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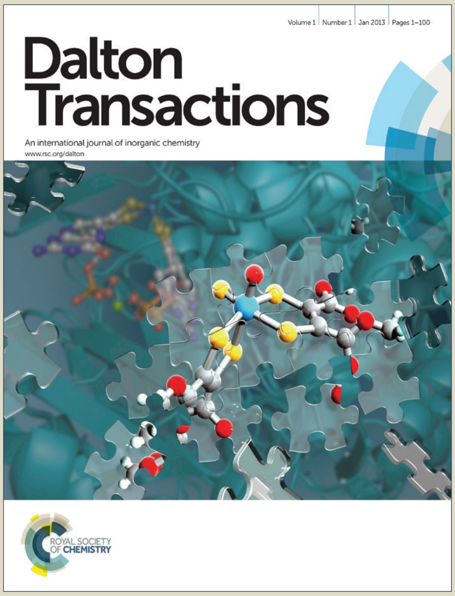

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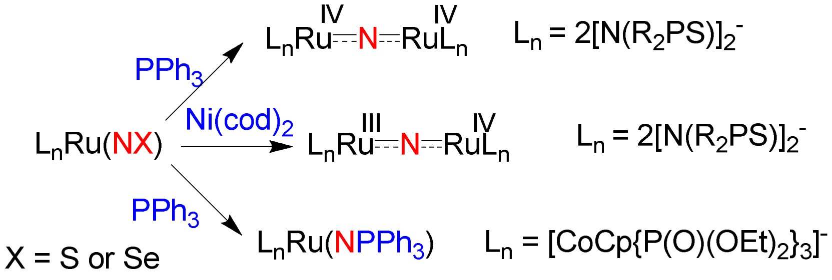

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Ruthenium thio- and seleno-nitrosyl complexes containing chelating sulfur and oxygen ligands have been synthesised and their de-chalogenation reactions have been studied. Reaction of *mer*-[Ru(N)Cl$_3$(AsPh$_3$)$_2$] with elemental sulfur and selenium in tetrahydrofuran at reflux afforded the chalcogenonitrosyl complexes *mer*-[Ru(NX)Cl$_3$(AsPh$_3$)$_2$] [X = S (**1**), Se (**2**)]. Treatment of **1** with KN(R$_2$PS)$_2$ afforded *trans*-[Ru(NS)Cl{N(R$_2$PS)$_2$}$_2$] [R = Ph (**3**), Pr^i (**4**), Bu^t (**5**)]. Alternatively, the thionitrosyl complex **5** was obtained from [Bu$^n_4$N][Ru(N)Cl$_4$] and KN(Bu$^t_2$PS)$_2$, presumably via sulfur atom transfer from [N(Bu$^t_2$PS)$_2$]$^-$ to the nitride. Reactions of **1** and **2** with NaL$_{OEt}$ (L$_{OEt}^-$ = [Co(η^5-C$_5$H$_5$){P(O)(L$_{OEt}$)$_2$}$_3$]$^-$) gave [Ru(NX)L$_{OEt}$Cl$_2$] (X = S (**8**), Se (**9**)). Treatment of [Bu$^n_4$N][Ru(N)Cl$_4$] with KN(R$_2$PS)$_2$ produced the Ru^{IV}-Ru^{IV} μ-nitrido complexes [Ru$_2$(μ-N){N(R$_2$PS)$_2$}$_4$Cl] [R = Ph (**6**), Pr^i (**7**)]. Reactions of **3** and **9** with PPh$_3$ afforded **6** and [Ru(NPPh$_3$)L$_{OEt}$Cl$_2$], respectively. The desulfurisation of **5** with [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) gave the mixed valance Ru^{III}-Ru^{IV} μ-nitrido complex [Ru$_2$(μ-N){N(Bu$^t_2$PS)$_2$}$_4$] (**10**) that was oxidised by [Cp$_2$Fe](PF$_6$) to give the Ru^{IV}-Ru^{IV} complex [Ru$_2$(μ-N){N(Bu$^t_2$PS)$_2$}$_4$](PF$_6$) ([**10**]PF$_6$). The crystal structures of **1**, **2**, **3**, **7**, **9** and **10** have been determined.

Introduction

While nitrosyl complexes of transition metals are well documented,[1] the chemistry of the heavier chalcogen analogues, namely, thionitrosyl and selenonitrosyl complexes, has received less attention[2-20] due, in part, to the difficulty of their preparations. Common synthetic routes to thionitrosyl complexes include (a) sulfur atom transfer to metal nitrides, (b) reaction of N$_3$S$_3$Cl$_3$ or NS$^+$ salts with metal complexes, (c) halide abstraction from thiazyl complexes, and (d) reaction of S$_4$N$_4$ with metal halides or nitrides.[19] Most of these preparations involve the use of highly moisture-sensitive thionitrosylating agents. Metal selenonitrosyl complexes are even less common. A selenonitrosyl species has been proposed as an intermediate in the formation of [W(NSeCl)Cl$_4$]$_2$ from the reaction of [WCl$_6$] with Se$_4$N$_4$.[21] Selenonitrosyl complexes can be obtained from the reaction of metal nitrides with selenium. To date, [Os(NSe)TpCl$_2$] (Tp$^-$ = hydrotris(pyrazol-1-yl)borate)[10] and [Ir(NSe)(PNP)]$^+$ (PNP = N(CHCHPBu$_2^t$)$_2$)[18] are the only isolated selenonitrosyl complexes that have been characterised by X-ray diffraction. To our knowledge, Ru selenonitrosyl complexes have not been reported.

We are interested in electrophilic nitrido complexes that are potentially useful in N-X (X = C or heteroatom) bond forming reactions. For example, ruthenium(VI) nitrido complexes supported by chelating ligands such as the Kläui tripodal ligand [Co(η^5-C$_5$H$_5$){P(O)(OEt)$_2$}$_3$]$^-$ (L$_{OEt}^-$) (Scheme 1) have been shown to exhibit electrophilic behaviour. Thus, the Ru^{VI} nitride [Ru(N)L$_{OEt}$Cl$_2$] reacted with nucleophilic S$_2$O$_3^{2-}$ and PPh$_3$ to afford [Ru(NS)L$_{OEt}$Cl$_2$] and [Ru(NPPh$_3$)L$_{OEt}$Cl$_2$], respectively.[22] However, our previous attempt to prepare ruthenium nitrides containing bidentate dithioimidodiphosphinate ligands, [N(R$_2$PS)$_2$]$^-$ (Scheme 1), failed. The treatment of [Ru(N)Cl$_4$]$^-$ with KN(R$_2$PS)$_2$ (R = Ph, Pr^i) in methanol led to formation [Ru{N(R$_2$PS)$_2$}$_3$], presumably via intermolecular N-N coupling of a reactive Ru^{VI} nitrido intermediates and subsequent ligand re-distribution.[23] Therefore, in an effort to synthesise Ru nitrides, the de-chalcogenation of Ru chalcogenonitrosyl complexes was attempted.

We here report a convenient synthetic route to *mer*-[Ru(NX)Cl$_3$(AsPh$_3$)$_2$] (X = S, Se) starting from *mer*-[Ru(N)Cl$_3$(AsPh$_3$)$_2$][24] and elemental sulfur or selenium. *mer*-[Ru(NX)Cl$_3$(AsPh$_3$)$_2$] proved to be useful starting materials for the synthesis of Ru chalcogenonitrosyl complexes with chelating ligands. In this work, the Ru chalcogenonitrosyl complexes [Ru(NS){N(R$_2$PS)$_2$}$_2$Cl] and [Ru(NX)L$_{OEt}$Cl$_2$] have been synthesised and their de-chalcogenation reactions have been studied. We found that the de-chalcogenation of [Ru(NS){N(R$_2$PS)$_2$}$_2$Cl] with PPh$_3$ and [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) afforded dinuclear Ru^{IV}-Ru^{IV} and Ru^{III}-Ru^{IV} nitrido complexes, respectively. On the other hand, the reaction of [Ru(NX)L$_{OEt}$Cl$_2$] with PPh$_3$ yielded the Ru^{IV} phosphoraniminato complex [Ru(NPPh$_3$)L$_{OEt}$Cl$_2$].

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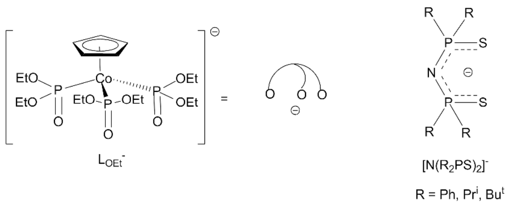
*CCDC 1401892-1401894, 1401895, 1401896 and 1401897 contain the supplementary crystallography data for complexes **1-3**, **7**, **9** and **10**. For crystallographic data in CIF or other electronic format see DOI: XX.*



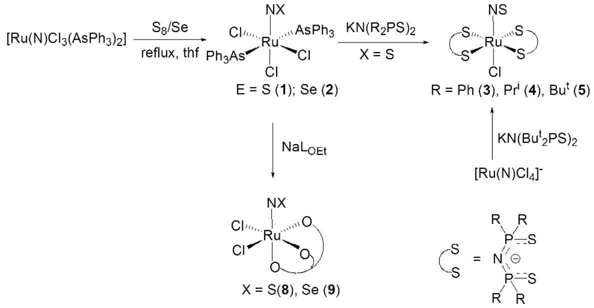
Scheme 1 Structures of the ligands, L_{OEt}^- and $[N(R_2PS)_2]^-$.

Results and Discussion

Syntheses of *mer*-$[Ru(NX)Cl_3(AsPh_3)_2]$ (X = S, Se)

The syntheses of ruthenium chalcogenonitrosyl complexes are summarised in Scheme 2. Previously, Agarwala and coworkers synthesised *mer*-$[Ru(NS)Cl_3(AsPh_3)_2]$ (**1**) by the reaction of $[RuCl_3(AsPh_3)_2L]$ (L = dimethylsulfoxide, *N*,*N*-dimethylformamide, tetrahydrofruan, *etc*.) with $N_3S_3Cl_3$.[4] We found that **1** could be synthesised more conveniently from *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$[24] without using corrosive $N_3S_3Cl_3$ (Scheme 2). Thus, refluxing *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$ with elemental sulfur in tetrahydrofuran (thf) led to isolation of **1** in 90% yield. Similarly, the selenonitrosyl analogue, *mer*-$[Ru(NSe)Cl_3(AsPh_3)_2]$ (**2**), was obtained in 82% yield by refluxing *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$ with selenium in thf. An attempt to prepare a telluronitrosyl complex by refluxing *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$ with tellurium in thf failed. **1** and **2** are air-stable in both the solid state and solution. They are diamagnetic and exhibit well-resolved signals in the ^1H NMR spectra, consistent with the $\{Ru(NX)\}^6$ (X = S, Se) configuration according to the Enermark-Feltham notation.[25] The IR spectra of **1** and **2** displayed a band at 1310 and 1137 cm^{-1}, respectively, which is absent in that of *mer*-$[Ru(NO)Cl_3(AsPh_3)_2]$. These bands are tentatively assigned as ν(N-S) and ν(N-Se), respectively. Similar stretching frequencies have been found in reported thio- and selenonitrosyl complexes.[10,18]

Both **1** and **2** have been characterised by X-ray diffraction. The molecular structures of **1** and **2** are shown in Figs 1 and 2, respectively. Selected bond lengths and angles of **1**, **2** and related nitrido[26] and nitrosyl[27] complexes are listed in Table 1 for comparison. The Ru-N distances in **1** [1.753(4) Å] and **2** [1.756(3) Å] are quite short, indicative of multiple bond character. They are similar to/slightly longer than that in *mer*-$[Ru^{II}(NO)Cl_3(AsPh_3)_2]$ [1.729(7) Å],[27] but significantly longer than that in *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$ [1.6161(15) Å][26] that



Scheme 2 Syntheses of ruthenium chalcogenonitrosyl complexes.

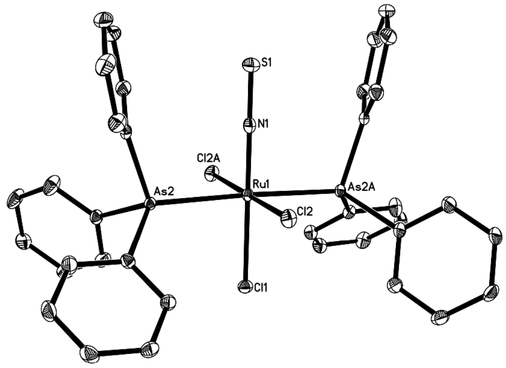


Fig. 1 Molecular structure of *mer*-$[Ru(NS)Cl_3(AsPh_3)_2]$ (**1**). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level.

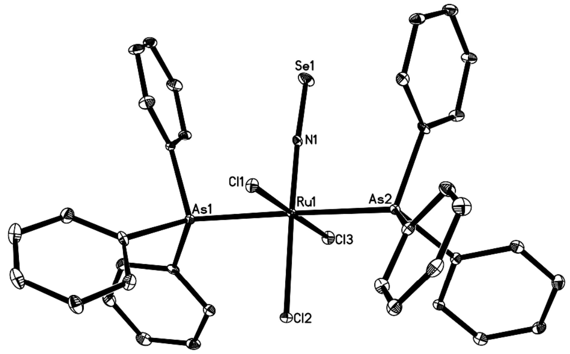


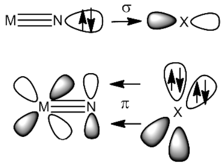
Fig. 2 Molecular structure of *mer*-$[Ru(NSe)Cl_3(AsPh_3)_2]$ (**2**). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for *mer*-$[Ru^{II}(NX)Cl_3(AsPh_3)_2]$ complexes.

X	Nothing[26]	O[27]	S (**1**)	Se (**2**)
		bond lengths		
Ru-N	1.6161(15)	1.729(7)	1.753(4)	1.756(3)
Ru-Cl (*trans* to N)	2.5020(4)	2.346(2)	2.3937(10)	2.3953(10)
Ru-Cl (*cis* to N)	2.3786(3)	2.384(1)	2.3887(7)	2.3708(9), 2.4108(9)
Ru-As	2.5533(3)	2.5198(6)	2.5194(4)	2.5103(5), 2.5071(5)
N-X	--	1.151(9)	1.502(4)	1.650(3)
		bond angles		
N-Ru-Cl(*trans*)	180.0	180.0	180.0	175.16(10)
N-Ru-Cl(*cis*)	93.325(7)	90.0(1)	89.790(19)	93.55(10), 86.30(10)
N-Ru-As	93.590(10)	91.5(1)	91.295(8)	91.62(10), 91.35(10)
Ru-N-X	--	180.0	180.0	171.2(2)

contains a Ru-N triple bond. By comparison, the Ir-N distances in $[Ir(NX)(PNP)]^+$ are 1.678(4), 1.749(2), 1.768(2), and 1.756(4) Å for X = nothing, O, S, and Se, respectively.[18] The short N-X distances in **1** [1.502(4) Å] and **2** [1.650(3) Å] (cf. 1.522(2) and 1.678(4) Å, respectively, in $[Ir(NX)(PNP)]^+$) are indicative of multiple bond character. A previous theoretical study indicated that nitrosyl complexes possess M=N=O (e.g. M = Re) covalent double bonds, whereas the N-X bonding in the M(NX) (X = S, Se) analogues can be considered as donor-acceptor interactions between M$\equiv$N and the X atom in the singlet state with two filled pπ orbitals (Scheme 3).[18,28,29] Also, it was suggested that the ratio of N-X (X = O, S, Se) stretching frequencies for M-NX complexes can provide insight into the M-NX bonding. For *mer*-$[Ru(NX)Cl_3(AsPh_3)_2]$, the ν(N-O)[27]:ν(N-S) ratio of 1.43 is similar to those of reported systems (1.40-1.47)[10,18,30] and significantly higher than the harmonic oscillator approximation(1.14) based on the reduced mass of NO and NS. This result is supportive of stronger N-X interaction in the nitrosyl complex (M=N=O) compared with that in the thionitrosyl congener that features a donor-acceptor interaction between M$\equiv$N and S.[18] By contrast, the ν(N-S):ν(N-Se) ratio (for **1** and **2**) of 1.1 agrees well with the harmonic oscillator approximation, indicating similar N-X bonding in the NS and NSe complexes.[10,18,28]

Like *mer*-$[Ru(NO)Cl_3(AsPh_3)_2]$,[26] in both **1** and **2**, the Ru-Cl(*trans* to N) distances [2.3937(10) and 2.3953(10) Å, respectively] are very similar to the Ru-Cl(*cis* to N) distances (av. 2.3887 and 2.3908 Å respectively), and the Ru centre roughly lies on the equatorial plane (defined by the two Cl and As atoms), indicating the absence of the trans influence of the NX ligands. This is in sharp contrast with *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$, in which the Ru-Cl(*trans* to N) bond is significantly longer than the Ru-Cl(*cis* to N) bonds and the Ru atom is displaced above the mean equatorial plane by 0.1483(2) Å, due to the trans influence of the nitride. A similar result has been observed in the $[Mn(NX)(CN)_5]^{3-}$ (X = nothing or O) system. The difference between the Mn-C(*trans* to N) and average Mn-C(*cis* to N) distance for $[Mn(N)(CN)_5]^{3-}$ is 0.253 Å, whereas that for $[Mn(NO)(CN)_5]^{3-}$ is only 0.04 Å.[31]



Scheme 3 Bonding description of M(NX) complexes in terms of orbital interactions between M$\equiv$N and X in the singlet state.[28]

Thionitrosyl Complexes

Complex **1** proved to be a useful starting material for Ru thionitrosyl complexes. For example, reaction of **1** with 2 equivalents of $KN(R_2PS)_2$ in methanol afforded *trans*-$[Ru(NS)\{N(R_2PS)_2\}_2Cl]$ (R = Ph (**3**), Pr^i (**4**), Bu^t (**5**)) in good yield (Scheme 2). The $^{31}P\{^1H\}$ spectra of **3**-**5** showed singlets at δ 37.8, 63.2 and 68.8 ppm, respectively, consistent with the *trans* geometry of these complexes. The N–S stretching frequencies of **3**-**5** (1281, 1304 and 1305 cm^{-1} respectively) are slightly lower than that in **1** (1310 cm^{-1}). The molecular structure of **3** is shown in Fig. 3. The geometry around Ru is *pseudo* octahedral with the NS ligand opposite to the chloride. The Ru–N–S unit is linear [177.0(6)°]. The Ru–Cl(*trans* to N) and Ru-N distances [2.397(3) and 1.745(9) Å] are similar to those in **1** [2.3937(10) and 1.753(4) Å, respectively]. The Ru-S distances [2.4307(9) and 2.4227(9) Å] are slightly longer than those in *trans*-$[Ru\{N(Ph_2PS)_2\}_2(NH_3)(H_2O)]$ (av. 2.411 Å).[32]

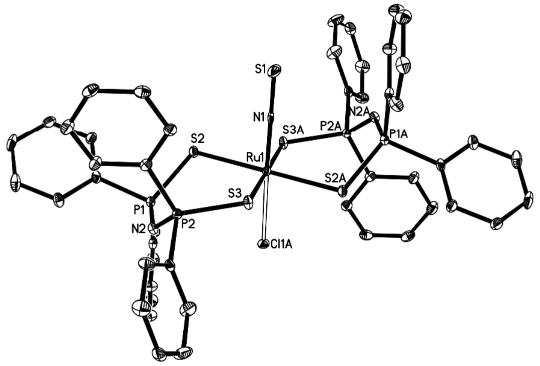


Fig. 3 Molecular structure of *trans*-$[Ru(NS)\{N(Ph_2PS)_2\}_2Cl]$ (**3**). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level. Symmetry code: #1: 1 - *x*, 2 - *y*, -*z*; #2: 1 - *x*, 1 - *y*, 1 - *z*

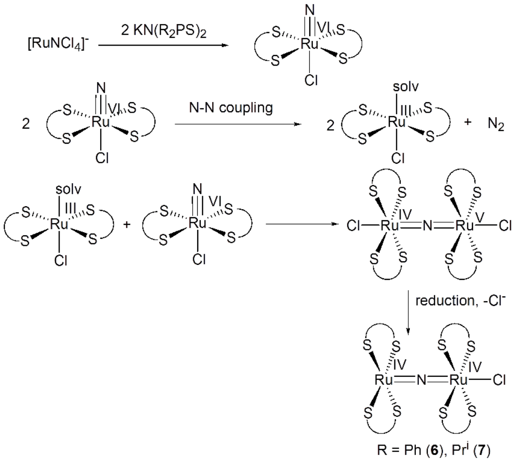
Table 2 Selected bond lengths (Å) and angles (°) for **3**.

bond lengths			
Ru(1)-N(1)	1.745(9)	Ru(1)-S(2)	2.4307(9)
Ru(1)-S(2A)	2.4307(9)	Ru(1)–S(3)	2.4227(9)
Ru(1)-S(3A)	2.4227(9)	Ru(1)–Cl(1A)	2.397(3)
N(1)-S(1)	1.478(9)		
bond angles			
S(1)-N(1)-Ru(1)	177.0(6)	N(1)-Ru(1)-S(2)	88.7(2)
N(1)-Ru(1)-S(2A)	91.3(2)	N(1)-Ru(1)-S(3)	88.7(2)
N(1)-Ru(1)-S(3A)	91.3(2)	N(1)-Ru(1)-Cl(1A)	180.0

Interestingly, complex **5** was also formed by reaction of the Ru^{VI} nitride $[Ru(N)Cl_4]^-$ with $KN(Bu^t{}_2PS)_2$. Thus, treatment of $[Bu^n{}_4N][Ru(N)Cl_4]$ with 2 equivalents of $KN(Bu^t{}_2PS)_2$ afforded **5** in ca. 25% yield. The thionitrosyl group in **5** was apparently formed by sulfur atom transfer from the dithioimidodiphosphinate ligand to a reactive nitrido intermediate, presumably "$[Ru(N)\{N(Bu^t{}_2PS)_2\}_2Cl]$". The sulfidation of transition metal nitrides with elemental sulfur to give thionitrosyl complexes has been reported.[2,10-12,14,19] Also, metal-mediated desulfurisation of dithioimidodiphosphinate ligands is well precedented.[33,34]

μ-Nitrido Complexes

In contrast with the *tert*-butyl analogue, the reactions of $KN(R_2PS)_2$ (R = Ph, Pr^i) with $[Ru(N)Cl_4]^-$ resulted in the formation of μ-nitrido complexes instead of sulfur atom transfer. Thus, the treatment of $[Bu_4N][Ru(N)Cl_4]$ with $KN(R_2PS)_2$ afforded the Ru^{IV}-Ru^{IV} μ-nitrido complexes $[Ru_2(\mu\text{-}N)\{N(R_2PS)_2\}_4Cl]$ [R = Ph (**6**), Pr^i (**7**)]. The formation of dinuclear nitrido complexes by N-N coupling of Ru^{VI} nitrido complexes is well precedented.[35-37] For example, refluxing $[Ru^{VI}(N)L_{OEt}Cl_2]$ in CCl_4 afforded $[Ru^{IV,V}{}_2(\mu\text{-}N)(L_{OEt})_2Cl_4]$. A plausible mechanism for the formation of **6** and **7** is shown in Scheme 4. The reaction of $[Ru(N)Cl_4]^-$ with $KN(R_2PS)_2$ initially gives a nitrido intermediate, "$[Ru(N)\{N(R_2PS)_2\}_2Cl]$", which undergoes rapid N-N coupling to give a Ru^{III} species, $[Ru\{N(R_2PS)_2\}_2Cl(solv)]$, and dinitrogen. Combination of the Ru^{III} species with the Ru nitride gives a mixed valence Ru^{IV}-Ru^{V} μ-nitrido species that is subsequently reduced to the more stable Ru^{IV}-Ru^{IV} complex (vide infra). It may be noted that the Ru^{IV}-Ru^{IV} nitrido complex $[Ru^{IV,IV}{}_2(\mu\text{-}N)(L_{OEt})_2Cl_4]^-$ has been obtained from the reduction of the Ru^{IV}-Ru^{V} precursor $[Ru^{V,IV}{}_2(\mu\text{-}N)(L_{OEt})_2Cl_4]$.[35]



Scheme 4 Plausible mechanism for the formation of the μ-nitrido complexes **6** and **7**.

As expected, complexes **6** and **7** are diamagnetic due to antiferromagnetic coupling of the two d^4 Ru^{IV} centres. In the ^{31}P $\{^1H\}$ NMR spectra of **6** and **7** two resonances were observed, consistent with the pseudo C_2 symmetry of the two compounds. The IR spectra of **6** and **7** displayed absorptions at 1026 and 1024 cm^{-1}, respectively, which are not found for other mononuclear $[Ru\{N(R_2PS)_2\}_2]$-type complexes. These IR bands are tentatively assigned as ν_{asym}(Ru-N-Ru). Similar ν_{asym}(Ru-N-Ru) stretching frequencies have been observed in the reported dinuclear Ru nitrido complexes.[38] The cyclic voltammogram of **7** in acetonitrile displayed a reversible couple at +0.79 V and an irreversible wave at –0.91 V, which are tentatively assigned as the $Ru^{IV}Ru^{V}$-$Ru^{IV}Ru^{IV}$ and $Ru^{IV}Ru^{IV}$-$Ru^{IV}Ru^{III}$ redox events, respectively. The observed high $Ru^{IV}Ru^{V}$-$Ru^{IV}Ru^{IV}$ potential indicates that the Ru^{V}-Ru^{IV} nitrido species can be reduced to the Ru^{IV}-Ru^{IV} complex **7** easily.

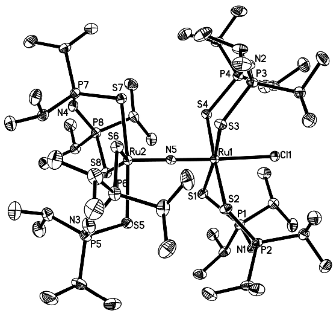


Fig. 4 Molecular structure of $[Ru_2(\mu\text{-}N)\{N(Pr^i{}_2PS)_2\}_4Cl]$ (**7**). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level.

Table 3 Selected bond lengths (Å) and angles (°) for **7**.

	bond lengths		
Ru(1)–N(5)	1.758(3)	Ru(1)–S(1)	2.4472(9)
Ru(1)–S(2)	2.4255(9)	Ru(1)–S(3)	2.4093(9)
Ru(1)–S(4)	2.4278(9)	Ru(1)–Cl(1)	2.4269(10)
Ru(2)–N(5)	1.717(3)	Ru(2)–S(5)	2.4464(10)
Ru(2)–S(6)	2.3543(9)	Ru(2)–S(7)	2.4515(9)
Ru(2)–S(8)	2.3495(9)		
	bond angles		
Ru(1)–N(5)–Ru(2)	179.13(18)	N(5)–Ru(1)–S(1)	86.86(9)
N(5)–Ru(1)–S(2)	92.74(9)	N(5)–Ru(1)–S(3)	86.74(9)
N(5)–Ru(1)–S(4)	89.87(9)	N(5)–Ru(1)–Cl(1)	176.88(9)
S(1)–Ru(1)–S(2)	93.29(3)	S(1)–Ru(1)–S(3)	173.43(4)
S(1)–Ru(1)–S(4)	85.49(3)	S(1)–Ru(1)–Cl(1)	96.26(3)
S(2)–Ru(1)–S(3)	85.55(3)	S(2)–Ru(1)–S(4)	177.05(4)
S(2)–Ru(1)–Cl(1)	87.28(3)	S(3)–Ru(1)–S(4)	95.96(3)
S(3)–Ru(1)–Cl(1)	90.15(3)	S(4)–Ru(1)–Cl(1)	90.18(3)
N(5)–Ru(2)–S(5)	91.66(9)	N(5)–Ru(2)–S(6)	106.82(10)
N(5)–Ru(2)–S(7)	94.99(9)	N(5)–Ru(2)–S(8)	104.96(10)
S(5)–Ru(2)–S(6)	98.09(3)	S(5)–Ru(2)–S(7)	173.35(4)
S(5)–Ru(2)–S(8)	81.05(3)	S(6)–Ru(2)–S(7)	79.90(3)
S(6)–Ru(2)–S(8)	148.21(4)	S(7)–Ru(2)–S(8)	97.28(3)

The crystal structure of **7** is shown in Fig. 4. Selected bond lengths and angles are listed in Table 3. The structure consists of a $\{RuCl[N(Pr^i{}_2PS)_2]_2\}$ fragment and a $\{Ru[N(Pr^i{}_2PS)_2]_2\}$ fragment bridged by a nitride. The Ru-N [1.713(3) Å] and Ru-S (av. 2.4004 Å) distances for the 5-coordinated Ru fragment is shorter than that in the 6-coordinated one [1.758(3) and av. 2.4275 Å, respectively]. The roughly symmetric and linear Ru-N-Ru bridge is indicative of the Ru^{IV}=N=Ru^{IV} bonding description. The Ru-Cl distance [2.4269(10) Å] in **7** is shorter than that in *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$, but longer than that in **3**, thus indicating the order of *trans* influence terminal nitrido > μ-nitrido > thionitrosyl.

Selenonitrosyl Complexes

Attempts to synthesise Ru selenonitrosyl dithioimidophosphinate complexes failed. Refluxing **2** with $KN(R_2PS)_2$ (R = Ph, Pr^i, Bu^t) in methanol gave dark materials that did not crystallize. On the other hand, heating **1** and **2** with NaL$_{OEt}$ in thf resulted in isolation of [Ru(NX)L$_{OEt}$Cl$_2$] [X = S (**8**), Se (**9**)] (Scheme 2). It may be noted that **8** has been previously prepared from [Ru(N)L$_{OEt}$Cl$_2$] and Na$_2$S$_2$O$_3$; however, an attempt to prepare **9** by reacting [Ru(N)L$_{OEt}$Cl$_2$] with selenium failed.[22] Complex **9** has been characterised by X-ray diffraction (Fig. 5). To our knowledge, **2** and **9** are the first isolated Ru selenonitrosyl complexes that have been characterised by X-ray diffraction. **9** is structurally related to the previously reported nitrido [Ru(N)L$_{OEt}$Cl$_2$] and nitrosyl [Ru(NO)L$_{OEt}$Cl$_2$] complexes.[22] The Ru-N distance in **9** [1.731(4) Å] is in similar to those in [Ru(NO)L$_{OEt}$Cl$_2$] [1.729(3) Å] and [Ru(N)L$_{OEt}$Cl$_2$] [1.573 (6) Å], indicative of multiple bond character. The Ru-O (av. 2.077 Å) and Ru-Cl (2.347 Å) distances in **9** are slightly longer than those in [Ru(NO)L$_{OEt}$Cl$_2$].

Dechalcogenation with PPh$_3$

Treatment of **3** in CDCl$_3$ with 1 equivalent of PPh$_3$ at room temperature resulted in a colour change from orange to green. The ^{31}P {^{1}H} NMR spectrum of the green solution displayed a singlet at δ 43.2 ppm due to SPPh$_3$ and two signals at δ 38.6 and 43.6 ppm attributable to **6**. In addition, a signal at δ 32.4 ppm due to an unknown species was found. Evaporation of the solvent and recrystallisation from CH$_2$Cl$_2$/hexanes led to isolation of **6** (Scheme 5). Since SPPh$_3$ was detected in the reaction mixture, it seems likely **3** is initially desulfurised by PPh$_3$ to a nitrido intermediate that dimerises rapidly to give **6**. This is in contrast with *trans*-[Ru(NO){N(R$_2$PS)$_2$}$_2$Cl] (R = Ph, Pr^i) that did not react with PPh$_3$ even under refluxing conditions.[39]

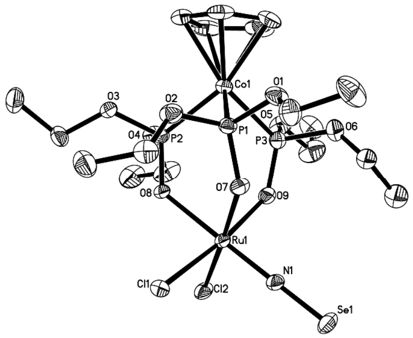
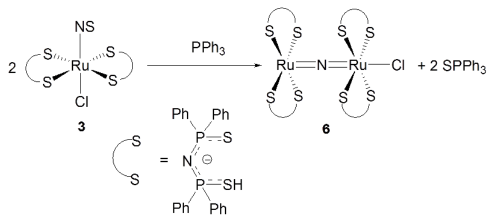


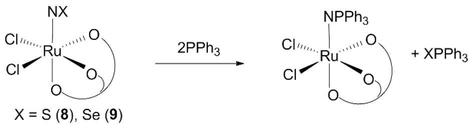
Fig. 5 Molecular structure of [Ru^{II}(NSe)L$_{OEt}$Cl$_2$] (**9**). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level.

Table 4 Selected bond lengths (Å) and angles (^{o}) for **9**.

bond lengths			
Ru(1)–N(1)	1.731(4)	Ru(1)–Cl(1)	2.3400(12)
Ru(1)–Cl(2)	2.3542(11)	Ru(1)–O(7)	2.073(3)
Ru(1)–O(8)	2.081(3)	Ru(1)–O(9)	2.078(3)
N(1)–Se(1)	1.651(4)		
bond angles			
N(1)–Ru(1)–Cl(1)	92.74(14)	N(1)–Ru(1)–Cl(2)	91.54(13)
N(1)–Ru(1)–O(7)	91.82(16)	N(1)–Ru(1)–O(8)	179.23(16)
N(1)–Ru(1)–O(9)	93.83(17)	Cl(1)–Ru(1)–Cl(2)	91.83(5)
Cl(1)–Ru(1)–O(7)	90.60(9)	Cl(1)–Ru(1)–O(8)	87.49(9)
Cl(1)–Ru(1)–O(9)	173.41(10)	Cl(2)–Ru(1)–O(7)	175.76(9)
Cl(2)–Ru(1)–O(8)	89.19(9)	Cl(2)–Ru(1)–O(9)	88.53(10)
O(7)–Ru(1)–O(8)	87.44(12)	O(7)–Ru(1)–O(9)	88.66(12)
O(8)–Ru(1)–O(9)	85.93(13)	Se(1)–N(1)–Ru(1)	178.4(3)



Scheme 5 Reaction of **3** with PPh$_3$.

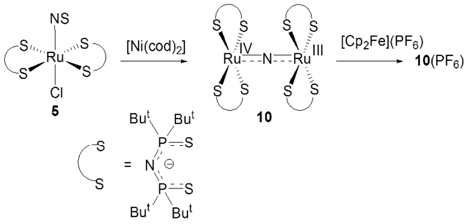


Scheme 6 Reaction of **8** or **9** with PPh$_3$.

Like [Ru(NS)L$_{OEt}$Cl$_2$], **9** reacted with PPh$_3$ to yield [Ru(NPPh$_3$)L$_{OEt}$Cl$_2$] and SePPh$_3$ (δ^P = 35.14 ppm) (Scheme 6). Our previous work showed that [Ru(N)L$_{OEt}$Cl$_2$] reacted with PPh$_3$ rapidly at room temperature to give [Ru(NPPh$_3$)L$_{OEt}$Cl$_2$],[22] the N-N coupling of [Ru(N)L$_{OEt}$Cl$_2$] to yield a μ-nitrido complex only occurred at refluxing CCl$_4$ (boiling point = 76.7 ^{o}C).[35] Therefore, it is understandable that the dechalcogenation of **8** or **9** with PPh$_3$ led to formation of a phosphoraniminate instead of a μ-nitrido complex.

Desulfurisation with [Ni(cod)$_2$]

Treatment of **3** or **4** with [Ni(cod)$_2$] led to a colour change from orange to dark brown. The ^{1}H NMR spectrum of the reaction mixture showed ill-resolved broad signals, indicating a paramagnetic species was produced. Unfortunately, we were not able to crystallise the brown species due to its poor solubility. On the other hand, the reaction of [Ni(cod)$_2$] with more soluble complex **5** resulted in a change of colour from orange to brown, and isolation of [Ru$_2$(μ-N){N(Bu$^t{}_2$PS)$_2$}$_4$] (**10**) (Scheme 7), which is formulated as a mixed valence Ru^{III}-Ru^{IV} μ-nitrido complex. The measured magnetic moment of **10** of ca. 1.6 μ_B (Evans method) is consistent with the S =1/2 spin state. While Ru^{IV}-Ru^{IV} μ-nitrido complexes are well documented,[40] not many mixed valance dinuclear Ru nitrides have been reported.[41] To our knowledge, apart from **10**, [Na$_4$(thf)$_3$][Ru$^{III,IV}{}_2$(μ-N)(Me$_8$N$_4$)$_2$] (Me$_8$N$_4{}^{2-}$ = meso-octamethylporphyinogen tetraanion) is the only reported Ru^{III}-Ru^{IV} nitrido complex characterised by X-ray diffraction.[41b] It seems likely that similar to PPh$_3$, [Ni(cod)$_2$] initially desulfurised **5** to give a Ru^{IV}-Ru^{IV} intermediate, **10**$^+$ (see later section), which was further reduced by [Ni(cod)$_2$] to yield **10**. Consistent with this proposal, reaction of **10**$^+$ with [Ni(cod)$_2$] led to formation of **10**.



Scheme 7 Reaction of **5** with [Ni(cod)$_2$].

The crystal structure of **10** (Fig. 6) features two symmetry-related [Ru{N(Bu$^t{}_2$PS)$_2$}$_2$] fragments and a bridged nitride lying on the C_2 axis. The Ru-N-Ru bridge is symmetric with the Ru-N distance of 1.75850(14) Å, which is longer than that in **7** (av. 1.738 Å). On the other hand, the Ru-S distances in **10** (av. 2.4193 Å) are slightly shorter than those in the [Ru{N(Pr$^i{}_2$PS)$_2$}$_2$] fragment of **7** (av. 2.4275 Å). The *tert*-butyl groups of the two [Ru{N(Bu$^t{}_2$PS)$_2$}$_2$] fragments in **10** adopt a staggered arrangement apparently because of steric effects.

10 is air-sensitive in both the solid state and solution. In CH$_2$Cl$_2$, it is rapidly air oxidised to a red species. The oxidation of **10** with [Cp$_2$Fe](PF$_6$) led to isolation of a diamagnetic red complex characterized as the Ru^{IV}-Ru^{IV} complex [Ru$_2$(μ-N){N(Bu$^t{}_2$PS)$_2$}$_4$] ([**10**]PF$_6$). The ^{31}P {^{1}H} NMR spectrum of **10**$^+$ exhibits a singlet at δ 68.95 ppm, indicative of the symmetric coordination environments of the two Ru centres. The cyclic voltammogram of **10**$^+$ displayed an irreversible redox wave at +0.8 V and a reversible reduction couple at -0.8 V, which are assigned as the Ru^{V}Ru^{IV}-Ru^{IV}Ru^{IV} and Ru^{IV}Ru^{IV}-Ru^{IV}Ru^{III} events, respectively. The observed low Ru^{IV}Ru^{IV}-Ru^{IV}Ru^{III} redox potential for **10** explains why the Ru^{III}-Ru^{IV} complex is air-sensitive and readily oxidised to **10**$^+$.

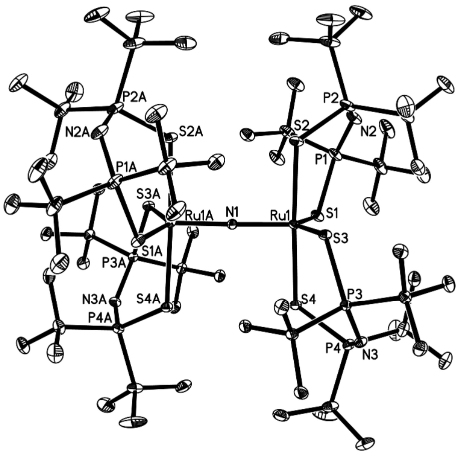


Fig. 6 Molecular structure of [Ru$^{IV,III}{}_2$(μ-N){N(Bu$^t{}_2$PS)$_2$}$_4$] (**10**). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level.

Table 5 Selected bond lengths (Å) and angles (^{o}) for **10**.

	bond lengths		
Ru(1)-N(1)	1.75850(14)	Ru(1)-S(1)	2.3945(4)
Ru(1)-S(2)	2.4369(5)	Ru(1)–S(3)	2.4129(4)
Ru(1)-S(4)	2.4330(4)		
	bond angles		
Ru(1)-N(1)-Ru(1A)	178.89(13)	S(1)-Ru(1)-S(2)	98.666(15)
S(1)-Ru(1)-S(3)	142.648(17)	S(1)-Ru(1)-S(4)	80.297(15)
S(2)-Ru(1)-S(3)	81.091(15)	S(2)-Ru(1)-S(4)	177.251(16)
S(3)-Ru(1)-S(4)	98.167(14)		

Conclusions

We have developed a convenient synthetic route to the Ru chalcogenonitrosyl complexes *mer*-[Ru(NX)Cl$_3$(AsPh$_3$)$_2$] (X = S, Se) starting from *mer*-[Ru(N)Cl$_3$(AsPh$_3$)$_2$] and elemental sulfur or selenium. X-ray diffraction studies indicate that like nitrosyl, the NX ligands have very weak *trans* influence. The bonding of the Ru(NX) complexes can be described as Ru=N=X or donor-acceptor interactions between Ru nitride and the chalcogen atom X (Scheme 3). *mer*-[Ru(NX)Cl$_3$(AsPh$_3$)$_2$] can be used as starting materials for Ru chalcogenonitrosyl complexes such as *trans*-[Ru(NS){N(R$_2$PS)$_2$}$_2$Cl] and [Ru(NX)L$_{OEt}$Cl$_2$]. The dechalcogenation of Ru chalcogenonitrosyl complexes with PPh$_3$ and [Ni(cod)$_2$] has been studied. The reaction of *trans*-[Ru(NS){N(Ph$_2$PS)$_2$}$_2$Cl] with PPh$_3$ and [Ni(cod)$_2$] gave dinuclear Ru^{IV}-Ru^{IV} and Ru^{III}-Ru^{IV} nitrido complexes, respectively, presumably via N-N coupling of a reactive Ru nitride intermediate. Selenium abstraction of [Ru(NSe)L$_{OEt}$Cl$_2$] with PPh$_3$ afforded the phosphoraniminato complex [Ru(NPPh$_3$)L$_{OEt}$Cl$_2$]. The investigation of the reactivity of ruthenium selenonitrosyl complexes is underway.

Experimental

General Considerations

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400.0, 376.5 and 162.0 MHz for ^{1}H ^{19}F and ^{31}P, respectively. Chemical shifts (*δ*, ppm) were reported with reference to SiMe$_4$ (^{1}H), CF$_3$C$_6$H$_5$ (^{19}F) and H$_3$PO$_4$ (^{31}P). IR spectra were recorded on a Perkin-Elmer 16 PC Fourier transform infrared spectrophotometer. Magnetic moments of paramagnetic complexes were determined by Evans method in CDCl$_3$ solutions at room temperature. Cyclic voltammetry was performed with a CH Instrument model 600D potentiostat. The working and reference electrodes were glassy carbon and Ag/AgNO$_3$ (0.1 mol dm^{-3} in acetonitrile) electrodes, respectively. Redox potentials ($E_{1/2}$) were reported with reference to the ferrocenium-ferrocene couple. Electrospray ionisation mass spectrometry was recorded on an Applied Bio-system QSTAR spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K.

The ligands $KN(R_2PS)_2$ (R = Ph,[42] Pr^i,[43] Bu^{t},[44]) and NaL_{OEt}[45] and the nitrido complexes $[Bu^n_4N][Ru(N)Cl_4]$[46] and *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$[24] were prepared according to literature methods.

Syntheses

***mer*-$[Ru(NS)Cl_3(AsPh_3)_2]$ (1).** A mixture of *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$ (83 mg, 0.1 mmol) and elemental sulfur (3.2 mg, 0.1 mmol) in thf (5 mL) was refluxed for 2 h. The orange solid was collected and washed with Et_2O. Recrystallisation in CH_2Cl_2/Et_2O afforded orange blocks which were suitable for the X-ray diffraction study. Yield: 78 mg (90 %). ^1H NMR ($CDCl_3$): δ 7.76-8.03 (m, 30H, Ph). IR (KBr, cm^{-1}): 1310 [ν(N-S)]. Anal. Calcd for $C_{36}H_{30}As_2Cl_3NRuS$: C, 49.93; H, 3.49, N, 1.62. Found: C, 49.50; H, 3.37; N, 1.63.

***mer*-$[Ru(NSe)Cl_3(AsPh_3)_2]$ (2).** A mixture of *mer*-$[Ru(N)Cl_3(AsPh_3)_2]$ (83 mg, 0.1 mmol) and selenium (7.9 mg, 0.1 mmol) in thf (5 mL) was refluxed overnight. The orange solid was collected and washed with Et_2O. Recrystallisation in CH_2Cl_2/Et_2O afforded orange blocks which were suitable for the X-ray diffraction study. Yield: 75 mg (82%). ^1H NMR ($CDCl_3$): δ 7.33-7.88 (m, 30H, Ph). IR (KBr, cm^{-1}): 1137 [ν(N-Se)]. Anal. Calcd for $C_{36}H_{30}As_2Cl_3NRuSe{\cdot}CH_2Cl_2$: C, 44.54; H, 3.23, N, 1.40. Found: C, 44.75; H, 3.22; N, 1.50.

***trans*-$[Ru(NS)\{N(R_2PS)_2\}_2Cl]$ (R = Ph (3), Pr^i (4)).** A mixture of **1** (86 mg, 0.1 mmol) and 2 equivalents of $KN(R_2PS)_2$ (97 mg for **3,** 70 mg for **4,** , 0.2 mmol) in thf (5 mL) was refluxed for 2 hr. The solvent was removed *in vacuo* the residue was extracted with CH_2Cl_2 (5 ml). Recrystallisation from CH_2Cl_2/hexanes (5 mL, v:v = 1:2) afforded orange crystals.

3: Yield: 82 mg (76 %). ^1H NMR ($CDCl_3$): δ 7.21-7.25 (m, 8H, Ph), 7.31-7.40 (m, 16H, Ph), 7.74-7.79 (m, 8H, Ph), 8.00-8.06 (m, 8H, Ph). ^{31}P {^1H} NMR ($CDCl_3$): δ 37.8 (s). IR (KBr, cm^{-1}): 1281 [ν(NS)]. Anal. Calcd for $C_{48}H_{40}ClN_3P_4RuS_5$: C, 53.40; H, 3.73, N, 3.89. Found: C, 53.10; H, 3.82; N, 3.56.

4: Yield: 59 mg (73 %). ^1H NMR ($CDCl_3$): δ 1.12-1.64 (m, 48H, $(C\mathit{H}_3)_2CH$), 1.93-2.13 (m, 4H, $(CH_3)_2C\mathit{H}$), 2.40-2.69 (m, 4H, $(CH_3)_2C\mathit{H}$). ^{31}P {^1H} NMR ($CDCl_3$): δ 63.2 (s). IR (KBr, cm^{-1}): 1304 [ν(NS)]. Anal. Calcd for $C_{24}H_{56}ClN_3P_4RuS_5$: C, 35.70; H, 6.99, N, 5.20. Found: C, 35.96; H, 6.93; N, 5.34.

***trans*-$[Ru(NS)\{N(Bu^t_2PS)_2\}_2Cl]$ (5).** *Method A*: A mixture of **1** (86 mg, 0.1 mmol) and 2 equivalents of $KN(Bu^t_2PS)_2$ (81 mg, 0.2 mmol) in thf (10 mL) was stirred at room temperature for overnight. The solvent was removed *in vacuo* the residue was extracted with CH_2Cl_2. Recrystallisation from CH_2Cl_2/hexanes gave red crystalline solid. Yield: 63 mg (68 %). ^1H NMR ($CDCl_3$): δ 1.22-1.27 (d, *J* = 8 Hz, 36H, CH_3), 1.54-1.60 (d, *J* = 8 Hz, 36H, CH_3). ^{31}P {^1H} NMR ($CDCl_3$): δ 68.8 (s). IR (KBr, cm^{-1}): 1305 [ν(NS)]. Anal. Calcd for $C_{32}H_{72}ClN_3P_4RuS_5{\cdot}0.5CH_2Cl_2{\cdot}0.5C_6H_{14}$: C, 42.42; H, 8.0; N, 4.18. Found: C, 42.48; H, 8.40; N, 3.93.

Method B: To a solution of $[Bu^n_4N][Ru(N)Cl_4]$ (50 mg, 0.1 mmol) in thf (5 mL) was added 3 equivalents of $KN(Bu^t_2PS)_2$ (81 mg, 0.2 mmol) and the mixture was stirred at room temperature for overnight. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2. Recrystallisation from CH_2Cl_2/hexanes gave red crystals. Yield: 23 mg (25 %).

$[Ru_2(\mu\text{-}N)\{N(R_2PS)_2\}_4Cl]$ (R = Ph (6), Pr^i (7)). To a solution of $[Bu^n_4N][Ru(N)Cl_4]$ (50 mg, 0.1 mmol) in thf (10 mL) was added 2 equivalents of $KN(R_2PS)_2$ (97 mg for **6,** 70 mg for **7**, 0.2 mmol) in thf (10 mL) dropwise at -78 ^oC. The purple solution was warmed to room temperature and stirred for overnight. The solvent was removed in vacuo and the residue was extracted with thf (for **6**) or Et_2O (for **7**). Recrystallisation from thf/hexanes (for **6**) or Et_2O/hexanes (for **7**) afforded a green crystalline solid.

6: Yield: 90 mg (45 %). ^1H NMR ($CDCl_3$): δ 6.71-6.75 (m, 12H, Ph), 6.88-6.92 (m, 16H, Ph), 6.98-7.14 (m, 20H, Ph), 7.56-7.70 (m, 16H, Ph), 7.74-7.81 (m, 16H, Ph), 7.83-7.87 (m, 4H, Ph). ^{31}P {^1H} NMR ($CDCl_3$): δ 38.6 (s), 43.6 (s). IR (KBr, cm^{-1}): 1026 [ν_{as}(RuNRu)]. Anal. Calcd for $C_{96}H_{80}ClN_5P_8Ru_2S_8$: C, 56.37; H, 3.94, N, 3.42. Found: C, 56.65; H, 3.91; N, 3.40.

7: Yield: 35 mg (23 %). ^1H NMR (benzene-*d*$_6$): δ 1.12-1.26 (m, 24H, $(C\mathit{H}_3)_2CH$), 1.35-1.58 (m, 72H, $(C\mathit{H}_3)_2CH$), 1.85 (m, 4H, $(CH_3)_2C\mathit{H}$), 2.33 (m, 4H, $(CH_3)_2C\mathit{H}$), 2.95 (m, 4H, $(CH_3)_2C\mathit{H}$), 3.26 (m, 4H, $(CH_3)_2C\mathit{H}$). ^{31}P {^1H} NMR (benzene-*d*$_6$): δ 62.5 (s), 62.6 (s). IR (KBr, cm^{-1}): 1024 [ν_{as}(RuNRu)]. Anal. Calcd for $C_{48}H_{112}ClN_5P_8Ru_2S_8$: C, 38.40; H, 7.52, N, 4.66. Found: C, 38.65; H, 7.73; N, 4.88. $E_{1/2}$: -0.91, 0.79 V (quasi-reversible).

$[Ru(NSe)L_{OEt}Cl_2]$ (9). A mixture of **2** (90 mg, 0.1 mmol) and 1 equivalent of NaL_{OEt} (55 mg, 0.1 mmol) in thf (5 mL) was refluxed for 2 h, during which a yellow solution was formed. Solvent was pumped off and the residue was extracted with CH_2Cl_2. Recrystallisation from CH_2Cl_2/hexanes afforded yellowish brown crystals. Yield: 48 mg (60%). ^1H NMR ($CDCl_3$): δ 1.28-1.37 (m, 18H, CH_3), 4.16-4.23 (m, 12H, CH_2), 5.07 (s, 5H, Cp). ^{31}P {^1H} NMR ($CDCl_3$): δ 119.3-120.6 (m). Yield: Anal. Calcd for $C_{17}H_{35}Cl_2CoNO_9P_3RuSe$: C, 25.51; H, 4.41, N, 1.75. Found: C, 25.34; H, 4.11; N, 1.83.

$[Ru_2(\mu\text{-}N)\{N(Bu^t_2PS)_2\}_4]$ (10). To a solution of **5** (50 mg, 0.054 mmol) in thf (10 mL) was added 1 equivalent of $[Ni(cod)_2]$ (15 mg, 0.054 mmol) at 0 ^oC, during which the orange solution turned brown. The solvent was pumped off and the residue was extracted with thf/hexanes (5 mL, 1:1, v/v). Concentration and cooling at -20 ^oC afforded dark brown crystals. Yield: 20 mg, 43%. μ_{eff} (Evans method, $CDCl_3$) = 1.58 μ_B. IR (KBr, cm^{-1}): 1018 [ν_{as}(RuNRu)]. Anal. Calcd for $C_{64}H_{144}N_5P_8Ru_2S_8{\cdot}1.5C_6H_{12}$: C, 48.27; H, 8.99, N, 3.86. Found: C, 47.78; H, 9.35; N, 3.51.

$[Ru_2(\mu\text{-}N)\{N(Bu^t_2PS)_2\}_4](PF_6)$ ([10]PF$_6$). To a solution of **10** (30 mg, 0.019 mmol) in thf (10 mL) was added 1 equivalent of ferrocenium hexafluorophosphate (6 mg, 0.019 mmol) during which the brown solution turned red. The red solution was stirred at room temperature for 2 h. The solvent was pumped off and the residue was washed with Et_2O and then extracted with CH_2Cl_2. Recrystallisation from CH_2Cl_2/Et_2O/hexanes afforded red crystals. Yield: 27 mg, 83%. ^1H NMR ($CDCl_3$): δ 1.24 (d, *J* = 15.2 Hz, 36H, CH_3), 1.57 (d, *J* = 15.6 Hz, 36H, CH_3). ^{31}P {^1H} NMR ($CDCl_3$): δ 68.95 (br. s), -144.49 (sept, *J* = 712 Hz, PF_6^-). ^{19}F {^1H} NMR ($CDCl_3$): δ -74.65 (d, *J* = 713 Hz). IR (KBr, cm^{-1}): 1014 [ν_{as}(RuNRu)]. Anal. Calcd for $C_{64}H_{144}F_6N_5P_9Ru_2S_8$: C, 41.88; H, 7.91, N, 3.82. Found: C, 41.65; H, 7.90; N, 3.72. $E_{1/2}$: -0.80, 0.80 V (irreversible).

Reaction of 3 with PPh$_3$. To a solution of **3** (20 mg, 0.019 mmol) in CH_2Cl_2 (0.5 mL) was added 1 equivalent of PPh_3 (4.9 mg, 0.019 mmol). The resulting brown solution was stirred at room temperature for 6 h. ^{31}P {^1H} NMR spectroscopy indicated that the reaction mixture contained **6** (δ 38.6 and 43.6 ppm), $SPPh_3$ (δ 43.2

ppm) and an unknown species (δ 32.4 ppm). The solvent was removed in vacuo, and residue was washed with Et_2O and extracted with CH_2Cl_2. Recrystallisation from CH_2Cl_2/hexanes afforded **6** (14 mg).

Reaction of 9 with PPh_3. To a solution of **9** (20 mg, 0.025 mmol) in CH_2Cl_2 (5 mL) was added 2 equivalents of PPh_3 (13 mg, 0.05 mmol). The reaction mixture was stirred at room temperature for 1 h, during which the yellow solution turned orange. The solvent was pumped off and the residue was washed with hexanes. Recrystallisation from CH_2Cl_2/hexanes afforded orange crystals, which were identified as $[Ru(NPPh_3)L_{OEt}Cl_2]$.[22] The $^{31}P\{^1H\}$ NMR spectrum of the mother liquor displayed a singlet at δ 35.14 ppm corresponding to $SePPh_3$.

Table 6 Crystallographic data and experimental details for **1, 2, 3, 7, 9** and **10**.

	1	**2**·CH_2Cl_2	**3**·CH_2Cl_2	**7**	**9**	**10**·$1.54C_6H_{12}$
Empirical formula	$C_{36}H_{30}As_2Cl_3N_3RuS$	$C_{37}H_{32}As_2Cl_5NRuSe$	$C_{49}H_{42}Cl_3N_3P_4RuS_5$	$C_{48}H_{112}ClN_5P_8Ru_2S_8$	$C_{17}H_{35}Cl_2CoNO_9P_3RuSe$	$C_{73.24}H_{162.48}N_5P_8Ru_2S_8$
Formula weight	865.93	997.76	1164.45	1501.26	795.19	1729.79
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	I2/a	P-1	P2(1)/n	P2(1)/n	Pca2(1)	C2/c
a, Å	116.0414(9)	10.7021(4)	14.3179(15)	13.3977(2)	14.40074(14)	22.7799(4)
b, Å	9.4516(3)	12.8930(5)	9.3685(10)	28.4018(4)	15.56830(18)	15.6193(3)
c, Å	22.7388(16)	13.9385(5)	18.4542(19)	19.9030(3)	13.23672(14)	27.8342(5)
α, deg	90	77.871(3)	90	90	90	90
β, deg	102.120(7)	87.759(3)	91.9680(10)	107.605(2)	90	102.8792(18)
γ, deg	90	78.802(3)	90	90	90	90
V, $Å^3$	3370.7(3)	1844.55(11)	2473.9(4)	7218.76(18)	2967.61(5)	9654.5(3)
Z	4	2	2	4	4	4
ρ_{calcd}, g cm^{-1}	1.706	1.796	1.563	1.381	1.780	1.252
Temp, K	173(2)	99.9(5)	100(2)	173(2)	203.01(10)	99.97(11)
F(000)	1720	980	1184	3152	1580	3892
μ, mm^{-1}	8.924	3.583	0.859	7.829	13.476	5.691
Total reflection	5222	12063	13599	26080	9310	22023
Indep. Reflection	2907	7195	5176	12841	4355	8589
R_{int}	0.0391	0.0394	0.0280	0.0507	0.0312	0.0257
GoF^a	1.011	1.002	1.002	1.010	1.003	1.004
$R_1{}^b$, $wR_2{}^c[I>2\sigma(I)]$	0.0321, 0.0907	0.0387, 0.0767	0.0483, 0.1065	0.0403 0.0936	0.0275, 0.0658	0.0250, 0.0660
R_1, wR_2 (all data)	0.0356, 0.0925	0.0521, 0.0825	0.0561, 0.1097	0.0513, 0.0958	0.0309, 0.0678	0.0285, 0.0678

^{a} GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. $^b R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

X-ray Crystallography

Crystal data and experimental details for **1, 2, 3, 7, 9** and **10** are summarised in Table 6. Preliminary examinations and intensity data collection were carried out on a Bruker SMART-APEX 1000 area-detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.70173 Å). The collected frames were processed with the software SAINT. The data was corrected for absorption using the program SADABS.[47] Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[48] Unless stated otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXL97 default parameters.

For **10**, effort was made to deduce the solvent content from the difference map. A clear fragment which showed the presence of methylcyclopentane as one of the solvent molecules was found but there were still a few high residual peaks around the fragment which made the disorder modelling to give a sensible structure more difficult. Squeeze was then applied in the Olex 2 programme suite with set completion applied. The total void accessible volume per unit cell is 1966.3 $Å^3$ [20.4%] with total electron per cell of 259.3, indicative of 3.09 molecules of methylcyclopentane per unit cell, or 1.54 molecules of methylcyclopentane per molecule of **10**.

Acknowledgements

The financial support from the Hong Kong Research Grants Council (project no. 603111) is gratefully acknowledged. We thank Mr. Kwok-Chung Law for assistance in the synthesis of Ru selenonitrosyl complexes.

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