# Selenolatovinylidene Complexes: Metal-Mediated Alkynyl Selenoether Rearrangements

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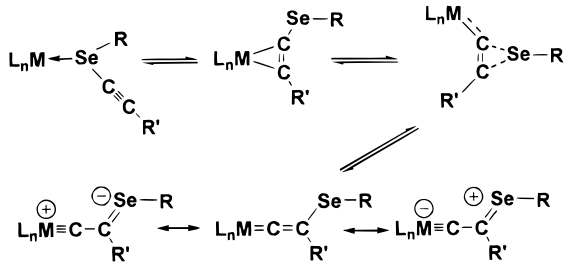
*Summary*: *The reactions of* $[RuCl_2(PPh_3)_3]$ *and* $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ *with* $PhC{\equiv}CSe^iPr$ *provide the selenolatovinylidene complexes* $[RuCl_2\{{=}C{=}C(Se^iPr)Ph\}(PPh_3)_2]$ *and* $[Ru\{{=}C{=}C(Se^iPr)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$. *The former, being coordinatively unsaturated, readily reacts with nitrogen and phosphorus donor ligands with retention of the selenolatovinylidene moiety; however, π-acid ligands induce facile elimination of* $PhC{\equiv}CSe^iPr$.



By far the majority of vinylidene ligands originate either from metal-mediated rearrangement of terminal alkynes or electrophilic attack at the β-carbon of σ-alkynyl ligands;[1] this is particularly true for the elements of group 8.[2] A similar intraligand mobility is displayed by the silyl group of alkynylsilanes,[1,3] and Werner has shown that this mobility increases on descending group 14 such that alkynylstannanes serve as effective precursors for group 9 stannyl-functionalized vinylidene complexes.[4] This migratory aptitude may be traced at least in part to the decrease in C-element bond strength on descending a p-block group. Silylvinylidene complexes notwithstanding, heteroatom-functionalized vinylidene complexes remain rare, being currently limited to (i) halovinylidene complexes arising from β-halogenation of the complex $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$[5] or rearrangement of iodoalkynes,[6] (ii) azovinylidenes via the reaction of $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$ with diazonium salts,[7] and (iii) the thiolatovinylidene complex $[Ru\{{=}C{=}C(SMe)_2\}(PMe_3)_2(\eta\text{-}C_5H_5)]^+$, which is obtained upon heating the alkynyl thioether complex $[Ru\{S(C{\equiv}CSMe)Me\}(PMe_3)_2(\eta\text{-}C_5H_5)]^+$. This complex, reported by Angelici,[8] is particularly noteworthy in that it serves as a precursor for a host of complexes of unusual organosulfur ligands. Herein we wish to report the confluence of the principles of Angelici (intraligand thiolate mobility) and Werner (increasing migratory aptitude down a group). This has allowed the synthesis and structural characterization of the first examples of selenolato-functionalized vinylidene complexes, including 16- and 18-valence-electron examples. Our interest in the possibility of such an alkynyl selenoether/selenolatovinylidene rearrangement process (Scheme 1) arises from our recent reports of alkynyl selenoether and chloroalkyne complexes of divalent ($d^4$) molybdenum and tungsten,[9] wherein the alkyne is required to serve as a 4-electron ligand such that rearrangement to a vinylidene would be accompanied by an unfavorable reduction in the overall valence electron count by 2 units.

**Scheme 1. Alkynyl Selenoether/Vinylidene Interconversion**



Heating a tetrahydrofuran solution of $[RuCl_2(PPh_3)_3]$ and $PhC{\equiv}CSe^iPr$ under reflux (2 h) provides (after chromatography) moderate yields (55%) of the vinylidene complex $[RuCl_2\{{=}C{=}C(Se^iPr)Ph\}(PPh_3)_2]$ (**1**) (Scheme 2). Although the formulation of **1** follows unambiguously from spectroscopic data,[10] it was further confirmed by a single-crystal structure determination.[11] The molecular geometry (Figure 1) may be described as severely distorted trigonal bipyramidal (*trans* bis-axial phosphines P(1)−Ru−P(2) = 173.07(5)°, diequatorial chlorides Cl(1)−Ru−Cl(2) = 148.89(6)°). This conformation is stabilized by the combination of a weak π-stacking between one of the phosphine phenyl groups and that of the vinylidene (centroid−centroid = 3.94 Å) and a C−H···π interaction between the *ortho* hydrogen of the adjacent phenyl group on the same phosphine and the vinylic C=C bond (H···π = 2.84 Å, C−H···π 141°, H···C(1) = 2.74 Å). This is analogous to what is observed for the isonitrile and phosphine ligands in the recently reported complex $[RuCl(CNCMe_3)(PPh_3)\{HB(pz)_3\}]$ (pz = pyrazol-1-yl).[12] Commensurate with significant Ru−C retrodative multiple bonding, the vinylidene ligand occupies an equatorial site, with Ru−C(1) at

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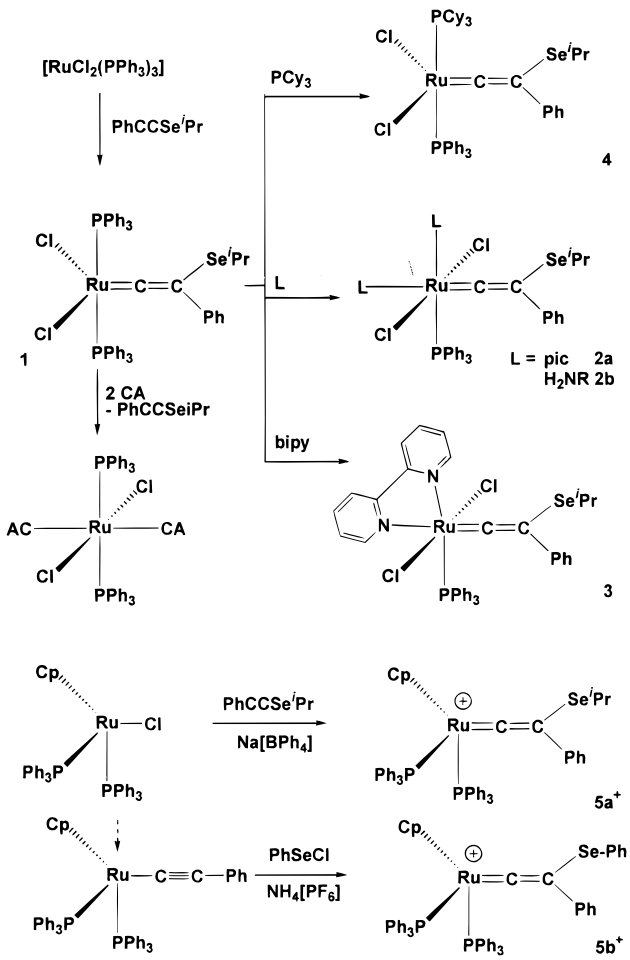
**Scheme 2. Synthesis of Selenolatovinylidene Complexes of Ruthenium(II)[a]**




[a] Legend: pic = $\gamma$-picoline, CA = CO, $CNC_6H_3Me_2$-2,6, bipy = 2,2′-bipyridyl, Cp = $\eta$-$C_5H_5$.

1.769(5) Å lying at the short end of reported ruthenium vinylidenes,[2] the majority of which are, however, cationic and/or coordinatively saturated. The vinylidene ligand is essentially linear with Ru−C(1)−C(2) = 175.2-(4)°, and the C(1)−C(2) bond length at 1.329(8) Å suggests multiple-bond character. The substitution at

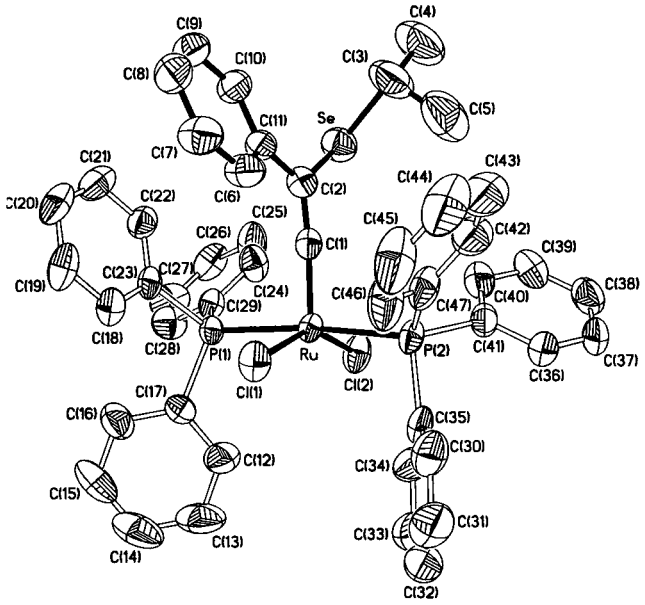



**Figure 1.** Molecular structure of **1**. Selected bond lengths (Å) and angles (deg): Ru−C(1) = 1.769(5), Ru−Cl(1) = 2.3228(13), Ru−Cl(2) = 2.3349(13), Ru−P(1) = 2.3854(11), Ru−P(2) = 2.3985(12); C(1)−Ru−Cl(1) = 104.7(2), C(1)−Ru−Cl(2) = 106.2(2), Cl(1)−Ru−Cl(2) = 148.89(6), C(1)−Ru−P(1) = 90.8(2), Cl(1)−Ru−P(1) = 86.42(4), Cl(2)−Ru−P(1) = 89.82(4), C(1)−Ru−P(2) = 94.9(2), Cl(1)−Ru−P(2) = 88.29(5), Cl(2)−Ru−P(2) = 92.40(5), P(1)−Ru−P(2) = 173.07(5).

C(2) is of primary interest, and the following points are noted: (i) the coordination is trigonal (angle sum 359.6°); (ii) the Se−C(2) bond length of 1.917(5) Å is significantly shorter than that to C(3) (2.017(11) Å), indicating an appreciable degree of multiple bonding in the former (Scheme 1). This perhaps accounts in part for the lack of conjugation of the phenyl substituent into the Ru=C=C cumulene system, which is rotated by ca. 21° out of the C(1)−C(2)−Se plane.

The coordinative unsaturation of the ruthenium center in **1** is reflected in reactions with potential ligands: Although simple 1:1 adducts might be expected to arise on treatment with the simple nitrogen donor ligands $\gamma$-picoline and *tert*.butylamine, these are not observed. Rather, one phosphine is also substituted to provide the coordinatively saturated octahedral complexes $[RuCl_2\{=C=C(Se^iPr)Ph\}(L)_2(PPh_3)]$ (L = $NC_5H_4$-Me-4 (**2a**), $NH_2CMe_3$ (**2b**)). The picoline derivative[10] is moderately stable, while attempted isolation of the *tert*-butylamine complex results primarily in reversion to **1**. In a similar manner, no tractable product resulted from the treatment of **1** with TMEDA, although a reaction ensued. The identity and stereochemistry of these complexes follows unambiguously from spectroscopic

(10) Selected spectroscopic data for new complexes (satisfactory elemental microanalysis obtained unless otherwise indicated; NMR data: $\delta$, $CDCl_3$, 25 °C, $^{13}C$ phosphine and phenyl resonances omitted. IR data: $\nu_{Ru=C=C}$ in $cm^{-1}$, Nujol. FAB-MS data: *m/z*, nba matrix, positive ion. **1**: $^1H$ NMR 1.10 (d, $^3J$ = 7.4 Hz, 6 H, $CH_3$), 2.77 (sept, 1 H, C*H*$Me_2$), 6.7−8.0 (m, 35 H, $C_6H_5$); $^{13}C\{^1H\}$ NMR 320.4 (t, $^2J$ = 16.2, Ru=*C*), 111.2 (t, $^3J$ = 5.4, Ru=C=*C*), 34.9 (s, *C*$HMe_2$), 23.7 (s, $CH_3$); $^{31}P\{^1H\}$ NMR 30.3; IR 1600 m, 1587 s; FAB-MS 920 $[M]^+$. **2a**: $^1H$ NMR 1.03 (d, 6 H, $^3J$ = 12.9 Hz, $CHCH_3$), 2.26 (s, 6 H, $CH_3$), 2.77 (sept, 1 H, C*H*$Me_2$), 6.7−8.6 (m, 23 H, $C_6H_5$, $C_5H_4N$); $^{13}C\{^1H\}$ NMR 328.6 (d, $^2J$ = 21.6 Hz, Ru=*C*), 111.5 (s, Ru=C=*C*), 35.1 (s, *C*$HMe_2$), 23.6 (s, *C*$HCH_3$), 20.8 (s, $NC_5H_4CH_3$); $^{31}P\{^1H\}$ NMR 41.7; IR 1618 m; FAB-MS 658 $[M - 2pic]^+$. **3**: $^1H$ NMR 1.31 (d, 6 H, $^3J$ = 6.9 Hz, $CH_3$), 3.19 (sept, 1 H, C*H*$Me_2$), 7.0−9.74 ($C_6H_5$ + bipy);$^{13}C\{^1H\}$ NMR: 333.0 (d, $^2J$ = 24.8 Hz, Ru=*C*), 113.8 (s, Ru=C=*C*), 35.7 (s, *C*$HMe_2$), 24.3 (s, $CH_3$); $^{31}P\{^1H\}$ NMR 39.0; IR 1620 m; FAB-MS 814 $[M]^+$. **4**: $^1H$ NMR 1.04 (d, 6 H, $^3J$ = 7.4 Hz, $CH_3$), 1.0−2.7 (m, $C_y$), 2.89 (sept, 1 H, *CH*$CH_3$), 6.7−7.8 (m, 5 H, $C_6H_5$); $^{13}C\{^1H\}$ NMR 320.4 (dd, $^2J$ = 15.3 Hz, Ru=*C*), 110.3 (dd, $^3J$ = 5.5 Hz, Ru=C=*C*), 34.4 (s, *C*$HMe_2$), 23.7 (s, $CH_3$); $^{31}P\{^1H\}$ NMR 29.6, 28.2 ($^2J$ = 357.9 Hz); IR 1580, 1562 m; FAB-MS 938 $[M]^+$. **5a**-$BPh_4$: $^1H$ NMR 1.31 (d, 6 H, $^3J$ = 7.6 Hz, $CH_3$), 2.96 (sept, 1 H, C*H*$Me_2$), 4.98 (s, 5 H, $C_5H_5$), 6.8−8.7 (m, 55 H, $C_6H_5$); $^{13}C\{^1H\}$ NMR 324.1 (t, $^3J$ = 15.1 Hz, Ru=*C*), 117.8 (s, Ru=C=*C*), 94.2 (s, $C_5H_5$), 35.8 (s, *C*$HMe_2$), 24.0 (s, $CH_3$); $^{31}P\{^1H\}$ NMR 41.4; IR 1621 m; FAB-MS 915 $[M]^+$. **5b**-$PF_6$: $^1H$ NMR 5.03 (s, 5H, $C_5H_5$), 6.7−8.0 (m, 40 H, $C_6H_5$); $^{13}C\{^1H\}$ NMR 324.2 (t, $^2J$ = 30.0 Hz, Ru=*C*) 117.7 (s, Ru=C=*C*), 94.4 ($C_5H_5$); $^{31}P\{^1H\}$ NMR 41.2; IR 1625 m; FAB-MS 949 $[M]^+$.

(11) Crystal data for **1**: $C_{47}H_{42}P_2Cl_2SeRu$, $M_r$ = 919.7, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 10.113(1) Å, $b$ = 12.296(1) Å, $c$ = 18.827(2) Å, $\alpha$ = 100.02(1)°, $\beta$ = 90.98(1)°, $\gamma$ = 114.05(1)°, $V$ = 2095.1(3) Å$^3$, $Z$ = 2, $D_c$ = 1.458 g $cm^{-3}$, $\mu$(Cu K$\alpha$) = 61.6 $cm^{-1}$, $F$(000) = 932, $T$ = 293 K; deep red prisms, 0.43 × 0.43 × 0.20 mm, Siemens P4/PC diffractometer, $\omega$-scans, 6112 independent reflections. The structure was solved by direct methods, and the major-occupancy non-hydrogen atoms were refined anisotropically using full-matrix least squares based on $F^2$ to give R1 = 0.046, wR2 = 0.108 for 5070 independent, observed, absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta$ = 120°) and 407 parameters.

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data; however, their lability in solution precluded us from obtaining structural or microanalytic data. The more robust adduct $[RuCl_2\{=C=C(Se^iPr)Ph\}(bipy)(PPh_3)]$ (**3**) was, however, obtained with 2,2′-bipyridyl and characterized by spectroscopy[10] and by a single-crystal X-ray structure determination.[13] The reaction of **1** with the bulky and basic phosphine $PCy_3$ is not clean, in contrast to those of Grubbs' alkylidene complexes $[RuCl_2(CHR)(PPh_3)_2]$ (R = Ph, $CH=CPh_2$), where disubstitution occurs readily.[14] Following chromatography, moderate yields of the mixed bis(phosphine) complex $[RuCl_2\{=C=C(Se^iPr)Ph\}(PCy_3)(PPh_3)]$ (**3**) may be obtained.[10]

The reactions of **1** with the carbon $\pi$-acids CO and $CNC_6H_3Me_2$-2,6 take a different and surprising course: if we recall that the alkynyl selenoether/vinylidene rearrangement leading to **1** required refluxing tetrahydrofuran, it is remarkable that treating a solution of **1** with CO (1 atm) at room temperature results in immediate (2 min) and spectroscopically quantitative formation of *all-trans*-$[RuCl_2(CO)_2(PPh_3)_2]$ (**4a**). A similar reaction occurs with $CNC_6H_3Me_2$-2,6 to provide *all-trans*-$[RuCl_2(CNC_6H_3Me_2\text{-}2,6)_2(PPh_3)_2]$ (**4b**); however, this proceeds more slowly and a red intermediate (presumably the adduct $[RuCl_2\{=C=C(Se^iPr)Ph\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$) may be transiently observed ($\nu$(CN) = 2176 $cm^{-1}$). Thus, it would appear that the coordination of a modest (CNR) or strong (CO) $\pi$-acid *trans* to the strongly $\pi$-acidic vinylidene ligand significantly destabilizes coordination of the latter. This may be alleviated by retroformation of the alkyne, which is then replaced by a second equivalent of the added ligand. In retrospect, this tallies with our previous observations that the reaction of *cct*-$[RuCl(C{\equiv}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2]$[15] with HCl does not provide a vinylidene complex but rather *cct*-$[RuCl_2(CO)_2(PPh_3)_2]$. Thus, loading a metal center with $\pi$-acidic ligands appears to destabilize vinylidene coordination with respect to rearrangement to a (labile) alkyne. Perusal of the vinylidene chemistry of group 8 metals[1,2] reveals that the overwhelming majority *do not* involve $\pi$-acidic co-ligands, none feature a *trans* disposition of vinylidene and $\pi$-acid, and those that do possess $\pi$-acid coligands are highly electrophilic (at $C^\alpha$).

The generality of the selenolatovinylidene/alkynyl selenoether rearrangement was briefly examined: the reaction of $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ (pz = pyrazol-1-yl)[12,16] with $PhC{\equiv}CSe^iPr$ is complex, with the major isolable product being $[RuCl(CO)(PPh_3)\{HB(pz)_3\}]$, which presumably arises from the precedented[1] hydrolysis of a vinylidene intermediate. Similarly, no clean product was obtained from the reaction of **1** with $K[HB(pz)_3]$. The complex $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$, however, reacts with $PhC{\equiv}CSe^iPr$ and $Na[BPh_4]$ to provide the isolable salt $[Ru\{=C=C(Se^iPr)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]BPh_4$ (**5a**-$BPh_4$) (Scheme 2).[10] The related salt $[Ru\{=C=C(SePh)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (**5b**-$PF_6$)[10] could be obtained via a complementary strategy involving electrophilic attack at the $\beta$-carbon of $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$ by PhSeCl followed by counteranion metathesis in ethanol with $[NH_4]PF_6$.

To conclude, the conversion of alkynyl selenoethers to selenolatovinylidenes within a transition-metal coordination sphere is facile, but so is the reverse reaction, in particular when *trans* $\pi$-acidic coligands are present. The results of Angelici,[8] which convincingly demonstrate the synthetic versatility of thiolatovinylidenes, presage a similarly rich chemistry for those based on more mobile selenolate substituents.

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**Supporting Information Available:** Tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for the complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Full details of this and related structures will be reported elsewhere: White, A. J. P.; Williams, D. J. Manuscript in preparation.

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