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Toward Permetalated Alkyne/Azide 3 + 2 or “Click” Cycloadducts

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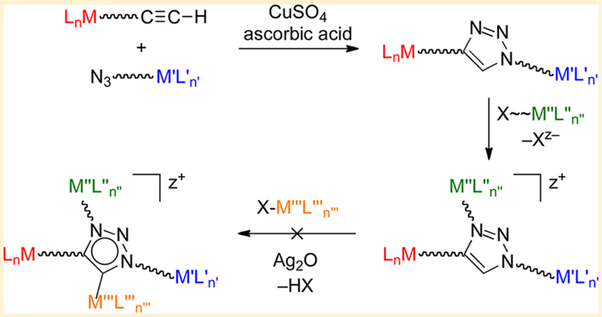
Supporting Information



ABSTRACT: The Cu(I)-catalyzed reaction of the platinum butadiynyl complex *trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_2H$ and rhenium cyclopentadienylazide complex $(\eta^5\text{-}C_5H_4N_3)Re(CO)_3$ yields the 1,2,3-triazole *trans*-$(C_6F_5)(p\text{-}tol_3P)_2PtC{\equiv}C\overline{C{=}CHN((\eta^5\text{-}C_5H_4)Re(CO)_3)N{=}N}$ (54%), which upon treatment with $Re(CO)_5OTf$ or $Re(CO)_5Br$ affords $Re(CO)_5{}^+TfO^-$ or *cis*-$Re(CO)_4Br$ adducts derived from attack at N(3) (84−98%). The crystal structures of solvates of these three complexes are compared, but attempts to metalate the =CH groups were unsuccessful. However, the reaction of monometallic *trans*-$(C_6F_5)(p\text{-}tol_3P)_2PtC{\equiv}C\overline{C{=}CHN(CH_2C_6H_5)N{=}N}$ and MeI gives an N(3)-methyl triazolium salt (81%), which upon addition of Ag_2O and $[RhCl(cod)]_2$ yields the N-heterocyclic carbene complex *trans*-$(C_6F_5)(p\text{-}tol_3P)_2PtC{\equiv}C\overline{C{\cdots}C(RhCl(cod)){\cdots}N(CH_2C_6H_5){\cdots}N{\cdots}N}(Me)$. Further experiments and analyses suggest that =CH derivatization is possible only when the ^1H NMR chemical shift is downfield of ca. δ 7.9 ppm. Electropositive metal fragments generally effect upfield shifts, meaning that insulating spacers, electronegative ligands, and/or new chemical methodologies will be required to construct tetrametallic arrays via click chemistry.

Molecular frameworks that can incorporate tailor-made heteromultimetallic arrays—to wit, M, M′, M″, M‴, M⁗ or, more ambitiously, *a*M, *b*M′, *c*M″, *d*M‴, *e*M⁗—might serve as precursors to unusual bulk or nanoscopic species. To our knowledge, the most advanced efforts along these lines are those of Lang,[1,2] who has synthesized a molecule with one of each of six different metal atoms: iron, ruthenium, rhenium, gold, copper, and titanium (**1**). As shown in Scheme 1 (top), this species features carbon-rich alkyne and/or arene bridging units. However, certain metal atoms in **1** would be challenging to vary; a number of limitations are obvious.

The copper catalyzed “click” 3 + 2 cycloaddition of terminal alkynes and azides to give 1,2,3-triazoles[3] is seeing ever-increasing use in metal coordination spheres,[4,5] and similar reactions without added catalysts have also been reported.[6,7] As depicted in Scheme 1 (middle), we have shown that the platinum polyynyl complexes *trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_nH$ (**2**; *n* = 2−6) efficiently undergo click reactions with organic azides to give **3**.[8] Others have employed ethynyl moieties appended to various metal ligands,[4] as well as azido species that incorporate metals.[4e,6,7] In any case, the resulting triazoles have two additional sites that are amenable to functionalization: (a) the nucleophilic lone pair of the unsubstituted nitrogen atom (N3) that is remote from the substituted nitrogen atom (N1) and (b) the moderately acidic proton of the =CH moiety,[9] abstraction of which can lead to an “abnormal” or “mesionic”[10] N-heterocyclic carbene complex.

Hence, 1,2,3-triazole cores could seemingly serve as versatile templates for assemblies containing four different transition-metal atoms, and we set out to explore protocols toward this end. In recent work, Viege has demonstrated that the gold azide and alkynyl complexes Ph_3PAuN_3 and $PhC{\equiv}CAuPPh_3$ undergo an uncatalyzed 3 + 2 cycloaddition at room temperature to give the digold complex **4** shown in Scheme 1 (bottom) in 88% yield after workup.[7] In this study, we report the first click-derived trimetallic triazole derivatives, attendant crystallographic data, and results relevant to further metalations.

Accordingly, equimolar quantities of the platinum butadiynyl complex *trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_2H$ (**2a**)[11] and the rhenium cyclopentadienylazide complex $(\eta^5\text{-}C_5H_4N_3)Re(CO)_3$ (**5**)[12] were combined in DMF. As shown in Scheme 2, $CuSO_4{\cdot}5H_2O$ (1.6 mol %), ascorbic acid (2.3 mol %), and water were added. Workup gave the anticipated product, the heterobimetallic cycloadduct **6**, as a white solid in 54% yield. Complex **6**, and all other new compounds isolated below, were characterized by NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy and microanalysis, as summarized in the Supporting Information. The spectroscopic properties of **6** combined features typical of monosubstituted cyclopentadienyl complexes of rhenium tricarbonyl with those of the adduct **3a** in Scheme 1.

The introduction of a third metal was sought. Accordingly, **6** was combined with 1.15 equiv of the rhenium triflate $Re(CO)_5OTf$[13] in CH_2Cl_2. After 5 days at room temperature, workup gave the triazolium triflate salt 7^+TfO^-, derived from electrophilic attack at N(3), as a white solid in 84% yield.

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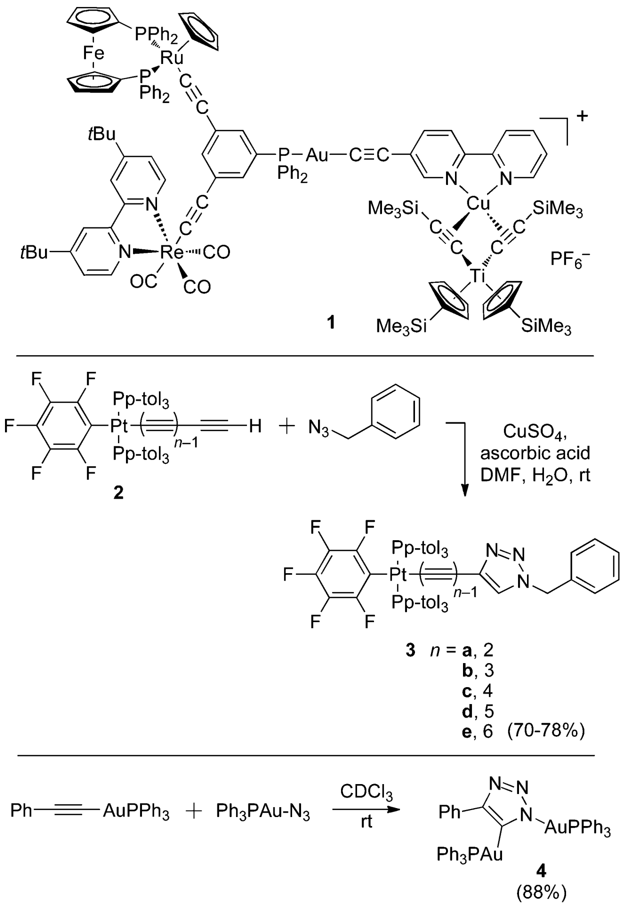
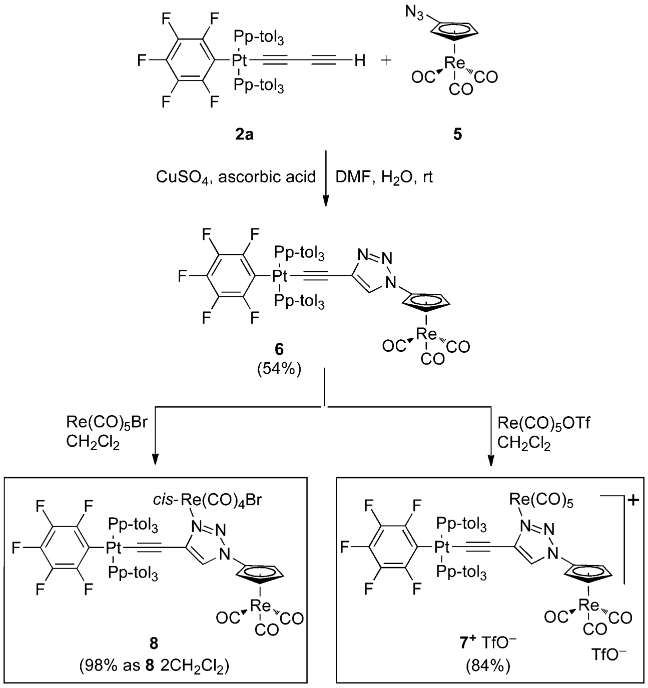
Scheme 1. A Complex with Six Different Transition-Metal Atoms (Top) and Some Previously Reported Alkyne/Azide 3 + 2 Cycloadditions in Metal Coordination Spheres (Middle, Catalyzed; Bottom, Uncatalyzed)



Scheme 2. Triply Metalated Alkyne/Azide 3 + 2 Cycloadducts



The NMR and IR properties of $7^{+}TfO^{-}$ were similar to those of **6**, but with signals characteristic of a $Re(CO)_5$ fragment, suggesting the structure depicted in Scheme 2. An analogous reaction of **6** and the less electrophilic rhenium bromide $Re(CO)_5Br$ was slower. After 10 days, workup gave the solvate **8**$\cdot 2CH_2Cl_2$ as a white solid in 98% yield. The IR and other data suggested the nonionic structure shown in Scheme 2.

Single crystals of the solvates **6**$\cdot 2CH_2Cl_2$, $7^{+}TfO^{-}\cdot CH_2Cl_2$, and **8**$\cdot 2CH_2Cl_2$ were grown, and the X-ray structures were determined as described in the Supporting Information. The thermal ellipsoid diagrams in Figures 1−3 confirm the proposed formulations. In the last structure, the bromide ligand of the *cis*-$Re(CO)_4Br$ moiety was disordered over two positions (84:16). With the cationic complex $7^{+}TfO^{-}\cdot CH_2Cl_2$, the N1−N2 and N2=N3 bond lengths (1.316(7) and 1.288(7) Å) were slightly shorter than those in the others (1.343(6)−1.348(4) and 1.323(6)−1.317(4) Å). Analogous N1−N2 contractions have been observed upon alkylations of triazoles.[14] As seen in most

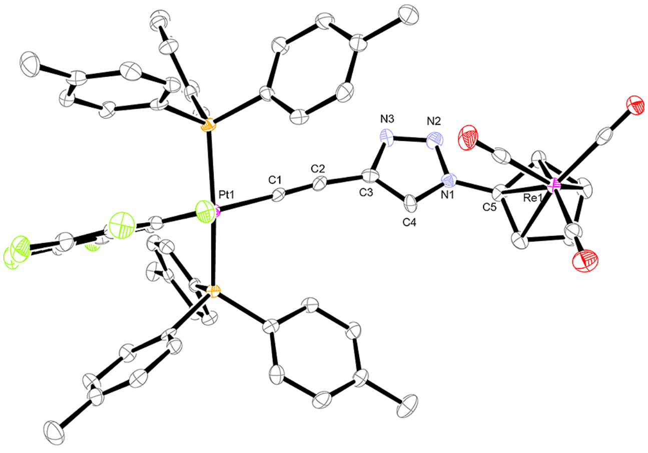


Figure 1. Thermal ellipsoid plot (50% probability level) of the molecular structure of **6**$\cdot 2CH_2Cl_2$ with the solvate molecule omitted. Key bond lengths and angles: Pt1−C1 = 1.998(4), C1≡C2 = 1.210(5), C2−C3 = 1.422(6), C3=C4 = 1.368(5), C4−N1 = 1.345(5), N1−N2 = 1.348(4), N2=N3 = 1.317(4), N3−C3 = 1.380(5); C_{ipso}−Pt1−C1 = 170.00(15), Pt1−C1−C2 = 167.7(3), C1−C2−C3 = 171.8(4).

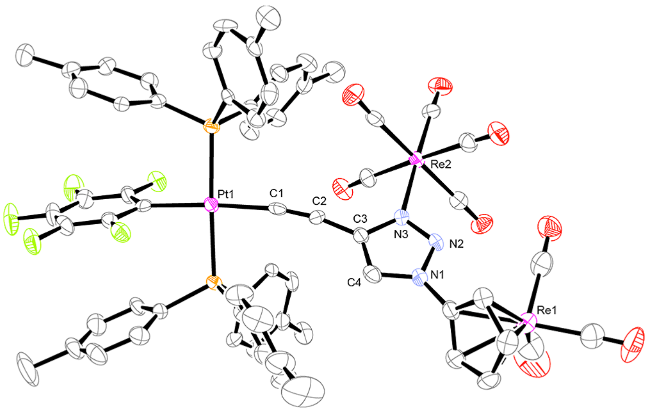


Figure 2. Thermal ellipsoid plot (50% probability level) of the molecular structure of $7^{+}TfO^{-}\cdot CH_2Cl_2$ with the anion and solvate molecule omitted. Key bond lengths and angles: Pt1−C1 = 2.001(7), C1≡C2 = 1.202(9), C2−C3 = 1.414(9), C3=C4 = 1.352(10), C4−N1 = 1.351(9), N1−N2 = 1.316(7), N2=N3 = 1.288(7), N3−C3 = 1.373(8); C_{ipso}−Pt1−C1 = 175.8(3), Pt1−C1−C2 = 171.7(6), C1−C2−C3 = 169.4(7).

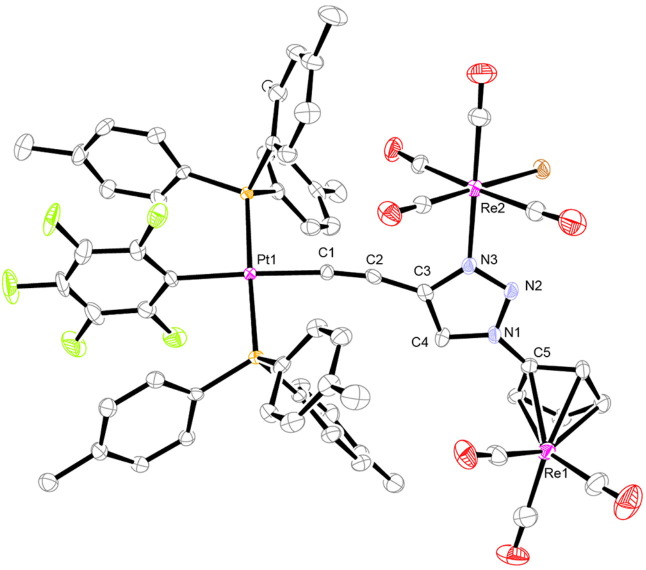


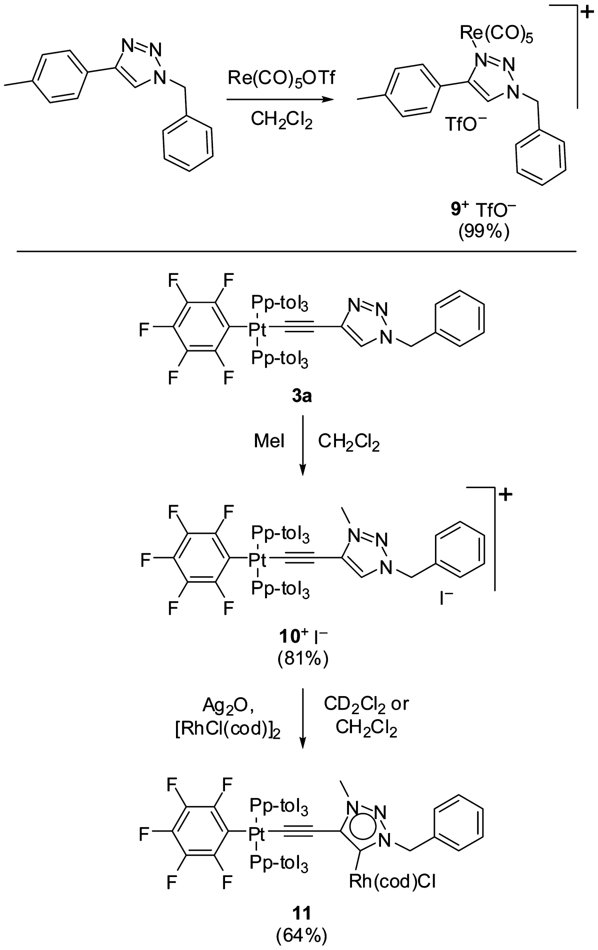
Figure 3. Thermal ellipsoid plot (50% probability level) of the dominant conformation of the molecular structure of **8**·$2CH_2Cl_2$ with the solvate molecules omitted. Key bond lengths and angles: Pt1−C1 = 1.995(5), C1≡C2 = 1.207(7), C2−C3 = 1.407(7), C3═C4 = 1.387(8), C4−N1 = 1.351(6), N1−N2 = 1.343(6), N2═N3 = 1.323(6), N3−C3 = 1.387(7); C_{ipso}−Pt1−C1 = 177.6(2), Pt1−C1−C2 = 173.4(4), C1−C2−C3 = 166.6(5).

other platinum complexes in this series, $C_6H_4CH_3/C_6F_5/C_6H_4CH_3$ stacking interactions were evident.[8]

Efforts were then directed at introducing a fourth metal at the triazole ═CH moiety. Recipes were tested that successfully afforded N-heterocyclic carbene complexes from 1,3,4-trisubstituted triazolium salts and related heterocycles.[9] Unfortunately, no reactions were observed upon treatment of 7^+TfO^- or **8**·$2CH_2Cl_2$ with Ag_2O or Cu_2O in CH_2Cl_2 at 25−40 °C. Combinations of Ag_2O and $[RhCl(cod)]_2$ or $PdCl_2(NCMe)_2$, or $[IrCl(cod)]_2$ and KO^{t}Bu,[15] also gave no reactions. In view of the structural data in Figures 1−3, and the successful metalation of triazolium salts with analogous arrays of organic substituents,[9] it was considered unlikely that these failures were due to steric effects. In order to probe for electronic effects, the monometallic triazolium salts $\mathbf{9}^+TfO^-$ and $\mathbf{10}^+I^-$ were prepared as shown in Scheme 3.

The ^1H NMR chemical shifts of the triazole or triazolium ═CH moieties in the preceding compounds proved to be particularly informative. These are summarized in Table 1, together with that of the purely organic salt $C_6H_5\overline{C{=}CHN(Et)N{=}N}(Me)]^+I^-$ ($\mathbf{12}^+I^-$).[9a] This compound readily reacts with Ag_2O to give a cationic bis(triazolylidene) silver complex that is easily transmetalated. Importantly, $\mathbf{12}^+I^-$ exhibits the most downfield ═CH signal (δ 9.52 ppm, $CDCl_3$), suggestive of the greatest acidity. In the remaining complexes, the ═CH signal generally shifts upfield as the number of electropositive metal substituents increases (δ 8.01−6.15 ppm for one metal fragment, δ 6.26 ppm for two, and δ 6.03−5.81 ppm for three).

Scheme 3. Reactions Relevant to a Fourth Metalation of Alkyne/Azide 3 + 2 Cycloadducts



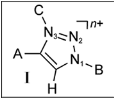
$\mathbf{9}^+$ TfO^- (99%)

3a

$\mathbf{10}^+$ I^- (81%)

11 (64%)

Table 1. ═CH ^1H NMR Data for Compounds with the Structural Unit I

	*n*	A	B	C	δ, ═CH (ppm)
8	0	$ArL_2PtC{\equiv}C^a$	$(C_5H_4)Re(CO)_3$	$Re(CO)_4Br$	5.81^c, 5.73^b
$\mathbf{7}^+$ TfO^-	1	$ArL_2PtC{\equiv}C^a$	$(C_5H_4)Re(CO)_3$	$Re(CO)_5$	6.03^c, 6.09^b
6	0	$ArL_2PtC{\equiv}C^a$	$(C_5H_4)Re(CO)_3$	---	6.26^b
3a	0	$ArL_2PtC{\equiv}C^a$	CH_2Ph	---	6.15^b
$\mathbf{9}^+$ TfO^-	1	$CH_3C_6H_5$	CH_2Ph	$Re(CO)_5$	7.83^b
$\mathbf{10}^+$ I^-	1	$ArL_2PtC{\equiv}C^a$	CH_2Ph	Me	8.01^c
$\mathbf{12}^+$ I^-	1	Ph	Et	Me	9.52^b

[a] ArL_2 = *trans*-$(C_6F_5)(p\text{-}tol_3P)_2$. [b] In $CDCl_3$. [c] In CD_2Cl_2.

The monometallic triazolium salt $\mathbf{9}^+TfO^-$ (δ 7.83 ppm, $CDCl_3$) was similarly inert under the conditions investigated for the further metalation of the trimetallic complexes **8**·$2CH_2Cl_2$ and $\mathbf{7}^+TfO^-$. However, the salt $\mathbf{10}^+I^-$, in which the metal fragment is insulated from the triazolium core by a C≡C unit, reacted with Ag_2O and $[RhCl(cod)]_2$. Clean conversion to the bimetallic N-heterocyclic carbene complex **11** shown in Scheme 3 occurred, as assayed by ^1H NMR and evidenced by a characteristic ^{13}C NMR signal at δ 168.6 ppm (d, $^1J_{CRh}$ = 46.9 Hz).[9a,c] Accordingly, $\mathbf{10}^+I^-$ exhibits the second most deshielded ═CH ^1H NMR signal in Table 1 (δ 8.01 ppm, CD_2Cl_2). Hence, a chemical shift of ca. δ 7.9 ppm seems to represent an operational cutoff for elaborating this carbon atom to a carbene complex under the conditions investigated.

In summary, this work has significantly expanded the scope of “click” chemistry in metal coordination spheres. Given that alkynyl, azide, and electrophilic derivatives of every transition metal are known, this methodology should allow the facile assembly of virtually any hetereotrimetallic combination. However, a comparatively versatile introduction of a fourth metal onto the triazole or triazolium core must await one of two developments. The most desirable would be the discovery of new =CH functionalization methodologies that are not as sensitive to proton acidity. Alternatively, more electronegative metal fragments could be employed, possibly in conjunction with spacers that would enhance insulation from the heterocycle core. Efforts toward these ends will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and tables giving experimental procedures and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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