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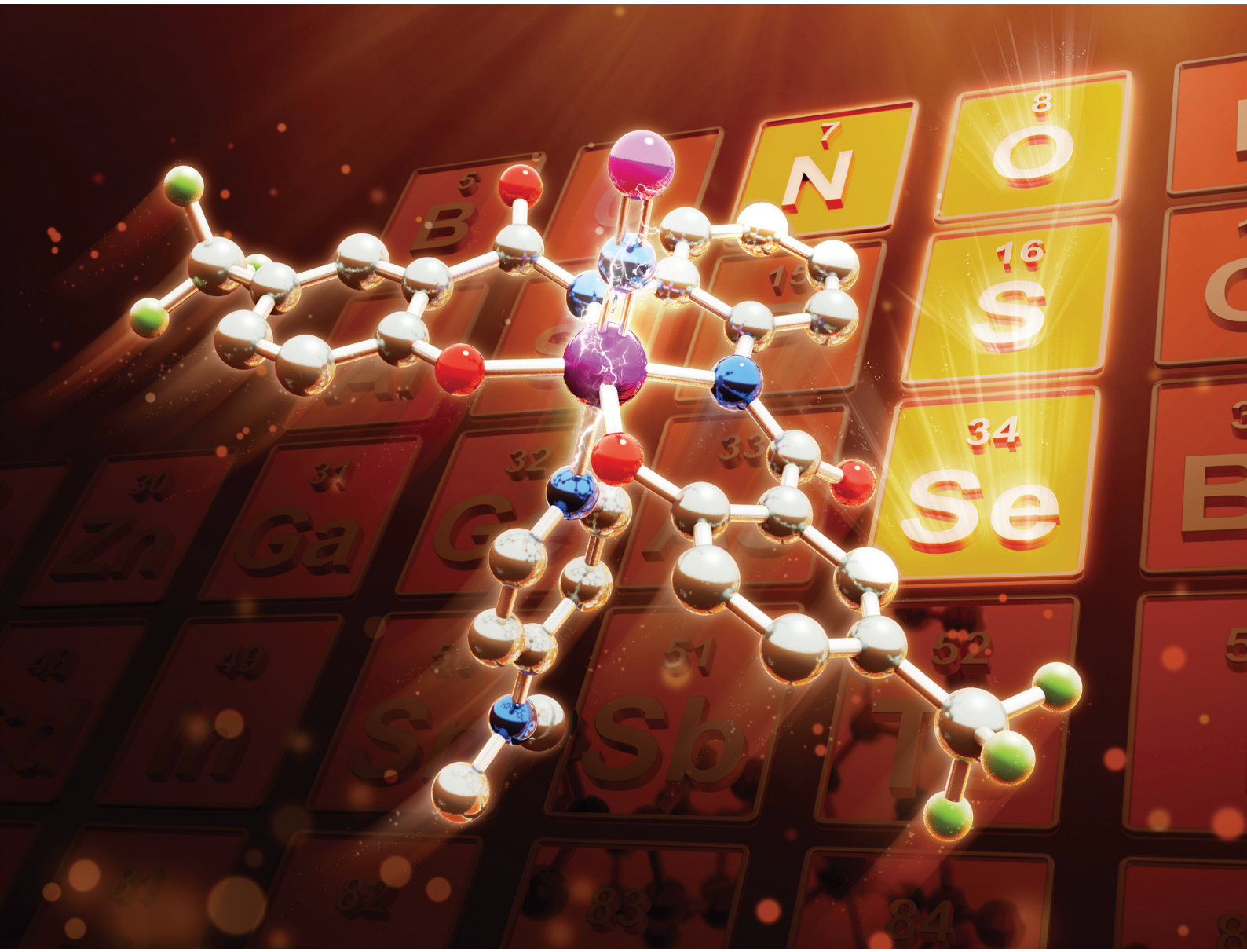

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Synthesis and properties of anionic ruthenium thionitrosyl and selenonitrosyl complexes that contain tetraanionic 2-hydroxybenzamidobenzene ligands†

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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 reportes, the NSe ligand in these complexes is a better π-acceptor than the NO and NS ligands and exhibits a stronger *trans* 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.[1] Accordingly, it is hardly surprising that numerous transition-metal complexes of NO have been studied in depth.[2] 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 matrixes.[3] 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,[4] 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 was obtained from the reaction of a molybdenum nitrido complex with elemental sulfur,[5] and other NS complexes have also been prepared by the treatment of the corresponding transition-metal nitrido complexes[6] with elemental sulfur[7] or its equivalents.[8,9] Moreover, reactions of metal complexes with trithiazyl chloride ($N_3S_3Cl_3$) as the NS source have been reported.[10] 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,[7a,c,d] albeit that this approach is less generic for NSe than for NS. For example, *cis*-[Ru(N)(Cl)L_2] (L = 2-[(2,6-diisopropylphenyl)imino]methyl-4,6-dibromophenolato), did not afford the corresponding NSe complex under reaction conditions similar to those for the reaction with NS.[7e]

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.[11] So far, only three series of NE complexes have been reported, which include neutral and cationic metal complexes of [Os(NE)Cl_2Tp] (Tp = hydrotris(1-pyrazolyl)borate),[7a] [Ru(NE)$Cl_3(AsPh_3)_2$][7d,12] and [Ir(NE){N(CHCHP^{t}Bu$_2$)$_2$}][PF_6][7c,13] (Fig. 1). Conversely, a series of anionic transition-metal NE complexes has not yet been reported. Examples of anionic NS complexes remain scarce,[14] 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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†Electronic supplementary information (ESI) available: Copies of NMR spectra, X-ray structures and computational data of **3d**, **4d**, **5d** and **6**. CCDC 1946037–1946040. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt04219a

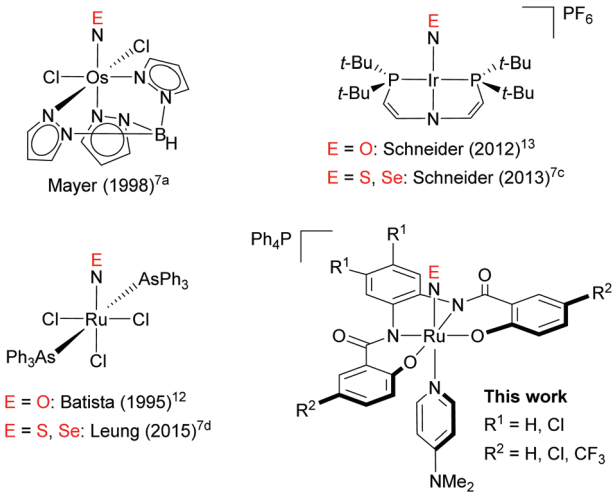
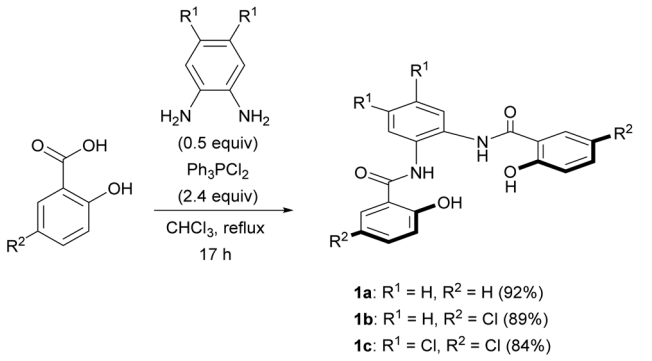
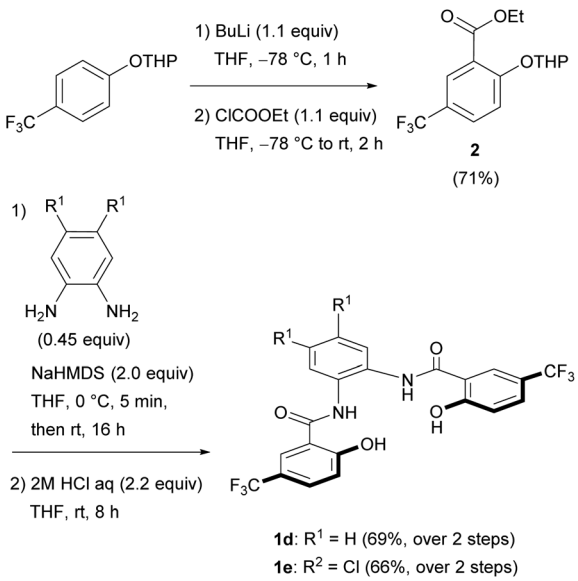


Fig. 1 Examples of a series of transition-metal NE (E = O, S, Se) complexes.

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.*, [Ph_4P][Ru(NE)(hybeb$^{R^1,R^2}$)(dmap)] (E = O, S, Se; hybeb = *N*,*N*′-(1,2-phenylene) bis(2-hydroxybenzamide), R^1 = H, Cl; R^2 = H, Cl, CF_3; dmap = 4-(*N*,*N*-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.[15]



Scheme 1 Synthesis of H_4hybeb$^{R^1,R^2}$ ligands **1a–c**.



Scheme 2 Synthesis of H_4hybeb$^{R^1,CF_3}$ ligands **1d** and **1e**.

Results and discussion

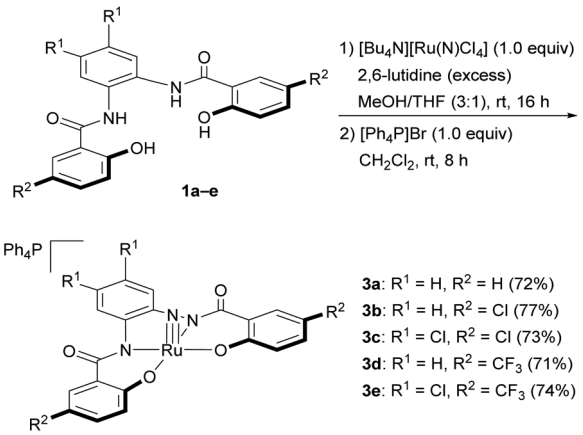
Syntheses of 2-hydroxybenzamidobenzene derivatives (H_4hybeb$^{R^1,R^2}$)

We selected the 2-hydroxybenzamidobenzene derivatives H_4hybeb$^{R^1,R^2}$ (**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 H_4hybeb^{H,H} (**1a**) was prepared in 92% yield by the Ph_3PCl_2-mediated condensation[16] of salicylic acid and 1,2-phenylenediamine (Scheme 1), and substituted H_4hybeb^{H,Cl} (**1b**) and H_4hybeb^{Cl,Cl} (**1c**) were prepared in good yield under similar reaction conditions.

Unexpectedly, the attempted synthesis of H_4hybeb derivatives with a CF_3 group at R^2 [**1d**: H_4hybeb^{H,CF_3}; **1e**: H_4hybeb^{Cl,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 H_4hybeb$^{R^1,CF_3}$. Finally, the THP group was removed under acidic conditions to generate **1d** and **1e** in good yield. The H_4hybeb$^{R^1,R^2}$ 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 [Ph_4P][Ru(N)(hybeb$^{R^1,R^2}$)] (3)

With H_4hybeb$^{R^1,R^2}$ 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),[19a] the reaction of **1a** and [Bu_4N][Ru(N)Cl_4][20] in the presence of an excess 2,6-lutidine in a mixture of MeOH/THF (3 : 1, v/v) afforded the tetrabutylammonium salt [Bu_4N][Ru(N)(hybeb^{H,H})],[19] which was treated with [Ph_4P]Br to afford nitrido complex [Ph_4P][Ru(N)(hybeb^{H,H})] (**3a**) in 72% yield. The cation metathesis was necessary to obtain



Scheme 3 Synthesis of nitrido complexes **3**.

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 $[Ph_4P][Ru(N)(hybeb^{H,CF_3})]$ (**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)), $[Bu_4N][Ru(N)(hybeb^{H,H})]$ (1.594(4) Å (ref. 19*a*)), $[Bu_4N][Ru(N)(O_2C_6H_4)_2]$ (1.603(4) Å (ref. 22)), and $[Bu_4N][Ru(N)(S_2C_6H_4)_2]$ (1.613(5) Å (ref. 23)).

Syntheses of the NS complexes $[Ph_4P][Ru(NS)(hybeb^{R^1,R^2})(dmap)]$ (4)

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 S_8 (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,

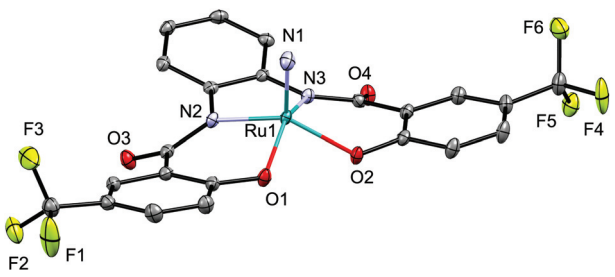
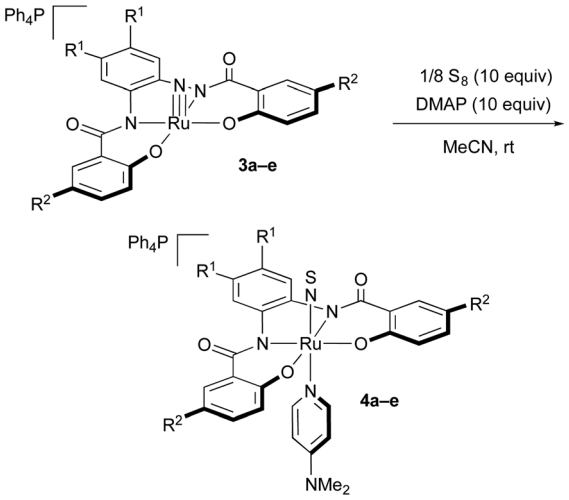


Fig. 2 Molecular structure of the anionic part of nitrido complex **3d**. Hydrogen atoms are omitted for clarity and only selected atoms are labelled. Selected bond length (Å): Ru1–N1 1.6040(15).

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	CF_3	0.25	**4d**	74
5	**3e**	Cl	CF_3	0.25	**4e**	69

and the NS complex $[Ph_4P][Ru(NS)(hybeb^{H,H})(dmap)]$ (**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 CF_3-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 unisolable intermediates of the type $[Ph_4P][Ru(NS)(hybeb^{R^1,R^2})]$,[14e] 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 *trans* 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 ^{1}H NMR spectroscopy. However, changes were not observed in these ^{1}H 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

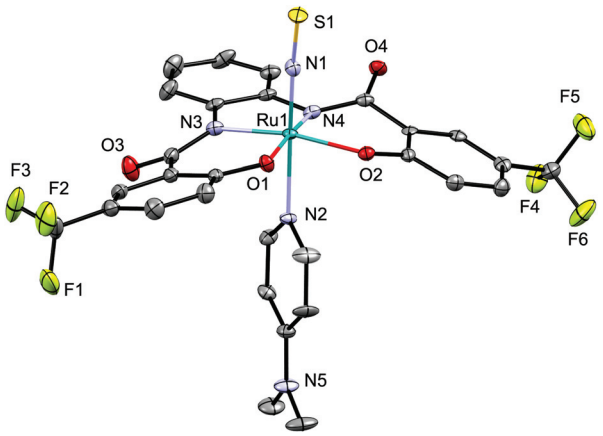


Fig. 3 Molecular structure of the anionic part of NS complex **4d**. Only one of the two independent anions per unit cell is shown. Hydrogen atoms are omitted for clarity and only selected atoms are labelled. Selected bond lengths (Å) and angles (°): S1–N1 1.511(4); N1–Ru1 1.746(4); Ru1–N2 2.155(4); S1–N1–Ru1 171.0(3); N1–Ru1–N2 173.53(19).

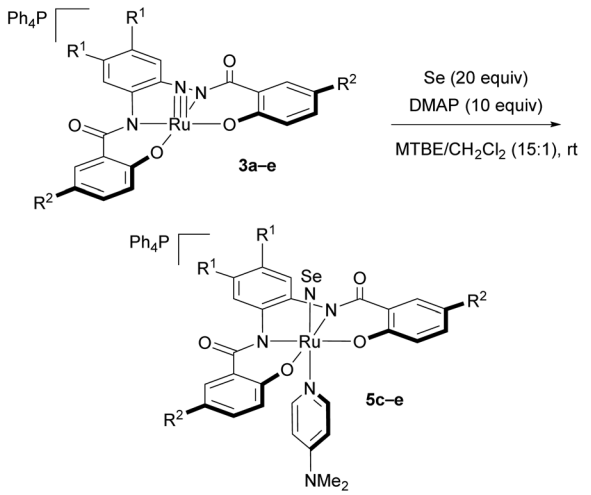
was confirmed, whereby the DMAP ligand is located *trans* to the NS ligand. The Ru–N–S angle is 171.0(3)/172.2(3)°, which confirms a terminal coordination and linear alignment of the NS ligand. The N–S bond length in **4d** [1.511(4)/1.516(6)] is similar to those in other NS complexes such as *mer*-[Ru(NS)$Cl_3(AsPh_3)_2$] (1.502(4) Å (ref. 7*d*)), [Ph_4P][Ru(NS)$Cl_4(H_2O)$] (1.504(4) Å (ref. 14*a*)), [Ph_4P][Os(NS)$Cl_4(H_2O)$] (1.514(5) Å (ref. 14*b*)), and [(Ir(NS){N(CHCHP^tBu_2)$_2$}][PF_6] (1.522(2) Å (ref. 7*c*)).

Syntheses of the NSe complexes [Ph_4P][Ru(NSe)(hybeb$^{R^1,R^2}$)(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 [Ph_4P][Ru(NSe)(hybeb$^{R^1,R^2}$)(dmap)] (**5a**: $R^1 = R^2 = H$; **5b**: $R^1 = H$, $R^2 = Cl$) 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 [Ph_4P][Ru(NSe)(hybeb^{Cl,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 hybeb$^{R^1,CF_3}$ ligands with a CF_3 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 [Ph_4P][Ru(NSe)(hybeb^{H,CF_3})(dmap)] (**5d**) and [Ph_4P][Ru(NSe)(hybeb^{Cl,CF_3})(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

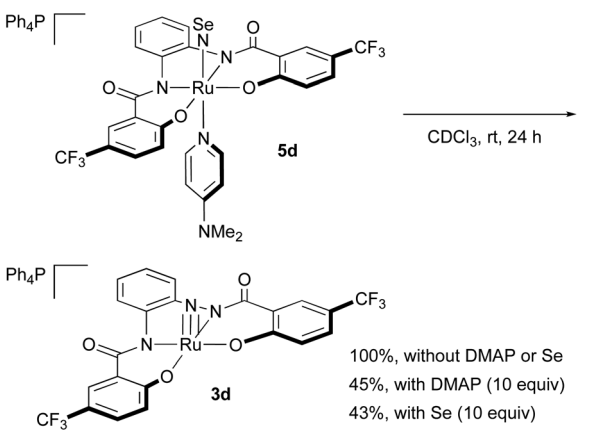
Table 2 Syntheses of NSe complexes **5c–e**



Entry	3	R^1	R^2	Time (h)	Product	Yield (%)
1	**3a**	H	H	72	**5a**	0
2	**3b**	H	Cl	72	**5b**	0
3	**3c**	Cl	Cl	36	**5c**	38
4	**3d**	H	CF_3	12	**5d**	46
5	**3e**	Cl	CF_3	12	**5e**	48

argon. When a $CDCl_3$ 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 $CDCl_3$ solution inhibited the decomposition, and only *ca.* 40% of **5d** was converted into **3d** after 24 h. An intermediate was not observed in the ^{1}H 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



Scheme 4 Decomposition of NSe complex **5d** in $CDCl_3$ into nitrido complex **3d**.

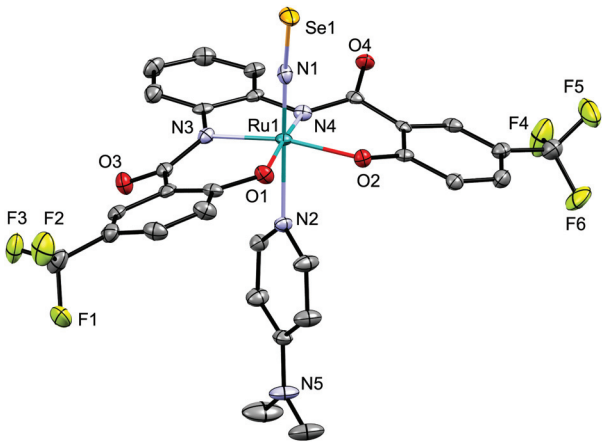
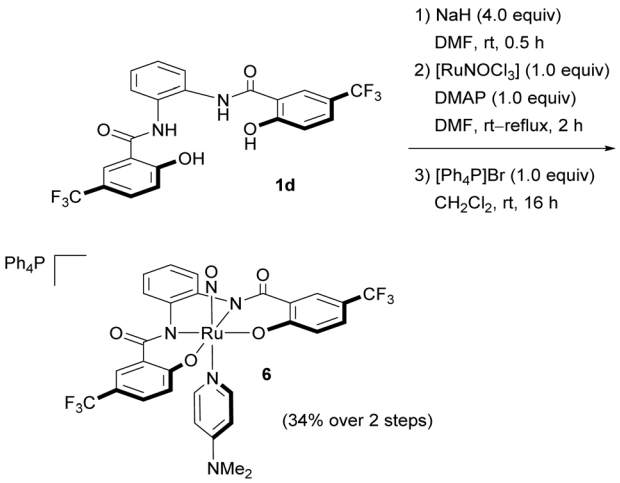


Fig. 4 Molecular structure of the anionic part of NSe complex **5d**. Only one of the two independent anions per unit cell is shown. Hydrogen atoms are omitted for clarity and only selected atoms are labelled. Selected bond lengths (Å) and angles (°): Se1–N1 1.670(4); N1–Ru1 1.734(4); Ru1–N2 2.173(4);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



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

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)Cl_2Tp] (1.629(10) Å (ref. 7*a*)) and *mer*-[Ru(NSe)Cl_3($AsPh_3$)$_2$] (1.650(3) Å (ref. 7*d*)), but similar to that in [(Ir(NSe){N(CHCHP^tBu_2)$_2$}][PF_6] (1.678(4) Å (ref. 7*c*)).

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.[7a,d]

Synthesis of the NO complex [Ph_4P][Ru(NO)(hybeb^{H,CF_3})(dmap)] (6)

To compare the structures of NS complex **4d** and NSe complex **5d** with the corresponding NO complex [Ph_4P][Ru(NO)(hybeb^{H,CF_3})(dmap)] (**6**), we attempted to synthesize **6** *via* the oxidation of **3d** using Me_3NO,[7a,e,13] H_2O_2 [25] or O_2 with Et_3B·DMAP,[4e] but all of these attempts were unsuccessful. Therefore, **6** was synthesized according to a modified literature method (Scheme 5):[26] **1d** was treated with sodium hydride, followed by [$RuNOCl_3$][26] and DMAP to generate the sodium salt Na[Ru(NO)(hybeb^{H,CF_3})(dmap)]. A subsequent cation metathesis with [Ph_4P]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 hybeb$^{R^1,R^2}$ ligand and the [Ph_4P]$^+$ 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)Cl_3($AsPh_3$)$_2$] (1.151(9) Å (ref. 12)) and [(Ir(NO){N(CHCHP^tBu_2)$_2$}][PF_6] (1.168(3) Å (ref. 7*c*)), but shorter than that in [Os(NO)Cl_2Tp] (1.19(4) Å (ref. 7*a*)).

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 lengths

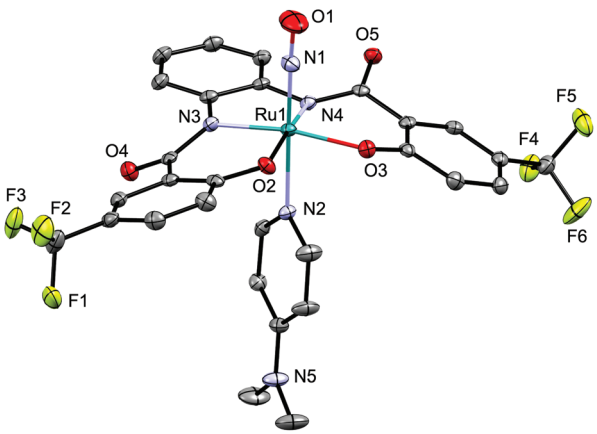


Fig. 5 Molecular structure of the anionic part of NO complex **6**. Only one of the two independent anions per unit cell is shown. Hydrogen atoms are omitted for clarity and only selected atoms are labelled. Selected bond lengths (Å) and angles (°): O1–N1 1.144(3); N1–Ru1 1.752(2); Ru1–N2 2.1325(19);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

Table 3 Selected bond lengths (Å),[a] angles (°),[a] WBIs[b] and NPA charges[b] for nitrido complex **3d** and NE complexes **6** (E = O), **4d** (E = S), **5d** (E = Se)

E	Nothing (**3d**)	O (**6**)	S (**4d**)	Se (**5d**)
Bond angles				
dmap–Ru–N	—	176.57(8)	173.53(19)	173.79(16)
		176.82(8)	173.78(19)	172.78(17)
Ru–N–E	—	174.9(2)	171.0(3)	171.2(3)
		177.27(19)	172.2(3)	169.9(3)
Bond lengths				
RuN–E	—	1.144(3)	1.511(4)	1.670(4)
		1.149(3)	1.516(4)	1.671(4)
Ru–NE	1.6040(15)	1.752(2)	1.746(4)	1.734(4)
		1.744(2)	1.746(4)	1.732(4)
N(dmap)–Ru	—	2.1325(19)	2.155(4)	2.173(4)
		2.1327(18)	2.157(4)	2.173(4)
Wiberg bond index				
RuN–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	0.980	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. [b] The calculation of WBIs and NPA charges were performed at the B3PW91/SBKJC(d) level of theory.

in **6**, **4d**, and **5d** 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 WBIs of the Ru–NE bonds in **6**, **4d**, and **5d** decrease compared to the Ru–N bond in **3d**. Considering the previously reported WBI for nitrido complex $[(Ir(N)\{N(CHCHP^tBu_2)_2\}][PF_6]$[13] and iridium NE complexes $[(Ir(NE)\{N(CHCHP^tBu_2)_2\}][PF_6]$,[7c,12] the Ru–N triple bond in **3d** should turn into a double bond after 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),[27] and the WBIs corroborate double-bond character for the Ru–NE bonds 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),[27] but similar to the corresponding double-bond radii (N═O: 1.17 Å; N═S: 1.54 Å; N═Se: 1.67 Å).[27] Taking the WBIs into account (N–O: 1.8352; 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.[28] However, it should also be noted here that this trend contradicts previous studies on complexes such as $[Cr(NS)(OH_2)_5]^{2+}$,[29] $[Os(NE)Cl_2Tp]$[7a] or $[Ru(NE)Cl_3(AsPh_3)_2]$,[7d,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 $[Ir(NE)\{N(CHCHP^tBu_2)_2\}][PF_6]$,[7c,13] where the π-acceptor ability of the NS ligand is lower than that of the NO and NSe ligands.[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)–RuNE 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 WBIs 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 $[Ru(NE)Cl_3(AsPh_3)_2]$ (E = O, S, Se)[7d,12] 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: $[Bu_4N][Ru(N)Cl_4]$,[20] tetrahydro-2-[4-(trifluoromethyl)phenoxy]-2*H*-pyran,[17] and $[Ru(NO)Cl_3]$.[26] Commercially available sulfur powder was recrystallized from benzene prior to use. TLC was performed on Merck TLC silica gel 60 F_{254} 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 (^{1}H: 400 MHz; ^{13}C: 100 MHz; ^{19}F: 375 MHz; ^{31}P: 161 MHz). Chemical shifts are reported in δ, relative to residual ^{1}H and $^{13}C\{^1H\}$ signals of $CDCl_3$ (^{1}H: δ 7.24; $^{13}C\{^1H\}$: 77.16) and $(CD_3)_2SO$ with 0.03% v/v TMS (^{1}H: δ 2.50; $^{13}C\{^1H\}$: δ 39.52) or to the external ^{19}F signal of C_6F_6 (δ −164.9) or $^{31}P\{^1H\}$ signal of H_3PO_4 (δ 0.00). ESI-HRMS were obtained on an FT-ICR mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyser. The number of solvent molecules in the products was determined by elemental analysis and ^{1}H NMR spectroscopy.

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

A previous reported procedure was slightly modified.[15] Ph_3PCl_2 (4.8 equiv.) was added to a $CHCl_3$ (40 mL) solution of phenylenediamine (1.0 equiv.) and salicylic acid (2.4 equiv.), and the mixture was stirred under reflux for 17 h. The resulting mixture was poured into iced water and extracted with EtOAc. The organic layer was consecutively treated with an aqueous solution of HCl (4 M), a saturated aqueous solution of $NaHCO_3$, and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was passed through silica gel (EtOAc) in order to remove Ph_3PO, and the fraction $R_f \approx 0.8$ was collected and concentrated *in vacuo*. The residual material was purified by column chromatography on silica gel (EtOAc/hexane) to afford the product as a white solid.

***N*,*N*′-(1,2-Phenylene)bis(2-hydroxybenzamide)·0.1EtOAc (1a·0.1EtOAc).** 1,2-Phenylenediamine (0.324 g, 3.00 mmol), salicylic acid (0.994 g, 7.20 mmol), and Ph_3PCl_2 (4.66 g, 14.0 mmol) were used as reagents. EtOAc/hexane = 1 : 1 was used as the eluent after Ph_3PO was removed. **1a**·0.1EtOAc was isolated as a white solid (0.981 g, 2.75 mmol, 92% yield). The NMR data of synthesized **1a** was consistent with reported data.[31]

***N*,*N*′-(1,2-Phenylene)bis(5-chloro-2-hydroxybenzamide)·0.1EtOAc (1b·0.1EtOAc).** 1,2-Phenylenediamine (0.324 g, 3.00 mmol), 5-chlorosalicylic acid (1.24 g, 7.20 mmol) and Ph_3PCl_2 (4.66 g, 14.0 mmol) were used as reagents. EtOAc/hexane = 1 : 1 was used as the eluent after Ph_3PO was removed. **1b**·0.1EtOAc was isolated as a white solid (1.14 g, 2.68 mmol, 89% yield). The ^{1}H NMR data matched those reported previously.[32] $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): δ 170.4 (EtOAc), 164.9, 157.0, 133.4, 131.0, 129.1, 126.0, 125.5, 123.1, 119.3, 118.7, 59.8 (EtOAc), 20.8 (EtOAc), 14.1 (EtOAc). HRMS (ESI−) *m*/*z*: $[M - H]^-$ calcd for $C_{20}H_{13}N_2O_4{}^{35}Cl_2$: 415.0255; found: 415.0258. IR (ATR, cm^{-1}): ν_{NH} = 3311, ν_{CO} = 1645. mp: 248.6–251.4 °C.

***N*,*N*′-(4,5-Dichloro-1,2-phenylene)bis(5-chloro-2-hydroxybenzamide)·0.1EtOAc (1c·0.1EtOAc).** 4,5-Dichlro-1,2-phenylenediamine (0.531 g, 3.00 mmol), 5-chlorosalicylic acid (1.24 g, 7.20 mmol) and Ph_3PCl_2 (4.66 g, 14.0 mmol) were used as reagents. EtOAc/hexane = 1 : 3 was used as the eluent after Ph_3PO was removed. **1c**·0.1EtOAc was isolated as white solid (1.24 g, 2.51 mmol, 84% yield). ^{1}H NMR ($(CD_3)_2SO$ 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, 0.2H, EtOAc), 1.98 (s, 0.3H, EtOAc), 1.17 (t, *J* = 7.1 Hz, 0.3H, EtOAc). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): δ 164.6, 156.6, 133.6, 131.0, 129.3, 127.4, 126.2, 123.2, 119.2, 118.6. HRMS (ESI−) *m*/*z*: $[M - H]^-$ calcd for $C_{20}H_{11}N_2O_4{}^{35}Cl_4$: 482.9477; found 482.9478. IR (ATR, cm^{-1}): ν_{NH} = 3332, ν_{CO} = 1636. mp: 284.7–286.7 °C.

Synthesis of ethyl 2-((tetrahydro-2*H*-pyran-2-yl)oxy)-5-(trifluoromethyl)benzoate (2). A previously reported procedure was slightly modified for the preparation of **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 tetrahydro-2-[4-(trifluoromethyl)phenoxy]-2*H*-pyran[16] (0.273 g, 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 Na_2SO_4, 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). ^{1}H NMR ($CDCl_3$): 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 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. ^{19}F NMR ($CDCl_3$): δ −60.3. HRMS (ESI+) *m*/*z*: $[M + Na]^+$ calcd for $C_{15}H_{17}O_4F_3Na^+$: 341.0974; found 341.0971. IR (ATR, cm^{-1}): ν_{CO} = 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.[18a] 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 to a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The organic layer was treated with

water and brine, dried over anhydrous Na_2SO_4, 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 $NaHCO_3$ and extracted with EtOAc. The organic layer was treated with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (EtOAc/hexane) to afford the product.

***N*,*N*′-(1,2-Phenylene)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). ^{1}H NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): δ 12.41 (s, 2H), 10.52 (s, 2H), 8.32 (s, 2H), 7.76–7.82 (m, 4H), 7.32 (q, J = 3.2, 2H), 7.16 (d, J = 8.7 Hz, 2H), 4.03 (q, J = 7.1, 0.4H, EtOAc), 1.99 (s, 0.6H, EtOAc), 1.17 (t, J = 7.1 Hz, 0.6H, EtOAc). ^{13}C{^{1}H} NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): 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). ^{19}F NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): δ −58.4. HRMS (ESI−) m/z: $[M - H]^-$ calcd for $C_{22}H_{13}N_2O_4F_6$: 483.0779, found 483.0785. IR (ATR, cm^{-1}): ν_{NH} = 3324, ν_{CO} = 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 : 3 was used as the eluent. **1e**·0.1EtOAc was isolated as pale yellow solid (0.284 g, 0.505 mmol, 66% yield over 2 steps). ^{1}H NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): δ 12.33 (s, 2H), 10.59 (s, 2H), 8.29 (s, 2H) 8.16 (s, 2H), 7.79 (d, J = 8.7, 2.3 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 4.03 (q, J = 7.1 Hz, 0.2H, EtOAc), 1.99 (s, 0.3H, EtOAc), 1.17 (t, J = 7.1 Hz, 0.3H, EtOAc). ^{13}C{^{1}H} NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): δ 171.1 (EtOAc), 164.6, 160.7, 131.1, 130.6, 127.6, 127.5, 126.4, 124.3 (q, J = 270.7 Hz), 120.1 (q, J = 32.8 Hz), 118.3, 117.8, 59.8 (EtOAc), 20.8 (EtOAc), 14.1 (EtOAc). ^{19}F NMR ($(CD_3)_2SO$ with 0.03% v/v TMS): δ −58.4. HRMS (ESI−) m/z: $[M - H]^-$ calcd for $C_{22}H_{11}N_2O_4F_6{}^{35}Cl_2$: 551.0008, found 551.0006. IR (ATR, cm^{-1}): ν_{NH} = 3357, ν_{CO} = 1647. mp: 274.6–277.5 °C.

General procedure for the syntheses of nitrido complexes [Ph$_4$P][RuN(hybeb$^{R^1,R^2}$)] (3)

Nitrido complexes **3** were synthesized according to a modified literature procedure.[19a] 2,6-Lutidine (excess, 0.73 mL) was added to a MeOH/THF = 3 : 1 (5.1 mL : 1.7 mL) solution of **1** (0.500 mmol, 1.00 equiv.) and [Bu$_4$N][Ru(N)Cl$_4$][19] (0.250 g, 0.500 mmol, 1.0 equiv.), and the mixture was stirred for 16 h at room temperature. The solvent was removed *in vacuo*, and the black/brown residue was purified by column chromatography on alumina ($CHCl_3$). The orange band was collected and concentrated *in vacuo*, and the residue was recrystallized from CH_2Cl_2/hexane to afford [Bu$_4$N][Ru(N)(hybeb^{H,H})] as an orange solid. The orange complex (1.0 equiv.) was dissolved in CH_2Cl_2 (10.0 mL per mmol) and [Ph$_4$P]Br (1.0 equiv.) was added. After stirring for 8 h, water was added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on alumina ($CHCl_3$) and recrystallized (CH_2Cl_2/hexane) to afford the product.

[Ph$_4$P][RuN(hybeb^{H,H})]·0.1CH$_2$Cl$_2$ (3a·0.1CH$_2$Cl$_2$). The tetrabutylammonium salt was synthesized from **1a**·0.1EtOAc (0.179 g, 0.500 mmol) in the first step. [Ph$_4$P]Br (0.164 g, 0.391 mmol) was used in the second step. The product was isolated as red crystals (0.291 g, 0.360 mmol, 72% yield from **1a**·0.1EtOAc). ^{1}H NMR ($CDCl_3$): δ 8.91 (td, J = 6.5, 3.2 Hz, 2H), 8.21 (dd, J = 8.2, 1.8 Hz, 2H), 7.66 (td, J = 7.5, 1.1 Hz, 4H), 7.51 (td, J = 8.0, 3.7 Hz, 8H), 7.27–7.35 (m, 10H), 7.19 (dd, J = 8.2, 0.9 Hz, 2H), 6.84–6.92 (m, 4H), 5.31 (s, 0.2H, CH_2Cl_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 169.2, 166.9, 146.0, 135.5, 134.2 (d, J = 10.6 Hz), 131.8, 131.7, 130.5 (d, J = 12.5 Hz), 124.7, 122.2, 121.8, 120.0, 118.5, 117.3 (d, J = 89.6 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.5. Anal. calcd for $C_{44.1}H_{32.2}Cl_{0.2}N_3O_4PRu$ (**3a**·0.1CH_2Cl_2): C, 65.61; H, 4.02; N, 5.21. Found: C, 65.41; H, 3.94; N, 5.19.

[Ph$_4$P][RuN(hybeb^{H,Cl})] (3b). The tetrabutylammonium salt was synthesized from **1b**·0.1EtOAc (0.213 g, 0.500 mmol) in the first step. [Ph$_4$P]Br (0.152 g, 0.363 mmol) was used in the second step. The product was isolated as red crystals (0.333 g, 0.384 mmol, 77% yield from **1b**·0.1EtOAc). ^{1}H NMR ($CDCl_3$): δ 8.83 (td, J = 6.6, 3.0 Hz, 2H), 8.08 (d, J = 2.7 Hz, 2H), 7.64–7.68 (m, 4H), 7.50 (td, J = 7.8, 3.7 Hz, 8H), 7.34 (dd, J = 13.0, 8.0 Hz, 8H), 7.16 (dd, J = 8.9, 2.5 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.88 (td, J = 6.6, 3.0 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.9, 165.4, 145.7, 135.6 (d, J = 2.9 Hz), 134.2 (d, J = 9.6 Hz), 131.6, 130.9, 130.5 (d, J = 12.5 Hz), 125.7, 123.2, 122.6, 121.8, 121.6, 117.7, 116.8. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.7. Anal. calcd for $C_{44}H_{30}Cl_2N_3O_4PRu$ (**3b**): C, 60.91; H, 3.49; N, 4.84. Found: C, 60.79; H, 3.24; N, 4.83.

[Ph$_4$P][RuN(hybeb^{Cl,Cl})] (3c). The tetrabutylammonium salt was synthesized from **1c**·0.1EtOAc (0.247 g, 0.500 mmol) in the first step. [Ph$_4$P]Br (0.162 g, 0.386 mmol) was used in the second step. The product was isolated as red crystals (0.344 g, 0.367 mmol, 73% yield from **1c**·0.1EtOAc). ^{1}H NMR ($CDCl_3$): δ 9.07 (s, 2H), 8.04 (d, J = 2.7 Hz, 2H), 7.69 (dd, J = 8.2, 6.8 Hz, 4H), 7.53 (td, J = 7.8, 3.5 Hz, 8H), 7.38 (dd, J = 13.0, 7.5 Hz, 8H), 7.17 (dd, J = 8.7, 2.7 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.7, 165.3, 145.1, 135.5 (d, J = 2.9 Hz), 134.2 (d, J = 10.6), 132.0, 130.7, 130.4 (d, J = 13.5), 124.9, 124.6, 123.4, 122.0, 121.6, 117.6, 116.7. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.7. Anal. calcd for $C_{44}H_{28}Cl_4N_3O_4PRu$ (**3c**): C, 55.50; H, 2.98; N, 4.49. Found: C, 55.85; H, 2.66; N, 4.29.

[Ph$_4$P][RuN(hybeb^{H,CF_3})] (3d). The tetrabutylammonium salt was synthesized from **1d**·0.2EtOAc (0.251 g, 0.500 mmol) in the first step. [Ph$_4$P]Br (0.164 g, 0.391 mmol) was used in the second step. The product was isolated as red crystals (0.330 g, 0.353 mmol, 71% yield from **1d**·0.2EtOAc). ^{1}H NMR ($CDCl_3$): δ 8.91 (td, J = 6.6, 3.5 Hz, 2H), 8.52 (d, J = 2.3 Hz, 2H), 7.69–7.73 (m, 4H), 7.50–7.58 (m, 10H), 7.37–7.42 (m, 8H), 7.29 (d, J = 9.1 Hz, 2H), 6.95 (td, J = 6.6, 3.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ

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. ^{19}F NMR ($CDCl_3$): δ −59.3. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7. Anal. calcd for $C_{44}H_{30}Cl_4N_3O_4PRu$ (**3d**): C, 59.10; H, 3.23; N, 4.50. Found: C, 59.47; H, 2.99; N, 4.50.

[Ph_4P][RuN(hybeb^{Cl,CF_3})] (3e). The tetrabutylammonium salt was synthesized from **1e**·0.1EtOAc (0.281 g, 0.500 mmol) in the first step. [Ph_4P]Br (0.164 g, 0.391 mmol) was used in the second step. The product was isolated as red crystals (0.370 g, 0.369 mmol, 74% yield from **1e**·0.1EtOAc). ^{1}H NMR ($CDCl_3$): δ 9.12 (s, 2H), 8.47 (d, J = 1.8 Hz, 2H), 7.73–7.77 (m, 4H), 7.59 (td, J = 7.8, 3.5 Hz, 8H), 7.54 (dd, J = 8.9, 2.1 Hz, 2H), 7.41–7.47 (m, 8H), 7.30 (d, J = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.1, 168.0, 145.1, 135.8 (d, J = 2.9 Hz), 134.2 (d, J = 9.6 Hz), 130.6 (d, J = 12.5 Hz), 129.9 (d, J = 3.9 Hz), 128.8 (d, J = 2.9 Hz), 125.1, 124.8 (q, J = 271.7 Hz), 123.8, 122.3, 121.1, 121.0 (q, J = 32.8 Hz), 117.8, 116.9. ^{19}F NMR ($CDCl_3$): δ −59.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.8. Anal. calcd for $C_{22}H_{12}Cl_2F_6N_2O_4$ (**3e**): C, 55.05; H, 2.81; N, 4.19. Found: C, 55.29; H, 2.47; N, 4.10.

General procedure for the syntheses of NS complexes [Ph_4P][Ru(NS)(hybeb$^{R^1,R^2}$)(dmap)] (4)

1/8 S_8 (0.160 g, 5.00 mmol, 10 equiv. as S) and DMAP (0.611 g, 5.00 mmol, 10 equiv.) were added to a MeCN solution (20 mL) of nitrido complex **3** (0.500 mmol, 1.0 equiv.). After the mixture was stirred at room temperature for the reaction time shown in Table 1, the solvent was removed *in vacuo*. The residue was dissolved in a small amount of acetone, and a large amount of water was added. The resulting brown solid was collected by filtration and recrystallized from acetone/MTBE (methyl *tert*-butyl ether) to afford **4** as black crystals.

[Ph_4P][Ru(NS)(hybeb^{H,H})(dmap)] (4a). **3a**·0.1CH_2Cl_2 (0.404 g, 0.500 mmol) was used. The reaction was completed after 40 h. The product was isolated as black crystals (0.320 g, 0.336 mmol, 67% yield). ^{1}H NMR ($CDCl_3$): δ 8.98 (td, J = 6.6, 3.0 Hz, 2H), 8.26 (dd, J = 8.2, 1.8 Hz, 2H), 7.75–7.78 (m, 6H), 7.62 (td, J = 8.0, 3.7 Hz, 8H), 7.39–7.44 (m, 8H), 7.07 (dd, J = 8.2, 1.4 Hz, 2H), 6.97–7.01 (m, 2H), 6.65 (td, J = 6.6, 3.0 Hz, 2H), 6.45–6.49 (m, 2H), 5.91 (d, J = 6.4 Hz, 2H), 2.68 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.2, 168.3, 154.3, 147.8, 146.6, 135.9 (d, J = 2.9 Hz), 134.4 (d, J = 10.6 Hz), 133.3, 130.9 (d, J = 13.49 Hz), 124.8, 122.6, 122.4, 121.4, 117.4 (d, J = 89.6 Hz), 114.9, 105.9, 39.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.6. HRMS (ESI−) m/z: $[M - Ph_4P - dmap]^-$ calcd for $C_{20}H_{12}N_3O_4RuS$: 491.9592; found 491.9604.

[Ph_4P][Ru(NS)(hybeb^{H,Cl})(dmap)] (4b). **3b** (0.434 g, 0.500 mmol) was used. The reaction was completed in 1.5 h. The product was isolated as black crystals (0.368 g, 0.360 mmol, 72% yield). ^{1}H NMR ($CDCl_3$): δ 8.92 (dd, J = 5.7, 3.9 Hz, 2H), 8.12 (s, 2H), 7.75 (t, J = 7.3 Hz, 4H), 7.66 (d, J = 6.4 Hz, 2H), 7.60 (td, J = 7.2, 3.3 Hz, 8H), 7.46 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.69 (q, J = 3.2 Hz, 2H), 5.84 (s, 2H), 2.60 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.8, 167.0, 154.3, 147.6, 146.3, 135.8 (d, J = 1.9 Hz), 134.4 (d, J = 10.6 Hz), 132.2, 130.8 (d, J = 13.5), 130.4, 125.6, 123.7, 122.5, 121.6, 119.1, 117.4 (d, J = 89.6 Hz), 105.7, 38.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.6. Anal. calcd for $C_{51}H_{40}Cl_2N_5O_4PRuS$ (**4b**): C, 59.54; H, 3.95; N, 6.85. Found: C, 59.73; H, 3.77; N, 6.61.

[Ph_4P][Ru(NS)(hybeb^{Cl,Cl})(dmap)]·0.5MTBE (4c·0.5MTBE). 3c (0.468 g, 0.500 mmol) was used. The reaction was completed in 30 min. The product was isolated as black crystals (0.414 g, 0.365 mmol, 73% yield). ^{1}H NMR ($CDCl_3$): δ 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 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, 123.6, 122.7, 119.5, 117.5 (d, J = 89.6 Hz), 105.9, 72.8 (MTBE), 49.6 (MTBE), 39.0, 27.1 (MTBE). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.8. Anal. calcd for $C_{53.5}H_{44}Cl_4N_5O_{4.5}PRuS$ (**4c**·0.5MTBE): C, 56.62; H, 4.00; N, 6.48. Found: C, 56.26; H, 3.77; N, 6.08.

[Ph_4P][Ru(NS)(hybeb^{H,CF_3})(dmap)] (4d). **3d** (0.467 g, 0.500 mmol) was used. The reaction was completed in 15 min. The product was isolated as black crystals (0.402 g, 0.369 mmol, 74% yield). ^{1}H NMR ($CDCl_3$): δ 8.96 (q, J = 3.3 Hz, 2H), 8.55 (s, 2H), 7.77 (dd, J = 8.2, 6.4 Hz, 4H), 7.70 (d, J = 6.8 Hz, 2H), 7.61 (td, J = 8.0, 3.7 Hz, 8H), 7.44–7.49 (m, 8H), 7.23 (d, J = 10.5 Hz, 4H), 7.14 (d, J = 8.7 Hz, 2H), 6.74 (td, J = 6.6, 3.0 Hz, 2H), 5.95 (s, 2H), 2.72 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.5, 167.1, 154.5, 147.6, 146.4, 135.9 (d, J = 2.9 Hz), 134.4 (d, J = 10.6 Hz), 131.5 (d, J = 3.9 Hz), 130.8 (d, J = 13.5 Hz), 127.2 (d, J = 2.9 Hz), 125.7 (q, J = 270.7 Hz), 124.1, 122.9, 122.7, 121.8, 117.4 (d, J = 89.6 Hz), 116.3 (q, J = 31.8 Hz), 105.9, 39.0. ^{19}F NMR ($CDCl_3$): δ −60.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7. Anal. calcd for $C_{53}H_{40}F_6N_5O_4PRuS$ (**4d**): C, 58.53; H, 3.78; N, 6.38. Found: C, 58.72; H, 3.59; N, 6.23.

[Ph_4P][Ru(NS)(hybeb^{Cl,CF_3})(dmap)] (4e). **3e** (0.502 g, 0.500 mmol) was used. The reaction was completed in 15 min. The product was isolated as black crystals (0.402 g, 0.347 mmol, 69% yield). ^{1}H NMR ($CDCl_3$): δ 9.25 (s, 2H), 8.53 (d, J = 2.3 Hz, 2H), 7.79 (dd, J = 8.2, 6.8 Hz, 4H), 7.60–7.65 (m, 10H), 7.51 (dd, J = 12.8, 7.3 Hz, 8H), 7.28 (dd, J = 8.7, 2.3 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H), 5.98 (d, J = 7.3 Hz, 2H), 2.74 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 171.4, 167.3, 154.6, 147.5, 145.8, 136.0 (d, J = 2.9 Hz), 134.5 (d, J = 9.6 Hz), 131.4 (d, J = 3.9 Hz), 130.9 (d, J = 2.9 Hz), 127.5, 125.6 (q, J = 270.7 Hz), 123.8, 123.5, 123.2, 117.5 (d, J = 89.6 Hz), 116.8 (q, J = 31.8 Hz), 106.0, 39.1. ^{19}F NMR ($CDCl_3$): δ −58.7. ^{31}P NMR ($CDCl_3$): δ 23.8. Anal. calcd for $C_{51}H_{38}Cl_2F_6N_5O_4PRuS$ (**4e**): C, 54.98; H, 3.31; N, 6.05. Found: C, 55.25; H, 3.46; N, 5.96.

General procedure for the syntheses of NSe complexes [Ph_4P][Ru(NSe)(hybeb$^{R^1,R^2}$)(dmap)] (5)

A 30 mL two-necked flask containing grey selenium powder (0.790 g, 10.0 mmol, 20 equiv.) was heated under vacuum, before argon gas was introduced. In a separate flask, nitrido complex **3** (0.500 mmol, 1.0 equiv.) and DMAP (0.611 g, 5.00 mmol, 10 equiv.) were dissolved in MTBE/CH_2Cl_2 (15 mL : 1 mL) at room temperature. The resulting solution was added to the flask containing the dried selenium, and the

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 CH_2Cl_2 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 $^{13}C\{^1H\}$ NMR spectra, **5c–e** decomposed to generate nitrido complexes **3c–e**, DMAP, and selenium. For this reason, the $^{13}C\{^1H\}$ NMR spectra exhibit signals of **5c–e** together with those of **3c** and DMAP (Fig. S32, S34, and S36, ESI†).

[Ph$_4$P][Ru(NSe)(hybeb^{Cl,Cl})(dmap)]·0.5MTBE (5c·0.5MTBE). **3c** (0.468 g, 0.500 mmol) was used. The reaction reached completion within 72 h. **5c**·0.5MTBE was isolated as black crystals (0.222 g, 0.188 mmol, 38% yield). ^1H NMR ($CDCl_3$): δ 9.19 (d, J = 0.91, 2H), 8.14 (q, J = 1.4 Hz, 2H), 7.80 (dd, J = 7.8, 5.9 Hz, 4H), 7.64 (td, J = 7.8, 3.7 Hz, 8H), 7.58 (d, J = 5.9 Hz, 2H), 7.49–7.54 (m, 8H), 7.01 (dd, J = 8.7, 2.7 Hz, 2H), 6.95 (td, J = 5.8, 2.9 Hz, 2H), 5.98 (dd, J = 6.6, 5.2 Hz, 2H), 3.19 (s, 3H, MTBE), 2.74 (s, 6H), 1.16 (s, 9H, MTBE). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.7, 167.1, 154.6, 147.5, 145.7, 135.9 (d, J = 2.9 Hz), 134.4 (d, J = 10.6 Hz), 132.1, 130.8 (d, J = 12.5 Hz), 125.1, 124.2, 124.1, 123.7, 122.9, 120.0, 118.0, 117.5 (d, J = 89.6 Hz), 106.0, 72.9 (MTBE), 49.6 (MTBE), 39.1, 27.1 (MTBE). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.8. Anal. calc. for $C_{51.5}H_{39.2}Cl_4N_5O_{4.1}PRuSe$ (**5c**·0.5MTBE): C, 53.95; H, 3.45; N, 6.11. Found: C, 53.69; H, 3.41; N, 5.93.

[Ph$_4$P][Ru(NSe)(hybeb^{H,CF_3})(dmap)]·0.5MTBE (5d·0.5MTBE). **3d** (0.467 g, 0.500 mmol) was used. The reaction reached completion within 36 h. **5d**·0.5MTBE was isolated as black crystals (0.270 g, 0.229 mmol, 46% yield). ^1H NMR ($CDCl_3$): δ 8.91 (td, J = 6.6, 3.2 Hz, 2H), 8.53 (d, J = 2.3 Hz, 2H), 7.76–7.80 (m, 4H), 7.66 (dd, J = 6.0, 1.4 Hz, 2H), 7.60–7.63 (m, 8H), 7.45–7.50 (m, 8H), 7.22 (d, J = 2.3 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.71 (td, J = 6.6, 3.2 Hz, 2H), 5.96 (dd, J = 6.0, 1.4 Hz, 2H), 3.19 (s, 1.5H, MTBE), 2.73 (s, 6H), 1.17 (s, 4.5H, MTBE). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.2, 167.1, 154.5, 147.5, 146.3, 135.8 (d, J = 1.9 Hz), 134.4 (d, J = 9.6 Hz), 131.4 (d, J = 4.8 Hz), 130.8 (d, J = 13.5 Hz), 127.2 (d, J = 2.9 Hz), 125.7 (q, J = 270.7 Hz), 124.2, 123.1, 122.8, 121.9, 117.5 (d, J = 89.6 Hz), 116.6 (q, J = 31.8 Hz), 105.97, 72.93 (MTBE), 49.60 (MTBE), 39.01, 27.12 (MTBE). ^{19}F NMR ($CDCl_3$): δ −58.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.7. Anal. calc. for $C_{55.5}H_{46}F_6N_5O_{4.5}PRuSe$ (**5d**·0.5MTBE): C, 56.49; H, 3.93; N, 6.10. Found: C, 56.07; H, 3.83; N, 5.89.

[Ph$_4$P][Ru(NSe)(hybeb^{Cl,CF_3})(dmap)]·0.6MTBE (5e·0.6MTBE). **3e** (0.502 g, 0.500 mmol) was used. The reaction reached completion within 36 h. **5e**·0.6MTBE was isolated as black crystals (0.304 g, 0.242 mmol, 48% yield). ^1H NMR ($CDCl_3$): δ 9.22 (d, J = 1.4 Hz, 2H), 8.53 (s, 2H), 7.80 (t, J = 7.5 Hz, 4H), 7.59–7.65 (m, 10H), 7.52 (dd, J = 13.0 Hz, 8.4 Hz, 8H), 7.29 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 6.00 (d, J = 6.4 Hz, 2H), 3.19 (s, 1.8H, MTBE), 2.77 (s, 6H), 1.17 (s, 5.4H, MTBE). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.3, 167.3, 154.6, 147.4, 145.7, 135.9 (d, J = 2.9 Hz), 134.4 (d, J = 9.6 Hz), 131.3 (d, J = 2.9 Hz), 130.8 (d, J = 9.6 Hz), 127.5 (d, J = 2.9 Hz), 125.6 (q, J = 270.7 Hz), 123.9, 123.6, 123.3, 122.9, 117.5 (d, J = 89.6 Hz), 116.9 (q, J = 32.8 Hz), 106.0, 72.9 (MTBE), 49.6 (MTBE), 39.1, 27.1 (MTBE). ^{19}F NMR ($CDCl_3$): δ −58.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.8. Anal. calc. for $C_{56}H_{45.2}Cl_2F_6N_5O_{4.6}PRuSe$ (**5e**·0.6MTBE): C, 53.38; H, 3.55; N, 5.61. Found: C, 53.28; H, 3.53; N, 5.45.

Synthesis of NO complex [Ph$_4$P][Ru(NO)(hybeb^{H,CF_3})(dmap)] (6)

Initially, a previously reported procedure was modified.[25] 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 $[RuNOCl_3]$[25] (0.0855 g, 0.360 mmol, 1.0 equiv.) and DMAP (0.0440 g, 0.360 mmol, 1.0 equiv.). 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 $[Ph_4P]Br$ (0.0717 g, 0.171 mmol, 1.0 equiv.) in CH_2Cl_2 (3 mL) was added and the mixture was stirred overnight. The mixture was transferred into water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on alumina ($CHCl_3$/MeOH = 20 : 1, v/v) and the product was recrystallized from CH_2Cl_2/MTBE to afford **6** as black crystals (0.132 g, 0.123 mmol, 34% yield from **1d**·0.1EtOAc). ^1H NMR ($CDCl_3$): δ 8.99 (td, J = 6.3, 2.7 Hz, 2H), 8.58 (d, J = 1.4 Hz, 2H), 7.83 (d, J = 7.3 Hz, 2H), 7.75 (dd, J = 7.9, 6.7 Hz, 4H), 7.59 (td, J = 7.8, 3.5 Hz, 8H), 7.42–7.47 (m, 8H), 7.21–7.24 (m, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.79 (q, J = 3.3 Hz, 2H), 6.00 (d, J = 6.8 Hz, 2H), 2.72 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.9, 166.7, 154.7, 147.3, 145.3, 135.9 (d, J = 2.9 Hz), 134.3 (d, J = 10.6 Hz), 131.5 (d, J = 3.9 Hz), 130.8 (d, J = 13.5 Hz), 127.1 (d, J = 1.9 Hz), 125.7 (q, J = 270.7 Hz), 124.2, 122.7, 122.6, 121.7, 117.4 (d, J = 89.6 Hz), 116.3 (q, J = 32.8 Hz), 105.9, 39.0. ^{19}F NMR ($CDCl_3$): δ −58.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.5. HRMS (ESI−) m/z: [M − Ph$_4$P − dmap]$^-$ calcd for $C_{22}H_{10}F_6N_3O_5Ru$: 611.9568; found 611.9582. IR (ATR, cm^{-1}): ν_{NO} = 1810.

X-ray diffraction studies

All 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-XG[33] graphical interface. The positions of the non-hydrogen atoms were determined by using the SHELXT[34] program and refined on F^2 by full-matrix least-squares techniques using the SHELXL-2018[35] 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.[36] 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[37] density functional with the effective core potential (ECP) proposed by Stevens *et al.*,[38] SBKJC, 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[39] and natural population analysis (NPA) charge distributions[40] were estimated using the NBO6.0 program[41] based on the optimized structures. Optimized Cartesian coordinates of anionic part for **4d**, **5d**, and **6** are summarized in Tables S5–S7 (ESI†).

Conflicts of interest

There are no conflicts to declare.

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