

Alkynyl Selenolate Complexes of Iron, Nickel, and Molybdenum

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The successive treatment of terminal alkynes, $HC \equiv CR$ ($R = C_6H_4Me-4$, $SiMe_3$), with "BuLi and gray selenium affords $LiSeC \equiv CR$, which in turn reacts with $[FeCl(CO)_2(\eta-C_5H_5)]$, $[NiCl(PPh_3)-(\eta-C_5H_5)]$, and $[MoI(CO)_3(\eta-C_5H_5)]$ to afford the alkynylselenolato complexes $[Fe(SeC \equiv CR)-(CO)_2(\eta-C_5H_5)]$, $[Ni(SeC \equiv CR)(PPh_3)(\eta-C_5H_5)]$, and $[Mo(SeC \equiv CR)(CO)_3(\eta-C_5H_5)]$, two examples of which have been structurally characterized. When $[MoI(CO)_3\{HB(pz)_3\}]$ (pz = pyrazol-1-yl) was however employed as the electrophile, low yields of the selenoketenyl complex $[Mo(\eta^2-C_5C'-SeCCR)(CO)_2\{HB(pz)_3\}]$ were obtained via the presumed intermediacy of the alkynylselenolato complex $[Mo(\sigma-SeC \equiv CR)(CO)_3\{HB(pz)_3\}]$, which is perhaps destabilized relative to the selenoketenyl complex by the octahedral enforcer character of the HB(pz)_3 ligand.

Introduction

We have previously reported the first examples of transition metal complexes of the alkynylselenolate ligand "SeC=CR" in two different coordination modes via disparate routes (Scheme 1).^{1,2}

The first approach involved the generation of the alkynylselenolate anion via the reaction of lithium alkynyls with gray selenium followed by treatment with Vaska's complex, [IrCl(CO)(PPh₃)₂], to afford [Ir(SeC=CR¹)(CO)(PPh₃)₂] (R¹ = C₆H₄Me-4). The alkynylselenolate ligand in this complex is coordinated solely through the selenium (σ -Se) atom despite the coordinative unsaturation of the d⁸-squareplanar iridium(I) center and is in many respects akin to more conventional selenolate ligands. In the interim other groups have provided further examples of this class of ligand accessed via this route,³⁻⁵ and these are summarized in Chart 1.

It is noteworthy that in all cases the alkynylselenolato ligand coordinates in the σ -Se manner. By way of contrast, we have also described the synthesis of complexes in which the "SeCCR" group coordinates side-on through the C–C

multiple bond, an arrangement that may be described as a selenoketenyl (η^2 -C,C'). The vast majority of ketenyl ligands, ⁵ and given that selenocarbonyl complexes are rare, and none to date also possess carbyne ligands, this approach is unattractive for the general synthesis of selenoketenyls. We chose an alternative synthetic strategy,² which involved conversion of a preformed ketenyl complex with Woollins' reagent (Ph₂P₂Se₄, obtained from PhPCl₂ and Li₂Se).⁷ This reagent has emerged as an effective selenating agent.⁸

With these two disparate coordination modes firmly established, in addition to the recent isolation of the first isoselenocarbonyls,⁹ which might also be described as alkylidynylselenolates (Scheme 2), we were eager to establish if these two modes were interconvertible. Ketenyl ligands may in some instances adopt a monodentate coordination mode; however this is generally through the carbon atom rather than oxygen,⁶ e.g., in the complex [W{ σ -C-C(=C=O) R¹}(CO)(PMe_3)₂(η -C₅H₅)],¹⁰ obtained from [W{ η^2 -C,C'-OCCR¹}(CO)(PMe_3)₂-(η -C₅H₅)] and excess PMe₃. We have therefore investigated further examples of alkynylselenolates based on nickel (d⁸), iron (d⁶), and molybdenum (d⁴) metal centers including one

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Scheme 1. Synthetic Routes to Alkynylselenolate¹ and Selenoketenyl² Complexes





example where it was indeed possible to infer the interconversion of σ -Se and η^2 -C,C' bonding modes, affording a new route to chalcoketenyl complexes.

Scheme 2. Synthesis of an Isoselenocarbonyl/Alkylidynylselenolate Complex⁸



Chart 2. Resonance Descriptions for (a) the Alkynylselenolate Anion and (b) Positively Mesomeric Heteroatom (D:)-Substituted Alkynes



Results and Discussion

The reaction of alkynyl lithium reagents (LiC≡CR) with elemental (gray) selenium proceeds via the presumed formation of the lithium alkynylselenolate (LiSeC=CR), which although not isolated, may be inferred through the nature of products obtained via subsequent reactions with electrophiles.¹¹ The alkynylselenolate anion is an ambidentate nucleophile (Chart 2), the behavior of which may be rationalized by two resonance contributors, which suggest that both the selenium and the β -carbon may be prone to electrophilic attack. The potential nucleophilicity of C_{β} is most clearly demonstrated in the case of protonation, which does not provide the selenohydryl acetylene RC=CSeH (though reversible kinetic protonation of the heteroatom should not be discounted), but rather heterocycles that may be viewed as forming via the highly reactive selenoketene (Se=C= CHR).¹² Selenoketenes are at present hypothetically inferred intermediates and due to their high reactivity are likely to remain so in condensed phases. However, selenoketenes have been assembled as ligands within the protective environment of transition metal coordination spheres.¹³ We shall return to the question of electrophilic attack at C_β subsequently; for the work to immediately follow, attack at the

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Figure 1. Molecular structure of 1 in a crystal of $1 \cdot (CHCl_3)_2$. Selected bond lengths (Å) and angles (deg): Ni–Se 2.3056(16), Ni–P 2.145(3), Se–C(1) 1.831(10), Se–Ni–P 91.71(7), Ni– Se–C(1) 105.0(3), Se–C(1)–C(2) 171.9(9), C(1)–C(2)–C(3) 177.2(11), P–Ni–Se–C(1)–157.6(3).

Scheme 3. Synthesis of Alkynylselenolato Complexes of Nickel(II) and Iron(II)



selenium appears to be the preferred mode for transition metal electrophiles.

Treating a solution of 4-ethynyltoluene (hereafter HC= $CC_6H_4Me-4 = HC \equiv CR^1$) in tetrahydrofuran with gray selenium provides a solution of LiSeC \equiv CR^1, which was used without isolation. Treating this solution with [NiCl(PPh₃)- $(\eta-C_5H_5)$]¹⁴ results in the clean formation of a red-brown compound formulated as the alkynylselenolato complex [Ni(SeC = CR¹)(PPh₃)(η -C₅H₅)] (1) (Scheme 3) on the basis of spectroscopic, elemental microanalytical, and crystallographic data (Figure 1). The infrared spectrum includes a single absorption at 2131 cm⁻¹, which may be assigned to the alkynyl group. The ¹H and ¹³C NMR spectra feature the expected signatures of the cyclopentadienyl, tolyl, and phosphine groups, while the chemical shifts of the alkynyl unit [$\delta_C = 92.6$ (CC=), 84.9 (SeC=)] are consistent with those for more conventional alkynylselenoethers.¹⁵ FAB-mass spectrometric data suggest that the complex is monomeric.

The formulation of 1 was confirmed in the solid state by a crystallographic study, the results of which are summarized in Figure 1. Geometric parameters associated with the "Ni- $(PPh_3)(\eta - C_5H_5)$ " unit are unremarkable, conform to precedent for chalcogenolato complexes of this fragment,^{16,17} and do not call for further comment. Structural data associated with the previously reported nickel selenolate complex $[Ni(SePh)(PPh_3)(\eta-C_5H_5)]^{17}$ include Ni–Se and Ni–P bond lengths of 2.301(1) and 2.136(1) Å with P-Ni-Se and Ni-Se-C angles of 91.4(1)° and 107.9(1)°. Thus the Ni-Se bond length of 2.3056(16) Å found for 1 is within the experimental accuracy, identical to that for the phenylselenolate example, while the Ni-Se-C angle of 105.0(3)° is also very similar. The C1=C2 bond length of 1.216(14) Å is somewhat longer than found for hydrocarbon alkynes, but within the range typical of alkynes bearing positively mesomeric (π -donor) heteroatom substituents (Chart 2b). Structural data for conventional acyclic alkynylselenoethers are somewhat sparse¹⁸ but typically span the ranges 1.17-1.21 Å (C≡C) and 1.81-1.85 Å (C-Se), within which those for 1 fall.

The reactions of LiSeC=CR (R = R¹, SiMe₃) with [FeCl-(CO)₂(η -C₅H₅)]¹⁹ provide in high yield khaki-olive green compounds formulated as the monomeric species [Fe-(SeC=CR)(CO)₂(η -C₅H₅)] (R = C₆H₄Me-4 **2a**, SiMe₃ **2b**). The compounds appear to be stable in solution (aerobic dichloromethane, 36 h, TLC, IR). The infrared spectrum of **2b** includes peaks at 2034 and 1990 cm⁻¹ due to the *cis* carbonyl ligands and one weaker absorption at 2061 cm⁻¹ that we attribute to the alkynyl group. The former may be compared with those for the selenolato complex [Fe(SePh)-(CO)₂(η -C₅H₅)] (cyclohexane: 2026, 1984 cm⁻¹)²⁰ and those for the alkynylthiolato complex [Fe(SC=C'Bu)(CO)₂-(η -C₅H₅)] (THF: 2032, 1987 cm⁻¹)²¹ described previously by Delgado.

The molecular structure of **2a** in the solid state is depicted in Figure 2, and selected geometric parameters for alkynylselenolate complexes are collated in Table S1 (Supporting Information). The geometry of the "Fe(CO)₂(η -C₅H₅)" moiety is unexceptional, with OC-Fe-Se and OC-Fe-CO angles close to 90° [87.7(3)-94.7(4)°] and the Fe-Se bond length of 2.4072(14) Å being close to that found for [Fe(SePh)(CO)₂(η -C₅H₅)] (2.413(3) Å)²² and other mononuclear 18-electron iron(II) selenolates.²³ The features of the Fe-Se-C=C spine (Se-C1 = 1.834(9), C α C = 1.188(13) Å)

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Figure 2. Molecular structure of 2a in a crystal. Selected bond distances (Å) and angles (deg.): Fe–Se 2.4072(14), Se–C(1) 1.834(9), C(1)–C(2) 1.188(13), Fe–Se–C(1) 103.0(2), Se–Fe–C(15) 92.7(3), Se–Fe–C(16) 87.7(3), Se–C(1)–C(2) 176.3(8), C(1)–C(2)–C(3) 178.4(8), C(15)–Fe–Se–C(1) 29.4(4), C(16)–Fe–Se–C(1) –65.2(4).

are comparable to those observed for **1**. The iron(II) center being d⁶-pseudo-octahderal has little inclination for any π -dative capacity on the part of the selenium center. Accordingly, the positively mesomeric influence of the selenium is rather directed toward the alkynyl group, which is lengthened toward the long end of the norms discussed above. The steric profile of the "Fe(CO)₂(η -C₅H₅)" group is modest, and accordingly the angle at selenium [103.0(2)°] is also comparable to that for **1**.

The reaction of $[MoI(CO)_3(\eta-C_5H_5)]^{24}$ with LiSeC=CR¹ affords the anticipated complex $[Mo(SeC \equiv CR^{1})(CO)_{3}(\eta - 1)]$ C_5H_5](3) by analogy with the reported reactions²⁵ of [MoX- $(CO)_3(\eta-C_5H_5)](X=Cl, Br, I)$ with RSe⁻, although the more common entry into the selenolate chemistry of the molybdenum cyclopentadienyl unit is typically via the reactions of $[Mo_2(CO)_x(\eta-C_5H_5)_2](x = 4, 6)$ with diselenides.²⁶ Alkynyl diselenides (RC=CSeSeC=CR), though a potentially interesting class of compounds, are not yet synthetically available, precluding the latter approach. Our choice of [MoI- $(CO)_3(\eta - C_5H_5)$] as the preferred substrate was based on the proclivity of the corresponding chloride to undergo outersphere single electron transfer reactions with strong reducing agents, including chalcogenolates, to provide $[Mo_2(CO)_6(\eta C_5H_5_2$]. The complex [MoI(CO)₃(η -C₅H₅)] performed well in this respect, with no indication (TLC, IR) for the formation of $[Mo_2(CO)_6(\eta - C_5H_5)_2]$.

Complex 3, being of the four-legged piano-stool variety, has the option of two possible ligand arrangements, a local $C_{3\nu}$ -Mo(CO)₃ arrangement of the three carbonyls, capped by the selenolato ligand, or alternatively a square-pyramidal

arrangement of the carbonyl and selenolate donors. The ${}^{13}C{}^{1}H{}$ NMR spectrum would appear to suggest the latter (CDCl₃: $\delta_{\rm C} = 235.3, 222.9$); however the infrared data are too numerous by one for this to be a simple case (2036, 1973, 1960, 1944 cm⁻¹). We suggest that perhaps there exist rotamers with respect to the Cp-Mo-Se-C spine that interconvert on the ${}^{13}C$ NMR time scale but are apparent on the IR time scale. The alkynyl group however gives rise to a single infrared absorption (CHCl₃: 2137 cm⁻¹).

Seven-coordinate geometry is common for complexes of the form $[MoL_4(\eta-C_5H_5)]$, designating the cyclopentadienyl as a facial pseudotridentate ligand. The hydrotris(pyrazolyl)borate ligand in contrast has been described as an octahedral enforcer.^{27–29} This would appear to be the case with respect to the reaction of $LiSeC \equiv CR^1$ with [MoI-(CO)₃{HB(pz)₃}], which proceeds distinctly from that involving the cyclopentadienyl analogue. Selenolates of the form $[Mo(SeR)(CO)_3(\eta$ -C₅H₅)] are well known,²⁵ as are binuclear species $[M_2(\mu - \text{SeR})_2(\text{CO})_x(\eta - \text{C}_5\text{H}_5)_2] (x = 2, 4).^{26,30}$ Within the poly(pyrazolyl)borate series, Templeton has described the thiolate complexes $[M(SR)(CO)_2 \{HB(pzMe_2)_3\}]$, which are stable monomeric, paramagnetic species,³¹ while Young has more generally considered group 6 poly(pyrazolyl)borates with a variety of chalcogen donors within the broader context of the biomimetic modeling of molybdenum and tungsten enzyme active sites.32

Treating the complex $[MoI(CO)_3\{HB(pz)_3\}]^{33}$ with one equivalent of LiSeC=CR¹ at -40 °C afforded in poor yield (ca. 10%) after cryogenic anaerobic chromatography (-30 °C, silica gel) a red compound formulated as the selenoketenyl complex $[Mo(\eta^2-SeCCR^1)(CO)_2\{HB(pz)_3\}]$ (4) on the basis of spectroscopic, (FAB) mass spectrometric, and elemental microanalytical data. Unfortunately, successive attempts to obtain crystallographic grade crystals from the trace amounts of product obtained were unsuccessful. Intermediate species could be observed spectroscopically (IR: $\nu_{CO} = 1984$, 1752, 1725, 1688 cm⁻¹) with a collective intense purple color. However, all attempts to intercept these species, including workup at -20 °C, failed to provide useful

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Scheme 4. Synthesis of Alkynylselenolato and Selenoketenyl Complexes of Molybdenum(II)^{*a*}



 ${}^{a}R^{1} = C_{6}H_{4}Me-4$; Tp = HB(pz)₃. Complexes **5a-c** (indicated by an asterisk) are alternative mechanistic postulates, none of which were isolated. The formulation of **4** rests on spectroscopic and analytical data.

results. In the absence of crystallographic data the formulation of 4 rests on spectroscopic and elemental microanalytical data, the interpretation of which is however substantiated by sparse data available for other selenoketenyl complexes of group 6 metals.² The dicarbonyl formulation follows from the observation of two ν_{CO} absorptions (Nujol: 1952vs, 1861vs cm^{-1}) in the infrared spectrum, the relative intensities of which are consistent with a cis-M(CO)₂ unit in close to octahedral geometry. The spectrum is however devoid of any further absorptions that might be attributable to a (free) alkynyl group. We tentatively assign the absorption at 1049 cm⁻¹ to a predominantly $\nu_{\rm CSe}$ mode; however the spectrum in this area is cluttered with fingerprint bands associated with the HB(pz)₃Mo cage, precluding more confident assignment. Complexes of carbon diselenide, in which one C=Se bond coordinates side-on leaving one exocyclic C=Se bond, have some topological similarity to selenoketenyl ligands, and the limited data available for such complexes suggest that the exocyclic C=Se stretch appears in the region 1000–1050 cm⁻¹, though again, many of these complexes have extraneous coligand absorptions in this region.

The remaining spectroscopic data associated with the "HB(pz)₃(CO)₂Mo" are either unremarkable or uninformative other than to note that the ¹³C{¹H} NMR spectrum indicates one pyrazolyl environment on this time scale. This is, however, not unusual in that complexes of the form [Mo(η^2 -XY)(CO)₂{HB(pz)₃}] are often fluxional, despite the low (*C_s*) symmetry of the ground state. The key spectroscopic data associated with the ligand of interest are somewhat equivocal. The two carbon resonances for the few known examples of selenoketenyl ligands appear within a narrow range in the ${}^{13}C{}^{1}H{}$ NMR spectrum,; for example, the complex [Mo(η^2 -SeCCR¹)(CO)(PPh₃){HB(pz)₃}] gives rise to two closely spaced resonances at 238.8 and 234.8 ppm.² On the basis of the intensity of the single broad absorption observed for 4 at 234.0 ppm relative to that observed at 215.1 ppm for the two carbonyl ligands, it would appear that the former corresponds to two overlapping resonances, presumably for the two carbon nuclei of a η^2 -C,C'-selenoketenyl ligand.

As to the nature of the intensely purple intermediate(s), three possibilities to consider include (i) the monodentate σ -Se alkynylselenolate complex [Mo(SeC=CR¹)(CO)₃{HB- $(pz)_{3}$ (5a); (ii) the monodentate selenoketenvl complex $[Mo\{\sigma-C-C(=C=Se)R^1\}(CO)_3\{HB(pz)_3\}]$ (5b), and (iii) the trihapto η^3 -Se,C,C' alkynylselenolate complex [Mo(η^3 -SeC= CR^{1} (CO)₂{HB(pz)₃}] (5c). We doubt that the last of these would be a persistent species since the barrier to rearrangement to 4 would involve little energy expenditure or atom reorganization. The possibility of electrophilic attack by molybdenum at C_{β} would seem to be sterically disfavored, leaving us with the first option, an alkynylselenolate complex akin to 1, 2, and 3 as the most plausible formulation. Selenolate complexes of the form [Mo(SeR)- $(CO)_{3}$ {HB(pz)₃] are presently unknown;^{28,29} however the complexes $[W(SR)(CO)_2 {HB(pzMe_2)_3}]^{31}$ have been reported to be exceptionally stable both thermally and aerobically. The reason for the apparent instability of 5a relative to the stable cyclopentadienyl analogue 4 may presumably be traced to the predilection of tris(pyrazolyl)borates toward octahedral geometry,²⁷ with higher coordination numbers being disfavored. For the $HB(pz)_3$ ligand, this is primarily an electronic argument (metal orbitals more orthogonally hybridized than for $M(\eta$ -C₅H₅)), while the inclusion of 3,5-pyrazolyl substituents introduces an additional steric component.

Preliminary reactivity studies on the complexes 1 and 2 have been carried out. First, complex 2a, while thermally stable, was found to undergo photochemical carbonyl ligand substitution by triphenylphosphine to provide the complex $[Fe(SeC=CR^1)(CO)(PPh_3)(\eta-C_5H_5)]$ (6, Scheme 5). The characterisational data for 6 do not call for comment, and superficially, this would appear to be a rather mundane reaction. However, the simplicity of the reaction outcome hides a significant point. Ketenyl complexes are prevalent within group 6, arising from thermally, photochemically, or nucleophile-induced coupling of carbyne and carbonyl ligands.⁶ Because this ligand coupling depletes the metal center of two valence electrons (Chart 3), the transient 16electron ketenyl intermediates are typically not observed, but are rather inferred from the nature of products obtained

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 a R¹ = C₆H₄Me-4.

when an extraneous ligand is provided. In contrast, mononuclear complexes of ketenyl ligands are rare for the later transition metals,³⁶ and none arise from carbyne–carbonyl coupling. It therefore remains to be seen if coordinatively unsaturated late transition metal ketenyls might serve as synthetic intermediates en route to carbyne complexes. However for the moment this remains conjecture.

The formation of **6** via photolysis of **2a** presumably proceeds via conventional carbonyl photoejection to afford a coordinatively unsaturated alkynylselenolate complex, and the failure of this complex to evolve to an observable selenoketenyl complex [Fe(η^2 -SeCCR¹)(CO)(η -C₅H₅)] ("7") is therefore noteworthy. Notably, [Mo(SePh)(CO)₃(η -C₅-H₅)] and [Fe(SePh)(CO)₂(η -C₅H₅)] both undergo photochemical CO dissociation to provide the selenolate-bridged binuclear species [Mo₂(μ -SePh)₂(CO)₄(η -C₅H₅)₂] and [Fe₂-(μ -SePh)₂(CO)₂(η -C₅H₅)₂], respectively.³⁷ While the possibility that "7" represents a perhaps reversible means of stabilizing the coordinative unsaturation, this would appear unlikely, given that *dihapto* ketenyls are on (rare) occasion opened by strong nucleophiles (e.g., PMe₃)¹⁰ to provide σ -Ccoordinated ketenyls.⁶

The nucleophilicity of the selenium atom in **2a** was investigated through reactions with iodomethane and methyl trifluoromethane sulfonate (MeOTf). In the case of iodomethane, loss of the alkynylselenolate was observed with formation of [FeI(CO)₂(η -C₅H₅)]. Presumably, this occurs via Se-alkylation to provide the iodide salt (8·I) of the labile selenoether complex [Fe{ σ -Se(Me)C=CR¹}(CO)₂(η -C₅H₅)]⁺ (8⁺), which evolves via selenoether dissociation to the neutral

Chart 3. Interconversion of Carbyne and Ketenyl Ligands



complex [FeI(CO)₂(η -C₅H₅)]. Support for this mechanism is provided by the reaction of 2a with MeOTf, which affords the marginally more stable salt 8. OTf, in which the triflate counteranion less readily replaces the alkynylselenoether. Nevertheless, the salt 8. OTf was also not isolated in pure form due to slow decomposition. It could however be spectroscopically characterized based on data obtained from a sample generated in situ. Thus treating a solution of 2a in CDCl₃ with excess MeOTf affords a complex with a resonance at $\delta_{\rm H} = 2.80$ ppm attributable to the selenoether methyl group (upfield of MeOTf, $\delta_{\rm H} = 4.18$) and a cyclopentadienyl resonance appearing at 5.47 ppm. The ${}^{13}C{}^{1}H$ NMR spectrum of 8. OTf included resonances at $\delta_{\rm C}$ = 103.6 and 64.4 (cf. 85.7, 75.0 for **2a**). While these data alone might not allow us to exclude formation of the alkyne salt $[Fe(\eta^2 - MeSeC \equiv CR^1)(CO)_2(\eta - C_5H_5)]OTf$, the absorption at 2169 cm^{-1} in the infrared spectrum is most consistent with the presence of a noncoordinated alkynyl group.

The alkynyl character of the alkynylselenolate ligand in **2a** was investigated with recourse to the classical addition of "Co₂(CO)₆" (from [Co₂(CO)₈]) across a C=C triple bond. Alkynylselenoethers have been previously shown to undergo this reaction, ³⁸ as does **2a**, to afford the dicobaltatetrahedrane [Fe(SeC{Co₂(CO)₆}CR¹)(CO)₂(η -C₅H₅)], **9** (Scheme 5). While the spectroscopic signatures (¹H, ¹³C NMR) for the cyclopentadienyl and 4-tolyl groups are only marginally shifted from those for **2a**, the resonances due to the alkynyl group are shifted markedly ($\delta_{\rm C} = 103.3$, 90.4 ppm) from those for **2a** ($\delta_{\rm C} = 85.7$, 85.4 ppm), indicating that this is the site of adduct formation, rather than coordination to the selenium center. Remaining data for **9** conform where applicable to the copious precedent for dicobaltatetrahedranes of the general form [Co₂(μ -RCCR)(CO)₆].³⁹

Concluding Remarks. The reactions of **2a** discussed above point to the alkynylselenolate ligand functioning as both a conventional selenolate and a conventional heteroatomsubstituted alkyne. In contrast, the failure to isolate an alkynylselenolate complex [Mo(σ -SeCCR¹)(CO)_n{HB(pz)₃}] (n =2, 3; cf. [Mo(SeC=CR¹)(CO)₃(η -C₅H₅)] (3)) in favor of the formation of the selenoketenyl complex [Mo(η^2 -SeCCR¹)-(CO)₂{HB(pz)₃}] (**4**) points toward a unique reactivity relying

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on both components of the "SeC=CR" unit. A further feature, yet to be explored, which may impinge on the reactivity profile of alkynylselenolates is the fragility of alkynylselenoether linkages in combination with transition metal centers. The facile rearrangement of alkynylselenoethers to selenatovinylidene ligands upon coordination to ruthenium(II) has been previously demonstrated.⁴⁰ Alkynylselenolatoalkylidyne complexes have been shown to react with zerovalent platinum via insertion of platinum into the alkynyl–selenoether linkage to afford isoselenocarbonyls.⁹ Furthermore, Tatsumi has demonstrated the insertion of zirconocene into the =C–Se bond of the alkynylselenolate complex [Ru(SeC=CPh)(PPh_3)₂(η -C₃H₅)].⁴ These observations, taken together, suggest that alkynylselenolate complexes represent an intriguing class of compound for further study.

Experimental Section

General Procedures. All manipulations, unless otherwise stated, were carried out under an atmosphere of dry prepurified dinitrogen using conventional Schlenk, vacuum line, and glovebox techniques. Solvents were purified, when necessary, by distillation from an appropriate drying agent (ethers and parafins from sodium/potassium alloy with benzophenone as indicator; halocarbons from CaH₂). Petroleum ether refers to that fraction of petroleum of boiling range 40–60 °C. ¹H and ³¹P{¹H} NMR spectra were recorded at 25 °C on JEOL JMX-270 (¹H: 270.0 MHz, ³¹P{¹H}: 121.5 MHz), Varian Gemini 300, or Mercury 300 (¹H: 300.1 MHz, ³¹P{¹H}: 121.469 MHz) spectrom-¹³C{¹H} spectra were recorded on Varian INOVA 300 eters. $({}^{13}C{}^{1}H{}; 75.42 \text{ MHz})$ or Varian INOVA 500 $({}^{13}C{}^{1}H{}; 125.7 \text{ MHz})$ spectrometers. ${}^{1}H$ and ${}^{13}C{}^{1}H{}$ NMR chemical shifts are reported relative to $\delta(SiMe_4) = 0$, internally referenced against deuterated (¹³C) or residual protiated (¹H) solvent peaks. ³¹P{¹H} NMR chemical shifts are reported relative to an external standard (D₃PO₄). Elemental microanalytical data were obtained from the ANU Research School of Chemistry or University of North London microanalytical services. FAB mass spectrometry was performed by the Imperial College mass spectrometry service with samples prepared in nitrobenzyl matrices. Electrospray mass spectrometry (ESI) was performed by the Research School of Chemistry mass spectrometry service. Samples for ESI were prepared by dissolving a solid in a small amount of CH₂Cl₂ and diluting with either acetonitrile or methanol. Mass spectrometric assignments were substantiated by simulation of isotopic distributions. IR spectra were recorded in the solid state (Nujol mulls) and in solution (CH2Cl2). Only bands associated with the chromophores of interest are reported. The complexes [NiCl(PPh₃)(η -C₅H₅)],¹⁴ [FeCl(CO)₂(η -C₅H₅)],¹⁹ and [MoI(CO)₃{HB(pz)₃)₃]⁴¹ were prepared according to published procedures. The complex [MoI(CO)₃(η -C₅H₅)] has been described previously,²⁴ but was in this instance prepared by the procedure outlined below. Caution: heavy metal alkynyls have on occasion been found to spontaneously detonate.

Synthesis of $[MoI(CO)_3(\eta-C_5H_5)]$. The following procedure is a minor modification of that described by Filippou.⁴¹ The modifications are of a practical nature. Rather than employing NaC₅H₅, which typically forms as a nonstoichiometric thf solvate that is difficult to completely free of the solvent, the freeflowing crystalline stoichiometric solvate NaC₅H₅·dme was used. Unreacted $[Mo(CO)_6]$ was removed by precipitation of the desired product from hexane in which the small amount of $[Mo(CO)_6]$ remains dissolved: A mixture of $[Mo(CO)_6]$ (10.00 g, 37.9 mmol) and NaC₅H₅·dme (6.75 g, 38.0 mmol) in tetrahydrofuran (100 mL) was heated under reflux for 12 h to afford a solution of Na[Mo(CO)₃(η -C₅H₅)]. The mixture was cooled in an ice bath and treated with one equivalent of iodine (9.64 g, 38.0 mmol) in one portion, causing a color change to deep redpurple. The solution was warmed to room temperature and diluted with hexane (50 mL). The precipitated NaI was removed by filtration, and the filtrate diluted with further hexane (50 mL) was concentrated on a rotary evaporator to precipitate the product as a red-purple crystalline solid. Yield: 11.51 g (82%, 30.9 mmol). The material, as formed, was spectroscopic data were comparable to those previously published.^{24,41}

Synthesis of $[Ni(SeC \equiv CC_6H_4Me-4)(PPh_3)(\eta-C_5H_5)]$ (1). A solution of 4-ethynyltoluene (0.271 g, 2.33 mmol) in tetrahydrofuran (20 mL) was cooled to 0 °C, treated dropwise with a solution of "BuLi in hexane (1.46 mL, 1.60 M, 2.33 mmol), and allowed to warm to room temperature and then recooled to 0 °C. Gray selenium (0.192 g, 2.41 g-atom) was added, and the mixture stirred until all the selenium had dissolved. The resulting yellow solution was cooled to -20 °C and transferred by filter cannula to a second vessel containing a solution of $[NiCl(PPh_3)(\eta C_5H_5$] (1.00 g, 2.40 mmol) in tetrahydrofuran (25 mL), which was also precooled to -20 °C. The mixture was allowed to warm slowly to room temperature, during which time it changed in color from purple to deep red-brown. After approximately 30 min stirring at room temperature, the solution was reduced in volume to ca. 15 mL under reduced pressure, resulting in the precipitation of the crude product. The supernatant was removed via filter cannulation to afford a red-brown powder that was washed with diethyl ether and then recrystallized from a mixture of dichloromethane and hexane to give 1 in an analytically pure form. Yield: 0.57 g (41%, 0.98 mmol). Crystals of the solvate 1 · (CHCl₃)₂ suitable for X-ray 0.98 limbol). Crystais of the solvate Γ⁴(CHCl₃)₂ subtable for X-fay diffraction analysis were grown by slow cooling of a concentrated chloroform solution of **1**. IR CH₂Cl₂: 2131 cm⁻¹ ν_{C≡C}. Nujol: 2127 cm⁻¹ ν_{C≡C}. NMR (CDCl₃, 25 °C): ¹H: δ_H 2.30 (s, 3 H, Cd₃), 5.25 (s, 5 H, C₅H₅), 7.03, 7.25 [(**AB**)₂, 4 H, C₆H₄, ³J_{**AB**} = 6.7 Hz), 7.30–7.9 (m, 15 H, C₆H₅). ¹³C{¹H}: δ_C 136.1 [C¹(C₆H₄)], 133.9 [d, C^{2.6}(C₆H₅), ²J_{PC} = 11.2], 132.5 [d, C¹(C₆H₅), ¹J_{PC} = 24.0], 131.5 [C^{3.5}(C₆H₄)], 130.5 [C⁴(C₆H₅)], 128.8 [C^{2.6}(C₆H₄)], 128.4 [d, C^{3.5}. $(C_6H_5)]$, ${}^{3}J_{PC} = 10.0 \text{ Hz}]$, 123.2 $[C^4(C_6H_4)]$, 95.1 (C_5H_5) , 92.6 $(CC \equiv)$, 84.9 $(SeC \equiv)$, 21.5 (CH_3) . ${}^{31}P\{{}^{1}H\}$: $\delta_P 40.1 \text{ ppm. FAB-MS}$ (+ve ion, nba matrix): m/z 580 [M]⁺, 515 [M - C₅H₅]⁺, 465 [M - CCR¹]⁺, 400 [M - C₅H₅ - CCR¹]⁺, 385 [M - SeCCR¹]⁺. Anal. Found: C, 66.11; H, 4.70. Calcd for C₃₂H₂₇PNiSe: C; 66.25, H; 4.69. Crystal data for 1: $C_{32}H_{27}NiPSe \cdot (CHCl_3)_2$, $M_w = 818.91$, monoclinic, $P2_1/c$ (no. 14), a = 14.164(6) Å, b = 17.521(6) Å, c = 15.348(10) Å, $\beta = 105.60(4)^\circ$, V = 3669(3) Å³, Z = 4, $D_c = 1.483$ Mg m⁻³, μ (Mo K α) = 2.024 mm⁻¹, T = 203 K, orange-red plates, Siemens P4 diffractometer; 4442 independent measured reflections $(R_{\text{int}}=0.0592), F^2$ refinement, $R_1(\text{obs})=0.0660, wR_2(\text{all})=0.1594,$ 2684 independent observed absorption-corrected reflections $[|F_{o}| > 4\sigma(|F_{o}|), 2\theta_{max} = 45^{\circ}], 509 \text{ parameters. CCDC 784169.}$ Synthesis of $[\text{Fe}(\text{SeC}=\text{CC}_{6}\text{H}_{4}\text{Me-4})(\text{CO})_{2}(\eta-\text{C}_{5}\text{H}_{5})]$ (2a). A

Synthesis of [Fe(SeC=CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (2a). A solution of 4-ethynyltoluene (2.00 g, 17.2 mmol) in tetrahydrofuran (20 mL) was cooled to 0 °C and treated dropwise with a solution of "BuLi in hexane (10.8 mL, 1.60 M, 17.3 mmol). The mixture was then allowed to warm to room temperature and stirred for 30 min before being recooled to 0 °C. Gray selenium (1.36 g, 17.2 g-atom) was added in one portion, and the mixture then stirred for 30 min, by which time all the selenium had dissolved and reacted. The solution was cooled to -20 °C and transferred dropwise by filter cannula to a precooled (-20 °C) solution of [FeCl(CO)₂(η -C₅H₅)] (3.67 g, 17.2 mmol) in diethyl ether (50 mL). The mixture was allowed to warm to room temperature with stirring, during which time, the color changed from red to deep green. After approximately 30 min stirring at room temperature, the solvent was removed *in vacuo*, and the

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residue was then extracted with dichloromethane (50 and 20 mL portions). The combined, filtered extracts were concentrated to ca. 20 mL and then diluted with light petroleum followed by further concentration to afford the crude product (green platelets), which was found to be slightly impure (IR, TLC). This crude material was then recrystallized from a mixture of diethyl ether and hexane to provide deep green platelets. Yield: 3.32 g (52%, 8.95 mmol). Crystals of 2a suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a concentrated solution of 1 in diethyl ether. IR Nujol: 2133 $\nu_{C\equiv C}$, 2026, 1979 ν_{CO} cm⁻¹. NMR (CDCl₃, 25 °C): ¹H: δ_{H} 2.30 (s, 3 H, CH₃), 5.00 (s, 5 H, C₅H₅), 7.03, 7.25 ((**AB**)₂, 4 H, C₆H₄, $J_{AB} = 7.8$ Hz). ¹³C{¹H}: δ_{C} 212.9 (CO), 137.0 [C⁴(C₆H₄)], 131.7 [C^{2,6}(C₆H₄)], 129.0 [C^{3,5}(C₆H₄)], 122.3 [C¹(C₆H₄)], 85.7 (CC \equiv) 85.4 (C₅H₅), 75.0 (SeC=), 21.5 (CH₃). FAB-MS (+ve ion, nba matrix): *m*/*z* 372 [M]⁺, 316 [M – 2CO]⁺. Anal. Found: C, 51.71; H, 3.33. Calcd for C₁₆H₁₂O₂FeSe: C, 51.79; H, 3.26. Crystal data for **2a**: $C_{16}H_{12}FeO_2Se$, $M_w = 371.07$, triclinic, $P\overline{1}$ (no. 2), a = 6.7194(5) Å, b = 8.6243(11) Å, c = 13.679(3) Å, α $105.948(10)^\circ, \beta = 97.141(11)^\circ, \gamma = 96.818(9)^\circ, V = 746.5(2) \text{ Å}^3,$ $Z = 2, D_c = 1.651 \text{ Mg m}^{-3}, \mu(\text{Cu K}\alpha) = 10.865 \text{ mm}^{-1}, T = 293$ K, orange prisms, Siemens P4 diffractometer; 2194 independent measured reflections ($R_{int} = 0.0968$), F^2 refinement, $R_1(obs) =$ 0.0625, $wR_2(all) = 0.1850$, 1704 independent observed absorption-corrected reflections $[|F_o| > 4\sigma(|F_o|), 2\theta_{max} = 120^\circ], 183$ parameters. CCDC 784170.

Synthesis of $[Fe(SeC \equiv CSiMe_3)(CO)_2(\eta - C_5H_5)]$ (2b). A solution of ethynyltrimethylsilane (2.00 mL, d = 0.695 g mL⁻¹ 1.40 g, 14.1 mmol) in tetrahydrofuran (20 mL) was cooled to 0 °C and treated dropwise with a solution of "BuLi in hexane (8.84 mL, 1.60 M, 14.1 mmol). The pale yellow solution was allowed to warm to room temperature (1 h) and then recooled to 0 °C. Gray selenium (1.125 g, 14.2 g-atom) was added in one portion, which dissolved within 15 min to provide an orange solution, which was then cooled (-60 °C). The solution was transferred (filter cannula) to a cooled (-60 °C) suspension of $[FeCl(CO)_2(\eta-C_5H_5)]$ (3.02 g, 14.2 mmol) in diethyl ether (50 mL). The mixture was allowed to warm to room temperature and stirred for 1 h with the development of an olive green color. TLC (silica gel, CH₂Cl₂/hexane, 1:1) indicated the presence of only one visible mobile component. The solvent was removed under reduced pressure, the resulting residue was extracted with dichloromethane (2×50 mL), and the combined extracts were filtered through diatomaceous earth. Addition of petroleum ether (40-60) to the filtrate and slow concentration provided a khaki microcrystalline powder that was spectroscopically pure (¹H NMR, IR) and suitable for subsequent investigations. A sample for elemental microanalysis was prepared by recrystallization of the mixture from a mixture of dichloromethane and *n*-hexane at -18 °C. Yield: 4.35 g (87%, 12.3 mmol). IR CH₂Cl₂: 2061 $\nu_{C=C}$, 2034, 1990 ν_{CO} cm⁻¹. Nujol: 2062 $\nu_{C=C}$, 2035, 1993 ν_{CO} cm⁻¹. NMR ¹H (C₆D₆): δ 3.94 (s, 5 H, C₅H₅), 0.25 (s, 9 H, SiCH₃) ppm. ¹³C{¹H} (CDCl₃): 212.5 (CO), 92.89, 92.78 (C=C), 85.34 (C₅H₅), 0.38 (SiCH₃) ppm. MS (ESI high-res, +ve ion, MeCN): m/z 353.9286. Anal. Calcd 353.9282. Found: C, 40.67; H, 4.20. Anal. Calcd for C₁₂H₁₄FeO₂SeSi: C, 40.82; H, 4.00.

Synthesis of [Mo(SeC=CC₆H₄Me-4)(CO)₃(η -C₅H₅)] (3). A solution of LiSeC=CC₆H₄Me-4 (from 0.94 g of 4-ethynyl-toluene, 1 equiv of 1.6 M BuLi, and 0.64 g of gray selenium as described above) was added via a filter cannula to a solution of [MoI(CO)₃(η -C₅H₅)] (3.00 g, 8.10 mmol, prepared as described above) in THF (25 mL), maintained at -40 °C. The mixture was then allowed to warm slowly to room temperature with stirring, during which time it changed slightly in color from red to purplered. After approximately 30 min stirring, the solvent was removed *in vacuo*, and the resulting red oil was redissolved in diethyl ether/light petroleum (4:1). The solution was applied to the top of a cryostatically cooled (-30 °C) chromatography column (silica gel/15 cm). Initial elution with the same solvent combination removed traces of unreacted starting material.

Subsequent elution with neat diethyl ether mobilized a broad, red fraction. This was diluted with light petroleum, and the solvent volume was reduced on a rotary evaporator until the product precipitated as deep red crystals. These were collected on a glass frit, washed with small portions of petroleum ether, and dried *in vacuo*. Yield: 1.51 g (42%, 3.44 mmol). IR Nujol: 2134 $v_{C=C}$, 2033, 1962, 1943 v_{CO} cm⁻¹. CHCl₃: 2137 $v_{C=C}$, 2050 (sh), 2036, 1976, 1960, 1934 (br) v_{CO} cm⁻¹. Hexane: 2142 $v_{C=C}$, 2036, 1973, 1960, 1944 (br) v_{CO} cm⁻¹. MMR (CDCl₃, 25 °C): ¹H: $\delta_{\rm H}$ 2.32 (s, 3 H, CH₃), 5.60 (s, 5 H, C₅H₅), 7.29, 7.55 [(AB)₂, 4 H, C₆H₄, ³J_{AB}=7.9 Hz]. ¹³C{¹H}: δ_{C} 235.3 (CO), 222.9 (CO), 137.0 [C⁴(C₆H₄)], 131.8 [C²⁻⁶(C₆H₄)], 129.1 [C^{3.5}(C₆H₄)], 121.8 [C¹-(C₆H₄)], 95.2 (C₅H₅), 92.1 (SeC=), 86.9 (CC=), 75.2 (SeC=), 21.6 (CH₃). Anal. Found: C, 46.31; H, 2.83. Calcd for C₁₇H₁₂MoO₃Se: C, 46.49; H, 2.75. FAB-MS (+ve ion): m/z 438 [M – 2H]⁺, 412 [M – CO]⁺, 383 [M – 2CO – H]⁺, 356 [M – 3CO]⁺.

Synthesis of $[Mo(\eta^2-C,C'-SeCCC_6H_4Me-4)(CO_2\{HB(pz)_3)]$ (4). The reaction of $LiSeC \equiv CR^1$ with $[MoI(CO)_3 \{HB(pz)_3\}]$. A solution of LiSeC= CC_6H_4Me-4 was prepared as described above by successive addition of "BuLi (2.40 mL, 1.6 M solution in hexane, 3.84 mmol) and gray selenium (0.30 g, 3.80 g.atom) to a solution of 4-ethynyltoluene (0.44 g, 3.91 mmol) in diethyl ether (15 mL) at 0 °C. This solution was added dropwise over 15 min to a solution of [MoI(CO)₃{HB(pz)₃}] (2.00 g, 3.81 mmol) in THF maintained at -40 °C. The solution was allowed to warm slowly to 0 °C, at which point all volatiles were removed in vacuo. The resulting oil was redissolved in diethyl ether and applied to a cryostatically cooled (-30 °C) silica gel chromatography column (15 cm). Elution with diethyl ether gave several minor unidentified vellow and brown fractions, followed by a deep red fraction, which was collected, concentrated in vacuo, and further diluted with light petroleum to give a red solid. Recrystallization from a mixture of dichloromethane and hexane gave a deep red, microcrystalline solid. Yield: 0.22 g (10%, 0.39 mmol). IR Nujol: 2479 (w) v_{BH}, 1952, 1861 v_{CO}, 1049 (m) $\nu_{C=Se}$ (tentative). NMR (CDCl₃, 25 °C): ¹H: δ_{H} 2.24 (s, 3 H, CH_3), 4.6 (s br, 1 H, BH), 6.0–8.6 (m, 13 H, C_6H_4 and pz). ¹³C{¹H}: δ_{C} 234.0 (br, Mo=CCSe, Mo=CCSe), 215.1 (CO), 150–125 [C^{3,5}(pz) and C₆H₄], 106.2 [C⁴(pz)], 21.4 (CH₃). Anal. Found: C, 43.07; H, 3.11; N, 15.05. Calcd for C₂₀H₁₇BMo-N₆O₂Se: C, 42.97; H, 3.06; N, 15.03. FAB-MS (+ve ion): m/z $504 [M - 2CO]^+, 467 [M - C_7H_7]^+, 388 [M - C_7H_7 - Se]^+$

Synthesis of $[Fe(SeC \equiv CC_6H_4Me-4)(CO)(PPh_3)(\eta-C_5H_5)]$ (6). A solution of [Fe(SeC=CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (**2a**: 0.25 g, 0.67 mmol) and triphenylphosphine (0.18 g, 0.69 mmol) in diethyl ether (25 mL) was irradiated with a domestic tungsten lamp, resulting in vigorous evolution of CO and a color change to red-brown within 30 s. Irradiation was continued until the complete consumption of 2a was indicated (IR, TLC). The solution was diluted with hexane and reduced in volume on a rotary evaporator to give the title compound as a red-brown solid, which was recrystallized from a mixture of dichloromethane and hexane (-18 °C). Yield: 0.30 g (72%, 0.50 mmol). IR CH₂Cl₂: 2129 $\nu_{C\equiv C}$, 1945 ν_{CO} cm⁻¹. Nujol: 2122 $\nu_{C\equiv C}$, 1945, 1933 ν_{CO} cm⁻¹. NMR (CDCl₃, 25 °C): ¹H: δ_{H} 2.30 (s, 3 H, CH₃), 4.55 (s, 5 H, C₅H₅), 7.01, 7.28 [(**AB**)₂, 4 H, C₆H₄, ${}^{3}J_{AB}$ = 7.0 Hz], 7.21–7.74 (m, 15 H, C₆H₅). ${}^{13}C{}^{1}H$: δ_{C} 219.8 (d, $\begin{array}{l} \text{CO}_{12}, \text{7.21} & \text{7.74} \text{ (III, 15 H}, \text{C}_{6}\text{H}_{5}\text{).} & \text{C}_{11}, \text{C}_{0}\text{C}_{11}\text{, 10}, \text{C}_{12}\text{, 10}, \text{C}_{11}\text{, 10}, \text{C}_{11}\text{, 10}, \text{C}_{11}\text{, 10}, \text{C}_{11}\text{, 10}, \text{C}_{11}\text{, 10}, \text{C}_{12}\text{, 10}, \text{C}_{11}\text{, 10}, \text{C}_{12}\text{, 11}, \text{C}_{$ ion, nba matrix) m/z 606 [M]⁺, 578 [M – CO]⁺, 513 [M – C₅H₅ $-CO]^+$, 463 $[M - CO - CCR^1]^+$, 411 $[M - SeCCR^1]^+$, 399 $[FePPh_3]^+$, 383 $[M - SeCCR^1 - CO]^+$, 316 $[M - PPh_3 - CO]^+$. Anal. Found: C, 65.52; H, 4.61. Calcd for C₃₃H₂₇OPFeSe: C, 65.48; H, 4.50.

Synthesis of [Fe(SeC{Co₂(CO)₆}CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (8). To a solution of [Fe(SeC \equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (2a: 0.30 g, 0.81 mmol) in diethyl ether (20 mL) was added $[Co_2(CO)_8]$ (0.28 g, 0.81 mmol) in one portion. Evolution of gas was observed, which ceased after 1–2 min. The volatiles were removed *in vacuo*, and the residue was redissolved in light petroleum and transferred via cannula filtration to a second Schlenk vessel. The solvent volume was reduced, and cooling (dry ice/ propanone) gave the title compound as a deep green microcrystalline solid. Yield: 0.52 g (98%, 0.79 mmol). IR Nujol: 2080, 2048, 2028, 2003, 1978 ν_{CO} cm⁻¹. NMR (CDCl₃, 25 °C) ¹H: δ_{H} 2.35 (s, 3 H, CH₃), 5.03 (s, 5 H, C₅H₅), 7.19, 7.74 [s br × 2, 2 H × 2, C₆H₄, ³*J*_{HH} not resolved). ¹³C{¹H}: δ_{C} 213.2 (FeCO), 199.8 (br, CoCO), 137.7 [C⁴(C₆H₄)], 136.2 [C¹(C₆H₄)], 128.9 [C^{2.6}(C₆H₄)], 128.7 [C^{3.5}(C₆H₄)], 103.3 (CC=C), 90.4 (SeC=C), 85.0 (C₅H₅), 21.5 (CH₃) ppm. FAB-MS (+ve ion, nba matrix): *m/z* 658 [M]⁺,

followed by peaks for successive loss of 8 \times CO. Anal. Found: C, 40.33; H, 1.88. Calcd for C₂₂H₁₂O₈Co₂FeSe: C, 40.22; H, 1.84.

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Supporting Information Available: Full details of the crystal structure determination of $1 \cdot (CHCl_3)_2$ (CCDC 784169) and 2a (CCDC 784170) in CIF format; ORTEP representations of the molecular structures of 1 and 2a; Tables S1 collating geometric parameters for alkynylselenolate complexes. This material is available free of charge via the Internet at http://pubs.acs.org.