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FULL PAPER

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Symmetrical and Non-symmetrical Pd (II) Pincer Complexes Bearing Mesoionic N-heterocyclic Thiones: Synthesis, Characterizations and Catalytic Properties

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In contrast to well-established symmetrical pincer complexes, non-symmetrical metal pincers with the loss of C_{2v} symmetry are much less studied. In this work, mesoionic NHTs (NHTs = N-heterocyclic thiones), which can be viewed as the sulfur adducts of mesoionic carbenes, are incorporated into pincer complexes for the first time. Two symmetrical and non-symmetrical phenylene-bridged bis (NHT) compounds **3a**/**3b** were synthesized as proligands via a “cycloaddition-alkylation-thionation” reaction sequence. In a case to access bis (NHT) compound **3c**, N-dealkylation reactions occurred. The carbene NMR signals of NHTs are only partially correlated to the π-accepting abilities of carbenes, which is different from Bertrand's carbene-phosphinidene system. The structural analysis of **3a**/**3b** indicates that they possess C-S partial double bonds. **3a** and **3b** served as the precursors to access two aryl anion-linked [SCS/S′] pincer complexes **6a**/**6b**. An external base proved to be essential for this cyclopalladation process. The catalytic properties of **6a**/**6b** in the cycloisomerizations of alkynoic acids have been examined. Finally, non-symmetrical complex **6a** shows superior catalytic performance in such transformations contrasting to its symmetrical counterpart **6b**.

KEYWORDS
Mesoionic, N-heterocyclic thione, non-symmetrical, pincer

1 | INTRODUCTION

The past 40 years have witnessed the rapid development of transition metal pincer chemistry.[] Notably, compared to [PXP]- and [NXN]-type analogues, sulfur-based [SXS] pincer frameworks are relatively less investigated.[2] A number of S-donors such as thioethers/thiolates,[3] phosphine sulfides[4] and thioamides[5] have been employed as arm donors to access various sulfur-containing pincer complexes (*e.g.* **I**, **II**, **III**, Figure 1), and they have found manifold applications spanning from catalytic organic transformations to photoluminescence.

However, it should be additionally noted that most of the reported [SXS] pincers are C_{2v}-symmetric, and non-symmetric [SXS']-type pincer frameworks with two different S-based functionalities remain largely unexplored.[6] The desymmetrization of pincer platforms undoubtedly further expands the structural diversity of pincer family. In addition, employing two arm-donors with different electron-releasing capacities can make one donor hemilabile

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Xuechao Yan and Bo Zhang, contribute equally to this work.

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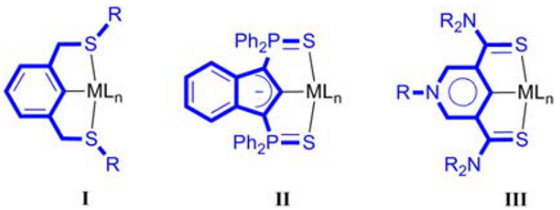


FIGURE 1 Some examples (**I/II/III**) of [SXS] pincer complexes

and help to generate a vacant coordination site. Such concept has been employed in a few non-symmetric pincers such as Milstein's PNN and PNS systems and proved to be successful.[1j,7]

NHTs (NHTs = N-heterocyclic thiones) such as imidazolin-2-thiones can be viewed as the sulfur adducts of NHCs (NHCs = N-heterocyclic carbenes) and have been extensively used as S-donors.[8] The strong interest in NHTs partially roots in the fact that they can be conveniently accessed by reacting well-established NHCs[9] with elemental sulfur. As such, odorous and toxic organosulfur compounds (*e.g.* thiols), which are typically used as sulfur sources to access S-based pincers, can be avoided. Furthermore, the fine steroelectronic tunability and convenient functionalization of NHCs also render their NHT derivatives highly appealing.

In contrast to classical NHTs, mesoionic NHTs (*e.g.* **i**, Figure 2) derived from mesoionic carbenes[10] are much less investigated. For mesoionic compounds, a totally uncharged canonical resonance structure cannot be represented,[11] and this unique type of molecules as well as their complexes have gained increasing interest in recent years.[12] For 1,2,3-triazole-derived mesoionic NHT **i**, a number of limiting resonance forms (*i.e.* thiolate or thione forms) can be deduced. Surprisingly, although the synthesis of **i** dates back to Begtrup's work almost 50 years ago,[13] its metal complexes and further catalytic applications have been rarely reported.[14]

Herein, we report the first examples of mesoionic NHT-based pincer complexes, and three pincer platforms are targeted (Figure 2). In addition to non-symmetrical SCS' pincer system **A** bearing two different mesoionic NHTs, two symmetrical counterparts (**B** and **C**) have also been accessed to make a systematic comparison. The preparation, reactivity and catalytic performance of their proligands as well as palladium (II) pincers are reported.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of non-symmetrical proligands

In aiming to access the non-symmetrical target ligand **A**, the corresponding dicationic precursor **2a** was synthesized via a sequence shown in Scheme 1. The copper-mediated click reaction using 3-aminophenyl-acetylene and benzyl azide as the starting materials gave the mono-triazole **a**. For this step, a well-defined copper carbene complex [CuCl (IPr)] (IPr = 1,3-bis-(2,6-diisopropylphenyl) imidazolin-2-ylidene) was used as the catalyst. Without isolation, compound **a** underwent diazotization, azidation followed by [3 + 2] click reaction successfully affording the non-symmetrical bis (triazoles) **1a** in good yield. The subsequent alkylation using Meerwein's salt $(CH_3)_3OBF_4$ yielded the desired dicationic proligand salt **2a** in moderate yield. In the ^1H NMR spectrum of **2a** in d^6-DMSO, two downfield singlets at 9.45 and 9.33 ppm were observed, which can be assigned to the two non-symmetrical $C_{triazole}$-H protons. Symmetrical 1,2,3-triazolium salts **2b** and **2c**, which have been previously reported by others and our group respectively,[15] are used herein as precursors of ligands **B** and **C** (see Supporting Information, Scheme S1).

2.2 | Mesoionic carbene-sulfur adducts

Then, **2a**-**2c** were used as precursors to access the target S-donors. The reactions of **2a**/**2b** with elemental sulfur in

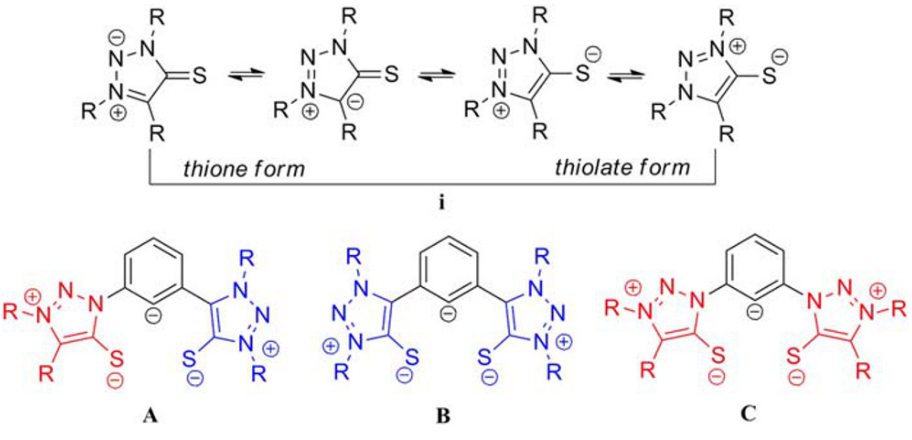
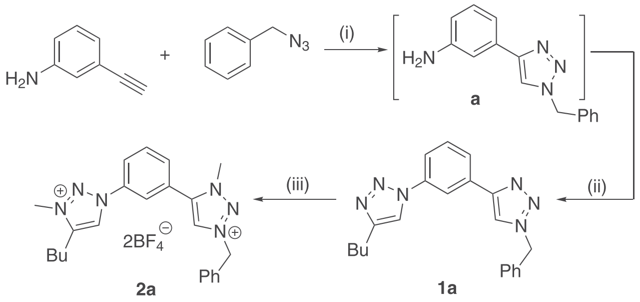


FIGURE 2 Resonance forms of mesoionic NHT **i** and three targeted ligand platforms (**A**-**C**)



SCHEME 1 Synthesis of **1a** and **2a**. Condition (i): [CuCl (IPr)], EtOH/H_2O; Condition (ii): NaNO2, HCl, and then NaN_3, and then 1-hexyne, [CuCl (IPr)], EtOH/H2O, 82% (two-step combined yield); Condition (iii): $(CH_3)_3OBF_4$, $C_2H_4Cl_2$, 56%

the presence of an external base were examined. KO^{t}Bu and an even weaker base K_2CO_3 proved to be effective. The desired non-symmetrical mesoionic bis (NHT) compound **3a** and the symmetrical analogue **3b** can be isolated as yellow solid in good yields (Scheme 2).

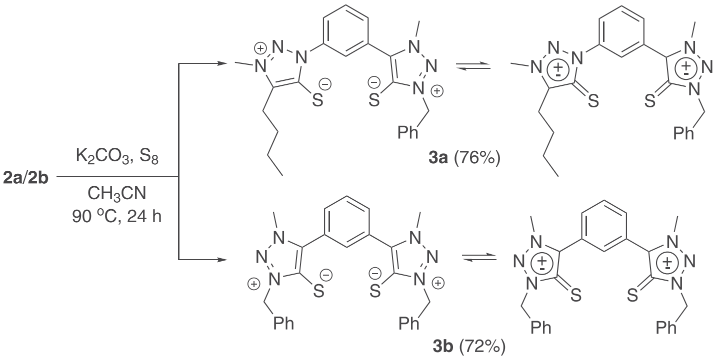
In sharp contrast, the reaction of **2c** with elemental sulfur in the presence of an external base produced a very complicated mixture (Scheme 3). ESI-MS analysis of the crude product suggested the formation of bis (NHT) compound **3c** as well as a number of demethylated products **1c**, **4c** and **5c** (Figure 3). Similar dealkylation process has been reported to occur during the course of the palladation of **2c**,[15c] and has also been observed in earlier work of Bertrand and others.[12a,16]

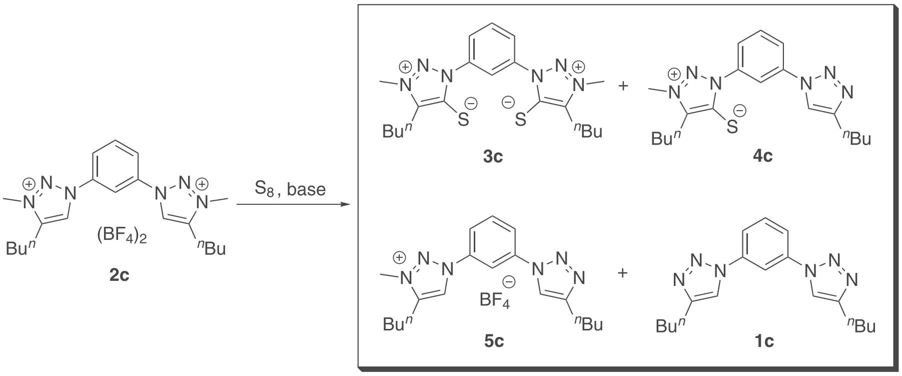
2.3 | Spectroscopic and structural features of 3a/3b

Compounds **3a**/**3b** are air-stable and readily soluble in EtOAc and CH_2Cl_2 but less soluble in Et_2O. Their formation was first corroborated by positive mode ESI mass spectrometric analysis. Two base peaks at m/z 451 and 485, which can be assigned to the corresponding protonated species $[M + H]^+$, were observed. In addition, in the ^1H NMR spectra of **3a**/**3b**, the downfield signals assigned to $C_{triazole}$-H protons disappeared, which indicate that the deprotonation processes have occurred. As expected, the two N-methyl groups of **3b** gave only one singlet (4.14 ppm), while two different NCH_3 signals (4.16 ppm and 3.99 ppm) were observed in the case of **3a** owing to the loss of C_{2v} symmetry.

In the ^{13}C NMR spectrum of **3a**, two downfield singlets at 157.2 ppm and 157.0 ppm were found, which can be assigned to the sulfur-attached $C_{carbene}$ atoms. Only one carbene signal was observed at 157.0 ppm in the case of **3b**. These signals are in agreement with that observed for monodentate mesoionic NHT **i** (Figure 4),[14] upfield than the related 'normal' thiones reported by Kühn et al,[18] and slightly downfield compared to those for

SCHEME 2 Synthesis of mesoionic carbene-sulfur adducts **3a** and **3b**





SCHEME 3 Attempt to synthesize **3c**

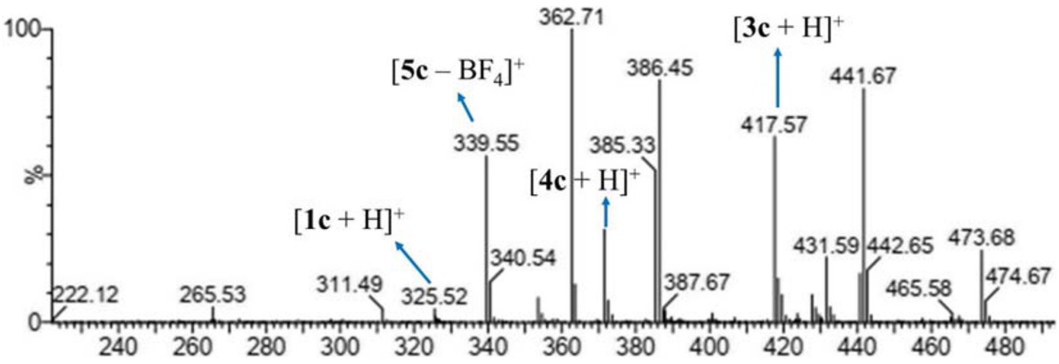


FIGURE 3 ESI-MS spectrum of the crude product for the attempt to synthesize **3c**

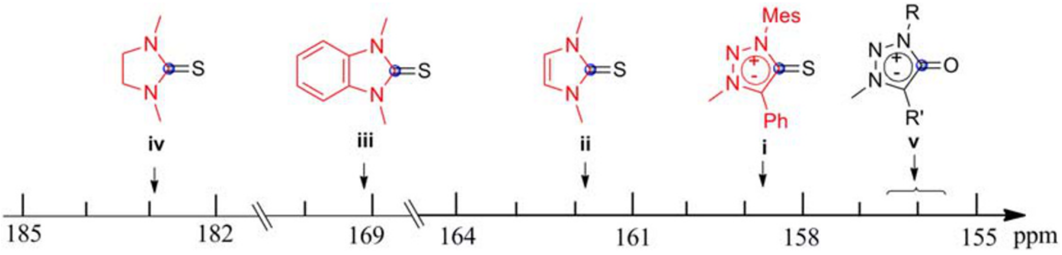


FIGURE 4 Comparison of $^{13}C_{carbene}$ NMR signals of mesoionic NHT **i** with other representative structurally relevant molecules. The data is from reference 14 (for **i**), reference 17 (for **ii**/**iii**/**iv**), reference 12a (for **v**). $CDCl_3$ was used as the solvent except **iii** (using d^6-DMSO)

mesoionic oxides (**v**, Figure 4) previously documented by Albrecht's group.[12a]

The mesoionic NHTs studied herein are highly related to Bertrand's carbene-phosphinidene system and Ganter's carbene-selenium system (Figure 5). In Bertrand's case,[9a, 19a] they have found that the $^{13}C_{carbene}$ NMR and ^{31}P NMR signals are both correlated to the π-accepting capacities of carbenes: C (XY). Generally, a more downfield shift was observed when a more π-accepting carbene was used in their system. In contrast, in Ganter's case, [9a, 19b, c] the π-accepting abilities can only be correlated to the ^{77}Se NMR resonances rather than the $^{13}C_{carbene}$ NMR signals.

The carbene signals of mesoionic NHT **i** was compared with a few representative non-mesoionic NHTs (**ii**-**iv**),[17] which is shown in Figure 4. The question that arises here, is: Is there a correlation between the $^{13}C_{carbene}$ signals of NHTs **i**-**iv** and the π-accepting abilities of carbenes? Previously, Frenking and Dutton *et al.* have used DFT calculations to reveal a trend of carbene π-accepting abilities, **iii** > **iv** > **ii** > **i**.[20] The benzannulated carbene in **iii** is expected to be the strongest π-acceptor, while the mesoionic carbene in **i** is expected to be the least π-accepting. However, this carbene π-accepting trend is only partially correlated to the carbene signals of **i**-**iv**. For example, mesoionic NHT **i**, bearing the least π-acidic carbene, indeed gives the most upfield carbene resonance. However, compound **iv**, although possessing the second strongest π-accepting carbene in **i**-**iv**, gives the most downfield carbene signal. These observations implicate the difference of spectroscopic features of NHT system versus Bertrand's carbene-phosphinidene system.

Several attempts to grow single crystals of **3a**/**3b** were to no avail, and thus DFT calculations were carried out to provide further insight into their structural features.

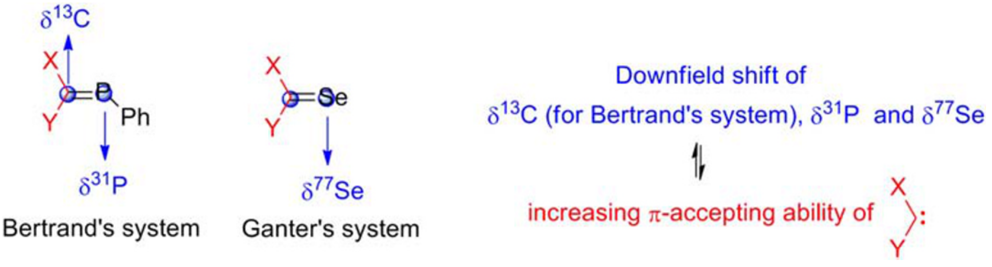


FIGURE 5 Bertrand and Ganter's systems to determine the π-accepting capacities of carbenes

The optimized molecular structures are depicted in Figure 6, and the calculated C-S bond lengths are listed in Table 1.

For both cases of **3a** and **3b**, the C-S moieties adopted an *anti*-configuration relative to the central phenylene group. In contrast, Hollis and Jia *et al.* have reported a series of bis (imidazolin-2-thione) analogues **Btb** (Table 1),[21] and a *syn* orientation was reported for ^{n}Bu-**Btb**.[21a] The calculated C-S bond distances up to 1.6975 Å is close to the typical C-S partial double bond distance (1.72 Å),[22] and thus the thiocarbonyl moieties of **3a**/**3b** are better described as partial double bonds. In addition, the C-S bond lengths of **3a**/**3b** are slightly longer than those for ^{n}Bu-**Btb** indicating a less pronounced C-S double bond character in the former case.

Finally, it should be noted that for Albrecht's mesoionic oxides **v** (Figure 4), the C-O bond length of 1.243 Å clearly indicates that the carbonyl moiety possesses a highly characteristic C-O double bond feature. The diminished carbon-chalcogen bond order of **3a**/**3b** (vs. **v**) can be rationalized by the poor overlap of C (2p) and S(3p) orbitals.[8] This also accounts for the higher reactivity of thioketones compared to ketones in general.

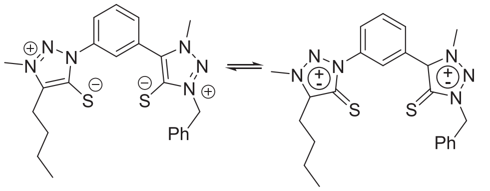
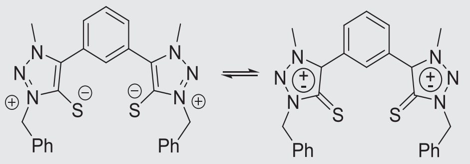
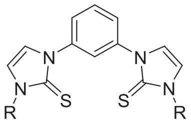
2.4 | Cyclopalladations to access [SCS] and [SCS′]-type complexes

Compounds **3a** and **3b** were then employed as ligand precursors to access cyclopalladated complexes bearing nonsymmetrical [SCS′] or symmetrical [SCS] pincer ligands, respectively (Scheme 4).

Heating **3a**/**3b** with $PdCl_2$ at 90 °C in the presence of NaOAc gave the desired complexes **6a** and **6b**, and the products can be isolated as yellow solid. Compared to **3a**/**3b**, complexes **6a**/**6b** show much decreased solubility in common organic solvents such as CH_2Cl_2.

In the ESI mass spectra of **6a** and **6b**, two base peaks at *m/z* 555 and 589 were observed respectively. These peaks can be assigned to the mono-cationic fragments $[M - Cl]^+$, which indicates the loss of Cl ligands and the retainment of metal pincer frameworks in the ESI-MS condition. In the ^1H NMR spectra of **6a**/**6b**, the signals of pincer central C-donors all show an upfield shift compared to those for the proligands **3a**/**3b**, owing to the greater shielding of the anionic aryl donors in the former cases.

TABLE 1 Comparison of C-S bond lengths of **3a**/**3b** versus **Btb**

Compd.		**C-S bond length (Å)**
 3a		1.6888[b] 1.6912[b]
 3b		1.6975[b] 1.6943[b]
 (Btb)[a]	R = ^{n}Bu	1.6758[c] 1.6842[c]
	R = Et	—
	R = Allyl	—

[a] **Btb** = 1,3-bis(3′-butylimidazolyl-2′-thione)benzene.
[b] DFT calculated.
[c] The data is from reference 21a.

Previously, Hollis, Jia *et al.* have reported the cyclopalladations of **Btb** (Scheme 5), in which cases

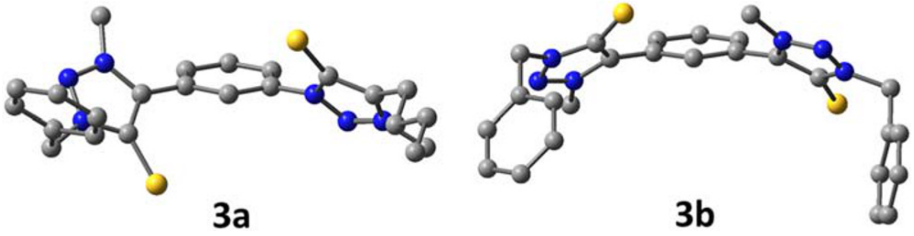
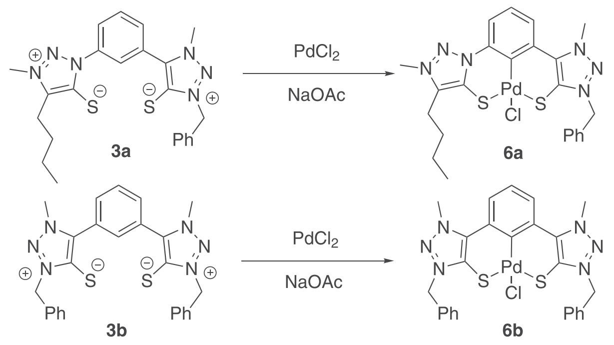
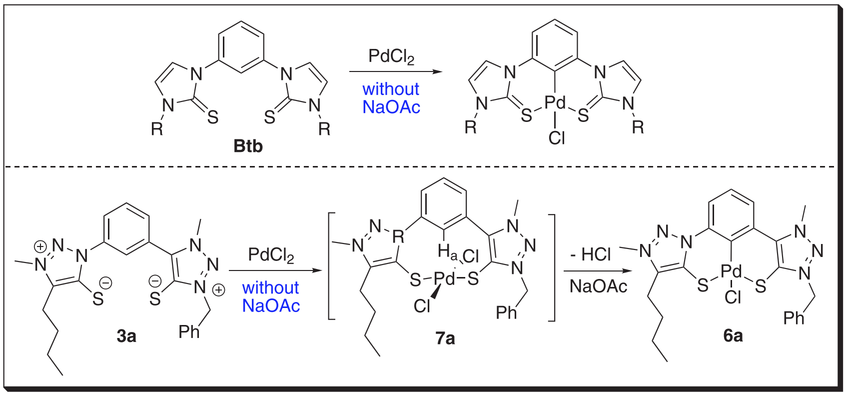


FIGURE 6 Optimized molecular structures of **3a**/**3b** based on DFT calculations. Atoms with yellow color (S), atoms with blue color (N), atoms with gray color (C)



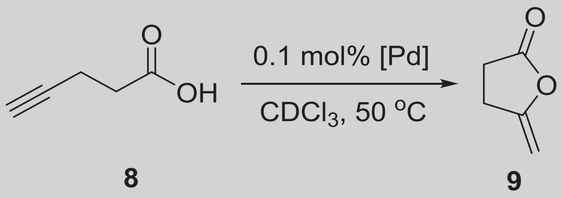
SCHEME 4 Synthesis of Pd bis (NHT) pincer complexes **6a** and **6b**

NaOAc was not utilized.[21] As such, **3a** was used as a representative, and under Hollis's condition, the metalation reactivity in the absence of NaOAc was examined. ^{1}H NMR spectrum of the as-formed product shows a very downfield singlet at 12.17 ppm, which is tentatively assigned to the C_{aryl}-H_a proton of non-cyclopalladated complex **7a**. The formation of **7a** can be further verified by ESI mass spectrometric analysis revealing a dominant peak at m/z 591 corresponding to [**7a** − Cl]$^+$. Further treating **7a** with NaOAc can afford the desired pincer complex **6a**. These observations indicate that in the current case OAc$^-$ plays an essential role in promoting the C_{aryl}-H activation and cyclopalladation.



SCHEME 5 Cyclopalladation reactivity comparison of previously reported non-mesoionic bis (NHT) and mesoionic bis (NHT) **3a**

TABLE 2 Catalytic condition screening of cycloisomerization of 4-pentynoic acid **8**[a]



Entry	Cat.	Cat. Loading	Et_3N (mol%)	t (hr)	Yield(%)[b]
1	–	–	–	12	3
2	**6a**	0.1%	–	12	38
3	**6a**	0.1%	–	2	6
4	**6b**	0.1%	–	12	37
5	**6a**	0.1%	2	12	>99
6	**6b**	0.1%	2	12	57

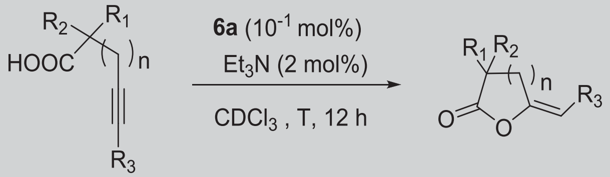
[a] Reaction condition: 0.2 mmol of 4-pentynoic acid, 0.5 ml of $CDCl_3$, 0.1 mol% of [Pd] (for entries 2–6), 2 mol% of Et_3N (for entries 5–6), 50 °C.
[b] Yields were determined using ^{1}H NMR spectroscopy.

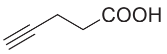
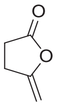
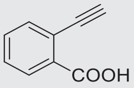
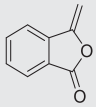
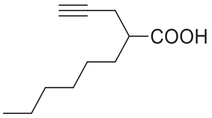
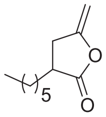
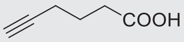
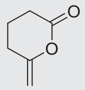
2.5 | Catalytic study

Intramolecular cycloisomerization of alkynoic acids is an important reaction of high atom economy to construct enol lactones. Such transformations have been known to be mediated by a few transition metals including Pd.[23] Particularly for structurally related [SCS] pincer systems, Bourissou *et al*. have documented a few symmetrical phosphine sulfide-based Pd pincer complexes of the type **II** (*vide supra*, Figure 1), and reported their catalytic cycloisomerization of alkynoic acids at a 5 mol% catalyst loading.[24] In a preliminary study and as a comparison, the newly synthesized pincer complexes **6a**/**6b** were tested for their catalytic performances in the same reaction (Table 2).

In the model reaction, 4-pentynoic acid **8** was used as the substrate. Without the addition of any Pd catalyst, a very low yield was obtained even after a reaction time of 12 hr (Entry 1). The yield of the enol lactone product **9** can be increased to 38% in the presence of only 0.1 mol % of catalyst **6a** (Entry 2). Shortening the reaction time to 2 hr gave a sharp decrease of yield (Entry 2 vs. Entry 3). Essentially the same yield was obtained using **6b** as the catalyst (Entry 4). These observations suggest that an external base was not necessary to drive this transformation. However, this reaction can be accelerated using Et_3N, and a nearly full conversion of **8** to **9** can be achieved under otherwise identical conditions. In contrast, when symmetrical complex **6b** was employed as the catalyst, only a moderate yield was obtained clearly

TABLE 3 Expanding the substrate scope of intramolecular cycloisomerization of alkynoic acids catalyzed by **6a**[a]



Entry	Substrate	Product	*T* (°C)	*t* (hr)	Yield(%)[b]
1			50	12	>99%
2			50	12	>99%
3			50	12	47
4			50	12	<1
5			90	12	<1

[a] Reaction condition: 0.2 mmol of alkynoic acid, 0.5 ml of $CDCl_3$, 0.1 mol% of [Pd], 2 mol% of Et_3N.
[b] Yields were determined using ^1H NMR spectroscopy.

indicating the superiority of non-symmetrical pincer catalyst **6a**.

Under the optimized condition, non-symmetrical complex **6a** served as the catalyst, and with a catalyst loading of 0.1 mol%, the cycloisomerization of a small selection of alkynoic acids were then tested (Table 3). 2-Ethynylbenzoic acid can undergo a complete conversion yielding the benzannulated enol lactone (Table 3, Entry 2). A moderate yield was obtained when a substrate with a long aliphatic tail was used (Entry 3). The cycloisomerization to construct a 6-membered enol lactone proved to be very sluggish even at an elevated temperature of 90 °C (Entries 4 and 5).

3 | CONCLUSION

In summary, the multi-step synthesis and characterizations of symmetrical or non-symmetrical bis (mesoionic NHT) compounds **3a**-**3b** as well as their complexes **6a**/**6b** has been described. In the case of **3c**, N-dealkylations were observed during the course of thionation. In contrast to Bertrand's carbene-phosphinidene system, the carbene signals of NHT system are not fully correlated to the π–accepting abilities of carbenes. DFT-assisted structural analysis of **3a**/**3b** indicates a diminished C-S double bond order. The comparative catalytic study of **6a**/**6b** in cycloisomerizations of alkynoic acids revealed the superiority of non-symmetrical **6a** over symmetrical **6b** in such transformations.

To the best of our knowledge, this report provides the first examples of mesoionic NHT-based pincer complexes, and also enriches the less studied non-symmetrical pincer chemistry. The synthetic, spectroscopic and catalytic study explored in the current work will facilitate the revisit of “old” mesoionic NHTs. Currently, our lab is engaged in further expanding the catalytic applications of the as-synthesized non-symmetrical pincer complexes.

4 | EXPERIMENTAL SECTION

4.1 | General considerations

If not mentioned otherwise, all reagents and solvents were used as received without further purification. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian 600 MHz spectrometer or Bruker 400 MHz spectrometer. The chemical shifts (*δ*) were internally referenced to the residual solvent signals. ESI mass spectra were measured using an Agilent 6,540 Q-TOF mass spectrometer. Elemental analyses were done on a vario EL cube elemental analyzer.

4.2 | Synthesis of a

Benzyl bromide (595 μL, 5 mmol), NaI (37.5 mg, 0.25 mmol) and DMF (5 ml) were mixed in a 25 ml round bottom flask. The reaction mixture was stirred at the ambient temperature for 20 min. Sodium azide (358 mg, 5.5 mmol) was added, and then the reaction mixture was stirred at the ambient temperature for another 2 hr. Diethyl ether and deionized H_2O were added, and the organic phase was dried in *vacuo* affording benzyl azide as a yellow liquid. Then, 3-ethynylaniline (570 μL, 4.5 mmol), CH_3CH_2OH (15 ml), H_2O (5 ml) and the catalyst [CuCl (IPr)] (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene, 25 mg, 0.05 mmol) were added. The mixture was stirred at 60 °C for 24 hr. The resulting precipitate was collected and dried in *vacuo* affording the mono-triazole product **a** as a dark solid, which was directly used for the next step without further purification.

4.3 | Synthesis of 1a

Compound **a** (ca. 5 mmol) was mixed with HCl (3.2 ml, 6 M in H_2O) at 0 °C in a flask charged with a magnetic stirring bar, and a solution of $NaNO_2$ (350 mg, 5.13 mmol) in deionized H_2O (1.8 ml) was added. After stirring for 10 min, a solution of NaN_3 (330 mg, 5.1 mmol) in deionized H_2O (1.8 ml) was added dropwise. The reaction mixture was stirred at the ambient temperature for 2 hr. Diethyl ether (10 mL × 3) was added, the organic phase was collected and dried *in vacuo* affording the azide intermediate as an off-white solid. Then 1-hexyne (555 μL, 5 mmol), CH_3CH_2OH (15 ml), H_2O (5 mL) and the catalyst [CuCl (IPr)] (25 mg, 0.05 mmol) were added. The mixture was stirred at 60 °C for 24 hr. The resulting precipitate was collected and dried in *vacuo* affording **1a** as a dark solid (4.1 mmol, 1.03 g, 82%).

^{1}H NMR (400 MHz, d^{6}-DMSO): δ 8.79 (s, 1H, Ar – H), 8.64 (s, 1H, Ar – H), 8.35 (s, 1H, Ar – H), 7.95 (d, 1H, Ar – H, $^{3}J_{H,H}$ = 7.6 Hz), 7.84 (dd, 1H, Ar – H, $^{3}J_{H,H}$ = 8 Hz, $^{3}J_{H,H}$ = 1.2 Hz), 7.64 (t, 1H, Ar – H, $^{3}J_{H,H}$ = 8 Hz), 7.42–7.33 (m, 5H, Ar – H), 5.69 (s, 2H, CH_2), 2.71 (t, 2H, $C\underline{H_2}CH_2CH_2CH_3$, $^{3}J_{H,H}$ = 7.8 Hz), 1.70–1.62 (m, 2H, $CH_2C\underline{H_2}CH_2CH_3$), 1.42–1.33 (m, 2H, $CH_2CH_2C\underline{H_2}CH_3$), 0.92 (t, 3H, $CH_2CH_2CH_2C\underline{H_3}$, $^{3}J_{H,H}$ = 7.2 Hz). ^{13}C NMR (100 MHz, d^{6}-DMSO): δ 148.2, 145.7, 137.4, 135.9, 132.3, 130.5, 128.8, 128.2, 128.0, 124.7, 122.4, 120.1, 119.0, 116.2 (Ar – C), 53.2 (N – CH_2), 30.9 ($\underline{C}H_2CH_2CH_2CH_3$), 24.7 ($CH_2\underline{C}H_2CH_2CH_3$), 21.7 ($CH_2CH_2\underline{C}H_2CH_3$), 13.7 ($CH_2CH_2CH_2\underline{C}H_3$).

4.4 | Synthesis of 2a

In a Schlenk tube, a mixture of compound **1a** (359 mg, 1 mmol), trimethyloxonium tetrafluoroborate (592 mg, 4 mmol) and 1,2-dichloroethane (1 mL) were stirred at 90 °C for 24 hr. After the mixture was cooled to the ambient temperature, CH_3OH (4 mL) was added and the resulting mixture was stirred at the ambient temperature for 30 min in order to remove the excessive oxonium salt. All the volatiles were removed *in vacuo*. The residue was washed with diethyl ether (3 × 10 mL), then dried under vacuum to give the product as an off-white solid (0.56 mmol, 350 mg, 56%).

^1H NMR (600 MHz, d^6-DMSO): δ 9.45 (s, 1H, H_{triazole}), 9.33 (s, 1H, H_{triazole}), 8.35 (s, 1H, Ar – H), 8.29 (d, 1H, Ar – H, $^3J_{\mathrm{H,H}} = 7.8$ Hz), 8.06–8.01 (m, 2H, Ar – H), 7.57 (d, 2H, Ar – H, $^3J_{\mathrm{H,H}} = 7.2$ Hz), 7.50–7.46 (m, 3H, Ar – H), 5.99 (s, 2H, CH_2), 4.35 (s, 3H, N – CH_3), 4.32 (s, 3H, N – CH_3), 2.95 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$, $^3J_{\mathrm{H,H}} = 6$ Hz), 1.78–1.73 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.51–1.45 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.98 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{\mathrm{H,H}} = 7.8$ Hz).^{13}C NMR (150 MHz, d^6-DMSO): δ 145.4, 140.9, 135.3, 132.8, 132.5, 131.5, 129.7, 129.4, 129.1, 129.0, 126.8, 124.6, 124.2, 122.5 (Ar – C), 56.4 (N – CH_2), 39.0, 37.9 (N – CH_3), 28.1 ($\underline{C}H_2CH_2CH_2CH_3$), 22.3 ($CH_2\underline{C}H_2CH_2CH_3$), 21.5 ($CH_2CH_2\underline{C}H_2CH_3$), 13.6 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI): *m/z* 194 $[M - 2BF_4]^{2+}$.

4.5 | General procedure for the synthesis of 3a and 3b

A 25 ml Schlenk tube was charged with compound **2a/2b** (0.1 mmol), K_2CO_3 (28 mg, 0.2 mmol), S (6.4 mg, 0.2 mmol) and CH_3CN (2 ml). The tube was sealed and the reaction mixture was stirred and heated at 90 °C for 20 hr. All the volatiles were removed *in vacuo*. To the residue, CH_2Cl_2 (5 ml) was added, then the crude product was purified using column chromatography (SiO_2, CH_2Cl_2/CH_3OH (V:V) = 40: 1) affording the product as an yellow solid.

3a. Yield: 76%. ^1H NMR (600 MHz, $CDCl_3$): δ 8.49 (s, 1H, Ar – H), 8.16 (d, 1H, Ar – H, $^3J_{\mathrm{H,H}} = 7.8$ Hz), 7.80 (d, 1H, Ar – H, $^3J_{\mathrm{H,H}} = 8.4$ Hz), 7.61 (t, 1H, Ar – H, $^3J_{\mathrm{H,H}} = 7.8$ Hz), 7.52 (d, 2H, Ar – H, $^3J_{\mathrm{H,H}} = 7.8$ Hz), 7.32–7.27 (m, 3H, Ar – H), 5.69 (s, 2H, N – CH_2), 4.16 (s, 3H, N – CH_3), 3.99 (s, 3H, N – CH_3), 2.80 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$, $^3J_{\mathrm{H,H}} = 7.8$ Hz), 1.66–1.61 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.42–1.38 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.91 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{\mathrm{H,H}} = 7.8$ Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.2, 157.0 (C – S), 139.7, 136.4, 135.6, 134.5, 131.1, 129.7, 129.2, 128.9, 128.6, 126.5, 125.9, 125.2 (Ar – C), 51.4 (N – CH_2), 39.5, 37.3 (N – CH_3), 29.0 ($\underline{C}H_2CH_2CH_2CH_3$), 24.3 ($CH_2\underline{C}H_2CH_2CH_3$), 22.7 ($CH_2CH_2\underline{C}H_2CH_3$), 13.9 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI) *m/z*: 451 $[M + H]^+$.

3b. Yield: 72%. ^1H NMR (600 MHz, $CDCl_3$): δ 8.16 (t, 1H, Ar – H, $^3J_{\mathrm{H,H}} = 1.8$ Hz), 7.81–7.80 (m, 2H, Ar – H), 7.64–7.62 (m, 1H, Ar – H), 7.57–7.55 (m, 4H, Ar – H), 7.37–7.32 (m, 6H, Ar – H), 5.73 (s, 4H, $PhCH_2$), 4.14 (s, 6H, NCH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.0 (C – S), 136.0, 134.4, 131.4, 130.4, 129.3, 129.2, 128.9, 128.6, 126.7 (Ar – C), 51.5 (N – CH_2), 39.2 (N – CH_3). MS (ESI) *m/z* 485 $[M + H]^+$.

4.6 | General procedure for the synthesis of 6a and 6b

In a 25 ml Schlenk tube, compounds **3a** or **3b** (0.5 mmol), $PdCl_2$ (0.5 mmol), NaOAc (1.5 mmol) and 2 ml of CH_3CN were added. The reaction mixture was stirred and heated at 90 °C for 24 hr. After cooling down to the ambient temperature, all the volatiles were removed *in vacuo*. CH_2Cl_2 (5 ml) was added to extract the crude product. All the insolubles were filtered off, and the organic phase was dried and further purified using column chromatography (SiO_2, CH_2Cl_2/CH_3OH (V:V) = 10: 1) affording the product as a yellow solid.

6a: Yield 26%. ^1H NMR (600 MHz, d^6-DMSO): δ 7.81 (br s, 1H, Ar – H), 7.52–7.51 (m, 3H, Ar – H), 7.43–7.35 (m, 4H, Ar – H), 5.70 (s, 2H, CH_2), 4.33 (s, 3H, NCH_3), 4.24 (s, 3H, NCH_3), 2.83 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$, $^3J_{\mathrm{H,H}} = 6.6$ Hz), 1.66–1.61 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.41–1.37 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.93 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{\mathrm{H,H}} = 7.2$ Hz). Due to the low solubility of this compound in common organic solvents, a satisfying ^{13}C NMR spectrum cannot be obtained even after long-time accumulation of signals. MS (ESI) *m/z*: 555 $[M - Cl]^+$. Anal. Calcd. for $C_{23}H_{25}ClN_6PdS_2$: C, 46.70; H, 4.26; N, 14.21; S, 10.84%; Found: C, 46.35; H, 4.46; N, 14.58; S, 11.21%.

6b: Yield 31%. ^1H NMR (600 MHz, $CDCl_3$): δ 7.55–7.54 (m, 4H, Ar – H), 7.33–7.30 (m, 8H, Ar – H), 7.14 (t, 1H, Ar – H, $^3J_{\mathrm{H,H}} = 7.2$ Hz), 5.62 (s, 4H, $PhCH_2$), 4.18 (s, 6H, NCH_3). Due to the low solubility of this compound in common organic solvents, a satisfying ^{13}C NMR spectrum cannot be obtained even after long-time accumulation of signals. MS (ESI) *m/z*: 589 $[M - Cl]^+$. Anal. Calcd. for $C_{26}H_{23}ClN_6PdS_2$: C, 49.93; H, 3.71; N, 13.44; S, 10.25%; Found: C, 49.58; H, 3.89; N, 13.16; S, 10.56%.

4.7 | General procedure for catalysis

Alkynoic acid (0.2 mmol), triethylamine (2 mol% if applicable) and Pd catalyst (the catalyst loading is as indicated in Table 2 and 3) were mixed in a NMR tube, to which 0.5 ml of $CDCl_3$ was added. The NMR tube was sealed, and then stirred and heated. After that, the reaction mixture was cooled to the ambient temperature, and subjected to ^{1}H NMR spectroscopic analysis and compared with the ^{1}H NMR data reported in the literature for each substrate.[24,25]

4.8 | DFT calculation

Compounds **3a/3b** were geometry optimized using density functionals at the B3LYP/6–311 + G* level of theory with empirical dispersion GD3.

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CONFLICT OF INTEREST

There are no conflicts to declare.

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REFERENCES

[1] For selected recent reviews, see:(a)D. Morales-Morales (Ed), *Pincer Compounds: Chemistry and Applications*, Elsevier, Amsterdam, Holland **2018**. (b)G. van Koten, *Top. Organomet. Chem.* **2013**, *40*, 1. (c)N. Selander, K. J. Szabó, *Chem. Rev.* **2011**, *111*, 2048. (d)E. Peris, R. H. Crabtree, *Chem. Soc. Rev.* **2018**, *47*, 1959. (e)L. González-Sebastián, D. Morales-Morales, *J. Organomet. Chem.* **2019**, *893*, 39. (f)J.-K. Liu, J.-F. Gong, M. P. Song, *Org. Biomol. Chem.* **2019**, *17*, 6069. (g)V. Charra, P. de Frémont, P. Braunstein, *Coord. Chem. Rev.* **2017**, *341*, 53. (h)R. E. Andrew, L. González-Sebastián, A. B. Chaplin, *Dalton Trans.* **2016**, *45*, 1299. (i)J.-Q. Liu, X.-X. Gou, Y.-F. Han, *Chem. – Asian J.* **2018**, *13*, 2257. (j)C. Gunanathan, D. Milstein, *Chem. Rev.* **2014**, *114*, 12024. (k)H. A. Younus, N. Ahmad, W. Su, F. Verpoort, *Coord. Chem. Rev.* **2014**, *276*, 112. (l)K. Farrell, M. Albrecht, *Top. Organomet. Chem.* **2015**, *54*, 45. (m)H. Li, T. P. Gonçalves, D. Lupp, K.-W. Huang, *ACS Catal.* **2019**, *9*, 1619. (n)S. Zhao, J. Wu, W. Chen, *J. Organomet. Chem.* **2017**, *848*, 249.

[2] For relevant reviews, see:(a)D. V. Aleksanyan, V. A. Kozlov, *Top. Organomet. Chem.* **2015**, *54*, 209. (b)D. Yuan, H. V. Huynh, *Molecules* **2012**, *17*, 2491. Also see reference 1a, Chapter 20, I. Castillo, Transition Metal Complexes With Anionic Sulfur-Based Pincer Ligands

[3] For recent examples, see:(a)K. E. Rosenkoetter, M. K. Wojnar, B. J. Charette, J. W. Ziller, A. F. Heyduk, *Inorg. Chem.* **2018**, *57*, 9728. (b)M. R. Elsby, K. Ghostine, U. K. Das, B. M. Gabidullin, R. T. Baker, *Organometallics* **2019**, *38*, 3844. (c)A. Fiebor, R. Tia, B. C. E. Makhubela, H. H. Kinfe, *Beilstein J. Org. Chem.* **2018**, *14*, 1859. (d)S. Götz, R. Geitner, M. Abend, M. Siegmann, S. Zechel, J. Vitz, S. Gräfe, M. Schmitt, J. Popp, M. D. Hager, U. S. Schubert, *Macromol. Rapid Commun.* **2018**, *39*, 1800495. (e)J. Schörgenhumer, A. Zimmermann, M. Waser, *Org. Process Res. Dev.* **2018**, *22*, 862.

[4] For recent examples, see(a)D. V. Aleksanyan, S. G. Churusova, Z. S. Klemenkova, R. R. Aysin, E. Y. Rybalkina, Y. V. Nelyubina, O. I. Artyushin, A. S. Peregudov, V. A. Kozlov, *Organometallics* **2019**, *38*, 1062. (b)J. Monot, N. Merceron-Saffon, B. Martin-Vaca, *J. Organomet. Chem.* **2017**, *829*, 37.

[5] For recent examples, see:(a)R. Shi, M. D. Wodrich, H.-J. Pan, F. F. Tirani, X. Hu, *Angew. Chem. Int. Ed.* **2019**, *58*, 16869. (b) T. Xu, M. D. Wodrich, R. Scopelliti, C. Corminboeuf, X. Hu, *Pnas* **2017**, *114*, 1242. (c)M. Hosseini-Kharat, D. Zargarian, A. M. Alizadeh, K. Karami, M. Saeidifar, S. Khalighfard, L. Dubrulle, M. Zakariazadeh, J.-P. Cloutier, Z. Sohrabijam, *Dalton Trans.* **2018**, *47*, 16944.

[6] For a relevant review, seeM. Asay, D. Morales-Morales, *Dalton Trans.* **2015**, *44*, 17432. Also see reference 1a, Chapter 22, G. Roffe, S. Boonseng, H. Cox, J. Spencer, Unsymmetrical Pincer Palladacycles Synthesis and Reactivity

[7] For selected examples of non-symmetrical pincers, see(a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840. (b)M. Gargir, Y. Ben-David, G. Leitus, Y. Diskin-Posner, L. J. W. Shimon, D. Milstein, *Organometallics* **2012**, *31*, 6207. (c)J. Shi, B. Hu, D. Gong, S. Shang, G. Hou, D. Chen, *Dalton Trans.* **2016**, *45*, 4828.

[8] For recent examples, see(a)A. H. Mageed, B. W. Skelton, A. N. Sobolev, M. V. Baker, *Tetrahedron* **2018**, *74*, 2956. (b) M. Ruamps, S. Bastin, L. Rechignat, A. Sournia-Saquet, D. A. Valyaev, J.-M. Mouesca, N. Lugan, V. Maurel, V. César, *Chem. Commun.* **2018**, *54*, 7653. For recent and relevant reviews, see(c)A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**, *119*, 6994. (d)V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**, *118*, 9678.

[9] For recent reviews on NHCs, see:(a)H. V. Huynh, *Chem. Rev.* **2018**, *118*, 9457. (b)M.-M. Gan, J.-Q. Liu, L. Zhang, Y.-Y. Wang, F. E. Hahn, Y.-F. Han, *Chem. Rev.* **2018**, *118*, 9587. (c)Q. Zhao, G. Meng, S. P. Nolan, M. Szostak, *Chem. Rev.* **2020**, *120*, 1981. (d)E. Peris, *Chem. Rev.* **2018**, *118*, 9988. (e)J. Cheng, L. Wang, P. Wang, L. Deng, *Chem. Rev.* **2018**, *118*, 9930. (f) W. Wang, L. Cui, P. Sun, L. Shi, C. Yue, F. Li, *Chem. Rev.* **2018**, *118*, 9843. (g)S. Kuwata, F. E. Hahn, *Chem. Rev.* **2018**, *118*, 9642. (h)W. Zhao, V. Ferro, M. V. Baker, *Coord. Chem. Rev.* **2017**, *339*, 1.

[10] For recent reviews on mesoionic NHCs, see:(a)S. C. Sau, P. K. Hota, S. K. Mandal, M. Soleilhavoup, G. Bertrand, *Chem. Soc. Rev.* **2020**, *49*, 1233. (b)Á. Vivancos, C. Segarra,

M. Albrecht, *Chem. Rev.* **2018**, *118*, 9493.

[11] According to IUPAC gold book, "mesoionic compounds" is defined as "dipolar five- (possibly six-) membered heterocyclic compounds in which both the negative and the positive charge are delocalized, for which a totally covalent structure cannot be written, and which cannot be represented satisfactorily by any one polar structure. The formal positive charge is associated with the ring atoms, and the formal negative charge is associated with ring atoms or an exocyclic nitrogen or chalcogen atom".

[12] For selected examples, see:(a)A. Petronilho, H. Müller-Bunz, M. Albrecht, *Chem. Commun.* **2012**, *48*, 6499. (b)M. Navarro, M. Li, S. Bernhard, M. Albrecht, *Dalton Trans.* **2018**, *47*, 659. (c)M. Navarro, V. Rosar, T. Montini, B. Milani, M. Albrecht, *Organometallics* **2018**, *37*, 3619. (d)K. F. Donnelly, C. Segarra, L.-X. Shao, R. Suen, H. Muller-Bunz, M. Albrecht, *Organometallics* **2015**, *34*, 4076. (e)M. Navarro, C. A. Smith, M. Albrecht, *Inorg. Chem.* **2017**, *56*, 11688. (f)G. Kleinhans, G. Guisado-Barrios, D. C. Liles, G. Bertrand, D. I. Bezuidenhout, *Chem. Commun.* **2016**, *52*, 3504. (g)G. Kleinhans, M. M. Hansmann, G. Guisado-Barrios, D. C. Liles, G. Bertrand, D. I. Bezuidenhout, *J. Am. Chem. Soc.* **2016**, *138*, 15873.

[13] M. Begtrup, *Tetrahedron Lett.* **1971**, *12*, 1577.

[14] M. Vaddamanu, K. Velappanb, G. Prabusankar, *New J. Chem.* **2020**, *44*, 129.

[15] (a)K. J. Kilpin, U. S. D. Paul, A.-L. Lee, J. D. Crowley, *Chem. Commun.* **2011**, *47*, 328. (b)J. D. Crowley, P. H. Bandeen, L. R. Hanton, *Polyhedron* **2010**, *29*, 70. (c)X. Yan, H. Wang, S. Guo, *Angew. Chem. Int. Ed.* **2019**, *58*, 16907.

[16] (a)J. Bouffard, B. K. Keitz, R. Tonner, G. Guisado-Barrios, G. Frenking, R. H. Grubbs, G. Bertrand, *Organometallics* **2011**, *30*, 2617. (b)Z. Monasterio, A. Irastorza, J. I. Miranda, J. M. Aizpurua, *Org. Lett.* **2016**, *18*, 2511. (c)G. Guisado-Barrios, M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* **2018**, *51*, 3236. (d)G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 4759.

[17] (a)R. Faure, E.-J. Vincent, G. Assef, J. Kister, J. Metzger, *Org. Reson. Chem.* **1977**, *9*, 688. (b)R. S. Balestrero, D. M. Forkey, J. G. Russell, *Magn. Reson. Chem.* **1986**, *24*, 651. (c)H.-O. Kalinowski, H. Kessler, *Org. Reson. Chem.* **1974**, *6*, 305.

[18] L.-A. Schaper, K. Öfele, R. Kadyrov, B. Bechlars, M. Drees, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Chem. Commun.* **2012**, *48*, 3857.

[19] (a)O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 2939. (b)A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269. (c)K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* **2015**, *2015*, 2416.

[20] (a)D. M. Andrada, N. Holzmann, T. Hamadi, G. Frenking, *Beilstein J. Org. Chem.* **2015**, *11*, 2727. (b)L. J. Romeo, A. Kaur, D. J. D. Wilson, C. D. Martin, J. L. Dutton, *Inorg. Chem.* **2019**, *58*, 16500.

[21] (a)G. E. Tyson, K. Tokmic, C. S. Oian, D. Rabinovich, H. U. Valle, T. K. Hollis, J. T. Kelly, K. A. Cuellar, L. E. McNamara, N. I. Hammer, C. E. Webster, A. G. Oliver, M. Zhang, *Dalton Trans.* **2015**, *44*, 14475. (b)W.-G. Jia, L.-L. Gao, Z.-B. Wang, L.-Y. Sun, Y.-F. Han, *Organometallics* **2019**, *38*, 1946.

[22] For the database of typical bond lengths, please refer to the website: http://www.csb.yale.edu/userguides/datamanip/uppsala/manuals.20020128/typical_bonds.html The data is from the Handbook of Chemistry and Physics (63rd edition mostly, some from the 75th edition).

[23] For a relevant review, see:(a)F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079. For some more recent examples, see:(b)Y. Huang, X. Zhang, X.-Q. Dong, X. Zhang, *Adv. Synth. Catal.* **2020**, *362*, 782. (c)Y. Zheng, M. Liu, G. Qiu, W. Xie, J. Wu, *Tetrahedron* **2019**, *75*, 1663.

[24] (a)N. Á. Espinosa-Jalapa, D. Ke, N. Nebra, L. L. Goanvic, S. Mallet-Ladeira, J. Monot, B. Martin-Vaca, D. Bourissou, *ACS Catal.* **2014**, *4*, 3605. (b)N. Nebra, J. Monot, R. Shaw, B. Martin-Vaca, D. Bourissou, *ACS Catal.* **2013**, *3*, 2930. (c) D. Ke, N. Á. Espinosa-Jalapa, S. Mallet-Ladeira, J. Monot, B. Martin-Vaca, D. Bourissou, *Adv. Synth. Catal.* **2016**, *358*, 2324.

[25] (a)H.-Y. Liao, C.-H. Cheng, *J. Org. Chem.* **1995**, *60*, 3711. (b) C. Lambert, K. Utimoto, H. Nozaki, *Tetrahedron Lett.* **1984**, *25*, 5323.

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