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1,6-Bis(trimethylsilyl)hexa-1,3,5-triyne as a precursor to ruthenium clusters containing highly ethynylated ligands[1]

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Abstract

The reaction of 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne (**1**) with $Ru_3(CO)_{12}$ results in the formation of the butterfly cluster $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**2**) and the yellow binuclear complex $Ru_2(CO)_6\{\mu\text{-}\eta^2\text{-}\eta^4\text{-}C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3)\}$ (**3**). Both complexes contain pendant ethynyl ligands that are potential sites for further reactivity. In the case of reaction of **1** with the tetranuclear cluster $Ru_4(\mu_4\text{-}PPh)(CO)_{13}$ (**4**), the open chain molecule $Ru_4(CO)_8(\mu_3\text{-}PPh)[\mu_4\text{-}\eta^2,\eta^4,\eta^2,\eta^4\text{-}(Me_3SiC{\equiv}C)CC(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C\text{-}CC(SiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)]$ (**6**) is formed, in which the co-ordination of a pendant ethynyl moiety has been realised. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium clusters; 1,6-Bis(trimethylsilyl)hexa-1,3,5-triyne; Ethynyl clusters

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1. Introduction

Recognition that metal complexes of highly conjugated polycarbon ligands, such as polyynes $R\text{–}(C{\equiv}C)_x\text{–}R$, polyynyls $R\text{–}(C{\equiv}C)_x\text{–}$, polyynediyls $\text{–}(C{\equiv}C)_x\text{–}$ and polyalkaenylidenes $={(C{=}C)_x}{=}CR_2$, may possess promising physical [1] and chemical [2] properties has spurred a renaissance in the organometallic chemistry of non-cyclic polyunsaturated molecules. In this regard, several groups have recently studied the reactions of conjugated 1,3-diynes with various metal complexes and clusters [3]. In most cases, the first formed products are ethynyl-substituted derivatives of the analogous complexes obtained from reactions with simple monoalkynes. In the case of asymmetrically substituted diynes, $RC{\equiv}CC{\equiv}CR'$, the reactions often produce both regioisomers arising from co-ordination of each $C{\equiv}C$ moiety [4,5]. Among the rare examples of selective co-ordination of one triple bond in an asymmetric diyne are the high valent tungsten complexes of $PhC{\equiv}CC{\equiv}CSiMe_3$ prepared by Dehnicke and co-workers [6], and rotomers of $Re(\eta^2\text{-}HC_2CC{\equiv}CSiMe_3)(NO)(PPh_3)(\eta^5\text{-}C_5Me_5)$ reported by Gladysz et al. [7]. To date 1,3,5-triynes have not been extensively explored as ligands to transition metal centres.

In cluster systems, the presence of a pendant ethynyl group may lead to further chemistry, including the incorporation of the second alkynyl moiety, as in the conversion of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}RC_2C{\equiv}CR)$ to $Ru_4(CO)_{10}(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^1,\eta^1,\eta^3,\eta^3\text{-}RC_2C_2R)$ ($R = Ph, SiMe_3$) [8]; C–C bond cleavage as observed in the thermolysis of the osmium clusters $Os_3(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}RC_2C{\equiv}CR')(\mu\text{-}CO)(CO)_9$ ($R = Ph$; $R' = Ph, SiMe_3$ [9], $W(CO)_3(\eta^5\text{-}C_5Me_5)$ [10]); oligomerisation of the diyne ligand or other C–C bond forming reactions, sometimes with cluster fragmentation as observed in the reactions of $Ru_3(CO)_{12}$ with $RC{\equiv}CC{\equiv}CR'$ ($R = R' = Ph$ [11], ferrocenyl [12]; $R = H$, $R' = W(CO)_3Cp$ [13]); and the formation of novel cluster frameworks as found in the reaction of $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)(\mu\text{-}CO)(CO)_9$ with $Co_2(CO)_8$ [14].

We are exploring the application of various complexes bearing pendant alkynyl and other polyynyl ligands as precursors to the assembly of metal-rich

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[1] Dedicated to Professor Michael Bruce, a respected colleague and valued friend, on the occasion of his 60th birthday.

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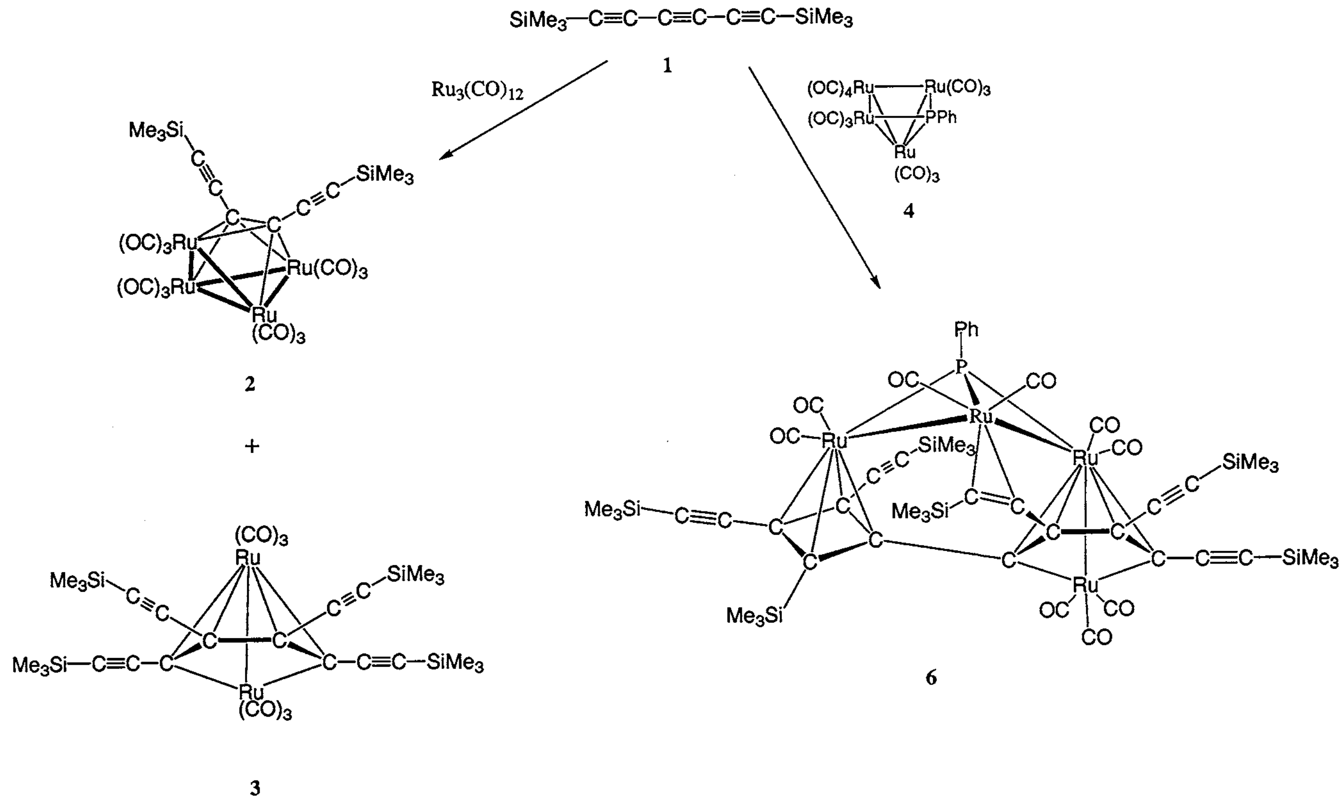

Scheme 1.

polycarbon systems [15]. We report herein the use of the air-stable, crystalline triacetylene 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne (**1**), a synthon of the vastly more sensitive compound hexa-1,3,5-triyne, as a reagent in the preparation of complexes bearing multiple pendant trimethylsilyl ethynyl groups.

The reaction of **1** with $Ru_3(CO)_{12}$ in refluxing hexane afforded two major products, isolated by chromatography on Florisil. These were identified as the red tetranuclear butterfly cluster $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**2**) (30%) and the yellow binuclear complex $Ru_2(CO)_6\{\mu\text{-}\eta^2,\eta^4\text{-}C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3)\}$ (**3**) (40%) (Scheme 1). The comparatively high yield of cluster **2** in this reaction is particularly notable. Related reactions of $Ru_3(CO)_{12}$ with alkynes $RC{\equiv}CR'$ ($R = Ph$, $R' = Me$, Et, Ph, $C{\equiv}CPh$; $R = R' = CH_2OMe$) afford similar clusters (vide infra), but in only 5–10% yields.

The identities of **2** and **3** were established spectroscopically[2] via comparison with the data reported for several analogous complexes, and confirmed by single crystal X-ray studies, the details of which will be reported elsewhere. For **2** the ^{13}C-NMR spectrum contained only three quaternary carbon resonances, consistent with a high degree of symmetry in the molecule. The carbon nuclei of the uncoordinated alkyne moieties gave rise to typical alkyne signals at δ 116.3 and 96.0, while the co-ordinated carbon atoms gave rise to a single low-field resonance at δ 153.8. The ^{13}C-NMR spectrum of ruthenole (**3**) contained six low-field resonances at δ 137.57, 111.85, 108.59, 107.23, 100.38 and 97.94, arising from the alkynyl and ruthenole ring carbon atoms, which could not be unambiguously assigned.

Complexes with related core structures are known from reactions of $Ru_3(CO)_{12}$ with both alkynes [16] and 1,3-diynes [11,12]. However, the reactions with 1,3-diynes are complicated by the formation of mixtures of isomers arising from the various possible head-to-head, head-to-tail and tail-to-tail coupling combinations. In contrast, **1**, which has three accessible triple bonds, affords only two products, both of which are derived

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[2] Selected spectrocopic data. **2**, IR (C_6H_{12}) $\nu(C{\equiv}C)$ 2140 vw; $\nu(CO)$ 2098 w, 2075 vs, 2050 s, 2024 vs, 2021 m, 1977 w cm^{-1}. FAB MS: (m/z) 960, M^+; 932–764, $[M\text{-}nCO]^+$ ($n = 1$–7). ^{1}H-NMR ($CDCl_3$): δ 0.19 (s, $SiMe_3$). ^{13}C-NMR ($CDCl_3$): δ 197.12 (s, CO); 190.57 (s, CO); 153.84 (s, C[3,4]); 116.30 (s, C[2]), 96.00 (s, C[1]), −0.35 (s, $SiMe_3$). **3**, IR (C_6H_{12}) $\nu(C{\equiv}C)$ 2159 vw, 2133 w; $\nu(CO)$ 2089 s, 2064 vs, 2027 vs, 2009 s, 1997 m, 1984 w cm^{-1}. FAB MS: (m/z) 808, M^+; 780–640, $[M\text{-}nCO]^+$ ($n = 1$–6). ^{1}H-NMR ($CDCl_3$): δ 0.28, 0.17 (2 s, 2 $SiMe_3$). ^{13}C-NMR ($CDCl_3$): δ 195.21, 194.02, 193.34 (3 s, 3 CO); 137.57, 111.85, 108.59, 107.23, 100.39, 97.94 [6 s, $C_4(C{\equiv}CSiMe_3)$]; −0.21, −0.49 (2 s, 2 $SiMe_3$). **6**, IR (C_6H_{12}) $\nu(C{\equiv}C)$ 2144 w, 2122 w; $\nu(CO)$ 2081 s, 2037 vs, 2023 vs, 2009 m, 2001 s, 1072 sh, 1966 m, 1949 m cm^{-1}. FAB MS; (m/z) 1420, M^+; 1392–1336, $[M\text{-}nCO]^+$ ($n = 1$–3). ^{1}H-NMR ($CDCl_3$): δ 0.06 (s, 9H, 3 $SiMe_3$), 0.27, 0.32, 0.78 (3 s, 3 $SiMe_3$). ^{31}P-NMR ($CDCl_3$): δ 427.28 (s, PPh).

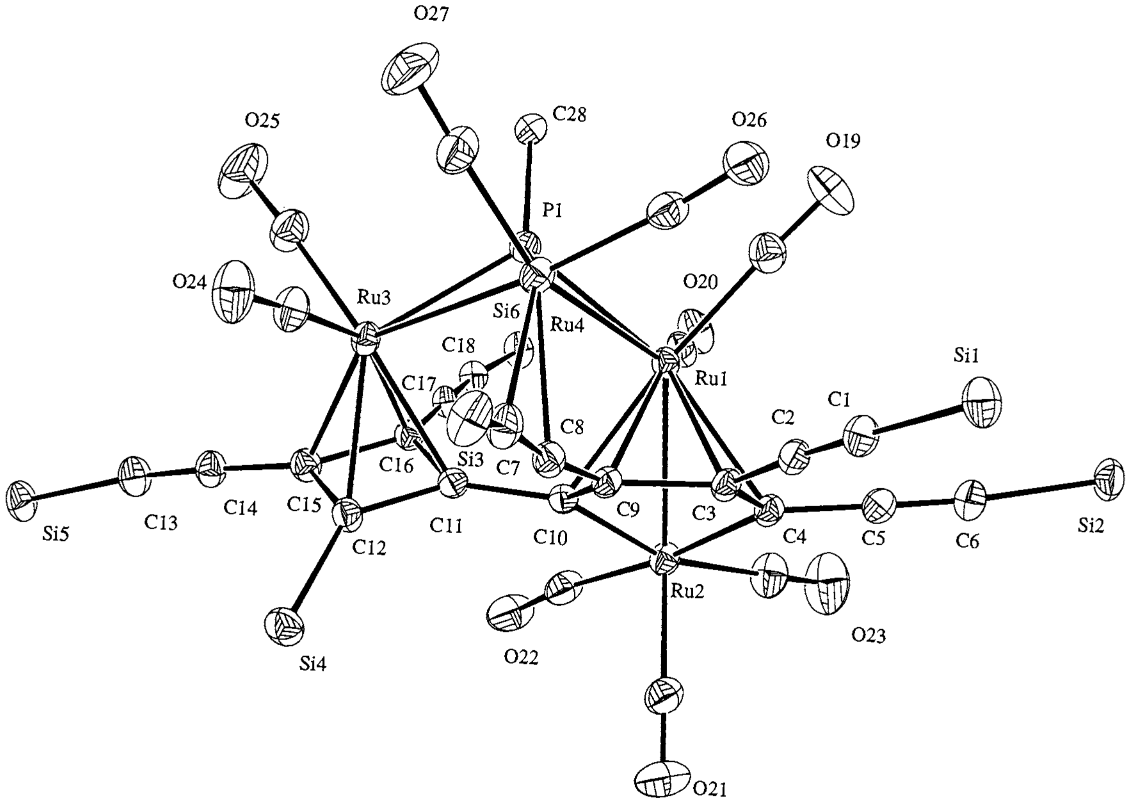

Fig. 1. View of the molecular structure of **6**. For clarity, only the *ipso*carbon of the phenyl group is shown, while the silyl methyl groups have been omitted. Ru(1)–Ru(2) 2.7912(4), Ru(1)–Ru(4) 2.9964(4), Ru(l)–P(1) 2.3393(8), Ru(1)–C(3) 2.312(3), Ru(1)–C(4) 2.315(3), Ru(1)–C(9) 2.310(3), Ru(1)–C(10) 2.191(3), Ru(2)–C(4) 2.073(3), Ru(2)–C(10) 2.082(3), Ru(4)–C(7) 2.394(3), Ru(4)–C(8) 2.263(3), Ru(4)–P(1) 2.2196(8), Ru(3)–C(11) 2.192(3), Ru(3)–C(12) 2.236(3), Ru(3)–C(15) 2.175(3), Ru(3)–C(16) 2.150(3), C(1)–C(2) 1.193(4), C(2)–C(3) 1.441(4), C(3)–C(4) 1.405(4), C(4)–C(5) 1.443(4), C(5)–C(6) 1.201(4), C(7)–C(8) 1.223(5), C(8)–C(9) 1.431(4), C(9)–C(10) 1.458(4), C(10)–C(11) 1.467(4), C(11)–C(12) 1.467(4), C(13)–C(14) 1.198(4), C(14)–C(15) 1.422(4), C(15)–C(16) 1.474(4), C(17)–C(18) 1.209(4) Å. Ru(2)–Ru(1)–Ru(4) 128.267(11), Ru(2)–Ru(1)–P(1) 127.537(23), Ru(1)–Ru(4)–Ru(3) 80.621(9), C(1)–C(2)–C(3) 174.7(3), C(2)–C(3)–C(4) 122.8(3), C(3)–C(4)–C(5) 119.2(3), C(4)–C(5)–C(6) 177.7(3), C(7)–C(8)–C(9) 171.8(3), C(13)–C(14)–C(15) 177.1(4), C(14)–C(15)–C(16) 133.0(3), C(16)–C(17)–C(18) 178.9(3) °.

from reaction exclusively at the internal C≡C triple bond. In fact, we have been unable to detect any products formed by co-ordination of the 'external' triple bonds. While some of this selectivity may no doubt be attributed to the steric influence of the $SiMe_3$ caps, it is also possible that hyper-conjugation of the Si d-orbitals with the triyne π-system occurs [17], a phenomenom that leads to reduced electron density at the triple bonds adjacent to silicon, and therefore deactivates these sites.

The selective reaction of the internal C≡C triple bond of **1** with $Ru_3(CO)_{12}$ prompted us to examine the reaction of the triyne with $Ru_4(\mu_4\text{-}PPh)(CO)_{13}$ (**4**). Cluster **4** has previously been shown to trimerise PhC≡C-C≡CPh to give $Ru_4(CO)_8(\mu_4\text{-}PPh)[\mu_4\text{-}\eta^2,\eta^4,\eta^2,\eta^4\text{-}(Ph)CC(C{\equiv}CPh)C(Ph)C\text{-}CC(Ph)C(Ph)C(C{\equiv}CPh)]$ (**5**), with the unusual C_{12} hydrocarbon ligands co-ordinated to a distorted Ru_4 square. The reaction of **4** with a threefold excess of **1** resulted in the formation of cluster $Ru_4(CO)_8(\mu_3\text{-}PPh)[\mu_4\text{-}\eta^2,\eta^4,\eta^2,\eta^4\text{-}(Me_3SiC{\equiv}C)CC(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C\text{-}CC(SiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)]$ (**6**) in high yield (Scheme 1). The structure was

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[3] Crystal data for $Ru_4(CO)_8(\mu_3\text{-}PPh)[\mu_4\text{-}\eta^2,\eta^4,\eta^2,\eta^4\text{-}(Me_3SiC{\equiv}C)CC(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C\text{-}CC(SiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)]$ (**6**): $Ru_4Si_6C_{51}O_9H_{59}$, $M = 1419.78$, monoclinic, space group $P2_1/n$, $a = 11.0862(5)$, $b = 22.5737(10)$, $c = 26.2829(12)$ Å, $\beta = 101.32(1)°$, $V = 6449.4(5)$ Å^3, $Z = 4$, $D_{calc.} = 1.462$ g cm^{-1}, $F(000) = 2831.41$, $\mu(\text{Mo–K}_\alpha) = 1.10$ mm^{-1}. A dark red block-shaped crystal ($0.10 \times 0.15 \times 0.30$ mm^3), obtained by diffusion of methanol into a CH_2Cl_2 solution of **6**, was used for the data collection on a Siemens SMART CCD diffractometer using the ω scan mode. Cell dimensions were obtained from 8192 reflections with 2θ in the range 3.00–57.50°. The h, k, l ranges used during the structure solution and refinement are h(min, max) -15, 14; k(min, max) 0, 30; l(min, max) 0, 35. Unique reflections: 16659, of which 12173 had $I \geq 2\sigma(I)$, were used. An empirical absorption correction was applied. Hydrogen atoms were placed in calculation positions, and allowed to ride on their parent atoms. The structure was solved by direct methods, and refined by full-matrix least-squares. The function minimised in the least-squares calculation was $\Sigma\, w(|F_O| - |F_C|)^2$. A weighting scheme of $w^{-1} = \sigma 2(F)$ was used. The last least-squares cycle was calculated with 130 atoms, 640 parameters and 13115 out of 16659 reflections. For all significant reflections $R_f = 0.039$, $R_w = 0.034$, goodness-of-fit = 2.14. For all reflections $R_f = 0.060$, $R_w = 0.037$, where $R_f = \Sigma(F_O - F_C)/\Sigma\, F_O$, $R_w = [\Sigma\{w(F_O - F_C)^2\}/\Sigma(wF_O^2)]^{1/2}$ and goodness-of-fit = $[\Sigma\{w(F_O - F_C)^2\}/(\text{No. of reflections} - \text{No. of parameters})]^{1/2}$. $(\Delta/\sigma)_{max} = 0.005$. Max/min residual density -0.540e, 0.740 Å^{-3}.

established by a single crystal X-ray study[3], and is shown in Fig. 1. The organic ligand in **6** is a trimer of **1** and is an unusual example of a co-ordinated, acyclic C_{18} fragment. The metal framework of the molecule consists of four ruthenium atoms in an open-chain arrangement. The metal atoms Ru(1), Ru(3) and Ru(4) form an open-triangular array, capped by a μ_3-phosphinidene ligand (^{31}P δ 427.28), with Ru(2) significantly displaced out of the plane defined by the other metal atoms. A tetraethynylated ruthenole, similar to **3**, is formed about Ru(1) and Ru(2) through the central triple bonds of two molecules of **1**. A cyclobutadiene ligand, presumably formed by [2 + 2] cycloaddition of one pendant ethynyl moiety of the ruthenole with the central triple bond of the third molecule of **1**, is co-ordinated in the usual η^4-mode to Ru(3). The fourth metal atom Ru(4) is co-ordinated by two carbonyl ligands, has metal–metal interactions to Ru(1) and Ru(3) and a two electron η^2 interaction from the C(7)–C(8) ethynyl group.

In **5** an agostic interaction from a C–Ph bond of the cyclobutadiene moiety is required to achieve electronic saturation at the metal centre related to Ru(4). It appears that the open metal framework of **6** may be attributed to the more flexible co-ordinating properties of the organic ligand in this case, resulting from the presence of the extra ethynyl moiety.

We believe that these are the first reactions to be reported between ruthenium carbonyl clusters and a conjugated triyne. The relatively high yields, simple product distributions and selectivity of the reactions lead us to believe that **1** will be a potentially valuable source of many other cluster species containing pendant ethynyl moieties. We are currently exploring the potential of metal complexes such as polyethynylated **2** and **3** as ligands for the sequestering of other metal fragments.

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