Azide alkyne cycloaddition facilitated by hexanuclear rhenium chalcogenide cluster complexes

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Azide alkyne cycloaddition facilitated by hexanuclear rhenium chalcogenide cluster complexes†

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Two hexanuclear rhenium clusters containing azide ligands, $[Re_6Se_8(PEt_3)_5(N_3)]BF_4$ and $[Re_6Se_8(PEt_3)_4(N_3)_2]$, were synthesized from the analogous pyridine complexes and fully characterized. Studies show that $[Re_6Se_8(PEt_3)_5(N_3)]BF_4$ reacts with activated alkynes, dimethyl acetylenedicarboxylate and methyl 4-hydroxy-hex-2-yneoate, to form the triazolate cluster complexes $[Re_6Se_8(PEt_3)_5(L1 \text{ or } L2)]BF_4$ (where L1 = 4,5-bis(methoxycarbonyl)-1,2,3-triazol-2-yl and L2 = 4-methoxycarbonyl-5-(1-propanol)-1,2,3-triazol-2-yl). The bis-triazolato complex, *cis*-$[Re_6Se_8(PEt_3)_4(L1)_2]$ was also prepared *via* a similar reaction starting with *cis*-$[Re_6Se_8(PEt_3)_4(N_3)_2]$ demonstrating that these clusters can promote two azide moieties to undergo heterocyclic ring formation. The structures of $[Re_6Se_8(PEt_3)_5(N_3)]BF_4$, $[Re_6Se_8(PEt_3)_4(N_3)_2]$, and $[Re_6Se_8(PEt_3)_5(L1)](BF_4)$, were determined by single-crystal X-ray diffraction analysis. In addition, studies involving the alkylation of $[Re_6Se_8(PEt_3)_5(L1)]BF_4$ with benzyl bromide and methyl iodide are reported.

Introduction

Since 2001 when Sharpless and co-workers introduced 'click chemistry', an innovative approach to organic synthesis,[1] it has become widespread, especially for its use in the formation carbon–heteroatom bonds.[2–7] Click reactions are modular, have simple reaction conditions, are stereospecific, and generate readily isolable products in high yield. Of the different classes of transformations in the click chemistry toolbox, cycloaddition reactions, such as 1,3-dipolar and hetero-Diels-Alder, lead to a wide range of 5 and 6 membered heterocyclic rings. In particular, the azide–alkyne cycloaddition (AAC) reaction which forms 1,2,3-triazoles has received the most attention.[3–5,8,9] This is due in part to the discovery of Cu(I) and Ru(II) catalysts which greatly increase the rate and selectivity of triazole formation (Scheme 1).[10–12] Other features which make this reaction favorable include: the synthetic ease with which azide and alkyne moieties can be introduced, the fact that the formation of the triazole ring is highly exothermic, the relative stability of azides and alkynes to nucleophilic and electrophilic attack, and that triazole rings are relatively robust to hydrolysis.[7,10–12] All of these factors have enabled the AAC reaction to be adapted for use in a wide variety of applications, including organic synthesis, medicinal chemistry, materials science and chemical biology.[13] The majority of these AAC reactions focus on organic azides reacting with alkynes in the presence of a catalyst or *in situ* (in the absence of metal ions) using template directed synthesis. The first report of a transition metal azide reacting with alkynes to form triazolate rings was reported in 1982;[14] since then there have been several reports of similar reactions with other transition metal azide complexes.[15–18] However, most of these studies involve the more electron rich (mostly organometallic) azide complexes.[15–17] Recent reports of cycloaddition reactions leading to the formation (triazolato)transition metal complexes

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†Electronic supplementary information (ESI) available: An alternative synthesis of **1** starting from $[Re_6Se_8(PEt_3)_5I]$. The ^1H and $^{31}P \{^1H\}$ NMR spectral data for the reaction mixture containing **3** and BnBr, as well as for the reaction of **3** and MeI. The ^1H and $^{31}P \{^1H\}$ NMR spectral data of **7**. IR spectral data for **2**, **3**, **6**, and **7**. CCDC 924492–924494. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50436k

Scheme 1 Azide–alkyne cycloaddition catalyzed by both Cu(I) to form 1,4-disubstituted-1,2,3-triazoles and by $Cp*Ru(PPh_3)_2Cl$ to form 1,5-disubstituted-1,2,3-triazoles.

include: [3 + 2] cycloaddition of gold(I) alkynyls,[19] the first all inorganic click (iClick) reaction,[20] and a study examining the AAC reactivity of first row transition metal azide complexes with biomimetic (*i.e.* N and O donor chelate) type ligands.[21]

Our interest in the AAC reaction began with our finding that rhenium based clusters can facilitate dipolar cycloaddition reactions between nitriles and azides. Specifically, nitriles (acetonitrile and various benzonitriles) coordinated to the $[Re_6Se_8]^{2+}$ cluster core react with inorganic azides to form tetrazolate rings (see eqn (1)), with some of the reactions occurring within minutes at room temperature.[22,23] The observed formation of tetrazolate rings on this cluster core made us curious whether or not triazolate ring formation could be promoted as well. Towards this end, we prepared both mono- and bis-azido $[Re_6Se_8]^{2+}$ cluster complexes and examined their reactivity with alkynes such as dimethyl acetylenedicarboxylate. To the best of our knowledge, there is only one report of an (azido)manganese complex reacting with an activated alkyne to form a triazolate ring.[24] There are reports of rhenium metal complexes being involved in click chemistry; however, there are no reports of Re–N$_3$ moieties undergoing cyclization reactions (instead, the reports involve AAC reactions taking place *outside* the primary coordination sphere).[25] Our study is significant in that it marks the first investigation into the reactivity of the (azido)rhenium moiety and is the first example of triazolate formation at a rhenium center.

$$(1)$$
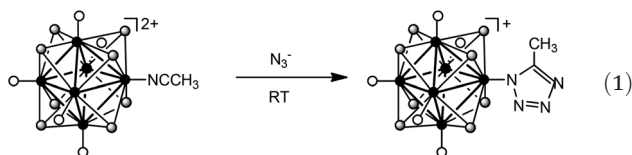
Experimental

EXTREME CAUTION. *Sodium azide can explode on heating, and contact of metal azides with acids liberates the highly toxic and explosive hydrazoic acid. In addition, reactions of silver(I) and sodium azide can lead to formation of the explosive silver azide. All reactions involving azides and triazoles should be treated as potentially explosive and shock sensitive, and handled in small quantities in an appropriate manner!*

General methods and materials

The rhenium cluster complex starting material, $[Re_6Se_8(PEt_3)_5I]I$ was prepared according to a previously published method.[26] The synthesis of the bis-pyridine complex *cis*-$[Re_6Se_8(PEt_3)_4(py)_2](BF_4)_2$ is an alternative synthesis to the previously reported preparation.[27] Rhenium metal was purchased from Cerac, and pyridine was distilled prior to use. Air and moisture-sensitive materials were stored under argon in an inert atmosphere glove box and all reactions were run under an atmosphere of $N_2(g)$. ^1H (and ^{31}P) spectra were recorded using a 400 MHz (162 MHz) Varian Mercury or a 500 MHz (202.5 MHz) Bruker Avance III NMR spectrometer equipped

with a tunable probe. All ^{31}P spectra were proton decoupled, unless otherwise noted, and externally referenced to an 85% (wt/wt) H_3PO_4 solution. Elemental analyses (EA) were performed by the Microanalysis Laboratory at the University of Illinois, Urbana; mass spectral data were also obtained at the University of Illinois. Infrared spectra (IR) were collected on a Perkin Elmer Spectrum One FT-IR spectrophotometer equipped with a germanium attenuated total reflection (Ge ATR) attachment.

X-ray crystallography

(a) General. All single crystals were grown *via* the vapor diffusion technique at −20 °C: $[Re_6Se_8(PEt_3)_5(N_3)]BF_4·3Et_2O$ were grown out of CH_3CN/Et_2O, $[Re_6Se_8(PEt_3)_4(N_3)_2]·1.5CH_2Cl_2$ utilized a mixture of $CH_2Cl_2–Et_2O$ and an acetone–Et_2O mixture was used to grow crystals of $[Re_6Se_8(PEt_3)_5(L1)]BF_4$. Crystals selected for diffraction experiments were coated with Paratone-N oil then placed under a cold N_2 gas stream on the diffractometer. All three data sets were obtained using a Bruker D8 diffractometer equipped with a SMART Apex II CCD detector with the crystals cooled to −100 °C and diffraction measurements obtained using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å). Data were corrected for absorption by Gaussian integration after face-indexing and measurement of crystal dimensions. The structures were all solved using Patterson methods and structure expansion (*DIRDIF-2008*).[28] Structures were refined by full-matrix least squares on F^2 with *SHELXL-97*.[29] Hydrogen atoms were included as riding atoms and were placed in geometrically idealized positions with isotropic displacement parameters 120% of those of the U_{eq} for their parent atoms. See Table 1 for a summary of crystallographic data.

(b) Special refinement details. (i) $[Re_6Se_8(PEt_3)_5(N_3)]BF_4·$3Et$_2$O and $[Re_6Se_8(PEt_3)_4(N_3)_2]·1.5CH_2Cl_2$: attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in PLATON.[30–32] For $[Re_6Se_8(PEt_3)_5(N_3)]BF_4·3Et_2O$ a total solvent-accessible void volume of 877.7 Å^3 with a total electron count of 591 (consistent with 12 molecules of solvent diethyl ether, or 3 molecules per formula unit of the hexarhenium complex ion) was found in the unit cell. For $[Re_6Se_8(PEt_3)_4(N_3)_2]·$1.5CH$_2Cl_2$ a total solvent-accessible void volume of 782.7 Å^3 with a total electron count of 251 (consistent with six molecules of solvent dichloromethane, or 1.5 molecules per formula unit of the hexarhenium complex ion) was found in the unit cell. (ii) $[Re_6Se_8(PEt_3)_5(L1)]BF_4$: The C1A–C3A and C1B–C3B distances were constrained to be equal (within 0.03 Å) during refinement. (b) F–B bond distances within the disordered tetrafluoroborate ion were constrained to be equal (within 0.03 Å) to a common refined value during refinement. (c) F···F distances (of F–B–F angles) within the disordered tetrafluoroborate ion were constrained to be equal (within 0.03 Å) to a common refined value during refinement.

Table 1 Crystallographic data for [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]BF$_4$·3Et$_2$O, cis-[Re$_6$Se$_8$(PEt$_3$)$_4$(N$_3$)$_2$]·1.5CH$_2$Cl$_2$ and [Re$_6$Se$_8$(PEt$_3$)$_5$(L1)]BF$_4$[a]

	[Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]BF$_4$·3Et$_2$O	cis-[Re$_6$Se$_8$(PEt$_3$)$_4$(N$_3$)$_2$]·1.5CH$_2$Cl$_2$	[Re$_6$Se$_8$(PEt$_3$)$_5$(L1)]BF$_4$
Formula	C$_{30}$H$_{75}$BF$_4$N$_3$P$_5$Re$_6$Se$_8$·3C$_4$H$_{10}$O	C$_{24}$H$_{60}$N$_6$P$_4$Re$_6$Se$_8$·1.5CH$_2$Cl$_2$	C$_{36}$H$_{81}$BF$_4$N$_3$O$_4$P$_5$Re$_6$Se$_8$
FW (g mol^{-1})	3913.26	2432.99	2610.64
Space group	C2 (No. 5)	P2$_1$/c (No. 14)	P1̄ (No. 2)
a (Å)	15.5343(8)	11.2984(6)	12.0855(6)
b (Å)	20.3729(11)	20.7624(12)	12.1341(6)
c (Å)	19.5681(11)	23.0471(13)	22.7645(11)
α (°)			98.7794(6)
β (°)	92.6900(7)	103.1417(7)	101.8551(5)
γ (°)			103.6671(6)
V (Å^3)	6186.1(6)	5264.8(5)	3102.8(3)
Z	4	4	2
T (°C)	−100	−100	−100
Radiation (λ Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ$_{calcd}$ (g cm^{-3})	2.889	3.069	2.794
μ (mm^{-1})	16.58	19.57	16.52
Flack parameter	0.024(9)		
R$_1$ [I ≥ 2σ(I)]	0.0284	0.0362	0.0285
wR$_2$ [all data]	0.0758	0.0810	0.0776

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; wR$_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^4)])^{1/2}$.

[Re$_6$Se$_8$(PEt$_3$)$_5$(py)](PF$_6$)$_2$ (1)

[Re$_6$Se$_8$(PEt$_3$)$_5$(MeCN)](PF$_6$)$_2$ (200 mg, 0.15 mmol) was dissolved in 5.0 mL of pyridine and heated at reflux for 3 d. After removal of the solvent, the solid was redissolved in CH$_2$Cl$_2$ and precipitated from Et$_2$O. Crystals (133 mg, 66%) were formed by vapor diffusion crystallization in CH$_2$Cl$_2$/Et$_2$O. δ$_H$ (400 MHz; CDCl$_3$; ppm) 9.22 (2H, d, py), 7.87 (1H, t, py), 7.34 (2H, t, py), 2.22 (24H, m, P-CH$_2$CH$_3$), 2.07 (6H, m, P-CH$_2$CH$_3$), 1.08 (45H, m, P-CH$_2$CH$_3$). δ$_P$ (162 MHz; CDCl$_3$; ppm) −25.97, −29.20. Found: C, 15.58; H, 2.76; N, 0.57. Calc. for C$_{35}$H$_{80}$NRe$_6$Se$_8$P$_7$F$_{12}$: C, 15.52; H, 2.98; N, 0.52%. ESI-MS: m/z 1209.5 ([M − 2PF$_6$]$^+$) (see the ESI† for an alternative synthesis starting from [Re$_6$Se$_8$(PEt$_3$)$_5$I]I).

[Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]BF$_4$ (2)

[Re$_6$Se$_8$(PEt$_3$)$_5$(py)](BF$_4$)$_2$ (253.6 mg, 0.103 mmol) was dissolved in 50 mL DMF in a 100 mL round bottom flask. A 105.0 mg sample of NaN$_3$ (1.62 mmol) was added to the flask and the reaction mixture was heated at reflux for 3 h. The solution was reduced to dryness in vacuo. The product was dissolved in minimal CH$_2$Cl$_2$, filtered through Celite to removed NaBF$_4$, and dripped into Et$_2$O to afford a solid (204.3 mg, 85% yield). δ$_H$ (500 MHz; CDCl$_3$; ppm) 2.11 (30H, m, P-CH$_2$CH$_3$), 1.08 (45H, m, P-CH$_2$CH$_3$). δ$_P$ (202.5 MHz; CDCl$_3$; ppm) −29.38, −29.94. MS (ESI(+)): m/z 2381.5 ([Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]$^+$). IR (Ge ATR) ν$_{max}$/cm^{-1} 2048 (N$_3$). Found: C, 15.10; H, 2.89; N, 1.76. Calc. for C$_{30}$H$_{75}$N$_3$P$_5$BF$_4$Re$_6$Se$_8$·0.1Et$_2$O C, 14.75; H, 3.09; N, 1.70%.

[Re$_6$Se$_8$(PEt$_3$)$_5$(L1)]BF$_4$ (3)

[Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]BF$_4$ (100.6 mg, 0.0408 mmol) was dissolved in 12.5 mL CH$_2$Cl$_2$ in a Schlenk flask. Subsequently, 99.8 μL dimethyl acetylenedicarboxylate (DMAD, C$_6$H$_6$O$_4$, 0.820 mmol) was added. The reaction mixture was stirred for 2 h at room temperature. The solution was reduced to dryness and precipitated from CH$_2$Cl$_2$ and Et$_2$O. Crystals were grown via vapor

diffusion crystallization in acetone/Et$_2$O to remove excess DMAD, resulting in an orange crystalline material (59.7 mg, 56% yield). δ$_H$ (500 MHz; CDCl$_3$; ppm) 3.82 (6H, s, −OCH$_3$), 2.12 (30H, m, P-CH$_2$CH$_3$), 1.10 (45H, m, P-CH$_2$CH$_3$). δ$_P$ (202.5 MHz; CDCl$_3$; ppm) −28.09, −30.21. IR (Ge ATR) ν$_{max}$/cm^{-1} 1728 (CO), 1499 (NN). MS (ESI(+)): m/z 2523.4 ([Re$_6$Se$_8$(PEt$_3$)$_5$(C$_6$H$_6$O$_4$N$_3$)]$^+$). Found: C, 16.57; H, 2.79; N, 1.65. Calc. for C$_{36}$H$_{81}$N$_3$O$_4$P$_5$BF$_4$Re$_6$Se$_8$: C, 16.56; H, 3.13; N, 1.61%.

[Re$_6$Se$_8$(PEt$_3$)$_5$(L2)]BF$_4$ (4)

A sample of [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]BF$_4$ (124.6 mg, 0.0505 mmol) was dissolved in 10 mL chlorobenzene in a round bottom flask. To the solution, 145 μL methyl 4-hydroxyhex-2-yneoate (C$_7$H$_{10}$O$_3$, 1.02 mmol) was added. The reaction mixture was heated at reflux for 2 days, and then reduced to dryness in vacuo. A crude solid was obtained after reprecipitating from CH$_2$Cl$_2$/Et$_2$O (73.8 mg). Crystals were grown via vapor diffusion using CH$_2$Cl$_2$/Et$_2$O, affording an orange crystalline material (50.2 mg, 38% yield). δ$_H$ (400 MHz; CDCl$_3$; ppm) 4.77 (1H, q, −CH−OH), 4.43 (1H, d, −CH−OH), 3.81 (3H, s, −OCH$_3$), 2.11 (30H, m, P-CH$_2$CH$_3$), 1.79 (2H, m, −CH−CH$_2$CH$_3$), 1.07 (45H, m, P-CH$_2$CH$_3$), 0.88 (3H, t, −CH−CH$_2$CH$_3$). δ$_P$ (162 MHz; CDCl$_3$; ppm) −28.38, −30.30. IR (Ge ATR) ν$_{max}$/cm^{-1} 1680 (CO), 1513 (NN). MS (ESI(+)): m/z 2524.6 ([Re$_6$Se$_8$(PEt$_3$)$_5$(C$_7$H$_{10}$O$_3$N$_3$)]$^+$). Found: C, 17.13; H, 3.12; N, 1.61. Calc. for C$_{37}$H$_{85}$N$_3$O$_3$P$_5$BF$_4$Re$_6$Se$_8$: C, 17.02; H, 3.28; N, 1.61%.

cis-[Re$_6$Se$_8$(PEt$_3$)$_4$(py)$_2$](BF$_4$)$_2$ (5)

cis-[Re$_6$Se$_8$(PEt$_3$)$_4$I$_2$] (893.9 mg, 0.2965 mmol) was dissolved in 50 mL of CH$_2$Cl$_2$ followed by a solution of 296.6 mg (1.524 mmol) of AgBF$_4$ dissolved in 25 mL of pyridine. The reaction mixture was stirred for 3 h at room temperature and the solution reduced to dryness. The product was isolated by reprecipitating from CH$_2$Cl$_2$/Et$_2$O and then dried in vacuo with heat (842.0 mg, 94% yield). δ$_H$ (500 MHz; CDCl$_3$; ppm) 9.43 (4H, m, py), 7.88 (2H, m, py), 7.41 (4H, t, py), 2.26 (12H, m,

P-CH_2CH$_3$), 2.18 (12H, m, P-CH_2CH$_3$), 1.12 (36H, m, P-CH$_2$CH_3); free pyridine is also present in the sample and appears at 8.73 (2H), 7.90 (1H), 7.52 (2H). δ_P (202.5 MHz; CDCl$_3$; ppm) −23.05, −25.99. MS (ESI(+)): m/z 1190.1 ([Re$_6$Se$_8$(PEt$_3$)$_4$(py)$_2$]$^{2+}$). Found: C, 16.77; H, 2.45; N, 1.59. Calc. for C$_{34}$H$_{70}$N$_2$P$_4$B$_2$F$_8$Re$_6$Se$_8$·0.75py C, 17.35; H, 2.85; N, 1.47%.

cis-[Re$_6$Se$_8$(PEt$_3$)$_4$(N$_3$)$_2$] (6)

A sample of cis-[Re$_6$Se$_8$(PEt$_3$)$_4$(py)](BF$_4$)$_2$ (302.2 mg, 0.1267 mmol) was dissolved in 70 mL of DMF. Subsequently, 134.8 mg (2.074 mmol) of NaN$_3$ was added to the solution. The reaction mixture was heated at reflux for 3 h and then stripped dry. After reprecipitating from CH$_2$Cl$_2$/Et$_2$O, the product was isolated (238.2 mg, 84.7% yield). δ_H (400 MHz; CDCl$_3$; ppm) 2.21 (12H, m, P-CH_2CH$_3$), 2.11 (12H, m, P-CH_2CH$_3$), 1.07 (36H, m, P-CH$_2$CH_3). δ_P (162 MHz; CDCl$_3$; ppm) −29.17, −31.06. IR (Ge ATR) ν_{max}/cm^{-1} 2045 (N$_3$). MS (MALDI(+)): m/z 2375.4 ([Re$_6$Se$_8$(PEt$_3$)$_4$](DHB)$^+$). Found: C, 12.78; H, 2.38; N, 3.52. Calc. for C$_{24}$H$_{60}$N$_6$P$_4$Re$_6$Se$_8$: C, 12.50; H, 2.62; N, 3.65%.

cis-[Re$_6$Se$_8$(PEt$_3$)$_4$(L1)$_2$] (7)

In a 250 mL Schlenk flask, 255.6 mg (0.1109 mmol) cis-[Re$_6$Se$_8$(PEt$_3$)$_4$(N$_3$)$_2$] was dissolved in 58 mL of chlorobenzene. To this solution, 260 μL of dimethyl acetylenedicarboxylate, was added. The solution was heated at reflux for 2.5 h. (Alternatively, the reaction could be conducted in CH$_2$Cl$_2$ at room temperature.) After cooling to room temperature the solvent was removed and the product reprecipitated from CH$_2$Cl$_2$/Et$_2$O (234.0 mg 86% yield). A portion of this sample was dried overnight at 100 °C prior to analysis. Major isomer: δ_H (400 MHz; CDCl$_3$; ppm) 3.83 (12H, s, –OCH$_3$), 2.17 (12H, m, P-CH_2CH$_3$), 2.09 (12H, m, P-CH_2CH$_3$), 1.10 (36H, t, P-CH$_2$CH_3). δ_P (162 MHz; CDCl$_3$; ppm) −26.43, −29.69. IR (Ge ATR) ν_{max}/cm^{-1} 1733 (CO), 1512 (NN). MS (ESI(+)): m/z 2613.1 (Na[Re$_6$Se$_8$(PEt$_3$)$_4$(L1)$_2$]$^+$). Found C, 17.44; H, 2.50; N, 2.88. Calc. for [C$_{36}$H$_{72}$N$_6$O$_8$P$_4$Re$_6$Se$_8$]: C, 16.70; H, 2.80; N, 3.25%.

Reaction of alkyl halides with [Re$_6$Se$_8$(PEt$_3$)$_5$(L1)]BF$_4$

A typical reaction involved dissolving 11 mg of [Re$_6$Se$_8$(PEt$_3$)$_5$(L1)]BF$_4$ in chloroform-d in a LPV NMR tube with a 20 fold excess of MeI or BnBr. Immediately upon mixing, spectral data was recorded. The sample was then placed in an oil bath at 100 °C and removed periodically to record both ^{31}P and ^{1}H NMR data.

Results and discussion

Cordier and coworkers were the first to report the preparation of a rhenium chalcogenide cluster complex containing azide ligands.[33] Their compound, Cs$_4$[Re$_6$S$_8$(N$_3$)$_6$], was prepared from a reaction of Cs$_4$[Re$_6$S$_8$Br$_6$] and NaN$_3$ in water. However, direct reaction of [Re$_6$Se$_8$(PEt$_3$)$_5$I]I and NaN$_3$, either in the presence or absence of Ag$^+$, did not lead to the formation of the mono-azido cluster complex, [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]$^+$. Next, we

attempted to substitute azide for coordinated acetonitrile in [Re$_6$Se$_8$(PEt$_3$)$_5$(MeCN)](BF$_4$)$_2$ which led to the discovery that the [Re$_6$Se$_8$]$^{2+}$ cluster core activates NCCH$_3$ and other nitriles to react with inorganic azides to form tetrazolate rings.[22,23] Ultimately, we were successful in preparing the desired azido complex via reaction of [Re$_6$Se$_8$(PEt$_3$)$_5$(py)](BF$_4$)$_2$ with NaN$_3$ at elevated temperatures. Likely, the substitution of pyridine for azide was successful since pyridine is not as susceptible to nucleophilic attack as are nitriles.

Although nitriles coordinated to the [Re$_6$Se$_8$]$^{2+}$ core undergo cycloaddition reactions with NaN$_3$ (as mentioned above) we found that [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]BF$_4$ does not react with free nitriles (MeCN, benzonitrile or p-nitrobenzonitrile) even after heating at 100 °C for 24 h. Notably, heterocyclic ring formation is observed when [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]BF$_4$ reacts with activated alkynes. As the cluster core is considered more electron withdrawing in nature, it is somewhat surprising that both [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]$^+$ and [Re$_6$Se$_8$(PEt$_3$)$_5$(NCCH$_3$)]$^{2+}$ facilitate heterocyclic ring formation. The mechanism of metal–azide cycloadditions with alkynes has not been studied in much detail. For organic transformations, molecular orbital theory requires π-orbital overlap in [3 + 2] cycloaddition reactions. However, 1,3-dipolar cycloadditions are somewhat unique in that the dipole can either act as a nucleophile or as an electrophile, depending on the nature of the dipolarophile.[34] For example, azide would act as a nucleophile towards dipolarophiles containing electron withdrawing substituents and as an electrophile towards those containing electron donating groups. We propose that coordination of nitriles to the [Re$_6$Se$_8$]$^{2+}$ cluster core make the nitrile more susceptible to nucleophilic attack, thus facilitating tetrazolate formation. However, coordination of azide to the same cluster core lowers the energy of the orbitals meaning it can only react with electron poor dipolarophiles. Thus, we see reaction of [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]$^+$ with activated alkynes like dimethyl acetylenedicarboxylate (DMAD), but we do not see reaction with free nitriles which are more electron rich.

The reactivity studies of [Re$_6$Se$_8$(PEt$_3$)$_5$(N$_3$)]$^+$ reported here complement our previous studies involving [Re$_6$Se$_8$(PEt$_3$)$_5$(L)]$^{2+}$ (L = NCCH$_3$, NCPh or substituted benzonitriles) in that all the compounds are analogous except for the coordination of the sixth ligand (azide vs. nitrile), see eqn (1)–(3). This is the first time the cycloaddition reactivity of such analogous octahedral complexes has been reported.
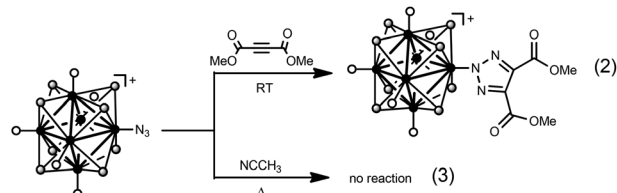
Cyclization of the coordinated azide with dimethyl acetylenedicarboxylate (DMAD) forms a coordinated 4,5-bis(methoxycarbonyl)-1,2,3-triazol-2-yl (L1, Fig. 1) and the reaction is complete within two hours at room temperature. The large
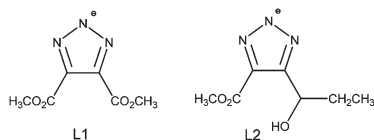
Fig. 1 Structures of 4,5-bis(methoxycarbonyl)-1,2,3-triazol-2-yl (L1) and 4-methoxycarbonyl-5-(1-propanol)-1,2,3-triazol-2-yl (L2).

singlet in the ^{1}H NMR spectrum (3.82 ppm), assigned to the methoxycarbonyl resonances, indicates N(2) coordination of the triazolate ring. This was supported by a single crystal X-ray diffraction study (*vide infra*). Upon careful examination of the ^{1}H NMR spectral data we do see two very small peaks indicative of the N(1) isomer (~2% based on ^{1}H NMR integration). Thus, the N(2) isomer is not formed exclusively. To date, there is only one report of a N(1) bound triazolate ligand;[35] thus, the N(2) bound ligand is by far the more stable isomer. Two other alkynes, methyl 4-hydroxyhex-2-yneoate and dichloro-2-butyne, show some reactivity with **2** after 20 h of reflux in chlorobenzene.

We pursued the reaction with methyl 4-hydroxyhex-2-yneoate and found that it took 2 days of heating at reflux in chlorobenzene to drive the reaction to completion. The NMR spectral data indicates a clean transformation where only one isomer is observed in the ^{1}H and ^{31}P NMR spectra. For steric reasons, this is likely the N(2) isomer, but the asymmetry of the ring makes it difficult to determine this conclusively; we were not able to obtain single crystals for a definite structure analysis. These mark the first (triazolato)rhenium complexes reported to date. One other alkyne, 1-methyl-2-phenylacetylene, and an alkene, diethylmaleate, did not react under the conditions tested. Therefore, it is clear that the substituents on the dipolarophile (see Fig. 2) are important in determining whether or not cycloaddition will occur.

In order to further understand the reactivity of these systems, we attempted to prepare a bis-azido cluster complex, to see if both azide moieties would react to form triazolate rings. Towards this end, we prepared the bis-pyridine cluster complex, *cis*-[Re$_6$Se$_8$(PEt$_3$)$_4$(py)$_2$](BF$_4$)$_2$. Our preparation requires milder conditions, has a much shorter reaction time (3 h compared to 4 d), and the yield is slightly higher compared to the previously reported synthesis.[27] However, our isolated solid does contain some residual pyridine, which in our case, was easily removed in the subsequent reaction. *cis*-[Re$_6$Se$_8$(PEt$_3$)$_4$(py)$_2$](BF$_4$)$_2$ was converted to the bis-azido complex, **6**, using a similar preparation as that used for the

mono-azido cluster complex. With the bis-azido cluster we only examined reactivity with one of the alkynes, DMAD, since it was the most active of those investigated with the mono-azido cluster. As expected, the starting bis-azido cluster shows two resonances of approximately equal intensity in the ^{31}P $\{^1$H$\}$ NMR spectrum (at −29.17 and −31.06 ppm) which represent the two unique environments for the phosphorus nuclei in *cis*-[Re$_6$Se$_8$(PEt$_3$)$_4$(N$_3$)$_2$]. After stirring at room temperature for 2 h in the presence of DMAD, the bis-azido cluster had reacted; however, the spectrum contained multiple resonances, not just two as expected for pure N(2) coordinated bis-triazolate complex, *cis*-[Re$_6$Se$_8$(PEt$_3$)$_4$(L1)$_2$]. We switched to a higher boiling solvent (chlorobenzene) and heated at reflux for 2.5 hours; however, the spectral data did not change. Other characterization techniques support the complete conversion of the azide moieties to triazolate rings. For example, the IR spectrum of **7** shows the presence of ν(CO) stretches from the substituents on the triazolate ring; the disappearance of the ν(N$_3$) stretches is also evident (see the ESI† for IR spectral data of **6** and **7**). The MS data also supports the [Re$_6$Se$_8$(PEt$_3$)$_4$(L1)$_2$] formulation. Thus, we believe isomers were generated which would be defined by the triazolate donor atoms (*i.e.* [N(1),N(1)], [N(1),N(2)] or [N(2),N(2)]). We propose that our product contains a mixture of symmetric *cis*-[Re$_6$Se$_8$(PEt$_3$)$_4$(L1)$_2$] with two N(2) coordinated triazolate ligands (this is the major isomer and is supported by one large isochronous methoxycarbonyl peak in the ^{1}H NMR spectrum at 3.83 ppm) and a [N(1),N(2)] bound isomer. Both the ^{1}H and ^{31}P $\{^1$H$\}$ NMR spectral data support this, as the minor peaks indicate a non-symmetric isomer (see ESI†). Kemmerich *et al.* mention the preparation of two bis-azido cobalt complexes and report that both azide ligands react with DMAD to form bis-triazolate complexes; however, the ^{1}H NMR and elemental analysis data provided do not support their conclusion.[14]

The X-ray structures of **2** and **6** are shown in Fig. 3 and the structure of **3** is shown in Fig. 4. Examining the X-ray structures of these three complexes we observe that the terminal ligands do not influence the structure of the core itself. Comparing the bond length and angles of the azide ligands (see Table 2), we note that the Re–N and N–N bond distances are within the range found for transition metal azide complexes.[36] Similarly, the N–N–N bond angles indicate a linear azide moiety. These distances and angles are consistent with those observed by Cordier and coworkers for Cs$_4$[Re$_6$S$_8$(N$_3$)$_6$]·H$_2$O, the only other Re(III) azide complex reported in the literature.[33] The Re–N(triazolate) bond distance in **3** is similar to the Re–N distance reported for the (tetrazolato)rhenium chalcogenide cluster complexes.[22,23] The heterocyclic ring in **3** does not show significant differences between the bond lengths indicating delocalization of the π electrons; most transition metal complexes containing monodentate triazolate based ligands also show similar delocalization within the ring.[15,16,37]

The coordinated triazolate ligand (L1) in [Re$_6$Se$_8$(PEt$_3$)$_5$(L1)]BF$_4$ does react with electrophilic reagents as has been shown for other similarly coordinated heterocyclic rings.[14,16,17] Separately, we tested the reaction of MeI and benzyl bromide
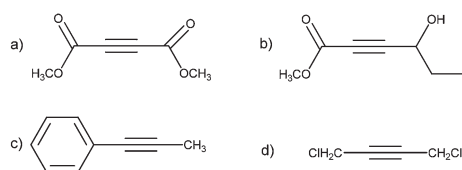

Fig. 2 Structures of the four alkynes tested: (a) dimethyl acetylenedicarboxylate, (b) methyl 4-hydroxyhex-2-yneoate, (c) 1-methyl-2-phenylacetylene, and (d) dichloro-2-butyne.
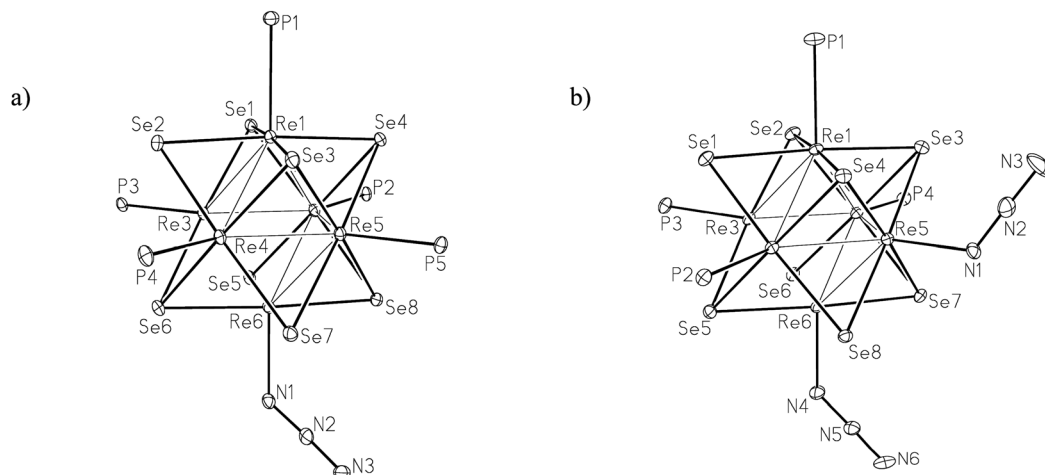
a)   b)

Fig. 3 Perspective view of (a) $[Re_6Se_8(PEt_3)_5(N_3)]^+$ and (b) $[Re_6Se_8(PEt_3)_4(N_3)_2]$ showing the atom labeling schemes. Carbon and hydrogen atoms omitted for clarity and Gaussian ellipsoids are at the 20% probability level.
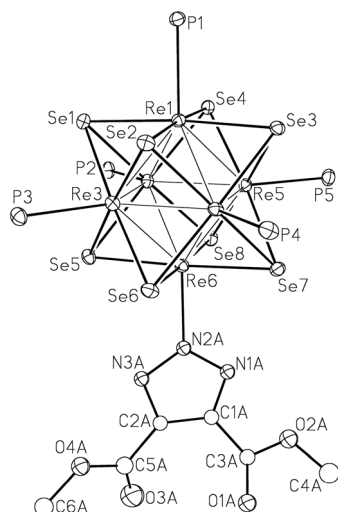
anisochronous methoxycarbonyl resonances indicative of alkylation at the N(1) position. Thus, the coordinated triazolate ring can be removed *via* reaction with electrophilic reagents as was shown previously for tetrazolate rings coordinated to the $[Re_6Se_8]^{2+}$ core.[23]

Recently, Mirica and coworkers investigated a series of transition metal azide complexes to see which undergo cycloaddition with DMAD.[21] For the compounds studied a correlation between cycloaddition reactivity and the difference between the long and short N–N bonds of the azide ligand (*i.e.* $N–N_{prox}$ and $N–N_{dist}$) was made. Specifically, when this difference was longer than 0.053 Å, the compounds did not undergo cycloaddition with DMAD at room temperature. In our system, the difference between the $N–N_{prox}$ and $N–N_{dist}$ distances of the azide ligands are 0.054 for **2**, and 0.055 and 0.059 for **6**, and all azide moieties react with DMAD at room temperature. Thus, the azide ligands coordinated to the $[Re_6Se_8]^{2+}$ cluster core fall under different criteria. We attempted to correlate the asymmetric stretch of the azide ligand ($\nu_a(N_3)$) with cycloaddition activity, but this does not provide a good correlation either. It appears that these predictors are useful within a given family of compounds, but cannot be applied across the board.

Fig. 4 Perspective view of $[Re_6Se_8(PEt_3)_5(L1)]^+$ showing the atom labeling scheme. Carbon and hydrogen atoms omitted for clarity and Gaussian ellipsoids are at the 20% probability level.

Conclusion

(BnBr) with **3**; the $^{31}P\{^1H\}$ NMR spectral data of the reaction mixtures taken at various time intervals can be seen in the ESI.† There does not appear to be any substantial difference in the relative rates of these reaction as both show product halide formation ($[Re_6Se_8(PEt_3)_5X]^+$ where X = I⁻ or Br⁻) within an hour, and the reactions appear complete within 24 hours. The ^1H NMR spectral data for both reactions show two

The ability of $[Re_6Se_8(PEt_3)_5(N_3)]^+$ to undergo cycloadditions with activated alkynes (but not nitriles) has been compared

Table 2 Selected bond distances for $[Re_6Se_8(PEt_3)_5(N_3)]BF_4·3Et_2O$ and $[Re_6Se_8(PEt_3)_4(N_3)_2]·1.5CH_2Cl_2$

$[Re_6Se_8(PEt_3)_5(N_3)]BF_4·3Et_2O$		$[Re_6Se_8(PEt_3)_4(N_3)_2]·1.5CH_2Cl_2$			
Re6–N1	2.112(8)	Re5–N1	2.113(7)	Re6–N4	2.122(8)
N1–N2	1.191(11)	N1–N2	1.205(12)	N4–N5	1.198(11)
N2–N3	1.137(12)	N2–N3	1.150(13)	N5–N6	1.139(12)
N1–N2–N3	177.6(10)	N1–N2–N3	178.3(14)	N4–N5–N6	176.2(11)

with the reactivity of $[Re_6Se_8(PEt_3)_5(nitrile)]^{2+}$ where coordinated nitriles readily undergo cycloaddition reactions with NaN_3. We propose that coordination to the $[Re_6Se_8]^{2+}$ cluster core is strongly electron withdrawing. Thus, coordination of azide to the $[Re_6Se_8]^{2+}$ core decreases its nucleophilicity so it only reacts with electron poor dipolarophiles. We are interested in testing this theory further by examining reactions of these cluster complexes with a wider range of dipolarophiles and potentially conducting some computational studies.

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