

# Facile Generation of Lithiocarbyne Complexes: [M(≡CLi)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (M = Mo, W; pz = Pyrazol-1-yl)

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Received July 31, 2008

**Summary:** The reactions of [M(≡CX)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (M = Mo, W; X = Cl, Br; pz = pyrazol-1-yl) with <sup>n</sup>BuLi provide the lithiocarbyne complexes [M(≡CLi)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}], which react with a range of electrophiles to provide variously functionalized carbyne and chalcocarbonyl complexes [Mo(≡CE)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (E = H, Me, SiMe<sub>3</sub>, SPh, SePh, Se<sup>-</sup>, Te<sup>-</sup>, Fe(CO)<sub>2</sub>Cp).

Terminal carbido complexes (Chart 1)<sup>1–4</sup> remain rare, and while they might conceptually provide the simplest access to variously substituted carbyne complexes from a late common synthetic intermediate, the syntheses of the known examples or their precursors are lengthy or nontrivial.

Templeton has demonstrated this principle with the complex [W(≡CLi)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (**1b**; pz = pyrazol-1-yl),<sup>1</sup> which reacts with a range of electrophiles to provide the alkylidyne complexes [W(≡CE)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (E = CH<sub>3</sub>, SiMe<sub>3</sub>, I, CPh<sub>2</sub>OH, CHPhOH, C(=O)Ph). However, the various synthetic routes to the precursor [W(≡CH)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (**2b**; Scheme 1)<sup>1,6</sup> in combination with its thermolability have perhaps contributed to the synthetic potential of **1b** not being more widely exploited. The corresponding molybdenum chemistry has yet to be explored in any detail beyond the implicit formation of **1a** en route to [Mo<sub>2</sub>(μ-CCH<sub>2</sub>)(CO)<sub>4</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}]<sub>2</sub> (**3a**)<sup>1b</sup> via fluoride-mediated protodesilylation of [Mo(≡CSiMe<sub>2</sub>Ph)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}].

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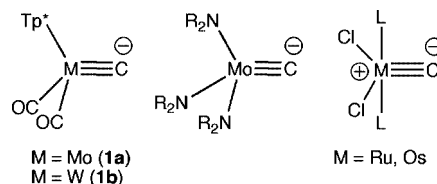
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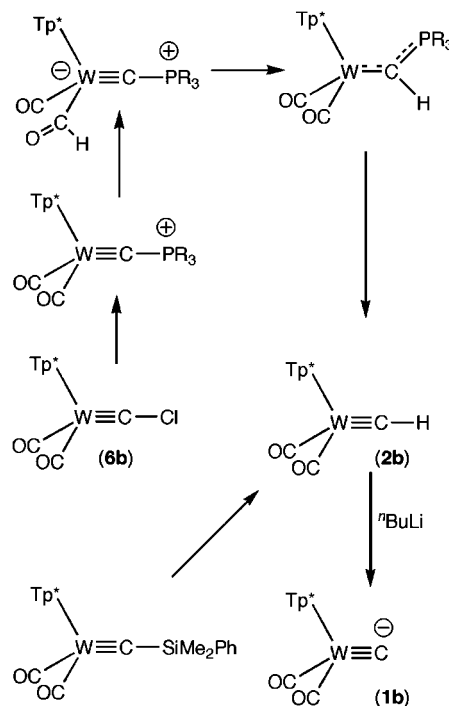
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## Chart 1. Terminal Carbido Complexes<sup>1–4 a</sup>



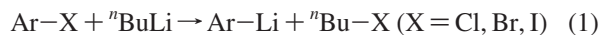
<sup>a</sup> Legend: Tp\* = HB(pzMe<sub>2</sub>-3,5)<sub>3</sub>, pz = pyrazol-1-yl, NR<sub>2</sub> = N<sup>t</sup>Bu(C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-3,5), L = phosphine, N-heterocyclic carbene. Hereafter M = Mo for the **a** series and M = W for the **b** series.

## Scheme 1. Templeton's Lithiocarbyne Syntheses<sup>1,5</sup>

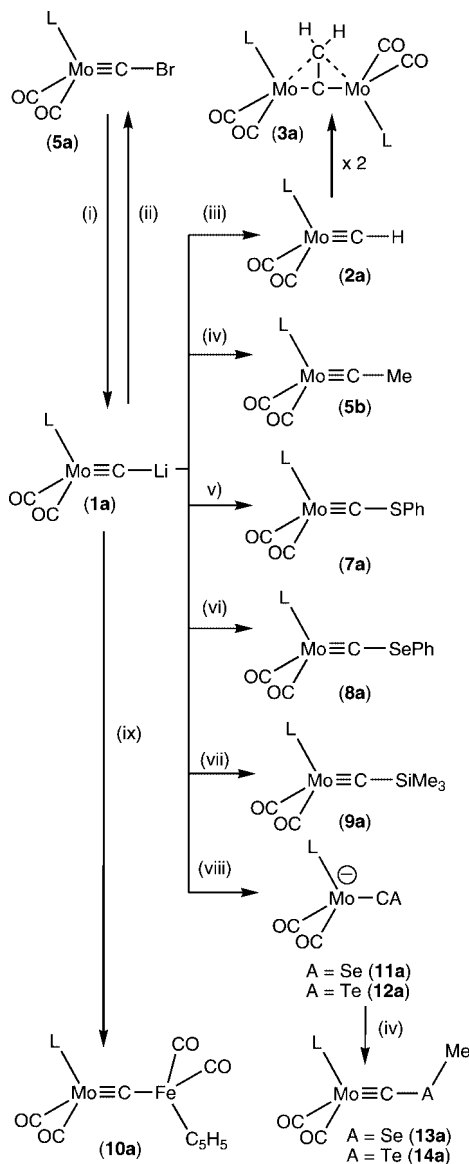


Herein we wish to report a convenient synthesis of **1a,b** and their conversion to a range of carbon and heteroatom functionalized carbyne or chalcocarbonyl complexes.

Lithium–halogen exchange (eq 1) is one of the most widely employed methods for generating organolithium reagents, often occurring rapidly at low temperatures.<sup>6</sup>



Given the ready availability of the bromocarbyne complexes [M(≡CBr)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (M = Mo (**4a**), W (**4b**)),<sup>7,8</sup> we considered whether lithium–halogen exchange might represent

**Scheme 2. Synthesis of Functionalized Carbyne Complexes via Electrophilic Attack at a Lithiocarbyne<sup>a</sup>**


<sup>a</sup>Legend: (i)  ${}^n\text{BuLi}$ ; (ii) *N*-bromosuccinimide; (iii)  $\text{H}_2\text{O}$ ; (iv)  $\text{MeI}$ ; (v)  $\text{PhSSPh}$ ; (vi)  $\text{PhSeSePh}$ ; (vii)  $\text{ClSiMe}_3$ ; (viii)  $1/n \text{A}_n$  ( $\text{A} = \text{Se}, \text{Te}$ ); (ix)  $\text{FeCl}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ .

a viable direct synthesis of **1b** and the unknown lithiocarbyne complex  $[\text{Mo}(\equiv\text{CLi})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$  (**1a**). Considering the notional relationship between alkynes and alkylidynes, lithium-halogen exchange with 1-haloalkynes has little to offer as a synthetic protocol for the former; haloalkynes are themselves generally prepared from the alkynyl anions and electrophilic halogen sources. Thus, the reaction would appear to be a synthetically retrograde step of doubtful utility in alkyne chemistry. However, treating a THF solution of **4a** ( $\nu_{\text{CO}}$  2001, 1917  $\text{cm}^{-1}$ ) at low temperature (dry ice, propanone) with commercial  ${}^n\text{BuLi}$  (2.5 M in hexane) results in the slow formation of a red-orange solution. Addition of  $\text{H}_2\text{O}$  followed by warming to room temperature results in the initial observation of the parent methylidyne complex  $[\text{Mo}(\equiv\text{CH})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$  (**2a**;  $\nu_{\text{CO}}$  2000, 1913  $\text{cm}^{-1}$ ), which evolves into the green nonclassical vinylidene-bridged dimer  $[\text{Mo}_2(\mu,\eta^2\text{-}\eta^2\text{-CCH}_2)(\text{CO})_4\{\text{HB}(\text{pzMe}_2)_3\}_2]$  (**3a**;  $\nu_{\text{CO}}$  1989, 1934, 1900, 1854  $\text{cm}^{-1}$ ; Scheme 2) in a process described previously by Templeton.<sup>1</sup> Solutions of the complex **1a** are unstable at room

temperature, evolving rapidly to **2a** and then, inter alia, **3a** even under strictly anhydrous conditions, suggesting that either the solvent is deprotonated or, more likely, **1a** acts as a base (rather than a nucleophile) toward the  ${}^n\text{BuBr}$  side product. Treating a solution of **1a** with iodomethane provides the ethylidyne complex  $[\text{Mo}(\equiv\text{CMe})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$  (**5a**;  $\nu_{\text{CO}}$  (THF) 1982, 1893  $\text{cm}^{-1}$ ), while similar treatment of  $[\text{W}(\equiv\text{CBr})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$  (**4b**) provides the tungsten analogue  $[\text{W}(\equiv\text{CMe})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$  (**5b**). The chlorocarbyne complex  $[\text{Mo}(\equiv\text{CCl})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$  (**6a**) also serves the same purpose, though not as well, resulting in approximately 45% conversion to the ethylidyne complex **5a**; i.e., lithium-bromide exchange is more effective than lithium-chloride exchange.

We have so far failed to isolate stable salts of either **1a** or **1b** by cation exchange; however, the various derivatives obtained substantiate the formulation as lithiocarbyne complexes, or at least functional synthetic equivalents. Furthermore, the respectable yields generally obtained in a single step obviate the need for isolation.

We have briefly explored the synthetic utility of **1a** as a precursor to variously functionalized carbyne complexes.<sup>11</sup> In general, due to the high reactivity of **1a** under these conditions, the preferred protocol involved the generation of **1a** at  $-78^\circ\text{C}$  from **4a** and addition of the desired electrophile at this same temperature followed by warming to ca.  $0^\circ\text{C}$ , at which temperature stirring is maintained until the completion of the reaction as monitored by IR spectroscopy. The reaction of **1a** with *N*-bromosuccinimide cleanly regenerates **4a**, this (crystalline) reagent being preferable to elemental bromine, which results in indiscriminate oxidation of the metal center<sup>12</sup> and partial 4-bromination of the pyrazolyl ring(s). The reactions of **1a** with diphenyl disulfide and diselenide provide the arylchal-

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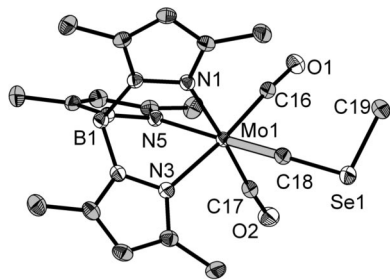
(8) We have refined the synthesis of **4a** to allow large amounts to be prepared directly from  $[\text{Mo}(\text{CO})_6]$  in 58% yield, minimizing losses associated with the isolation and purification of  $[\text{Et}_4\text{N}][\text{Mo}(\text{CO})_3\{\text{HB}(\text{pzMe}_2)_3\}]$ : a mixture of  $[\text{Mo}(\text{CO})_6]$  (26.0 g, 98.0 mmol) and  $\text{K}[\text{HB}(\text{pzMe}_2)_3]$  (44.0 g, 131.0 mmol) in 1,2-dimethoxyethane (400 mL) was heated under reflux for 4 h and then freed of solvent under reduced pressure. The residue was dissolved in bromoform (100 mL), the solution was treated with mesityli-diazonium tetrafluoroborate (23.0 g, 98.0 mmol), and the resulting suspension was stirred for 18 h. The volatiles were removed under reduced pressure, and the solid residue was chromatographed on silica gel with a mixture of dichloromethane and petroleum spirit (10:1) as eluent. The yellow-orange fraction was collected, concentrated, and cooled ( $-18^\circ\text{C}$ ) to provide yellow crystals, which were isolated by filtration, washed with cold petroleum ether, and dried in vacuo. Yield: 31.0 g (58%). Spectroscopic data (IR,  ${}^1\text{H}$  and  ${}^{13}\text{C}\{{}^1\text{H}\}$  NMR) conform to those that have been previously reported.<sup>7</sup>

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(11) General procedure for the generation and electrophilic quenching of **1a**: to a precooled (dry ice/propanone) solution of **4a** (0.20 g, 0.37 mmol) in anhydrous THF (10 mL) was added a solution of  ${}^n\text{BuLi}$  (0.15 mL, Aldrich, 2.50 M in hexane, 0.37 mmol). The mixture was stirred for 30 min, treated with the requisite electrophile (0.37 mmol), and then warmed to  $0^\circ\text{C}$  and stirred until the completion of the reaction, as indicated by in situ IR spectroscopy. The volatiles were removed under reduced pressure, and the desired product was isolated by extraction with dichloromethane, filtration through diatomaceous earth, dilution with hexane, concentration, and cooling. The products were generally obtained in spectroscopically pure form; however, if necessary, further purification could be effected by column chromatography on silica gel with an increasing dichloromethane/hexane gradient as eluent.

(12) For bromination of carbyne complexes of the form  $[\text{M}(\equiv\text{CR})(\text{CO})_2(\text{L})]$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{L} = \text{HB}(\text{pz})_3, \text{HB}(\text{pzMe}_2)_3$ ), see: (a) Ahn, S.; Mayr, A. *J. Am. Chem. Soc.* **1996**, 118, 7408. (b) Filippou, A. C.; Hofmann, P.; Kiprof, P.; Schmidt, H. R.; Wagner, C. *J. Organomet. Chem.* **1993**, 459, 233. (c) Anderson, S.; Cook, D. J.; Hill, A. F.; Malget, J. M.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, 23, 2552.



**Figure 1.** Molecular structure of **13a** in a crystal of **13a** · OEt<sub>2</sub> (100 K, 50% displacement ellipsoids, hydrogen atoms omitted, carbon atoms in gray). Selected bond lengths (Å) and angles (deg): Mo1–C18 = 1.823(2), Mo1–N3 = 2.216(2), Mo1–N1 = 2.230(2), Mo1–N5 = 2.293(2), Se1–C18 = 1.848(2), Se1–C19 = 1.955(2); C18–Mo1–C17 = 80.99(9), C18–Mo1–C16 = 83.09(9), C17–Mo1–C16 = 84.32(9), C18–Mo1–N3 = 103.84(8), C17–Mo1–N3 = 96.71(8), C18–Mo1–N1 = 104.48(8), C16–Mo1–N1 = 96.00(8), C18–Se1–C19 = 98.92(10), Mo1–C18–Se1 = 167.98(14).

cogenolatoalkylidynes [Mo(≡CSPH)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (**7a**) (previously obtained from **4a** and HN(SPh)<sub>2</sub>)<sup>13</sup> and [Mo(≡CSePh)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (**8a**) (previously obtained from **6a** and NaSePh).<sup>14</sup> With Me<sub>3</sub>SiCl the silylcarbyne complex [Mo(≡CSiMe<sub>3</sub>)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (**9a**) is obtained, which is related to the complex [Mo(≡CSiMe<sub>2</sub>Ph)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}]; the latter complex, however, was only previously obtained in low yield via a Fischer–Mayr protocol (ca. 19%).<sup>1b</sup> Templeton has described the synthesis of the binuclear carbido complex [Mo(≡CFe(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>))(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (**10a**) via the reaction of **6a** with K[Fe(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)]. This same complex **10a** may now be obtained via an “Umpolung” approach involving the reaction of **1a** with [FeCl(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)], a reaction that promises some generality for the synthesis of further heterobimetallic carbido complexes.

The lithiocarbyne complex **1a** also provides an alternative entry into chalcocarbonyl chemistry via reactions with elemental (gray) selenium or tellurium to cleanly provide Li[Mo(CA)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (A = Se (**11a**), Te (**12b**)), which were previously prepared via the reactions of the chlorocarbyne complex [Mo(≡CCl)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] with Li<sub>2</sub>A.<sup>16</sup> The current approach avoids the generation and manipulation of highly air sensitive chalcogenide solutions and proceeds in high yields, such that the lithium chalcocarbonylates may be generated and used in situ. Alkylation of the chalcocarbonylates **11a** and **12a** with iodomethane afford the methylchalcogenolato alkylidynes [Mo(≡CAME)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (A = Se (**13a**), Te (**14a**)). The characterization of **13a**<sup>17</sup> included a crystallographic study of **13a** · OEt<sub>2</sub>, the results of which are summarized in Figure 1.

There exist copious and recently compiled<sup>5</sup> structural data for alkylidyne complexes of the form [M(≡CR)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (M = Mo, W), to which those for **13a** conform. Crystallographic data for selenolatoalkylidynes remain sparse and are limited to those for the complex [Mo(≡CSeC≡CSiMe<sub>3</sub>)(CO)<sub>2</sub>{HB(pzMe<sub>2</sub>)<sub>3</sub>}] (**15a**), which we have recently obtained via an alternative route: viz., the reaction

of LiSeC≡CSiMe<sub>3</sub> with **6a**.<sup>18</sup> Both the Mo≡C18 separation (1.823(2) Å) and Mo–C18–Se1 angle (167.98(14)°) found in **13a** are comparable to those observed for **15a** (1.805(12) Å and 162.4(8)°, respectively), while in both complexes the angles at selenium are close to orthogonal (**13a**, 98.92(10)°; **15a**, 93.4(6)°). A degree of C18–Se1 multiple bonding would appear to be reflected in this bond length being markedly shorter (54 esd) than that between Se1 and C19, though the respective hybridizations, i.e., coordination numbers, of C18 and C19 will contribute in part to this disparity. The characteristic trans influence of the alkylidyne ligand is manifested in a modest lengthening of Mo1–N5 (2.2930(17) Å) relative to Mo1–N3 (2.2157(18) Å) and Mo1–N1 (2.2303(18) Å).

To conclude, a convenient method of generating the lithiocarbyne complexes **1** has been developed. The synthetic utility of **1a** has been demonstrated, affording high yields of a range of alkylidyne complexes previously accessed via multistep strategies in addition to chalcocarbonyl complexes that serve as precursors to further alkylidynes via electrophilic alkylation of the chalcogen. It may be noted that the majority of Fischer-type carbyne syntheses involve the installation of the carbyne substituent via nucleophilic attack at either a carbonyl (Fischer) or a halocarbyne (Lalor) ligand with attendant synthetic limitations. The alternative strategy, pioneered by Templeton and now made conveniently accessible by the present methodology, allows carbyne substituents to be installed in electrophilic form, thereby significantly widening the potential variety of accessible alkylidyne complexes.

**Acknowledgment.** This work was supported by a fellowship within the Post-Doctoral Programme of the German Academic Exchange Service (DAAD) and by the Australian Research Council (Grant No. DP0556236).

**Supporting Information Available:** A CIF file giving crystallographic data for **13a** · OEt<sub>2</sub> (CCDC 693015) and text and figures giving experimental procedures, a commentary on the modifications of the synthesis of **5a**, and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) To a solution of **1a** (0.37 mmol) in THF (10 mL) prepared as described above<sup>11</sup> at –78 °C was added elemental (gray) selenium (30 mg, 0.37 mmol). The mixture was warmed to room temperature with stirring. When all of the elemental selenium had dissolved, iodomethane (0.2 mL, excess) was added and the mixture stirred for a further 30 min. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (2 × 5 mL). The combined extracts were chromatographed on silica gel, with dichloromethane as eluent, to provide an orange band, which was concentrated and cooled (–18 °C) to provide **13a** as a red-orange powder. Yield: 0.18 g (83%). NMR (298 K, CDCl<sub>3</sub>): δ<sub>H</sub> 2.31 (s, 3 H, pzCH<sub>3</sub>), 2.35 (s, 6 H, pzCH<sub>3</sub>), 2.56 (s, 6 H, pzCH<sub>3</sub>), 2.61 (s, 3 H, pzCH<sub>3</sub>), 5.72 (s, 1 H, pzH), 5.85 (s, 2 H, pzH); δ<sub>C</sub> 269.2 (Mo≡C), 226.2 (CO), 151.4, 151.1, 145.0, 144.4 (C<sup>3-5</sup>(pz)), 106.3, 106.2 (C<sup>4</sup>(pz)), 15.8, 14.6, 12.7, 9.7 (pzCH<sub>3</sub>), 1.0 (SeCH<sub>3</sub>). ES(+)-MS (*m/z*): 579.0 [M + Na]<sup>+</sup>, 525.7 [M + Na – 2CO]<sup>+</sup>. IR (THF): ν<sub>CO</sub> 1987 s, 1905 vs cm<sup>-1</sup>. IR (Nujol): ν<sub>CO</sub> 1988 s, 1907 vs 1892 sh (solid state splitting) cm<sup>-1</sup>. Crystals of a diethyl ether monosolvate suitable for diffractometry and elemental microanalysis were obtained via slow evaporation of a solution of **13a** in diethyl ether. Anal. Found: C, 44.01; H, 5.34; N, 13.68%. Calcd for C<sub>19</sub>H<sub>25</sub>BMoN<sub>6</sub>O<sub>2</sub>Se · OC<sub>4</sub>H<sub>10</sub>: C, 43.90; H, 5.61; N, 13.35. Crystal data for **13a** · OEt<sub>2</sub>: C<sub>23</sub>H<sub>35</sub>BMoN<sub>6</sub>O<sub>3</sub>Se, *M<sub>w</sub>* = 629.28, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 8.0591(1) Å, *b* = 18.4282(3) Å, *c* = 18.6374(3) Å, β = 99.198(1)°, *V* = 2732.34(7) Å<sup>3</sup>, *Z* = 4, *D<sub>calcd</sub>* = 1.530 Mg m<sup>-3</sup>, μ(Mo Kα) = 1.847 mm<sup>-1</sup>, *T* = 100(2) K, orange needle, 0.28 × 0.10 × 0.08 mm, 7956 independent reflections. *F*<sup>2</sup> refinement, *R* = 0.034, *R<sub>w</sub>* = 0.088 for 6738 reflections (*I* > 2σ(*I*)), 2θ<sub>max</sub> = 60°, 325 parameters, CCDC 693015.

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