



Direct C-metallation of *N*-substituted triazoles promoted by mercury acetate. An alternative route to *N*-heterocyclic carbene complexes†

Nai-Chieh Lin, Herbert J. H. Syu,* Abbas Raja Naziruddin, Fu-Chen Liu* and Ivan J. B. Lin

C-Metallation of neutral mono-substituted triazoles could be induced by $\text{Hg}(\text{OAc})_2$ to give a near quantitative yield of *C,N*-bonded mercury complexes. Initial *N*-coordination to mercury(II) is confirmed by NMR spectroscopy. Subsequent acetate assisted deprotonation–metallation is a viable route to C-metallated products. $\text{Hg}(\text{OAc})_2$ is unique for this reaction. Metal salts of Ag_2O , $\text{Ag}(\text{OAc})$, $\text{Pd}(\text{OAc})_2$ or HgCl_2 in combination with bases of NaOH and K_2CO_3 did not yield triazolate complexes. Further reaction of one of these mercury(II)–*C,N*-triazolate complexes with a source of methyl cation yielded a monomeric *N*-heterocyclic carbene complex. Therefore the facile reaction of triazole with $\text{Hg}(\text{OAc})_2$ followed by alkylation is a handy alternative way to prepare Hg–NHCs.

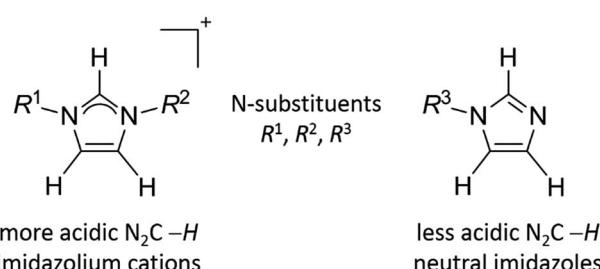
Received 5th January 2017
Accepted 9th February 2017

DOI: 10.1039/c7ra00163k
rsc.li/rsc-advances

Introduction

A plethora of methodologies that facilitate the metallation of N_2C carbon of imidazolium cations are known.¹ In contrast to the large library of *C*-metallation of these cations, examples of similar occurrence for mono-*N*-substituted neutral imidazoles are limited (see Scheme 1 for structural formula of imidazolium cations and imidazoles).^{2–9} This is because the N_2C –H proton of the neutral imidazoles is less acidic than that of the imidazolium cations and hence is more difficult to be deprotonated. A strong base such as BuLi ,^{10–12} $\text{KN}(\text{SiMe}_3)_2$,^{13,14} $\text{KO}^\text{t}\text{Bu}$,^{15,16} or LiHMDS ¹⁷ (HMDS = hexamethyldisilazide) is

often required to remove the N_2C –H proton of mono-*N*-substituted imidazoles. Alternatively, functionalization of benzimidazoles or imidazoles at *N*-side arms with tethered phosphine,^{18–21} pyridine^{20,21} or olefin²² donor ligands is known to promote the activation of N_2C –H bond to give *C*-metallated products. As a different approach, azoles bearing more reactive N_2C –X (X = Cl/Br/I) bonds are also known to undergo oxidative addition into lower valent metal ions to provide azolate complexes, which upon further protonation or methylation could afford NHC complexes.^{6,7,23,24} In an attempt to use a Rh(I) catalyst to couple *N*-methyl benzimidazole with iodobenzene, an intermediate complex, $[(\text{H-bimy-Me})\text{RhCl}(\text{PCy}_3)_2]$, bearing a protic NHC ligand was isolated.²⁵ In an earlier report, acid has been found to promote the rearrangement of *N*-metallated Ru(II) into its *C*-bound tautomer.²⁶ Computational results suggest that there is a thermodynamic preference of *C*-binding over *N*-coordination for the second and third row transition metals.²⁷ Recently we have reported the isolation of *C,N*-bonded, 12-membered mercuramacrocycles from the reactions of *N*-substituted benzimidazoles with $\text{Hg}(\text{OAc})_2$ and NaBr . This reaction presumably proceeds through an initial *N*-complexation of benzimidazoles to mercury bromide, which in turn favors the deprotonation of N_2C –H.²⁸ In the present study, we describe the direct reaction of neutral triazoles with $\text{Hg}(\text{OAc})_2$ to prepare mercury–*C,N*-triazolate complexes. This method could evolve as an important synthetic tool to attain *C*-metallation of triazoles. A subsequent methylation by $[\text{Me}_3\text{O}]$ $[\text{BF}_4]$ generates mercury(II)–NHC complex, which is possible to form other NHC complexes *via* the known transmetallation reaction.²⁹



Scheme 1 A representation of imidazolium cations and mono-*N*-substituted neutral imidazoles.

Department of Chemistry National Dong Hwa University, No. 1, Sec. 2, Da Hsueh Rd. Shoufeng, Hualien 97401, Taiwan, Republic of China. E-mail: fcliu@gms.ndhu.edu.tw; d9812001@gms.ndhu.edu.tw

† Electronic supplementary information (ESI) available. CCDC 1507775 and 1507776. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra00163k



Results and discussion

Ligand precursors of **R-TazH**, (R = phenyl, pyridyl and methyl) were prepared according to the literature protocols.^{30,31} Reactions of these ligand precursors with an equi-molar stoichiometry of $\text{Hg}(\text{OAc})_2$ in methanol under reflux conditions gave complexes of type $[\text{Hg}_2(\text{R-Taz})(\text{OAc})_2]_\infty$ (**1a**, R = phenyl; **1b**, R = pyridyl; **1c**, R = methyl) with yields >95% (Scheme 2). The occurrence of C-metallation at **R-TazH** was supported by the absence of C^5 -proton (see Scheme 2 for triazole atom numberings) resonances and the large downfield shift of the C^5 signals at *ca.* δ 175 ppm in ^{13}C NMR as compared to those of the ligand precursors. Single crystals of **1a** were obtained *via* slow evaporation of its tetrahydrofuran solution. Crystals of **1b** and **1c** suitable for X-ray diffraction study could not be obtained, in spite of repeated attempts. The structure of **1a** is depicted in Fig. 1, along with the important bonding parameters listed in the caption. **1a** exhibits a polymeric structure with repeating $(\text{Hg-RTaz})_2$ units. In each unit, one can consider that two $\text{Hg}(\text{II})$ centers are bridged by two triazolates with alternating C- and N-bond. Each $(\text{Hg-RTaz})_2$ unit is further linked by four acetates with neighboring units to form a polymer. The $\text{C}(1)-\text{Hg}(1)$ bond distance of **1a** (2.046(6) Å) is comparable to those of reported mercury NHC complexes.³²⁻³⁶ The $\text{N}(1)-\text{C}(1)-\text{N}(3)$ bond angle of 108.5(5) $^\circ$ is larger than those in other related Hg-NHC complexes (*ca.* 106 $^\circ$).³² The expansion of C-N-C bond angles is attributed to the formation of carbenolate complexes.²³ Notably, two trans disposed $\text{C}(1)$ and $\text{O}(1)$ atoms are in a nearly linear configuration with a $\text{C}(1)-\text{Hg}(1)-\text{O}(1)$ bond angle of 176.8(2) $^\circ$. This leads to a seesaw type coordination in the Hg center. Unlike **1a**, **1b** has a pyridyl group, one might wonder whether the pyridyl moiety would participate in the coordination sphere of $\text{Hg}(\text{II})$. However, this possibility is very slim as evidenced by the nearly unaltered ^1H NMR signals for the pyridyl moiety between **1b** and **Py-TazH**.

Upon treating **1a**, **1b** and **1c** with LiCl , the bridging acetato ligand was substituted by Cl^- ligand, with a nearly quantitative

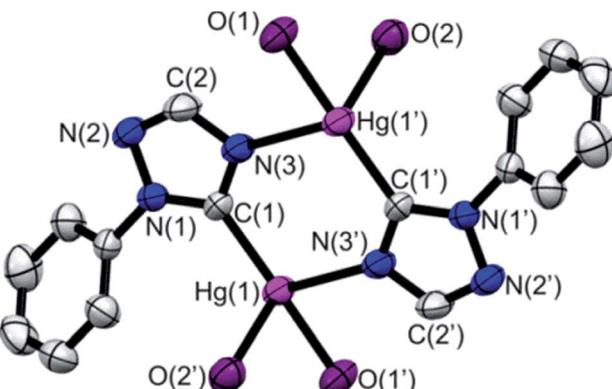
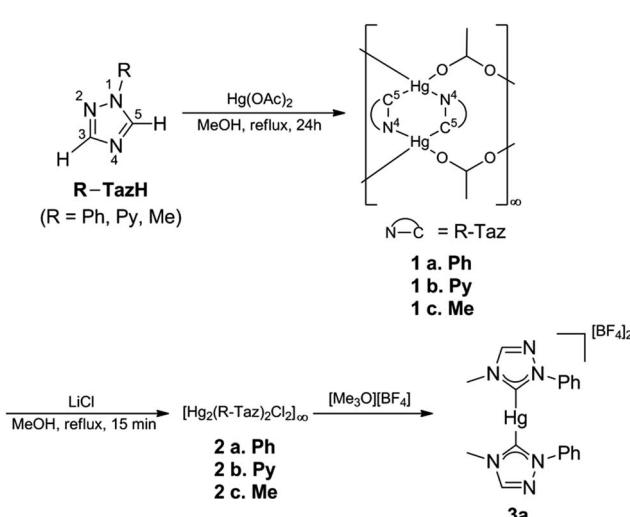


Fig. 1 ORTEP of **1a**, depicted with 50% polarizability ellipsoids with the carbon atoms in the acetyl moiety and hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [$^\circ$]: $\text{Hg}(1)-\text{C}(1)$ 2.046(6); $\text{Hg}(1)-\text{O}(1)$ 2.079(4); $\text{Hg}(1)-\text{N}(3')$ 2.583(5); $\text{N}(1)-\text{C}(1)-\text{N}(3)$ 108.5(5); $\text{C}(1)-\text{Hg}(1)-\text{O}(1)$ 176.8(2); $\text{C}(1)-\text{Hg}(1)-\text{O}(2)$ 100.3(2); $\text{C}(1)-\text{Hg}(1)-\text{N}(3)$ 100.8(2).

formation of $[\text{Hg}_2(\text{R-Taz})_2(\text{Cl})_2]_\infty$ (**2a**, **2b** and **2c**). Formation of **2a**, **2b**, and **2c** are accompanied by the loss of coordinated acetato singlet resonance in the range of δ 1.92–1.87 ppm, that otherwise would appear in the ^1H NMR spectra of **1a**, **1b** and **1c**. The solubility of **2a**, **2b** or **2c** in common organic solvents is poor. In DMSO-d_6 , increasing the temperature (≈ 80 $^\circ\text{C}$) could enhance their solubility. However, well resolved ^{13}C signals are achievable only for **2a** and **2b**. The C^5 ^{13}C NMR signals of **2a** and **2b** appear at δ 171.5 and 170.0 ppm, respectively, which are relatively up-field compared to those previously reported $\text{Hg}(\text{II})$ -1,2,4-triazol-5-ylidene complexes (δ 183.8 in DMSO-d_6)³² due to the relative shielding caused by the anionic nature of the triazolates. We notice that there is a clear shift in the pyridyl ^{13}C signals of **2b** relative to those of **1b** and **Py-TazH**. This observation allows us to propose that while the pyridyl wingtip in **1b** is dangling, it coordinates to the $\text{Hg}(\text{II})$ center in **2b**, as also supported by its crystal structure, discussed as follows. Single crystals of **2b** suitable for structural determination were obtained by diffusing ethanol vapor into its DMSO solution. We have been unable to obtain crystals of **2a** and **2c** in spite of repeated attempts. Crystal structure of **2b** is depicted in Fig. 2, along with important bonding parameters in the caption. **2b** also adopts a polymeric structure composed of repeating single $\text{Hg}(\text{II})$ unit. In each four coordinated $\text{Hg}(\text{II})$ unit, there is a chelating C^5N donor set, a terminal chloride, and an N atom from the neighboring triazolate. These units are thus linked by the bridging triazolates. Most of the bond lengths and angles of **2b** are comparable to those of **1a**, except a slight bending in the $\text{C}(1)-\text{Hg}(1)-\text{Cl}(1)$ bonds (168.5(7) $^\circ$), in comparison to the $\text{C}(1)-\text{Hg}(1)-\text{O}(1)$ bond angle of 176.8(2) $^\circ$ in **1a**.

The structure information of **2b** cannot be applied to those of **2a** and **2c**, where no additional donor group at the wingtip is available for the coordination. We believe that the $\text{Hg}(\text{II})$ center is also four coordinated in **2a** and **2c**. To fulfill this condition, a bridging rather than a terminal chloride is likely. Raman spectroscopy was employed to justify this notion. Raman modes involving Hg-Cl-Hg stretching are known to appear bands



Scheme 2 Synthetic scheme depicting the preparation of complexes and atom numberings for triazoles.



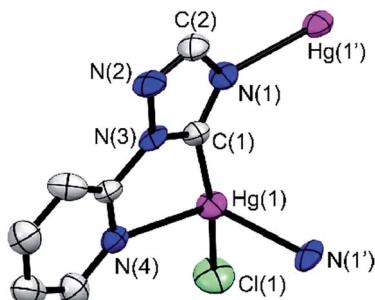


Fig. 2 ORTEP of **2b**, depicted with 50% polarizability ellipsoids with hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [°]: Hg(1)–C(1) 2.060(2); Hg(1)–Cl(1) 2.301(6); Hg(1)–N(4) 2.750(2); Hg(1)–N(1') 2.560(2); N(1)–C(1)–N(3) 108.0(2); C(1)–Hg(1)–N(4) 69.4(8); C(1)–Hg(1)–N(1') 96.4(8); Cl(1)–Hg(1)–N(1') 95.0(5); Cl(1)–Hg(1)–N(4) 109.8(5); C(1)–Hg(1)–Cl(1) 168.5(7).

below 200 cm^{-1} , whereas those of terminal Hg–Cl bonds appear at higher wavenumbers ($273\text{--}307\text{ cm}^{-1}$).³⁷ The observation of Raman bands of **2a** at 187 cm^{-1} and **2c** at 162 cm^{-1} is hence consistent to a bridging Hg–Cl–Hg unit, and suggests a four coordinated structure consisting of a C⁵ and an N atom from two independent triazolates and two bridging chlorides.

Further reaction of **2a** with trimethyloxonium-tetrafluoroborate gave **3a** featuring neutral NHC ligand. The ¹³C NMR resonance of the carbenoid carbon atom of **3a** occurs at 177.8 ppm which is downfield relative to that with triazolate donors (*vide supra*). In the crystals structure of **3a**, a residue density of $4.37\text{ e}\text{\AA}^{-3}$ could not be fitted. Nonetheless, the main frame of this structure is correct and depicted in Fig. S1.[†] While **1a** featuring an anionic carbon donor adopts a four coordinated Hg atom, **3a** bearing a neutral NHC donor adopts a two-coordinated linear geometry at Hg atom, as often observed for other bis-NHC Hg compounds.^{29,38}

To understand how this reaction proceeds, the reaction of **Me-TazH** and Hg(OAc)₂ at room temperature was monitored by ¹H NMR. **Me-TazH** in CD₃OD shows three resonances corresponding to ring C⁵–H and C³–H protons and N–CH₃ protons at δ 6.85, 6.40 and 2.38 ppm, respectively, with a relative intensity of 1 : 1 : 3 shown in Fig. 3(a). Addition of an equimolar quantity of Hg(OAc)₂ causes a substantial shift of the triazole signals to δ 7.26, 6.65 and 2.48 ppm again with 1 : 1 : 3 relative intensity (Fig. 3(b)). N-Coordination apparently occurs and that the larger downfield shift of the signal of C⁵–H relative to C³–H suggests an N⁴ rather than N² coordination. After 1.5 h (Fig. 3(c)), two new signals at δ 6.81 and 2.58 ppm appear, which grow with time (Fig. 3(d–h)), and could be attributed to the formation of the triazolate product. In addition, for those unreacted triazoles the relative intensity of the C⁵–H to C³–H and CH₃ signals gradually decreases along with time. This observation is again consistent with an N⁴ coordination, which gives a more acidic C⁵–H proton, such that H–D exchange between the C⁵–H proton and the deuterated solvent occurs. Then the weak base acetate deprotonates the C⁵–H proton. However, the role of the acetate ion needs further comment. Reactions of **Me-TazH** with HgCl₂ in the presence of several weak bases were examined. While using NaOAc as a base could indeed produce **2c**, other bases

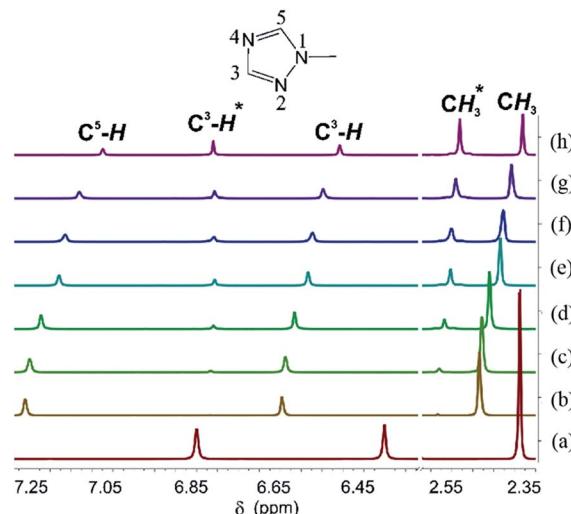
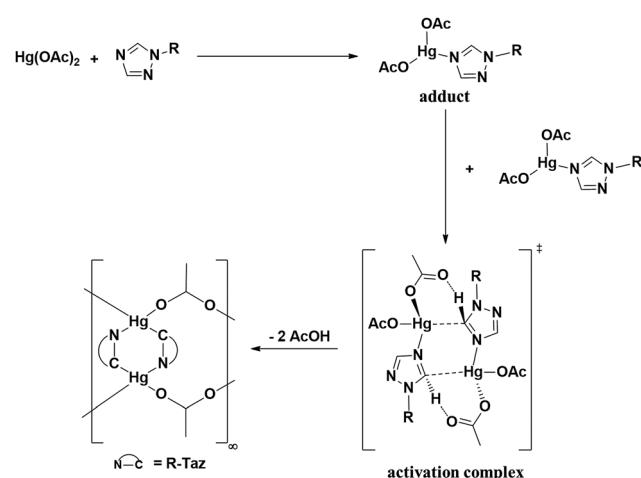


Fig. 3 Ambient temperature ¹H NMR spectra showing the interaction of **Me-TazH** (a) with Hg(OAc)₂ measured at: (b) $t = 0\text{ h}$, (c) 1.5 h. (d) 6.0 h. (e) 24.0 h. (f) 36.0 h. (g) 48.0 h. (h) 72.0 h. Signals of product (*).

such as K₂CO₃ or NaOH could not yield C-metallation products. Attempts to react **R-TazH** with other metal sources of Ag₂O, Ag(OAc) and Pd(OAc)₂ containing basic ligands always produce black metallic powder, but no C-metallation products. Among the few bases and metal ions tried, the combination of Hg(II) and acetate is unique to proceed this facile reaction. A proposed mechanism to account for this reaction is given in Scheme 3. Firstly, N⁴ coordination of a triazole to Hg(OAc)₂ gives a [Hg(OAc)₂·R-TazH] adduct. Then two of these adducts form an activation complex, where both (1) weakening of the acidic C⁵–H bond *via* hydrogen bonding interaction with neighboring acetate oxygen atom, and (2) forming a partial C⁵–Hg bond with a neighboring Hg atom occur simultaneously. The former interaction is favored by the possible formation of a six-membered HgOCOHC ring. The latter interaction is presumably facilitated by the favorable Hg–C–triazolate bond formation.



Scheme 3 Proposed mechanism via concerted metallation–deprotonation pathway.



These two factors may contribute to part of the reasons to stabilize the activation complex. Subsequent elimination of HOAc from the coordination sphere *via* abstraction of the C⁵-H proton by acetate yields the product. A similar concerted-metallation deprotonation process has been proposed for a Pd(OAc)₂ promoted C-C coupling reaction.³⁹

Conclusions

In summary, neutral *N*-substituted triazoles could react under ambient conditions with Hg(OAc)₂ to afford *C,N*-bound triazole complexes *via* processes of deprotonation and *C*-metallation, which otherwise cannot be achieved easily for other metal ions and simple bases. These Hg(II) complexes could be transformed into Hg(II) *N*-heterocyclic carbene complexes. Furthermore, the transfer of NHC from mercury complexes to other metal centers has been known,²⁹ we thus foresee the role of these Hg-triazolate complexes as an alternative bench top precursor to prepare *NR,NR'*-NHC complexes, which is a subject for future investigations.

Experimental section

General information

Ligand precursors were prepared according to the literature procedures.^{30,31} Analytical reagent grade chemicals and solvents were purchased from Alfa Aesar, Acros Organics, and Mallinckrodt Chemicals Co. and were used without further purifications. NMR spectra were recorded on Advanced DXP-Bruker spectrometers (300 MHz) and Bruker Avance^{II} spectrometer (400 MHz). Elemental microanalyses were performed at the Taiwan Instrumentation Center. Single crystal data collection was carried out on a Bruker SMART APEX II diffractometer equipped with a SMART CCD array detector with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) in ϕ and ω scan modes. All the structures were refined by a full matrix least squares method based on F^2 values using the SHELX-97 program.⁴⁰ Crystallographic data are summarized in ESI.[†]

Synthesis of 1

A mixture of Hg(OAc)₂ (0.96 g, 3.0 mmol) and an equimolar amount of the *N*-functionalized triazole-NHC precursors of **Ph-TazH** (0.44 g, 3.0 mmol), or **Py-TazH** (0.44 g, 3.0 mmol), or **Me-TazH** (0.25 g, 3.0 mmol) was dissolved in methanol (20.0 mL) and heated under reflux for 24 h. Cooling the reaction mixture to room temperature and subsequent filtration afforded the products of **1a**, **1b** and **1c** as colorless solids.

[Hg₂(Ph-Taz)₂(OAc)₂]_∞ (1a). Yield 98% (1.19 g) ¹H NMR (300 MHz, DMSO-d₆): $\delta = 8.29$ (s, 1H, taz), 7.81–7.84 (m, 2H, Ph), 7.45–7.52 (m, 3H, Ph), 1.92 (s, 3H, OAc). ¹³C NMR (100 MHz, DMSO-d₆): $\delta = 175.1$ (NCN), 165.8 (taz), 152.8 (CO), 139.4, 129.9, 128.7, 123.7 (Ph), 22.8 (CH₃). Anal. calcd for C₁₀H₉HgN₃O₂: C, 29.75; H, 2.25; N, 10.41. Found: C, 30.02; H, 2.01; N, 10.53%.

[Hg₂(Py-Taz)₂(OAc)₂]_∞ (1b). Yield 98% (1.19 g) ¹H NMR (300 MHz, DMSO-d₆): $\delta = 8.48$ (d, $J = 6.0$ Hz, 1H, Py), 8.36 (s, 1H,

taz), 8.09 (t, $J = 6.0$ Hz, 1H, Py), 7.92 (d, $J = 9.0$ Hz, 1H, Py), 7.50 (t, $J = 6.0$ Hz, 1H, Py), 1.92 (s, 3H, OAc). ¹³C NMR (100 MHz, DMSO-d₆): $\delta = 174.1$ (NCN), 163.4 (taz), 153.0 (CO), 149.1, 147.3, 140.1, 123.0, 112.8 (Py), 21.8 (CH₃). Anal. calcd for C₉H₈HgN₄O₂: C, 26.62; H, 1.87; N, 13.91. Found: C, 26.71; H, 1.99; N, 13.84%.

[Hg₂(Me-Taz)₂(OAc)₂]_∞ (1c). Yield 95% (0.98 g) ¹H NMR (300 MHz, DMSO-d₆): $\delta = 8.08$ (s, 1H, taz), 3.95 (s, 3H, CH₃), 1.87 (s, 3H, OAc). ¹³C NMR (100 MHz, DMSO-d₆): $\delta = 175.0$ (NCN), 167.4 (taz), 150.9 (CO), 37.2 (CH₃), 23.5 (CH₃-C(=O)-O-). Anal. calcd for C₅H₇HgN₃O₂: C, 17.57; H, 2.06; N, 12.30. Found: C, 17.27; H, 2.31; N, 12.08%.

Synthesis of 2

A solution of **1a** (0.61 g, 1.5 mmol), or **1b** (0.61 g, 1.5 mmol), or **1c** (0.51 g, 1.50 mmol) in ethanol (50.0 mL) was added to a solution of LiCl (0.13 g, 3.0 mmol) in methanol (25.0 mL). The mixture was heated under reflux for 15 minutes and immediately filtered thereafter, to obtain colourless solids, which were further washed with methanol (20 mL \times 3), ethanol (20 mL \times 3), and subsequently dried *in vacuo* to obtain the product of **2a**, **2b** or **2c** as colourless solids.

[Hg₂(Ph-Taz)₂(Cl)₂]_∞ (2a). Yield 98% (0.58 g) ¹H NMR (300 MHz, DMSO-d₆): $\delta = 8.30$ (s, 1H, taz), 7.81 (d, $J = 9.0$ Hz, 2H, Ph), 7.45–7.52 (m, 3H, Ph). ¹³C NMR (100 MHz, DMSO-d₆): $\delta = 171.5$ (NCN), 152.7 (taz), 139.6, 130.0, 128.9, 124.0, 123.6 (Ph). Anal. calcd for C₈H₆HgClN₃: C, 25.27; H, 1.59; N, 11.05. Found: C, 25.26; H, 1.49; N, 10.68%.

[Hg₂(Py-Taz)₂(Cl)₂]_∞ (2b). Yield 98% (0.47 g) ¹H NMR (300 MHz, DMSO-d₆): $\delta = 8.46$ (d, 1H, Py), 8.35 (s, 1H, taz), 8.11 (t, $J = 7.5$ Hz, 1H, Py), 7.93 (d, $J = 4.5$ Hz, 1H, Py), 7.52 (t, $J = 6.0$ Hz, 1H, Py). ¹³C NMR (100 MHz, DMSO-d₆): $\delta = 170.0$ (NCN), 153.8 (taz), 150.0, 147.7, 141.1, 124.1, 113.8 (Py). Anal. calcd for C₇H₅HgClN₄: C, 22.06; H, 1.32; N, 14.70. Found: C, 22.36; H, 1.24; N, 14.48%.

[Hg₂(Me-Taz)₂(Cl)₂]_∞ (2c). Yield 98% (0.58 g) ¹H NMR (300 MHz, DMSO-d₆): $\delta = 7.92$ (s, 1H, taz), 3.84 (s, 3H, CH₃). Anal. calcd for C₃H₄HgClN₃: C, 11.33; H, 1.27; N, 13.21. Found: C, 11.06; H, 1.51; N, 13.48%. Note: Due to the poor solubility of **2c** in DMSO-d₆ even at 80 °C, its ¹³C NMR could not be obtained.

Synthesis of [(Ph-Taz-Me)₂Hg][BF₄]₂ (3a)

Reaction was carried out in a dry box. To a suspension of **2a** (190.2 mg, 0.50 mmol) in dichloromethane (30 mL), trimethyloxonium tetrafluoroborate (85.0 mg, 0.58 mmol) was added. The resultant cloudy mixture was stirred overnight (12 h) and filtered using a cannula. The filtrate was dried *in vacuo*, and the resultant solids were washed with about 5 mL of diethyl ether. Solids were again dried in high vacuum to obtain the mercury-NHC complex **3a** of [(Ph-Taz-Me)₂Hg][BF₄]₂. Yield 44% (0.76 g) ¹H NMR (400 MHz, CD₃CN): $\delta = 8.23$ (s, 1H, CH), 7.66 (m, 5H, Ph), 4.05 (s, 3H, CH₃). ¹³C NMR (100 MHz, CD₃CN): $\delta = 177.8$ (NCN), 146.8 (taz), 137.7, 131.4, 130.5, 124.4 (Ph), 35.9 (CH₃). Anal. calcd for C₁₈H₁₈B₂F₈HgN₆: C, 31.22; H, 2.62; N, 12.13. Found: C, 31.02; H, 2.69; N, 12.03%.



Acknowledgements

We thanks the Ministry of Science and Technology, Taiwan (MOST 104-2113-M-259-004-) and (MOST 104-2113-M-259-010-).

Notes and references

- 1 F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172.
- 2 F. E. Hahn, *ChemCatChem*, 2013, **5**, 419–430.
- 3 S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey and J. M. J. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 13702–13703.
- 4 V. Miranda-Soto, D. B. Grotjahn, A. G. DiPasquale and A. L. Rheingold, *J. Am. Chem. Soc.*, 2008, **130**, 13200–13201.
- 5 A. R. Naziruddin, A. Hepp, T. Pape and F. E. Hahn, *Organometallics*, 2011, **30**, 5859–5866.
- 6 T. Kösterke, T. Pape and F. E. Hahn, *J. Am. Chem. Soc.*, 2011, **133**, 2112–2115.
- 7 R. Das, C. G. Daniliuc and F. E. Hahn, *Angew. Chem., Int. Ed.*, 2014, **53**, 1163–1166.
- 8 M. C. Jahnke and F. E. Hahn, *Coord. Chem. Rev.*, 2015, **293–294**, 95–115.
- 9 M. C. Jahnke and F. E. Hahn, *Chem. Lett.*, 2015, **44**, 226–237.
- 10 F. Bonati, A. Burini, B. R. Pietroni and B. Bovio, *J. Organomet. Chem.*, 1989, **375**, 147–160.
- 11 H. G. Raubenheimer and S. Cronje, *J. Organomet. Chem.*, 2001, **617–618**, 170–181.
- 12 N. Meier, F. E. Hahn, T. Pape, C. Siering and S. R. Waldvogel, *Eur. J. Inorg. Chem.*, 2007, **2007**, 1210–1214.
- 13 M. A. Huertos, J. Pérez, L. Riera, J. Díaz and R. López, *Angew. Chem., Int. Ed.*, 2010, **49**, 6409–6412.
- 14 M. A. Huertos, J. Pérez, L. Riera and A. Menéndez-Velázquez, *J. Am. Chem. Soc.*, 2008, **130**, 13530–13531.
- 15 J. Ruiz and B. F. Perandones, *J. Am. Chem. Soc.*, 2007, **129**, 9298–9299.
- 16 J. Ruiz, B. F. Perandones, J. F. Van der Maelen and S. García-Granda, *Organometallics*, 2010, **29**, 4639–4642.
- 17 G. E. Dobereiner, C. A. Chamberlin, N. D. Schley and R. H. Crabtree, *Organometallics*, 2010, **29**, 5728–5731.
- 18 S. E. Flowers and B. M. Cossairt, *Organometallics*, 2014, **33**, 4341–4344.
- 19 M. Brill, J. Díaz, M. A. Huertos, R. López, J. Pérez and L. Riera, *Chem.–Eur. J.*, 2011, **17**, 8584–8595.
- 20 S. Kuwata and T. Ikariya, *Chem. Commun.*, 2014, **50**, 14290–14300.
- 21 K. Araki, S. Kuwata and T. Ikariya, *Organometallics*, 2008, **27**, 2176–2178.
- 22 K. L. Tan, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2002, **124**, 3202–3203.
- 23 D. Brackemeyer, A. Hervé, C. Schulte to Brinke, M. C. Jahnke and F. E. Hahn, *J. Am. Chem. Soc.*, 2014, **136**, 7841–7844.
- 24 T. Kösterke, J. Kösters, E.-U. Würthwein, C. Mück-Lichtenfeld, C. Schulte to Brinke, F. Lahoz and F. E. Hahn, *Chem.–Eur. J.*, 2012, **18**, 14594–14598.
- 25 J. C. Lewis, S. H. Wiedemann, R. G. Bergman and J. A. Ellman, *Org. Lett.*, 2004, **6**, 35–38.
- 26 R. J. Sundberg, R. F. Bryan, I. F. Taylor and H. Taube, *J. Am. Chem. Soc.*, 1974, **96**, 381–392.
- 27 G. Sini, O. Eisenstein and R. H. Crabtree, *Inorg. Chem.*, 2002, **41**, 602–604.
- 28 M.-H. Yu, H.-H. Yang, A. R. Naziruddin, S. Kanne, B.-H. Wang, F.-C. Liu, I. J. B. Lin and G.-H. Lee, *Eur. J. Inorg. Chem.*, 2016, 4829–4834.
- 29 M. V. Baker, D. H. Brown, R. A. Haque, P. V. Simpson, B. W. Skelton, A. H. White and C. C. Williams, *Organometallics*, 2009, **28**, 3793–3803.
- 30 D. Wang, F. Zhang, D. Kuang, J. Yu and J. Li, *Green Chem.*, 2012, **14**, 1268–1271.
- 31 L. Zhu, P. Guo, G. Li, J. Lan, R. Xie and J. You, *J. Org. Chem.*, 2007, **72**, 8535–8538.
- 32 C. Buron, L. Stelzig, O. Guerret, H. Gornitzka, V. Romanenko and G. Bertrand, *J. Organomet. Chem.*, 2002, **664**, 70–76.
- 33 J. C. C. Chen and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 839–840.
- 34 S. Budagumpi and S. Endud, *Organometallics*, 2013, **32**, 1537–1562.
- 35 S. Pelz and F. Mohr, *Organometallics*, 2011, **30**, 383–385.
- 36 M. M. D. Roy, M. J. Ferguson and E. Rivard, *Z. Anorg. Allg. Chem.*, 2016, **642**, 1232–1235.
- 37 P. Biscarini, L. Fusina and G. D. Nivellini, *J. Chem. Soc., Dalton Trans.*, 1972, 1003–1008.
- 38 C.-X. Lin, L. Guo, Q.-S. Li, Z.-Z. Zhang, Y.-F. Yuan and F.-B. Xu, *J. Organomet. Chem.*, 2014, **749**, 180–187.
- 39 T. Gensch, M. N. Hopkinson, F. Glorius and J. Wencel-Delord, *Chem. Soc. Rev.*, 2016, **45**, 2900–2936.
- 40 G. Sheldrick, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 2008, **64**, 112–122.

