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Synthesis and properties of anionic ruthenium thionitrosyl and selenonitrosyl complexes that contain tetraanionic 2-hydroxybenzamidobenzene ligands†

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Although transition-metal complexes that contain thiocarbonyl (CS) and selenocarbonyl (CSe) ligands have been well studied, only three neutral or cationic selenonitrosyl (NSe) complexes have been reported, while anionic NSe complexes remain elusive. Herein, we report the first examples of anionic NSe-ligated ruthenium complexes, which were obtained from the reaction of anionic ruthenium nitrido complexes, elemental selenium, and 4-(N,N-dimethylamino)pyridine (DMAP). The structures of one of these ruthenium NSe complexes, as well as of the corresponding thionitrosyl (NS) and nitrosyl (NO) complexes, were systematically examined by X-ray diffraction analyses and theoretical calculations. In contrast to previous reports, the NSe ligand in these complexes is a better \( \pi \)-acceptor than the NO and NS ligands and exhibits a stronger \( \pi \)-influence.

Introduction

The chemistry of nitric oxide (NO) is well investigated, primarily due to the importance of NO in a biological context, e.g. in cell signalling and other physiological functions in living organisms. Accordingly, it is hardly surprising that numerous transition-metal complexes of NO have been studied in depth. Yet, the chemistry of the heavier isologues of NO, i.e., nitric sulfide (NS) and nitric selenide (NSe), has attracted less attention, as these species can only be detected in harsh environments such as low-temperature matrices. Stabilizing these fleeting species in transition-metal complexes would afford an opportunity to study the properties of these thionitrosyl (M–NS) and selenonitrosyl complexes (M–NSe) and thus broaden our understanding of the chemistry of NS and NSe.

In contrast to the chemistry of thiocarbonyl (CS) and selenocarbonyl (CSe) transition-metal complexes, that of NS and NSe complexes has been much less developed, which is probably due to the scarcity of NS and NSe complexes. The first transition-metal complexes of NS were obtained from the reaction of a molybdenum nitrido complex with elemental sulfur, and other NS complexes have also been prepared by the treatment of the corresponding transition-metal nitrido complexes with elemental sulfur or its equivalents. Moreover, reactions of metal complexes with trithiazyl chloride (N3S3Cl3) as the NS source have been reported. Following the successful synthesis of NS complexes from the corresponding nitrido complexes, a few NSe complexes were prepared by the reaction of nitrido complexes with elemental selenium, albeit that this approach is less generic for NSe than for NS. For example, cis-[Ru(N)(Cl)L2] \( (L = 2\text{-}(2,6\text{-diisopropylphenyl})\text{limino}\text{methyl}4,6\text{-dibromophenolato}) \) did not afford the corresponding NSe complex under reaction conditions similar to those for the reaction with NS.

To investigate the properties of the chalcogenonitrosyls (NE; E = O, S, Se) in transition-metal complexes, systematic studies on a series of NE complexes would be highly desirable. So far, only three series of NE complexes have been reported, which include neutral and cationic metal complexes of [Os(NE)Cl2Tp] \( (Tp = \text{hydrotris}[1\text{-pyrazolyl}]\text{borate}) \) and \([Ru(NE)\text{Cl}_3(\text{AsPh}_3)_2]\) \( (E = O, S, Se) \) and \([\text{Ir}(NE)(N(\text{CHCHP}_{\text{Bu}_2})_2)][\text{PF}_6]^\cdot\) (Fig. 1). Conversely, a series of anionic transition-metal NE complexes has not yet been reported. Examples of anionic NS complexes remain scarce, while anionic NSe complexes remain elusive. The synthesis of such a series of anionic NE \( (E = O, S, Se) \) complexes should thus be important to gain deeper insight into

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the chemistry of NE, particularly with respect to the question how the overall charge influence the properties of such NE complexes. Herein, we report the synthesis of anionic ruthenium NE (E = O, S, Se) complexes that bear tetraanionic 2-hydroxybenzamidobenzene ligands, i.e., \([\text{Ph}_4\text{P}] \left[ \text{Ru(NE)}(\text{hybebR}_1,R_2)(\text{dmap}) \right] \) (E = O, S, Se; hybeb = \(N,N'-(1,2\text{-phenylene})\)bis(2-hydroxybenzamide), \(R_1 = \text{H, Cl} \); \(R_2 = \text{H, Cl, CF}_3 \); dmap = 4-(\(N,N'\text{-dimethylamino}\)pyridine). The structures of some of these NE complexes were determined in detail by a combination of single-crystal X-ray diffraction analyses and theoretical calculations. All the Ru–NE complexes obtained in this study are classified as \{RuNE\}_6 according to the Enemark-Feltham notation.

Results and discussion

Syntheses of 2-hydroxybenzamidobenzene derivatives (\(\text{H}_4\text{hybeb}^{R_1,R_2} \))

We selected the 2-hydroxybenzamidobenzene derivatives \(\text{H}_4\text{hybeb}^{R_1,R_2} \) (1) as tetradentate ligands for the synthesis of anionic NE complexes of ruthenium, as they can be readily prepared, and offer an opportunity to study the electronic effect on the properties of the complexes. Moreover, when such ligands coordinate to transition metals, a rigid structure is usually formed. Unsubstituted \(\text{H}_4\text{hybeb}^{\text{H},\text{H}} \) (1a) was prepared in 92% yield by the \(\text{Ph}_3\text{PCl}_2\)-mediated condensation \(\text{(NaHMDS)}^{18} \) of salicylic acid and 1,2-phenylenediamine (Scheme 1), and substituted \(\text{H}_4\text{hybeb}^{\text{H},\text{Cl}} \) (1b) and \(\text{H}_4\text{hybeb}^{\text{Cl},\text{Cl}} \) (1c) were prepared in good yield under similar reaction conditions.

Unexpectedly, the attempted synthesis of \(\text{H}_4\text{hybeb} \) derivatives with a CF\(_3\) group at \(R_2 \) [1d: \(\text{H}_4\text{hybeb}^{\text{H},\text{CF}_3} \); 1e: \(\text{H}_4\text{hybeb}^{\text{Cl},\text{CF}_3} \)] failed under the conditions shown in Scheme 1. To prepare these compounds, we treated THP-protected 4-(trifluoromethyl)phenol with BuLi and ethyl chloroformate to afford ester 2 (Scheme 2).\(^{17}\) Subsequently, 2 was treated with 1,2-phenylenediamine derivatives in the presence of sodium bis(trimethylsilyl)amide (NaHMDS)\(^{18} \) to furnish the corresponding THP-protected \(\text{H}_4\text{hybeb}^{\text{R_1},\text{CF}_3} \). Finally, the THP group was removed under acidic conditions to generate 1d and 1e in good yield. The \(\text{H}_4\text{hybeb}^{\text{R_1},\text{R_2}} \) ligands 1a–e contained a small amount of solvent molecules (hexane or EtOAc) that could not be removed (Fig. S1–S4 and S7–S10, ESI†).

Syntheses of the nitrido complexes \([\text{Ph}_4\text{P}]\left[\text{Ru(N)(hybeb}^{R_1,R_2}\right]\) (3)

With \(\text{H}_4\text{hybeb}^{\text{R_1},\text{R_2}} \) ligands 1a–e in hand, we focused on the preparation of nitrido complexes that bear tetraanionic hybeb\(^{R_1,R_2}\) ligands as precursors for the synthesis of the corresponding NS and NSe complexes. Based on a modified literature procedure (Scheme 3),\(^{19} \) the reaction of 1a and \([\text{Bu}_4\text{N}]\left[\text{Ru(N)}\right]^{20} \) in the presence of an excess 2,6-lutidine in a mixture of MeOH/THF (3:1, v/v) afforded the tetraethylammonium salt \([\text{Bu}_4\text{N}]\left[\text{Ru(N)}\right]^{20} \) which was treated with \([\text{Ph}_4\text{P}]\) Br to afford nitrido complex \([\text{Ph}_4\text{P}]\left[\text{Ru(N)}\right]^{20} \) (3a) in 72% yield. The cation metathesis was necessary to obtain
single crystals suitable for an X-ray diffraction analysis. Nitrido complexes 3b–e were prepared in a similar fashion and obtained as orange/red crystals, which are air- and moisture-stable in both the solid state and in solution.

The molecular structure of nitrido complex [Ph₄P][Ru(N)\(\text{hybeb}^{1H,CF_3}\)] (3d) was unambiguously determined by a single-crystal X-ray diffraction analysis. Complex 3d exhibits a distorted square-pyramidal coordination geometry in which the nitride ligand is located at the apical position (Fig. 2). Based on this analysis, the ruthenium center in 3 exhibits a 16-electron configuration with the formal oxidation state of +6. The length of the Ru1–N1 bond in 3d (1.6040(15) Å) falls in the range of previously reported five-coordinate anionic ruthenium nitrido complexes such as [Na(dme)][Ru(N)(meso-octamethylporphyrinogen)] (1.569(6) Å (ref. 21)), [Bu₄N][Ru(N)(hybeb)\(^{1H,1H}\)] (1.594(4) Å (ref. 19a)), [Bu₄N][Ru(N)(O₂C₆H₄)\(_2\)] (1.603(4) Å (ref. 22)), and [Bu₄N][Ru(N)(S₂C₆H₄)\(_2\)] (1.613(5) Å (ref. 23)).

Subsequently, we synthesized NS complexes via the reaction of 3 with elemental sulfur (Table 1). When 3a was treated at room temperature with 1/8 \(S₈\) (10 equiv.) in the presence of DMAP (10 equiv.), the colour of the mixture gradually turned from orange to black. The reaction reached completion after 40 h, and the NS complex [Ph₄P][Ru(NS)(hybeb\(^{1H,1H}\))(dmap)] (4a) was isolated in 67% yield in the form of black plates (entry 1). An acceleration of the reaction progress was observed when nitrido complexes with electron-withdrawing groups on the hybeb ligands were used (entries 2 and 3). After 0.5–1.5 h, the reactions of 3b and 3c with sulfur and DMAP smoothly furnished good yields of 4b and 4c, respectively. The reactivity of CF₃-substituted complexes 3d and 3e was very high, and the reactions were complete after 15 min (entries 4 and 5). The formation of NS complexes was not observed when the reaction was carried out in the absence of DMAP.

Two possible pathways can be considered for the formation of these NS complexes. A sulfurization of the nitrido complexes would most likely result in the formation of unsoluble intermediates of the type [Ph₄P][Ru(NS)(hybeb\(^{1H,1H}\))],\(^{14c}\) followed by coordination of DMAP to stabilize these unsaturated complexes, which would lead to the coordinatively saturated product 4. Alternatively, the reactivity of the nitrido ligand in 3 would be increased upon coordination of DMAP to the nitrido ligand prior to the formation of the nitrogen–sulfur bond.\(^{6d}\) In order to examine the pathway and the role of DMAP toward the formation of 4, we monitored the reactions of 3 with (a) sulfur in the absence of DMAP, and with (b) DMAP in the absence of sulfur by \(^1H\) NMR spectroscopy. However, changes were not observed in these \(^1H\) NMR spectra: the mechanism of this reaction and the role of DMAP remains unclear at this stage.

The molecular structure of 4d was unequivocally determined by a single-crystal X-ray diffraction analysis (Fig. 3). The six-coordinate octahedral geometry of the ruthenium center

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**Table 1** Syntheses of NS complexes 4a–e

| Entry | 3 | R\(^1\) | R\(^2\) | Time (h) | Product | Yield (%) |
|-------|---|--------|--------|---------|---------|-----------|
| 1     | 3a | H      | H      | 40      | 4a      | 67        |
| 2     | 3b | H      | Cl     | 1.5     | 4b      | 72        |
| 3     | 3c | Cl     | Cl     | 0.5     | 4c      | 73        |
| 4     | 3d | H      | CF₃    | 0.25    | 4d      | 74        |
| 5     | 3e | Cl     | CF₃    | 0.25    | 4e      | 69        |

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**Fig. 2** Molecular structure of the anionic part of nitrido complex 3d. Hydrogen atoms are omitted for clarity and only selected atoms are labelled. Selected bond length (Å): Ru1–N1 1.6040(15).

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**Scheme 3** Synthesis of nitrido complexes 3.
was confirmed, whereby the DMAP ligand is located trans to the NS ligand. The Ru–N–S angle is 171.0(3)/172.2(3)°, which confirms a terminal coordination and linear alignment of the NS ligand. The N–S bond length in 4d [1.511(4)/1.516(6)] is similar to those in other NS complexes such as mer-[Ru(NS)Cl4(AsPh3)2] (1.502(4) Å (ref. 7d)), [Ph4P][Ru(NS)Cl4(H2O)] (1.504(4) Å (ref. 14a)), [Ph4P][Os(NS)Cl4(H2O)] (1.514(5) Å (ref. 14b)), and [[Ir(NS)(N(CH2CHPh2)2)]][PF6] (1.522(2) Å (ref. 7c)).

Syntheses of the NSe complexes [Ph4P][Ru(NSe)(hybebR1,R2)(dmap)] (5)

Next, we attempted to synthesize NSe complexes via a similar approach, using elemental selenium instead of sulfur (Table 2). As expected, in accordance with the aforementioned low reactivity of 3a and 3b, the corresponding NSe complexes [Ph4P][Ru(NSe)(hybebR1,R2)(dmap)] (5a: R1 = R2 = H; 5b: R1 = H, R2 = Cl) were not formed (entries 1 and 2). The reaction of 3c with selenium and DMAP proceeded sluggishly and led only to the formation of an equilibrium mixture between 3c and the product [Ph4P][Ru(NSe)(hybebCl,Cl)(dmap)] (5c) in a ratio of 60 : 40 after 36 h. From the mixture, 5c could be isolated in 38% yield in the form of black microcrystals (entry 3). Considering the electrophilic nature of the nitrido ligand in high-valent ruthenium complexes,24 we anticipated that hybebR1,CF3 ligands with a CF3 group should enhance the reactivity of the nitrido complexes. In fact, when 3d and 3e were treated with selenium in the presence of DMAP, full conversion of 3d and 3e was observed after 12 h. The corresponding anionic ruthenium NSe complexes [Ph4P][Ru(NSe)(hybebR1,CF3)(dmap)] (5d) and [Ph4P][Ru(NSe)(hybebCl,CF3)(dmap)] (5e) were obtained in 46% and 48% yields, respectively (entries 4 and 5), and these represent the first examples of anionic transition-metal NSe complexes.

NSe complexes 5c–e are stable in the solid state under air and at low temperature in solution. However, 5c–e decompose in solution at room temperature, even under an atmosphere of argon. When a CDCl3 solution of 5d was kept standing at room temperature (Scheme 4), the gradual liberation of DMAP under concomitant formation of nitrido complex 3d and a black precipitate (presumably elemental selenium) was observed. The addition of DMAP (10 equiv.) or selenium (10 equiv.) to the CDCl3 solution inhibited the decomposition, and only ca. 40% of 5d was converted into 3d after 24 h. An intermediate was not observed in the 1H NMR spectrum of the reaction mixture. Due to the instability of the NSe complexes, it was necessary to work up the reaction rapidly, and the recrystallization had to be conducted at low temperature.

The molecular structure of 5d was determined by crystallographic measurements (Fig. 4). Structural features similar to...
those of NS complex 4d were observed for NSe complex 5d, which exhibits a six-coordinate octahedral coordination geometry with a linear Ru–N–Se linkage [171.2(3)/169.9(3)°] and short Ru–NSe and N–Se distances. The N–Se bond distance in 5d [1.670(4)/1.671(4) Å] is longer than those in [Os(NSe)Cl2Tp] (1.629(10) Å (ref. 7a)) and mer-[Ru(NSe)Cl2(AsPh3)2] (1.650(3) Å (ref. 7d)), but similar to that in [[Ir(NSe)3(N(CH2)2Ph)2]2][PF6] (1.678(4) Å (ref. 7b)).

Encouraged by the successful synthesis of these NSe complexes, we further studied the synthesis of hitherto unprecedented tellurium analogues of NO complexes, i.e., telluronitrosyl (NTe) complexes. However, all attempts to synthesize NTe complexes via the reaction of 3 and elemental tellurium in the presence of pyridines failed, which might be attributed to the low solubility of elemental tellurium in common organic solvents. It should be noted here that this result is consistent with previously reported results on the reactions of osmium and neutral ruthenium nitrido complexes.7c,7d

**Synthesis of the NO complex [Ph4P][Ru(NO)hybebH,CF3](dmap) (6)**

To compare the structures of NS complex 4d and NSe complex 5d with the corresponding NO complex [Ph4P][Ru(NO)(hybebH,CF3)](dmap) (6), we attempted to synthesize 6 via the oxidation of 3d using Me2NO,17,18 H2O2 or O2, with Et3B·DMAP,19 but all of these attempts were unsuccessful. Therefore, 6 was synthesized according to a modified literature method (Scheme 5).20 1d was treated with sodium hydride, followed by [Ru(NO)Cl2]29 and DMAP to generate the sodium salt Na[Ru(NO)(hybebH,CF3)](dmap). A subsequent cation metathesis with [Ph4P]Br afforded the targeted NO complex 6 in the form of black crystals (34% yield over two steps).

In its IR spectrum, NO complex 6 exhibits a ν(NO) absorption at 1810 cm⁻¹, while the ν(NS) and the ν(NSe) bands of 4d and 5d, respectively could not be clearly identified due to the overlap with vibrational stretches arising from the hybebH,CF3 ligand and the [Ph4P]⁺ ion. The molecular structure of 6 was determined by a single-crystal X-ray diffraction analysis (Fig. 5). The alignment of the Ru–N–O moiety is almost linear [174.9(2)/177.27(19)°] with an N–O bond distance of 1.144(3)/1.149(3) Å, which is similar to that in other NO complexes such as mer-[Ru(NO)Cl2(AsPh3)2] (1.151(9) Å (ref. 12)) and [[Ir(NO)3(N(CH2)2Ph)2][PF6] (1.168(3) Å (ref. 7c)), but shorter than that in [Os(NO)2Cl2(Tp)] (1.19(4) Å (ref. 7a)).

**Properties of a series of NE complexes**

The selected metric parameters, Wiberg bond indices (WBI) and the natural population analysis (NPA) charge distributions for a series of the obtained NE complexes (E = O, 6; E = S, 4d; E = Se, 5d) are summarized in Table 3 together with those of nitrido complex 3d for comparison. The Ru–NE bond

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**Fig. 4** Molecular structure of the anionic part of NSe complex 5d. Only one of the two independent anions per unit cell is shown. Hydrogen atoms are omitted for clarity and only selected atoms are labelled. Selected bond lengths (Å) and angles (°): Se1–N1 1.670(4); N1–Ru1 1.734(4); Ru1–N2 2.173(4); Se1–N1–Ru1 171.2(3); N1–Ru1–N2 173.79(16).

**Scheme 5** Synthesis of NO complex 6.

**Fig. 5** Molecular structure of the anionic part of NO complex 6. Only one of the two independent anions per unit cell is shown. Hydrogen atoms are omitted for clarity and only selected atoms are labelled. Selected bond lengths (Å) and angles (°): O1–N1 1.144(3); N1–Ru1 1.752(2); Ru1–N2 2.1325(19); O1–N1–Ru1 174.9(2); N1–Ru1–N2 176.57(8).

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**Table 3** Properties of a series of NE complexes.
### Table 3

| E        | Nothing (3d) | O (6) | S (4d) | Se (5d) |
|----------|--------------|-------|--------|---------|
| Bond angles |              |       |        |         |
| dmap-Ru–N | 176.57[8]    | 173.53(19) | 173.79(16) |         |
| Ru–N–E   | 174.9(2)     | 171.0(5) | 171.2(3) |         |
| Ru–NE    | 177.27(19)   | 172.2(3) | 169.9(3) |         |
| Bond lengths |            |       |        |         |
| Ru–E     | 1.144(3)     | 1.511(4) | 1.670(4) |         |
| Ru–NE    | 1.752(2)     | 1.746(4) | 1.734(4) |         |
| N(dmap)–Ru | 2.1325(19) | 2.155(4) | 2.173(4) |         |
| Wiberg bond index |      |       |        |         |
| Ru–E     | 1.8352       | 1.6889 | 1.5792 |         |
| Ru–NE    | 2.3049       | 1.4144 | 1.3629 | 1.4072  |
| N(dmap)–Ru | 0.3154   | 0.2881 | 0.2753 |         |
| NPA charges |            |       |        |         |
| Ru       | 1.111        | 0.883 | 0.909  | 1.006   |
| N (NE)   | –0.065       | 0.401 | –0.348 | –0.409  |
| E        | –0.224       | 0.370 | 0.390  |         |

a Distances and bond angles of both molecules per unit cell are shown. The calculation of WBI and NPA charges were performed at the B3PW91/SBKJC(d) level of theory.

in 6, 4d, and 5d and are longer compared to the Ru–N bond length in 3d [Ru–N (3d): 1.6040(15) Å; Ru–NO (6): 1.75 Å (mean); Ru–NS (4d): 1.75 Å (mean); Ru–NSe (5d): 1.73 Å (mean)]. The WBI of the Ru–NE bond in 6, 4d, and 5d decrease compared to the Ru–N bond in 3d. Considering the previously reported WBI for nitrido complex \([\text{Ir(N)(N(CHCHP}3\text{Bu}2)_3])\lbrack\text{PF}_6\rbrack^3\) and iridium NE complexes \([\text{Ir(N)(N(CHCHP}3\text{Bu}2)_3])\lbrack\text{PF}_6\rbrack^3\) the Ru–N triple bond in 3d should turn into a double bond and the nitrido ligand bonds with chalcogen atoms to generate 4d and 5d.

The Ru–NE bond lengths are comparable to the sum of the covalent double-bond radii (Ru= N: 1.74 Å),\textsuperscript{27} and the WBI of double-bound character bond for the Ru–N bond in the NE complexes (Ru–NO: 1.4144; Ru–NS: 1.3629; Ru–NSe: 1.4072). The N–E bond lengths [N–O: 1.15 Å (mean); N–S: 1.51 Å (mean); N–Se: 1.67 Å (mean)] are longer than the calculated covalent triple-bond radii (N–O: 1.07 Å; N–S: 1.49 Å; N–Se: 1.61 Å),\textsuperscript{27} but similar to the corresponding double-bond radii (N–O: 1.17 Å; N–S: 1.54 Å; N–Se: 1.67 Å).\textsuperscript{27} Taking the WBI into account (N–O: 1.8332; N–S: 1.6889; N–Se: 1.5792), the N–E bonds in 4d, 5d, and 6 exhibit double-bond character.

The obtained data revealed characteristic features of the NE ligands, i.e., the order of π-back donation and trans influence of the NE ligands. The length of the Ru–NSe bond in 5d slightly decreases compared to the corresponding Ru–NO and Ru–NS bonds in 6 and 4d [Ru–NO (6): 1.75 Å (mean); Ru–NS (4d): 1.75 Å (mean); Ru–NSe (5d): 1.73 Å (mean)]. This result could be explained in terms of an increased π-back donation from the ruthenium center to the NSe ligand, which appears to reflect a better π-accepting character of the NSe ligand relative to the lighter chalcogen homologues. This trend is consistent with previously reported estimations based on theoretical calculations.\textsuperscript{28} However, it should also be noted here that this trend contradicts previous studies on complexes such as \([\text{Cr(NE)(OH}2])_3]^{2+},\textsuperscript{29} [\text{Os(NE)Cl}2\text{Tp}]^{7+}\) or \([\text{Ru(NE)Cl}3(\text{AsPh}3)_2]^{7,12}\) in which the respective NO ligands appear to be better π-acceptors than the NS and NSe ligands, as well as the studies on \([\text{Ir(NE)(N(CHCHP}3\text{Bu}2)_3])\lbrack\text{PF}_6\rbrack^{7c,11}\) where the π-acceptor ability of the NS ligand is lower than that of the NO and NSe ligands.\textsuperscript{30}

The aforementioned π-accepting nature of the NSe ligand in 5d was corroborated by the NPA charge distribution on the RuNSe moiety. The positive charge on the ruthenium atom is greater in 5d than in 6 and 4d [RuNO (6): 0.883; RuNS (4d): 0.980; RuNSe (5d): 1.006], while the negative charge on the nitrogen atom of the NE ligand is greater in 5d than in 6 and 4d [RuNO (6): 0.401; RuNS (4d): –0.348; RuNSe (5d): –0.409]. Therefore, the NSe ligand appears to be a better π-acceptor than the NO and NS ligands.

The NSe ligand in 5d exhibits a stronger trans influence than the NO and NS ligands in 6 and 4d, respectively. The N(dmap)–RuNSe bond length slightly increases in the order E = O < S < Se [N–RuNO (6): 2.13 Å (mean); N–RuNS (4d): 2.16 Å (mean); N–RuNSe (5d): 2.17 Å (mean)], and the corresponding WBI of N(dmap)–Ru decrease in the same order [N–RuNO (6): 0.3154; N–RuNS (4d): 0.2880; N–RuNSe (5d): 0.2753]. Considering the order of trans influence, the NSe ligand appears to exhibit a better σ-donating ability than the lighter chalcogen homologues. This trend is consistent with the data obtained for \([\text{Ru(NO)}\text{Cl}3(\text{AsPh}3)_2]^{6}\) wherein the NS and NSe ligands exert a stronger trans influence than the NO ligand.

### Conclusions

Anionic ruthenium NS and NSe complexes were synthesized via the reaction of the corresponding nitrido complexes with elemental sulfur or selenium in the presence of DMAP, which provided the first anionic NSe complexes. The structural properties of these NE [E = O, S, Se] complexes were determined by single-crystal X-ray diffraction analyses and theoretical calculations, which revealed that in these complexes, the NSe ligand is the best π-acceptor with the strongest trans influence.

### Experimental

#### General considerations

Unless otherwise noted, all reactions were performed in oven-dried (110 °C) glassware under an atmosphere of dry argon (balloon). Reagents were obtained from common commercial sources and used as received. Anhydrous solvents for reactions were purchased from Kanto Chemical Co., Inc. and used as received. Solvents for workup, column chromatography, and recrystallization were of ‘reagent grade’. The following com-
pounds were prepared as described in the literature: [Bu₄N][Ru(N[C]₁₇₃)₂₆ tetraydro-2-[4-(trifluoromethyl)phenoxy]-2H-pyranyl-1,₁₇ and [Ru(NO)[C]₁₇₃].₂₆ Commercially available sulfur powder was recrystallized from benzene prior to use. TLC was performed on Merck TLC silica gel 60 F₃₅₈ plates. Silica gel used for flash column chromatography (silica gel 60N; spherical; neutral; 40–50 μm) was obtained from Kanto Chemical Co., Inc. Alumina used for column chromatography (Aluminium Oxide 90; active neutral; 63–200 μm) was obtained from Merck.

Melting points are uncorrected. IR spectra were recorded using a diamond-attenuated total reflectance (ATR) unit and are corrected. NMR spectra were recorded at ambient temperature on a JEOL ECZ 400 spectrometer (1H: 400 MHz; 13C: 100 MHz; 19F: 375 MHz; 31P: 161 MHz). Chemical shifts are reported in δ, relative to residual 1H and 13C{1H} signals of C6D₆ (δ = 7.24; 13C{1H}: 77.16) and (CD3)2SO with 0.03% v/v TMS (1H: δ = 2.50; 13C{1H}: δ = 39.52) or to the external 19F signal (δ = −164.9) or 31P{1H} signal of H3PO4 (δ = 0.00). ESI-HRMS were obtained on an FT-ICR mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 furnace elemental analyzer.

General procedure for the syntheses of N,N’(1,2-phenylene)bis(2-hydroxybenzamide) and derivatives (1a–c)

A previously reported procedure was slightly modified.₁³ Ph3PCl₂ (4.66 g, 14.0 mmol) were used as reagents. EtOAc/hexane = 1 : 1 was used as the eluent after Ph3PO was removed. 1a.0.1EtOAc was isolated as white solid (1.14 g, 2.68 mmol, 89% yield). 1H NMR ((CD3)2SO with 0.03% v/v TMS): δ 11.81 (s, 2H), 10.53 (s, 2H), 8.16 (s, 2H), 7.99 (d, J = 2.6 Hz, 2H), 7.49 (dd, J = 8.8, 2.7 Hz, 2H), 7.03 (d, J = 8.9 Hz, 2H), 4.02 (q, J = 7.1, 2.9 Hz, 2H), 3.60 (d, J = 7.1 Hz, 3H). 13C{1H} NMR ((CD3)2SO with 0.03% v/v TMS): δ 164.6, 156.6, 133.6, 131.0, 129.3, 127.4, 126.2, 132.2, 119.2, 118.6. HRMS (ESI−) m/z: [M – H]− 415.0254; found: 415.0258. IR (ATR, cm−¹): νNH = 3311, νCO = 1645. mp: 248.6–251.4 °C.

Synthesis of ethyl 2-[(tetrahydro-2H-pyran-2-yl)oxy]-5-(trifluoromethyl)benzoate (2). A previously reported procedure was used to prepare 2.₁⁶ BuLi (1.55 M solution in hexane, 0.79 mL, 1.22 mmol, 1.1 equiv.) was added dropwise to a THF (6.7 mL) solution of tetraydro-2-[4-(trifluoromethyl)phenox]-2H-pyranyl (0.783 mg, 1.11 mmol, 1.0 equiv.) at −78 °C, where the mixture was stirred for 1 h. The mixture was then transferred into a −78 °C solution of ethyl chloroformate (0.132 g, 1.22 mmol, 1.1 equiv.) in THF (1.9 mL), allowed to warm to room temperature, where it was stirred for 2 h. The resulting mixture was added into water and extracted with EtOAc. The organic layer was treated with water and brine, dried over anhydrous Na2SO4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane = 1:10, v/v) to afford 2 as a colourless oil (0.251 g, 0.789 mmol, 71% yield). 1H NMR (CDCl3): δ 8.02 (d, J = 2.3 Hz, 1H), 7.63 (dd, J = 8.9, 2.5 Hz, 1H), 7.29 (d, J = 8.7 Hz, 1H), 5.58 (t, J = 2.7 Hz, 1H), 4.36 (qd, J = 7.1, 1.9 Hz, 2H), 3.83 (dd, J = 11.2, 3.0 Hz, 1H), 3.60 (d, J = 11.0 Hz, 1H), 1.61–2.04 (m, 6H), 1.37 (t, J = 7.1 Hz, 3H). 13C{1H} NMR (CDCl3): δ 165.5, 158.7, 130.0 (dd, J = 3.9, 2.9 Hz, 128.8 (q, J = 3.9 Hz, 124.0 (q, J = 271.7 Hz), 123.2 (q, J = 33.7 Hz), 121.8, 116.2, 96.6, 61.9, 61.4, 30.1, 25.2, 18.1, 14.4. 19F NMR (CDCl3): δ −60.3. HRMS (ESI−) m/z: [M + Na]⁺ calculated for C₁₄H₁₅O₆F₃Na⁺: 341.0974; found 341.0971. IR (ATR, cm−¹): νCO = 1732.

General procedure for the syntheses of N,N’(1,2-phenylene)bis(5-trifluoromethyl-2-hydroxybenzamide) derivatives 1d and 1e

A previous reported procedure was slightly modified.₁₈ NaHMDS (1.0 M solution in hexane, 2.0 equiv.) was added dropwise to a THF (2.0 mL) solution of 2 (1.0 equiv.) and phenylenediamine (0.45 equiv.) at 0 °C. The mixture was stirred for 5 min at 0 °C before it was allowed to warm to room temperature, where it was stirred for 16 h. The resulting mixture was added into a saturated aqueous solution of NH₄Cl and extracted with EtOAc. The organic layer was treated with
water and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo* to leave a red residue.

This residue was dissolved in THF (1.0 mL) and 2 M HCl (1.9 mL, 2.2 equiv.) was added. The mixture was stirred at room temperature for 8 h. The resulting mixture was added to a saturated aqueous solution of NaHCO₃ and extracted with EtOAc. The organic layer was treated with water and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (EtOAC/hexane) to afford the product.

**N,N′-(1,2-Phenylenedi)-bis(5-trifluoromethyl-2-hydroxybenzamide)-0.2EtOAc (1d-0.2EtOAc).**

2 (0.541 g, 1.70 mmol) and 1,2-phenylenediamine (0.0827 g, 0.765 mmol) were used as reagents. EtOAC/hexane = 1:1 was used as the eluent. 

1d-0.2EtOAc was isolated as a pale yellow solid (0.258 g, 0.514 mmol, 69% yield over 2 steps).  

1H NMR (CDCl₃) δ 7.75 (s, 2H), 116.8, 112.3, 7.38 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 7.1 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 4.03 (q, J = 7.1, 0.4 Hz, EtOAc), 1.99 (s, 0.6H, EtOAc), 1.17 (t, J = 7.1, 0.6 Hz, EtOAc). 13C{¹H} NMR (CDCl₃) δ 170.4 (EtOAc), 164.9, 161.1, 131.0, 130.4, 127.5, 126.1, 125.6, 124.3 (q, J = 271.7 Hz), 120.1 (q, J = 32.8 Hz), 118.3, 117.8, 59.8 (EtOAc), 20.7 (EtOAc), 14.1 (EtOAc).

IR (ATR, cm⁻¹): νmax = 3324, νCO = 1615. mp: 234.2–237.0 °C.

**N,N′-(4,5-Dichloro-1,2-phenylene)-bis(5-trifluoromethyl-2-hydroxybenzamide)-0.1EtOAc (1e-0.1EtOAc).**

2 (0.541 g, 1.70 mmol) and 4,5-dichloro-1,2-phenylenediamine (0.135 g, 0.765 mmol) were used as reagents. EtOAC/hexane = 1:1 was used as the eluent.  

1e-0.1EtOAc was isolated as a pale yellow solid (0.284 g, 0.505 mmol, 66% yield over 2 steps).  

1H NMR (CDCl₃) δ 170.2 (EtOAc), 164.8, 161.1, 131.0, 130.4, 127.5, 126.1, 125.6, 124.3 (q, J = 271.7 Hz), 120.1 (q, J = 32.8 Hz), 118.3, 117.8, 59.8 (EtOAc), 20.7 (EtOAc), 14.1 (EtOAc). 13C{¹H} NMR (CDCl₃) δ 170.2 (EtOAc), 164.8, 161.1, 131.0, 130.4, 127.5, 126.1, 125.6, 124.3 (q, J = 271.7 Hz), 120.1 (q, J = 32.8 Hz), 118.3, 117.8, 59.8 (EtOAc), 20.7 (EtOAc), 14.1 (EtOAc).

IR (ATR, cm⁻¹): νmax = 3324, νCO = 1615. mp: 234.2–237.0 °C.

General procedure for the synthesis of nitroben complexes

**[Ph₄P][Ru(nhybeb⁴⁺n)] (3).**

Nitro complexes 3 were synthesized according to a modified literature procedure.  

**[Ph₄P][Ru(nhybeb⁴⁺n)] (3).**

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Nitro complexes 3 were synthesized according to a modified literature procedure.  

**[Ph₄P][Ru(nhybeb⁴⁺n)] (3).**

Nitro complexes 3 were synthesized according to a modified literature procedure.
Dalton Transactions

169.1, 168.0, 145.6, 135.7 (d, J = 2.9 Hz), 134.2 (d, J = 9.6 Hz), 130.6 (d, J = 12.5 Hz), 130.0 (d, J = 3.9 Hz), 125.0 (q, J = 270.7 Hz), 128.4 (d, J = 2.9 Hz), 124.5, 122.8, 121.8, 120.6 (q, J = 32.8 Hz), 120.9, 117.7, 116.9. \( ^{31}P \) NMR (CDCl\(_3\)): \( \delta = 59.3. \) \( ^{31}P(\text{H}) \) NMR (CDCl\(_3\)): \( \delta = 23.7. \) Anal. calcld for C\(_{44}H_{30}Cl_{4}N_{3}O_{4}PRu (3d): C, 59.10; H, 3.23; N, 4.50. Found: C, 59.47; H, 2.99; N, 4.50.

\( ^{1}H \) NMR (CDCl\(_3\)): 0.369 mmol, 74% yield from 0.360 mmol, 72% yield). \( ^{1}H \) NMR (CDCl\(_3\)): \( \delta = 9.22 (s, 2H), 8.13 (d, J = 2.7 Hz, 2H), 7.76–7.80 (m, 4H), 7.60–7.65 (m, 10H), 7.48–7.53 (m, 8H), 7.01 (d, J = 8.7 Hz, 2H), 6.92 (dd, J = 8.9, 3.0 Hz, 2H), 5.93 (d, J = 7.1 Hz, 2H), 3.18 (s, 1.5H, MTBE), 2.69 (s, 6H), 1.16 (s, 4.5H, MTBE). \( ^{31}P \) (\text{H}) NMR (CDCl\(_3\)): \( \delta = 167.9, 167.2, 154.5, 147.6, 145.8, 135.9 (d, J = 3.1 Hz), 134.4 (d, J = 9.6 Hz), 132.1, 130.8 (d, J = 12.5 Hz), 125.0, 123.9, 126.3, 122.7, 119.5, 117.5 (d, J = 89.6 Hz), 105.9, 72.8 (MTBE), 49.6 (MTBE), 39.0, 27.1 (MTBE). \( ^{3}P \) (\text{H}) NMR (CDCl\(_3\)): \( \delta = 23.8. \) Anal. calcld for C\(_{53,3}H_{44}Cl_{4}N_{5}O_{4}PRuS (4c): C, 56.62; H, 4.00; N, 6.48. Found: C, 56.26; H, 3.77; N, 6.08.

\[ \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{Cl,c}})\text{)(dmap)}] (3e) \] \( \text{The tetrabutylammonium salt was synthesized from 1e-0.1EtOAc (0.281 g, 0.500 mmol) in the first step. Ph}_2\text{PBr (0.164 g, 0.391 mmol) was used in the second step. The product was isolated as red crystals (0.370 g, 74% yield from 0.369 mmol).} \]

\[ \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{Cl,c}})\text{)(dmap)}] (3d) \] \( \text{The product was isolated as black crystals (0.402 g, 0.369 mmol, 74% yield).} \]

\[ \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4d) \] \( \text{The product was isolated as black crystals (0.414 g, 0.365 mmol, 73% yield).} \]

\[ \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4a) \] \( \text{The product was isolated as black crystals (0.420 g, 0.369 mmol, 74% yield).} \]

\[ \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4e) \] \( \text{The product was isolated as black crystals (0.402 g, 0.369 mmol, 74% yield).} \]

\[ \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4b) \] \( \text{The product was isolated as black crystals (0.370 g, 0.369 mmol, 72% yield).} \]

\[ \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4c) \] \( \text{The product was isolated as black crystals (0.420 g, 0.369 mmol, 74% yield).} \]

General procedure for the syntheses of NS complexes \( \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4a) \] \( \text{The product was isolated as black crystals (0.420 g, 0.369 mmol, 74% yield).} \]

General procedure for the syntheses of NS complexes \( \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4b) \] \( \text{The product was isolated as black crystals (0.420 g, 0.369 mmol, 74% yield).} \]

General procedure for the syntheses of NS complexes \( \text{Ph}_2\text{P}[\text{Ru(N}(\text{hybeb}^{\text{H}})\text{)(dmap)}] (4c) \] \( \text{The product was isolated as black crystals (0.420 g, 0.369 mmol, 74% yield).} \]

A 30 mL two-necked flask containing grey selenium powder (0.434 g, 2.00 mmol) was used. After heating under vacuum, before argon gas was introduced. In a separate flask, nitrido complex 3 (0.500 mmol, 10 equiv.) and DMAP (0.611 g, 5.00 mmol, 10 equiv.) were dissolved in MTBE/CH\(_2\)Cl\(_2\) (15 mL: 1 mL) at room temperature. The resulting solution was added to the flask containing the dried selenium, and the

Paper

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mixture was stirred at room temperature for the reaction time shown in Table 2. The solvent was removed in vacuo to leave a black residue. During the subsequent manipulations, the temperature of the solution containing the product should be kept below 0 °C. To remove the selenium powder, the residue was suspended at 0 °C in CH2Cl2 and filtered through a pad of Celite into a glass tube that was kept at 0 °C. The filtrate was layered with MTBE and stored in a refrigerator (0 °C) for one day to afford 5 as black crystals, which were collected by suction filtration or decantation, and dried under vacuum.

During the measurements of the 13C{1H} NMR spectra, 5c-e decomposed to generate nitrido complexes 3c-e, DMAP, and selenium. For this reason, the 13C{1H} NMR spectra exhibit signals of 5c-e together with those of 3c and DMAP (Fig. S32, S34, and S36, ESIF†).

\[ \text{[Ph}_4\text{P][Ru(NSe)(hybebCl,Cl)(dmap)]·0.5MTBE (5c·0.5MTBE).} \]

\[ \text{[Ph}_4\text{P][Ru(NSe)(hybebH,CF}_3\text{)(dmap)]·0.5MTBE (5d·0.5MTBE).} \]

\[ \text{[Ph}_4\text{P][Ru(NO)(hybebH,CF}_3\text{)(dmap)] (6).} \]

Synthesis of NO complex \([\text{Ph}_4\text{P][Ru(NO)(hybebH,CF}_3\text{)(dmap)] (6)} \]

Initially, a previously reported procedure was modified. A solution of 1d·0.1EtOAc (0.178 g, 0.360 mmol, 1.0 equiv.) in DMF (12 mL) was added to NaH, and the mixture was stirred for 0.5 h. The colour of the mixture changed from yellow to brown. The mixture was then transferred to a DMF (5 mL) solution of \([\text{Ru(NOCl}_3]\) (0.0855 g, 0.360 mmol, 1.0 equiv.) and DMAP (0.0440 g, 0.360 mmol, 1.0 equiv.) in vacuo. The mixture was stirred under reflux for 2 h, before the solvent was removed by distillation. The black residue was dissolved in acetonitrile and filtered, before the filtrate was concentrated in vacuo. The crude product was purified by recrystallization from acetone/MTBE to yield the sodium salt as a black solid.

Next, a solution of \([\text{Ph}_4\text{P][Br (0.0717 g, 0.171 mmol, 1.0 equiv.) in CH}_2\text{Cl}_2 (3 mL)} \]

was used. The reaction reached completion within 36 h. The mixture was filtered, before the filtrate was concentrated in vacuo. The mixture was washed with MTBE to yield the sodium salt as a black solid.

X-ray diffraction studies

All X-ray diffraction data were collected at −173 °C on a Bruker Apex II Ultra X-ray diffractometer equipped with a Mo-Kα radiation (λ = 0.71073 Å) source. Intensity data were processed using the Apex3 software suite. The solution of the structures and the corresponding refinements were carried out using the Yadokari-XG13 graphical interface. The positions of the non-hydrogen atoms were determined by using the SHELXTL program and refined on \( F^2 \) by full-matrix least-squares techniques using the SHELXL-2018 program. All non-hydrogen atoms were refined with anisotropic thermal parameters, while all hydrogen atoms were placed using AFIX instructions.
Details of the diffraction data are summarized in Tables S1–S4 (ESI†). For 4d and 5d, the structures were refined as an inversion twin. Although two residual peaks slightly above 1 e Å⁻³ were observed in the final difference map, these have no chemical meaning.

**Computational details**

All density functional theory (DFT) calculations were performed using the Gaussian 09 package. The computers used in this study are part of the computer facilities of the Academic Center for Computing Media Studies (ACCMS) at Kyoto University (Japan). The geometries of the anionic part of 4d, 5d, and 6 were fully optimized using the B3PW91 density functional with the effective core potential (ECP) proposed by Stevens et al., with double-ζ polarization functions, which is denoted SBKJC(d) in this paper. Vibrational analyses based on force constant matrices (Hessians) were carried out at the stationary points in order to identify minima (all positive constants), transition states (one negative force constant), or higher-order saddle points. NAO-based Wiberg bond indices were observed in the final di...
