39**, 5213; (*e*) A. Poulain, D. Canseco-Gonzalez, R. Hynes-Roche, H. Müller-Bunz, O. Schuster, H. Stoeckli-Evans, A. Neels and M. Albrecht, *Organometallics*, 2011, **30**, 1021; (*f*) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, *Science*, 2009, **326**, 556.
10 O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445 and references therein.
11 (*a*) A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller and R. H. Crabtree, *Organometallics*, 2004, **23**, 2461; (*b*) H. V. Huynh, Y. Han, R. Jothibasu and J. A. Yang, *Organometallics*, 2009, **28**, 5395.
12 M. Heckenroth, E. Kluser, A. Neels and M. Albrecht, *Angew. Chem., Int. Ed.*, 2007, **46**, 6293.
13 *SMART version 5.628*, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
14 *SAINT+ version 6.22a*, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
15 G. W. Sheldrick, *SADABS version 2.10*, University of Göttingen, 2001.
16 *SHELXTL version 6.14*, Bruker AXS Inc., Madison, Wisconsin, USA, 2000.