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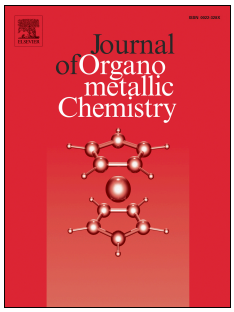

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Synthesis of a new class of cationic Pd(II) complexes with 1,2,3-triazol-5-ylidene ligand and their catalytic application in the conversion of internal alkynes to 1,2-diketones

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Abstract

A new class of cationicPd(II) complexes of the type $[Pd(Tz)(Cl)(bipy)]^{+}Cl^{-}$ and $[Pd(Tz)(Cl)(phen)]^{+}Cl^{-}$ (Tz = 1,4-diaryl-3-methyl-1,2,3-triazol-5-ylidene , bipy = 2,2'-bipyridine and phen = 1,10-phenanthroline) with various wing tip groups were synthesized from the corresponding 1,2,3-triazolium iodide via the corresponding chloro bridged dinuclear complexes $[(Tz)(Cl)Pd(\mu\text{-}Cl)_2Pd(Cl)(Tz)]$. The synthesized cationic complexes were screened for their catalytic activity of hydration of alkynes and found to be excellent towards the selective conversion of internal alkynes to the corresponding 1,2-diketones in good yields. A plausible mechanism was proposed for this conversion.

Keywords

Alkyne, cationic Pd complex,1,2-diketone,hydration,NHC-Pd complex,1,2,3-triazol-5-ylidene,

1. Introduction

N-Heterocyclic carbenes (NHCs) have gained exclusive, rapid popularity and emerged as versatile ligands for a wide variety of metal complexes.[1] The success achieved by NHCs is because of their strong *σ*-electron donating capacity which will allow them to form strong NHC-metal bonds. Due to their stability to air, moisture and strong σ-donor but poor π-acceptor abilities NHCs have been receiving a great amount of attention and becoming a very important

class of ligands in transition metal catalysis.[2] Over past few years 1,2,3-triazol-5-ylidenes have attracted many research groups and emerged as promising ligands for transition metal chemistry, these ligands are often referred as abnormal (*a*NHCs) or mesoioniccarbenes (MICs) due to the fact that their structures can only be represented as zwitter ions and not in the neutral canonical form.[3] Albrecht first reported the synthesis and structural characterization of 1,2,3-triazol-5-ylidene-metal (Pd, Rh and Ir) complexes.[3a] The first example of chiral and chelate type palladium-1,2,3-triazol-5-ylidene complexes and their catalytic activity in Suzuki-Miyaura coupling was reported by our group.[3b]

π-Complexes of palladium (II) are widely used in organic transformations.[4] Coordination of Pd (II) to π bond increases the reactivity of the π-bond towards nucelophilic attack.[5] In this regard cationic palladium complexes are catalytically more reactive than their neutral counter parts.[6] They have been primarily used in the catalytic activation of alkenes and alkynes towards addition of nucelophiles.[7] Catalysis of copolymerization of olefins and carbon monoxide,[8] hetero Diels-Alder reaction[9] and telomerization of butadiene[10] are few of the reactions catalyzed by cationic palladium (II) complexes. Cationic palladium (II) complexes bearing *N*-heterocyclic carbene (NHC) ligands have been reported in the literature,[10b,11] especially imidazol-2-ylidene based complexes are common.[10b,11c-j,11l,11m] In addition to imidazole-2-ylidene ligands these complexes contained a variety of other ligands that include phosphanes,[11f,11j,11m] allyl, thiolate,[10b,11b] 2,2'-bipyridine,[11b] quinolone[11k] and pyridine.[11d,11f-g] Cationic palladium (II) complexes containing chelating bis-imidazol-2-ylidene ligands were also reported.[11c-d, 11h-i] Cationic palladium complexes of 1,2,3-triazol-5-ylidene ligands are less explored in comparison to the cationic complexes of imidazole-2-ylidene ligands. The first example of cationic Pd(II) and Pt(II) complexes of 1,2,3-triazol-5-

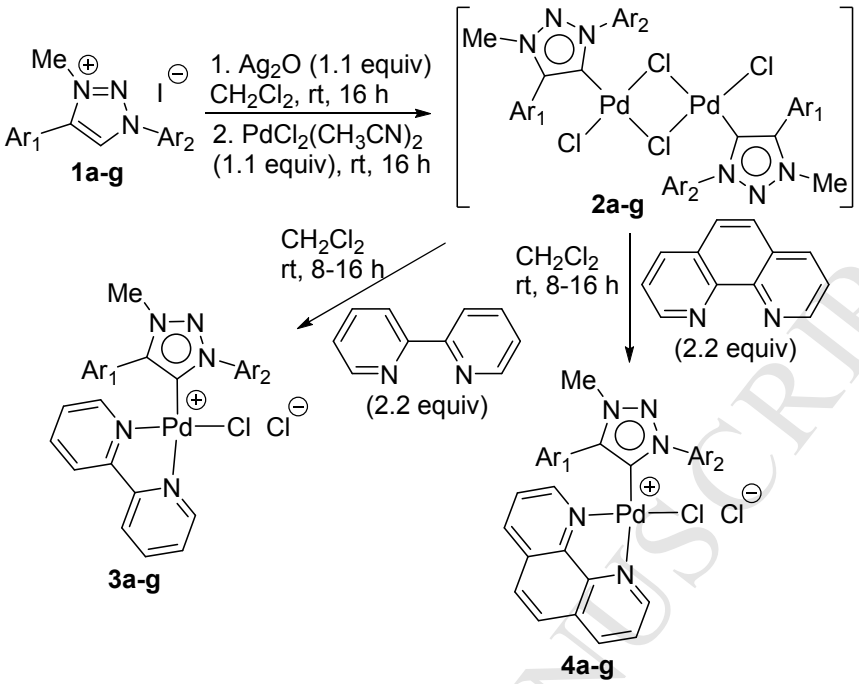
ylidene ligands has been reported by Gandelman.[12] An unconventional approach involving post-synthesis modification of Pd(II) and Pt(II) complexes containing PCP-pincer ligands was used as the methodology for the synthesis of cationic Pd and Pt complexes. Conventional synthesis of chiral cationic 1,2,3-triazol-5-ylidene-Pd complex from the corresponding triazoliumtriflate has also been reported.[13] 1,2-Diketones are important building blocks in organic synthesis, valuable motifs often found in many natural products and biologically active compounds.[14] Several synthetic methods have been reported with different Pd-catalysts for the catalytic oxidation of alkynes to 1,2-diketones.[15]In this study we report the synthesis of a new class of cationic palladium (II) complexes of the type $[Pd(Tz)(Cl)(bipy)]^{+}Cl^{-}$ and $[Pd(Tz)(Cl)(phen)]^{+}Cl^{-}$ (Tz = 1,4-diaryl-3-methyl-1,2,3-triazol-5-ylidene, bipy = 2,2'-bipyridine and phen = 1,10-phenanthroline) and explore their catalytic activity towards the conversion of internal alkynes to 1,2-diketones.To the best of our knowledge this is the first example for the oxidation of alkynes to 1,2-diketones catalyzed by cationic Pd-complexes bearing 1,2,3-triazol-5-ylidne ligands.

2. Results and discussion

2.1. Synthesis of cationic palladium complexes bearing 1,2,3-triazol-5-ylidene ligands.

1,4-Diphenyl-3-methyl-1,2,3-triazolium iodide (**1a**) was treated with freshly prepared silver oxide in dichloromethane at room temperature. Formation of the corresponding silver triazolylidenecarbene complex was inferred from the disappearance of the triazolium proton signal at 9.61 ppm in the ^{1}H NMR spectrum of the crude product obtained by working up a aliquot of the reaction mixture.[3a-b,16] Typically after stirring for 16 h at room temperature, complete disappearance of the starting material was observed. The silver carbene complex thus generated was not isolated. It was directly treated with 1 equivalent of $Pd(Cl)_2(CH_3CN)_2$ and

stirred for additional 16 h at room temperature. After workup the crude product was obtained as a pale yellow solid. It was identified as the chloro bridged dinuclear complex **2a**.[17] Complex **2a** was further treated with 2 equivalent of either 2,2'-bipyridine or 1,10-phenanthroline to obtain the corresponding cationic complex **3a** or **4a**, respectively (Scheme 1)[17,18].In this preparation it was not necessary to isolate **2a**. It can be *in situ* treated with 2,2'-bipyridine or 1,10-phenanthroline to obtain **3a** or **4a,** respectively without any detrimental effect in the yield. Triazolium iodides (**1a-g**) bearing different wing-tip groups were treated in asimilar manner to obtain the corresponding cationic complexes **3a-g** and **4a-g**in excellent yields (Table 1).All the complexes were fully characterized by spectroscopic methods. In addition, complex **3a** was also characterized by single crystal XRD data. Complex **3a** crystallized in P-1 space group and triclinic crystal system. The geometry around palladium was distorted square planar (Figure 1). The unit cell contained two molecules of **3a** and four molecules of chloroform, solvent of crystallization. In the crystal structure of 3a one of the chloride ion was bonded to the palladium atom and the other chloride ion remained free, clearly indicating the cationic nature of the palladium center in **3a.**



Scheme 1.Synthesis of cationic palladium (II) complexes through chloro bridged dinuclear complex.

Table 1.Synthesis of cationic palladium (II) complexes**3a-g** and **4a-g**

1	Ar_1	Ar_2	Product	Duration (h)[a]	Isolated yield (%)
1a	Phenyl	Phenyl	**3a**	8	98%
1b	Phenyl	Mesityl	**3b**	8	97%
1c	Phenyl	1-Naphthyl	**3c**	16	93%
1d	Mesityl	Mesityl	**3d**	8	96%
1e	1-Naphthyl	Phenyl	**3e**	8	97%
1f	1-Naphthyl	Mesityl	**3f**	8	94%
1g	1-Napthyl	1-Naphthyl	**3g**	16	92%
1a	Phenyl	Phenyl	**4a**	8	95%
1b	Phenyl	Mesityl	**4b**	8	97%
1c	Phenyl	1-Naphthyl	**4c**	16	92%
1d	Mesityl	Mesityl	**4d**	8	96%
1e	1-Naphthyl	Phenyl	**4e**	8	94%
1f	1-Naphthyl	Mesityl	**4f**	8	94%

1g	1-Napthyl	1-Naphthyl	**4g**	16	92%

[a]corresponds to conversion of **2a-g** to **3a-g** and **4a-g**.

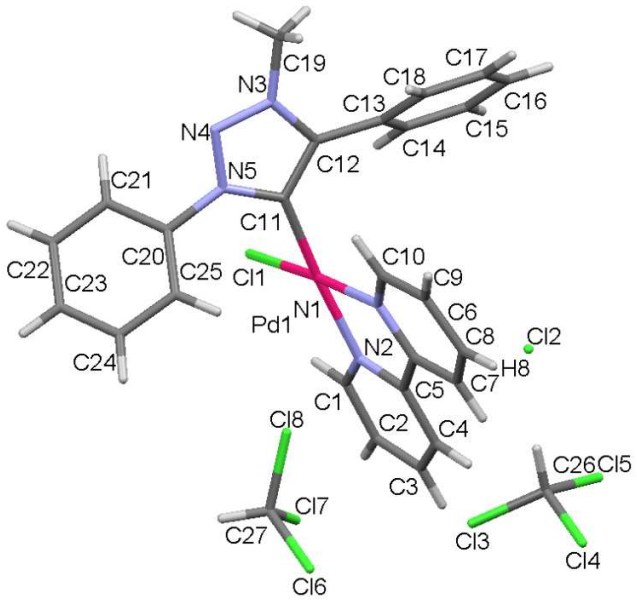
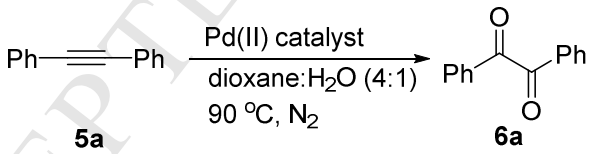


Figure 1. Stick representation of structure of [**3a**-2$CHCl_3$] in the crystal. Hydrogen atoms are not labeled for clarity. Selected bond angles: N1-Pd-N2 79.92(15)^o, N1-Pd-C11 96.10(11)^o, C11-Pd-$C_{carbene}$ 88.15(11)^o, N2-Pd-$C_{carbene}$ 95.87(14)^o, Selected bond lengths: Pd-$C_{carbene}$ 197.6(4) pm, Pd-Cl1 230.12(10) pm.

2.2. Catalytic conversion of internal alkynes to 1,2-diketones

Initially we aimed at the addition of water as a nucleophile to the internal alkynes catalyzed by the cationic palladium complexes.1,2-Diphenylacetylene (**5a**) was chosen as the model substrate for the optimization of reaction conditions. When the reaction was carried out in the presence of 2 mol% of **3a** in 1,4-dioxane-water mixture (4:1 v/v) as solvent under N_2 atmosphere from room temperature to refluxing conditions (rt to 110 ^{o}C) only starting material remained intact even after prolonged period (Table 2, entry 1). Addition of 2 mol% of $AgNO_3$ to the same reaction mixture at 90 ^{o}C for 36 h surprisingly yielded benzil (**6a**) as the only product in 32% yield and the balance being the unreacted starting alkyne (Table 2, entry 2). The course of the reaction was

followed by TLC which indicated formation of benzil (**6a**) as the only product. Careful comparison of the TLC of the crude product with authentic samples of benzoin, hydrobenzoin and deoxybenzoin (as possible byproducts) revealed that none of these compounds were formed in the reaction. Upon addition of $AgNO_3$a white precipitate was observed immediately due to the formation of AgCl. The yield of **6a** increased to 69% when the reaction was carried out in the presence of 4 mol% of $AgNO_3$. Finally in the presence of 4 mol% of the catalyst **3a** and 8 mol% of $AgNO_3$ the yield of **6a** increased to 94% (Table 2, entry 3 and 4). Control experiments clearly showed that there was no reaction in the absence of **3a**(Table 2, entry 5), only starting material was recovered after prolonged period. Neither Ag(OTf) nor $CuSO_4$(as oxidant to convert any Pd(0) formed during course of the reaction to Pd(II)) was as effective as $AgNO_3$ as additive (Table 2, entry 6 and 7). Similarly other palladium sources, namely $PdCl_2$ and $Pd(OAc)_2$ were not as effective as **3a** as catalyst for this reaction (Table 2, entry 8 and 9). The presence of cationic palladium complex **3a** and $AgNO_3$ in the mole ratio of 1:2, respectively was essential for the success of the transformation shown in Scheme 2.



Scheme 2.Catalytic conversion of diphenylacetylene (**5a**) to benzil (**6a**).

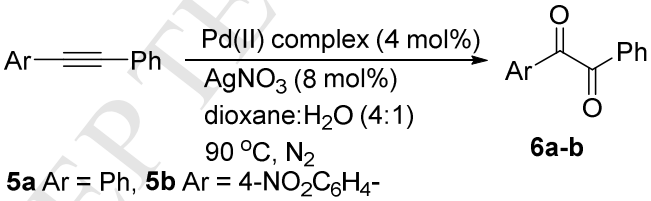
Table 2. Optimization of reaction conditions for the catalytic conversion of diphenylacetylene (**5a**) to benzil (**6a**).

Entry[a]	Pd(II) source	Additive	Temp/duration	Yield of benzil[b] (**6a**) (%)
1	complex **3a** (2 mol%)	none	rt to 100 °C/36 h	no reaction
2	complex **3a** (2 mol%)	$AgNO_3$ (2 mol%)	90 °C / 36 h	32%
3	complex **3a** (2 mol%)	$AgNO_3$ (4 mol%)	90 °C / 36 h	69%

4	complex **3a** (4mol%)	$AgNO_3$ (8 mol%)	90 ^oC / 16 h	94%
5	none	$AgNO_3$ (8 mol%)	90 ^oC / 36 h	no reaction
6	complex **3a** (4 mol%)	Ag(OTf) (8 mol%)	90 ^oC / 36 h	no reaction
7	complex **3a** (4 mol%)	$CuSO_4$ (8 mol%)	90 ^oC / 36 h	no reaction
8	$PdCl_2$ (4 mol%)	$AgNO_3$ (8 mol%)	90 ^oC / 48 h	trace amount
9	$Pd(OAc)_2$ (4 mol%)	$AgNO_3$ (8 mol%)	90 ^oC / 48 h	trace amount

[a]all reactions were carried out on a 100 mg (0.56 mmol) scale in 1,4-dioxane:H_2O (4 mL:1mL) under N_2atm, [b]isolated yield of **6a**.

The catalytic activities of complexes **3a-c** and **4a-c** were tested under optimized reaction conditions (Table 2, entry 4) for the conversion of **5a** and **5b** to **6a** and **6b**, respectively. **5b** (with electron withdrawing NO_2 group) reacted slower than **5a**in all cases. Complex **3a** was found to be more active than other catalysts as evident from time taken for the completion of the reaction under identical conditions (Table 3, entry 1). Therefore complex **3a** was used as the catalyst for further studies.



Scheme 3. Screening of Pd(II) complexes for the conversion of internal alkynes (**5a-b**) to 1,2-diketones (**6a-b**).

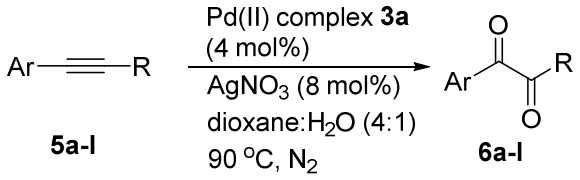
Table 3.Screening of Pd(II) complexes for the conversion of internal alkynes (**5a-b**) to 1,2-diketones (**6a-b**).

Entry[a]	Pd(II) complex	Substrate	Duration (h)	Product/ Yield (%)[b]
1	**3a**	**5a**	16	**6a**/ 94
2	**3b**	**5a**	16	**6a**/94
3	**3c**	**5a**	24	**6a**/91

4	**4a**	**5a**	24	**6a**/89
5	**4b**	**5a**	24	**6a**/ 90
6	**4c**	**5a**	24	**6a**/85
7	**3a**	**5b**	21	**6b**/80
8	**3b**	**5b**	24	**6b**/78
9	**3c**	**5b**	36	**6b**/74
10	**4a**	**5b**	36	**6b**/72
11	**4b**	**5b**	36	**6b**/72
12	**4c**	**5b**	36	**6b**/71

[a]substrate (100 mg), Pd complex (4 mol%), $AgNO_3$ (8 mol%), 1,4-dioxane:H_2O (5 mL, 4:1 v/v). N_2 atm. 90 ^oC, [b]isolated yield of the product.

To demonstrate the scope of substrates for the conversion of internal alkyne to 1,2-diketones a variety of 1,2-diarylalkynes bearing electron donating, electron withdrawing groups and easily oxidizable group were chosen. In all the cases the reaction proceeded smoothly to furnish the corresponding 1,2-diketones (Table 4). The easily oxidizable aldehyde group in **5c** remained intact during the course of this reaction and **6c** was formed in good yield (Table 4, entry 3). Sterically hindered substrates **5f** and **5l**reacted slower and gave moderate yields of the corresponding diketones**6f** and **6l**, respectively (Table 4, entry 6, 10 and 12). 1-alkyl-2-arylalkynes **5h** and **5i** also reacted to furnish the corresponding diketones**6h** and **6i**, respectively in excellent yields (Table 4, entry 8 and 9). Conversion of **5a** to **6a** was carried out in 500 mg scale. After 19 h 551 mg (93%) of **6a** was isolated along with 28 mg (94% conversion) of unreacted **5a** after column chromatographic separation. Similarly conversion of **5b** to **6b** was carried out in 1 gram scale. After 28 h 871 mg (76%) of **6b** was isolated along with 217 mg (78% conversion) of **5b** after column chromatographic sepearation.



Scheme 4.Substrate scope on the catalytic conversion of internal alkynes to 1,2-diketones.

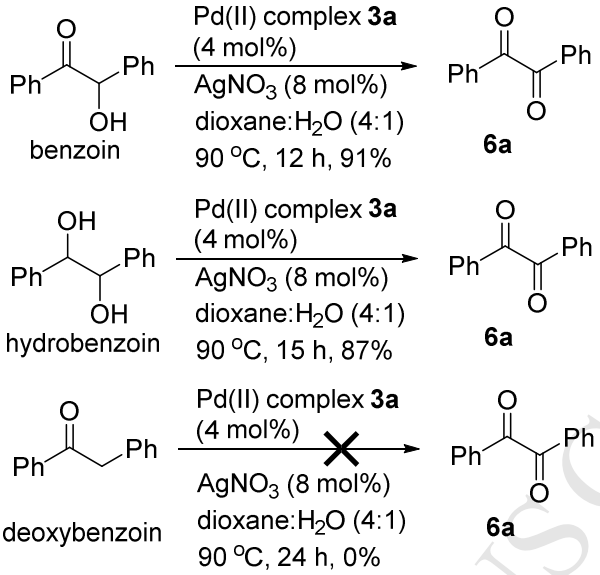
Table 4. Catalytic conversion of internal alkynes to 1,2-diketones. Substrate scope.

Entry	Substrate/Ar/R[a]	Product	Duration (h)	Yield (%)
1	**5a** / Ph /Ph	**6a**	16 (19)[b]	94 (93)[b]
2	**5b** / Ph / 4-$NO_2C_6H_4$-	**6b**	21 (28)[c]	80 (76)[c]
3	**5c** / Ph / 4-$CHOC_6H_4$-	**6c**	21	83
4	**5d** / Ph / 2-MeC_6H_4-	**6d**	19	89
5	**5e** / Ph / 4-MeC_6H_4-	**6e**	18	91
6	**5f** / Ph / mesityl	**6f**	30	48
7	**5g** / Ph / -1-naphthyl	**6g**	28	81
8	**5h** / Ph / Me	**6h**	14	94
9	**5i** / Ph / *n*-Bu	**6i**	14	92
10	**5j** / 2-MeC_6H_4- / 2-MeC_6H_4-	**6j**	48	63
11	**5k** / 4-MeC_6H_4- / 4-MeC_6H_4-	**6k**	48	69
12	**5l** / 1-naphthyl / 1-Naphthyl	**6l**	60	52

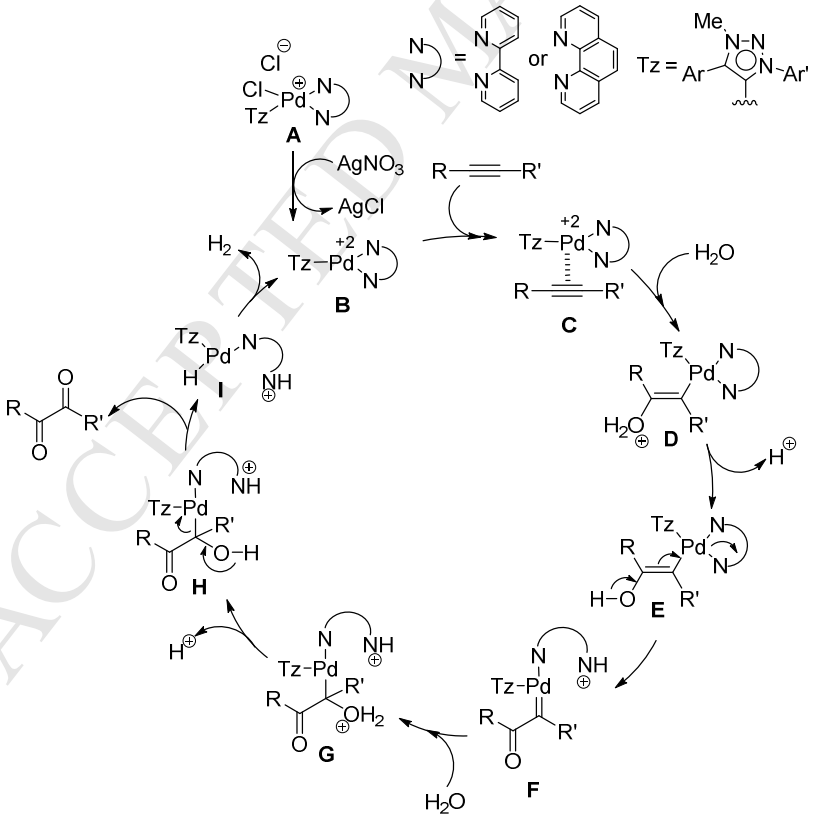
[a]all reactions were carried out on a 100 mg scale of substrate, [b]on a 500 mg scale reaction with 94% conversion, [c]on a 1 gram scale reaction with 78% conversion.

Both *trans*-stilbene and 1,4-diphenylbuta-1,4-diyne did not react even after prolonged period of time under conditions described in Scheme 4. We have clearly established by TLC analysis of the crude product and its comparison with authentic samples of benzoin, hydrobenzoin and deoxybenzoin that they were not formed in the conversion of **5a** to **6a.** Nevertheless their formation and involvement as short lived intermediates cannot be ruled out. Control experiments were carried out to test the above hypothesis. Benzoin, hydrobenzoin and deoxybenzoin were separately reacted in the presence of **3a** as the catalyst under optimized conditions as described

in Scheme 4 (Scheme 5). While benzoin and hydrobenzoin reacted to furnish benzil as the sole product, deoxybenzoin did not react even after prolonged period (Scheme 5). Thus the formation of deoxybenzoin as a possible intermediate through Pd(II) catalyzed hydration of **5a** can be clearly ruled out in the conversion of **5a** to **6a**. The involvement of benzoin and hydrobenzoin in the conversion of **5a** to **6a** as short lived intermediates cannot be ruled out. A plausible mechanism of the catalytic process is depicted in Scheme 6. Initially silver nitrate removes the chloride ions as insoluble AgClto generate the dicationic intermediate **B** which coordinates to the alkyne forming the π-complex produce intermediate **C**. Addition of water to the triple bond followed by deprotonation results in the formation of intermediate **E** which undergoes deprotonation to yield Pd-carbene intermediate **F**. This electrophilic Pd-carbeneintermediate undergoes addition of water to give intermediate **G** which on β-elimination releases the observed product. The resulting palladium hydrido complex loses hydrogen to give back the catalytically active species **B** completing the catalytic cycle. It is effectively the sequential addition of water molecules to the alkyne that results in the formation of 1,2-diketone as the product. Such an addition of water as a nucleophile to alkyne is catalyzed by electrophilic cationic palladium complex.



Scheme 5.Control experiments to test the involvement of benzoin, hydrobenzoin and deoxybenzoin in the conversion of **5a** to **6a.**



Scheme 6. Plausible mechanism for the catalytic conversion of alkyne to 1,2-diketone

3. Conclusions

A new class of cationic palladium-NHC complexes containing mixed 1,2,3-triazol-5-ylidene (bearing a variety of wingtip groups) and 2,2'-bipyridine/1,10-phenanthroline ligands were synthesized from the corresponding 1,2,3-triazolium iodide via the silver carbene complex and chlorobridgeddinuclear palladium complex. Complex **3a** was structurally characterized by single crystal XRD data and all the others were characterized thoroughly by spectroscopic data. These cationic complexes showed excellent catalytic activity for the conversion of internal alkynes to 1,2-diketones in excellent yield with $AgNO_3$ as an additive in 1,4-dioxane-water mixture. Several symmetrical and unsymmetrical aryl and alkyl substituted 1,2-diketones were synthesized using these cationic complexes. A plausible mechanism involving hydration of triple bond catalyzed by the electrophilic cationic Pd complex was proposed.

4. Experimental section

General instrumentation used in the study has been described elsewhere.[13a]

Synthesis of complex **2a**

1,4-Diphenyl-3-methyl-1,2,3-triazolium iodide (**1a**) (2.18 g, 6 mmol) was treated with freshly prepared silver oxide (1.67 g, 7.2 mmol, 1.1 equiv.) in CH_2Cl_2 (35 mL). The solution was stirred at room temperature in the dark for 16 h under nitrogen atmosphere. The silver carbene complex thus generated was not isolated, it was directly treated with $Pd(CH_3CN)_2Cl_2$ (1.71 g, 6.6 mmol, 1.1 equiv.) and stirred for 8 h. The reaction mixture was passed through a bed of celite, and then removal of CH_2Cl_2 gave complex **2a**as a pale yellow solid (1.19 g) in 96% yield. mp: 189-191 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.35 (m, 4H), 7.97-7.95 (m, 4H), 7.58 (s, 12H), 4.06 (s, 6H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 138.5, 130.7, 130.6, 129.6, 129.3, 125.3, 38.0; ESI-MS: HRMS: *m/*zcalcd for $C_{30}H_{27}N_6Pd_2Cl_4$ $[M+H]^+$ 822.9121, found 822.9136.

Synthesis of complex**3a**

To a solution of complex **2a** (825 mg, 1 mmol) in 20 mL dichloromethane 2,2'-bipyridine (343 mg, 2.2 mmol) was added and the reaction mixture was stirred for 8 h at room temperature to give complex **3a** as a pale yellow solid (556 mg, 0.97 mmol) in 98%. Crystals of **3a**suitable for

single-crystal diffraction were grown by slow evaporation of a solution of **3a**from chloroform. Complexes **3b-g**were synthesized using similar procedure. Complexes **4a-g** were also synthesized using similar procedure using 1,10-phenanthroline instead of 2,2-bipyridine.

Complex **3a**: mp: 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.35 (d, *J* = 6.8 Hz, 2H), 8.27 (d, *J* = 7.2 Hz, 2H), 8.14-8.02 (m, 3H), 7.88-7.79 (m, 2H), 7.55 (t, *J* = 6.0 Hz, 1H), 7.51-7.46 (m, 6H), 4.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 155.1, 154.4, 149.2, 144.5, 141.8, 140.9, 140.3, 139.0, 131.2, 130.5, 130.4, 129.7, 129.5, 129.1, 126.5, 126.4, 125.7, 123.4, 122.9, 38.7; ESI-MS: HRMS: *m/z*calcd for $C_{25}H_{21}N_5ClPd$ $[M-Cl]^+$ 528.0542, found 528.0560.

Complex **3b**

Prepared from 1,2,3-triazolium iodide**2b** (405 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 2,2'-bipyridine (343 mg, 2.2 equiv.). Yield 592 mg, 97%, mp: 195 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (dd, *J* = 6, 1 Hz, 1H), 8.95 (t, *J* = 3 Hz, 1H), 8.48 (d, *J* = 7.5 Hz, 2H), 8.11 (d, *J* = 8 Hz, 1H), 8.07-8.03 (m, 2H), 7.97-7.95 (m, 2H), 7.52-7.49 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 6.89 (s, 1H), 4.48 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 155.17, 155.12, 149.6, 144.1, 144.0, 140.48, 140.41, 140.1, 136.4, 135.2, 134.8, 131.4, 130.2, 129.8, 129.5, 129.3, 129.0, 126.4, 126.3, 122.6, 122.1, 38.9, 21.3, 19.1, 18.8; ESI-MS: HRMS: *m/z*calcd for $C_{28}H_{27}N_5ClPd$ $[M-Cl]^+$ 574.0990, found 574.0993.

Complex **3c**

Prepared from 1,2,3-triazolium iodide**2c** (413 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 2,2'-bipyridine (343 mg, 2.2 equiv.). Yield 576 mg, 93%,light brown solid,mp: 201-202 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02-8.98 (m, 2H), 8.49-8.42 (m, 3H), 8.27 (d, *J* = 7 Hz, 1H), 7.94 (d, *J* = 8 Hz, 2H), 7.84-7.73 (m, 4H), 7.67-7.66 (m, 2H), 7.59-7.53 (m, 3H), 7.45 (t, *J* = 7 Hz, 3H), 4.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 154.9, 154.8, 149.3, 144.5, 144.4, 140.4, 139.8, 135.3, 133.9, 131.7, 131.3, 130.3, 129.9, 129.1, 128.7, 127.7, 127.4, 127.0, 126.4, 126.3, 124.7, 124.4, 122.4, 122.0, 39.2; ESI-MS: HRMS: *m/z*calcd for $C_{29}H_{23}N_5ClPd$ $[M-Cl]^+$ 582.0677, found 582.0665.

Complex **3d**

Prepared from 1,2,3-triazolium iodide**2d** (447 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 2,2'-bipyridine (343 mg, 2.2 equiv.). Yield 627 mg,

96%,off white solid,mp: 197-199 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (d, *J* = 8 Hz, 1H), 8.99 (d, *J* = 5.5 Hz, 1H), 8.88 (d, *J* = 8 Hz, 1H), 8.42 (t, *J* = 6.5 Hz, 1H), 8.14 (t, *J* = 8 Hz, 1H), 8.01 (d, *J* = 5.5 Hz, 1H), 7.61 (t, *J* = 6.5 Hz, 1H), 7.44 (t, *J* = 7 Hz, 1H), 7.04 (s, 1H), 7.03 (s, 1H), 6.97 (s, 1H), 6.95 (s, 1H), 4.05 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 155.1, 151.5, 151.2, 149.0, 147.3, 144.0, 142.4, 141.5, 141.3, 141.1, 140.0, 136.9, 136.4, 135.1, 133.0, 130.2, 130.1, 129.6, 129.2, 126.9, 126.5, 126.1, 124.6, 121.1, 37.5, 21.9, 21.3, 21.1, 19.37, 19.32; ESI-MS: HRMS: *m/z*calcd for $C_{31}H_{33}N_5ClPd$ $[M\text{-}Cl]^+$ 616.1459, found 616.1481.

Complex **3e**

Prepared from 1,2,3-triazolium iodide**2e** (413 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 2,2'-bipyridine (343 mg, 2.2 equiv.). Yield 600 mg, 97%'pale yellow solid, mp: 185-187 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (d, *J* = 5.5 Hz, 1H), 8.98 (d, *J* = 5.5 Hz, 1H), 8.51 (d, *J* = 7.5 Hz, 2H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 7 Hz, 1H), 7.96-7.92 (m, 2H), 7.81 (t, *J* = 6.5 Hz, 1H), 7.82-7.77 (m, 2H), 7.69 (t, *J* = 8 Hz, 1H), 7.65-7.61 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.46-7.41 (m, 3H), 4.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 154.8, 154.7, 149.2, 144.4, 144.3, 140.5, 139.7, 135.3, 133.8, 131.6, 131.2, 130.3, 129.7, 129.0, 128.7, 127.7, 127.4, 126.9, 126.5, 126.3, 124.7, 124.3, 122.3, 122.0, 39.1; ESI-MS: HRMS: *m/z*calcd for $C_{29}H_{23}N_5ClPd$ $[M\text{-}Cl]^+$ 582.0677, found 582.0690.

Complex **3f**

Prepared from 1,2,3-triazolium iodide**2f** (455 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 2,2'-bipyridine (343 mg, 2.2 equiv.). Yield 621 mg, 94%,pale yellow solid, mp: 204 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (d, *J* = 3.3 Hz, 1H), 8.95-8.93 (m, 2H), 8.19-8.18 (m, 2H), 8.02-7.95 (m, 1H), 7.90 (t, *J* = 8 Hz, 4H), 7.84 (d, *J* = 8 Hz, 1H), 7.61-7.57 (m, 2H), 7.52-7.49 (m, 1H), 7.35-7.32 (m, 1H), 7.04 (s, 1H), 6.92 (s, 1H), 4.27 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 154.9, 149.5, 140.4, 140.1, 140.0, 136.6, 134.9, 133.7, 132.5, 131.7, 131.1, 129.8, 129.47, 129.41, 128.2, 127.4, 126.8, 126.2, 125.8, 123.2, 122.3, 121.9, 38.7, 21.4, 19.4, 19.0; ESI-MS: HRMS: *m/z*calcd for $C_{32}H_{29}N_5ClPd$ $[M\text{-}Cl]^+$ 624.1146, found 624.1119.

Complex **3g**

Prepared from 1,2,3-triazolium iodide**2g** (463 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 2,2'-bipyridine (343 mg, 2.2 equiv.). Yield 616 mg, 92%,yellow solid, mp: 208-210 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.15-8.56 (m, 2H), 8.44-8.02 (m, 12H), 7.83-7.53 (m, 8H), 4.14 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 156.5, 155.8, 155.7, 154.37, 154.34, 153.0, 152.5, 149.8, 148.2, 148.1, 146.5, 143.0, 142.4, 141.48, 141.46, 141.41, 134.97, 134.91, 133.7, 133.6, 133.4, 133.2, 132.0, 131.76, 131.71, 131.6, 131.4, 131.3, 130.2, 129.0, 128.4, 128.37, 128.32, 128.1, 128.0, 127.9, 127.7, 127.6, 127.59, 127.52, 127.45, 127.41, 127.1, 126.9, 126.6, 126.4, 126.3, 125.7, 125.6, 125.3, 125.2, 124.3, 124.2, 124.0, 123.7, 123.6, 123.4, 123.3, 123.1, 123.0, 38.5, 38.2; ESI-MS: HRMS: *m/z*calcd for $C_{33}H_{25}N_5ClPd$ $[M-Cl]^+$ 632.0833, found 632.0834.

Complex **4a**

Prepared from 1,2,3-triazolium iodide **2a** (447 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 1,10-phenanthroline (436 mg, 2.2 equiv.). Yield 563 mg, 95%,pale yellow solid,mp: 231 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (d, *J* = 4.4 Hz, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 8.89 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 4.8 Hz, 1H), 8.25 (d, *J* = 7.2 Hz, 2H), 8.22 (d, *J* = 4.8 Hz, 2H), 8.13 (dd, *J* = 8, 4.8 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.89-7.86 (m, 1H), 7.61-7.46 (m, 6H), 4.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.6, 149.3, 146.3, 145.1, 144.2, 141.2, 140.4, 140.3, 138.4, 130.7, 130.4, 130.3, 130.2, 129.8, 129.0, 127.8, 127.5, 126.4, 126.2, 124.7, 38.5; ESI-MS: HRMS: *m/z*calcd for $C_{27}H_{21}N_5ClPd$ $[M-Cl]^+$ 556.0520, found 556.0505.

Complex **4b**

Prepared from 1,2,3-triazolium iodide **2b** (405 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 1,10-phenanthroline (436 mg, 2.2 equiv.). Yield 616 mg, 97%,off white solid, mp: 213-215 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (d, *J* = 5 Hz, 1H), 9.33 (dd, *J* = 5, 1 Hz, 1H), 8.57 (d, *J* = 7 Hz, 2H), 8.50 (dd, *J* = 8.5, 1 Hz, 1H), 8.42 (d, *J* = 8 Hz, 1H), 8.33 (dd, *J* = 8, 5.5 Hz, 1H), 7.91 (s, 2H), 7.82 (dd, *J* = 8, 5 Hz, 1H), 7.42 (t, *J* = 8 Hz, 2H), 7.30 (t, *J* = 8 Hz, 1H), 7.02 (s, 1H), 6.84 (s, 1H), 4.54 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 149.7, 146.5, 146.0, 144.3, 142.8, 140.4, 138.9, 138.6, 136.4, 135.3, 135.1, 131.6, 130.19, 130.12, 129.7, 129.4, 129.2, 128.9, 128.5, 127.6, 126.7, 126.5, 125.0, 39.0, 21.3, 19.2, 18.8; ESI-MS: HRMS: *m/z*calcd for $C_{30}H_{27}N_5ClPd$ $[M-Cl]^+$ 598.0990, found 598.0984.

Complex **4c**

Prepared from 1,2,3-triazolium iodide **2c** (413 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 1,10-phenanthroline (436 mg, 2.2 equiv.). Yield 592 mg, 92%,yellow solid, mp: 225 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 9.28 (dd, *J* = 5, 1.5 Hz, 1H), 8.55 (d, *J* = 7 Hz, 3H), 8.40 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.35 (d, *J* = 7.5 Hz, 1H), 8.29-8.26 (m, 2H), 7.93 (d, *J* = 8 Hz, 1H), 7.79-7.75 (m, 4H), 7.69 (t, *J* = 8 Hz, 1H), 7.58 (t, *J* = 8 Hz, 1H), 7.51 (t, *J* = 7 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H) 4.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 149.5, 144.7, 143.4, 138.8, 138.4, 133.9, 131.7, 131.2, 130.2, 129.6, 129.0, 128.8, 128.4, 127.6, 127.5, 127.4, 127.0, 126.6, 124.9, 124.7, 124.4, 39.2; ESI-MS: HRMS: *m/z*calcd for $C_{31}H_{23}N_5ClPd$ $[M\text{-}Cl]^+$ 606.0677, found 606.0682.

Complex **4d**

Prepared from 1,2,3-triazolium iodide **2d** (447 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 1,10-phenanthroline (436 mg, 2.2 equiv.). Yield 650 mg, 96%, off white solid, mp: 196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (dd, *J* = 5, 1 Hz, 1H), 9.10 (d, *J* = 8 Hz, 1H), 8.70 (d, *J* = 8, 1 Hz, 1H), 8.43 (dd, *J* = 8.5, 5.5 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 8.79 (dd, *J* = 8.5, 5 Hz, 1H), 7.02 (s, 1H), 6.97 (s, 1H), 6.94 (s, 1H), 6.89 (s, 1H), 4.10 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H), 2.27 (s, 3H), 2.25 (s, 6H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 149.5, 146.7, 145.9, 145.5, 144.0, 141.4, 141.2, 140.8, 139.9, 139.4, 138.0, 136.6, 135.2, 133.7, 131.0, 130.1, 129.9, 129.7, 129.6, 129.3, 128.3, 127.4, 127.1, 125.1, 121.5, 37.7, 21.7, 21.6, 21.3, 19.5, 19.2; ESI-MS: HRMS: *m/z*calcd for $C_{33}H_{33}N_5ClPd$ $[M\text{-}Cl]^+$ 640.1459, found 640.1473.

Complex **4e**

Prepared from 1,2,3-triazolium iodide **2e** (413 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 1,10-phenanthroline (436 mg, 2.2 equiv.). Yield 605 mg, 94%,yellow solid, mp: 207-209 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.98 (d, *J* = 5.5 Hz, 1H), 8.51 (d, *J* = 4.5 Hz, 2H), 8.45 (s, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.82-7.41 (m, 12H) 4.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 144.7, 143.4, 138.8, 138.4, 133.9, 131.7, 131.2, 130.2, 129.6, 129.0, 128.8, 128.4, 127.6, 127.5, 127.4, 127.0, 126.6, 126.5, 124.9, 124.7, 124.5, 39.2; ESI-MS: HRMS: *m/z*calcd for $C_{31}H_{23}N_5ClPd$ $[M\text{-}Cl]^+$ 606.0677, found 606.0697.

Complex **4f**

Prepared from 1,2,3-triazolium iodide **2f** (455 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 1,10-phenanthroline (436 mg, 2.2 equiv.). Yield 644 mg, 94%,pale yellow solid, mp: 219-221 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (d, *J* = 4.5 Hz, 1H), 9.17 (dd, *J* = 5, 1.5 Hz, 1H), 9.13 (d, *J* = 6.5 Hz, 1H), 8.51-8.43 (m, 2H), 8.32 (dd, *J* = 8, 1.5 Hz, 1H), 8.26 (d, *J* = 8 Hz, 1H), 7.84 (t, *J* = 8 Hz, 2H), 7.78-7.76 (m, 2H), 7.66-7.57 (m, 3H), 7.49-7.45 (m, 1H), 7.06 (s, 1H), 6.88 (s, 1H), 4.33 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 149.6, 146.5, 145.9, 144.4, 142.2, 140.4, 138.69, 138.63, 136.6, 135.6, 135.1, 133.7, 132.6, 131.8, 130.9, 130.1, 129.67, 129.61, 129.4, 129.3, 128.4, 128.1, 127.5, 127.3, 126.9, 126.79, 126.72, 125.9, 124.8, 123.3, 38.8, 21.4, 19.4, 19.0; ESI-MS: HRMS: *m/z*calcd for $C_{34}H_{29}N_5ClPd$ $[M\text{-}Cl]^+$ 648.1146, found 648.1147.

Complex **4g**

Prepared from 1,2,3-triazolium iodide **2g** (463 mg, 1 mmol), Ag_2O (256 mg, 1.1 equiv.), $Pd(CH_3CN)_2Cl_2$(286 mg, 1.1 equiv.), 1,10-phenanthroline (436 mg, 2.2 equiv.). Yield 638 mg, 92%, light brown solid, mp: 221-223 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.29-9.22 (m, 1H), 9.02-8.40 (m, 4H), 8.23-7.84 (m, 12H), 7.78-7.59 (m, 6H), 4.16 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d6) δ 153.3, 152.7, 150.1, 148.9, 148.8, 146.6, 145.9, 145.8, 145.56, 145.54, 144.6, 143.1, 142.4, 140.5, 140.0, 139.9, 132.0, 131.7, 131.5, 131.4, 131.3, 131.2, 131.1, 130.26, 130.20, 130.1, 129.87, 129.84, 128.80, 128.3, 128.19, 128.15, 128.0, 127.8, 127.64, 127.61, 127.55, 127.50, 127.4, 127.34, 127.30, 127.2, 126.9, 126.8, 126.6, 126.4, 126.3, 126.1, 125.9, 125.88, 125.81, 125.6, 125.5, 125.25, 125.21, 123.38, 123.34, 123.0, 38.4, 38.3; ESI-MS: HRMS: *m/z*calcd for $C_{35}H_{25}N_5ClPd$ $[M\text{-}Cl]^+$ 656.0833, found 656.0857.

Representative procedure for the conversion of internal alkynes to 1,2-diketones:

To a solution of 1,2-diphenylethyne (**5a**) (500 mg, 2.808 mmol) in 1,4-dioxane, water (20 mL:5 mL v/v), complex **3a** (63 mg, 0.112 mmol, 4 mol%), $AgNO_3$ (38 mg, 0.224 mmol, 8 mol%) were added and the reaction mixture was stirred at 90 ^{o}C, the progress of the reaction was monitored by TLC. After 19 h the reaction mixture was cooled to room temperature, diluted with water and extracted with CH_2Cl_2. The separated organic layer was dried over Na_2SO_4, concentrated under vacuum. The residue was subjected to silica gel column chromatography by using hexane/EtOAc (9:1, v/v) as eluent to give benzil (**6a**) (551 mg, 2.623 mmol) as a yellow solid in 93% yield. Similarly to a solution of **5b** (1000 mg, 4.48 mmol) in 1,4-dioxane, water (40 mL:10 mL v/v),

complex **3a** (102 mg, 0.179 mmol, 61 mg, 4 mol%), $AgNO_3$ (61 mg, 0.358 mmol, 8 mol%) were added and the reaction mixture was stirred at 90 $^oC+$ for 28 h to give **6b** (871 mg, 3.415 mmol) as a yellow solid in 76% yield. The characterization data for all the 1,2-diketones (**6a-l)** are given in the supporting information.

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Appendix A. Supplementary material

The following is the supplementary data related to this article:

Spectroscopic data for**6a-l**. CCDC number1484554contain the supplementary crystallographic data for compound**3a**. 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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Synthesis of a new class of cationic Pd(II) complexes with 1,2,3-triazol-5-ylidene ligand and their catalytic application in the conversion of internal alkynes to 1,2-diketones

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Highlights

- Synthesis of cationic Pd(II) complexes with 1,2,3-triazolylidene ligands is reported
- Cationic Pd(II) complexes bear bipyridine and 1,10-phenanthroline as co-ligands
- One of the cationic complex is structurally characterized by single crystal XRD data
- Cationic complexes are catalytically active for the conversion of alkynes to 1,2-diketones
- Catalytic conversion of 1,2-diarylalkynes to benzil derivatives is highly selective