

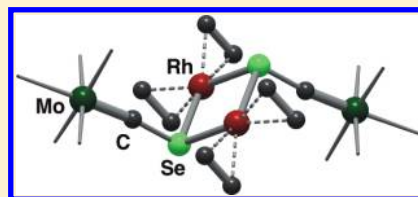
# Novel Carbon Monochalcogenide Coordination Mode: $[\text{Rh}_2\{\mu\text{-SeCMo}(\text{CO})_2(\text{Tp}^*)\}_2(\eta^4\text{-cod})_2]$ ( $\text{Tp}^* = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$ ; $\text{cod} = \text{cyclo-octa-1,5-diene}$ )

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## Supporting Information

**ABSTRACT:** The reaction of  $[\text{Et}_4\text{N}][\text{Mo}(\text{CSe})(\text{CO})_2(\text{Tp}^*)]$  ( $\text{Tp}^* = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$ ) with  $[\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$  ( $\text{cod} = \text{cyclo-octa-1,5-diene}$ ) results in the formation of the tetrametallic complex  $[\text{Rh}_2\{\text{SeCMo}(\text{CO})_2(\text{Tp}^*)\}_2(\eta^4\text{-cod})_2]$  in which the CSe ligand adopts a crystallographically confirmed and unprecedented  $\mu_3:\sigma,\sigma'(\text{Se}),\sigma''(\text{C})$  coordination mode.



## INTRODUCTION

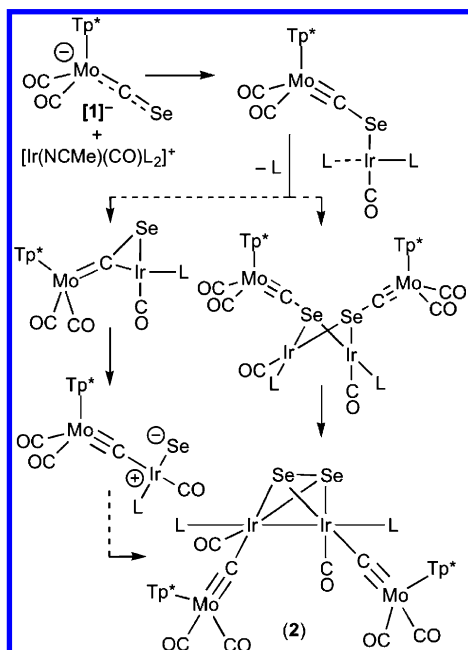
We have previously described<sup>1</sup> an unusual reaction between the selenocarbonyl salt  $[\text{Et}_4\text{N}][\text{Mo}(\text{CSe})(\text{CO})_2(\text{Tp}^*)]$ ,<sup>2</sup>  $[\text{NEt}_4][\mathbf{1}]$  ( $\text{Tp}^* = \kappa^3\text{-hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$ ), and  $[\text{Ir}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ ,<sup>3</sup> which results in unexpected C–Se cleavage to afford a tetrametallic bis( $\mu$ -carbido) species,  $[\text{Ir}_2(\mu\text{-Se}_2)\{\text{C}\equiv\text{Mo}(\text{CO})_2(\text{Tp}^*)\}_2(\text{CO})_2(\text{PPh}_3)_2]$  (**2**).

Our mechanistic conjecture on the route to **2** (Scheme 1) might have sufficed were it not for the attention that carbon–chalcogen bond cleavage reactions of the heavier carbon monochalcogenides

have enjoyed of late.<sup>4,5</sup> Accordingly, we have pursued phenomena to reinforce or revise our proposal. A key step involves the formation of selenocarbonyl complexes in which the CSe ligand is activated by coordination to two or possibly more metal centers. We have also had occasion to implicate a bridging selenocarbonyl ligand in the unusual rearrangement of an alkynylselenolatocarbene to a binuclear selenoacyl complex.<sup>6a</sup> Previously, however, bridging selenocarbonyl ligands were limited to the complexes *cis*- and *trans*- $[\text{Pt}\{\text{SeCMo}(\text{CO})_2(\text{Tp}^*)\}(\text{C}\equiv\text{CBu})(\text{PPh}_3)_2]$ , which arise via insertion of platinum(0) into the C–Se bond of the alkynylselenolatocarbene complex  $[\text{Mo}(\text{C}\equiv\text{CSeC}\equiv\text{C}'\text{Bu})\text{-(CO)}_2(\text{Tp}^*)]$ .<sup>6b,c</sup>

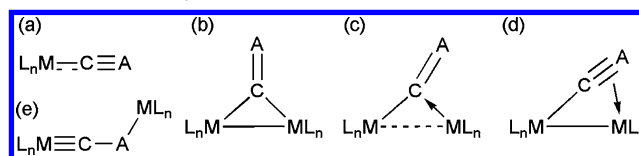
In contrast, a range of bridging modes have been identified<sup>7,8</sup> for carbon monosulfide (Chart 1). These in general have parallels

**Scheme 1. Mechanistic Proposal for the Formation of a Carbido Complex (2) via C–Se Bond Cleavage<sup>a</sup>**



<sup>a</sup>L = PPh<sub>3</sub>.

**Chart 1. Coordination Modes for Carbon Monochalcogenide (CA: A = S, Se): (a) Terminal; (b) Bridging; (c) Semibridging; (d)  $\sigma$ - $\pi$ -Bridging; (e) Isochalcocarbonyl<sup>7,8</sup>**



in the chemistry of CO, though the propensity for bridging is more enhanced for CS compared with CO ligands.<sup>9</sup>

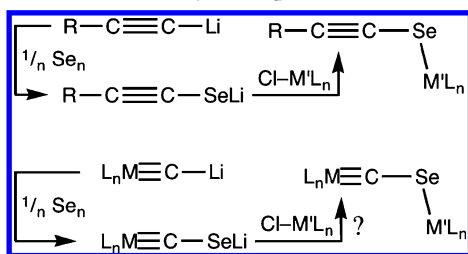
Herein, we report the isolation of a bridging seleno carbonyl complex in which the CSe diatomic bonds in a manner not previously seen for either CS or CO.

## RESULTS AND DISCUSSION

The reactions of alkynylselenolate anions with transition metal halides afford  $\sigma$ -(Se)-alkynylselenolato complexes (Scheme 2),<sup>10,11</sup>

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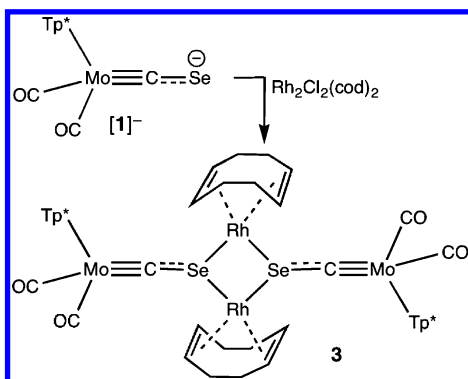
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**Scheme 2. Alkynylselenolato Complexes and a Possible Route to Isoselenocarbonyl Complexes<sup>10 a</sup>**


<sup>a</sup>R = C<sub>6</sub>H<sub>4</sub>Me-4, SiMe<sub>3</sub>, ML<sub>n</sub> = Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>, Mo(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), Ni(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>).

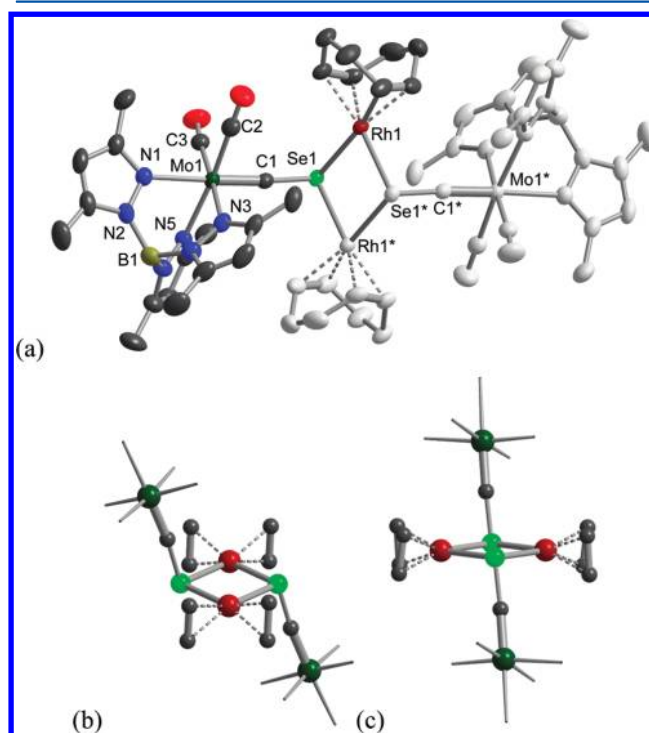
and the complex [Ir(SeC≡CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>10a</sup> provided the initial motivation for exploring the reaction of [Et<sub>4</sub>N][1] with [Ir(NCMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> in the hopes of isolating an analogous isoselenocarbonyl (Chart 1e) complex. Reasoning that the electron-rich nature of the phosphine-ligated iridium center might have facilitated the C–Se bond cleavage, to deter this, the reaction of [Et<sub>4</sub>N][1] with [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(η<sup>4</sup>-cod)<sub>2</sub>]<sup>12</sup> (cod = cyclo-octa-1,5-diene) was investigated. It has long been established that the bridging chlorides in [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(η<sup>4</sup>-cod)<sub>2</sub>] may be displaced to form thiolato-bridged complexes [Rh<sub>2</sub>(μ-SR)<sub>2</sub>(η<sup>4</sup>-cod)<sub>2</sub>] with ultimate retention of the binuclear arrangement.<sup>13</sup>

A slow reaction ensues between [Et<sub>4</sub>N][1] and [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(η<sup>4</sup>-cod)<sub>2</sub>] in THF, accompanied by the development of new infrared absorption bands at 1982, 1974, and 1901 cm<sup>-1</sup>. Column chromatography yielded a bright orange band, from which was isolated a complex formulated as the tetrametallic species [Rh<sub>2</sub>{μ-SeCMo(CO)<sub>2</sub>(Tp\*)}<sub>2</sub>(η<sup>4</sup>-cod)<sub>2</sub>] (3, Scheme 3) on the basis of spectroscopic and mass spectrometric data.

**Scheme 3. Synthesis of CSe-Bridged Tetrametallic Complex 3**


The ESI-mass spectrum shows ions with isotopic distributions consistent with [M + K]<sup>+</sup>, [M + Na]<sup>+</sup>, [M]<sup>2+</sup>, and [M – 4CO]<sup>2+</sup> ions for the tetrametallic ensemble. The NMR spectra confirmed a 1:1 ratio of Tp\* and cod ligands, but could not provide unequivocal information about the connectivity within the complex. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, a poor signal-to-noise ratio due to low solubility precluded the unambiguous identification of a selenocarbonyl resonance, and therefore the potentially informative multiplicity and J<sub>RhC</sub> coupling could not be identified with confidence. The <sup>77</sup>Se{<sup>1</sup>H} NMR spectrum showed one broad resonance (~100 Hz width at half-height) that did not show discernible <sup>1</sup>J<sub>RhSe</sub> coupling. The likelihood that this coupling is simply too modest to resolve is supported by

studies of the complex [RhCl(CO)(dppmSe)] (dppmSe = Ph<sub>2</sub>P(Se)CH<sub>2</sub>PPh<sub>2</sub>), for which the <sup>1</sup>J<sub>RhSe</sub> coupling was found to be only 20 Hz.<sup>14</sup> The broadness of the <sup>77</sup>Se resonance quite possibly reflects the onset of fluxional behavior, perhaps involving inversion of the pyramidal selenium centers and the possibility of *exo* and *endo* dispositions (*vide infra*) of the bulky molybdenum groups with respect to the Rh<sub>2</sub>Se<sub>2</sub> core. Since the first isolation of geometric isomers of [Fe<sub>2</sub>(SMe)<sub>2</sub>(CO)<sub>6</sub>] by King,<sup>15</sup> the fluxionality of M<sub>2</sub>(μ-ER)<sub>2</sub> cores (E = S, Se, Te) has become a common feature of this motif across the transition series. The operation of such a fluxional process is implicit in the appearance of a single <sup>13</sup>C resonance for the vinylic carbon nuclei of the cod ligands (δ<sub>C</sub> = 80.4, <sup>1</sup>J<sub>RhC</sub> = 12 Hz). The formulation of 3 was eventually confirmed through a crystallographic study, the results of which are summarized in Figure 1.

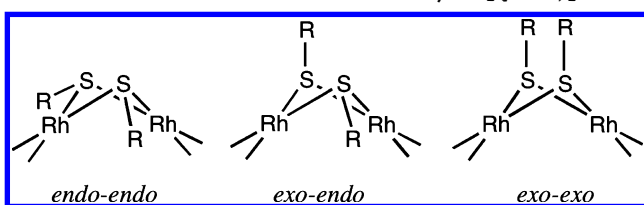


**Figure 1.** Molecular structure of 3 in a crystal (a) with 50% displacement ellipsoids and hydrogen atoms omitted (light gray and asterisked atoms generated by *P* $\bar{1}$  symmetry). (b and c) Alternative views of the Rh<sub>2</sub>Se<sub>2</sub> core. Selected bond lengths (Å) and angles (deg): C1–Mo1 1.815(3), C1–Se1 1.854(3), Rh1–Rh1\* 3.7112(5), Rh1–Se1\* 2.5275(4), Rh1–Se1 2.5163(4), Mo1–C1–Se1 173.07(18), Se1–Rh1–Rh1\* 42.509(8), Se1–Rh1–Se1\* 85.253(12), Rh1–Rh1\*–Se1 42.743(8), C1–Se1–Rh1 95.51(9), C1–Se1–Rh1\* 104.15(9), Rh1–Se1–Rh1\* 94.75(1).

The molecular structure of 3 has a crystallographically imposed inversion center (*P* $\bar{1}$ ) with only half the molecule being crystallographically unique. The geometric parameters associated with the “Tp\*(CO)<sub>2</sub>Mo” fragments conform to the copious precedent for carbyne complexes of this moiety, which have been recently surveyed.<sup>16a</sup> While the planarity of the Rh<sub>2</sub>Se<sub>2</sub> unit is a crystallographic requirement, the bridging is not perfectly rhombic (Rh1–Se1\* 2.5275(4), Rh1–Se1 2.5163(4) Å; Δ = 28 esd). The coordinatively unsaturated rhodium centers approximate to distorted square-planar geometry. The Se1...Se1\* (3.416 Å) and Rh1...Rh1\* (3.711 Å) separations are well beyond any suggestion of *trans*-annular bonding. Consistent with the lone pair character on selenium, the geometry at selenium is pyramidal with the angle

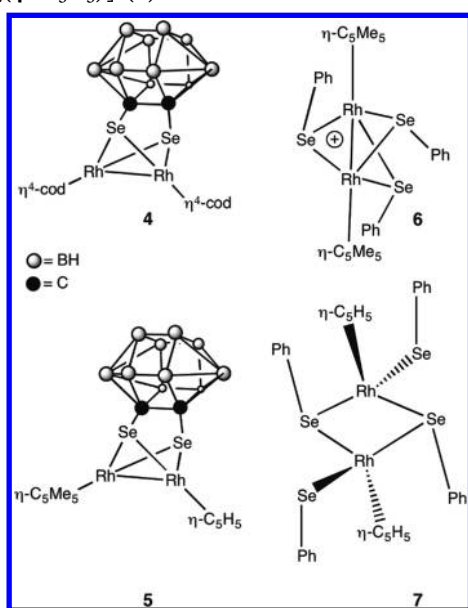
sum (294.4°) being typical of the orthogonality of substituents normally observed for the heavier chalcogens. The C1–Se bond length of 1.854(3) Å is very close to that observed for the simple methylselenolato-carbyne complex  $[\text{Mo}(\equiv\text{CSeCH}_3)(\text{CO})_2(\text{Tp}^*)]^{2b}$  (1.848(2) Å) despite the increased coordination number at Se1. More conventional selenolates have a strong propensity for adopting bridging roles, and while comparative structural data are not yet available for simple selenolates of the form  $[\text{Rh}_2(\mu\text{-SeR})_2(\eta^4\text{-cod})_2]$ , many examples of the corresponding thiolates  $[\text{Rh}_2(\mu\text{-SR})_2(\eta^4\text{-cod})_2]$  have been structurally characterized.<sup>17–19</sup> From these data, the general observations may be made that (i) none involve planar  $\text{Rh}_2\text{S}_2$  cores and (ii) with respect to the disposition of thiolate substituents, the situations where these both lie *endo*<sup>17</sup> or both lie *exo*<sup>18</sup> to the  $\text{Rh}_2\text{S}_2$  butterfly core are each well-represented, but there are not yet any *exo-endo* examples (Chart 2).<sup>19</sup>

Chart 2. Geometric Isomers for Butterfly  $\text{Rh}_2(\mu\text{-SR})_2$  Cores



Within the structural chemistry of rhodium the complexes  $[\text{Rh}_2(\mu\text{-Se}_2\text{C}_2\text{B}_9\text{H}_9)(\eta^4\text{-cod})_2]$  (**4**),<sup>21</sup>  $[\text{Rh}_2(\mu\text{-Se}_2\text{C}_2\text{B}_9\text{H}_9)(\eta\text{-C}_5\text{Me}_5)_2]$  (**5**),<sup>22</sup>  $[\text{Rh}_2(\mu\text{-SePh})_3(\eta\text{-C}_5\text{Me}_5)_2]^+$  (**6**),<sup>23</sup> and  $[\text{Rh}_2(\mu\text{-SePh})_2(\text{SePh})_2(\eta\text{-C}_5\text{H}_5)_2]$  (**7**) (Chart 3, Table S1

Chart 3. Structurally Characterized Selenolato-Bridged Rhodium Complexes: (a)  $[\text{Rh}_2(\mu\text{-Se}_2\text{C}_2\text{B}_9\text{H}_9)(\eta^4\text{-cod})_2]$  (**4**);<sup>20</sup> (b)  $[\text{Rh}_2(\mu\text{-Se}_2\text{C}_2\text{B}_9\text{H}_9)(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)]$  (**5**);<sup>21</sup> (c)  $[\text{Rh}_2(\mu\text{-SePh})_3(\eta^5\text{-C}_5\text{Me}_5)_2]^+$  (**6**);<sup>22</sup> (d)  $[\text{Rh}_2(\mu\text{-SePh})_2(\text{SePh})_2(\eta^5\text{-C}_5\text{H}_5)_2]$  (**7**)<sup>22</sup>



Supporting Information)<sup>24</sup> serve as the only available benchmarks. Of these, only **7** has a  $\text{Rh}_2\text{Se}_2$  core that approaches planarity, and although the rhodium centers have a higher formal oxidation number ( $d^6$  for **7** compared with  $d^8$  for **3**), it also features both terminal (mean  $\text{Rh}-\text{Se} = 2.488$  Å) and bridging

selenolate ligands (2.481 Å) with remarkably similar  $\text{Rh}-\text{Se}$  bond lengths despite the different coordination numbers at selenium.

The bridging mode adopted by the selenocarbonyl ligand in **3** is unprecedented for any chalcocarbonyls. Some loose analogy might be entertained with isoselenocyanates ( $\text{L}_n\text{M}-\text{SeC}\equiv\text{N}$ ) and alkynylselenolates ( $\text{L}_n\text{M}-\text{SeC}\equiv\text{CR}$ ),<sup>10,11</sup> which each also involve selenium bound to an  $sp$ -hybridized carbon. Other than for a single polymeric copper selenocyanate,<sup>23</sup> no structural data are available for either of these ligands bridging transition metals. There is copious precedent for bridging thiocyanato ligands<sup>24</sup> and limited data for bridging alkynylthiolato ligands<sup>11b,25,26</sup> in particular within the area of cluster chemistry developed by Delgado.<sup>26</sup>

To conclude, the origin of interstitial carbido atoms in clusters is often traced to the cleavage of  $\text{CO}$ ; however this typically requires forcing conditions. Recently, Johnson has demonstrated the synthesis of terminal carbido complexes of ruthenium and osmium via sulfur abstraction from thiocarbonyl ligands by early transition metal siloxides or amides, most likely via isothiocarbonyl-bridged intermediates.<sup>4</sup> The isolation of **3** provides mechanistic insight into the early stages of how a selenocarbonyl ligand might be cleaved en route to the carbido complex **2**. In addition, **3** features a coordination mode not yet seen for other chalcocarbonyls, pointing toward greater coordinative flexibility for the heavier, more polarizable chalcogens.

## EXPERIMENTAL SECTION

**General Procedures.** Manipulations were carried out under an atmosphere of prepurified and dried nitrogen using standard Schlenk and vacuum line techniques unless otherwise indicated. Dichloromethane and tetrahydrofuran were distilled from calcium hydride and sodium benzophenone ketyl, respectively, under  $\text{N}_2$ .  $^1\text{H}$  (299.9 MHz),  $^{13}\text{C}\{\text{H}\}$  (75.42 MHz), and  $^{77}\text{Se}\{\text{H}\}$  (57.26 MHz) NMR spectra were recorded on Varian Inova 300 or Mercury 300 spectrometers to provide chemical shifts, which are reported relative to residual solvent peaks ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or an external reference ( $\text{PhSeSePh}$ :  $\delta_{\text{Se}} = 0$ ).

**Synthesis of  $[\text{Rh}_2(\mu\text{-SeC}(\text{CO})_2(\text{Tp}^*))_2(\eta^4\text{-cod})_2]$  (**3**).** A mixture of  $[\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]^{12}$  (0.140 g, 0.224 mmol) and  $[\text{Et}_3\text{N}][\text{I}]^2$  (0.300 g, 0.448 mmol) in THF (20 mL) was stirred for 36 h, filter-cannulated, and then freed of volatiles under reduced pressure. The residue was chromatographed on silica gel using a 20% mixture of dichloromethane in *n*-hexane as eluent. An orange band was collected, from which the solvent was removed under reduced pressure to yield an orange microcrystalline powder. Yield: 0.116 g (34%). IR ( $\text{cm}^{-1}$ ): 1964, 1880  $\nu_{\text{CO}}$ , 1542  $\nu_{\text{CN}}$ . THF: 1982, 1974, 1901  $\nu_{\text{CO}}$ , 1543  $\nu_{\text{CN}}$ . An absorption corresponding primarily to the  $\nu_{\text{CSe}}$  mode could only be tentatively identified.<sup>27</sup> Terminal selenocarbonyls typically give rise to strong absorptions in the region 1070–1205  $\text{cm}^{-1}$ . NMR ( $\text{C}_6\text{D}_6$ , 298 K)  $^1\text{H}$ :  $\delta_{\text{H}}$  1.63 (d, 4 H,  $\text{C}_2\text{H}_4$ ,  $J_{\text{HH}} = 5.40$  Hz), 2.03 (s, 3 H,  $\text{pzCH}_3$ ), 2.09 (s, 6 H,  $\text{pzCH}_3$ ), 2.23 (br, 4 H,  $\text{C}_2\text{H}_4$ ), 2.37 (s, 3 H,  $\text{pzCH}_3$ ), 2.96 (s, 6 H,  $\text{pzCH}_3$ ), 5.04 (br, 4 H,  $\text{CH}=\text{CH}$ ), 5.30 (s, 1 H,  $\text{pzH}$ ), 5.70 (s, 2 H,  $\text{pzH}$ );  $^{13}\text{C}\{\text{H}\}$ :  $\delta_{\text{C}}$  228.8 (CO), 151.8, 151.5, 144.3, 144.2 [2:1:1:2,  $\text{C}^{3,5}(\text{pz})$ ], 106.6, 106.5 [1:2,  $\text{C}^4(\text{pz})$ ], 80.4 (d,  $\text{CH}=\text{CH}$ ,  $J_{\text{RHC}} = 12$  Hz), 31.6 ( $\text{C}_2\text{H}_4$ ), 16.9, 14.7, 12.7, 12.4 (2:1:2:1,  $\text{pzCH}_3$ );  $^{77}\text{Se}\{\text{H}\}$ :  $\delta_{\text{Se}}$  521.2. ESI-MS (+ve ion, MeCN):  $m/z = 1540.8$  [ $\text{M} + \text{K}$ ]<sup>+</sup>, 1524.8 [ $\text{M} + \text{Na}$ ]<sup>+</sup>, 751.5 [ $\text{M}$ ]<sup>2+</sup>, 696.5 [ $\text{M} - 4\text{CO}$ ]<sup>2+</sup>. Acc. Mass: found 754.0131 [ $\text{M}$ ]<sup>2+</sup>; calcd for  $1/2[\text{C}_{52}\text{H}_{68}\text{O}_4^{11}\text{B}_2^9\text{Mo}_2^{14}\text{N}_{12}^{80}\text{Se}_2^{103}\text{Rh}_2]$  754.0111. Anal. Found: C, 41.77; H, 4.62; N, 10.93. Calcd for  $\text{C}_{52}\text{H}_{68}\text{B}_2\text{Mo}_2\text{N}_{12}\text{O}_4\text{Rh}_2\text{Se}_2$ : C, 41.57; H, 4.56; N, 11.19. Crystal data for  $\text{C}_{52}\text{H}_{68}\text{B}_2\text{Mo}_2\text{N}_{12}\text{O}_4\text{Rh}_2\text{Se}_2$ :  $M_r = 1502.42$ , triclinic,  $\text{P}\bar{1}$  (No. 2),  $a = 10.5793(2)$  Å,  $b = 10.6046(3)$  Å,  $c = 15.4375(4)$  Å,  $\alpha = 82.0374(11)^\circ$ ,  $\beta = 72.8897(14)^\circ$ ,  $\gamma = 61.3733(13)^\circ$ ,  $V = 1452.92(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.717$  Mg  $\text{m}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 2.286$  mm<sup>-1</sup>,  $T = 200(2)$  K, orange plate,  $0.03 \times 0.10 \times 0.18$  mm; 30 194 absorption-corrected reflections [ $2\theta \leq 55^\circ$ ] provided 6694 independent reflections, 5495 of which were observed [ $I/I > 2\sigma(I)$ ].  $F^2$  refinement on all independent reflections using 343 parameters gave

$R_1 = 0.0329$ ,  $wR_2 = 0.0743$  with residual electron densities between  $-1.02$  and  $+0.97$  e  $\text{\AA}^{-3}$  (CCDC 860900).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Crystallographic data for **3** (CCDC 860900) in CIF format; tabulation of structural data for rhodium-bridging selenolate complexes. This information 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.

## ■ ACKNOWLEDGMENTS

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