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Templated Synthesis and Intact Coordination of a Diorganotriselenane: $[RuCl_2(PPh_3)\{\kappa^3\text{-}Se,N,N'\text{-}Se(mt^{Se})_2\}]$ (mt^{Se} = selenomethimazolyl)

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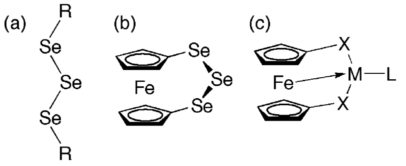
Summary: The reaction of $[RuCl_2(PPh_3)_3]$ *with methimazole (Hmt) under basic conditions provides the simple bis(chelate) complex* $[Ru(\kappa^2\text{-}S,N\text{-}mt)_2(PPh_3)_2]$*, while the selenium analogue* Hmt^{Se} *provides an intact coordinated diorganotriselenane* $[Ru\{\kappa^3\text{-}Se,N,N'\text{-}Se(mt^{Se})_2\}Cl_2(PPh_3)]$*. Bidentate* mt^{Se} *coordination is however observed in the complexes* $[RuR(\kappa^2\text{-}Se,N)(CO)(PPh_3)_2]$ *(R = H, CH=CHC$_6$H$_4$Me-4).*

Diorganotriselenanes, RSeSeSeR, are a well-established class of organoselenium compound,[1] the coordination chemistry of which is however essentially unexplored. The exception involves triselenometallocenophanes,[2] which in reactions with zerovalent complexes of platinum and palladium proceed via rupture of the CSe_3C spine by analogy with Seyferth's palladadithiaferrocenophane synthesis (Chart 1).[3] Given that even in the absence of transition metal reagents diorganotriselenanes can be prone to redistribution and selenium extrusion,[1] this factor alone may have discouraged the study of the organotransition metal chemistry of such species. We have however, inadvertently encountered a stable example of a complex of an intact diorganotriselenane, which we describe herein. Of particular note is the implication that the triselenane was actually constructed at the metal center.

We have for some time explored the unusual proclivity of Reglinski's poly(methimazolyl)borate ligand HB(mt)$_3$ (Hmt = methimazole, mt = methimazolyl)[4,5] to enter into B−H activation processes, which ultimately lead to the formation of "metallaboratranes", i.e., cage compounds involving transannular metal−boron dative bonding.[6] We have attributed this phenomenon to the geometric features of methimazolyl-derived chelates A(mt)$_n$, which bring the bridgehead group A into close proximity to the metal center upon coordination, e.g., as illustrated for the isoelectronic complexes $[Rh(cod)\{A(mt)_2\}]$ (cod = 1,5-cyclooctadiene, A = BH_2, CH_2^+), which feature three-center, two-electron B−H−Rh and C−H−Rh interactions.[7] Thus the complex $[RuH(CO)(PPh_3)\{HB(mt)_3\}]$ (**1**), a precursor to the archetypal ruthenaboratrane $[Ru(CO)(PPh_3)\{B(mt)_3\}](Ru{\rightarrow}B)^8$ (**2**) features κ^3-*H,S,S′* rather than the anticipated κ^3-*S,S′,S″* borate coordination.[6b,8,9] Given that **2** arose from the reaction of $[RuCl(R)(CO)(PPh_3)_2]$ (R = aryl, vinyl)[6a] with Na[HB(mt)$_3$] and that $[Pt(PPh_3)\{B(mt)_3\}](Pt{\rightarrow}B)$[10] is obtained similarly from $[PtCl_2(PPh_3)_2]$ under basic conditions,[6f] it was of interest to ascertain whether the reaction of $[RuCl_2(PPh_3)_3]$ would provide a metallaboratrane $[Ru(PPh_3)_2\{B(mt)_3\}](Ru{\rightarrow}B)^8$ or a simple scor-

Chart 1. (a) Diorganotriselenanes; (b) Triselenaferrocenophane; (c) Metalladichalcaferrocenophanes (X = S, Se; M = Pd, Pt; L = PPh$_3$)[2c,3]



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(8) To obviate confusion that might arise as to the assignment of oxidation number, d-configuration, and metal valency for metallaboratranes, it is recommended that line formulas for such compounds carry the suffix $(M{\rightarrow}B)^n$, where *n* denotes the total number of d-electrons, including the pair involved (to some variable extent) in donation to the boron.[9] In a similar manner, describing Seyferth's palladadithiaferrocenophane[3] as $(Fe{\rightarrow}Pd)^8$ circumvents such issues.

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10.1021/om0608511 CCC: $33.50

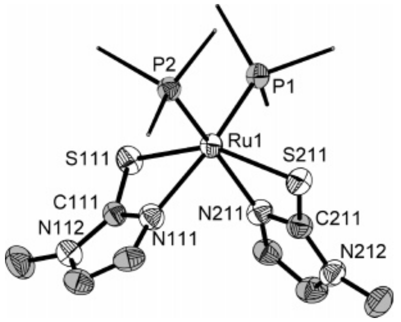

Figure 1. Molecular geometry of **3** in a crystal (50% displacement ellipsoids, phenyl groups and hydrogen atoms omitted). Selected bond distances (Å) and angles (deg): Ru1−N211 2.141(3), Ru1−N111 2.187(3), Ru1−P1 2.2833(8), Ru1−P2 2.3057(9), Ru1−S111 2.4615(9), Ru1−S211 2.4918(8), S111−C111 1.731(3), N111−C111 1.325(4), C111−N112 1.357(4), S211−C211 1.725(3), N211−C211 1.332(4), C211−N212 1.343(4), P1−Ru1−P2 101.69(3), N111−Ru1−S111 67.90(7), P1−Ru1−S111 94.18(3), P2−Ru1−S111 103.51(3), N211−Ru1−S211 67.57(8), N111−Ru1−S211 95.95(7), P1−Ru1−S211 98.56(3), P2−Ru1−S211 97.80(3), S111−Ru1−S211 152.36(3), C111−S111−Ru1 78.12(10), C111−N111−Ru1 97.56(19), N111−C111−N112 111.6(3), N111−C111−S111 116.4(2), N112−C111−S111 131.9(2), C211−S211−Ru1 77.21(11), C211−N211−Ru1 99.3(2), C212−N211−Ru1 153.2(2), N211−C211−N212 111.0(3), N211−C211−S211 115.4(2), N212−C211−S211 133.6(3).

pionate derivative [RuCl(PPh$_3$)$_2${HB(mt)$_3$}] analogous to the synthetically versatile complex [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (pz = pyrazolyl).[10] In practice, neither occurs, but, rather, fragmentation of the pro-ligand occurs to provide, inter alia, traces of the simple bis(chelate) complex [Ru(mt)$_2$(PPh$_3$)$_2$] (**3**).[11,12] Methimazolyl complexes of ruthenium have recently received attention,[13,14] and **3** provides a simpler analogue of the previously reported complex [Ru(mt)$_2${κ^2-*P,P′*-MeC(CH$_2$PPh$_2$)$_3$}].[13] Figure 1 depicts the inner coordination sphere geometry of **3**, which however calls for little comment, with metrical parameters for the chelates falling within expected norms for bidentate mt coordination.[12−15]

The isolation of **3** suggested the possible extension to the selenium analogue of methimazole (Hmt^{Se}).[16] While the coordination chemistry of saturated cyclic selenoureas is well-developed,[17] no complexes of the unsaturated heterocycle Hmt^{Se} or its conjugate base have been reported. We find that the reaction of [RuH(NCMe)$_2$(CO)(PPh$_3$)$_2$]BF$_4$ with Hmt^{Se} under basic conditions does indeed provide a selenomethimazolyl complex [RuH(κ^2-*N,Se*-mt^{Se})(CO)(PPh$_3$)$_2$] (**4**).[18] In parallel with the analogous mt complex[14,19] this complex hydrometalates ethynyl toluene under ambient conditions to provide the organometallic derivative [Ru(CH=CHC$_6$H$_4$Me-4)(κ^2-*N,Se*-mt^{Se})(CO)(PPh$_3$)$_2$] (**5**) (Scheme 1).[20] Surprisingly however, the reaction of Hmt^{Se} with [RuCl$_2$(PPh$_3$)$_3$] under basic conditions does not parallel the formation of **3**. Rather a dark brown compound was isolated in modest yield and characterized as the novel diorganotriselenane complex [RuCl$_2$(PPh$_3$){κ^3-*Se,N,N′*-Se(mt^{Se})$_2$}] (**6**).[21] The yield of **6** could be increased (ca. 63%) by carrying out the reaction in the presence of excess elemental selenium (4 equiv). The molecular geometry of the inner coordination sphere is depicted in Figure 2 and shows that the pseudo-octahedral complex has no element of symmetry, with two distinct mt^{Se} environments. The respective *trans* influences of the phosphine and Cl2 are reflected in the modest lengthening (8 esd) of the Ru−N bond *trans* to the former. The features of note relate to the triselenane linkage and its coordination to

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(11) **3**: This compound was only ever obtained in trace amounts sufficient for crystallographic characterization. *Crystal Data for* **3**: $C_{44}H_{40}N_4P_2RuS_2$, M_w = 851.93 gmol^{-1}, monoclinic, $P2_1/a$, a = 18.5682(6) Å, b = 10.8947(4) Å, c = 19.3594(8) Å, β = 97.332(1)°, V = 3883.9 Å^3, Z = 4, T = 200(2) K, orange prsim, D_c = 1.457 Mg m^{-3}, μ(Mo Kα) = 0.632 mm^{-1}, 7924 independent absorption-corrected reflections, R = 0.0423, R_w = 0.0993 [6022 reflections with $I > 2\sigma(I)$, $2\theta < 52.74°$], 480 parameters; CCDC 620515.

(12) We have on numerous occasions encountered the cleavage of mt groups from the salts Na[H$_2$B(mt)$_2$], Na[HB(mt)$_3$], e.g.: (a) Hill, A. F.; Smith, M. K. *Chem. Commun.* **2005**, 1920. (b) Hill, A. F.; Smith, M. K. *Dalton Trans.* **2006**, 28.

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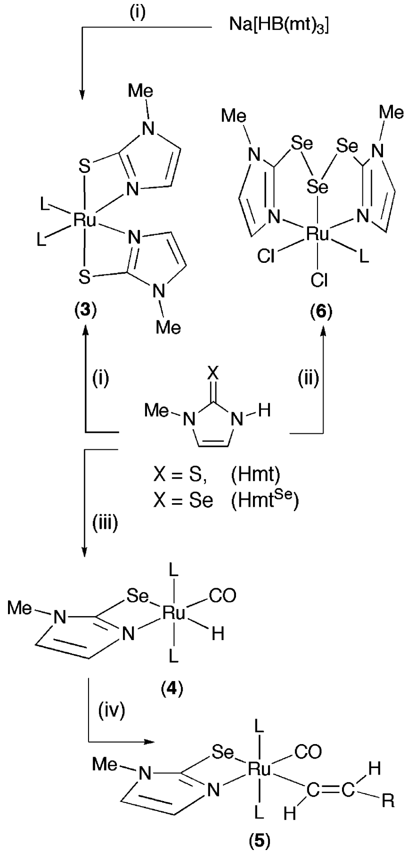
(18) **4**: [RuH(NCMe)$_2$(CO)(PPh$_3$)$_2$]BF$_4$ (250 mg, 0.31 mmol), Hmt^{Se} (50 mg, 0.31 mmol), and DBU (200 mg, 1.31 mmol) in CH$_2$Cl$_2$ (100 mL) were stirred anaerobically for 48 h, diluted with ethanol (100 mL), and slowly concentrated (ca. 50 mL) to provide pale orange crystals. Recrystallized (CH$_2$Cl$_2$/EtOH) yield 147 mg (59%). Anal. Found: C, 60.01; H, 4.73; N, 3.60. Calcd for $C_{41}H_{36}N_2OP_2RuSe$: C, 60.44; H, 4.45; N, 3.44. IR (Nujol): 1962w (ν_{RuH}), 1899vs (ν_{CO}) cm^{-1}. NMR (CDCl$_3$, 25 °C) ^{1}H: δ_H 7.70−7.22 (m, 30 H, C$_6$H$_5$), 5.74, 5.49 (d × 2, 1 H × 2, NCH=CH, $^3J_{HH}$ = 1.5), 2.70 (s, 3H, NCH$_3$), −12.87 (t, 1 H, $^2J_{PH}$ = 19.2 Hz, RuH). ^{31}P{^{1}H}: δ_P 49.79.

(19) The complex [RuH(mt)(CO)(PPh$_3$)$_2$] displays a rich chemistry derived from both the reactivity of the hydride ligand and the hemilability ($\kappa^2-\kappa^1$) of the mt ligand: Foreman, M. R. St.-J.; Hill, A. F.; Smith, M. K. Manuscript in preparation.

(20) **5**: Ethynyltoluene (100 mg, 0.86 mmol) and **4** (70 mg, 0.086 mmol) in toluene (5 mL) were stirred for 18 h and then diluted with methanol (30 mL) to precipitate the product. Recrystallized yield (acetone/Et$_2$O): 29 mg (47%). Anal. Found: C, 64.04; H, 4.61; N, 3.28. Calcd for $C_{50}H_{44}N_2OP_2RuSe$: C, 64.51; H, 4.76; N, 3.01. IR (Nujol): 1905vs (ν_{CO}) cm^{-1}. NMR (CDCl$_3$, 25 °C) ^{1}H: δ_H 7.83 (dt, 1 H, $^3J_{HH}$ = 17.1, $^3J_{PH}$ not resolved, RuCH), 7.64, 7.46, 7.23 (m × 3, 30 H, C$_6$H$_5$), 6.82, 6.36 (d × 2, 2 H × 2, $^3J_{HH}$ = 7.4, C$_6$H$_4$), 6.27, 5.80 (s br × 2, 1 H × 2, NCHCH), 5.85 (d, 1 H, $^3J_{HH}$ = 16.8, RuCH=C*H*), 2.51 (s, 3 H, NCH$_3$), 2.22 (s, 3 H, CCH$_3$). ^{31}P{^{1}H}: δ_P 43.02.

(21) **6**: [RuCl$_2$(PPh$_3$)$_3$] (261 mg, 0.27 mmol), Hmt^{Se} (87 mg, 0.55 mmol), Na$_2$CO$_3$ (51 mg, 0.48 mmol), and gray selenium (80 mg, 1.01 g-atom) were stirred anaerobically in CH$_2$Cl$_2$ (50 mL) for 48 h, filtered through diatomaceous earth, concentrated to ca. 20 mL, layered with light petroleum, and cooled to −20 °C overnight to provide black crystals. Yield: 142 mg (63%). Anal. Found: C, 34.85; H, 2.97; N, 5.72. Calcd for $C_{26}H_{25}N_4PCl_2RuSe_3 \cdot CH_2Cl_2$: C, 35.24; H, 3.18; N, 6.09. NMR (CDCl$_3$, 25 °C) ^{1}H: δ_H 8,15 (s br, 1 H, NCH=CH) 7.22 (d, 1 H, $^3J_{HH}$ = 2.1, NCH=CH), 6.91 (s br, 1 H, NCH=CH), 6.39 (d, 1 H, $^3J_{HH}$ = 1.5 Hz, NCH=CH), 7.86−7.18 (m, 15 H, C$_6$H$_5$), 3.64, 3.43 (s × 2, 3H × 2, NCH$_3$). ^{31}P{^{1}H}: δ_P 34.22. *Crystal data for* **6**: $C_{26}H_{25}N_4PCl_2Se_3Ru \cdot 2CH_2Cl_2$, M_w = 1003.17, monoclinic, $P2_1/n$, a = 11.579(2) Å, b =17.835(4) Å, c = 17.212(3) Å, β = 101.30(3)°, V = 3485.6(12) Å^3, Z = 4, T = 200(2) K, black prism, D_c = 1.912 Mg m^{-3}, μ(Mo Kα) = 4.116 mm^{-1}, 6141 independent absorption-corrected reflections, R_1 = 0.049, wR_2 = 0.138 [6141 reflections with $I > 2\sigma(I)$, $2\theta < 50.1°$], 390 parameters; CCDC 620516.

Scheme 1. Synthesis of Methimazolyl, Selenomethimazolyl, and Triselenane Complexes (L = PPh_3)[a]



[a] (i) $RuCl_2L_3$; (ii) $RuCl_2L_3$, Na_2CO_3, Se; (iii) $[RuHCl(CO)L_3]$ or $[RuH(NCMe)_2(CO)L_2]BF_4$, DBU; (iv) HC≡CR (R = C_6H_4Me-4).

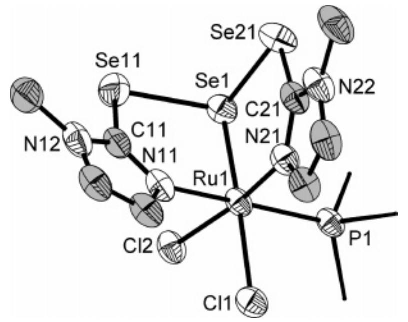
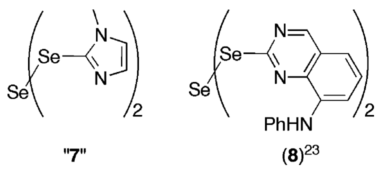


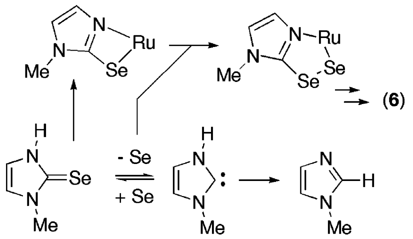
Figure 2. Molecular geometry of **6** in a crystal of **6**·$(CH_2Cl_2)_2$ (50% displacement ellipsoids, phenyl groups and hydrogen atoms omitted). Selected bond distances (Å) and angles (deg): Ru1−N21 2.062(6), Ru1−N11 2.112(5), Ru1−Se1 2.2998(10), Ru1−P1 2.3333(18), Ru1−Cl1 2.4241(18), Ru1−Cl2 2.4439(17), Se1−Se21 2.4161(11), Se1−Se11 2.4311(11), Se11−C11 1.879(7), Se21−C21 1.876(8), N21−Ru1−N11 83.7(2), N21−Ru1−Se1 91.14(16), N11−Ru1−Se1 88.71(17), N21−Ru1−P1 92.00(16), Se1−Ru1−P1 94.82(5), N21−Ru1−Cl1 91.23(17), N11−Ru1−Cl1 90.15(17), P1−Ru1−Cl1 86.51(6), Se1−Ru1−Cl2 86.86(5), P1−Ru1−Cl2 95.49(6), Cl1−Ru1−Cl2 90.61(6), Ru1−Se1−Se21 102.73(4), Ru1−Se1−Se11 101.82(4), Se21−Se1−Se11 104.44(4), C11−Se11−Se1 91.9(2), C21−Se21−Se1 93.3(2).

ruthenium. The Ru−Se1 separation of 2.2998(10) Å is significantly shorter than typical values for selenoether coordination to octahedral ruthenium(II) (2.40−2.50 Å, mean 2.46 Å).[22] Although the free molecule $Se(mt^{Se})_2$ "**7**" is unknown, the closest point of comparison is provided by the recently reported bis(4-(phenylamino)quinazolin-2-yl)triselenane (**8**, see Chart 2).[23] Assuming that the disparity in imidazolyl and quinazolinyl heterocyclic substituents contributes only a modest perturbation, the primary differences between the free and coordinated CSe_3C linkage involve elongations in the Se−Se bond lengths (**6**: 2.4311(11), 2.4161(11) Å vs **8**: 2.324 Å) and C−Se−Se bond angles (**6**: 91.9(2)°, 93.3(2)° vs **8**: 102.9°), with the angles at the unique selenium being comparable (**6**: 104.44(4)° vs **8**: 103.54°). These variations are most likely simple corollaries of the constraints of chelation, although retrodonation into the σ^*-(SeSe) orbital(s) could contribute to the significant lengthening of the Se−Se bonds. This interpretation, i.e., $d\pi \rightarrow \sigma^*$ retrodonation, is consistent with the comparative shortening (11 esd) of the π-donor Ru−Cl1 bond *trans* to Se1, relative to that *trans* to N21.

Chart 2



Scheme 2. Possible Decomposition Routes for Hmt^{Se}



The origin of the third selenium atom of the triselenane ligand, in the absence of added selenium, is of note given the well-established activation of chalcogens by *N*-alkylimidazoles.[24] We might speculate that an equilibrium could operate, undetected, relating Hmt^{Se} to the free *N*-heterocyclic carbene (NHC) and elemental selenium. Were the liberated selenium to be consumed, the NHC would simply tautomerize to *N*-methylimidazole (Scheme 2). The reverse of this reaction could thus account for the activating effect of *N*-methylimidazole on elemental selenium. It should be noted that ruthenium has a long tradition of effecting imidazole/imidazolylidene tautomerism.[25] Under the mild conditions in which **6** is formed, the combination of elemental selenium with either Hmt^{Se} or $(mt^{Se})_2$ does not appear to lead to the formation of the free triselenane (excess selenium is present during the synthesis of Hmt^{Se}), i.e., the metal plays a pivotal role in either the templating or the trapping of the triselenane. An alternative interpretation is that the metal plays a more intimate role in the activation of the C═Se bond of Hmt^{Se}, given that the reverse reaction, i.e., addition of elemental selenium to a carbene complex has

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[22] Cambridge Crystallographic Data Centre, Conquest, May 2006 release.

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precedent,[26] as does the metal-mediated transfer of selenium between isoselenocyanates and carbene[27] or carbyne[28] ligands. Furthermore, the spontaneous extrusion of tellurium from a SCTe complex has been noted.[29] Finally, thioureas have been shown to serve as carbene precursors in low-valent ruthenium chemistry via C═S bond cleavage.[30]

To conclude, the first complex of an intact neutral diorganotriselenane Se(mt^{Se})$_2$ has been isolated from a reaction that appears to involve metal-mediated triselenane assembly. The mechanism of formation remains obscure; however the metal center is necessary. Furthermore, the first complexes of the conjugate base mt^{Se} have been isolated, allowing a demonstration that the bidentate coordination mode is hemilabile, allowing alkyne hydrometalation to occur with an otherwise coordinatively saturated complex.

Supporting Information Available: Crystallographic data in CIF format for **3** (CCDC 620515) and **6** (CCDC 620516). This material is available free of charge via the Internet at http://pubs.acs.org.

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