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Preparation of a Family of Hexanuclear Rhenium Cluster Complexes Containing 5-(Phenyl)tetrazol-2-yl Ligands and Alkylation of 5-Substituted Tetrazolate Ligands

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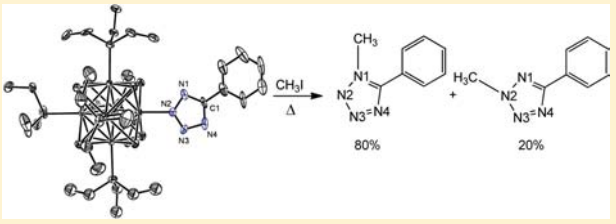
Supporting Information

ABSTRACT: The preparation of two new families of hexanuclear rhenium cluster complexes containing benzonitrile and phenyl-substituted tetrazolate ligands is described. Specifically, we report the preparation of a series of cluster complexes with the formula $[Re_6Se_8(PEt_3)_5L]^{2+}$ where L = benzonitrile, *p*-aminobenzonitrile, *p*-methoxybenzonitrile, *p*-acetylbenzonitrile, or *p*-nitrobenzonitrile. All of these complexes undergo a [2 + 3] cycloaddition with N_3^- to generate the corresponding $[Re_6Se_8(PEt_3)_5$(5-(*p*-X-phenyl)tetrazol-2-yl)$]^+$ (or $[Re_6Se_8(PEt_3)_5$(2,5-*p*-X-phenyltetrazolate)$]^+$) cluster complexes, where X = NH_2, OMe, H, $COCH_3$, or NO_2. Crystal structure data are reported for three compounds: $[Re_6Se_8(PEt_3)_5$(*p*-acetylbenzonitrile)$](BF_4)_2 \bullet MeCN$, $[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$](BF_4) \bullet CH_2Cl_2$, and $[Re_6Se_8(PEt_3)_5$(2,5-*p*-aminophenyltetrazolate)$](BF_4)$. Treatment of $[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$](BF_4)$ with HBF_4 in CD_3CN at 100 °C leads to protonation of the tetrazolate ring and formation of $[Re_6Se_8(PEt_3)_5(CD_3CN)]^{2+}$. Surprisingly, alkylation of the phenyl and methyl tetrazolate complexes ($[Re_6Se_8(PEt_3)_5(2,5\text{-}N_4CPh)](BF_4)$ and $[Re_6Se_8(PEt_3)_5(1,5\text{-}N_4CMe)](BF_4)$) with methyl iodide and benzyl bromide, leads to the formation of mixtures of 1,5- and 2,5-disubstituted tetrazoles.



INTRODUCTION

Tetrazoles are an important class of compounds that have important applications in organic synthesis and medicinal chemistry, as well as the explosives industry.[1−3] In particular, 1,5-disubstituted tetrazoles are of interest because they often serve as allosteric replacements for carboxylic acids in pharmaceuticals or as surrogates for the *cis* amide bond in peptides.[4,5] In addition, transition metal complexes and coordination polymers containing tetrazolate ligands have been shown to display interesting physical properties.[6] For example, Dunbar, Zubietta, and co-workers prepared a microporous framework ($[Co_2(H_{0.67}bdt)_3] \bullet 20H_2O$) containing 5,5′-(1,4-phenylene)bis-(tetrazolate) that displays single-chain magnetism.[7] Because the formation of tetrazoles via a direct reaction of nitriles and azides often requires long reaction times, toxic substances, and harsh conditions,[8] there has been interest in examining more efficient synthetic pathways.[9] Select transition metals are capable of facilitating the reaction between azides and nitriles to form tetrazoles, and the advent of "click chemistry" brought these synthetic routes to the forefront.[10] A handful of metals have been employed; however, the most common include Zn^{2+}, Pd^{2+}, and Pt^{2+}.[10−12] Little is known regarding the ability of Re to activate nitriles to undergo similar reactions with azide. There have been reports of single metal and small cluster rhenium(III) complexes containing nitrile ligands undergoing hydrolysis.[13] For example, a Re(III) dimer bridged by a benzamidate ligand was reported in 1998; the benzamidate ligand was formed via the hydrolysis of a coordinated benzonitrile ligand.[13a] More recently, the preparation and study of a series of Re(I) tetrazolate complexes was reported by Massi and co-workers.[14] However, these complexes were prepared by the direct substitution of MeCN by the 5-aryltetrazolate anion.

In 2007, two manuscripts describing how the hexarhenium cluster core, $[Re_6Se_8]^{2+}$, can activate coordinated acetonitrile ligands to react with nucleophiles were published (Scheme 1).[15,16] Zheng and co-workers reported the addition of alcohols to the coordinated MeCN ligands of $[Re_6Se_8(PEt_3)_{6-n}(MeCN)_n]^{2+}$ (n = 1, 2) forming imino ester ligands.[15] That same year, we reported the formation of tetrazolate ligands via the reaction of inorganic azides with $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$.[16] Here, the cluster activates the MeCN to undergo a cycloaddition with azide to form a tetrazolate ring. This was the first example of a rhenium-based complex facilitating the formation of a heterocyclic ring. Most notable is the fact that heterocyclic formation occurs within minutes at room temperature. Under these conditions, the N1 isomer can be generated in high yield.

Following up on our studies involving inorganic azides, Zheng and co-workers examined the reaction of organic azides with $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ and other analogous acetonitrile

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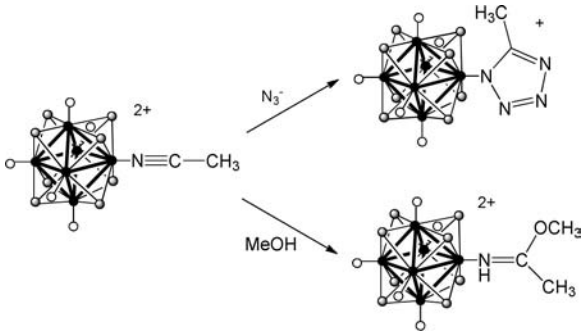
Scheme 1



cluster complexes.[17] The expectation was that organic azides would lead to the formation of functionalized tetrazole ligands.[18] However, it was found that instead of forming the tetrazole ring, a reversible ligand substitution of the organic azide for the nitrile occurred. The cluster-azido intermediate that formed was then found to undergo a photodecomposition reaction involving the migration of the organic moiety and elimination of N_2 leading to the formation of an imino complex. For example, the reaction of $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ with (1-azidoethyl)benzene led to the quantitative formation of the imino complex, $[Re_6Se_8(PEt_3)_5(PhN{=}CHCH_3)]^{2+}$. This unexpected result emphasizes the need for further studies involving the reactivity of nitrile ligands.

We now extend our initial report[16] involving the preparation of methyltetrazolate complexes to an investigation of the reactivity of coordinated benzonitrile and substituted benzonitrile ligands. Both the preparation and reactivity of the benzonitrile complex, $[Re_6Se_8(PEt_3)_5(PhCN)]^{2+}$, and cluster complexes containing *para*-substituted benzonitrile ligands (Figure 1),

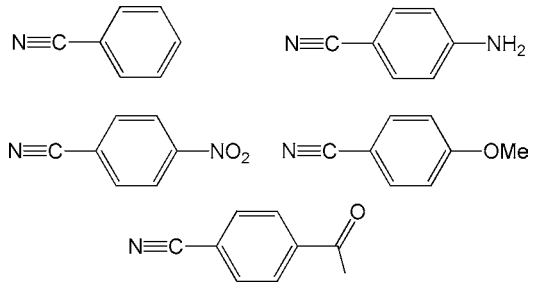


Figure 1.

p-aminobenzonitrile, *p*-acetylbenzonitrile, *p*-methoxybenzonitrile, and *p*-nitrobenzonitrile, will be discussed. These coordinated nitriles were also found to undergo reaction with inorganic azides to form the corresponding tetrazolate complexes (Scheme 2). Reactivity studies involving the $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$ complex shows that free 2,5-phenyltetrazole can be generated via heating a solution of this complex in the presence of acid. We also report our findings involving the reaction of both $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ and $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$ with alkylating agents, leading to the formation of disubstituted tetrazoles. It is important to note that while great strides have been made in the area of octahedral hexanuclear clusters over the past 25 years, studies involving the reactivity of these complexes (i.e., other than ligand substitution) are severely lacking.[19] Therefore, the studies described herein are important in that they explore fundamental chemistry associated with these hexarhenium cluster systems.

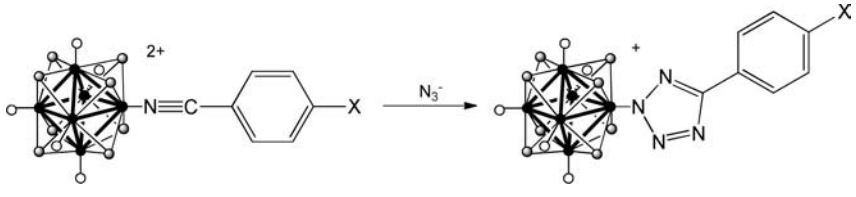
EXPERIMENTAL SECTION

Caution! *Sodium azide can explode on heating, and contact of metal azides with acids liberates the highly toxic and explosive hydrazoic acid. All reactions involving azides and tetrazoles should be treated as potentially explosive and handled in an appropriate manner!*

General Information. $[Re_6Se_8(PEt_3)_5I]I$ was prepared according to a previously published procedure.[20] ^1H NMR spectra were recorded at either 400 or 500 MHz. Those collected using at 400 MHz were collected on a Varian 400 Mercury or a Bruker Avance III 400 MHz NMR spectrometer, while the spectra collected at 500 MHz were collected on a Bruker Avance III 500 MHz NMR spectrometer. All ^{31}P NMR spectra were proton decoupled and externally referenced to 85% H_3PO_4. ^{31}P spectra were collected on the same instruments at either 162 or 202.5 MHz, respectively. All chromatography was performed using silica gel as the solid support. Elemental analyses (EA) were performed by the Microanalysis Laboratory at the University of Illinois, Urbana; mass spectral data was also obtained at the University of Illinois. UV−visible spectra were collected on a Varian Cary 5E UV−vis-NIR instrument. Infrared spectra (IR) were collected on a Perkin-Elmer Spectrum One FT-IR spectrophotometer using a KBr pellet (some of the IR spectra contain a broad peak at approximately 3500 cm^{-1}, which is attributed to water contamination in the KBr). X-ray diffractometry data sets were collected and solved by Dr. Robert McDonald at the University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Electrochemical measurements were conducted in 0.2 M Bu_4NBF_4/CH_2Cl_2 with Pt working and auxiliary and a Ag/AgCl reference electrode. The window scanned was 0.0−1.50 V vs Ag/AgCl. All reported potentials were referenced to the $FeCp_2^+/FeCp_2$ couple, which was measured under identical conditions. Steady state emission spectra were obtained using a Perkin-Elmer LS55 fluorimeter at excitation wavelengths that corresponded to the absorption wavelength.

$[Re_6Se_8(PEt_3)_5(p\text{-aminobenzonitrile})](BF_4)_2$ (1). $[Re_6Se_8(PEt_3)_5I]I$ (500 mg, 0.193 mmol) and 456.8 mg of *p*-aminobenzonitrile ($C_7H_6N_2$, 3.87 mmol) were dissolved in 12 mL of CH_2Cl_2. Separately, 189 mg of $AgBF_4$ (0.972 mmol) was dissolved in 8 mL of acetone. These solutions were combined, covered with aluminum foil, and heated at reflux for 3 h. The resulting mixture was cooled to room temperature and filtered through Celite. The filtrate was reduced to dryness and then precipitated using CH_2Cl_2 and Et_2O. Purification was accomplished via column chromatography; a 95:5 CH_2Cl_2:MeCN mixture was used to elute an impurity, and then the product band was eluted with a 85:15 CH_2Cl_2:MeCN mixture. The product fraction was stripped of solvent via rotary evaporation and precipitated with CH_2Cl_2 in Et_2O. Crystals were obtained via vapor diffusion crystallization using MeCN and Et_2O (180.4 mg, 35% yield). ^1H NMR (400 MHz, acetone-d_6, ppm): 7.48 (2H, d, $-C_6H_4$), 6.85 (2H, d, $-C_6H_4$), 6.29 (2H, s, $-NH_2$), 2.34 (24H, m, $-CH_2CH_3$), 2.26 (6H, m, $-CH_2CH_3$),

Scheme 2



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1.16 (45H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (162 MHz, acetone-d_6, ppm): −24.71, −28.53. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 224 (69,000), 273 (27,000), 308 (28,000). MS (ESI(+)): m/z 1228.9 ($[Re_6Se_8(PEt_3)_5(C_7H_6N_2)]^{2+}$). IR (KBr): 2227 ($-C\equiv N$) cm^{-1}. Anal. Calcd for $C_{37}H_{81}N_2P_5B_2F_8Re_6Se_8$: C, 16.89; H, 3.10; N, 1.06. Found: C, 16.50; H, 2.82; N, 1.10.

$[Re_6Se_8(PEt_3)_5$(*p*-methoxybenzonitrile)$](BF_4)_2$ (2). $[Re_6Se_8(PEt_3)_5I]I$ (149.4 mg, 0.058 mmol) and 69.7 mg of 4-methoxybenzonitrile (C_8H_7NO, 0.523 mmol) was dissolved in 10 mL of CH_2Cl_2. Separately, 30.1 mg of $AgBF_4$ (0.155 mmol) was dissolved in 5 mL of chlorobenzene. These solutions were combined, covered with aluminum foil, and stirred at room temperature for 3 h. The resulting mixture was then filtered through Celite; the filtrate was stripped of solvent on the Schlenk line. The remaining residue was dissolved in 1.5 mL of nitromethane and dripped into Et_2O to afford a crude solid (124.9 mg, 82% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.71 (2H, d, $-C_6H_4$), 7.13 (2H, d, $-C_6H_4$), 3.91 (3H, s, $-OCH_3$), 2.21 (24H, m, $-CH_2CH_3$), 2.09 (6H, m, $-CH_2CH_3$), 1.10 (45H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): −25.79, −29.41. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 223 (71,000), 239 sh, 277 (42,000), 335 sh. MS (ESI(+)): m/z 1236.7 ($[Re_6Se_8(PEt_3)_5(C_8H_7NO)]^{2+}$). IR (KBr): 2247 ($-C\equiv N$) cm^{-1}. Anal. Calcd for $C_{38}H_{82}NOP_5B_2F_8Re_6Se_8$: C, 17.25; H, 3.12; N, 0.53. Found: C, 17.14; H, 2.99; N, 0.55.

$[Re_6Se_8(PEt_3)_5$(NCPh)$](BF_4)_2$ (3). In a 25 mL round bottom, 60.7 mg of $AgBF_4$ was dissolved in 0.8 mL of benzonitrile. In a separate vial, $[Re_6Se_8(PEt_3)_5I]I$ (306.1 mg, 0.118 mmol) was dissolved in 8 mL of CH_2Cl_2 and added to the stirring $AgBF_4$ solution. The reaction mixture was stirred for 3 h, with exclusion of light, at room temperature. The solution was then filtered through Celite. The filtrate was reduced to dryness by rotary evaporation, which afforded the product in residual benzonitrile. The crude product was further purified by column chromatography; an initial 10:90 acetone:CH_2Cl_2 mixture was used to elute residual benzonitrile and then changed to 50:50 acetone:CH_2Cl_2 to elute the product band. The product was reduced to dryness by rotary evaporation and precipitated with CH_2Cl_2 and Et_2O. Crystals were obtained via vapor diffusion using a CH_2Cl_2/Et_2O mixture and Et_2O (252.2 mg, 82% yield). ^1H NMR (500 MHz, $CDCl_3$, ppm): 7.80 (2H, d, $-C_6H_5$), 7.72 (1H, t, $-C_6H_5$), 7.63 (2H, t, $-C_6H_5$), 2.22 (24H, m, $-CH_2CH_3$), 2.10 (6H, m, $-CH_2CH_3$), 1.13 (45H, m, $-CH_2CH_3$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$ ppm): −25.61, −29.48. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 225 (73,000), 271, 240, 403 sh. MS (ESI(+)): m/z 1221.7 ($[Re_6Se_8(PEt_3)_5(NCC_6H_5)]^{2+}$). IR (KBr): 2253 ($-C\equiv N$) cm^{-1}. Anal. Calcd for $C_{37}H_{80}NP_5B_2F_8Re_6Se_8$: C, 16.98; H, 3.08; N, 0.54. Found: C, 16.78; H, 2.95; N, 0.58.

$[Re_6Se_8(PEt_3)_5$(*p*-acetylbenzonitrile)$](BF_4)_2$ (4). $[Re_6Se_8(PEt_3)_5I]I$ (202.1 mg, 0.078 mmol) and 113.8 mg of 4-acetylbenzonitrile (C_9H_7NO, 0.784 mmol) was dissolved in 10 mL of CH_2Cl_2. Separately, 44.8 mg of $AgBF_4$ (0.230 mmol) was dissolved in 5 mL of chlorobenzene. These solutions were combined, covered with aluminum foil, and stirred at room temperature for 2 h. The resulting mixture was then filtered through Celite. The filtrate was stripped of solvent on the Schlenk line, and the crude product isolated via precipitation from CH_3NO_2 and Et_2O. A second precipitation was required to remove residual 4-acetylbenzonitrile (132.2 mg, 64% yield). ^1H NMR (500 MHz, $CDCl_3$, ppm): 8.21 (2H, d, $-C_6H_4$), 7.97 (2H, d, $-C_6H_4$), 2.66 (3H, s, $-CH_3$), 2.22 (24H, m, $-CH_2CH_3$), 2.11 (6H, m, $-CH_2CH_3$), 1.10 (45H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, ppm): −25.69, −29.31. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 224 (72,000), 242, 273, 340 sh. MS (ESI(+)): m/z 1241.6 ($[Re_6Se_8(PEt_3)_5(C_9H_7NO)]^{2+}$). IR (KBr): 2256 ($-C\equiv N$), 1687 ($C{=}O$) cm^{-1}. Anal. Calcd for $C_{39}H_{82}NOP_5B_2F_8Re_6Se_8$: C, 17.62; H, 3.11; N, 0.53. Found: C, 17.31; H, 2.88; N, 0.51.

$[Re_6Se_8(PEt_3)_5$(*p*-nitrobenzonitrile)$](BF_4)_2$ (5). $[Re_6Se_8(PEt_3)_5I]I$ (154.8 mg, 0.060 mmol) and 89.0 mg of 4-nitrobenzonitrile ($C_7H_4N_2O_2$, 0.601 mmol) was dissolved in 10 mL of CH_2Cl_2. Separately, 33.2 mg of $AgBF_4$ (0.170 mmol) was dissolved in 5 mL of chlorobenzene. These solutions were combined, covered with aluminum foil, and stirred at room temperature for 1 h. The resulting mixture was then filtered through Celite; the filtrate was stripped of solvent on the Schlenk line. The remaining residue was dissolved in 1.5 mL of CH_3NO_2 and dripped into Et_2O to afford a solid (124.8 mg, 79% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.43 (2H, d, $-C_6H_4$), 8.17 (2H, d, $-C_6H_4$), 2.21 (24H, m, $-CH_2CH_3$), 2.09 (6H, m, $-CH_2CH_3$), 1.12 (45H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): −25.54, −29.55. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 225 (71,000), 240, 281, 340 sh. IR (KBr): 2265 ($-C\equiv N$), 1524 and 1344 ($-NO_2$) cm^{-1}. Anal. Calcd for $C_{37}H_{79}N_2O_2P_5B_2F_8Re_6Se_8$: C, 16.70; H, 2.99; N, 1.05. Found: C, 16.64; H, 2.90; N, 1.12.

$[Re_6Se_8(PEt_3)_5$(2,5-*p*-aminophenyltetrazolate)$](BF_4)$ (6). A sample of **1** (297 mg, 0.113 mmol) was dissolved in 10 mL of acetone. Separately, 11.2 mg of NaN_3 (0.172 mmol) was dissolved in minimal DI water. These solutions were combined and stirred at room temperature for 15 min. The solution was then filtered through Celite and reduced to dryness. The resulting solid was precipitated using acetone and Et_2O and collected under a blanket of $N_{2(g)}$ (160.4 mg, 55% yield). ^1H NMR (400 MHz, acetone-d_6, ppm): 7.76 (2H, d, $-C_6H_4$), 6.70 (2H, d, $-C_6H_4$), 4.77 (2H, s, $-NH_2$), 2.27 (30H, m, $-CH_2CH_3$), 1.15 (45H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (162 MHz, acetone-d_6, ppm) −27.10, −29.90. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 224 (75,000) 272 (43,000). MS (ESI(+)): m/z 2499.6 ($[Re_6Se_8(PEt_3)_5(C_7H_6N_5)]^+$). Anal. Calcd for $C_{37}H_{81}N_5P_5BF_4Re_6Se_8\bullet 2.5H_2O$: C, 16.88; H, 3.29; N, 2.66. Found: C, 16.53; H, 2.93; N, 2.45.

$[Re_6Se_8(PEt_3)_5$(2,5-*p*-methoxyphenyltetrazolate)$](BF_4)$ (7). A sample of **2** (136.3 mg, 0.052 mmol) was dissolved in 3 mL of acetone. Separately, 5.2 mg of NaN_3 (0.080 mmol) was dissolved in minimal DI water. These solutions were combined and stirred at room temperature for 30 min. The resulting mixture was then filtered through Celite into stirring Et_2O to afford a crude solid (122.8 mg, 89% yield). This solid was purified via column chromatography; the desired product was collected as the first band, which was eluted with a 4:1 CH_2Cl_2/acetone mixture. The product was dissolved in minimal CH_3NO_2 and dripped into Et_2O to afford a solid (79.1 mg, 57% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.98 (2H, d, $-C_6H_4$), 6.89 (2H, d, $-C_6H_4$), 3.81 (3H, s, $-OCH_3$), 2.09 (30H, m, $-CH_2CH_3$), 1.10 (45H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): −28.21, −30.21. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 225 (72,000), 241, 257, 367 sh. MS (ESI(+)): m/z 2518.0 ($[Re_6Se_8(PEt_3)_5(C_8H_7N_4O)]^+$). Anal. Calcd for $C_{38}H_{82}N_4OP_5BF_4Re_6Se_8$: C, 17.54; H, 3.18; N, 2.15. Found: C, 17.66; H, 2.87; N, 2.12.

$[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$](BF_4)$ (8). A solution containing 228 mg of (**3**) (0.0872 mmol) in 6.0 mL of acetone was combined with a solution of NaN_3 (16.1 mg, 0.248 mmol) in 30 drops of DI water. The reaction mixture was stirred for 15 min at room temperature. The solution was then filtered through Celite. The filtrate was reduced to dryness by rotary evaporation and then precipitated using acetone and Et_2O. The product was further purified by column chromatography; a mixture of 20:80 acetone:CH_2Cl_2 was used to elute the product band. This band was reduced to dryness by rotary evaporation and precipitated with CH_2Cl_2 and Et_2O. Crystals were obtained by vapor diffusion using acetone/Et_2O mixture and Et_2O (120 mg, 54% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.07 (2H, d, $-C_6H_5$), 7.36 (2H, t, $-C_6H_5$), 7.26 (1H, t, $-C_6H_5$), 2.16 (30H, m, $-CH_2CH_3$), 1.10 (45H, m, $-CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 163.7 (s, $N_4CC_6H_5$), 130.2 (s, $N_4CC_6H_5$), 128.5 (s, $N_4CC_6H_5$), 126.7 (s, $N_4CC_6H_5$), 25.8 (m, $-CH_2CH_3$), 8.9 (m, $-CH_2CH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): −28.17, −30.15. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 225 (81,000), 240, 265, 396 sh. MS (ESI(+)): m/z 2484.2 ($[Re_6Se_8(PEt_3)_5(N_4CC_6H_5)]^+$). Anal. Calcd for $C_{37}H_{80}N_4P_5BF_4Re_6Se_8$: C, 17.28; H, 3.14; N, 2.18. Found: C, 17.37; H, 2.91; N, 2.07.

$[Re_6Se_8(PEt_3)_5$(2,5-*p*-acetylphenyltetrazolate)$](BF_4)$ (9). A sample of **4** (250 mg, 0.094 mmol) was dissolved in 10 mL of CH_3NO_2. Separately, 9.2 mg of NaN_3 (0.14 mmol) was dissolved in minimal DI water. These solutions were combined and stirred vigorously at room temperature for 15 min. The mixture was then filtered through Celite, and the filtrate was stripped dry via rotary evaporation. Upon dissolving in 1.5 mL of CH_3NO_2, a second filtration through Celite was required before the product was precipitated by dripping

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the solution into Et_2O (217.4 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.17 (2H, d, $-C_6H_4$), 7.96 (2H, d, $-C_6H_4$), 2.62 (3H, s, $-CH_3$), 2.16 (30H, m, $-CH_2CH_3$), 1.13 (48H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): −27.97, −29.99. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 223 (75,000), 278 (35,000). MS (ESI(+)): m/z 2525.8 ($[Re_6Se_8(PEt_3)_5(C_9H_7N_4O)]^+$). Anal. Calcd for $C_{39}H_{82}N_4OP_5BF_4Re_6Se_8$: C, 17.92; H, 3.16; N, 2.14. Found: C, 17.64; H, 3.11; N, 2.01.

$[Re_6Se_8(PEt_3)_5$(2,5-*p*-nitrophenyltetrazolate)$](BF_4)$ (10). A 169.1 mg sample of **5** (0.064 mmol) was dissolved in 7.5 mL of CH_3NO_2. Separately, 6.4 mg of NaN_3 (0.098 mmol) was dissolved in minimal DI water. These solutions were combined and stirred at room temperature for 30 min. The resulting mixture was then filtered through Celite. The filtrate was stripped of solvent, and the remaining residue was dissolved in 1.5 mL of CH_3NO_2 and dripped into Et_2O to afford a solid (146.6 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.22 (4H, $-C_6H_4$), 2.14 (30H, m, $-CH_2CH_3$), 1.10 (45H, m, $-CH_2CH_3$). ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): −27.86, −29.90. UV−vis (CH_3CN) nm (ε in M^{-1} cm^{-1}): 224 (75,000), 273 (23,000), 316 sh. Anal. Calcd for $C_{37}H_{79}N_5O_2P_5BF_4Re_6Se_8$: C, 16.98; H, 3.04; N, 2.68. Found: C, 16.78; H, 2.78; N, 2.34.

X-ray Crystallography. *General.* Single crystals of $[Re_6S_8(PEt_3)_5$(*p*-acetylbenzonitrile)$](BF_4)_2\cdot NCCH_3$ and $[Re_6S_8(PEt_3)_5$(2,5-*p*-aminophenyltetrazolate)$]BF_4$ were grown via the vapor diffusion technique using CH_3CN and Et_2O at −20 °C. Crystals of $[Re_6S_8(PEt_3)_5$(2,5-phenyltetrazolate)$]BF_4\cdot CH_2Cl_2$ were grown from an acetone−Et_2O mixture at room temperature also using vapor diffusion (the residual CH_2Cl_2 that was present came from the previous reprecipitation steps). 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 SMART 1000 CCD detector/PLATFORM diffractometer with the crystals cooled to −80 °C and diffraction measurements obtained using graphite-monochromated Mo Kα (λ = 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-99[21] (**8**•CH_2Cl_2) or DIRDIF-2008[22] (**4**•MeCN, **6**). Structures were refined by full-matrix least-squares on F^2 with SHELXL-97.[23] 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.

Special Refinement Details. $[Re_6S_8(PEt_3)_5$(p-acetylbenzonitrile)$](BF_4)_2\cdot NCCH_3$. Distances within a disordered PEt_3 ethyl group were fixed or restrained during refinement: d(P2−C25A) = d(P2−C25A) = 1.82(1) Å; d(C25A−C26A) = d(C25B−C26B) = 1.54(1) Å; and d(P2···C26A) = d(P2···C26B) (within 0.01 Å). F−B distances within the disordered BF_4^- ion (d(F5A−B2A), d(F6A−B2A), d(F7A−B2A), d(F7A−B2A), d(F5B−B2B), d(F6B−B2B), d(F7B−B2B), and d(F8B−B2B)) were constrained to be equal (within 0.01 Å) to a common value during refinement. F···F distances within the minor (40%) conformer of this disordered BF_4^- ion (d(F5B···F6B), d(F5B···F7B), d(F5B···F8B), d(F6B···F7B), d(F6B···F8B), and d(F7B···F8B)) were constrained to be equal (within 0.01 Å) to a common value during refinement. Distances within the disordered solvent acetonitrile molecule were fixed during refinement: d(N1SA−C1SA) = d(N1SB−C1SB) = 1.13(1) Å; d(C1SA−C2SA) = d(C1SB−C2SB) = 1.45(1) Å; and d(N1SA···C2SA) = d(N1SB···C2SB) = 2.58(1) Å.

$Re_6S_8(PEt_3)_5$(2,5-phenyltetrazolate)$]BF_4\bullet CH_2Cl_2$. Attempts to refine peaks of residual electron density as solvent dichloromethane carbon or chlorine atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in PLATON.[24−26] A total solvent-accessible void volume of 254.5 Å^3 with a total electron count of 100 (consistent with two molecules of solvent dichloromethane or one molecule per formula unit of the hexarhenium complex ion) was found in the unit cell. The following distance restraints were applied to impose an idealized geometry upon the disordered PEt_3 group attached to Re2: d(P2−C7A) = d(P2−C9A) = d(P2−C11A) = d(P2−C7B) = d(P2−C9B) = d(P2−C11B) = 1.84 Å; d(C7A−C8A) = d(C9A−C10A) = d(C11A−C12A) = d(C7B−C8B) = d(C9B−C10B) = d(C11B−C12B) = 1.54 Å; d(Re2...C7A) = d(Re2...C9A) = d(Re2...C11A) = d(Re2...C7B) = d(Re2...C9B) = d(Re2...C11B) = 3.65 Å; d(P2...C8A) = d(P2...C10A) = d(P2...C12A) = d(P2...C8B) = d(P2...C10B) = d(P2...C12B) = 2.85 Å; and d(C7A...C9A) = d(C7A...C11A) = d(C9A...C11A) = d(C7B...C9B) = d(C7B...C11B) = d(C9B...C11B) = 2.84 Å. Restraints were also applied to a disordered ethyl group of the PEt_3 ligand bound to Re5: d(P5−C29) = 1.84 Å; d(C29−C30A) = d(C29−C30B) = 1.54 Å; d(P5...C30A) = d(P5...C30B) = 2.85 Å. The F−B distances within the disordered BF4− ion (d(F1A−B1A), d(F2A−B1A), ... d(F4B−B1B)) were fixed at 1.35 Å during refinement.

$[Re_6S_8(PEt_3)_5$(2,5-p-aminophenyltetrazolate)$]BF_4$. Distances within the disordered PEt_3 ethyl groups were fixed during refinement: d(P1A−C11A) = d(P1A−C13A) = d(P1A−C15A) = d(P1B−C11B) = d(P1B−C13B) = d(P1B−C15B) = 1.82(1) Å; and d(C11A−C12A) = d(C13A−C14A) = d(C15A−C16A) = d(C11B−C12B) = d(C13B−C14B) = d(C15B−C16B) = d(C35A−C36A) = d(C35B−C36B) = 1.54(1) Å.

Table 1. Crystallographic Data for $[Re_6Se_8(PEt_3)_5$(*p*-acetylbenzonitrile)$](BF_4)_2\bullet$MeCN (4**•$NCCH_3$), $[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$](BF_4)\bullet CH_2Cl_2$, (**8**•CH_2Cl_2), and $[Re_6Se_8(PEt_3)_5$(2,5-*p*-aminophenyltetrazolate)$](BF_4)$ (6)**

	4•$NCCH_3$	8•CH_2Cl_2	6
formula	$C_{39}H_{82}B_2F_8NOP_5Re_6Se_8\cdot NCCH_3$	$C_{37}H_{80}BF_4N_4P_5Re_6Se_8\cdot CH_2Cl_2$	$C_{37}H_{81}BF_4N_5P_5Re_6Se_8$
FW (g mol^{-1})	2699.46	2656.52	2586.61
space group	$P2_1/n$	$P\bar{1}$	$Pna2_1$
a (Å)	12.2340(10)	11.8298(7)	25.2743(27)
b (Å)	19.9378(17)	15.2084(8)	19.7358(14)
c (Å)	27.756(2)	18.4824(10)	12.2496(8)
α (deg)		88.1099(10)	
β (deg)	91.6087(13)	81.9099(9)	
γ (deg)		81.7607(10)	
V (Å^3)	6767.5(10)	3257.9(3)	6110.2(7)
Z	4	2	4
T (°C)	−80	−80	−80
radiation (λ (Å))	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ_{calcd} (g cm^{-3})	2.649	2.708	2.812
μ (mm^{-1})	15.16	15.81	16.78
Flack parameter			−0.017(7)
R_1 [$I \geq 2\sigma(I)$]	0.0366	0.0428	0.0254
wR_2 [all data]	0.0839	0.1263	0.0518

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Protonation of (8). $[Re_6Se_8(PEt_3)_5(2,5\text{-}N_4CPh)](BF_4)$ (~5 mg) was dissolved in ~1.5 mL CD_3CN in a stoppered NMR tube (Wilmad Pyrex LPV). One drop of HBF_4 (48% aqueous solution) was added to the solution and the tube was sealed. Within minutes of mixing the ^1H and ^{31}P NMR spectra were recorded ($t = 0$). The samples were then placed in an oil bath at 100 °C; at various time intervals the samples were removed from the oil bath, cooled, and subjected to NMR spectral analysis.

Alkylation Studies. The alkylation reactions that were monitored via NMR spectroscopy involved combining 5−10 mg of $[Re_6Se_8(PEt_3)_5(2,5\text{-}N_4CPh)](BF_4)$ or $[Re_6Se_8(PEt_3)_5(1,5\text{-}N_4CMe)](BF_4)$ and 20 equivalents of MeI or BnBr in 1.5−2.0 mL of $CDCl_3$ in a stoppered NMR tube (Wilmad Pyrex LPV). These reactions were monitored in a manner similar to the protonation studies described above.

RESULTS AND DISCUSSION

Synthesis. The synthesis of $[Re_6Se_8(PEt_3)_5(NCPh)]^{2+}$ was modeled after the preparation of the analogous acetonitrile complex,[20] $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ and involves combining a CH_2Cl_2 solution of $[Re_6Se_8(PEt_3)_5I]I$ with a benzonitrile solution of $AgBF_4$. Because of the fact that the *para*-substituted benzonitriles are solids and $AgBF_4$ is only sparing soluble in CH_2Cl_2, another solvent was needed to dissolve the silver salt in these reactions. Chlorobenzene was found to work well in the preparation of the *p*-methoxy, *p*-nitro, and *p*-acetyl benzonitrile complexes, leading to complete conversion of the starting material within 3 h or less. However, using the same conditions, the substitution reaction involving *p*-aminobenzonitrile in CH_2Cl_2/chlorobenzene only led to a 50% conversion after 3 h (even after 17 h some starting material still remained). Monitoring these substitution reactions via NMR spectroscopy at 1 h intervals, we observed an opposite trend from what we expected. The benzonitrile with the most electron withdrawing substituent (nitro) was complete in the shortest amount of time (1 h), while reaction with the most electron donating substituent (amino) did not completely convert. We believe this trend is due to a combination of the less polar solvent mixture causing the $AgBF_4$ to remain ion paired and the ability of the more electron-donating nitriles to coordinate more strongly to Ag(I) making it less reactive toward the cluster.[27] The synthesis of $[Re_6Se_8(PEt_3)_5(p\text{-aminobenzonitrile})]^{2+}$ was finally achieved using a more polar solvent mixture (CH_2Cl_2/acetone); however, unidentified impurities were difficult to remove, resulting in a much lower yield compared to the other preparations. The ^{31}P NMR spectra of the new nitrile complexes show two resonances in a 4:1 ratio, which is characteristic of the pentaphosphine cluster complexes.[16,20,28] The IR spectral data of compounds **1**−**5** all show the ν(CN) stretch for the coordinated nitriles, which is higher than that of the free nitriles, which was expected.[29]

In order to test the impact of the *para* substituent of the benzonitrile ligand on the electronic nature of the cluster complex, electrochemical measurements were obtained for all of the newly prepared benzonitrile complexes. Cyclic voltammetric data were recorded, and each of the five new complexes showed a single oxidative redox process, assigned to the Re(IV)Re(III)$_5$/Re(III)$_6$ couple, in the window scanned. Notably, all five complexes had couples with $E_{1/2} = 0.767 \pm 0.002$ V (vs $FeCp_2^+/FeCp_2$ in CH_2Cl_2) indicating that the *para* substituent has minimal impact on the redox properties of the cluster (Figures S1−S5, Supporting Information). This is likely due to the fact that the effect of the *para* substituent is distributed over the entire cluster and is, therefore, reduced compared to the impact on a single metal center.[30] However, the potentials of the benzonitrile complexes are a little higher than that reported for the acetonitrile complex, $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$, which has an $E_{1/2} = 0.754$ V vs $FeCp_2^+/FeCp_2$ under the same conditions.[16] Acetonitrile is a stronger donor (higher donor number[31]) than benzonitrile; therefore, it is not surprising that the monoacetonitrile complex is slightly easier to oxidize than the benzonitrile complexes reported here.

Even though the electronic effect of the *para* substituent on the $E_{1/2}$ value of this family of complexes is not measurable, the substituent does have an effect on the donating ability of the benzonitrile ligand as was shown in the following ligand substitution experiments. Because MeCN is the stronger Lewis base, we anticipated that it would substitute for the weaker benzonitrile ligands. To test this, we prepared three separate samples of $[Re_6Se_8(PEt_3)_5(p\text{-nitrobenzonitrile})]^{2+}$, $[Re_6Se_8(PEt_3)_5(NCPh)]^{2+}$, and $[Re_6Se_8(PEt_3)_5(p\text{-methoxybenzonitrile})]^{2+}$ each in CD_3CN and monitored them via ^{31}P NMR spectroscopy. Within 8 h, the solution containing the *p*-nitrobenzonitrile complex (resonances at −24.41 and −28.71 ppm) already showed the presence of some $[Re_6Se_8(PEt_3)_5(CD_3CN)]^{2+}$ (resonances at −24.76 and −28.88 ppm). Within 2 days, about 50% of the material had been converted, and within 7 days substitution was almost complete (Figure 2a). In contrast, it took 7 days for 50% of $[Re_6Se_8(PEt_3)_5(NCPh)]^{2+}$ to be converted to $[Re_6Se_8(PEt_3)_5(CD_3CN)]^{2+}$ (Figure 2b) and a little more than 7 weeks for complete conversion (Figure S6, Supporting Information). Monitoring the substitution of the $[Re_6Se_8(PEt_3)_5(p\text{-methoxybenzonitrile})]^{2+}$ complex was more difficult because the chemical shifts are so close to those of $[Re_6Se_8(PEt_3)_5(CD_3CN)]^{2+}$ that the peaks overlap. However, it is clear that at 7 weeks about two-thirds of the *p*-methoxybenzonitrile ligand had been substituted (Figure S7, Supporting Information). Therefore, the *para* substituent does have an impact on the reactivity of the coordinated nitrile ligand.

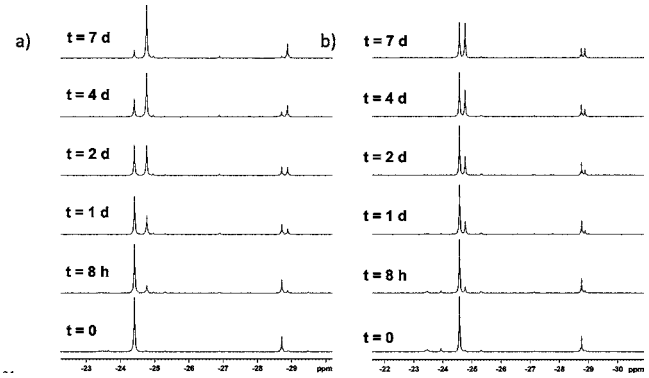

Figure 2. ^{31}P spectral data of samples taken at different time intervals in the substitution reaction of (a) $[Re_6Se_8(PEt_3)_5(p\text{-nitrobenzonitrile})](BF_4)_2$ and (b) $[Re_6Se_8(PEt_3)_5(NCPh)](BF_4)_2$ in CD_3CN. Resonances at −24.76 and −28.88 are due to $[Re_6Se_8(PEt_3)_5(CD_3CN)](BF_4)_2$.

In our initial preparation of the phenyltetrazolate complex, $[Re_6Se_8(PEt_3)_5(2,5\text{-}N_4CPh)]^+$, we combined $[Re_6Se_8(PEt_3)_5(NCPh)]^{2+}$ and Bu_4NN_3 and allowed the reaction to stir for 2 h at room temperature. This led to the complete conversion to the tetrazolate complex, demonstrating that benzonitrile ligands are also activated by the $[Re_6Se_8]^{2+}$ cluster core to undergo [2 + 3] cycloaddition reactions with inorganic azides. Later, we observed that sodium azide worked just as well and that the reaction occurred more rapidly than we thought

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(i.e., the reaction involving the benzonitrile complex was complete within minutes). Unlike the cyclization involving $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$ and N_3^- which leads to the exclusive formation of the N1-bound tetrazolate ligand within 15 min at room temperature, only the N2-bound tetrazolate was isolated for the phenyltetrazolate complexes reported here. Monitoring the reaction of $[Re_6Se_8(PEt_3)_5(NCPh)]^{2+}$ with sodium azide in acetone-d_6 via ^{31}P NMR spectroscopy, we see that all of the benzonitrile complex is gone within the first 5 min of the reaction (Figure S8, Supporting Information); at this time, the major product is $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$ at −28.42 and −31.39 ppm. In addition, there are two smaller peaks at −28.81 and −31.03 ppm. The peak at −28.81 ppm disappears after 30 min; this could possibly be the N1 isomer, but we did not attempt to isolate it as it was such a small fraction of the overall product. The other peak appears to be an impurity, which is removed via column chromatography. Ellis and Purcell also report that N1 to N2 isomerization of coordinated 5-phenyltetrazolate is faster than 5-methyltetrazolate.[32] The ^{13}C NMR spectral data for $[Re_6Se_8(PEt_3)_5(2,5\text{-}N_4CPh)]^+$ also supports N2 coordination. The tetrazole ring carbon in the ^{13}C NMR spectrum was observed at 163.7 ppm and falls with the range reported by Butler for 5-phenyl or pyridyl-substituted tetrazolate ligands coordinated through the N2 position.[33] Finally, the X-ray structure analyses of **8** and **6** also show that the phenyltetrazolate and the *p*-aminophenyltetrazolate ligands are coordinated through the N2 nitrogen. We believe this isomer is favored because of the steric size of the phenyl substituent. As expected, the ^{31}P NMR spectra of all of the tetrazolate complexes show two resonances in a 4:1 ratio, which are indicative of the 5:1 site-differentiation. Compared to the analogous dicationic benzonitrile complexes, there is an upfield shift of the ^{31}P resonances upon formation of the tetrazolate complexes; this upfield shift of the resonances of the more electron-rich monocationic complexes has been observed previously.[16,20] Also, there is a strong correlation between the chemical shift of the larger peak in the ^{31}P spectrum vs the Hammett parameters (R^2 = 0.97), demonstrating that the electronic effect of the *para* substituent does impact the phosphine ligands. The ^1H NMR spectral data for all newly prepared complexes is fairly straightforward to interpret. However, it is interesting that the ^1H NMR spectrum of $[Re_6Se_8(PEt_3)_5(2,5\text{-}p\text{-nitrophenyltetrazolate})]^+$ is different from the ^1H NMR spectra of the other *para*-substituted complexes. Instead of the expected pattern of doublets in the aromatic region, there is only one large peak that integrates for the same number of protons. Evidently, the two different sets of phenyl protons are nearly magnetically equivalent, resulting in almost no first-order coupling. This is supported by our simulation of the aromatic region of the ^1H NMR spectrum assuming near magnetic equivalency (Figure S9, Supporting Information). It is difficult to identify the stretches of the tetrazolate ring itself in the IR spectra of complexes **6** − **10**. However, for all but the $[Re_6Se_8(PEt_3)_5(2,5\text{-}p\text{-aminophenyltetrazolate})]^+$ complex, the $\nu(C{\equiv}N)$ stretch of the coordinated nitrile is absent in the IR spectra of the corresponding tetrazolate complexes. Because the spectral and elemental analysis data for this complex do not indicate any impurities, we believe that the complex is decomposing under pressure applied in preparing either a KBr pellet or collecting data via ATR.

The electrochemical properties of $[Re_6Se_8(PEt_3)_5(2,5\text{-}N_4CPh)]^+$ were investigated via cyclic voltammetry. In scanning from −0.30 to 1.00 V vs $FeCp_2^+/FeCp_2$, one quasi-reversible wave at 0.588 V is observed (Figure 3a), which has been assigned to the $Re(IV)Re(III)_5/Re(III)_6$ couple. We were able to determine the ligand electronic parameter, E_L, for 2,5-phenyltetrazolate (−0.10) using our previously reported relationship between $E_{1/2}$ and $\sum E_L$; this parameter is very similar to the value determined for 1,5-methyltetrazolate (E_L = −0.05).[16] Scanning out to a more positive potential, an irreversible peak at 1.239 V is evident, and on the return scan, a new cathodic peak near 0.684 V appears. Repeat scans within this window show a decrease in the intensity of the couple at 0.588 V and the growth of a new quasi-reversible wave at 0.715 V (Figure 3b).

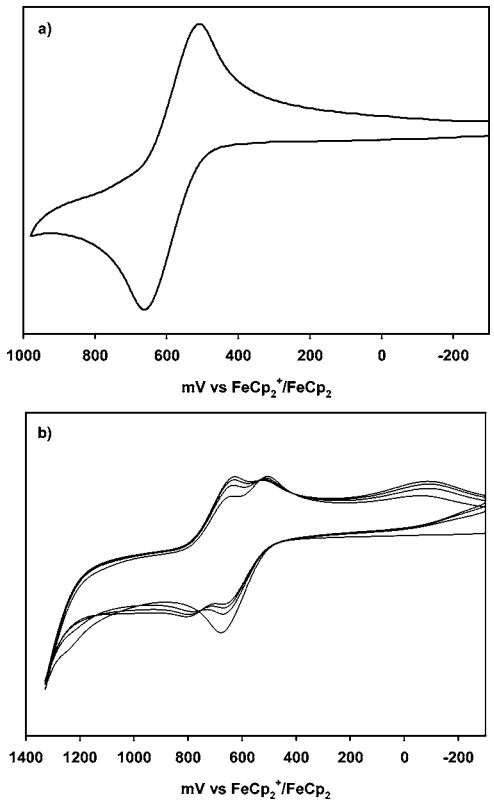

Figure 3. Cyclic voltammograms of $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})](BF_4)$ in CH_2Cl_2, at a) 100 mV/s and b) 400 mV/s (multiple scans).

The electrochemical study of $[Re_6Se_8(PEt_3)_5(1,5\text{-}N_4CMe)]^+$ showed similar decomposition after accessing the second oxidative process. At the time, we proposed that the tetrazolate ligand was decomposing back to the corresponding nitrile, $[Re_6Se_8(PEt_3)_5(NCMe)]^{2+}$, because the $E_{1/2}$ values of the decomposition product and the acetonitrile complex were so similar (within 15 mV). For the phenyltetrazolate complex, the redox potential of the decomposition product ($E_{1/2}$ = 0.715 V) is not the same as that of the corresponding benzonitrile complex $[Re_6Se_8(PEt_3)_5(NCPh)]^{2+}$ ($E_{1/2}$ = 0.754 V). Thus, we are no longer certain of the decomposition process.

The UV−vis spectra of the benzonitrile complexes all show one large absorbance at 225 nm in MeCN and multiple additional absorbances between 225 and 400 nm. The UV−vis spectral data of the phenyltetrazolate complexes look similar in that they also contain a large absorbance around 225 nm and then show numerous smaller absorptions that trail off at about 425 nm (Figures S10−S14, Supporting Information). Compounds **1**−**10** all display luminescent properties. We are

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currently conducting a detailed study on the excited state lifetimes and quantum yields of these cluster complexes.

Structure Analysis. Single crystals of **4**•$NCCH_3$, **8**•CH_2Cl_2, and **6** were grown via vapor diffusion technique and analyzed by X-ray diffraction. These complexes show core bond lengths (Re−Re) and (Re−Se) and angles (Re−Re−Re, Re−Re−Se, Se−Re−Se, and Re−Se−Re) that are not out of the ordinary for $[Re_6Se_8]^{2+}$-based cluster complexes.[34]

Table 2 shows the rhenium metal-terminal ligand bond lengths as well as the bond lengths of the tetrazolate rings. The

Table 2. Selected Bond Lengths for $[Re_6Se_8(PEt_3)_5$-(*p*-acetylbenzonitrile)$](BF_4)_2$•MeCN (4•$NCCH_3$), $[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$](BF_4)_2$•CH_2Cl_2, (8•CH_2Cl_2), and $[Re_6Se_8(PEt_3)_5$(2,5-*p*-aminophenyl-tetrazolate)$](BF_4)_2$ (6)

	4•$NCCH_3$	8•CH_2Cl_2	6
Re−P (mean)	2.474(2)−2.482(2) 2.479(1)	2.4262(2)−2.482(40) 2.467(10)	2.470(2)−2.482(2) 2.479(3)
Re6−N1	2.125(7)	–	–
Re6−N2	–	2.151(11)	2.137(7)
N1−N2	–	1.335(15)	1.350(10)
N2−N3	–	1.320(15)	1.311(9)
N3−N4	–	1.356(16)	1.322(10)
N4−C31/C1	–	1.310(19)	1.339(11)
C31/C1−N1	–	1.349(17)	1.329(10)

observed Re−P bond lengths fall within the 2.414−2.512 Å range observed for PEt_3 ligands coordinated to the $[Re_6Se_8]^{2+}$ cluster cores.[20,35] The Re−N(*p*-acetylbenzonitrile) bond distance in **4**•$NCCH_3$ is 2.151(11) Å; this is on the high end of bond lengths observed for single cluster Re-$NCCH_3$ ligands, which range from 2.09(2)−2.146(11) Å.[20,34] The ORTEP diagram of $[Re_6Se_8(PEt_3)_5$(*p*-acetylbenzonitrile)$]^{2+}$ is shown in Figure 4. The structures of the phenyltetrazolate complexes,

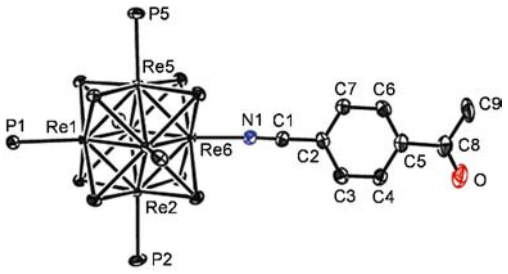

Figure 4. The ORTEP diagram of the $[Re_6Se_8(PEt_3)_5$(*p*-acetylbenzonitrile)$]^{2+}$ ion showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Hydrogen atoms and the carbon atoms of the PEt_3 ligands were omitted for clarity.

$[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$]^+$ and $[Re_6Se_8(PEt_3)_5$-(2,5-*p*-aminophenyltetrazolate)$]^+$, favor the N2 isomer as shown in Figure 5. The Re6−N2 bond lengths for these tetrazolate complexes are 2.151(11) and 2.137(7) Å for **8**•CH_2Cl_2 and **6**, respectively. This compares to a Re−N bond length of 2.143(8) Å reported earlier for the methyltetrazolate complex, $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$.[16] There is no significant difference between the bond lengths within the phenyltetrazolate ring themselves, indicating delocalization of the π electrons. This is what is commonly observed for nonbridging tetrazolate

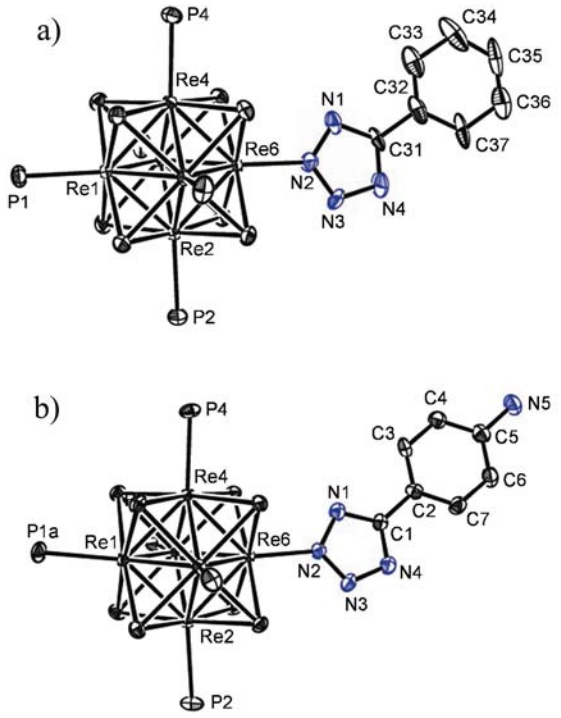

Figure 5. ORTEP diagrams of (a) $[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$]^+$ and (b) $[Re_6Se_8(PEt_3)_5$(2,5-*p*-aminophenyltetrazolate)$]^+$ showing the atom-labeling schemes. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Hydrogen atoms and the carbon atoms of the PEt_3 ligands were omitted for clarity.

ligands.[36] In contrast, $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ showed significant differences between bond lengths within the methyltetrazolate ring.[16] The planarity of the ring is not what is causing the difference, as all three complexes show planar tetrazolate rings. In addition, the phenyl and tetrazolate rings for both tetrazolate complexes nearly coplanar as indicated by the dihedral angles between the phenyl and tetrazolate ring for both of these structures (1.7(5)° for **6** and 7.7(10)° for **8**•CH_2Cl_2).

Reactivity Studies. Because of the various applications of free mono- and disubstituted tetrazoles,[37] we were interested in removing the newly formed heterocyclic rings from the $[Re_6Se_8]^{2+}$ cluster core. All reactivity studies were monitored via ^1H and ^{31}P NMR spectroscopy so that product formation could be observed over a period of time. The ^{31}P NMR data gave us insight into the transformation of the cluster complex, while the ^1H NMR spectral data enabled us to determine the outcome of the product heterocyclic rings.

Reaction of 8 with HBF_4. For the reaction of $[Re_6Se_8(PEt_3)_5$(2,5-phenyltetrazolate)$]^+$ with HBF_4 (conducted in CD_3CN, see Experimental Section for further details), the ^{31}P data was more useful because it was difficult to see the −NH hydrogen from the product in the ^1H NMR spectra. Figure 6 shows the ^{31}P spectral data for this reaction. Initially (t = 0) only the starting rhenium cluster (**8**) is present (peaks at −24.56 and −29.24 ppm). However, within 10 min a substantial amount of the product $[Re_6Se_8$-$(PEt_3)_5(NCCD_3)]^{2+}$ (peaks at −24.78 and −28.89 ppm) had formed, and the reaction was complete within 30 min. Because the reaction proceeded so quickly at 100 °C, we tested to see if the reaction would proceed at room temperature. Even after 6 h at ∼22 °C, there was no trace of the product cluster,

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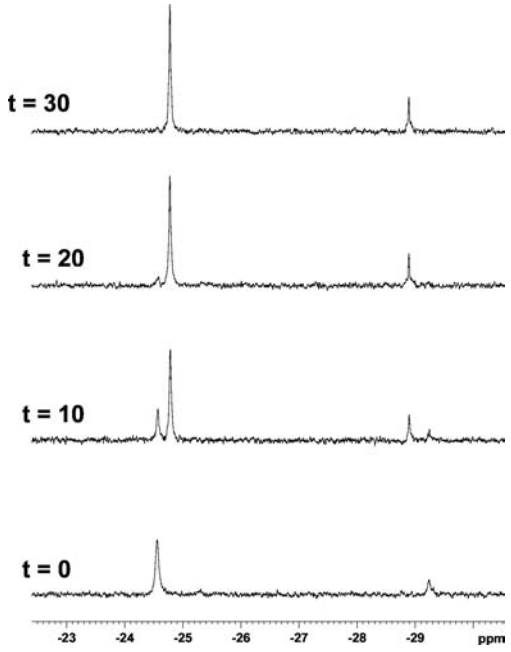


Figure 6. ^{31}P spectral data of the a CD_3CN solution containing $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$ with HBF_4 monitored over a 30 min time period. Resonances at −24.78 and −28.89 ppm are assigned to $[Re_6Se_8(PEt_3)_5(CD_3CN)]^{2+}$.

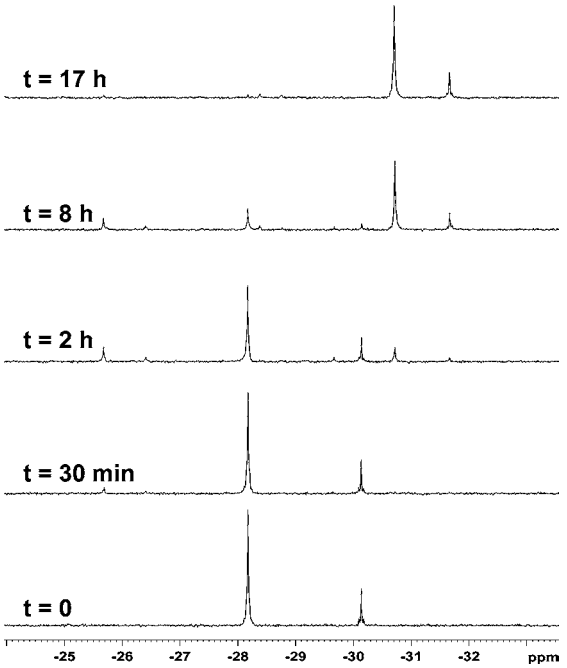
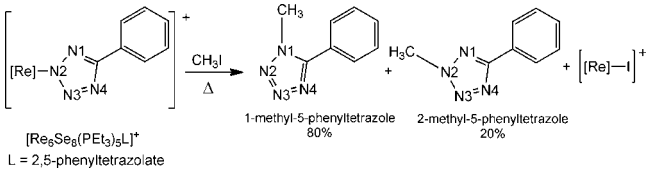


Figure 7. Reaction of $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$ and MeI in $CDCl_3$ monitored via ^{31}P NMR spectroscopy at different time intervals. Resonances at −30.71 and −31.66 ppm are due to $[Re_6Se_8(PEt_3)_5I]^+$.

$[Re_6Se_8(PEt_3)_5(NCCD_3)]^{2+}$. Thus, heat is necessary for this reaction to proceed. In 2007, we reported the displacement of free 5-methyltetrazole after heating a MeCN solution of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ and HCl at reflux for 48 h.[16] At that time, we did not monitor the reaction. Here, we found that after monitoring the reaction of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ with HBF_4 in CD_3CN (sealed NMR tube at 100 °C) by ^{31}P NMR spectroscopy, the reaction was complete within 12 h (i.e., complete conversion to $[Re_6Se_8(PEt_3)_5(NCCD_3)]^{2+}$). Comparing the protonation of these two tetrazolate complexes (2,5-phenyltetrazolate vs 1,5-methyltetrazolate), we see that protonation of the phenyl-substituted complex occurs much more quickly. This is likely caused by differences in the substituent on the tetrazolate ring. It is reasonable to assume that the methyl-substituted tetrazolate ligand would be a stronger Lewis base than the phenyl tetrazolate ligand because of the electron-donating nature of the methyl group, thus, making it more difficult to substitute, even when protonated.

Alkylation Studies. Alkylation of the tetrazolate ring also resulted in removal of these rings from the cluster core. The ^{31}P NMR spectral data for the reaction of $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})](BF_4)$ with MeI is shown in Figure 7. Over a 17 h time period, the resonances due to **8** decrease in intensity, while the resonances due to the formation of the $[Re_6Se_8(PEt_3)_5I]^+$ product increase in intensity. The ^1H NMR spectrum of the solution at 17 h shows the presence of two new resonances in the region expected for the $-NCH_3$ substituent, one at 4.38 and the other at 4.17 ppm (Figure S15, Supporting Information). Comparing our data with the previously reported values for the 1,5- and 2,5-disubstituted products, we concluded that a mixture of free tetrazoles, i.e., 2-methyl-5-phenyltetrazole ($N-CH_3$ at 4.38 ppm) and 1-methyl-5-phenyltetrazole ($N-CH_3$ at 4.17 ppm) actually formed (see Scheme 3).[38] The major product is 1-methyl-5-phenyltetrazole (80%) as determined by

Scheme 3



the integration of the proton resonances. The ^{31}P NMR spectral data obtained from the reaction of **8** with benzylbromide (BnBr) in $CDCl_3$ was similar to the MeI reaction in that the resonances of the PEt_3 ligands of **8** disappear over time as the resonances due to the $[Re_6Se_8(PEt_3)_5Br]^+$ product grow in (Figure S16, Supporting Information). The reaction takes about the same amount of time as the MeI reaction (24 h). The ^1H NMR spectrum taken at 24 h also shows the presence of both isomers of the alkylated product. Specifically, 1-benzyl-5-phenyltetrazole was present in 91% ($-CH_2-$ protons appear at 5.52 ppm) and the 2-benzyl-5-phenyltetrazole isomer in 9% ($-CH_2-$ protons appear at 5.70 ppm).[38,39] In both alkylation reactions, a very small set of peaks downfield of the starting complex begins to appear at ∼30 min to 1 h, increases in intensity at 4 h, and then decreases again. These peaks are no longer present once the reaction is over. We propose these are due to an intermediate, possibly the cluster complex containing the disubstituted tetrazole (vide infra).

We also investigated the reactivity of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ with both MeI and BnBr for comparison with the reactivity of **8**. Monitoring the reaction of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ with MeI via ^{31}P NMR spectroscopy, we see that within 30 min almost all of the starting cluster complex has been converted to what we believe is an intermediate whose peaks are shifted downfield from

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the starting material. Over the remainder of the reaction period (24 h), this cluster intermediate is slowly converted into the product iodo complex, $[Re_6Se_8(PEt_3)_5I]^+$ (Figure 8).

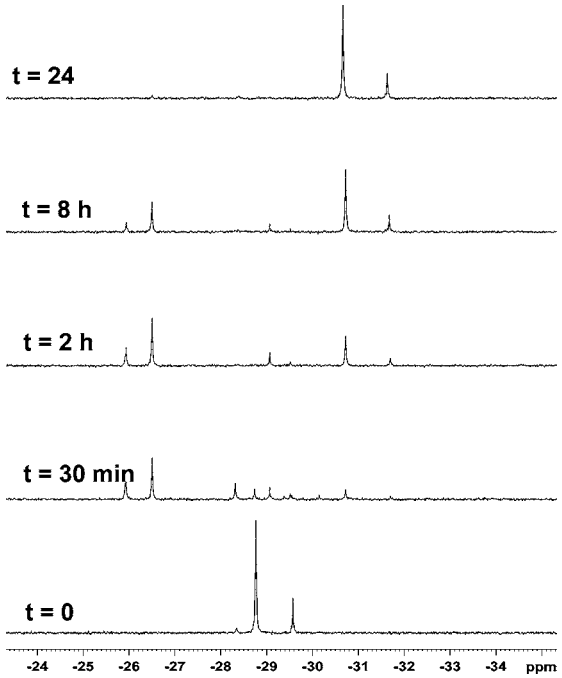

Figure 8. Reaction of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ and MeI in $CDCl_3$ monitored via ^{31}P NMR spectroscopy at different time intervals. Resonances at −30.67 and −31.63 ppm due to $[Re_6Se_8(PEt_3)_5I]^+$.

$[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$, which contains the N1 coordinated tetrazolate, is known to isomerize to a 50:50 mixture of the N1 and N2 coordinated tetrazolate ligands. Because we do not observe the formation of $[Re_6Se_8(PEt_3)_5(2,5\text{-methyltetrazolate})]^+$, the rapid conversion to this intermediate species must be faster than linkage isomerization. In terms of the alkylated products generated in this reaction, a mixture of free tetrazole isomers (72% 1-methyl-5-methyltetrazole and 28% 2-methyl-5-methyltetrazole) is shown in the ^1H NMR spectrum at 24 h (Figure S17, Supporting Information). These isomers were identified by both methyl substituents on the free tetrazole ring, i.e., 1-methyl-5-methyltetrazole appears at 2.55 ppm ($-CCH_3$) and 3.97 ppm ($-NCH_3$)), while 2-methyl-5-methyltetrazole appears at 2.50 ppm ($-CCH_3$) and 4.26 ppm ($-NCH_3$)).[38,40] The reaction of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ with BnBr is similar to that of MeI in that within an hour the ^{31}P resonances of the initial tetrazolate complex have disappeared and an intermediate has formed. Over the next 20 h, the conversion of the intermediate to the product complex, $[Re_6Se_8(PEt_3)_5Br]^+$, is observed (Figure S18, Supporting Information). Analysis of the ^1H NMR spectrum at 20 h shows the major organic product to be 1-benzyl-5-methyltetrazole generated in 74%. The resonances observed appear at 2.39 ($-CH_3$) and 5.44 ppm ($N-CH_3$) and match those observed by Nelson and coworkers.[38] We also observe a second set of peaks at 2.45 and 5.64 ppm, which we believe are due to the 2-benzyl-5-methyltetrazole.[41]

The intermediates observed in the above reactions are believed to be the cluster complex containing coordinated tetrazoles (i.e., the ring after it has been alkylated). For example, in the reaction of the $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ with MeI the intermediate would be $[Re_6Se_8(PEt_3)_5(1\text{-methyl-5-methyltetrazole})]^{2+}$. There are examples of metal complexes containing neutral tetrazole rings; in most cases, these have been generated via the alkylation or protonation of metal tetrazolate complexes with electrophilic reagents containing weakly coordinating anions (i.e., CF_3SO_3Me instead of MeI for the alkylating agent).[33,42] While intermediates are observed in all four of our alkylation reactions, they are most prominent in reactions containing the 1,5-methyltetrazolate ligand. Thus, we propose that alkylation of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ is relatively fast and subsequent substitution of the tetrazole ring by the halide is comparatively slow, i.e., $k_1 > k_2$ (Scheme 4a). Our data supports this theory as we see that the starting tetrazolate complex ($[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$) has completely reacted within ~1 h. (There actually appears to be a mixture of intermediates in these reactions, which could be assigned to the $[Re_6Se_8(PEt_3)_5(1,5\text{-dimethyltetrazole})]^{2+}$ and $[Re_6Se_8(PEt_3)_5(2,5\text{-dimethyltetrazole})]^{2+}$ isomers.) In contrast, it appears as though alkylation of $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$ is relatively slow. Therefore, we observe only small amounts of the intermediate. As soon as the phenyltetrazolate ring is alkylated, it is replaced by the halide ion in solution leading to the formation of the free tetrazole and the product cluster complex (Scheme 4b, $k_1 < k_2$). This behavior is likely a combination of both steric and electronic effects. The methyltetrazolate ring is more electron rich and less sterically hindered than the phenyltetrazolate ring. Therefore, we anticipated that the tetrazolate ring in $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ would be alkylated more quickly than that of $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$. Similarly, slow substitution of the neutral tetrazole ring in the intermediate shown in Scheme 4a, compared to Scheme 4b, is also consistent with this argument.

Even more interesting is the fact that these alkylations lead to the formation of a mixture of isomeric tetrazoles (i.e., 1,5-disubstituted and 2,5-disubstituted tetrazoles) as shown in Scheme 3. Nelson and co-workers reported the exclusive formation of 1,5-disubstituted tetrazoles when reacting $[Co(P(nBu)_3)(dmgH)_2(5\text{-R-tetrazolate})]$ (dmgH = monoanion of dimethylglyoxime, and R = CH_3, C_6H_5, etc.) with MeI and BnBr.[38] They concluded that sole formation of the 1,5-disubstituted isomer was indirect evidence of strictly N2 coordination of the anionic tetrazolate ligands (alkylation of the N1 or N4 nitrogen and subsequent removal would lead to the 1,5-disubstituted product). Other studies have also shown that alkylation or protonation occurs exclusively at the N4 site on both N1 and N2 coordinated tetrazolates[43] and show the formation of 1,5-disubstituted tetrazoles from N2 coordinated tetrazolates.[44] Mixtures of disubstituted tetrazoles are typically seen with alkali metal salts or metals containing a mixture of the N1 and N2 coordinated tetrazolate rings.[45] Although the free 1,5-disubstituted tetrazole is the major product in all of our alkylation studies, we do see 20% or more of the 2,5-disubstituted isomer in at least three of the reactions described here. In the case of $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$, we are aware that the coordinated ligand will undergo isomerization to a 50:50 mixture of the N1 and N2 tetrazolates in $CDCl_3$, which might explain the generation of both the 1,5- and 2,5-disubstituted products. However, we are certain that $[Re_6Se_8(PEt_3)_5(2,5\text{-phenyltetrazolate})]^+$ only contains the N2 coordinated tetrazolate; therefore, we were expecting to see the

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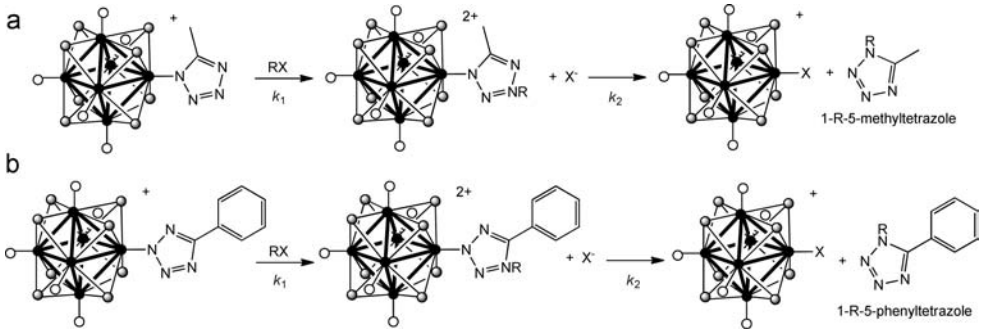
Scheme 4



exclusive formation of 1,5-disubstituted tetrazoles. In the reaction of **8** with MeI and BnBr, we observed formation of 20% of the 2-methyl-5-phenyltetrazole and 8% of 2-benzyl-5-phenyltetrazole, respectively. This indicates an isomerization process is taking place. There are some examples of disubstituted tetrazoles undergoing isomerization when one of the nitrogen atoms contains an imino substituent but only one known report involving the isomerization of dialkyl (or aryl) tetrazoles.[46,47] Isida et al. reported that 1-methyl-5-phenyltetrazole was quantitatively converted to 2-methyl-5-phenyltetrazole when heated at 130 °C in MeI for 10 h.[47] However, heating 1-methyl-5-phenyltetrazole at 70 °C for 20 h led to a mixture of 2-methyl-5-phenyltetrazole (27%) and the 1,4-dimethyl-5-phenyltetrazolium salt (35%).

Considering the possibility of this type of isomerization taking place, we examined the data obtained from the reaction of **8** with MeI more carefully. It is necessary for us to point out that there is some discrepancy in the literature values reported for the 2-methyl-5-phenyltetrazole (but not for 1-methyl-5-phenyltetrazole). Therefore, while we are certain that the resonance at 4.17 ppm is due to 1-methyl-5-phenyltetrazole, it is difficult for us to unambiguously assign the resonance at 4.38 ppm, i.e., is it the 2,5-disubstituted product or the 1,4-dimethyl-5-phenyltetrazolium salt? Nelson reports free 2-methyl-5-phenyltetrazolate at 4.35 ppm, while Fraser and Haque report it at 4.25 ppm, and the methyl resonances of the 1,4-dimethyl-5-phenyltetrazolium salt appears at 4.30 ppm according to Isida.[38,47,48] On the basis of Isida's isomerization study, we would expect the 1,5-disubstituted isomer to be generated early on in the reaction, and then the 1,5-disubstituted tetrazole would isomerize into the 2,5-disubstituted isomer. In addition, we would expect to see only the 2-methyl-5-phenyltetrazole product or a mixture of the 2,5-disubstituted isomer and the tetrazolium salt. However, the 1,5-disubstituted tetrazole is the major product in this and all alkylation reactions. Therefore, we propose that a different mechanism for isomerization is in play. It seems likely that the $[Re_6Se_8]^{2+}$ cluster core is facilitating the isomerization process. Possibilities include π bonded tetrazole or tetrazolate intermediates.[49] However, further studies need to be conducted to elucidate the exact mechanism.

Summary. All of newly reported benzonitrile complexes (compounds **1**−**5**) undergo cycloaddition reactions with inorganic azides to form 5-phenyltetrazolate rings. There is no noticeable effect of the *para* substituent on the redox properties or the cycloaddition reactivity of the benzonitrile complexes. However, the *para* substituent does influence the rate of substitution of the benzonitrile ligand by MeCN. The tetrazolate complexes, **8** and $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$, undergo reaction with electrophilic reagents leading to the formation of free (noncoordinated) tetrazoles. Alkylation studies revealed the formation of 1,5- and 2,5-disbustituted tetrazoles. This unexpected result indicates an isomerization process taking place; the data indicate the possibility of the cluster complex facilitating this isomerization process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cyclic voltammograms of compounds **1**−**5** (Figures S1−S5), ^{31}P NMR spectra of **3** and **5** in CD_3CN after 7 weeks (Figure S6), ^{31}P NMR spectra of **2** in CD_3CN at different time intervals (Figure S7), ^{31}P NMR spectra of **3** plus NaN_3 in acetone-d_6 at different time intervals (Figure S8), simulated and experimental ^1H NMR spectrum of **10** (Figure S9), UV−vis spectra of all compounds (Figures S10−S14), ^1H NMR spectrum at 17 h of the reaction between **8** and MeI (Figure S15), ^{31}P NMR spectra data of the reaction between **8** and BnBr (Figure S16), ^1H NMR spectrum at 24 h of the reaction between $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ and MeI (Figure S17), and ^{31}P NMR spectra data of the reaction between $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolate})]^+$ and BnBr (Figure S18). The X-ray crystallographic files in CIF format for **4**•$NCCH_3$, **8**•CH_2Cl_2, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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