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Ruthenium Chalcogenonitrosyl and Bridged Nitrido Complexes Containing Chelating Sulfur and Oxygen Ligands

Ho-Yuen Ng, Wai-Man Cheung*, Enrique Kwan Huang, Kang-Long Wong, Herman H.-Y. Sung, Ian D. Williams and Wa-Hung Leung*

\[
\begin{align*}
\text{PPh}_3 & \quad \text{L}_n\text{Ru}^\text{IV}\text{N} = \text{N} = \text{Ru} \text{L}_n & \quad L_n = 2\text{N} (\text{R}_2\text{PS}) \text{L}_2^- \\
\text{L}_n\text{Ru}(\text{NX}) & \quad \text{Ni(cod)}_2 & \quad \text{L}_n\text{Ru}^\text{III}\text{N} = \text{N} = \text{Ru} \text{L}_n & \quad L_n = 2\text{N} (\text{R}_2\text{PS}) \text{L}_2^- \\
\text{PPh}_3 & \quad \text{L}_n\text{Ru}(\text{NPPh}_3) & \quad L_n = [\text{CoCp}(\text{P(O)(OEt)}_2)_3]^+ \\
X = \text{S or Se}
\end{align*}
\]
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Their de-chalcogenation 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, Se). Treatment of 1 with KN[R(S)] afforded trans-[Ru(N(S)Cl)(N(R))] [R = Ph (3), Pr' (4), Bu'' (5)]. Alternatively, the thionitrosyl complex 5 was obtained from [Bu''(N)]Ru(N)Cl_3 and KN[Bu''(S)], presumably via sulfur atom transfer from [N(Bu'')(S)] to the nitrile. Reactions of 1 and 2 with NaL([L] = [Co(η^1-C_5H_4)(P(O)(L))] or [Co(η^1-C_5H_4)(P(O)(L))]) gave [Ru(NX)Cl_2L] (X = S, Se) (9). Treatment of [Bu''(N)]Ru(N)Cl_3 with KN[R(S)] produced the Ru''-Ru'' μ-nitrido complexes [Ru(Ru)-N][N[R(R)]Cl_3] (R = Ph (6), Pr' (7)). Reactions of 3 and 9 with PPh_3 afforded 6 and [Ru(NPPh_3)Cl_2L_2], respectively. The desulfurisation of 5 with [Ni(cod)_3] (cod = 1,5-cyclooctadiene) gave the mixed valence Ru''-Ru'' μ-nitrido complex [Ru(Ru)-N][N(Bu''(S))], which was oxidised by [CP,Fe](PF_6) to give the Ru''-Ru'' complex [Ru(Ru)-N][N(Bu''(S))](PF_6) (10). The crystal structures of 1, 2, 3, 7, 9 and 10 have been determined.

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 and [Co(η^1-C_5H_4)(P(O)(L))] have been shown to exhibit electrophilic behaviour. Thus, the Ru'' nitride [Ru(N)_2Cl_2] reacted with nuclyphilic S_2O_3^2- and PPh_3 to afford [Ru(N)=N]=S_2O_3 and [Ru(NPPh_3)_2Cl_2], respectively. However, our previous attempt to prepare ruthenium nitrides containing bidentate dithioimidodiphosphinate ligands, [N(R)]Cl_3 (Scheme 1), failed. The treatment of [Ru(N)Cl_3] with KN[R(S)] (R = Ph, Pr) in methanol led to formation [Ru(N)[R(S)]_2Cl_2], presumably via intermolecular N-S coupling of a reactive Ru'' nitrido intermediates and subsequent ligand re-distribution. 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] 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(S)N][R(S)Cl_2] and [Ru(NX)Cl_2] have been synthesised and their de-chalcogenation reactions have been studied. We found that the de-chalcogenation of [Ru(NS)[R(S)Cl_2] with PPh_3 and [Ni(cod)_3] (cod = 1,5-cyclooctadiene) afforded dinuclear Ru''-Ru'' and Ru''-Ru'' nitrido complexes, respectively. On the other hand, the reaction of [Ru(NX)Cl_2] with PPh_3 yielded the Ru'' phosphoraniminato complex [Ru(NPPh_3)_2Cl_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.
Results and Discussion

Syntheses of mer-[Ru(NX)Cl₂(AsPh₃)₃] (X = S, Se)

The syntheses of ruthenium chalcogenonitrosyl complexes are summarised in Scheme 2. Previously, Agarwala and coworkers synthesised mer-[Ru(NS)Cl₃(AsPh₃)₃] (1) by the reaction of [RuCl₃(AsPh₃)₂L] (L = dimethylosulfoxide, N,N-dimethylformamide, tetrahydrofuran, etc.) with N₂S₅Cl₂.⁴ We found that 1 could be synthesised more conveniently from mer-[Ru(NCl)Cl₃(AsPh₃)₃] without using corrosive N₂S₅Cl₂ (Scheme 2). Thus, refluxing mer-[Ru(NCl)Cl₃(AsPh₃)₃] with elemental sulfur in tetrahydrofuran (thf) led to isolation of 1 in 90% yield. Similarly, the selenonitrosyl analogue, mer-[Ru(NSe)Cl₃(AsPh₃)₃] (2), was obtained in 82% yield by refluxing mer-[Ru(NCl)Cl₃(AsPh₃)₃] with selenium in thf. An attempt to prepare a telluronitrosyl complex by refluxing mer-[Ru(NCl)Cl₃(AsPh₃)₃] 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)} 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)Cl₃(AsPh₃)₃]. 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 nitrido²⁶ and nitrosyl²⁷ 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(NO)Cl₃(AsPh₃)₃] [1.729(7) Å],²⁷ but significantly longer than that in mer-[Ru(NCl)Cl₃(AsPh₃)₃] [1.616(15) Å]²⁶ that...
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. 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=N and the X atom in the singlet state with two filled π orbitals (Scheme 3). 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)Cl2(AsPh3)3], the ν(N-O):ν(N-S) ratio of 1.43 is similar to those of reported systems (1.40-1.47) 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=N and S. 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.

Like mer-[Ru(NO)Cl2(AsPh3)3], 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 N ligands. This is in sharp contrast with mer-[Ru(N)(Cl2)(AsPh3)3], 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)2]+ (X = nothing or O) system. The difference between the Mn-Cl(trans to N) and average Mn-Cl(cis to N) distance for [Mn(N)(CN)2] is 0.253 Å, whereas that for [Mn(NO)(CN)2] is only 0.04 Å.

Scheme 3  Bonding description of M(NX) complexes in terms of orbital interactions between M=N and X in the singlet state.

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(RPS)2 in methanol afforded trans-[Ru(NS)(N(RPS)2)Cl] (R = Ph (3), Pr4 (4), Bu4 (5)) in good yield (Scheme 2). The 31P (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 [2.393(3) and 1.745(9) Å] are similar to those in 1 [2.393(10) and 1.753(4) Å, respectively]. The Ru-S distances [2.430(9) and 2.4272(9) Å] are slightly longer than those in trans-[Ru(N(PhPS)2)2(NH3)]H2O] (av. 2.411 Å).

Interestingly, complex 5 was also formed by reaction of the RuII nitride [Ru(NCl4)2] with KN(Bu4PS)2. Thus, treatment of [Bu4N][Ru(NCl4)2] with 2 equivalents of KN(Bu4PS)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(Bu4PS)2)Cl]”. The sulfidation of transition metal nitrides with elemental sulfur to give thionitrosyl complexes has been reported.2,5,10,12,14,19 Also, metal-mediated desulfurisation of dithioimidodiphosphinate ligands is well preceded.2,34

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

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<thead>
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<th>bond lengths</th>
<th>bond angles</th>
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<tr>
<td>Ru(1)-N(1) 1.745(9)</td>
<td>S(1)-N(1)-Ru(1) 177.0(6)</td>
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<tr>
<td>Ru(1)-S(2A) 2.4307(9)</td>
<td>N(1)-Ru(1)-S(2) 88.7(2)</td>
</tr>
<tr>
<td>Ru(1)-S(3A) 2.4227(9)</td>
<td>N(1)-Ru(1)-S(3) 88.7(2)</td>
</tr>
<tr>
<td>H               1.478(9)</td>
<td>N(1)-Ru(1)-S(1A) 180.0</td>
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Fig. 3  Molecular structure of trans-[Ru(NS)(N(PhPS)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.
µ-Nitrido Complexes

In contrast with the tert-butyl analogue, the reactions of K[R(N)Cl]₂ (R = Ph, Pr₃) with [Ru(N)Cl]⁺ resulted in the formation of µ-nitrido complexes instead of sulfur atom transfer. Thus, the treatment of [Ru₂(N)(RuCl)₂] with KN(R₂PS)₂ afforded the Ru⁴-Ru⁴ µ-nitrido complexes [Ru₂(µ-N)(N(R₂PS))₂Cl] (R = Ph, Pr₃). The formation of dinuclear nitrido complexes by N-N coupling of Ru⁴ nitrido complexes is well preceded.⁵⁻³⁷ For example, refluxing [Ru⁴(N)]Cl₂ in CCl₄ afforded [Ru⁴(µ-N)(L₂)₂Cl]₂. A plausible mechanism for the formation of 6 and 7 is shown in Scheme 4. The reaction of [Ru(N)Cl]⁺ with KN(R₂PS)₂ initially gives a nitrido intermediate, “[Ru(N)(N(R₂PS)₂)]Cl”, which undergoes rapid N-N coupling to give a Ru⁴ species, [Ru(N(R₂PS)₃)]Cl(solvent), and dinitrogen. Combination of the Ru⁴ species with the Ru nitride gives a mixed valence Ru⁴-Ru⁴ µ-nitrido species that is subsequently reduced to the more stable Ru⁴-Ru⁴ complex (vide infra). It may be noted that the Ru⁴-Ru⁴ nitrido complex [Ru⁴(µ-N)(L₂)₂Cl] has been obtained from the reduction of the Ru⁴-Ru⁴ precursor [Ru⁴(µ-N)(L₂)₂Cl].³⁵

As expected, complexes 6 and 7 are diamagnetic due to antiferromagnetic coupling of the two d⁴ Ru⁴ centres. In the ⁴¹P [¹H] NMR spectra of 6 and 7 two resonances were observed, consistent with the pseudo C₂ 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(R₂PS)₃)]Cl-type complexes. These IR bands are tentatively assigned as νasym(Ru-N-Ru). Similar νasym(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 Ru⁴-Ru⁴+ and Ru⁴-Ru⁴⁻ reduction events, respectively. The observed high Ru⁴-Ru⁴⁴ potential indicates that the Ru⁴-Ru⁴ nitrido species can be reduced to the Ru⁴-Ru⁴ complex 7 easily.

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

Fig. 4  Molecular structure of [Ru₂(µ-N)(N(R₂PS)₃)_2]Cl (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.

<table>
<thead>
<tr>
<th>bond lengths</th>
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<tr>
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<tr>
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<td>148.21(4)</td>
</tr>
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</table>

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(R₂PS)₃)] fragment and a [Ru(N(R₂PS)₃)] fragment bridged by a nitride. The Ru-N [1.713(3) Å] and Ru-S [av. 2.400 Å] distances for the 5-coordinated Ru fragment is shorter than that in the 6-coordinated one [1.758(3) Å and av. 2.4275 Å, respectively]. The roughly symmetric and linear Ru-N-Ru bridge is indicative of the Ru⁴-N=Ru⁴ bonding description. The Ru-Cl distance [2.4269(10) Å] in 7 is shorter than that in mer-[Ru(NICl₂AsPh₃)]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 dithiomidophosphinate complexes failed. Refluxing 2 with KN(R₂PS)₂ (R = Ph, Pr₃, Bu₃) in methanol gave dark materials.
that did not crystallize. On the other hand, heating 1 and 2 with NaOEt in thf resulted in isolation of [Ru(NX)OEtCl₂] [X = S (8), Se (9)] (Scheme 2). It may be noted that 8 has been previously prepared from [Ru(N)OEtCl₂] and Na₂S₂O₃ however, an attempt to prepare 9 by reacting [Ru(N)OEtCl₂] with selenium failed. 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)L₂Cl] and nitrosyl [Ru(NO)L₆OEtCl] complexes. The Ru-N distance in 9 [1.731(4) Å] is in similar to those in [Ru(NO)L₂OEtCl] [1.729(3) Å] and [Ru(N)L₆OEtCl] [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)L₆OEtCl].

Dehalogenation with PPh₃

Treatment of 3 in CDCl₃ with 1 equivalent of PPh₃ at room temperature resulted in a colour change from orange to green. The ³¹P (¹H) NMR spectrum of the green solution displayed a singlet at δ 43.2 ppm due to SPPh₂ 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 CH₂Cl₂/hexanes led to isolation of 6 (Scheme 5). Since SPPPh₃ was detected in the reaction mixture, it seems likely 3 is initially desulphurised by PPh₃ to a nitrido intermediate that dimerises rapidly to give 6. This is in contrast with trans-[Ru(NO)(N(R₉PS)₂Cl)] (R = Ph, Pr) that did not react with PPh₃ even under refluxing conditions.

Like [Ru(N)L₆OEtCl]₂ 9 reacted with PPh₃ to yield [Ru(NPPh₃)L₆OEtCl] and SePPh₃ (δ Se = 35.14 ppm) (Scheme 6). Our previous work showed that [Ru(N)L₆OEtCl] reacted with PPh₃ rapidly at room temperature to give [Ru(NPPh₃)L₆OEtCl]. The N-N coupling of [Ru(N)L₆OEtCl] to yield a μ-nitrido complex only occurred at refluxing CCl₄ (boiling point = 76.7 °C). Therefore, it is understandable that the dehalogenation of 8 or 9 with PPh₃ led to formation of a phosphoraniminate instead of a μ-nitrido complex.

Desulphurisation with [Ni(cod)₂]

Treatment of 3 or 4 with [Ni(cod)₂] led to a colour change from orange to dark brown. The ¹H 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)]₄ with more soluble complex 5 resulted in a change of colour from orange to brown, and isolation of [Ru₂(μ-N)(N(Bu’₃PS)₂)] (10) (Scheme 7), which is formulated as a mixed valence RuIV-RuIV μ-nitrido complex. The measured magnetic moment of 10 of ca. 1.6 μ₄B (Evans method) is consistent with the 5 = 1/2 spin state. While RuIV-RuIV μ-nitrido complexes are well documented, not many mixed valence dinuclear Ru nitrides have been reported. To our knowledge, apart from 10, [Na₄(thf)][Ru₂(μ-N)(Me₃S)₂] (Me₃S = meso-octamethylporphyrinogen tetraanion) is the only reported RuII₂ nitrido complex characterised by X-ray diffraction. It seems likely that similar to PPh₃, [Ni(cod)₂] initially desulphurised 5 to give a RuIV-RuIV intermediate, 10 (see later

![Figure 5 Molecular structure of [Ru(NSe)L₆OEtCl] (9). All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level.](image-url)
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)₃PS)₂] complexes and a bridged nitride lying on the C₂ axis. The Ru-N-Ru bridge is symmetric with the Ru-N distance of 1.7585(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(Pt)₂PS)₂] fragments of 7 (av. 2.4275 Å). The tert-butyl groups of the two [Ru(N(Bu)₃PS)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 CH₂Cl₂, it is rapidly air oxidised to a red species. The oxidation of 10 with [Cp₂Fe][PF₆] led to isolation of a diamagnetic red complex characterized as the RuⅣ⁻RuⅣ complex [Ru₂(μ-N)(N(Bu)₃PS)₄] ((10)PF₆). The ³¹P (¹H) 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 RuⅣ⁻RuⅣ and RuⅣ⁻RuⅣ events, respectively. The observed low RuⅣ⁻RuⅣ redox potential for 10 explains why the RuⅢ⁻RuⅣ complex is air-sensitive and readily oxidised to 10’.

Conclusions
We have developed a convenient synthetic route to the Ru chalcogenonitrosyl complexes mer-[Ru(NX)Cl₃(AsPh₃)] (X = S, Se) starting from mer-[Ru(NCl)₃(AsPh₃)] 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=NX or donor-acceptor interactions between Ru nitride and the chalcogen atom X (Scheme 3). mer-[Ru(NX)Cl₃(AsPh₃)] can be used as starting materials for Ru chalcogenonitrosyl complexes such as trans-[Ru(NS)(NR₂PS)₂Cl] and [Ru(NX)₂Cl₂].

The dechalcogenation of Ru chalcogenonitrosyl complexes with PPH₃ and [Ni(cod)]₂ has been studied. The reaction of trans-[Ru(NS)(NPh₂PS)₂Cl] with PPH₃ and [Ni(cod)]₂ gave dinuclear RuⅣ⁻RuⅣ and RuⅢ⁻RuⅣ nitrido complexes, respectively, presumably via N-N coupling of a reactive Ru nitride intermediate. Selenium abstraction of [Ru(NSe)₂Cl₂] with PPH₃ afforded the phosphoramidinate complex [Ru(NPPh₃)₂Cl₂]. 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 ¹H, ¹³C and ³¹P, respectively. Chemical shifts (δ, ppm) were reported with reference to SiMe₄ (¹H), CF₃CO₂H (¹³C) and H₂PO₄ (³¹P). 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 CDCl₃ 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/AgNO₃ (0.1 mol dm⁻³ in acetonitrile) electrodes, respectively. Redox potentials (E½) were reported with reference to the ferrocenium-ferrocene couple. Electrospray ionisation mass spectrometry was recorded on an Applied Biosystem QSTAR spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K.
The ligands KN(R\textsubscript{1}PS\textsubscript{1}) (R = Ph,\textsuperscript{42} Pr\textsuperscript{1},\textsuperscript{43} Bu\textsuperscript{1,44}) and NaLO\textsubscript{1}\textsubscript{OE}\textsuperscript{45} and the nitrido complexes [Bu\textsubscript{2}N]N[Ru(N)Cl\textsubscript{4}]\textsuperscript{16} and mer-[Ru(N)(Cl\textsubscript{4})(AsPh\textsubscript{3})\textsubscript{2}]\textsuperscript{24} were prepared according to literature methods.

**Syntheses**

**mer-[Ru(NS)]Cl\textsubscript{4}(AsPh\textsubscript{3})\textsubscript{2}** (1). A mixture of mer-[Ru(N)]Cl\textsubscript{4}(AsPh\textsubscript{3})\textsubscript{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\textsubscript{2}O. Recrystallisation in CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O afforded orange blocks which were suitable for the X-ray diffraction study. Yield: 78 mg (90 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta 7.76-8.03\) (m, 30H, Ph). IR (KBr, cm\textsuperscript{-1}): 1310 [\nu(N-S)]. Anal. Calcd for C\textsubscript{37}H\textsubscript{38}AsCl\textsubscript{3}N\textsubscript{4}Ru: C, 49.45; H, 3.17; N, 1.40. Found: C, 49.60; H, 3.17; N, 1.36.

**mer-[Ru(NSe)]Cl\textsubscript{4}(AsPh\textsubscript{3})\textsubscript{2}** (2). A mixture of mer-[Ru(N)]Cl\textsubscript{4}(AsPh\textsubscript{3})\textsubscript{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\textsubscript{2}O. Recrystallisation in CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O afforded orange blocks which were suitable for the X-ray diffraction study. Yield: 75 mg (82%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta 7.33-7.88\) (m, 30H, Ph). IR (KBr, cm\textsuperscript{-1}): 1137 [\nu(N-Se)]. Anal. Calcd for C\textsubscript{37}H\textsubscript{38}AsCl\textsubscript{3}N\textsubscript{4}RuSe: C, 44.54; H, 3.23; N, 1.40. Found: C, 44.75; H, 3.22; N, 1.50.

**trans-[Ru:NS]Cl\textsubscript{3}(N(RPS)\textsubscript{2})Cl** (R = Ph (3), Pr\textsuperscript{1} (4)). A mixture of 1 (86 mg, 0.1 mmol) and 2 equivalents of KN(R\textsubscript{1}PS\textsubscript{1}); (73 mg, 0.1 mmol) in thf (5 mL) was refluxed for 2 h. The solvent was removed in vacuo the residue was extracted with CH\textsubscript{2}Cl\textsubscript{2}. Recrystallisation from CH\textsubscript{2}Cl\textsubscript{2}/hexanes (5 mL, v:v = 1:2) afforded orange crystals.

3: Yield: 82 mg (76 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta 7.21-7.25\) (m, 8H, Ph), 7.31-7.40 (m, 16H, Ph), 7.74-7.79 (m, 8H, Ph), 8.00-8.06 (m, 8H, Ph). \textsuperscript{31}P \textsuperscript{(1)}H NMR (CDCl\textsubscript{3}): \(\delta 37.8\) (s). IR (KBr, cm\textsuperscript{-1}): 1281 [\nu(NPS)]. Anal. Calcd for C\textsubscript{37}H\textsubscript{38}Cl\textsubscript{3}N\textsubscript{4}P\textsubscript{2}Ru\textsubscript{2}: C, 53.40; H, 3.73, N, 3.89. Found: C, 53.10; H, 3.82; N, 3.56.

4: Yield: 59 mg (73 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta 1.12-1.64\) (m, 48H, (CH\textsubscript{2})\textsubscript{4}Cl), 1.93-2.13 (m, 4H, (CH\textsubscript{2})\textsubscript{2}Cl), 2.40-2.69 (m, 4H, (CH\textsubscript{2})\textsubscript{2}Cl). \textsuperscript{31}P \textsuperscript{(1)}H NMR (CDCl\textsubscript{3}): \(\delta 63.2\) (s). IR (KBr, cm\textsuperscript{-1}): 1304 [\nu(NPS)]. Anal. Calcd for C\textsubscript{45}H\textsubscript{52}Cl\textsubscript{4}N\textsubscript{4}P\textsubscript{2}Ru\textsubscript{2}: C, 35.70; H, 6.99; N, 5.20. Found: C, 35.96; H, 6.93; N, 5.34.

**trans-[Ru:NS]Cl\textsubscript{3}(N(RPS)\textsubscript{2})Cl** (5). **Method A:** A mixture of 1 (86 mg, 0.1 mmol) and 2 equivalents of KN(R\textsubscript{1}PS\textsubscript{1}); (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\textsubscript{2}Cl\textsubscript{2}. Recrystallisation from CH\textsubscript{2}Cl\textsubscript{2}/hexanes gave red crystalline solid. Yield: 63 mg (68 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta 1.22-1.27\) (d, \(J = 8\) Hz, 36H, CH\textsubscript{3}), 1.54-1.60 (d, \(J = 8\) Hz, 36H, CH\textsubscript{3}). \textsuperscript{31}P \textsuperscript{(1)}H NMR (CDCl\textsubscript{3}): \(\delta 68.8\) (s). IR (KBr, cm\textsuperscript{-1}): 1305 [\nu(NPS)]. Anal. Calcd for C\textsubscript{37}H\textsubscript{38}Cl\textsubscript{3}N\textsubscript{4}P\textsubscript{2}Ru\textsubscript{2}: 0.5CH\textsubscript{2}Cl\textsubscript{2}0.5CH\textsubscript{3}H\textsubscript{2}O. Found: C, 42.42; H, 8.00; N, 4.18. Found: C, 42.48; H, 8.40; N, 3.93.

**Method B:** To a solution of [Bu\textsubscript{2}N]\textsuperscript{N}[Ru(N)]Cl\textsubscript{3} (50 mg, 0.1 mmol) in thf (5 mL) was added 3 equivalents of KN(R\textsubscript{1}PS\textsubscript{1}); (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\textsubscript{2}Cl\textsubscript{2}. Recrystallisation from CH\textsubscript{2}Cl\textsubscript{2}/hexanes gave red crystals. Yield: 23 mg (25 %).
ppm) and an unknown species ($\delta$ 32.4 ppm). The solvent was removed in vacuo, and residue was washed with Et$_2$O and extracted with CH$_2$Cl$_2$. Recrystallisation from CH$_2$Cl$_2$/hexanes afforded 6 (14 mg).

**Reaction of 9 with PPh$_3$.** To a solution of 9 (20 mg, 0.025 mmol) in CH$_2$Cl$_2$ (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$_2$Cl$_2$/hexanes afforded orange crystals, which were identified as [Ru(NPPh$_3$)$_2$Cl$_2$]$_2$. The $^{31}$P (1H) NMR spectrum of the mother liquor displayed a singlet at $\delta$ 35.14 ppm corresponding to SePPh$_3$.

**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-K$_\alpha$ radiation ($\lambda = 0.70737$ Å). The collected frames were processed with the software SAINT. The data was corrected for absorption using the program SADABS. Structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELXTL software package. 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.

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**References**


