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Mono- and dinuclear palladium(II) complexes incorporating 1,2,3-triazole-derived mesoionic carbenes: syntheses, solid-state structures and catalytic applications

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Abstract
Two 1,2,3-triazole-derived monocationic salts **3** and **4** bearing N-aryl wingtips were prepared using copper-catalyzed "click" reactions followed by alkylations with iodomethane. Employing a silver–carbene transfer method, two dinuclear palladium(II) complexes of triazolin-5-ylidenes (**5/6**) were obtained, the former of which has been reported previously. Bridge-cleavage reaction of **5** as a representative with PPh_3 yielded *cis*-configured mesoionic carbene/phosphine hybrid complex *cis*-**7** and homoleptic bis(phosphine) complex **8**, suggesting the presence of a ligand exchange process. In contrast, bridge breakages of **5/6** with pyridine cleanly afforded PEPPSI-type complexes **9** and **10** in near quantitative yields. Finally, all complexes were exploited to catalyze Mizoroki–Heck coupling reactions with aryl bromides as the substrates, and PEPPSI-type complex **9** was found to be the best performer generally giving good to excellent yields.

Introduction

Palladium chemistry of NHCs (NHCs = N-heterocyclic carbenes) has gained rapidly growing interest in the past decade, which has found manifold applications, especially in transition-metal-mediated catalysis.[1] Up to date, a large number of well-defined palladium(II) NHCs have been reported, and most of them bear imidazolin-2-ylidenes or benzimidazolin-2- ylidenes as the supporting ligands (**A**, Fig. 1). In this regard, *trans*- or *cis*-oriented heteroleptic complexes of the type **I** (Fig. 1) are quite promising motifs,[2] since they combine the structural and stereoelectronic features of NHCs and a second class of ancillary ligands L. For example, PEPPSI (PEPPSI = Pyridine-Enhanced Precatalyst Preparation Stabilization and Initiation) complexes, generally bearing NHCs and *trans*-standing pyridines, have exhibited remarkable catalytic performances in various organic transformations.[3]

In contrast to classical Arduengo-type[4] NHCs of the type **A**, MICs (MICs = mesoionic carbenes, **B–E**, Fig. 1), which require additional charges in all their canonical resonance structures and are thus also named as *abnormal* NHCs, have been much less investigated.[5] Generally, MICs are stronger donors compared to normal NHCs according to the Tolman's[6] and Huynh's [15][7] electronic parameters. In this context, 1,2,3-triazolin-5-ylidenes (**E**) have gained increasing attention in recent years due to the intriguing reactivities and remarkable catalytic behaviors of their transition-metal complexes.[8] In addition, 1,2,3-triazoles, which typically serve as the ligand precursors of **E**, can be regioselectively and facilely constructed through copper-catalyzed "click"

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[1] For selected reviews, see [1–10].

[2] For selected examples of the type **I** with imdazolin-2-ylidenes as the supporting ligands, see [11–13]. For selected examples of the type **I** with benzimdazolin-2-ylidenes as the supporting ligands, see [14, 15].

[3] For selected reviews on PEPPSI-type complexes, see [16, 17].

[4] See [18].

[5] For selected reviews on mesoionic carbenes, see [19–24].

[6] See [25–27].

[7] See [28].

[8] For the paper providing the first example of 1,2,3-triazolin-5-ylidene complex, see [29]. For selected reviews on 1,2,3-triazolin-5-ylidenes and their complexes, see [30, 31].

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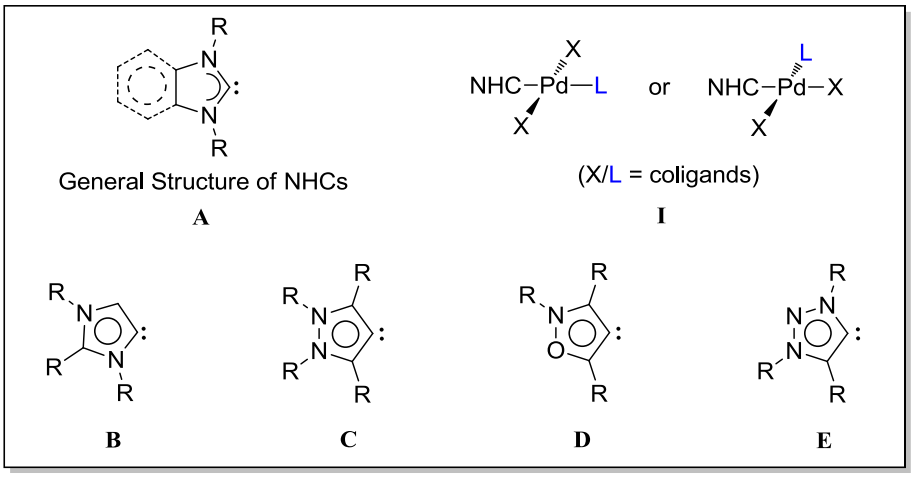
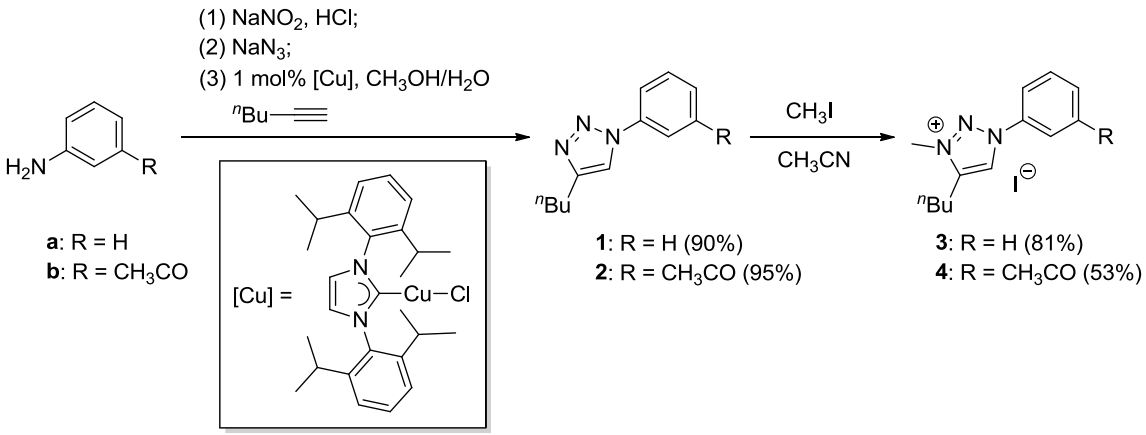


Fig. 1 General structure of NHCs (**A**), hybrid complexes of the type **I** and some hitherto known examples of mesoionic carbenes (**B**–**E**)



Scheme 1 Syntheses of triazole-based ligand precursors **3** and **4**

reactions.[9] Various substituents R can be incorporated rendering ligands of the type **E** electronically and sterically easily tunable.

Notably, previous studies predominantly focused on hybrid complexes **I** bearing normal NHCs (vide supra) [11–15]. In recent years, this type of motif has been further extended to 1,2,3-triazolin-5-ylidenes (**E**) by Albrecht and others,[10] and the structural diversities and reactivity studies of the corresponding complexes remain largely unexplored. As our contribution to this area and in line with our continuous interest in mesoionic carbene chemistry, herein we report the syntheses and reactivities of a series of new palladium(II) triazolin-5-ylidene complexes with phosphines/pyridines as ancillary ligands. In addition, comparative catalytic studies in Mizoroki–Heck coupling reactions were also carried out employing all newly synthesized palladium MICs as precatalysts.

Results and discussion

Carbene precursors

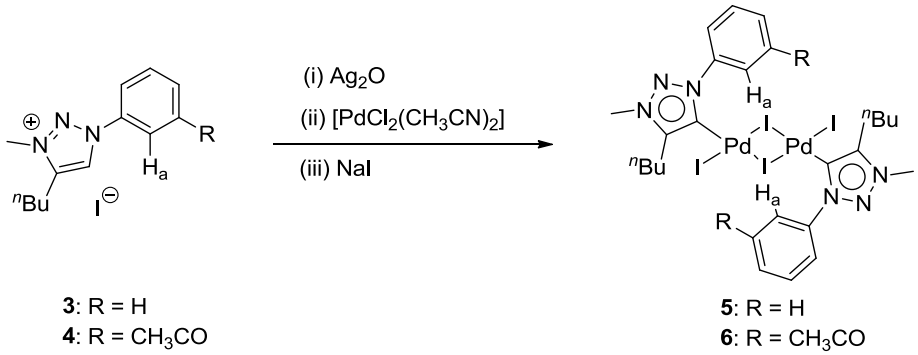
Monocationic triazole-derived salts **3** and **4**, which can serve as ligand precursors in the present work, were synthesized via a two-step procedure (Scheme 1).

In the first step, azidations of aromatic amines **a**/**b** followed by CuAACs (CuAACs = copper-catalyzed azide-alkyne cycloadditions) afforded the desired triazoles **1** and **2** in high yields of ≥ 90%. For this reaction, a copper(I)–NHC complex [CuCl(IPr)]

[9] For selected reviews on copper-catalyzed click reactions, see [32–34].

[10] For selected examples of hybrid complexes bearing MICs in analogy to **I**, see [35–39].

Scheme 2 Syntheses of dimeric complexes **5** and **6**



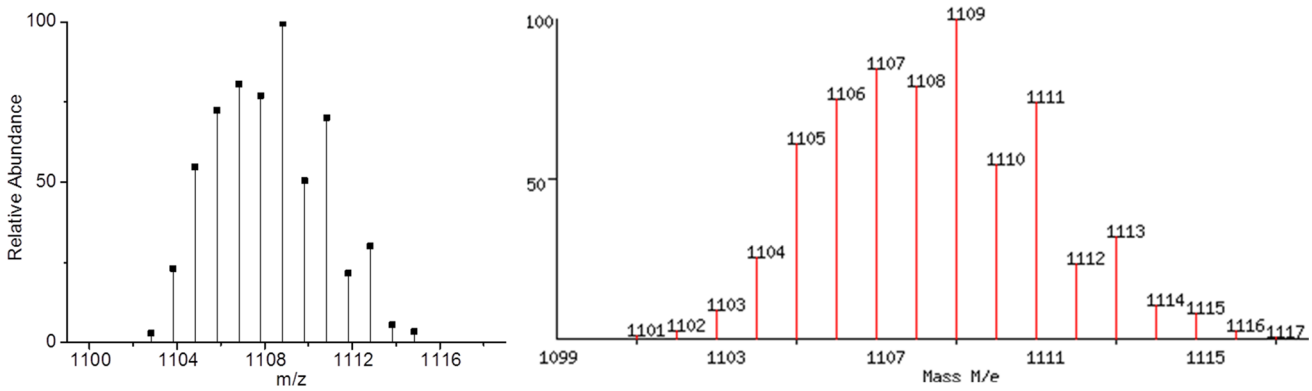


Fig. 2 Isotopic pattern of the $[\mathbf{6} - I]^+$ species in the positive ESI mass spectrometry (left) and simulated pattern (right)

(IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene)[11] was utilized instead of a copper(II) salts/reducing agent system, the latter of which was typically used for such "click" reactions [32–34]. Subsequent alkylations with iodomethane successfully produced triazolium salts **3** and **4** in good and moderate yields, respectively. Compounds **1** and **3** have been previously synthesized,[12] and acetyl-functionalized triazole **2** and its derivative **4** are reported for the first time. In the ^{1}H NMR spectrum of compound **4** in $CDCl_3$, the C–H proton of the triazole ring gives a characteristic signal at 9.67 ppm, which shows a significant downfield shift compared to that (*cf.* 7.97 ppm) for precursor **2**. A singlet at 2.66 ppm is observed which can be assigned to the methyl group of the acetyl moiety. The ESI mass spectrum of **4** shows the expected peak at *m/z* 258 corresponding to the monocationic species $[\mathbf{4} - I]^+$.

Dinuclear complexes of palladium(II)

By employing an Ag–carbene transfer protocol, two dinuclear palladium complexes **5** and **6** were successfully prepared (Scheme 2). It should be noted that the former has been reported by Albrecht et al. [43]. The newly synthesized complex **6** was fully characterized by ^{1}H, ^{13}C NMR spectroscopy, ESI mass spectrometry and elemental analysis.

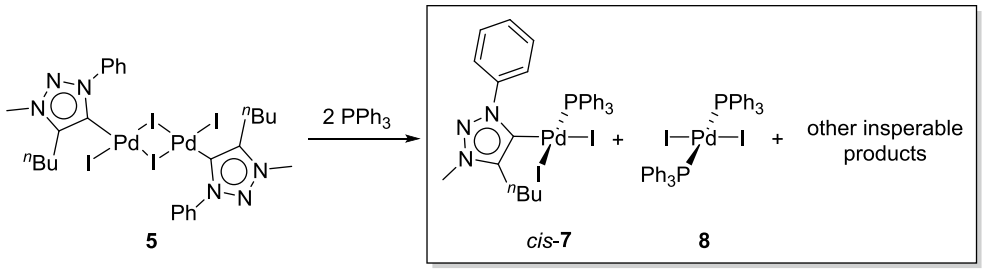
Positive-mode ESI mass spectrometric analysis of complex **6** provided the first evidence for its formation. In the mass spectrum, a base peak at *m/z* 1109 assigned to the monocationic fragment $[\mathbf{6} - I]^+$ was observed, which implies that the dinuclear structure can be retained in the gas phase surviving from bridge cleavages. The observed and simulated isotopic patterns are shown in Fig. 2.

In the ^{1}H NMR spectrum of **6**, the signal characteristic for the C–H proton of the triazole ring observed for precursor **4** is absent, which is indicative of successful palladation. The most downfield singlet[13] at 9.03 ppm can be assigned

[11] Complex [CuCl(IPr)] has been previously employed to catalyze azide-alkyne cycloaddition reactions. For selected papers and reviews, see [40–42].

[12] For earlier reports on the syntheses and characterizations of triazole **1** and salt **3**, see [43–45].

[13] The aryl C–H_a proton expectedly give a doublet with a small coupling constant of ~ 2–3 Hz, due to (i) the absence of protons attached to the C_{ortho} atoms and (ii) the splitting by C–H protons of the C_{meta} atoms. In our case, a singlet was observed probably due to the low resolution of NMR spectrometer.



Scheme 3 Attempt to synthesize a MIC/phosphine hybrid complex of palladium(II)

to the aryl C–H_a proton (Scheme 2). Interestingly, this resonance shows a significant downfield shift ($\Delta\delta_H = 0.53$ ppm) compared to that (*cf.* 8.50 ppm) for precursor **4**. This spectroscopic feature may indicate a C–H_a···Pd anagostic interaction, which is known to be evidenced by a downfield shift of C–H protons upon ligand coordination.[14] A similar interaction was also observed in the pyridine-ligated derivative of complex **6**, which was additionally characterized by X-ray diffraction analysis (vide infra). In the ^{13}C NMR spectrum of **6**, the carbonyl carbon atom of **6** gives a characteristic singlet at 196.8 ppm, and the $^{13}C_{carbene}$ signal was not detected.

Bridge-cleavage reactions with phosphines

Halido-bridged dimeric complexes **5/6** can be employed as potential precursors to yield triazolin-5-ylidene hybrid complexes of the type **I** (vide supra) upon bridge cleavage by incoming donors. Phosphines are ubiquitous ancillary ligands in organometallic chemistry and palladium-mediated catalysis. Hence, dinuclear complex **5** was chosen as a representative and treated with two equivalents of PPh_3 in aiming to prepare a MIC/phosphine mixed complex as an initial attempt (Scheme 3).

Slow evaporation from a solution of the crude product in a mixture of CH_2Cl_2 and *n*-hexane gives two sorts of X-ray quality single crystals, which were both structurally characterized, and proved to be a heteroleptic complex *cis*-**7** and homoleptic bis (phosphine) complex **8**. The molecular structure of *cis*-**7** and its intermolecular stacking are depicted in Fig. 3. Selected important crystallographic data are summarized in Table 1. The crystal data of **8** were previously reported[15] and thus not discussed herein.

As expected, the complex adopts an essentially square-planar geometry. The triazole-derived MIC ligand is *cis* to the phosphine donor, which is expected owing to the strong *transphobia effect*[16] induced by the electron-releasing carbene ligand. Similar orientations have been also observed for some analogue complexes of the type [PdX_2(tazy)(PR_3)] (X = halido ligand, tazy = triazolin-5-ylidene) [38].[17] The Pd1–I2 bond distance amounting to 2.6488(4) Å is found to be shorter than that (2.6699(4) Å) of the Pd1–I1 bond, although the former is excepted to be longer due to a stronger structural *trans* effect of carbene versus phosphine ligands [25–28]. The triazole ring is almost perpendicular to the [PdI_2CP] coordination plane with a dihedral angle of ca. 79°. The Pd–$C_{carbene}$ bond length of 2.000(4) Å is found to be comparable to that observed in the parent complex **5** [35]. In addition, as shown in the figure (the lower one), two molecules of complex *cis*-**7** are found to aggregate through a π–π interaction of N1-phenyl groups. The two participating phenyl rings are found to be parallel as clearly indicated by a dihedral angle of 0°. The centroid–centroid separation measured as 3.619 Å falls in the range typically observed for those molecules featuring π–π stackings.[18]

The formation of bis(phosphine) complex **8** is probably due to the ligand redistribution of *cis*-**7**. Similar processes have been observed for palladium(II) NHC/phosphine hybrid complexes reported by Hermann et al.[19] Several attempts to isolate analytically pure compound *cis*-**7** were to no avail.

Bridge-cleavage reactions with pyridines

When pyridine was utilized as an electron donor to break the iodido bridges, the reactions proceeded smoothly and cleanly with formation of the PEPPSI-type complexes **9** and **10** in near quantitative yields (Scheme 4). Compounds **9/10** were isolated as red brownish powders, which are fairly stable and readily soluble in common polar organic solvents such as chlorinated solvents and DMSO. Finally,

[14] For a review on agostic and anagostic interactions, see [46].

[15] For selected publications reporting the crystal data of *trans*-[$PdI_2(PPh_3)_2$], see [47, 48].

[16] The term "*transphobia effect*" was first coined by Vicente and Jones's groups. For this paper, see [49].

[17] For selected examples, see [50, 51].

[18] For a paper on the definition of π–π stacking, see [52].

[19] See [53].

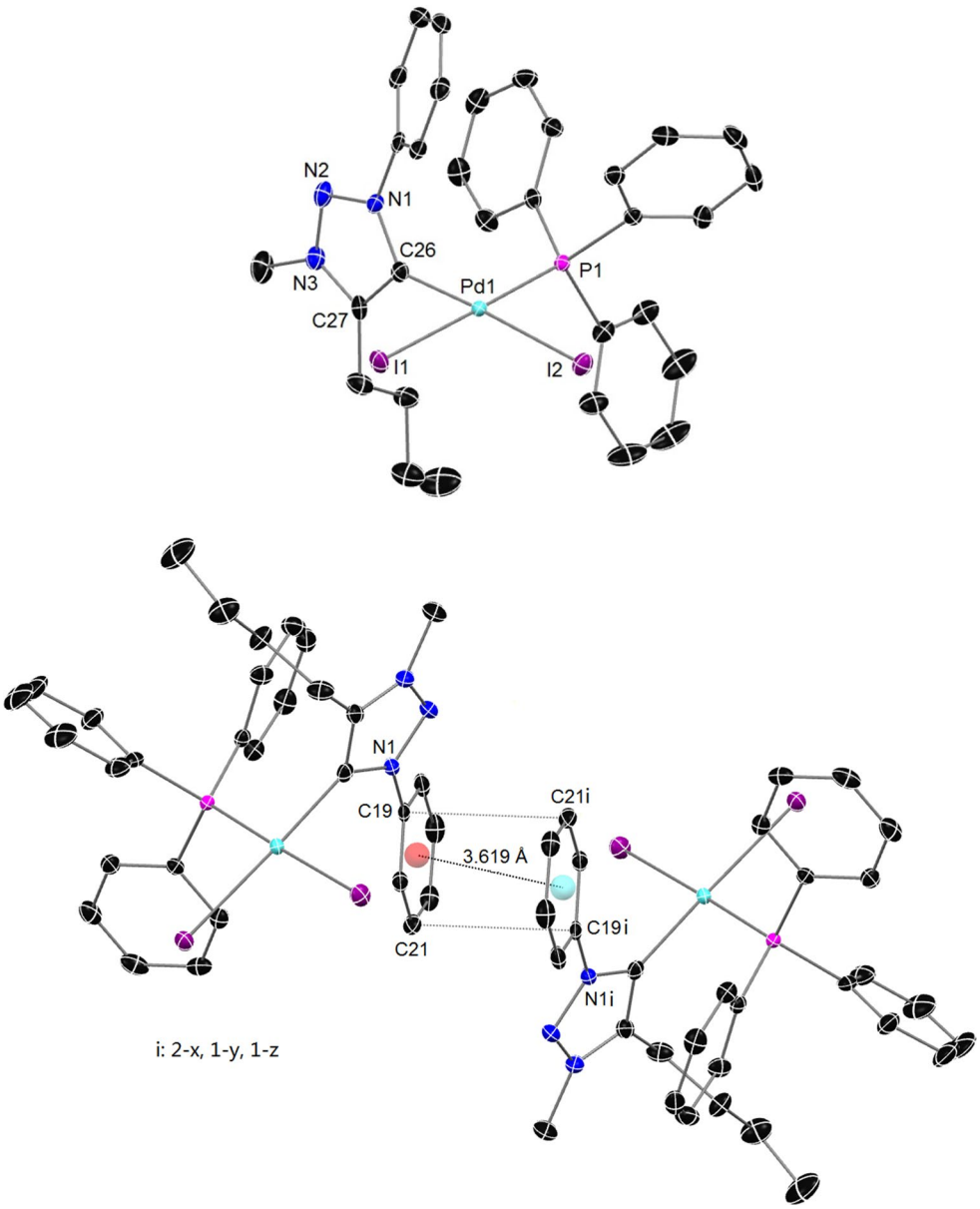


Fig. 3 Molecular structure and stacked packing (symmetry operator: 2 – x, 1 – y, 1 – z) of *cis*-**7** showing 50% probability ellipsoids. Hydrogen atoms, solvent molecules and the disordered atoms are omitted for clarity. Selected bond (Å) and angles (deg): Pd1–I1 2.6699(4), Pd1–I2 2.6488(4), Pd1–P1 2.2789(10), Pd1–C26 2.000(4); I2–Pd1–I1 92.633(14), P1–Pd1–I1 178.57(3), P1–Pd1–I2 88.73(3), C26–Pd1–I1 86.80(11), C26–Pd1–I2 176.96(11), C26–Pd1–P1 91.82(11)

in contrast to phosphine/MIC mixed complex *cis*-**7**, no ligand redistribution product was found for the PEPPSI-type complexes.

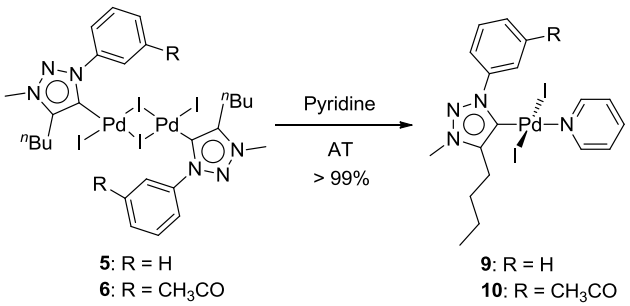
The ^{1}H NMR spectra of complexes **9/10** essentially resemble those of **5/6** except for the presence of the signals from pyridine moieties. The aryl C–H_a proton of **10** (vide supra) gives a triplet at 9.21 ppm with an expected coupling constant of ~ 2 Hz. Again, this resonance shows a marked downfield shift compared to that (*cf.* 8.50 ppm) observed for the ligand precursor **4**, which is also likely owing to a C–H_a···Pd anagostic interaction. Additional evidences can be provided by the bond parameters obtained by X-ray diffraction analysis of complex **10** (vide infra). The $^{13}C_{carbene}$ signals were not observed despite overnight accumulation of the ^{13}C NMR signals.

The formations of **9** and **10** were further verified by their positive ESI mass spectra. In the gas phase, losses of pyridine as well as iodido ligands and further captures of CH_3CN molecules from the solvents were observed giving rise to the monocationic species $[M - Pyr - I + CH_3CN]^+$, as indicated by the dominant peaks at *m/z* 488 (for **9**) and 531 (for **10**).

The single crystals of complex **10** were grown via slow evaporation of a saturated solution in CH_2Cl_2. The molecular structure and its intermolecular stacking are depicted in Fig. 4, and selected important crystallographic data are summarized in Table 1. The palladium metal center is coordinated by a triazolin-5-ylidene donor, a *trans*-standing pyridine and two anionic iodido co-ligands. The Pd–C and Pd–N bond lengths are comparable to those observed for

Table 1 Selected X-ray crystallographic data for compounds *cis*-**7** and **10**

Comp.	*cis*-**7**	**10**
Formula	$C_{33}H_{36}Cl_4I_2N_3PPd$	$C_{20}H_{24}I_2N_4OPd$
Formula weight	1007.62	696.63
Color, habit	Yellow, block	Orange, block
Crystal size (mm)	0.43×0.40×0.18	0.15×0.1×0.05
Temperature (K)	105.3	100.00 (10)
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	10.3150 (7)	8.0922 (4)
b (Å)	10.9619 (7)	10.0607 (7)
c (Å)	18.5705 (7)	15.2554 (10)
α (°)	86.879 (4)	73.695 (6)
β (°)	84.429 (4)	86.100 (5)
γ (°)	62.426 (7)	82.258 (5)
V (Å^3)	1852.41 (18)	1180.58 (13)
Z	2	2
D_c (g·cm^{-3})	1.807	1.960
Radiation used	Mo-Kα (λ = 0.7107)	Cu-Kα (λ = 1.54184)
μ (mm^{-1})	2.527	27.005
θ range (°)	6.12−52	4.613−73.343
Reflections collected	7275	8020
Final R indices (I > 2σ(I))	R_1 = 0.0337, wR_2 = 0.0692	R_1 = 0.0445, wR_2 = 0.1153
R indices (all data)	R_1 = 0.0363, wR_2 = 0.0705	R_1 = 0.0477, wR_2 = 0.1204
goodness of fit on F^2	1.142	1.059
Peak/hole (e·Å^{-3})	1.742/− 1.791	1.48/− 2.38



Scheme 4 Syntheses of PEPPSI-type complexes **9/10**

earlier reported analogues [35–37, 39]. The C6–N2–C7–C8 torsion angle measured as ca. 21° indicates that the N–aryl ring is far from perpendicular to the carbene backbone. This is interesting since such twisting is expected to enhance the steric repulsion between the N-aryl moiety and the [PdI$_2$CN] coordination plane. The C–H···Pd angle and Pd1···H8 distance amounting to ca. 129° and ca. 2.58 Å, respectively, fall in the range of structural parameters characteristic for anagostic interactions [46]. The molecules are found to dimerize in the solid state through a π–π interaction [52] of two essentially parallel pyridine rings, and the centroid–centroid separation is measured as 3.651 Å.

Catalytic studies

All isolated mesoionic carbene complexes reported herein were employed as catalyst precursors to catalyze Mizoroki–Heck couplings, and the results are summarized in Table 2. In a model reaction, 4-bromobenzaldehyde and tert-butyl acrylate were chosen as the substrates, and 1 mol % of mononuclear palladium complex (or 0.5 mol % of dinuclear palladium complex) was employed as the precatalyst. All complexes (**5**, **6**, **9** and **10**) proved to be catalytically active in this cross-coupling reaction, giving good to excellent yields. Complexes **6** and **10** are found to be inferior performers compared to their counterparts **5** and **9** (entries 1/3 vs. entries 2/4), highlighting the influence of N-wingtips in the MIC supporting ligands. Thus, the catalytic behaviors of complexes **5** and **9** were further compared. When a less activated aryl halide (4′-bromoacetophenone) was used as the substrate, sharp decreases in yields were observed (entries 5–6). The yields were significantly improved when TBAB (TBAB = tetra-*n*-butylammonium bromide) was utilized as an additive (entries 7–8). Finally, with complex **9** as the precatalyst, a decent yield was obtained even when a deactivated aryl bromide was employed (entry 9).

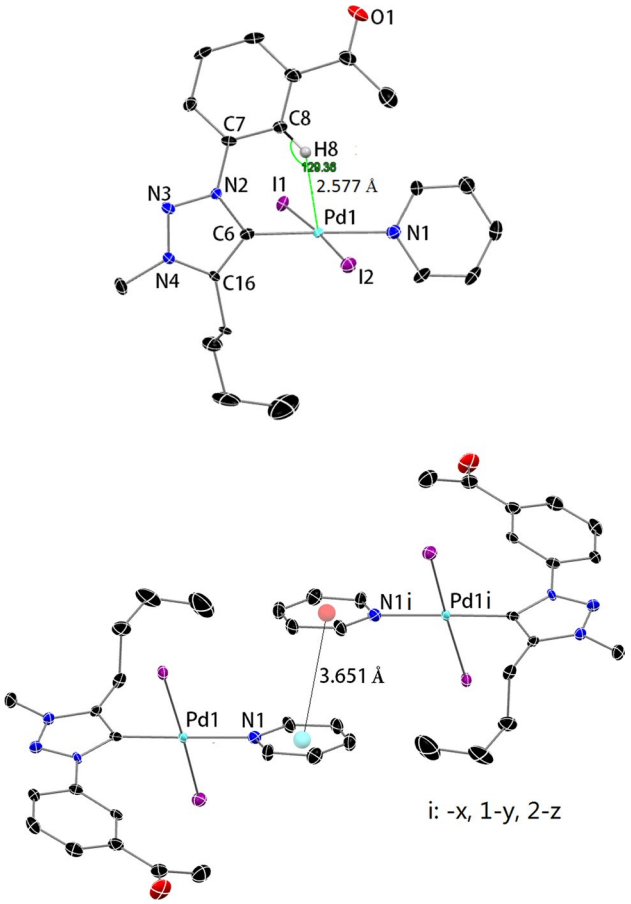


Fig. 4 Molecular structure and stacked packing (symmetry operator: −x, 1−y, 2−z) of complex **10** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond (Å) and angles (deg): Pd1–I1 2.6016(4), Pd1–I2 2.6007(4), Pd1–C6 1.969(5), Pd1–N1 2.091(4); C6–Pd1–I1 88.35(14), C6–Pd1–I2 88.57(14),N1–Pd1–I1 91.76(12), N1–Pd1–I2 91.28(12); C6–Pd1–N1 178.94(17), I1–Pd1–I2 176.294(16)

Conclusion

In summary, we have reported a series of new heteroleptic palladium(II) complexes bearing 1,2,3-triazole-based mesoionic carbenes and phosphine/pyridine ancillary ligands. These complexes can be conveniently accessed via bridge-cleavage reactions with dimeric triazolin-5-ylidene complexes as precursors. In the case of phosphine/MIC mixed complex *cis*-**7**, a ligand redistribution process occurred leading to the formation of homoleptic bis(phosphine) complex **8**. For *cis*-**7** and PEPPSI-type complex **10**, the solid-state structures were determined revealing π–π interactions in both cases. Finally, in a preliminary catalytic study, a remarkable influence of N-wingtips of carbenes on catalytic performance was observed.

This report provides additional examples of heteroleptic palladium complexes bearing less studied mesoionic carbenes. The reactivities, ligand redistributions, and catalytic behaviors unraveled herein have obvious implications for the syntheses and applications of triazolin-5-ylidene complexes as well as related MIC motifs. Further expansion of complex scope and detailed elucidations of ligand effect on catalytic behaviors are currently under way in our laboratory.

Experimental section

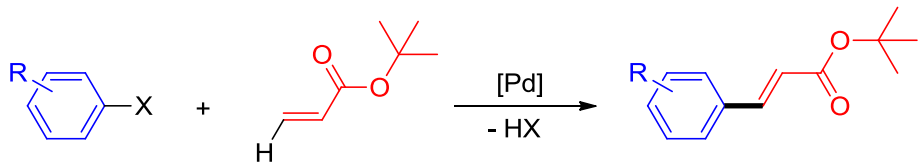
General considerations

All the manipulations were carried out without taking precautions to exclude air and moisture. All chemicals were used as received without further purification if not mentioned otherwise. All reagents (AR) were purchased from Alfa Aesar Chemical Co. Ltd., Adamas Reagent Co. Ltd. and Accela ChemBio Co. Ltd. Solvents (AR) were purchased from Beijing Chemical Works. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 600 MHz spectrometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to $(CH_3)_4Si$ (^{1}H,^{13}C). ESI mass spectra were measured using an Agilent 6540 Q-TOF mass spectrometer. X-ray single-crystal diffraction studies were done using a SuperNova, Dual, Cu at zero and AtlasS2 diffractometer. Elemental analyses were obtained on a vario EL analyzer of Elementar Analysensysteme GmbH at the Analytical Instrumentation Center of Peking University.

Synthesis of compound 2

A 100-mL round-bottom flask was charged with a hydrochloric acid solution (3.2 mL, 6 M), and 3-aminoacetophenone (676 mg, 5 mmol) was added. This mixture was cooled to 0 °C with an ice bath, and a solution of $NaNO_2$ (350 mg, 5.13 mmol) in H_2O (1.8 mL) was added. The reaction mixture was stirred for 10 min, and a solution of NaN_3 (330 mg, 5.1 mmol) in H_2O (1.8 mL) was added dropwise. The ice bath was removed, and the reaction mixture was stirred at ambient temperature for 2 h. Diethyl ether (10 mL × 3) was added, and the organic phase was dried *in vacuo* affording the azide intermediate as a dark brown liquid. To the flask charged with organic azide, 1-hexyne (555 μL, 5 mmol), complex [CuCl(IPr)] as the precatalyst (25 mg, 0.05 mmol), MeOH (2 mL) and H_2O (1 mL) were successively added. The reaction mixture was stirred and heated at 60 °C for 24 h. After cooling down to ambient temperature, the resulting precipitate was collected and dried *in vacuo* affording the product as a dark brown liquid **2** (1.024 g, 3.2 mmol, 95%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (s, 1H, Ar–H), 7.77 (s, 1H, Ar–H), 7.68–7.62 (m, 2H, Ar–H), 7.27–7.25 (m, Ar–H, 1H), 2.45 (br s, 2H, $CH_2CH_2CH_2CH_3$),

Table 2 Mizoroki–Heck reactions catalyzed by palladium complexes **5**, **6**, **9** and **10**



Entry	Aryl Halide	Precatalyst	Additive	Yield (%)[a]
1	4-bromobenzaldehyde	**5**	–	> 99
2	4-bromobenzaldehyde	**6**	–	72
3	4-bromobenzaldehyde	**9**	–	> 99
4	4-bromobenzaldehyde	**10**	–	58
5	4′-bromoacetophenone	**5**	–	26
6	4′-bromoacetophenone	**9**	–	17
7[b]	4′-bromoacetophenone	**5**	TBAB	87
8[b]	4′-bromoacetophenone	**9**	TBAB	> 99
9[b]	4-bromoanisole	**9**	TBAB	78

Reaction conditions generally not optimized. Reaction conditions: 1.0 mmol aryl halide, 1.5 mmol of tert-butyl acrylate, 1 mol % of mononuclear palladium complex (or 0.5 mol % of dinuclear palladium complex), 1.5 mmol of NaOAc, DMF (3 mL), 24 h, 120 °C

[a]Yields were determined by ^{1}H NMR spectroscopy. [b]With addition of 0.2 equiv. of TBAB

2.31 (s, 3H, $COCH_3$), 1.38 (t, 2H, $CH_2C\underline{H}_2CH_2CH_3$, $^{3}J_{H,H}=6$ Hz), 1.09–1.08 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.60 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^{3}J_{H,H}=6$ Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.6 (CO), 149.3, 138.3, 137.5, 130.1, 130.0, 127.9, 124.2, 119.3 (Ar–C), 31.4 ($\underline{C}H_2CH_2CH_2CH_3$), 26.6 ($CO\underline{C}H_3$), 25.3 ($CH_2\underline{C}H_2CH_2CH_3$), 22.2 ($CH_2CH_2\underline{C}H_2CH_3$), 13.8 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI): *m/z* 244 $[M+H]^+$.

Synthesis of compound 4

A 25-mL Schlenk tube was charged with compound **2** (932.2 mmol, 3.8 mmol), CH_3I (38 mmol, 2.4 mL) and CH_3CN (1 mL). The reaction mixture was stirred and heated at 90 °C for 3 d. After cooling down to ambient temperature, all the volatiles were removed *in vacuo*. The residue was washed with diethyl ether (20 mL × 3) and dried *in vacuo* affording the product as a yellow powder (777.4 mg, 2 mmol, 53%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.67 (s, 1H, Ar–H), 8.50 (s, 1H, Ar–H), 8.28 (d, 1H, Ar–H, $^{3}J_{H,H}=8$ Hz), 8.07 (d, 1H, Ar–H, $^{3}J_{H,H}=8$ Hz), 7.66 (t, 1H, Ar–H, $^{3}J_{H,H}=8$ Hz), 4.40 (s, 3H, N–CH_3), 2.98 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$, $^{3}J_{H,H}=8$ Hz), 2.66 (s, 3H, $COCH_3$), 1.83 (t, 2H, $CH_2C\underline{H}_2CH_2CH_3$, $^{3}J_{H,H}=7$ Hz), 1.43–1.39 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.88 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^{3}J_{H,H}=7$ Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.8 (CO), 146.7, 139.1, 135.5, 131.6, 131.4, 128.4, 126.4, 121.8 (Ar–C), 40.1 (N–CH_3), 29.5 ($\underline{C}H_2CH_2CH_2CH_3$), 28.2 ($CO\underline{C}H_3$), 24.4 ($CH_2\underline{C}H_2CH_2CH_3$), 22.7 ($CH_2CH_2\underline{C}H_2CH_3$), 14.1 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI): *m/z* 258 $[M-I]^+$.

Synthesis of complex 6

A round-bottom flask was charged with salt **4** (462 mg, 1.2 mmol), Ag_2O (139 mg, 0.6 mmol) and CH_2Cl_2 (10 mL). The reaction mixture was stirred in the dark at ambient temperature for 24 h. A solution of $[PdCl_2(CH_3CN)_2]$ (212.6 mg, 1.2 mmol), which was prepared by heating $PdCl_2$ (212 mg, 1.2 mmol) in CH_3CN (5 mL) at 80 °C, was added. The reaction mixture was stirred for 16 h, and a solution of NaI (1079.2 mg, 7.2 mmol) in acetone was added. The resulting suspension was stirred for another 4 h. All the volatiles were removed *in vacuo*. The crude product was extracted with CH_2Cl_2 (10 mL × 3), and purified using column chromatography (SiO_2, CH_2Cl_2) affording the product as a brown red powder (278 mg, 0.22 mmol, 37%). ^{1}H NMR (600 MHz, d^6–DMSO): δ 9.03 (s, 2H, Ar–H), 8.38 (d, 2H, Ar–H, $^{3}J_{H,H}=7.8$ Hz), 8.16 (d, 2H, Ar–H, $^{3}J_{H,H}=7.2$ Hz), 7.83 (t, 2H, Ar–H, $^{3}J_{H,H}=7.8$ Hz), 4.21 (s, 6H, N–CH_3), 2.99 (t, 4H, $C\underline{H}_2CH_2CH_2CH_3$, $^{3}J_{H,H}=7.8$ Hz), 2.68 (s, 6H, $COCH_3$), 1.94 (t, 4H, $CH_2C\underline{H}_2CH_2CH_3$, $^{3}J_{H,H}=7.5$ Hz), 1.45–1.42 (m, 4H, $CH_2CH_2C\underline{H}_2CH_3$), 0.97 (t, 6H, $CH_2CH_2CH_2C\underline{H}_3$, $^{3}J_{H,H}=7.2$ Hz). ^{13}C NMR (150 MHz, d^6–DMSO): δ 196.8 (CO), 144.5, 139.3, 137.1, 129.8, 129.5, 128.3, 123.8 (Ar–C), 37.2 (N–CH_3), 29.0 ($\underline{C}H_2CH_2CH_2CH_3$), 27.1 ($CO\underline{C}H_3$), 24.7 ($CH_2\underline{C}H_2CH_2CH_3$), 21.9 ($CH_2CH_2\underline{C}H_2CH_3$), 13.6 ($CH_2CH_2CH_2\underline{C}H_3$). The $^{13}C_{carbene}$ signal was not observed. MS (ESI): *m/z* 1109 $[M-I]^+$. Anal. Calcd. for $C_{30}H_{38}I_4N_6O_2Pd_2$: C, 29.17; H, 3.10; N, 6.80%; Found: C, 29.83; H, 3.57; N, 6.65%.

Synthesis of complex 9

Pyridine (22 µL, 0.25 mmol) was added to a stirred solution of **5** (135.4 mg, 0.1 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at ambient temperature for 5 min. All the volatiles were removed *in vacuo*, and then the resulting mixture was washed with diethyl ether (10 mL). The residue was dried under vacuum to afford the product as a brown powder in a near quantitative yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.91 (d, 2H, Ar–H, $^3J_{H,H}$ = 6 Hz), 8.36 (d, 2H, Ar–H, $^3J_{H,H}$ = 6 Hz), 7.67 (t, 1H, Ar–H, $^3J_{H,H}$ = 6 Hz), 7.62–7.59 (m, 2H, Ar–H), 7.56–7.53 (m, 1H, Ar–H), 7.27–7.24 (m, 2H, Ar–H), 4.06 (s, 3H, NCH_3), 3.11 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$, $^3J_{H,H}$ = 12 Hz), 2.12–2.09 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.59–1.55 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 1.08 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 154.5, 145.4, 140.5, 138.0, 133.8, 130.6, 129.5, 126.1, 125.5, 125.0 (Ar–C), 37.3 ($N\underline{C}H_3$), 30.6 ($\underline{C}H_2CH_2CH_2CH_3$), 26.6 ($CH_2\underline{C}H_2CH_2CH_3$), 23.4 ($CH_2CH_2\underline{C}H_2CH_3$), 14.5 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI): *m/z* 488 $[M - I - Pyr + CH_3CN]^+$. Anal. Calcd. for $C_{18}H_{22}I_2N_4Pd$: C, 33.03%, H, 3.39%, N, 8.56%; Found: C, 33.46%, H, 3.68%, N, 8.28%.

Synthesis of complex 10

This compound was synthesized by an analogous method to complex **9**. Red powder, near quantitative yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.21 (t, 1H, Ar–H, $^3J_{H,H}$ = 1.8 Hz), 8.90–8.89 (m, 2H, Pyr–H), 8.49–8.47 (m, 1H, Ar–H), 8.14–8.12 (m, 1H, Ar–H), 7.70–7.65 (m, 2H, Ar–H and Pyr–H), 7.27–7.24 (m, 2H, Pyr–H), 4.07 (s, 3H, N–CH_3), 3.11 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$, $^3J_{H,H}$ = 8 Hz), 2.71 (s, 3H, $COCH_3$), 2.14–2.07 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.58–1.52 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 1.06 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.6 (CO), 154.4 (Pyr–C), 145.7, 140.7, 138.09, 138.06, 134.7, 129.9, 129.8, 126.2, 125.0 (Ar–C), 37.4 (N–CH_3), 30.5 ($\underline{C}H_2CH_2CH_2CH_3$), 27.9 ($CO\underline{C}H_3$), 26.5 ($CH_2\underline{C}H_2CH_2CH_3$), 23.3 ($CH_2CH_2\underline{C}H_2CH_3$), 14.4 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI): *m/z* 531 $[M - I - Pyr + CH_3CN]^+$. Anal. Calcd. for $C_{20}H_{24}I_2N_4OPd$: C, 34.48; H, 3.47; N, 8.04%; Found: C, 34.52; H, 3.43; N, 7.90%.

General procedure for Heck couplings

In a typical run, a 25-mL Schlenk tube was charged with a mixture of aryl halide (1 mmol), sodium acetate (1.5 mmol), tert-butyl acrylate (1.5 mmol), precatalyst (0.01 mmol for mononuclear complex or 0.005 mmol for dinuclear complex) and DMF (3 mL). The reaction mixture was stirred for 24 h at 120 °C. Dichloromethane (5 mL) and deionized water (10 mL) were added, and the aqueous phase was then washed with dichloromethane (3 × 3 mL). All the organic phase was collected and dried over Na_2SO_4. The solvent was removed under vacuum to give a crude product, which was analyzed by ^{1}H NMR spectroscopy.

X-ray diffraction studies

For complex *cis*-**7**, the data were collected on an Agilent Xcalibur Eos Gemini diffractometer using Mo-Kα radiation. For complex **10**, the data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Cu-Kα radiation. Structural solution was carried out with the Olex2 program.[20] All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table 1. CCDC 1555284 and 1847545 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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