Alkynylselenolatoalkylidynes: [Mo(≡CSeC≡CR)(CO)$_2${HB(pzMe$_2$)$_3$}] (R = CMe$_3$, SiMe$_3$; pzMe$_2$ = 3,5-Dimethylpyrazol-1-yl)

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The reactions of [Mo(≡CCl)(CO)$_2${HB(pzMe$_2$)$_3$}] (pz = 3,5-dimethylpyrazol-1-yl) with lithium alkynylselenolates (LiSeC≡CR; R = CMe$_3$, SiMe$_3$) provide the alkynylselenolatoalkylidyne complexes [Mo(≡CSeC≡CR)(CO)$_2${HB(pzMe$_2$)$_3$}]. Cobalt carbonyl adds across the C≡C rather than the Mo≡C multiple bond to provide [Mo{≡CSeCC(CMe$_3$)Co$_2$(CO)$_6$}(CO)$_2${HB(pzMe$_2$)$_3$}], which upon reaction with dppm affords the complex [Mo{≡CSeCC(CMe$_3$)Co$_2$(CO)$_4$(dppm)}(CO)$_2${HB(pzMe$_2$)$_3$}] in addition to traces of the selenium extrusion product [Mo{≡CCC(CMe$_3$)Co$_2$(CO)$_4$(dppm)}(CO)$_2${HB(pzMe$_2$)$_3$}].

Alkynyl selenoethers, RSeC≡CR′, are a potentially intriguing class of reagents for organotransition-metal chemistry in that they combine both selenoether and alkyne functional groups, each potentially with their own chemistry, coupled with the expected fragility of the C−Se bond. To date, however, the organometallic chemistry of these species has only been briefly addressed. A small number of simple mononuclear[1] and dinuclear[2] complexes has been described without further reactivity studies, although alkynyl selenoethers have been shown to serve as precursors to selenolatovinylidene complexes via reversible metal-mediated rearrangements.[3] The isolobal analogy that relates carbon−carbon (C≡C) and metal–carbon (L$_n$M≡C) triple bonds has inspired much research, in particular with respect to the strategic synthesis by Stone of numerous polymetallic species supported by bridging alkylidyne ligands.[4] With this perspective in mind, we have considered the possibility of constructing molecules that contain both C≡C and M≡C bonds connected directly to the same selenium atom: viz. the alkynylselenolatoalkylidynes L$_n$M≡CSeC≡CR. The selenolatoalkylidynes L$_n$M≡CSeR in general remain rare, the single reported example being [Mo(≡CSePh)(CO)$_2${HB(pzMe$_2$)$_3$}] (pzMe$_2$ = 3,5-dimethylpyrazol-1-yl), which is obtained via the reaction of [Mo(≡CCl)(CO)$_2${HB(pzMe$_2$)$_3$}] (**1**) with sodium phenylselenolate (from Ph$_2$Se$_2$, NaBH$_4$, NaOH, and [Et$_3$NCH$_2$Ph]Br under phase transfer conditions).[5] We report herein the first examples of alkynylselenolatoalkylidyne complexes and their reactions with cobalt carbonyl, a reagent known to react variously with alkynes, alkylidynes, and selenoethers.

Results and Discussion

Successive treatment of terminal alkynes HC≡CR (R = CMe$_3$, SiMe$_3$, C$_6$H$_4$Me-4) with ^{n}BuLi, gray selenium, and **1** provides, following cryostatic chromatography (silica gel, −30 °C), the alkynylselenolatoalkylidynes [Mo(≡CSeC≡CR)(CO)$_2${HB(pzMe$_2$)$_3$}] (R = CMe$_3$ (**2a**; 76%), SiMe$_3$ (**2b**; 61%), C$_6$H$_4$Me-4 (**2c**; 59%)) in addition to ca. 10% recovered **1** (Scheme 1). In the case of **2b**, increasing the stoichiometry of LiSeC≡CSiMe$_3$ to **1** to 2:1 provided a comparable yield of **2b** (63%), in addition to traces (4%) of [Mo(≡CC≡CSiMe$_3$)(CO)$_2${HB(pzMe$_2$)$_3$}] (**3b**). The propargylidyne complex **3b** has been recently prepared by Bruce[6] via extension of our earlier protocol for the synthesis of [Mo(≡CC≡CCMe$_3$)(CO)$_2${HB(pzMe$_2$)$_3$}] (**3a**);[7] however, its formation under the present conditions is curious, given that Lalor has claimed that **1** is unreactive toward LiC≡CPh.[5a] The formulations of **2** follow from spectroscopic data, among which a low-field resonance in the ^{13}C{^{1}H} NMR spectrum (**2a**, 245.0 ppm; **2b**, 244.8 ppm) is characteristic of alkylidynes. The alkynyl nuclei are observed in regions typical of conventional alkynyl selenoethers[8] (**2a**, 114.7, 52.0 ppm; **1b**, 113.8, 78.7 ppm), with that bound to selenium appearing to higher field. For **1b** the formulation was confirmed by a crystallographic study, the results of which are summarized in Figure 1. The molecular geometry is as expected, with structural features associated with the "{HB(pzMe$_2$)$_3$}Mo(CO)$_2$" unit conforming to copious precedent.[9] Interest therefore focuses on the distortions of the Mo≡CSeC≡CSi spine, in which the angles at the sp-hybridized carbon atoms C1 (162.4(8)°), C11 (171.6(15)°), and C12 (166.8(11)°) are considerably less than 180°. The angle at Se1 (93.4(6)°) is also contracted somewhat

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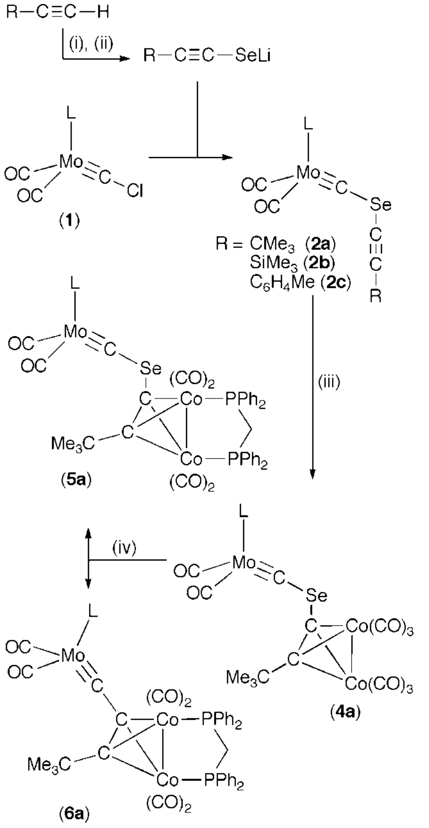
10.1021/om7008342 CCC: $40.75

Scheme 1. Syntheses of Alkynylselenolatoalkylidynes[a]



[a] L = HB(pzMe$_2$)$_3$. Legend: (i) ^{n}BuLi; (ii) Se; (iii) [Co$_2$(CO)$_8$]; (iv) dppm.

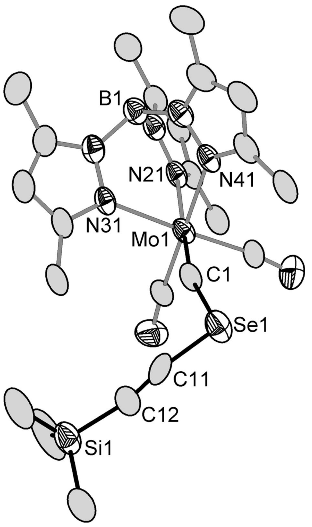


Figure 1. Molecular geometry of **2b** in the crystal state (hydrogen atoms omitted, 40% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mo–N21 = 2.312(8), Mo–N31 = 2.222(8), Mo–N41 = 2.227(8), Mo–C1 = 1.805(12), C1–Se1 = 1.887(12), Se1–C11 = 1.874(14), C11–C12 = 1.175(17), C12–Si1 = 1.838(15); Mo–C1–Se1 = 162.4(8), C1–Se1–C11 = 93.4(6), Se1–C11–C12 = 171.6(15), C11–C12–Si1 = 166.8(11).

from that range typically observed (99–101°) for structurally characterized selenocyanates (RSeC≡N), acyclic selenoethers, and the small number of acyclic alkynyl selenoethers, RSeC≡CR′, that have been structurally characterized.[10] Given the sterically imposing nature of the "CMo(CO)$_2${HB(pzMe$_2$)$_3$}" unit, this angular contraction is notable. The two Se–C separations are equivalent in length to, though marginally longer than, those observed for acyclic alkynyl selenoethers to date (1.822–1.841 Å).[10] Thus, from a structural standpoint, the Mo≡CSeC≡CSi spine appears to mimic conventional alkynyl selenoether features.

A classic reaction of alkynes, including a simple alkynyl selenoether,[2b] is the addition of cobalt carbonyl across the triple bond to provide a dicobaltatetrahedrane: e.g., the complex [Co$_2$(μ-PhSeCCPh)(CO)$_6$].[2b] The analogy between M≡C and C≡C bonds extends to this reaction such that group 6 alkylidynes react with cobalt carbonyl to provide metalladicobaltatetrahedranes.[11] We have previously shown that for propargylidynes L(CO)$_2$M(≡CC≡CCMe$_3$) i.e., compounds with conjugated M≡C and C≡C bonds, the site of dicobalt addition is dependent upon the choice of coligand "L". For sterically encumbered L = HB(pz)$_3$, HB(pzMe$_2$)$_3$, the site of addition is the C≡C bond, while for the more sterically modest L = Cp, addition occurs across the M≡C bond.[7] By way of contrast, the reactions of silylpropargylidynes with metal reagents under desilylating conditions (F$^-$, MeO$^-$) proceed with retention of the intact L$_n$M≡CC≡C– linkage and formation of linear tricarbido-bridged bi- and trimetallic compounds.[12] The reaction of **2a** with [Co$_2$(CO)$_8$] proceeds vigorously in diethyl ether at room temperature to provide a brown compound in 81% yield, which on the basis of spectroscopic data is formulated as the trimetallic complex [Mo{≡CSeC$_2$(CMe$_3$)Co$_2$(CO)$_6$}(CO)$_2${HB(pzMe$_2$)$_3$}] (**4a**). The formulation was further supported by the subsequent reaction of **4a** with bis(diphenylphosphino)methane (dppm) to provide [Mo{≡CSeC$_2$(CMe$_3$)Co$_2$(CO)$_4$(μ-dppm)}(CO)$_2${HB(pzMe$_2$)$_3$}] (**5a**), which was spectroscopically and crystallographically characterized (Figure 2). Notably, in addition to the major product **5a**, small amounts of the selenium extrusion product [Mo{≡CC$_2$(CMe$_3$)Co$_2$(CO)$_4$(μ-dppm)}(CO)$_2${HB(pzMe$_2$)$_3$}] (**6a**) were also obtained and identified on the basis of spectroscopic and (limited) crystallographic data (Figure 3;

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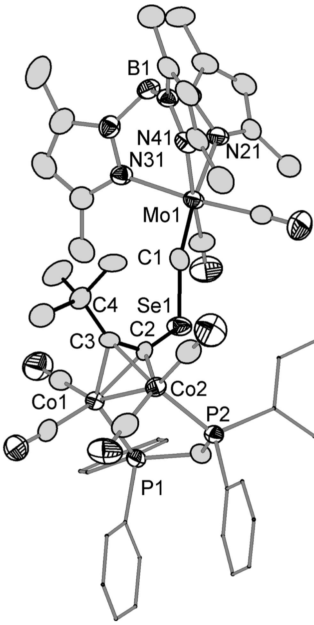

Figure 2. Molecular geometry of **5a** in the crystal state (hydrogen atoms omitted, phenyl groups simplified, 40% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mo1−N21 = 2.289(4), Mo1−N31 = 2.224(4), Mo1−N41 = 2.227(5), Mo1−C1 = 1.823(5), C1−Se1 = 1.857(5), Se1−C2 = 1.903(5), Co1−Co2 = 2.4586(10), Co1−P1 = 2.2265(15), Co1−C2 = 1.954(5), Co1−C3 = 1.982(5), Co2−P2 = 2.2247(15), Co2−C2 = 1.948(5), Co2−C3 = 1.987(5), C2−C3 = 1.338(7); N21−Mo1−N31 = 82.05(16), N21−Mo1−N41 = 83.14(16), N31−Mo1−N41 = 83.92(17), N31−Mo1−C1 = 101.0(2), N41−Mo1−C1 = 111.2(2), C1−Mo1−C20 = 85.1(2), C1−Mo1−C30 = 78.0(2), C1−Se1−C2 = 109.0(2), Se1−C1−Mo1 = 152.3(3), Se1−C2−Co1 = 125.4(3), C2−C3−C4 = 141.6(5).

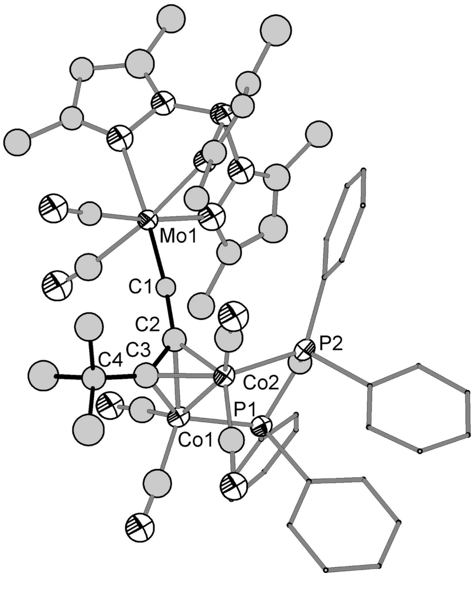

Figure 3. Molecular geometry of **6a** in the crystal state (hydrogen atoms omitted, phenyl groups simplified, 30% displacement ellipsoids).

see the Experimental Section). The related complex $[W\{\equiv CC_2(CMe_3)Co_2(CO)_4(\mu\text{-dppm})\}(CO)_2\{HB(pz)_3\}]$ has been previously obtained from the sequential reaction of $[W(\equiv CC\equiv CCMe_3)(CO)_2\{HB(pz)_3\}]$ with $[Co_2(CO)_8]$ and dppm.[7]

The molecular structure of **5a** (Figure 2) confirms that the "Co_2" fragment has indeed added across the C≡C rather than Mo≡C bond of the alkynylselenolatoalkylidyne chain. It may be surmised that this regioselectivity is steric in origin, given that such factors play a key role in determining the stability of metalladicobaltatetrahedranes[13] and that these are exaggerated in the case of the $HB(pzMe_2)_3$ ligand. The geometry of the dicobaltatetrahedrane core is essentially comparable to that observed for $[Co_2(\mu\text{-PhSeC}\equiv\text{CPh})(CO)_6]$,[2b] with the minor perturbations expected to result from the inclusion of the dppm bridging ligand.[14] As expected as a result of alkyne coordination, the C≡C bond of the alkyne is lengthened (1.338(7) Å) relative to that found in **2b** (1.175(17) Å), while the (sp^3) C2−Se bond length of 1.903(5) Å is also lengthened relative to the (sp) C−Se bond lengths in **2b**. Notably, this lengthening is attended by a contraction in C1−Se (1.857(5) Å), which would be consistent with the π-basicity of the selenium atom (shared between the sp carbons of **2**) now being directed solely toward the alkylidyne carbon in **5a**. Were this the case, then it might be expected that the Mo≡C bond became elongated, which is indeed what is observed, though at the limits of statistical significance. Coordination of the alkyne unit also results in an opening of the C1−Se−C2 angle (109.0(2)°) and substantial bending of the Mo−C1−Se angle (152.3(3)°)—the most severe deformation observed to date for pyrazolylborate-ligated alkylidyne complexes.[9] These deformations are presumably steric in origin, reflecting the nonbonded unfavorable interactions between the CMe_3 group and the two pyrazolyl rings between which it is required to nestle. It is perhaps noteworthy that, despite the severe bending of the alkylidyne unit in **5a**, this is not reflected in an unusually long Mo−C1 separation: i.e., nonlinear alkylidyne coordination does not appear to appreciably compromise effective multiple bonding.

The above results indicate that alkynylselenolatoalkylidynes are viable cumulenic systems for study. Nevertheless, given the observation of significant, albeit small, amounts of **6a** accompanying the formation of **5a** and of **3b** with **2b**, the C−Se bonds would appear to be susceptible to cleavage and selenium extrusion, a feature we are currently exploring.

Experimental Section

All manipulations, unless otherwise stated, were carried out under an atmosphere of prepurified and dried N_2 using conventional Schlenk and glovebox techniques. Dichloromethane and chloroform were dried over CaH_2 and distilled under nitrogen. Diethyl ether, hexane, and tetrahydrofuran (THF) were distilled from Na/benzophenone under N_2. Reactions were carried out at room temperature unless stated otherwise. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Inova 300 or Gemini 300 spectrometers (^1H, 300.1 MHz; $^{31}P\{^1H\}$, 121.4 MHz; $^{13}C\{^1H,\}$ 75.42 MHz). ^1H and $^{13}C\{^1H\}$ NMR chemical shifts (δ) are reported relative to residual solvent signals. $^{31}P\{^1H\}$ NMR chemical shifts are reported relative to an external 85% H_3PO_4 reference. Elemental microanalytical data were obtained from the Research School of Chemistry microanalytical service. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer. The complex **1** was prepared according to a published procedure.[5] All other reagents were used as obtained from commercial sources.

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[14] For comparison, the complex $[Co_2(\mu\text{-PhCCPPh}_2)(\mu\text{-dppm})(CO)_4]$ has one π-basic heteroatom alkyne substituent with Co−Co = 2.4711(16), C−C = 1.371(10), Co−C = 1.945(8)–1.996(8), and Co−P = 2.225(2), 2.242(3) Å: Hong, F.-E.; Ho, Y.-J.; Chang, Y.-C.; Lai, Y.-C. *Tetrahedron* **2004**, *60*, 2639.

Synthesis of [Mo(≡CSeC≡C^{t}Bu)(CO)$_2${HB(pzMe$_2$)$_3$}] (2a). A solution of 3,3-dimethylbut-1-yne (0.50 mL, 4.03 mmol) in tetrahydrofuran (5 mL) at −78 °C was treated dropwise (with stirring) with *n*-butyllithium (2.5 mL, 1.6 mol dm^{-3} solution in hexane, 4.0 mmol). The resultant pale yellow mixture was warmed to ambient temperature and stirred for a further 1 h, after which time it was cooled to 0 °C and elemental selenium (0.317 g, 4.02 g atom) added (N.B.: the mixture deepened in color over approximately 15 min as the selenium powder was consumed). The yellow reaction mixture was then cooled to −78 °C and transferred via a filter cannula into a separate flask containing a suspension of [Mo(≡CCl)(CO)$_2${HB(pzMe$_2$)$_3$}] (**1**; 2.00 g, 4.03 mmol) in diethyl ether (150 mL) at the same temperature. The cooling bath was removed, and the resultant yellow mixture warmed to ambient temperature with stirring. After 24 h, the cloudy orange solution was filtered through diatomaceous earth and solvent removed under reduced pressure to afford a reddish orange residue. The residue was redissolved in dichloromethane (3 mL) and transferred to a chromatography column (silica gel, −33 °C). Elution with dichloromethane−hexane (1:5) afforded an initial yellow fraction, corresponding to recovered [Mo(≡CCl)(CO)$_2${HB(pzMe$_2$)$_3$}] (**1**: IR (CH$_2$Cl$_2$) 2002, 1915 (ν_{CO}) cm^{-1}; cf. literature[5] data, IR (cyclohexane) 2005, 1921 cm^{-1}) (0.264 g, 13%), closely followed by a second broad orange band. Removal of solvent from the orange band and recrystallization from chloroform−hexane afforded **2a** as an orange powder. Yield: 1.889 g (76%). IR (CH$_2$Cl$_2$): 2000, 1916 (ν_{CO}) cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ_{H} 5.85, 5.73 (s × 2, 2:1 H, H^4(pz)), 2.54, 2.37, 2.36, 2.32 (s × 4, 6:3:6:3 H, pzCH$_3$), 1.23 (s, 9 H, CMe$_3$); ^{13}C{^{1}H}, δ_{C} 245.0 (Mo≡C), 225.1 (MoCO), 151.5, 151.1, 145.1, 144.4 (1:2:1:2, C^{3,5}(pz)), 106.4, 106.2 (1:2, C^4(pz)), 114.7 (*C*≡CSe), 52.0 (C≡*C*Se), 30.7 (C(*C*H$_3$)$_3$), 29.3 (*C*(CH$_3$)$_3$), 16.0, 14.6, 12.6 (2:1:3, pzCH$_3$). MS (ESI): *m/z* (%) 566.0 (100) [M − 2CO]$^+$. Anal. Found: C, 45.14; H, 5.02; N, 13.00. Calcd for C$_{24}$H$_{31}$BMoN$_6$O$_2$Se: C, 46.40; H, 5.03; N, 13.53. Calcd for C$_{24}$H$_{31}$BMoN$_6$O$_2$Se·H$_2$O: C, 45.09; H, 5.20; N, 13.15. N.B.: despite the use of dried solvents and prolonged storage under high vacuum, spectroscopic data (IR, ^{1}H NMR) indicated the presence of ca. 1 equiv of water, presumably originating from the chromatography support (silica gel).

Synthesis of [Mo(≡CSeC≡CSiMe$_3$)(CO)$_2${HB(pzMe$_2$)$_3$}] (2b). (a) Compound **2b** was prepared as an orange powder by following the procedure described for **2a** above from ethynyltrimethylsilane (0.075 mL, 0.530 mmol) in tetrahydrofuran (10 mL), *n*-butyllithium (0.34 mL of a 1.6 M solution in hexane), elemental selenium (0.042 g, 0.532 g atom), and [Mo(≡CCl)(CO)$_2${HB(pzMe$_2$)$_3$}] (**1**; 0.264 g, 0.532 mmol) in diethyl ether (15 mL). Yield: 0.128 g (61% based on recovered **1**).

(b) Compound **2b** was similarly prepared as an orange powder by following the procedure described above from 2 equiv of ethynyltrimethylsilane (0.569 mL, 4.03 mmol) in tetrahydrofuran (20 mL), *n*-butyllithium (0.34 mL of a 1.6 M solution in hexane), elemental selenium (0.317 g, 4.015 mmol) and [Mo(≡CCl)(CO)$_2$-{HB(pzMe$_2$)$_3$}] (**1**; 1.00 g, 2.02 mmol) in diethyl ether (50 mL). In addition to unreacted **1** (0.01 g, 10% recovery) and **2b** (0.805 g, 63%), chromatography afforded an intermediate red fraction, corresponding to [Mo(≡CC≡CSiMe$_3$)(CO)$_2${HB(pzMe$_2$)$_3$}] (**3a**), identified by comparison of spectroscopic data with those previously published.[5] Yield: 0.045 (4%). Data for **2b** are as follows. IR (Nujol): 2093 ($\nu_{\mathrm{C\equiv C}}$), 1996, 1910 (ν_{CO}), 1543 (ν_{CN}) cm^{-1}. IR (CH$_2$Cl$_2$): 2092 ($\nu_{\mathrm{C\equiv C}}$), 2002, 1919 (ν_{CO}) cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ_{H} 5.85, 5.73 (s × 2, 2:1 H, pzH), 2.52, 2.36, 2.35, 2.31 (s × 4, 6:3:6:3 H, pzCH$_3$), 0.22 (s, 9 H, SiCH$_3$); ^{13}C{^{1}H} δ_{C} 244.8 (Mo≡C), 224.8 (CO), 151.6, 151.2, 145.2, 144.5 (1:2:1:2, C^{3,5}(pz)), 106.5, 106.3 (1:2, C^4(pz)), 113.8 (*C*≡CSe), 78.7 (C≡*C*Se), 16.0, 14.6, 12.6 (1:2:3, pz*C*H$_3$), −0.25 (SiCH$_3$). MS (ESI): *m/z* (%) 582.9 (80) [M − 2CO]$^+$, 484.9 (18) [M − 2CO − C≡CSiMe$_3$]$^+$. Anal. Found: C, 43.40; H, 4.93; N, 12.96. Calcd for C$_{23}$H$_{31}$BMoN$_6$O$_2$SeSi: C, 43.34; H, 4.90; N, 13.19. Crystal data for **2b**: C$_{23}$H$_{31}$BMoN$_6$O$_2$SeSi: M_{r} = 637.33, orthorhombic, $P2_12_12_1$, a = 8.0112(4) Å, b = 17.7072(1) Å, c = 20.381(1) Å, V = 2891.1(3) Å^3, Z = 4, ρ_{calcd} = 1.464 Mg m^{-3}, μ(Mo Kα) = 1.784 mm^{-1}, T = 200(2) K, brown needle, 5092 independent measured reflections ($2\theta \leq 54°$), R1 = 0.062, wR2 = 0.092 for 3124 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 239 parameters. The crystal was refined in terms of a 0.545(29):0.455 twin assuming a volume fraction of 0.518(4):0.482 of a $P2_12_12_1$ structure and a 1:1 disordered *Pmnb* structure using reflections indexed for a smaller cell. A full discussion of the details of the nonstandard refinement will be published elsewhere.[15]

Synthesis of [Mo(≡CSeC≡CC$_6$H$_4$Me-4)(CO)$_2$HB(pzMe$_2$)$_3$}] (2c). The complex **2c** was prepared as an orange microcrystalline powder by following the procedure described above for **2a** from 4-ethynyltoluene (0.070 g, 0.603 mmol) in tetrahydrofuran (10 mL), *n*-butyllithium (0.38 mL of a 1.6 M solution in hexane), elemental selenium (0.048 g, 0.608 g atom), and [Mo(≡CCl)(CO)$_2$-{HB([pzMe$_2$)$_3$}] (**1**; 0.300 g, 0.604 mmol) in diethyl ether (100 mL). Yield: 0.106 g (59% based on recovered **1**). IR (Nujol): 2000 s, 1920 s (ν_{CO}) cm^{-1}. IR (CH$_2$Cl$_2$): 2001 s, 1918 s (ν_{CO}) cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ 7.36, 7.13 (d × 2, 4 H, C$_6$*H*$_4$), 5.84, 5.72 (s × 2, 2:1 H, H^4(pz)), 2.52, 2.36, 2.35, 2.31 (s × 4, 6:6:6:3 H, pzCH$_3$, C$_6$H$_4$C*H*$_3$); ^{13}C{^{1}H}, δ 246.6 (Mo≡C), 225.0 (MoCO), 151.5, 151.2, 145.2, 144.5 (1:2:1:2, C^{3,5}(pz)), 138.7, 131.5, 129.0 (C$_6$H$_4$), 106.4, 106.3 (1:2, C^4(pz)), 119.9 (*C*≡CSe), 63.8 (C≡*C*Se), 21.5 (C$_6$H$_4$CH$_3$), 15.9, 14.6, 12.6 (2:1:3, pz*C*H$_3$). MS (ESI): *m/z* (%) 600.9 (19) [M − 2CO]$^+$, 413.1 (90) [HB(pzMe$_2$)$_3$ + C$_2$C$_6$H$_4$Me]$^+$. MS (ESI): *m/z* (%) 656.07 (11) [M]$^+$, 578.15 (45) [M − Se]$^+$, 296.26 (100) [HB(pzMe$_2$)$_3$]$^+$, 282.28 (95) [HB(pzMe$_2$)$_3$ − CH$_3$]$^+$.

Synthesis of [Mo{≡CSeC$_2$^{t}BuCo$_2$(CO)$_6$}(CO)$_2${HB(pzMe$_2$)$_3$}] (4a). A mixture of [Mo(≡CSeC≡C^{t}Bu)(CO)$_2${HB(pzMe$_2$)$_3$}] (**2a**; 0.200 g, 0.322 mmol) and [Co$_2$(CO)$_8$] (0.110 g, 0.322 mmol) were stirred together in diethyl ether (15 mL) for 1 h, during which time a period of CO evolution was observed. The dark brown mixture was transferred via filter cannula into a new flask, and solvent was removed to give a brown solid comprising **4a**. Yield: 0.234 g (81%). IR (hexane): 2091 m, 2055 vs, 2034 s, 2024 s, 1999 m, 1921 s (ν_{CO}) cm^{-1}. IR (KBr): 2088 m, 2053 m, 2029 m, 2021 m, 2005 m, 1985 s, 1957 vs, 1898 vs (ν_{CO}) cm^{-1}. NMR (CD$_2$Cl$_2$, 25 °C):. ^{1}H, δ_{H} 5.90, 5.77 (s × 2, 2:1 H, pzH), 2.61, 2.37, 2.32, 2.30 (s × 4, 6:6:3:3 H, pzCH$_3$), 1.30 (s, 9 H, ^{t}Bu); ^{13}C{^{1}H}, δ_{C} 261.7 (Mo≡C), 227.2 (MoCO), 199.9 (br, CoCO), 152.0, 151.8, 146.2, 145.3 (2:1:1:2, C^{3,5}(pz)), 106.7, 106.5 (1:2, C^4(pz)), 113.7 (*C*≡CSe), 85.6 (C≡*C*Se), 36.8, (*C*(CH$_3$)$_3$), 32.2 (C(*C*H$_3$)$_3$), 16.2, 14.6, 12.8 (2:1:3, pz*C*H$_3$). MS (ESI): *m/z* (%) 946.9 (1) [M + K]$^+$, 850.2 (4) (M − CMe$_3$]$^+$. Accurate mass: *m/z* 946.8897 (calcd for [M + K]$^+$ 946.8839). Anal. Found: C, 39.00; H, 4.07; N, 8.34. Calcd for C$_{30}$H$_{31}$BCo$_2$MoN$_6$O$_8$Se: C, 39.72; H, 3.44; N, 9.26. Calcd for C$_{30}$H$_{31}$BCo$_2$MoN$_6$O$_8$Se·1.5H$_2$O: C, 38.57; H, 3.67; N, 9.00. N.B.: despite the use of dried solvents and prolonged storage under high vacuum, spectroscopic data (IR, ^{1}H NMR) indicated the presence of ca. 1.5 equiv of water, presumably originating from the chromatography support (silica gel).

Synthesis of [Mo{≡CSeC$_2$^{t}BuCo$_2$(CO)$_4$(dppm)}(CO)$_2${HB-(pzMe$_2$)$_3$}] (5a) and [Mo{≡CC$_2$^{t}BuCo$_2$(CO)$_4$(dppm)}(CO)$_2${HB-(pzMe$_2$)$_3$}] (6a). A mixture of [Mo{≡CSeC$_2$^{t}BuCo$_2$(CO)$_6$}(CO)$_2$-{HB(pzMe$_2$)$_3$}](**4a**; 0.216 g, 0.235 mmol) and bis(diphenylphosphino)methane (dppm; 0.092 g, 0.239 mmol) in dichloromethane (15 mL) was heated at reflux for 3.5 h, after which time all of the **4a** had been consumed (TLC). The solvent volume was reduced to ca. 3 mL and the orange solution transferred to a chromatography column (silica gel, −33 °C). Elution with CH$_2$Cl$_2$−hexane (1:1) afforded a major brown-orange fraction and a minor green band.

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[15] Caldwell, L. M.; Hill, A. F.; Rae, A. D.; Willis, A. C. To be submitted for publication in *Acta Crystallogr. Sect. E.*

Solvent removal from the brown fraction provided **5a** as a brown solid: Yield: 0.145 g (49%). Solvent removal from the narrow green fraction provided **6a** as a green solid. Yield: 0.006 g (2%). Data for **5a** are as follows. IR (CH_2Cl_2): 2022 m, 1995 s (br), 1968 m, 1907 m (br) (ν_{CO}) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ_H 7.44, 7.29, 7.20, 7.15, 7.02 (m × 5, 20 H, C_6H_5), 5.77, 5.69 (s × 2, 2:1 H, H^4(pz)), 3.35, 3.25 (m × 2, 2 H, CH_2P_2), 2.46, 2.36, 2.32, 2.29 (s × 4, 6:6:3:3 H, pzCH_3), 1.40 (s, 9 H, ^{t}Bu; $^{13}C\{^1H\}$, δ_C 268.8 ($Mo{\equiv}C$), 226.8 (MoCO), 207.1, 202.5 (br, CoCO), 151.8, 151.0, 144.9, 144.1 (2:1:1:2, $C^{3,5}$(pz)), 137.8 (vt, J_{PC} = 23.7 Hz, $C^1(C_6H_5)$), 134.6 (vt, J_{PC} = 16.6 Hz, $C^{1'}(C_6H_5)$), 132.6 (vt, J_{PC} = 6.1 Hz, $C^{2,6}(C_6H_5)$), 131.0 (vt, J_{PC} = 5.7 Hz, $C^{2',6'}(C_6H_5)$), 129.6, 129.3 ($C^{4,4'}(C_6H_5)$), 128.4, 127.9 (vt × 2, $C^{3,5,3',5'}(C_6H_5)$), 106.2, 106.0 (1:2, C^4(pz)), 119.2 (t br, $\mathit{C}{\equiv}\mathrm{CSe}$) 83.9 (t br, $\mathrm{C}{\equiv}\mathit{C}\mathrm{Se}$), 37.2 ($\mathit{C}(\mathrm{CH_3})_3$), 35.2 (t, CH_2P_2), 32.5 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 16.4, 14.6, 12.7 (2:1:3, pz$\mathit{C}\mathrm{H_3}$); $^{31}P\{^1H\}$, δ_P 38.25 (br). MS (ESI): *m/z* (%) 1258.0 (5) [M + Na]$^+$, 662.9 (63) [$Co_2C_2(CO)_6$(dppm) + Na]$^+$, 439.1 (100) [HB$(pzMe_2)_3Co_2C_2$]$^+$. Anal. Found: C, 52.94; H, 4.77; N, 6.72. Calcd for $C_{53}H_{53}BCo_2MoN_6O_6P_2Se\cdot{}^1/_2C_6H_{14}$: C, 52.60; H, 4.73; N, 6.57. C_8H_{14} confirmed by ^{1}H NMR. Crystals suitable for diffractometry were obtained by slow diffusion of hexane into a dichloromethane solution of the complex. Crystal data for **5a**: $C_{53}H_{53}BCo_2MoN_6O_6P_2Se$, M_r = 1235.57, triclinic, $P\bar{1}$, a = 9.1891(2) Å, b = 12.9671(4) Å, c = 23.1494(6) Å, α = 87.108(1)°, β = 81.193(2)°, γ = 84.996(2)°, V = 2714.3(2) Å^3, Z = 2, ρ_{calcd} = 1.512 Mg m^{-3}, μ(Mo Kα) = 1.615 mm^{-1}, T = 200(2) K, brown needle, 9597 independent measured reflections ($2\theta \leq 50°$), R1 = 0.0512, wR2 = 0.0527 for 6081 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 650 parameters. The crystal was twinned and refined accordingly (final twin ratio 0.589(6):0.411) (CCDC 656954).

Data for **6a** are as follows. IR (CH_2Cl_2): 2024 m, 1999 s (br), 1974 m, 1962 (sh), 1884 m (br) (ν_{CO}) cm^{-1}. NMR ($CDCl_3$, 25 °C): δ_H, 7.34, 7.12, 6.99 (m × 3, 20 H, C_6H_5), 5.70, 5.65 (s × 2, 2:1 H, pzH), 3.65, 3.45 (m × 2, 2 H, CH_2P_2), 2.39, 2.38, 2.29, 2.27, 2.27 (s × 4, 6:3:3:3:3 H, pzCH_3), 1.40 (s, 9 H, ^{t}Bu); ^{13}C, δ_C 255.5 ($Mo{\equiv}C$), 230.2 (MoCO), 219.9, 195.0 (br, CoCO), 151.4, 151.2, 144.0, 143.9 (2:1:1:2, $C^{3,5}$(pz)), 136.8 (vt, $C^1(C_6H_5)$), 131.5 ($C^{3,5}(C_6H_5)$), 129.3 ($C^4(C_6H_5)$), 128.0 ($C^{2,6}(C_6H_5)$), 112.7 (t br, $\mathit{C}\mathrm{CC}{\equiv}\mathrm{Mo}$), 106.0, 105.8 (1:2, C^4(pz)), 86.2 (t br, $\mathrm{C}\mathit{C}\mathrm{C}{\equiv}\mathrm{Mo}$), 38.9 ($\mathit{C}(\mathrm{CH_3})_3$), 37.2 (t, CH_2P_2), 33.6 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 16.7, 14.6, 12.8, 12.6 (2:1:2:1, pz$\mathit{C}\mathrm{H_3}$); ^{31}P, δ_P 33.47 (br). Crystals suitable for diffractometry were grown via slow diffusion of ethanol into a dichloromethane solution of the complex. Crystal data for **6a**: $C_{53}H_{53}BCo_2MoN_6O_6P_2$, M_r = 1156.59, monoclinic, $P2_1/n$, a = 14.093(4) Å, b = 19.431(5) Å, c = 20.150(5) Å, β = 109.277(8)°, V = 5209(2) Å^3, Z = 4, ρ_{calcd} = 1.475 Mg m^{-3}, μ(Mo Kα) = 0.983 mm^{-1}, T = 200(2) K, green needle, 7148 independent measured reflections ($2\theta \leq 46°$), R1 = 0.1322, wR2 = 0.1046 for 2607 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 311 parameters (CCDC 656955). Poor-quality diffraction data led to an imprecise structural model that nevertheless unambiguously established the identity of the compound.

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Supporting Information Available: CIF files giving full details of the crystal structure determinations of **5a** (CCDC 656954) and **6a** (CCDC 656955). This material is available free of charge via the Internet at http://pubs.acs.org.

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