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COMMUNICATION

1,2,3-Triazolylidene based complexes *via* **post-modification of pincer click ligands**[†]

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Preparation of 1,2,3-triazolylidene metal complexes by simple alkylation of triazolyl based parent species was demonstrated for the first time. Based on this post-modification approach, unprecedented tridentate Pd and Pt complexes bearing a 1,2,3-triazolylidene core were synthesized.

Tridentate pincer-type ligands D^1CD^2 have found a variety of valuable applications in different areas of chemistry (Scheme 1, 1).¹ The pincer structure affords its metal complex a high stability, which is widely attributed to the protective, sheltered environment in which the metal is situated. Additionally, steric and electronic properties of the metal center can be fine-tuned by versatile selection of the chelating arms of the pincer ligand. The backbone of the pincer systems can also be used for remote electronic modulation of metal center. All these intrinsic features of the pincer system have generated extensive research into the use of these complexes.

Recently, we reported the preparation of a new class of pincer ligands utilizing a triazole unit as the central core motif (Fig. 1, 2).² Apart from the conceptually distinct route to the preparation of the tridentate ligands, our system 2 differs from the conventional species 1 by bearing a functional triazole backbone. Indeed, we have demonstrated that the triazole-based ligands 2 can be complexed to late-transition metals in both tridentate and bidentate (involving nitrogen atoms of triazole) coordination modes.³ The "non-innocent" behavior of the triazole backbone sparked our interest in further exploring the ability to modify this core and thus affect its ligand properties.



Fig. 1 Typical phenyl- (1) and triazolyl-based (2) pincer ligands. D represents donor groups.

Since the inception of stable carbenes, they have received extraordinary attention in homogeneous catalysis both as free molecules⁴ and as ligands for transition metals.⁵ In addition to classical N-heterocyclic carbenes **3**, those with lesser degrees of heteroatom stabilization, known as abnormal carbenes (species **4**–**6**), have been recently of great interest.⁶ Albrecht and coworkers have recently extended the family of abnormal carbene ligands by preparation of 1,2,3-triazolylidene metal complexes (Fig. 2, ii) from the corresponding 1,2,3-triazolium salt.^{7,8} This type of carbenes is especially attractive due to the simplicity and versatility of preparation of the triazole scaffold by click chemistry. Moreover, Bertrand and coworkers successfully isolated these free "mesoionic carbenes" **5** by deprotonation of their triazolium precursors, and probed their electronic properties.⁹



Fig. 2 (i) Some selected examples of abnormal carbenes. (ii) Albrecht's Pd-triazolylidene complex from the triazolium salt.

While there exist a variety of methods to prepare conventional and abnormal carbene ligands, most of them utilize corresponding free heterocyclic derivatives as a starting material, which after some manipulations result in a metal-carbene species. The most popular approach in this respect is activation of C–H or C-halogen bond of the heterocyclic salts. Although there are few instances when carbenes are prepared by post-modification of a covalently bound heterocyclic ring (*e.g.*, alkylation or protonation of pyridyl and pyrolyl ligands),¹⁰ the approach has not yet been explored for the preparation of 1,2,3-triazolylidene complexes. Here we report that 1,2,3-triazolylidene ligands can be prepared by simple postmodification of triazolyl-transition metal complexes. Namely, we

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demonstrate that the covalently metal σ -bonded triazolyl ligand can be converted to its carbene-type counterpart by alkylation of the triazole ring. The palladium and platinum complexes prepared by this route represent the first example of tridentate chelating system bearing a mesoionic carbene.

Ligands 8 and 9 were prepared based upon the Cu(1)-catalyzed [2 + 3] cycloaddition of azides and alkynes ("click" chemistry),¹¹ decorated with donor arms, to form triazole as the main tool for ligand assembly (Scheme 1).^{12,2} Utilization of the "click" reaction is advantageous because it allows for the simple and selective preparation of a diverse family of ligands from a small group of monomers.



Scheme 1 Synthesis of pincer click ligands.

Palladation of ligand 8 in a selective tridentate manner was achieved by its thermal reaction with $(tmeda)PdCl_2$ (tmeda =tetramethylethylenediamine) in the presence of a base.² In order to address post-modification feasibility of the triazole backbone of 10 we performed reactions with alkylating agents. Thus, when compound 10 was exposed to an excess of methyl iodide at 70 °C, smooth formation of triazolylidene complex 11 was observed (Scheme 2).[‡] The selective methylation of the triazole ring was obtained, and no Pd(IV) methylated species was observed.¹³ Methylation of the triazole nitrogen in solution was confirmed by NMR spectroscopy. The methyl group of 11 gives rise to a singlet at 4.14 ppm in ¹H NMR and $\delta_{\rm C}$ 38.7 ppm in ¹³C NMR, which is comparable to other reported methyl- triazolylidene systems.^{7,8} In general, spectroscopic and structural (vide infra) characteristics of the triazolylidene motif in complex 11 are in good agreement with those of reported Pd complex 7.8 Complex 7 is most relevant for comparison to our systems due to its similar trans triazolylidene-Pd-I geometry. Specifically, the ipso carbon of 11 appears at $\delta_{\rm C}$ 148.6, as compared with the carbene resonance $\delta_{\rm C}$ 154.6 in complex 7.



Scheme 2 Synthesis of Pd-triazolylidene complex 11 by post-modification of triazolyl-Pd 10.

The molecular structure of **11** was unambiguously confirmed by X-ray spectroscopy of a single crystal. Crystals suitable for X-ray

analysis were obtained by slow cooling of a chloroform solution of **11** (Fig. 3).



Fig. 3 Perspective view of a molecule of 11. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 1.902(9), Pd1–P1 2.306(2), Pd1–P2 2.334(2), Pd1–I1 2.6241(11), P1–Pd1–P2, 159.24(9), C1–Pd1–I1, 179.2(3), P2–Pd1–I1 99.97(6), P1–Pd1–I1 100.72(7).

The palladium center has a slightly distorted square planar geometry, as expected for d^8 Pd(II) complexes. The geometry of the atoms coordinated around the palladium center is essentially planar, with the sum of angles equal to 360.6°. As compared with the non-methylated parent species **10**, in species **11** the N1–N2 and N2–N3 bonds equalize, which is anticipated for mesoionic carbene complexes.

Importantly, the C1–Pd bond is shortened from 1.929 Å in **10** to 1.902 Å in **11**, indicating the increased contribution of carbene character of this bond. This Pd–C1 bond is significantly shorter than the analogous Pd–C bond in complex **7** (1.902 Å *vs.* 1.997 Å). This is likely due to the restriction imposed by coordination of rigid phosphine arms of pincer framework to the palladium center. However, the Pd–I bond in cationic complex **11** is shorter than that of neutral complex **10** (2.624 Å *vs.* 2.651 Å).

Preparation of triazolylidene-metal species by postmodification of triazole-metal precursors was also demonstrated on platinum complexes. Complex 12 was prepared by reaction of ligand 9 with a Pt(II) precursor in the presence of triethyl amine in DMF (Scheme 3). Reaction of this complex with methyl iodide caused precipitation (the putative cationic Pt methylated species are likely to be low soluble). In order to increase solubility of the desired triazolylidene product, 4-(trifluoromethyl)benzyl bromide was used as an alkylating agent. Thus, when Pt complex 12 was reacted with 4-(trifluoromethyl)benzyl bromide in acetonitrile, selective formation of 13 was observed. This complex was fully characterized by multinuclear NMR techniques. The benzyl protons resonate at 5.91 ppm, indicative of an N-alkylated species. This novel complex is the first example of a 1,2,3triazolylidene-Pt compound, extending the list of known Pd, Rh, Ir and Au-triazolylidene species.7,8

Platinum-195 NMR proved useful in observing changes in the electronic environment of the platinum center.¹⁴ Alkylated *cationic* complex **13** exhibits a doublet of doublets due to its coupling to two nonsymmetric phosphines at δ_{Pt} –4347 ppm. This is an effective upfield shift of approximately 100 ppm relative to starting *neutral* complex **12** (Fig. 4a and b). Addition of *one equivalent* of silver



Scheme 3 Synthesis of Pt-triazolylidene complex 13 by alkylation of triazolyl-Pt 12.



triflate to **13** resulted in new complex **15** as was indicated by ³¹P NMR. However, there was no observable change in ¹⁹⁵Pt NMR (Fig. 4b and c), indicating that the Br ion is not situated in the Pt first coordination sphere. Further addition of a *second equivalent* of silver triflate to **15** in acetonitrile gave complex **16** (Scheme 4). The formation of this stable biscationic complex is confirmed by an effective upfield ¹⁹⁵Pt NMR shift of approximately 100 ppm relative to alkylated species **13** and **15** (Fig. 4d).

When complex 13 was reacted with two equivalents of silver triflate in THF, and subsequently exposed to a CO atmosphere, biscationic Pt carbonyl complex 14 was obtained. This complex was analyzed by IR and multinuclear NMR techniques. The CO ligand located *trans* to the carbene unit exhibited a CO stretch in IR at 2124 cm⁻¹. Interestingly, triazolylidenes have

been highlighted as some of the strongest σ -donors as compared to other N-heterocyclic carbenes. The relatively high IR stretch of the carbonyl ligand in complex 14 may be attributed to the high positive charge on the biscationic Pt center.¹⁵ It would be valuable to compare triazolylidene donor strength of complex 14 to the triazolyl ligand in parent complex 12. Unfortunately, our attempts to remove the Cl ligand of 12 with a silver salt in order to prepare the corresponding carbonyl complex were unsuccessful, because of immediate formation of an insoluble orange precipitate. We presume that this precipitate is an oligomer formed by coordination of another triazole unit to the naked cationic metal center.¹⁶

In summary, we have demonstrated the first example of 1,2,3triazolylidene preparation by alkylation of a metal-bound triazolyl ligand. This is also the first example of pincer-based complexes bearing triazolidene carbenes as a central motif. This method not only expands the versatility of our triazole-based ligands as bidentate, tridentate, or carbene-type systems, but also highlights postmodification as a method for altering the existing metal complex properties. Further studies are underway in our laboratories to explore the catalytic activity of these compounds.

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Experimental

Synthesis of 11

To a solution of **10** (13 mg, 0.028 mmol) in chloroform (1 mL) was added MeI (3.2 μ L, 0.051 mmol). The mixture was heated to 70 °C in a closed vessel. After 18 h, the product had fully precipitated from solution. The precipitate was filtered to give **11** (12.5 mg, 92%) as a white crystalline solid. ¹H NMR (CD₃CN) δ : 1.15–1.38 (24H, m), 2.54–2.66 (4H, m, CH), 3.22 (2H, d, J_{HP} = 8.4 Hz), 4.14 (3H, s, CH₃–N), 4.91 (2H, d, J_{HP} = 5.7 Hz, CH₂). ¹³C NMR (CD₃CN) δ : 17.1 (dd, J_{CP} = 9.3, 2.0 Hz), 17.7 (dd, J_{CP} = 4.0, 10.0 Hz), 19.9 (d, J_{CP} = 24.0 Hz), 24.7 (dd, J_{CP} = 3.8, 19.4 Hz), 25.5 (dd, J_{CP} = 3.8, 18.5 Hz), 38.7, 48.8 (d, J_{CP} = 27.5 Hz), 148.6 (C-*ipso*). ³¹P NMR (CD₃CN) δ : 62.6 (1P, d, J_{PP} = 400 Hz), 73.16 (1P, d, J_{PP} = 400 Hz).

Synthesis of 13

To a solution of **12** (35.5 mg, 0.051 mmol) in acetonitrile (1 mL) was added a solution of 4-(trifluoromethyl)benzyl bromide



Scheme 4 Preparation of Pt carbonyl complex 14 bearing a triazolylidene ligand *trans* to CO.

(13.4 mg, 0.102 mmol, 1.1 eq) in acetonitrile (0.5 mL). The resulting solution was heated in a closed vessel at 70 °C for 48 h. ³¹P{¹H} NMR showed quantitative formation of **13** as a single product. The solvent was evaporated and the residue was washed with hexane and toluene (3 × 3 ml) and extracted with THF (3 × 3 ml). The combined fractions were evaporated resulting in pure complex **13** (36 mg, 73%). ¹H NMR (CD₃CN) δ : 4.0 (2H, d, J_{HP} = 9.9 Hz), 5.5 (2H, d, J_{HP} = 7.2 Hz), 5.91 (2H, s), 7.52–7.89 (24H, m). ¹³C NMR (CD₃CN) δ : 30.4 (d, J_{CP} = 37.5 Hz), 44.7 (d, J_{CP} = 43.3 Hz), 125.8 (q, CF₃), 129.1, 129.3, 129.5, 129.7, 132.3 (d, J_{CP} = 2.5 Hz), 132.7 (d, J_{CP} = 2.6 Hz), 133.2 (d, J_{CP} = 2.4 Hz), 133.3 (d, J_{CP} = 2.3 Hz), 133.5 (d, J_{CP} = 2.3 Hz), 133.7(d, J_{CP} = 2.4 Hz), 136.3, 147.3 (C-*ipso*). ¹⁹F NMR (CDCl₃) δ : -62.5. ³¹P NMR (CDCl₃) δ : 44.4 (1P, d, J_{PP} = 436 Hz), 31.28 (1P, d, J_{PP} = 436 Hz). *m/z* (HRMS-ESI) M-H 931.0328, C₃₆H₂₉N₃F₃P₂ClPt calcd: 931.0309.

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‡ Crystal data for 11: pale-brown plates, $C_{17}H_{35}I_2N_3P_2Pd$, M = 703.62, triclinic, a = 8.545(2), b = 11.233(2), c = 13.533(3) Å, $\alpha = 9.60(2)$, $\beta = 88.03(2)$, $\gamma = 85.80(2)^\circ$, U = 1294.7(5) Å³, T = 293 K, space group $P\overline{1}$ (no 2), Z = 2, 10612 reflections were measured, 4442 unique ($R_{int} = 0.0726$) which were used in all calculations. The final *R*-factors was 0.0569 for reflections with $I > 2\sigma(I)$ and 0.0934 (all data).

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