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Inorganic click (iClick) synthesis of heterotrinuclear Pt^{II}/Au^{I}_2 complexes†

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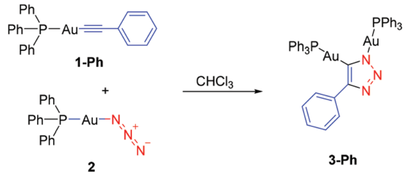
Metal-azide–metal-acetylide cycloaddition (iClick) reactions to synthesize heterotrimetallics and an unexpected novel tetranuclear gold(I) complex, are described. In addition, a discussion regarding the connection between traditional azide–alkyne cycloaddition reactions and iClick is presented focusing on applications towards linking multiple metal ions.

Few reactions rival the utility of the Click[1] classified Cu^I-catalyzed azide–alkyne cycloaddition (CuAAC)[2] for its ease of use in building molecules with high yield, regiospecificity, and atom economy. Multiple review articles detail the diverse applications of both the Huisgen 1,3-dipolar cycloaddition[3] and CuAAC,[2] with special attention given to building macromolecules.[4] It is exciting to imagine the extension of this powerful synthetic tool by incorporating metal ions. Azide–alkyne cycloadditions within a metal coordination sphere[5] and pendant ligands are known,[6] though only recently the direct linking of *two* metal ions *via* azide–acetylide cycloaddition was achieved.[6] We reported the iClick reaction involving the cycloaddition of a metal-azide‡ with a metal-acetylide to yield a 1,4,5-substituted 1,2,3-triazolate bridged dimetallic complex. Specifically, $PPh_3Au^IN_3$ (**1-Ph**) reacts with $PPh_3Au^IC{\equiv}CC_6H_5$ (**2**) to give 1-5-$[PPh_3Au^I]_2(\mu\text{-}N_3C_2\text{-}4\text{-}C_6H_5)$ (**3-Ph**; where, N_3C_2 = 1,2,3-triazolate) in 88% isolated yield (eqn (1)).[6]



(1)

Fig. 1 describes an analogy between iClick and the most notable Click reaction, CuAAC. Importantly, it shows how this synthetic technique potentially translates to the construction of *multi-metallic* materials. One notable difference is CuAAC reactions normally provide disubstituted 1,4-triazoles, whereas in iClick reactions, trisubstituted 1,4,5-triazoles form selectively. Fig. 1**A** depicts a prototypical CuAAC and the analogous reaction between a metal-azide and a metal-acetylide. In Fig. 1**B**, a metal-diacetylide reacts with two equivalents of metal-azide or *vice versa* (not drawn) to give trimetallic complexes, analogous to a double azide cycloaddition to an arenediyne. Another illustration of this concept appears in Fig. 1**C**. A mixed metal-azide–acetylide combines to create a metallopolymer, analogous to step-growth polymerization of azide–alkyne monomers.[4a–d] In the case where M = M′ a homometallic material forms; in the case of M ≠ M′ the result is a perfectly alternating heterometallic material. In Fig. 1**D**, step growth of organo-diazides with diacetylenes[4a–d] are akin to a reaction between a metal-diazide ($M{-}(N_3)_2$) and a metal-diacetylide ($M'{-}(C{\equiv}CR)_2$).

Here, we present significant progress towards realizing this new synthetic method for linking metal ions between triazolate bridges by extending, both literally and figuratively, iClick to the synthesis and characterization of heterotrimetallic Pt^{II}/Au^{I}_2 complexes.

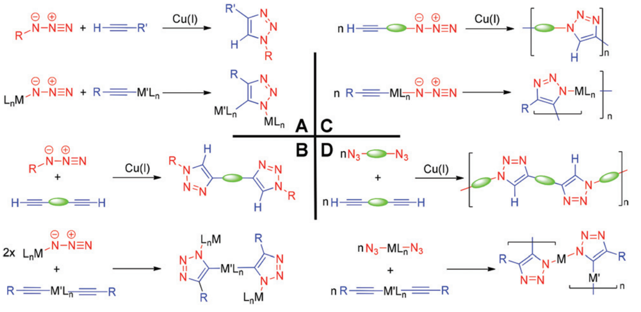


Fig. 1 CuAAC analogy with metal-azide–metal-acetylide iClick reactions.

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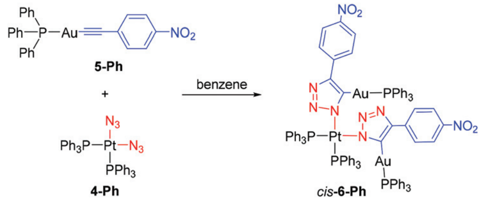


(2)

In an example of case **B** (Fig. 1), treating *cis*-$(PPh_3)_2Pt^{II}(N_3)_2$ (**4-Ph**)[7] with two equivalents of $PPh_3Au^IC{\equiv}CC_6H_4NO_2$ (**5-Ph**; where $C_6H_4NO_2$ = *p*-nitrophenyl)[8] in benzene (50 °C) provides the yellow heterotrimetallic complex *cis*-$(PPh_3)_2Pt^{II}$-1,5-$[PPh_3Au^I(\mu\text{-}N_3C_2\text{-}4\text{-}C_6H_4NO_2)]_2$ (*cis*-**6-Ph**) in 92% isolated yield *via* convenient filtration from the reaction medium (eqn (1)). A $^{31}P\{^1H\}$ NMR spectrum of *cis*-**6-Ph** exhibits two resonances, a singlet at 43.53 ppm for PPh_3 ligands bonded to Au^I, and a singlet at 7.79 ppm featuring satellites (J_{PtP} = 3095.32 Hz), for the PPh_3 with platinum connectivity. This reaction embodies the Click mantra, as it proceeds in very high yields, with high regioselectivity, and provides an isolable product that is synthesized from easily obtained starting materials. ^{31}P NMR data indicates a single cycloaddition occurs first; the phosphorous resonance due to **4-Ph** disappears with concomitant appearance of two doublets at 8.09 (J_{PP} = 21.27; J_{PtP} = 3093.47 Hz) and 11.19 ppm (J_{PP} = 21.99; J_{PtP} = 3573.66 Hz), indicating the phosphorus nuclei bound to Pt^{II} are no longer equivalent. As the reaction proceeds, resonances attributable to the single cycloaddition product diminish concomitant with the emergence of *cis*-**6-Ph** signals.

The X-ray crystal structure of *cis*-**6-Ph**, confirms the result of a double iClick (Fig. 2). The asymmetric unit cell consists of four chemically equivalent, but crystallographically independent molecules, each of which have a very similar geometry (as such, and for clarity, only one of these structures is shown in Fig. 2). Complex *cis*-**6-Ph** comprises a pseudo-C_2-symmetric square-planar Pt^{II} ion bearing *cis*-PPh_3 groups and two triazolate bridges to Au^IPPh_3 units. Interestingly, the triazolate-Au-PPh_3 ligands are positioned on opposite (*anti*) sides of the Pt^{II} square plane. This is consistent with a single cycloaddition product forming first, followed by attack of the second equivalent of **5-Ph** from the opposite, less sterically hindered, side of the square plane.

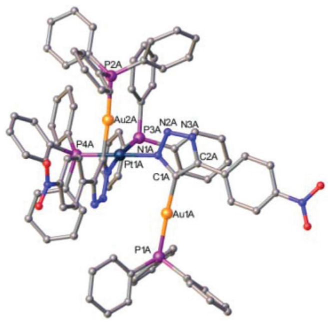
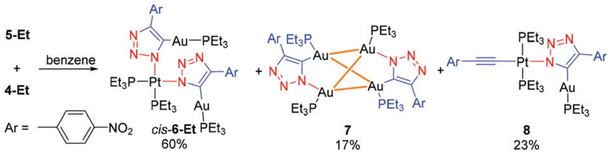


Fig. 2 Solid state molecular structure of *cis*-**6-Ph**. Hydrogen atoms and lattice solvent molecules are removed for clarity. Only one of four chemically equivalent, but crystallographically independent complexes from the asymmetric unit cell is depicted in the figure. Selected bond lengths (Å) and angles (°): Pt1–N1 = 2.040(7), Pt1–N5 = 2.073(7), Au1–C1 = 2.036(10), Au2–C27 = 2.020(10), N1–Pt1–N5 = 86.2(3), N5–Pt1–P4 = 89.3(2), P4–Pt1–P3 = 98.25(9), P3–Pt1–N1 = 86.3(2), C1–Au1–P1 = 176.0(3), C27–Au2–P2 = 173.6(3).



(3)

Replacing all the PPh_3 ligands with more basic, yet conically smaller PEt_3 ligands alters the chemistry in a notable way. Treating *cis*-$(PEt_3)_2Pt^{II}(N_3)_2$ (**4-Et**)[9] in benzene with two equivalents of $PEt_3Au^IC{\equiv}CC_6H_4NO_2$ (**5-Et**) provides the yellow heterotrimetallic complex *cis*-$(Et_3P)_2Pt^{II}$-1,5-$[PEt_3Au^I(\mu\text{-}N_3C_2\text{-}4\text{-}C_6H_4NO_2)]_2$ (*cis*-**6-Et**) as a crystalline solid. However, two other products also precipitate from the reaction mixture (in the ratios depicted in eqn (3)), as determined by $^{31}P\{^1H\}$ NMR spectroscopy ($CDCl_3$), and both are identifiable (see ESI†) (eqn (3)). Fortunately, the major component of the mixture, the double iClick product *cis*-**6-Et**, is isolable in 35% yield as single crystals *via* fractional crystallization from benzene. Again, the product contains a pseudo-C_2-symmetric square planar Pt^{II} ion with *cis*-phosphines and triazolate links to *anti* disposed Au^IPEt_3 units. A notable structural difference between *cis*-**6-Et** (Fig. 3) and *cis*-**6-Ph** is that the triazolate rings in *cis*-**6-Ph** are nearly perpendicular (~83.71°) to the square plane, whereas in *cis*-**6-Et** the rings are significantly canted (~66.20°), most likely a result of the relaxed steric congestion within *cis*-**6-Et**.

A minor product that is the result of ligand exchange is complex **8**. Azide exchange for acetylide at the Pt^{II} ion, and a single cycloaddition provides complex **8**. Multinuclear and 2-D NMR spectroscopy data provides reasonable evidence for the identity of **8**, though its isolation from the product mixture was not possible. In a somewhat cleaner reaction, treating *trans*-$(PEt_3)_2Pt(N_3)_2$ with two equivalents of **5-Et** provides **8**; however, a small amount of inseparable **7** (5%; NMR) also forms, thus precluding combustion analysis.

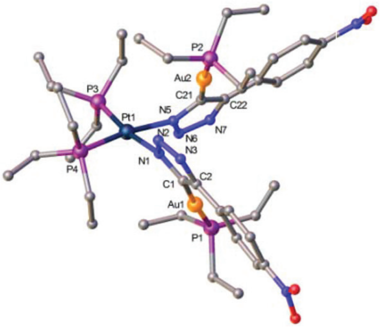
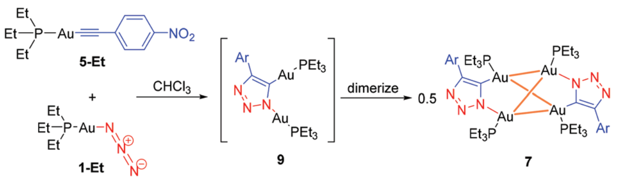


Fig. 3 Solid state molecular structure of *cis*-**6-Et**. Hydrogen atoms and disordered atoms are removed for clarity. Selected bond lengths (Å) and angles (°): Pt1–N1 = 2.064(7), Pt1–N5 = 2.057(7), Au1–C1 = 2.044(9), Au2–C27 = 2.017(9), N1–Pt1–N5 = 87.1(3), N5–Pt1–P3 = 85.9(2), P3–Pt1–P4 = 102.05(8), P4–Pt1–N1 = 85.3(2), C1–Au1–P1 = 175.9(3), C27–Au2–P2 = 175.4(3).

The third component, complex **7**, forms from Au^{I}-acetylide–azide ligand exchange and subsequent homo Au^{I}–Au^{I} cycloaddition to provide the intermediate digold complex **9**, which then dimerizes to yield the unique tetragold cluster complex **7**. Evidence for this sequence of events comes from an alternative synthesis of **7** by employing **9**[10] purposely generated *in situ* (eqn (3)). Treating **5-Et** with PEt$_3$Au^{I}N$_3$ (**1-Et**) provides **7** in 88% yield.



(4)

An X-ray crystal structure of **7** provides its solid state structure, which comprises two dinuclear gold units held together by aurophilic interactions to create a pseudo C_2-symmetric distorted tetrahedral geometry of Au^{I} ions (Fig. 4). The four Au–Au interactions range from 3.0099(11) to 3.0923(11) Å with an average of 3.0527(11) Å, well within the acceptable length for a bond.[11] Distortion from a pure tetrahedron is due to the triazolate bridges that prevent close contacts between Au1–Au3 (3.9357(11) Å) and Au2–Au4 (3.9121(11) Å), which are well above the sum of two van der Waals radii for Au^{I} (3.80 Å).

In both *cis*-**6-Ph** and *cis*-**6-Et**, the Au^{I} ions orient *anti* relative to each other. To create a Au^{I}–Au^{I} interaction, and to demonstrate the synthetic diversity of iClick, we sought to forcibly constrain the Au^{I} ions on the same side of the Pt^{II} square plane. Tethering the Au^{I}-acetylide units across a bis(diphenylphosphino)methane (dppm) bridge provides the necessary structural constraint. Treating **4-Et** with [Au^{I}(C≡CC$_6$H$_4$NO$_2$)]$_2$(μ-dppm) (**10**) provides the trimetallic Pt^{II}/Au$^{I}_2$ complex **11** in 36% yield.

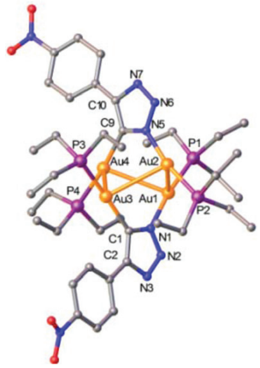
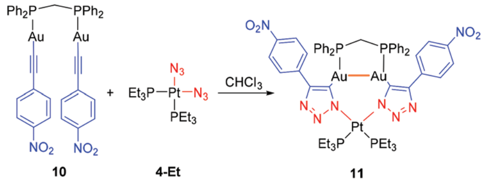


Fig. 4 Solid state molecular structure of **7**. Hydrogen atoms and disordered atoms are removed for clarity. Selected bond lengths (Å) and angles (°): Au1–N1 = 2.062(12), Au2–N5 = 2.052(13), Au3–C1 = 2.039(15), Au4–C9 = 2.061(18), Au1–Au2 = 3.0245(11), Au2–Au3 = 3.0842(11), Au3–Au4 = 3.0099(11), Au4–Au1 = 3.0923(11), Au1–Au3 = 3.9360(11), Au2–Au4 = 3.9120(11), P1–Au1–N1 = 171.9(6), P2–Au2–N5 = 170.1(7), P3–Au3–C1 = 172.1(7), P4–Au4–C9 = 173.0(7).



(5)

Orange single crystals of **11** deposit from the reaction medium (CHCl$_3$) over the course of 48 h. Evidence for the identity and purity of **11** comes from a X-ray diffraction experiment performed on a single crystal (Fig. 5), NMR spectroscopy in DMSO-d_6 (**11** has low solubility in benzene, chloroform, and ethereal solvents), and combustion analysis. Complex **11** contains a square-planar Pt^{II} ion with *cis*-PEt$_3$ ligands, and a unique chelating bis-triazolate ligand that features a Au^{I}–Au^{I} interaction within the chelating fragment. The average Au–Au distance of 3.1878(10) Å is within the range of similar crystallographically characterized Au^{I}–Au^{I} diphosphine bridged complexes.[11]

Complex **11** is C_1-symmetric in the solid state, but is C_s-symmetric in solution. A ^{1}H NMR spectrum of **11** features diastereotopic methylene protons that are well separated and appear as a doublet of triplets, indicative of the C_s-symmetry and their unique chemical environments (δ 5.20 ppm, dt, J_{PH} = 13.4 and 13.4 Hz; δ 3.70 ppm, dt, J = 14.5 and 10.9 Hz). A ^{31}P{^{1}H} NMR spectrum of **11** indicates each set of phosphorous atoms are equivalent (Au–P = 36.4 ppm; Pt–P = −1.6 ppm); a fluxional ring flip occurs in solution resulting in a mirror plane of symmetry that bisects the methylene carbon and Pt^{II} ion.

In conclusion this work establishes iClick as a convenient method for linking multiple metal ions across triazolate bridges to build heterotrimetallic complexes. In the vein of building multi-metallic materials, the iClick reaction is unique because the synthesis of well-defined heterometallic complexes is possible by simple choice of metal-azide–metal-acetylide pairing. In one case presented, smaller and more basic PR$_3$ ancillary ligands lead to a mixture of products including the unique tetragold cluster **7**. A point worthy of discussion is the observed exclusive formation of 1,4,5-triazolate isomers, in

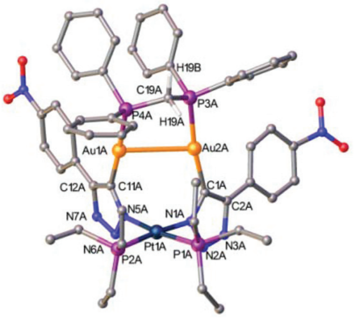
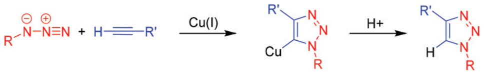
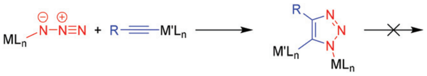


Fig. 5 Solid state molecular structure of **11**. Hydrogen atoms and disordered atoms are removed for clarity. Selected bond lengths (Å) and angles (°): Au1–Au2 = 3.1631(11), Pt1–N1 = 2.025(15), Pt1–N5 = 2.042(14), Au1–C11 = 2.055(14), Au2–C1 = 2.036(16), P1–Pt1–P2 = 94.4(3), P2–Pt1–N5 = 92.7(5), N5–Pt1–N1 = 84.7(6), N1–Pt1–P1 = 88.5(4).

which the Au^I ion is in the 5-position. At first this may appear to conflict with the regiospecific formation of 1,4-triazoles in CuAAC. However, in the generally accepted CuAAC mechanism, a Cu^I substituted 1,4,5-triazolate intermediate forms; subsequent hydrolysis places a proton in the 5-position producing the 1,4-triazole isomer (eqn (5)). In iClick (eqn (6)), hydrolysis does not occur (though it could, depending on the choice of metal ion and conditions), thus arresting the reaction at the 1,4,5-triazolate intermediate, which coincidentally provides indirect support for the role of Cu^I in CuAAC. Work continues to elucidate conditions and reagents that produce multimetallic complexes with iClick according to Fig. 1**C** and **D**.



(6)



(7)

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Notes and references

‡Note: metal-azides are known to be explosive and should be handled with the appropriate level of precaution and safety measures.

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