

## Rhenium Complexes

Rhenium(V) Complexes with Selenolato- and Telluolato-Substituted Schiff Bases – Released PPh<sub>3</sub> as a Facile ReductantMaximilian Roca Jungfer,<sup>[a]</sup> Adelheid Hagenbach,<sup>[a]</sup> Ernesto Schulz Lang,<sup>[b]</sup> and Ulrich Abram\*<sup>[a]</sup>

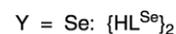
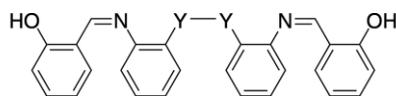
**Abstract:** The salicylidene Schiff bases of bis(2-aminophenyl)-diselenide and -ditelluride react with [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] or the arylimidorhenium(V) compounds [Re(NPhR)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (R = H, F, CF<sub>3</sub>) with formation of rhenium(V) complexes with tridentate {O,N,Se/Te} chalcogenolato ligands. The ligands adopt a *facial* coordination mode with the oxygen donors *trans* to the multiply bonded O<sup>2-</sup> or NPhR<sup>2-</sup> ligands. The reduction of the dichalcogenides and the formation of the chalcogenolato ligands oc-

curs *in situ* by released PPh<sub>3</sub> ligands. The absence of additional reducing agents provides good yields of products with rhenium in the high formal oxidation state "+5". A mechanism for the dichalcogenide reduction is proposed on the basis of the experimental results. In accordance with the proposed mechanism, best yields are obtained with a strict exclusion of oxygen, but in the presence of water.

## Introduction

In contrast to the large number of alcoholato or thiolato complexes, organoselenolato and -telluolato complexes of rhenium are rare. Only a few of such compounds have been characterized crystallographically.<sup>[1]</sup> The majority of them contains the metal in low oxidation states and tricarbonylrhenium(I) species dominate.<sup>[2–14]</sup> Organoselenolato and -telluolato complexes with rhenium in higher oxidation states are even more scarce despite their proposed potentially beneficial catalytic properties.<sup>[15–17]</sup> They mainly contain simple, unsubstituted phenylselenolato ligands.<sup>[18–21]</sup> A few more rhenium(V) complexes with special ligands such as acylselenoureas, a diselenolate, and pyridine-2-selenolate have been reported.<sup>[22–24]</sup> The rarity of these reports may result from the more complicated syntheses of heavier organochalcogenolato ligands. For some organochalcogenolates, such as alkynylselenolates, exist some special synthetic routes.<sup>[25,26]</sup> But commonly, the corresponding selenols and tellurols are unstable and prepared by reduction of the corresponding diorganodichalcogenides directly before the complex formation. The reaction conditions of such procedures

must be controlled carefully in order to avoid the parallel reduction of the transition metal ions. This problem has been described in detail for the synthesis of complexes of the composition (NBu<sub>4</sub>)[M<sup>VO</sup>(arylselenolate)<sub>4</sub>] (M = Tc, Re), where the use of Li(BH<sub>4</sub>) in THF proved to be a suitable and easy to control reductant.<sup>[27,28]</sup> Recently, an oxidorhenium(V) complex with pyridylselenolato ligands was prepared by the reaction of the corresponding diselenide with [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] without the addition of a reducing agent. Obviously, the released PPh<sub>3</sub> acted as a selective reducing agent for dipyriddyldiselenide, while the oxidation state of rhenium was retained.<sup>[24]</sup>



In the present work, we demonstrate that the assumed reaction pathway can be extended to other diorganodiselenides and -ditellurides. Thereto, we performed reactions of [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] and [Re(NPhR)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (R = 4-H, 4-F or 4-CF<sub>3</sub>) with the Schiff bases prepared from salicylaldehyde and bis(2-aminophenyl)diselenide ({HL<sup>Se</sup>}<sub>2</sub>) and -ditelluride ({HL<sup>Te</sup>}<sub>2</sub>).

## Results and Discussion

The salicylidene Schiff base of bis(2-aminophenyl)diselenide {HL<sup>Se</sup>}<sub>2</sub> was prepared by a reaction of di(2-aminophenyl)diselenide with two equivalents of salicylaldehyde in boiling ethanol. For the synthesis of {HL<sup>Te</sup>}<sub>2</sub>, an excess of the aldehyde (about 3:1) was used to obtain good yields. The products precipitated as yellow-orange ({HL<sup>Se</sup>}<sub>2</sub>) or orange-red ({HL<sup>Te</sup>}<sub>2</sub>) solids and were recrystallized from CHCl<sub>3</sub>/EtOH. The synthetic route is simi-

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lar to previous reports,<sup>[29,30]</sup> but the optimized conditions described in the Experimental Part give better yields and pure products. The purity of the dichalcogenides can readily be checked by their <sup>77</sup>Se and <sup>125</sup>Te NMR spectra giving resonances at 363 ppm ( $\{HL^{Se}\}_2$ ) and 228 ppm ( $\{HL^{Te}\}_2$ ). The other spectral features match the previously reported data.

Single crystals of  $\{HL^{Se}\}_2$  and  $\{HL^{Te}\}_2$  suitable for X-ray diffraction were grown from  $CHCl_3/EtOH$  mixtures. Figure 1a shows an ellipsoid representation of the selenium compound with the atomic labelling scheme, which has also been applied for  $\{HL^{Te}\}_2$ . A unit cell of the latter compound is shown in Figure 1b. It clearly illustrates that the ditelluride crystallizes in the present tetragonal polymorph with well-separated molecules. This is in contrast to the situation in the previously studied orthorhombic polymorph, in which each two molecules are connected by  $Te\cdots Te$  interactions of 4.054 Å. In the compound under study, the shortest intermolecular  $Te-Te$  distances are larger than 6.5 Å.

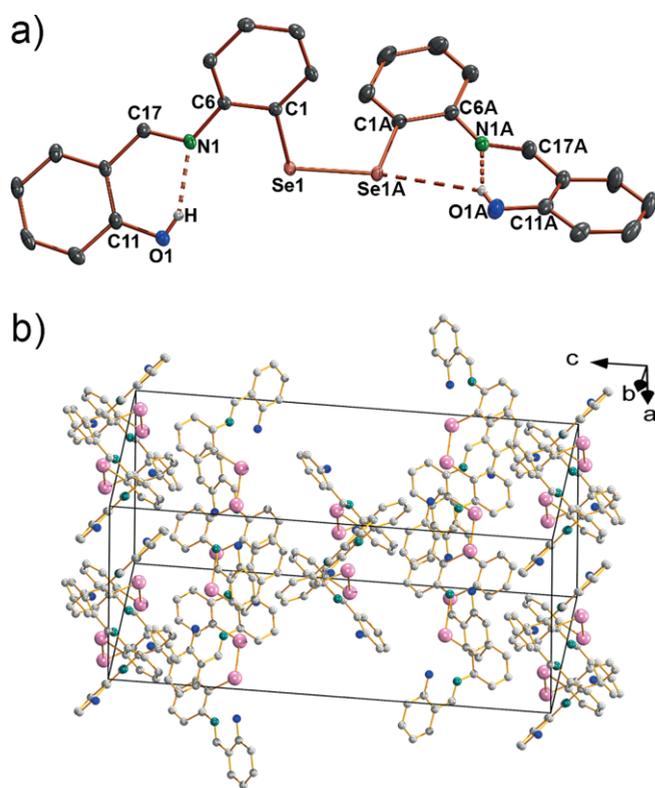


Figure 1. (a) Molecular structure of  $\{HL^{Se}\}_2$ . Ellipsoids represent 50 % probability. Hydrogen atoms bonded to carbon atoms are omitted for clarity. (b) Unit cell plot of  $\{HL^{Te}\}_2$  illustrating the absence of intermolecular  $Te\cdots Te$  interactions.

Some fundamental bond lengths of the dichalcogenides are compared with those in the rhenium complexes in Table 1 and Table 2. Some more details are summarized in the Supporting Information.

Reactions of the two functionalized dichalcogenides with oxido- and arylimidorhenium(V) complexes show that they are reduced during such procedures and form tridentate selenolato and telluroolato ligands, which bind tridentate to the  $\{ReO_3\}^{3+}$  or  $\{Re(NPhR)\}^{3+}$  cores. A summary of the performed reactions and

obtained products is shown in Scheme 1. Although all reactions worked at room temperature and without the addition of a supporting base, they are slow and the yields of the products are in many cases unsatisfactorily low. This comes, however, not completely unexpected with regard to the low solubility of most of the starting materials used. But surprisingly, also the use of the better soluble, fluorinated starting complex  $[Re(NPhF)Cl_3(PPh_3)]$  does not necessarily improve the yields. This means that the conditions for the individual reactions had to be optimized in terms of solvent, temperature and reaction time. Generally, we found that the presence of traces of water and the absence of oxygen are mandatory for good yields.

Reactions of  $[ReOCl_3(PPh_3)_2]$  with  $\{HL^{Se}\}_2$  give yields of  $[ReO(L^{Se})Cl(PPh_3)]$  in the range of 70 %, when the reaction is performed at room temperature in moist  $CH_2Cl_2$  under inert conditions. Interestingly, the yields are significantly lower (only about 20 %) when the reaction is done in dry solvent or on air. Since such a behavior suggests a sophisticated mechanism, we followed the course of the reaction by <sup>31</sup>P NMR spectroscopy. And indeed we found evidence for the formation of various phosphorus-containing species depending on the reaction time and the reaction conditions (presence of air and/or water). These experiments allow to propose a potential mechanism for the formation of  $[ReO(L^{Se})Cl(PPh_3)]$ , which is given in Scheme 2).

Initially, some phosphine (most probably together with one  $Cl^-$  ligand) dissociates from  $[ReOCl_3(PPh_3)_2]$  under replacement by a diselenide. The phosphine attacks the coordinated diselenide with formation of an intermediate, which may be assigned to  $\{Ph_3PSe(C_6H_4)-2-N=CH(C_6H_4)-2-OH\}^+Cl^-$ , and the liberation of a  $\{L^{Se}\}_2^{2-}$  ligand. The recorded chemical shift of 30 ppm of this potential intermediate is in the range where also the <sup>31</sup>P resonances of the related organoseleno-phosphonium species  $\{Ph_3PSePh\}Br$  (37 ppm),<sup>[31]</sup>  $\{Bu_3PSeMe\}$  (50 ppm),<sup>[32]</sup>  $\{Ph_3PSePh\}[GaCl_4]$  (38 ppm)<sup>[33]</sup> and  $\{Ph_3PSeMe\}(BF_4)$  (36 ppm)<sup>[34]</sup> are found. The reduction of disulfides and diselenides with phosphines with formation of phosphonium-chalcogenolate ion pairs or bis(organochalcogen)phosphoranes has been observed before.<sup>[34–37]</sup> In the reactions of the present study, the phosphonium species seems to have a remarkably high formation probability and is also found as a fragment of high intensity in the ESI+ mass spectra taken from  $CH_2Cl_2$  solutions of  $[ReO(L^{Se})Cl(PPh_3)]$ . Therefore, we consider the formation of an intermediate phosphonium species as highly probable, although an reaction pathway via a coordinated phosphorane cannot completely be excluded.

The intermediate can either decompose slowly in the anhydrous pathway with formation of triphenylphosphine selenide or it can quickly hydrolyze and give triphenylphosphine oxide and the respective selenol. The highly air-sensitive selenol is quickly re-oxidized to the diselenide in air. Thus, for the formation of the rhenium chalcogenolato complex, the exclusion of air is required and the presence of water supports the formation of  $OPPh_3$  instead of  $SePPh_3$ . Both reactions, which lead to  $OPPh_3$  or  $SePPh_3$  can be understood as nucleophilic attacks of  $H_2O$  or  $RSe^-$  on the phosphorus atom of the  $\{Ph_3PSe(C_6H_4)-2-N=CH(C_6H_4)-2-OH\}^+$  ion. In the case of water, the resulting pentacoordinate phosphorus species

Table 1. Selected bond lengths [Å] and angles (°) in  $\{HL^{Se}\}_2$ ,  $[ReO(L^{Se})Cl(PPh_3)]$ ,  $[Re(NPhF)(L^{Se})Cl(PPh_3)]$  and  $[Re(NPhCF_3)(L^{Se})Cl(PPh_3)]$ .

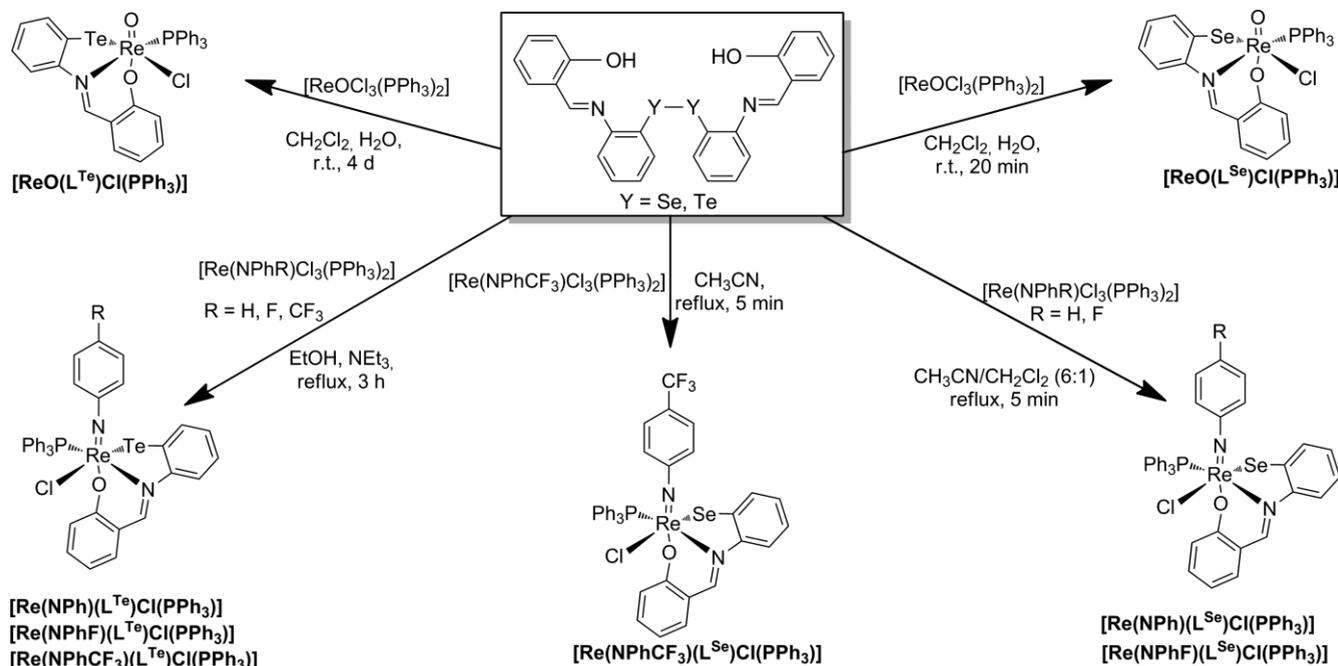
	$\{HL^{Se}\}_2$	$[ReO(L^{Se})Cl(PPh_3)]$	$[Re(NPhF)(L^{Se})Cl(PPh_3)]^{[a]}$	$[Re(NPhCF_3)(L^{Se})Cl(PPh_3)]$
Se1–C1	1.929(2)/1.933(2)	1.924(8)	1.923(2)	1.936(5)
O1–C11	1.356(2)/1.349(2)	1.332(9)	1.332(2)	1.341(5)
N1–C6	1.415(2)/1.415(2)	1.45(1)	1.443(3)	1.445(6)
N1–C17	1.287(2)/1.283(2)	1.302(9)	1.305(3)	1.299(6)
Re1–O10/N10	–	1.688(5)	1.728(2)	1.723(4)
Re1–O1	–	1.992(5)	2.020(2)	2.006(3)
Re1–P1	–	2.461(2)	2.4471(7)	2.430(1)
Re1–Cl1	–	2.537(2)	2.4967(7)	2.483(1)
Re1–N1	–	2.104(6)	2.117(2)	2.111(4)
Re1–Se1	–	2.439(1)	2.4923(5)	2.5003(6)
O1–Re1–O10/N10	–	161.3(3)	171.53(7)	172.3(2)
Re1–N10–C51	–	–	176.8(2)	174.1(4)
C1–Se1–Re1	–	92.9(3)	91.22(7)	90.4(1)

[a] Values taken from  $[Re(NPhF)(L^{Se})Cl(PPh_3)] \cdot CH_3CN$ .

Table 2. Selected bond lengths [Å] and angles (°) in  $\{HL^{Te}\}_2$ ,  $[ReO(L^{Te})Cl(PPh_3)]$ ,  $[Re(NPh)(L^{Te})Cl(PPh_3)]$  and  $[Re(NPhF)(L^{Te})Cl(PPh_3)]$ .

Bond lengths/Å	$\{HL^{Te}\}_2$	$[ReO(L^{Te})Cl(PPh_3)]^{[a]}$	$[Re(NPh)(L^{Te})Cl(PPh_3)]$	$[Re(NPhF)(L^{Te})Cl(PPh_3)]$
Te1–C1	2.127(2)	2.119(8)/2.123(8)	2.132(3)	2.128(4)
O1–C11	1.356(3)	1.33(1)/1.325(9)	1.332(4)	1.328(4)
N1–C6	1.415(3)	1.45(1)/1.44(1)	1.447(4)	1.449(5)
N1–C17	1.287(3)	1.30(1)/1.30(1)	1.296(4)	1.299(5)
Re1–O10/N10	–	1.699(6)/1.695(6)	1.726(3)	1.720(3)
Re1–O1	–	1.962(6)/1.985(6)	1.994(2)	1.990(2)
Re1–P1	–	2.469(2)/2.458(2)	2.4422(8)	2.4437(9)
Re1–Cl1	–	2.539(2)/2.527(2)	2.5045(9)	2.498(1)
Re1–N1	–	2.120(6)/2.105(7)	2.115(3)	2.107(3)
Re1–Te1	–	2.6416(6)/2.6469(6)	2.6899(3)	2.6869(3)
O1–Re1–O10/N10	–	166.4(3)/164.1(3)	169.6(1)	172.2(1)
Re1–N10–C51	–	–	168.1(3)	172.3(3)
C1–Te1–Re1	–	86.1(2)/85.7(2)	86.2(1)	85.7(1)

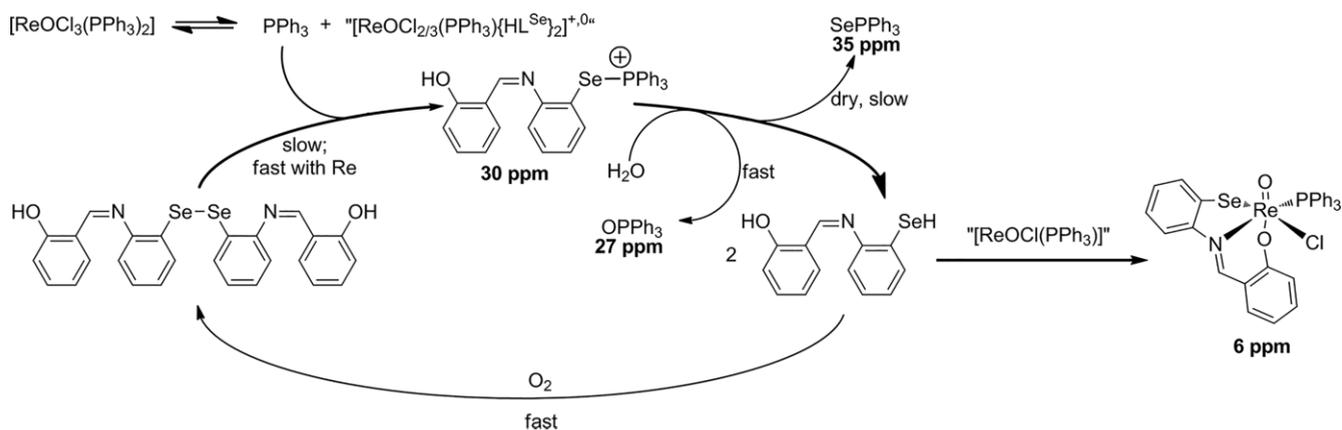
[a] Values for two independent species.



Scheme 1. Synthesis of the rhenium(V) selenolato and telluroloato complexes (all reactions were performed under argon).

$\{Ph_3P(OH)_2(Se(C_6H_4)-2-N=CH(C_6H_4)-2-OH)\}^+$  eliminates the free selenol ( $H_2L^{Se}$ ), HCl and  $OPPh_3$  as a consequence of the forma-

tion of the very stable  $P=O$  bond. The analogous  $Ph_3P(Se-R)$  ( $Se(C_6H_4)-2-N=CH(C_6H_4)-2-OH$ ) probably follows the same path-



Scheme 2. Proposed mechanism for the reaction between  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  and  $\{\text{HLSe}\}_2$  in  $\text{CH}_2\text{Cl}_2$ . Chemical shifts refer to  $^{31}\text{P}$ .

way with formation of  $\text{Se}\{(\text{C}_6\text{H}_4)\text{-2-N=CH}(\text{C}_6\text{H}_4)\text{-2-OH}\}_2$  and  $\text{SePPh}_3$ . The formation of such chalcogenoethers from organochalcogeno-phosphonium starting materials with formation of a formal phosphorus-chalcogen double bond is well-established.<sup>[34–37]</sup>

It should be noted that the relative rates of the described reactions are only valid in the presence of the rhenium complex. Reactions of  $\{\text{HL}^{\text{Se}}\}_2$  with pure  $\text{PPh}_3$  are very slow and form under the same conditions considerable amounts of  $\text{OPPh}_3$  only within days or weeks.

The same general course of the reaction as outlined in Scheme 2 can also be assumed for the phenylimido starting complexes and also for reactions with  $\{\text{HL}^{\text{Te}}\}_2$ . It should be mentioned that the reaction times may significantly differ and particularly the used solvent plays a crucial role. While  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  and  $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2]$  are sparingly soluble in most solvents, it proved to be favorable to reduce the solubility of the fluorinated phenylimido complexes for the reactions under study. For example,  $[\text{Re}(\text{NPhF})(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$  is formed only in low yields from reactions in  $\text{CH}_2\text{Cl}_2$ , in which the starting complex  $[\text{Re}(\text{NPhF})\text{Cl}_3(\text{PPh}_3)_2]$  is readily soluble. Higher yields are obtained in a  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1:6) mixture, in which the starting material is less soluble.

The red to brown complexes are stable as solids. In solution, however, they show gradual decomposition, which is normally higher in non-degassed solvents and can be understood by the re-formation of the dichalcogenides on air. The instability of some of the products and (in some cases) their low solubility prevent from the measurement of  $^{13}\text{C}$ ,  $^{77}\text{Se}$  and  $^{125}\text{Te}$  NMR spectra of sufficient quality.  $[\text{ReO}(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$  is the most unstable compound of our series and in the related NMR spectra appear signals of decomposition products directly after dissolution, even when measured in dry, degassed  $\text{CD}_2\text{Cl}_2$ . In turn, the related tellurium complex is stable in solution for several hours. The highest stability was found for  $[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$ , which shows no decomposition after several days in wet, non-degassed solvents.

The  $^{77}\text{Se}$  signals of the coordinated selenolato ligands appear between 360 and 395 ppm and the corresponding  $^{125}\text{Te}$  resonances are found between 378 and 695 ppm. In the spectra of the well-soluble fluorinated complexes  $[\text{Re}(\text{NPhF})(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$

and  $[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$ , the  $^{77}\text{Se}$  resonances are observed as doublets at 360 ppm ( $^2J_{\text{Se,P}} = 22$  Hz) and 395 ppm ( $^2J_{\text{Se,P}} = 24$  Hz). The coupling constants are within the magnitude of couplings, which have previously been observed for mixed selenolato/phosphine complexes of platinum.<sup>[38,39]</sup> The  $^{125}\text{Te}$  NMR spectra show signals with a  $^2J_{\text{Te,P}}$  coupling of 50–60 Hz, which is also in accord with the situation in similar Pt(II) compounds.<sup>[38]</sup> The  $^{77}\text{Se}$  and  $^{125}\text{Te}$  couplings could not be observed in the respective  $^{31}\text{P}$  NMR spectra.

A key feature in the proton NMR spectra of Schiff base complexes is the resonance of their unique imine proton. It is well-separated from the remaining aromatic resonances. The imine protons in the selenolato complexes are more deshielded compared to those in the telluroolato complexes, which is similar to the situation in the corresponding dichalcogenides  $\{\text{HL}^{\text{Se}}\}_2$  and  $\{\text{HL}^{\text{Te}}\}_2$ . Additionally, the imine protons are more deshielded in the oxido complexes compared to the phenylimido complexes. These observations can be attributed to the better donor abilities of the phenylimido ligands as compared to oxido ligands. In complexes with imine and phosphine ligands, the imine protons often couple to the  $^{31}\text{P}$  nuclei. This is also the case in the reported complexes with coupling constants of about 8 Hz and allows an *in situ* control of the complex formation. The  $^{31}\text{P}$  chemical shifts observed for the rhenium complexes are correlated to the donor strength of the rhenium multiple bonded cores. It is highest for the oxido complexes and decreases by 5 ppm to the phenylimido complexes. ESI+ mass spectra of the rhenium complexes under study show intense signals of their  $[\text{M} - \text{Cl}]^+$  ions. Typically, fragment peaks are observed, which correspond to ions with chalcogen–phosphorus bonds, such as  $\{\text{Ph}_3\text{PSe}(\text{C}_6\text{H}_4)\text{-2-N=CHC}_6\text{H}_4\text{-2-OH}\}^+$  ( $m/z = 538.0818$ ) or  $\{\text{Ph}_3\text{PSe}(\text{C}_6\text{H}_4)\text{-2-NH}_2\}^+$  ( $m/z = 343.0556$ ). The number and the intensities of such fragments depend on the stability of the complexes in solution.

Crystallographic studies on single-crystals of  $[\text{ReO}(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$ ,  $[\text{Re}(\text{NPhF})(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)] \cdot \text{CH}_3\text{CN}$ ,  $[\text{Re}(\text{NPhF})(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)] \cdot 0.5\text{CH}_2\text{Cl}_2$ ,  $[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$ ,  $[\text{ReO}(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)] \cdot \text{CH}_2\text{Cl}_2$ ,  $[\text{Re}(\text{NPh})(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)] \cdot \text{CHCl}_3$  and  $[\text{Re}(\text{NPhF})(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)]$  have been undertaken. All complexes show the same general structure with facially bonded tridentate ligands. The hydroxylic group of the organic tridentate ligand is in *trans* position to the oxido or

phenylimido ligand in all compounds.  $\text{PPh}_3$  and  $\text{Cl}^-$  ligands complete the equatorial coordination spheres of rhenium with the latter ligand being arranged *trans* to the selenium or tellurium atoms of the Schiff base. The molecular structures of  $[\text{ReO}(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)]$  and  $[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$  are shown in Figure 2 and Figure 3 as representatives for the complexes with the selenium- and tellurium-containing ligands. Since the general features of the other oxido and phenylimido complexes with the tridentate ligands are similar, their structures are not shown here. They can be found in the Supplementary Information. Selected bond lengths and angles of all complexes and the corresponding dichalcogenides are summarized in Table 1 (selenium compounds) and Table 2 (tellurium compounds).

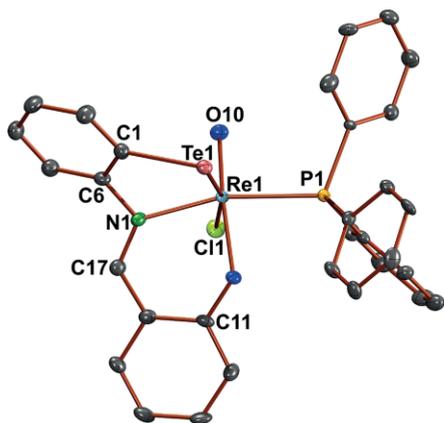


Figure 2. Molecular structure of  $[\text{ReO}(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)]$ . Ellipsoids are depicted at 50 % probability. Hydrogen atoms are omitted for clarity.

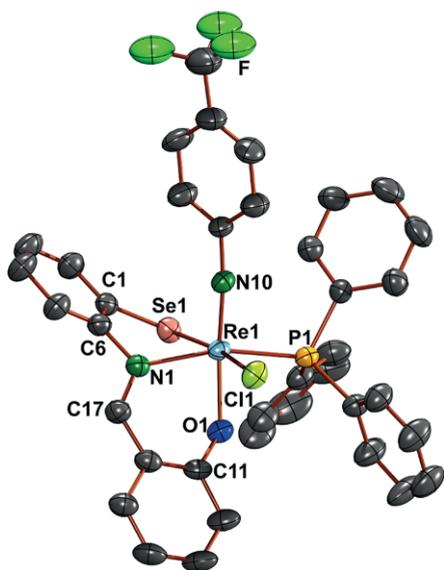


Figure 3. Molecular structure of  $[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$ . Ellipsoids are depicted at 50 % probability. Hydrogen atoms are omitted for clarity.

The rhenium atoms in the complexes have distorted octahedral coordination environments. Main distortions come from the restrictions caused by the facially coordinated tridentate ligands. The  $\text{N1}-\text{Re1}-\text{Se1/Te1}$  angles are between  $79.1$  and  $80.6^\circ$  and the  $\text{N1}-\text{Re1}-\text{O1}$  angles are between  $82.2$  and  $83.6^\circ$ . The angles between the axially bonded atoms  $\text{O10}$  or  $\text{N10}$  and

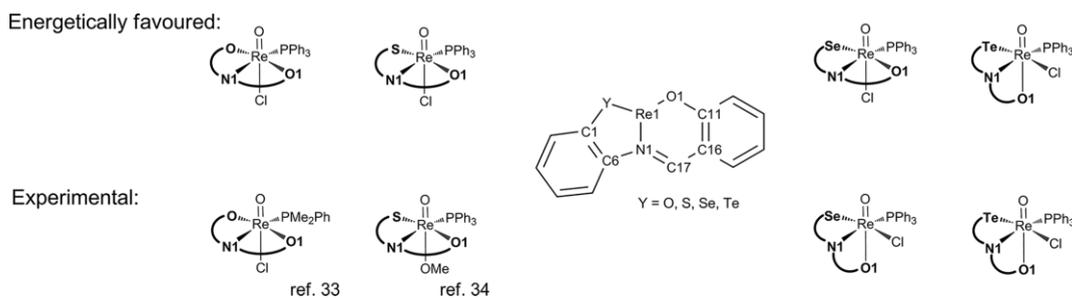
the donor atoms of the tridentate ligands in the equatorial coordination sphere are all larger than  $90^\circ$ . This is a consequence of the steric demand of the double bonds, which are established between rhenium and the oxido and arylimido ligands.

Similar results have been found in a series of related complexes before.<sup>[40–43]</sup> The corresponding  $\text{Re1}-\text{O10}$  ( $1.688(5)$ – $1.699(5)$  Å) and  $\text{Re1}-\text{N10}$  bonds ( $1.720(3)$ – $1.728(3)$  Å) are in the usual ranges and the imido ligands are linear.<sup>[40]</sup> It is interesting to note that all  $\text{Re1}-\text{O1}$  bonds are in the range or smaller than 2 Å. Such values are somewhat smaller than expected for  $\text{Re}-\text{O}$  single bonds, but not unusual for oxido or arylimido complexes of rhenium(V), since similar features are found with about 50 per cent of the crystallographically studied compounds of these types.<sup>[1]</sup> The effect is commonly explained by a partial transfer of electron density from the  $\text{Re}-\text{O/N}$  double bonds to the *trans*  $\text{Re}-\text{O}$  bond.<sup>[40,44–46]</sup>

The  $\text{Re}-\text{Se}$  bonds between  $2.439(1)$  and  $2.5003(6)$  Å are relatively short and similar bond lengths have hitherto only been found in some rare examples of  $\text{Re(V)}$  complexes with terminal phenylselenolato complexes,<sup>[19,21,28]</sup> while in the majority of their rhenium complexes such ligands bridge two low-valent rhenium atoms and the related  $\text{Re}-\text{Se}$  bond are in the range of 2.6 Å or longer.<sup>[1]</sup> Short  $\text{Re}-\text{Se}$  bonds are also established in binuclear rhenium compounds with  $\text{Re}-\text{Re}$  bonds or diselenolene complexes.<sup>[18,23]</sup> Most of the few rhenium complexes with tellurolo ligands are carbonyl compounds of  $\text{Re(I)}$  and they have  $\text{Re}-\text{Te}$  bond lengths between 2.760 and 2.811 Å.<sup>[3,6,8,11–14]</sup> Very recently, a series of  $[\text{Re}^{\text{VO}}(\text{aryltelluroate})_4]^-$  and  $[\text{Re}^{\text{III}}(\text{aryltelluroate})_3(\text{PPh}_3)(\text{CH}_3\text{CN})]$  complexes was prepared and structurally characterized.<sup>[28]</sup> The  $\text{Re}-\text{Te}$  bond lengths in the  $\text{Re(V)}$  complexes are very similar to the values for the compounds of the present study.

An interesting feature is the bond length distribution in the six-membered chelate rings of the  $[\text{ReO}(\text{L}^{\text{Y}})\text{Cl}(\text{PPh}_3)]$  and  $[\text{Re}(\text{NPhR})(\text{L}^{\text{Y}})\text{Cl}(\text{PPh}_3)]$  complexes ( $\text{Y} = \text{Se}, \text{Te}; \text{R} = \text{H}, \text{F}, \text{CF}_3$ ). The  $\text{N1}-\text{C17}$  bonds are only slightly lengthened compared to the related bonds in  $\{\text{HL}^{\text{Se}}\}_2$  and  $\{\text{HL}^{\text{Te}}\}_2$ . This means that the imine double bonds remain mainly localized and no significant delocalization of  $\pi$ -electron density is observed in this chelate ring. A similar bonding situation is observed in analogous oxidorhenium(V) complexes with the salicylidene Schiff bases derived from 2-aminophenol ( $\{\text{L}^{\text{O}}\}_2^-$ ) or 2-aminothiophenol ( $\{\text{L}^{\text{S}}\}_2^-$ ),<sup>[47,48]</sup> despite the fact that the tridentate  $\text{O,N,O}$  and  $\text{O,N,S}$  ligands are both coordinated in a *meridional* arrangement.

Since all hitherto structurally studied  $\text{Re(V)}$  complexes with the  $\{\text{L}^{\text{O}}\}_2^-$  and  $\{\text{L}^{\text{S}}\}_2^-$  show a *mer*-arrangement of these ligands,<sup>[47–55]</sup> and the complexes with their selenium and tellurium analogues of the present study contain the tridentate ligand exclusively in a *facial* coordination mode, we undertook a series of DFT calculations on the B3LYP level for both isomers of the  $[\text{ReO}(\text{L}^{\text{Y}})\text{Cl}(\text{PPh}_3)]$  ( $\text{Y} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ) complexes. Frequency calculations after the optimizations showed convergence of at least two out of four criteria in all cases and full convergence on the experimentally expected isomers. No negative frequencies were obtained. The calculated bonding parameters for the facial isomers with  $\{\text{L}^{\text{Se}}\}_2^-$  and  $\{\text{L}^{\text{Te}}\}_2^-$  match the determined crystal structures of *fac*- $[\text{ReO}(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)]$  and *fac*- $[\text{ReO}(\text{L}^{\text{Te}})$



Scheme 3. Calculated and experimentally isolated isomers for  $[\text{ReO}(\text{L}^{\text{Y}})\text{X}(\text{PR}_3)_2]$  complexes (Y = O, S, Se, Te; X = Cl or OMe).

$\text{Cl}(\text{PPh}_3)_2]$  on average within 0.037 Å. The deviations are highest with an average of 0.053 Å for the coordination sphere of rhenium, which is expected for a gas phase calculation.

Table 3 contains a comparison of the calculated over-all energies for the respective isomers and Scheme 3 visualizes the results. It becomes evident that the meridional isomers are more stable for the complexes with the phenolato, thiophenolato and selenophenolato ligands, while the *fac* compound is preferred for the tellurolato complex. But it is also clear that the calculated energy differences are small and are only suitable for the justification of the preferred formation of the *mer* complex in the case of  $[\text{ReO}(\text{L}^{\text{O}})\text{Cl}(\text{PPh}_3)_2]$ . Nevertheless, the trend found in the experiments, namely that the stability of the *facial* isomers increases for the heavier chalcogens, is well reflected by the computational results, even when the crystallized products for the Se-containing complexes show *fac* and not *mer* coordination.

Table 3. Energies for the *mer* and *fac* isomers the  $[\text{ReO}(\text{L}^{\text{Y}})\text{Cl}(\text{PPh}_3)_2]$  complexes (Y = O, S, Se, Te). The energies of the most stable geometries are in bold.

	$E_{\text{mer}}/\text{Hartree}$	$E_{\text{fac}}/\text{Hartree}$	$\Delta E/\text{kJ mol}^{-1}$
Y = O	<b>-1577.20576</b>	-1577.19178	36.8
Y = S	<b>-1512.08892</b>	-1512.08631	6.7
Y = Se	<b>-1511.20096</b>	-1511.19872	5.9
Y = Te	-1510.00999	<b>-1510.01209</b>	-5.4

A possible reason for this result might be given by the well-known labilization of the coordination positions *trans* to the multiple-bonded oxido or arylimido ligands. It is generally accepted, that ligand exchange reactions at complexes with the  $[\text{ReO}/\text{NAr}]^{3+}$  cores start with the substitution of the *trans*-ligand. Therefore, complexes with the *fac*-coordinated ligands should be the initial products in such reactions. As the reactions with the oxido complexes were performed under mild conditions, which means under kinetic control, a rationale for the observation of the *fac* complexes is given. Obviously, the formation of such intermediates at room temperature is faster than their subsequent isomerization. As the complexes tend to decompose at prolonged times of higher temperatures an isomerization to the *mer*-isomers could not be observed.

It would be interesting to study similar reactions with corresponding technetium compounds, where the kinetics of ligand exchange reactions is commonly faster. Unfortunately, there exists no oxidotechnetium(V) analogue to  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  and the phenylimido complex  $[\text{Tc}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2]$  is almost insoluble.

But recently the synthesis of two fluorinated arylimidotechnetium(V) complexes,  $[\text{Tc}(\text{NPh-4-F})\text{Cl}_3(\text{PPh}_3)_2]$  and  $[\text{Tc}(\text{NPh-4-CF}_3)\text{Cl}_3(\text{PPh}_3)_2]$ , has been reported.<sup>[43]</sup> Reactions between these novel precursors and dichalcogenides are planned for the future and their results may give a deeper insight into the mechanism of such reactions.

## Conclusions

Rhenium(V) complexes with tridentate selenolato- and tellurolato-substituted Schiff base ligands are formed during reactions of the corresponding dichalcogenides  $\{\text{HL}^{\text{Se}}\}_2$  or  $\{\text{HL}^{\text{Te}}\}_2$  with phosphine-containing rhenium(V) complexes such as  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  or  $[\text{Re}(\text{NAr})\text{Cl}_3(\text{PPh}_3)_2]$  (Ar = Ph, PhF,  $\text{PhCF}_3$ ). The resulting  $[\text{ReO}(\text{L}^{\text{Y}})\text{Cl}(\text{PPh}_3)_2]$  or  $[\text{Re}(\text{NAr})(\text{L}^{\text{Y}})\text{Cl}(\text{PPh}_3)_2]$  complexes (Y = Se, Te) contain the tridentate ligands in a *facial* arrangement.

A mechanism for such reactions has been deduced, in which released  $\text{PPh}_3$  acts as reducing agent for the dichalcogenides. Optimal yields are obtained in the presence of water and under strict exclusion of dioxygen. The method is well-suited for the synthesis of high-valent rhenium complexes.

## Experimental Section

$(\text{NBu}_4)[\text{ReOCl}_4]$ ,<sup>[56]</sup>  $[\text{ReOCl}_3(\text{PPh}_3)_2]$ ,<sup>[57]</sup>  $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2]$ ,<sup>[58]</sup>  $[\text{Re}(\text{NPhF})\text{Cl}_3(\text{PPh}_3)_2]$ ,<sup>[42]</sup> bis(2-aminophenyl)diselenide and bis(2-aminophenyl)dite lluride were prepared according to literature procedures.<sup>[59–61]</sup> All other chemicals were reagent grade and used as received. Reactions involving oxygen- or water-sensitive compounds were performed with standard Schlenk technique.

NMR spectra were recorded at 25 °C on JEOL 400 MHz ECS-400 or JNM-ECA400II spectrometers. Chemical shifts ( $\delta$ ) are given relative to the signals of external standards (tetramethylsilane, ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{ClCF}_3$  ( $^{19}\text{F}$ ), 85 % phosphoric acid ( $^{31}\text{P}$ ), dimethylselenide ( $^{77}\text{Se}$ ) and dimethyltelluride ( $^{125}\text{Te}$ ).

IR-Spectra were recorded with an FT-IR spectrometer (Nicolet iS10, Thermo Scientific). Intensities are classified as vs. = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

Electrospray ionization mass spectrometry (ESI MS) was carried out with the ESI MSD TOF unit of an Agilent 6210 TOF LC/MS system. The measurements were performed in  $\text{CHCl}_3$ ,  $\text{CDCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , MeOH or mixtures of them.

Elemental analyses were performed using a vario EL III CHN elemental analyzer (Elementar Analysensysteme GmbH) or a vario MICRO cube CHNS elemental analyzer.

Single crystal X-ray diffraction data were collected on a Bruker D8 Venture or a STOE IPDS II T. Absorption corrections were carried out by the multiscan (Bruker D8 Venture) or integration methods (STOE IPDS II T).<sup>[62,63]</sup> Structure solutions and refinements were done with the SHELX-2008 program packages.<sup>[64,65]</sup> Hydrogen atom positions at heteroatoms or the imino carbon atoms were taken from the Fourier maps when possible or placed at calculated positions and refined by a riding model. All other hydrogen atoms were placed at calculated positions and refined by a riding model. The visualization of the molecular structures was done using the program DIAMOND 4.2.2.<sup>[66]</sup>

CCDC 1956176–1956184 (see Supporting Information for the reference number of each compound) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

DFT calculations were performed on the high-performance computing systems of the Freie Universität Berlin ZEDAT (Soroban, Curta) using the program packages GAUSSIAN 09 and GAUSSIAN 16.<sup>[67,68]</sup> The gas phase geometry optimizations were performed using coordinates derived from the X-ray crystal structures or have been modelled with the use of crystal structure fragments using GAUSSVIEW.<sup>[69]</sup> The calculations were performed with the hybrid density functional B3LYP.<sup>[70–72]</sup> The double- $\zeta$  pseudopotential LANL2DZ basis set with the respective effective core potential (ECP) was applied to Re as well as S, Se and Te.<sup>[73]</sup> The 6-311G\*\*basis set was applied for all other atoms.<sup>[74–76]</sup> The LANL2DZ and 6-311G\*\* basis sets as well as the ECPs were obtained from the EMSL database.<sup>[77]</sup>

**{HL<sup>Se</sup>}<sub>2</sub>**. Salicylaldehyde (0.12 mL, 1.16 mmol) was added to a stirred suspension of bis(2-aminophenyl)diselenide (200 mg, 0.58 mmol) in 18 mL of EtOH. The mixture was heated under reflux for 4 h. A yellow solid precipitated over this period. After cooling to room temperature, the solid was filtered off. Before crystallization from EtOH/CHCl<sub>3</sub>, traces of elemental selenium must be removed by filtration of the hot solution. Orange-yellow crystals. Yield: 172 mg (53 %).

Alternatively, if no precipitate is observed after one hour, the addition of dry MgSO<sub>4</sub> starts the reaction. The procedure is followed as described above. The precipitate is extracted with CH<sub>2</sub>Cl<sub>2</sub> until the extract is colorless, the solvent is removed in vacuo and the residue recrystallized from EtOH/CHCl<sub>3</sub>.

Elemental analysis: Calculated for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Se<sub>2</sub>: C 56.7, H 3.7, N 5.1 %; Found C 56.6, H 3.7, N 5.1 %. IR (cm<sup>-1</sup>):  $\tilde{\nu}$  = 1608 (s) C=N, 1579 (m), 1562 (s), 1490 (m), 1461 (s), 1437 (m), 1362 (m), 1275 (s), 1226 (m), 1183 (s), 1147 (s), 1110 (w), 1044 (w), 1029 (m), 970 (m), 936 (w), 907 (s), 862 (w), 843 (m), 781 (m), 746 (vs), 706 (s), 672 (m), 641 (m), 601 (w), 576 (w), 569 (w), 553 cm<sup>-1</sup> (s). ESI+ MS (*m/z*): 552.9959 (calc. 552.9937) [M + H]<sup>+</sup>, 574.9786 (calc. 574.9757) [M + Na]<sup>+</sup>, 590.9524 (calc. 590.9496) [M + K]<sup>+</sup>, 1124.9671 (calc. 1124.9640) [2M+Na]<sup>+</sup>, 1140.9407 (calc. 1140.9379) [2M+K]<sup>+</sup>. ESI-MS (*m/z*): 550.9759 (calc. 550.9781) [M – H]<sup>-</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 12.74 (2H, br, OH), 8.60 (2H, s, HCR=NR), 7.75–7.69 (2H, m, *o*-Se-*m*-NR-ArH), 7.45–7.38 (4H, m, *o*-CNR-*m*-OH-ArH; *p*-CNR-*m*-OH-ArH), 7.29–7.38 (2H, m, *p*-Se-*m*-NR-ArH), 7.17–7.09 (4H, m, *m*-Se-*p*-NR-ArH; *m*-CNR-*p*-OH-ArH), 7.08–7.04 (2H, m, *m*-CNR-*o*-OH-ArH), 6.99–6.93 (2H, m, *m*-Se-*o*-NR-ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 163.2 (s, HCR=NR), 161.2 (s, R<sub>2</sub>C<sub>Ar</sub>-OH), 147.5 (s, NR-C<sub>Ar</sub>R<sub>2</sub>), 133.9 (s, *m*-NC-*o*-Se-R<sub>2</sub>C<sub>Ar</sub>), 132.8 (s, *m*-OH-*p*-CN-R<sub>2</sub>C<sub>Ar</sub>), 131.0 (s, *m*-OH-*o*-CN-R<sub>2</sub>C<sub>Ar</sub>), 128.4 (s, *p*-NC-*m*-Se-R<sub>2</sub>C<sub>Ar</sub>), 128.2 (s, *m*-NC-*p*-Se-R<sub>2</sub>C<sub>Ar</sub>), 126.8 (s, R<sub>2</sub>C<sub>Ar</sub>-Se), 119.4 (s, *o*-NC-*m*-Se-R<sub>2</sub>C<sub>Ar</sub>), 119.2 (s, *p*-OH-*m*-CN-R<sub>2</sub>C<sub>Ar</sub>), 117.7 (s, *o*-OH-R<sub>2</sub>C<sub>Ar</sub>-CNR), 117.6 (s, *o*-OH-*m*-CN-R<sub>2</sub>C<sub>Ar</sub>). <sup>77</sup>Se NMR (CDCl<sub>3</sub>, ppm): 363 (s).

**{HL<sup>Te</sup>}<sub>2</sub>**. Salicylaldehyde (0.15 mL, 1.41 mmol) was added to a suspension of bis(2-aminophenyl)ditelluride (200 mg, 0.46 mmol) in

dry, degassed MeOH (9 mL) whilst stirring. It was heated under reflux for 3 h. An orange-red solid precipitated over this period. After cooling to room temperature, the pure product was filtered off and dried in vacuo. The product can be recrystallized from hot EtOH/CHCl<sub>3</sub>. Orange-red crystals. Yield: 240 mg (0.44 mmol, 96 %).

Alternatively, if no precipitate is observed after one hour, the addition of dry MgSO<sub>4</sub> starts the reaction. The procedure is followed as described above. The precipitate is extracted with CH<sub>2</sub>Cl<sub>2</sub> until the extract is colorless, the solvent is removed in vacuo and the residue recrystallized from EtOH/CHCl<sub>3</sub>.

Elemental analysis: Calculated for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: C 48.2, H 3.1, N 4.3 %; Found C 48.1, H 3.2, N 4.3 %. IR (cm<sup>-1</sup>):  $\tilde{\nu}$  = 1605 (s) C=N, 1578 (m), 1558 (m), 1492 (m), 1457 (m), 1435 (m), 1384 (m), 1361 (m), 1274 (s), 1239 (w), 1225 (m), 1179 (m), 1154 (m), 1146 (m), 1108 (m), 1034 (m), 1018 (m), 975 (w), 937 (w), 905 (m), 853 (m), 841 (m), 779 (m), 747 (vs), 732 (sh), 708 (s), 666 (m), 638 (m), 575 (m), 551 (s). ESI+ MS (*m/z*): 648.9699 (calc. 648.9701) [M + H]<sup>+</sup>, 670.9532 (calc. 670.9521) [M + Na]<sup>+</sup>, 686.9269 (calc. 686.9259) [M + K]<sup>+</sup>, 1318.9152 (calc. 1318.9147) [2M+Na]<sup>+</sup>, 1334.8862 (calc. 1334.8885) [2M+K]<sup>+</sup>. ESI- MS (*m/z*): 646.9514 (calc. 646.9545) [M – H]<sup>-</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 12.53 (2H, s, OH), 8.55 (2H, s, HCR=NR), 7.94–7.85 (2H, m, *o*-Te-*m*-NR-ArH), 7.47–7.38 (4H, m, *o*-CNR-*m*-OH-ArH; *p*-CNR-*m*-OH-ArH), 7.34–7.27 (2H, m, *p*-Te-*m*-NR-ArH) 7.12–6.93 (8H, m, *m*-Te-*p*-NR-ArH; *m*-CNR-*p*-OH-ArH, *m*-CNR-*o*-OH-ArH, *m*-Te-*o*-NR-ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 163.7 (s, HCR=NR), 161.0 (s, R<sub>2</sub>C<sub>Ar</sub>-OH), 150.6 (s, NR-C<sub>Ar</sub>R<sub>2</sub>), 138.3 (s, *m*-NC-*o*-Te-R<sub>2</sub>C<sub>Ar</sub>), 134.0 (s, *m*-OH-*p*-CN-R<sub>2</sub>C<sub>Ar</sub>), 133.0 (s, *m*-OH-*o*-CN-R<sub>2</sub>C<sub>Ar</sub>), 129.4 (s, *p*-NC-*m*-Te-R<sub>2</sub>C<sub>Ar</sub>), 128.5 (s, *m*-NC-*p*-Te-R<sub>2</sub>C<sub>Ar</sub>), 119.6 (s, *o*-NC-*m*-Te-R<sub>2</sub>C<sub>Ar</sub>), 119.1 (s, *p*-OH-*m*-CN-R<sub>2</sub>C<sub>Ar</sub>), 117.6 (s, *o*-OH-R<sub>2</sub>C<sub>Ar</sub>-CNR), 117.1 (s, *o*-OH-*m*-CN-R<sub>2</sub>C<sub>Ar</sub>), 107.5 (s, R<sub>2</sub>C<sub>Ar</sub>-Te). <sup>125</sup>Te NMR (CDCl<sub>3</sub>, ppm): 228 (s).

**[ReO(L<sup>Se</sup>)Cl(PPh<sub>3</sub>)<sub>2</sub>]**. {HL<sup>Se</sup>}<sub>2</sub> (44 mg, 0.08 mmol) was dissolved in a degassed mixture of CH<sub>2</sub>Cl<sub>2</sub> (6 mL) and water (1 drop). [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (88 mg, 0.1 mmol) was added whilst stirring. The color changed from light yellow to dark brown and after 20 min of stirring at room temperature, the suspension became a clear brown solution. The mixture was overlaid with degassed diethyl ether (12 mL) and left in the freezer for slow diffusion. The formed crystals of [ReO(L<sup>Se</sup>)Cl(PPh<sub>3</sub>)<sub>2</sub>] were filtered off and washed with diethyl ether. Red-brown plates. Yield: 50 mg (68 %).

Elemental analysis: Calculated for C<sub>31</sub>H<sub>24</sub>CINO<sub>2</sub>PrSe: C 48.1, H 3.1, N 1.8 %; Found C 48.0, H 3.2, N 1.5 %. IR (cm<sup>-1</sup>):  $\tilde{\nu}$  = 3046 (w), 1601 (m) C=N, 1582 (m), 1567 (m), 1532 (m), 1481 (m), 1454 (m), 1432 (m), 1373 (m), 1283 (m), 1230 (w), 1175 (m), 1157 (m), 1148 (m), 1119 (m), 1094 (s), 1027 (m), 998 (m), 967 (sh), 955 (s) Re=O, 926 (m), 858 (m), 804 (m), 746 (vs), 718 (sh), 707 (sh), 690 (vs), 615 (s), 595 (m), 559 (s), 544 (m). ESI+ MS (*m/z*): 740.0224 (calc. 740.0267) [M – Cl]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 8.69 (1H, s, HCR=NR), 8.00–6.96 (23H, m, ArH). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 6.1 (s).

**[ReO(L<sup>Te</sup>)Cl(PPh<sub>3</sub>)<sub>2</sub>]**. {HL<sup>Te</sup>}<sub>2</sub> (64 mg, 0.1 mmol) was added to a suspension of [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (88 mg, 0.1 mmol) in a degassed mixture of CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and water (1 drop) whilst stirring. The color changed from light yellow to brown-yellow over a period of 2 h. The mixture was stirred at room temperature for 3 days. During this time, an orange-red powder precipitated. The volume was reduced to 2 mL and the orange-red precipitate was filtered off. Diethyl ether (12 mL) was added to the mixture and the solvent was reduced in a stream of dry argon to approximately 8 mL. An additional amount of degassed diethyl ether (12 mL) was added. The procedure was repeated four times. Finally, dark red crystals were formed. They were filtered off and washed subsequently with diethyl ether and hexane. Dark red plates. Yield: 15 mg (20 %).

Elemental analysis: Calculated for  $C_{32}H_{26}Cl_3NO_2PReTe$ : C 44.7, H 3.1, N 1.6 %; Found C 45.1, H 3.1, N 1.6 %. IR ( $cm^{-1}$ ):  $\tilde{\nu} = 3054$  (w), 1602 (s) C=N, 1583 (s), 1566 (m), 1537 (s), 1481 (m), 1452 (m), 1432 (s), 1373 (m), 1341 (w), 1289 (s), 1263 (m), 1231 (w), 1189 (w), 1177 (w), 1160 (w), 1148 (m), 1121 (w), 1094 (s), 1072 (sh), 1028 (m), 998 (m), 961 (s) Re=O, 944 (s), 927 (m), 892 (w), 862 (m), 806 (m), 749 (vs), 732 (vs), 704 (sh), 690 (vs), 641 (w), 617 (s), 598 (m), 574 (w), 559 (m), 544 (vs). ESI+ MS ( $m/z$ ): 788.0143 (calc. 788.0147)  $[M - Cl]^+$ .  $^1H$  NMR ( $CDCl_3$ , ppm): 8.60 (1H, d,  $^4J_{H,P} = 7.71$  Hz, HCR=NR), 8.10–7.31 (25H, m, ArH), 7.20–7.09 (1H, m,  $^1ArH$ ), 7.07–7.03 (1H, m,  $^1ArH$ ), 6.18–6.00 (1H, m,  $^1ArH$ ).  $^{13}C$  NMR ( $CDCl_3$ , ppm): 169.8 (s,  $R_2C_{ar}-O$ ), 162.2 (s, RC-NR), 160.8 (s,  $R_2C_{ar}-NCR$ ), 137.7 (s,  $p-CN-m-O-C_{ar}$ ), 136.4 ( $R_2C_{ar}-Te$ ), 135.7 (s,  $^1C_{ar}$ ), 134.9 (d,  $^3J_{C,P} = 10$  Hz,  $m-P-C_{ar}$ ), 132.8 (s,  $^1C_{ar}$ ), 132.2 (s,  $^1C_{ar}$ ), 131.3 (d,  $^4J_{C,P} = 0$  Hz,  $p-P-C_{ar}$ ), 128.7, (d,  $^2J_{C,P} = 11$  Hz,  $o-P-C_{ar}$ ), 128.6 (s,  $^1C_{ar}$ ), 128.1 (s,  $^1C_{ar}$ ), 127.1 (s,  $^1C_{ar}$ ), 122.4, (s,  $^1C_{ar}$ ), 119.5 (d,  $^1J_{C,P} = 12$  Hz,  $P-C_{ar}$ ), 119.3 (s,  $^1C_{ar}$ ).  $^{31}P$  NMR ( $CDCl_3$ , ppm): 6.3 (s).  $^{125}Te$  NMR ( $CDCl_3$ , ppm): 695 (d,  $^2J_{Te,P} = 59$  Hz).

**[Re(NPh)(L<sup>Se</sup>)Cl(PPh<sub>3</sub>)<sub>2</sub>]**.  $[Re(NPh)Cl_3(PPh_3)_2]$  (88 mg, 0.1 mmol) was suspended in a degassed mixture of  $CH_3CN$  (6 mL) and water (1 drop).  $\{HL^{Se}\}_2$  (44 mg, 0.08 mmol) was added as a solid after heating this mixture to reflux. The color changed from dark green to red-violet immediately and a red-brown solid precipitated together with unreacted  $\{HL^{Se}\}_2$ . After 3 min,  $CH_2Cl_2$  (1 mL) was added, which dissolved the remaining diselenide. The  $CH_2Cl_2$  was removed in a stream of argon. The mixture was cooled to room temperature and the product was filtered off as a brown powder. After washing with diethyl ether (10 mL) to remove potentially remaining  $\{HL^{Se}\}_2$ , a brown-violet powder was obtained. Yield: 44 mg (54 %).

Elemental analysis: Calculated for  $C_{37}H_{29}ClN_2OPReSe$ : C 52.3, H 3.4, N 3.3 %; Found C 50.7, H 3.5, N 3.4 %. IR ( $cm^{-1}$ ):  $\tilde{\nu} = 3043$  (w), 1599 (m) C=N, 1586 (m), 1570 (m), 1534 (m), 1478 (m), 1456 (m), 1435 (s), 1380 (m), 1334 (m), 1291 (s), 1246 (w), 1234 (w), 1223 (w), 1188 (m), 1179 (m), 1158 (m), 1148 (m), 1120 (m), 1095 (s), 1066 (m), 1025 (m), 1011 (w), 991 (w), 965 (m), 947 (w), 925 (m), 859 (m), 804 (m), 770 (s), 762 (sh), 753 (vs), 743 (vs), 720 (m), 703 (sh), 693 (vs), 683 (vs), 625 (w), 613 (s), 604 (m), 567 (w), 556 (s), 544 (m). ESI+ MS ( $m/z$ ): 815.0793 (calc. 815.0741)  $[M - Cl]^+$ , 833.0700 (calc. 833.0847)  $[M - Cl + H_2O]^+$ .  $^1H$  NMR ( $CD_2Cl_2$ , ppm): 8.34 (1H, d,  $^4J_{H,P} = 8.02$  Hz, HCR=NR), 7.89–7.80 (6H, m,  $m-P-ArH$ ), 7.67–7.60 (1H, m,  $^1ArH$ ), 7.60–7.51 (2H, m, 2  $^1ArH$ ), 7.44–7.30 (10H, m,  $o,p-P-ArH$ ,  $^{NPh}ArH$ ), 7.30–7.20 (2H, m, 2  $^1ArH$ ), 7.13–7.05 (1H, m,  $^1ArH$ ), 7.05–6.94 (1H, m,  $^1ArH$ ), 6.97–6.78 (2H, m,  $^{NPh}ArH$ ), 6.44–6.39 (1H, m,  $^1ArH$ ), 6.39–6.32 (2H, m,  $^{NPh}ArH$ ).  $^{13}C$  NMR ( $CD_2Cl_2$ , ppm): 166.7 (s,  $R_2C_{ar}-O$ ), 164.1 (s, RC-NR), 160.2 (s,  $R_2C_{ar}-NCR$ ), 149.8 (s,  $^1C_{ar}$ ), 136.8 (s,  $R_2C_{ar}-Se$ ), 135.1 (br,  $^{NPh}C_{ar}$ ), 135.1 (d,  $^3J_{C,P} = 10$  Hz,  $m-P-C_{ar}$ ), 134.2 (s,  $^1C_{ar}$ ), 133.7 (s,  $^1C_{ar}$ ), 131.3 (s,  $p-P-C_{ar}$ ), 129.0 (s,  $^1C_{ar}$ ), 128.7 (d,  $^2J_{C,P} = 10$  Hz,  $o-P-C_{ar}$ ), 128.6 (s,  $^1C_{ar}$ ), 128.5 (s,  $^{NPh}C_{ar}$ ), 125.9 (s,  $^{NPh}C_{ar}$ ), 124.8 (m,  $P-C_{ar}$ ), 123.0 (s,  $^1C_{ar}$ ), 120.3 (s,  $^1C_{ar}$ ), 118.5 (s,  $^1C_{ar}$ ), 118.2 (s,  $^1C_{ar}$ ), 97.7 (s,  $^{NPh}C_{ar}$ ).  $^{31}P$  NMR ( $CDCl_3$ , ppm): 2.4 (s).

**[Re(NPh)(L<sup>Te</sup>)Cl(PPh<sub>3</sub>)<sub>2</sub>]**. A mixture of  $[Re(NPh)Cl_3(PPh_3)_2]$  (91 mg, 0.1 mmol),  $\{HL^{Te}\}_2$  (52 mg, 0.08 mmol), water (1 drop) and  $NEt_3$  (1 drop) was suspended in degassed EtOH (3 mL) and heated to reflux whilst stirring. Degassed  $CH_2Cl_2$  (2 mL) was added. The mixture was heated for 5 h under reflux. The grey-brown precipitate formed was separated by filtration. This mixture of  $[Re(NPh)Cl_3(PPh_3)_2]$  and  $[Re(NPh)(L^{Te})Cl(PPh_3)_2]$  (approximate ratio: 1:2) was washed with EtOH, diethyl ether and hexane. After drying, it was charged on a column of neutral alumina ( $d = 1$  cm,  $h = 12$  cm) and eluted with  $CH_2Cl_2$  containing 0.1 % MeOH. A brown band was collected and the solvent was evaporated in vacuo. The residue was re-dissolved

in a minimum amount of  $CH_2Cl_2$  and a mixture of diethyl ether and EtOH (1:1) was added. After evaporation,  $[Re(NPh)(L^{Te})Cl(PPh_3)_2]$  precipitated as a red powder from the remaining EtOH. It was filtered off, washed with EtOH, diethyl ether and hexane and dried in vacuo. Red-brown powder. Recrystallization can be done from  $CH_2Cl_2$ /hexane or  $CH_2Cl_2$ /diethyl ether. Yield: 24 mg (27 %).

Elemental analysis: Calculated for  $C_{37}H_{29}ClN_2OPReTe$ : C 49.5, H 3.3, N 3.1 %; Found C 50.7, H 3.4, N 2.8 %. IR ( $cm^{-1}$ ):  $\tilde{\nu} = 3051$  (w), 1600 (m) C=N, 1584 (m), 1567 (m), 1538 (m), 1483 (m), 1474 (m), 1451 (m), 1434 (s), 1372 (m), 1335 (m), 1312 (w), 1293 (s), 1262 (w), 1220 (w), 1188 (m), 1177 (m), 1161 (m), 1148 (m), 1122 (m), 1095 (s), 1066 (m), 1024 (m), 990 (w), 968 (w), 936 (sh), 926 (s), 859 (m), 804 (s), 768 (s), 758 (s), 743 (s), 718 (w), 706 (m), 689 (vs), 625 (w), 615 (s), 603 (s), 572 (w), 560 (s), 545 (s). ESI+ MS ( $m/z$ ): 863.0679 (calc. 863.0621)  $[M - Cl]^+$ .  $^1H$  NMR ( $CD_2Cl_2$ , ppm): 8.28 (1H, d,  $^4J_{H,P} = 8.20$  Hz, HCR=NR), 7.91–7.83 (6H, m,  $m-P-ArH$ ), 7.72–7.64 (1H, m,  $^1ArH$ ), 7.52–7.45 (2H, m, 2  $^1ArH$ ), 7.40–7.21 (11H, m, integral corrected for  $CHCl_3$ ,  $o,p-P-ArH$ ,  $^{NPh}ArH$ ,  $^1ArH$ ), 7.15–7.05 (2H, m, 2  $^1ArH$ ), 7.02–6.95 (1H, m,  $^1ArH$ ), 6.79–6.70 (2H, m,  $^{NPh}ArH$ ), 6.51–6.44 (1H, m,  $^1ArH$ ), 6.44–6.33 (2H, m,  $^{NPh}ArH$ ).  $^{13}C$  NMR ( $CDCl_3$ , ppm): 171.1 (s,  $^{NPh}C_{ar}$ ), 166.8 (s,  $R_2C_{ar}-O$ ), 163.2 (s, RC-NR), 162.2 (m,  $^1C_{ar}$ ), 156.0 (s,  $R_2C_{ar}-NCR$ ), 136.4 (s,  $R_2C_{ar}-Te$ ), 136.2 (s,  $^1C_{ar}$ ), 135.3 (s,  $^{NPh}C_{ar}$ ), 134.8 (s,  $^{NPh}C_{ar}$ ), 134.4 (d,  $^3J_{C,P} = 10$  Hz,  $m-P-C_{ar}$ ), 134.4 (s,  $^1C_{ar}$ ), 130.6 ( $^4J_{C,P} = 2$  Hz,  $p-P-C_{ar}$ ), 128.2 (d,  $^2J_{C,P} = 10$  Hz,  $o-P-C_{ar}$ ), 127.7 (d,  $J = 3$  Hz,  $^1C_{ar}$ ), 126.5 (s,  $P-C_{ar}$ ), 124.8 (s,  $^1C_{ar}$ ), 124.0 (d,  $J = 2$  Hz,  $^1C_{ar}$ ), 122.0 (s,  $^1C_{ar}$ ), 119.9 (s,  $^1C_{ar}$ ), 118.6 (s,  $^{NPh}C_{ar}$ ), 118.1 (s,  $^1C_{ar}$ ).  $^{31}P$  NMR ( $CDCl_3$ , ppm): 1.5 (s).  $^{125}Te$  NMR ( $CDCl_3$ , ppm): 378 (d,  $^2J_{Te,P} = 50$  Hz).

**[Re(NPhF)(L<sup>Se</sup>)Cl(PPh<sub>3</sub>)<sub>2</sub>]**. A mixture of  $[Re(NPhF)Cl_3(PPh_3)_2]$  (92 mg, 0.1 mmol) and  $\{HL^{Se}\}_2$  (45 mg, 0.08 mmol) was suspended in a mixture of  $CH_3CN$  (3 mL) and  $CH_2Cl_2$  (0.5 mL) and heated under reflux for 10 min. After cooling to room temperature, the mixture was overlaid with diethyl ether (6 mL) and left in the freezer for slow diffusion. The formed crystals of  $[Re(NPhF)(L^{Se})Cl(PPh_3)_2] \cdot CH_3CN$  were filtered off, washed with diethyl ether and dried. From the combined filtrates and washing solutions, a second crop of crystals was obtained by slow evaporation. Red-brown plates. Yield: 73 mg (83 %).

Elemental analysis: Calculated for  $C_{37}H_{28}ClFN_2OPReSe$ : C 51.2, H 3.3, N 3.2 %; Found C 50.7, H 3.7, N 3.2 %. IR ( $cm^{-1}$ ):  $\tilde{\nu} = 3056$  (w), 2973 (w), 1599 (m) C=N, 1584 (m), 1569 (m), 1536 (m), 1507 (m), 1481 (m), 1455 (m), 1434 (s), 1377 (m), 1334 (w), 1312 (w), 1285 (m), 1265 (sh), 1228 (s), 1179 (m), 1146 (s), 1119 (m), 1093 (s), 1070 (w), 1045 (w), 1027 (m), 1006 (m), 997 (m), 963 (m), 935 (w), 925 (m), 859 (m), 845 (s), 803 (m), 749 (vs), 740 (sh), 721 (m), 711 (sh), 692 (vs), 647 (m), 612 (s), 603 (s), 584 (sh), 576 (w), 556 (s), 540 (s), 527 (vs). ESI+ MS ( $m/z$ ): 833.0675 (calc. 833.0647)  $[M - Cl]^+$ .  $^1H$  NMR ( $CD_2Cl_2$ , ppm): 8.34 (1H, d,  $^4J_{H,P} = 8.14$  Hz, HCR=NR), 7.90–6.31 (27H, m, ArH).  $^{13}C$  NMR ( $CD_2Cl_2$ , ppm): 166.7 (s,  $R_2C_{ar}-O$ ), 164.2 (s, RC-NR), 161.5 (d,  $^1J_{C,F} = 256$  Hz,  $^{NPhF}C_{ar}-F$ ), 158.6 (s,  $R_2C_{ar}-NCR$ ), 153.3 (s,  $^{NPhF}C_{ar}$ ), 136.9 (s,  $^1C_{ar}$ ), 135.5 ( $R_2C_{ar}-Se$ ), 135.1 (d,  $^3J_{C,P} = 10$  Hz,  $m-P-C_{ar}$ ), 134.2 (s,  $^1C_{ar}$ ), 133.7 (s,  $^1C_{ar}$ ), 132.6 (s,  $^1C_{ar}$ ), 132.5 (s,  $^1C_{ar}$ ), 131.3 (s,  $p-P-C_{ar}$ ), 129.1 (d,  $^3J_{C,F} = 12$  Hz,  $^{NPhF}C_{ar}$ ), 128.7, (d,  $^2J_{C,P} = 10$  Hz,  $P-C_{ar}$ ), 126.9 (d,  $^3J_{C,P} = 8$  Hz,  $o-P-C_{ar}$ ), 125.9 (s,  $^1C_{ar}$ ), 120.4 (s,  $^1C_{ar}$ ), 118.6 (s,  $^1C_{ar}$ ), 118.2 (s,  $^1C_{ar}$ ), 116.3 (d,  $^2J_{C,F} = 23.9$  Hz,  $^{NPhF}C_{ar}$ ).  $^{19}F$  NMR ( $CD_2Cl_2$ , ppm): -107.7 (s).  $^{31}P$  NMR ( $CD_2Cl_2$ , ppm): 1.8 (s).  $^{77}Se$  NMR ( $CD_2Cl_2$ , ppm): 360 (d,  $^2J_{Se,P} = 22$  Hz).

**[Re(NPhF)(L<sup>Te</sup>)Cl(PPh<sub>3</sub>)<sub>2</sub>]**. A mixture of  $[Re(NPhF)Cl_3(PPh_3)_2]$  (92 mg, 0.1 mmol),  $\{HL^{Te}\}_2$  (52 mg, 0.08 mmol), water (1 drop) and  $NEt_3$  (1 drop) was suspended in degassed EtOH (3 mL). Degassed  $CH_2Cl_2$  (2 mL) was added. The mixture was heated under reflux for 6 h. The formed grey-brown solid consisting of a mixture of  $[Re(NPhF)Cl_3(PPh_3)_2]$  and  $[Re(NPhF)(L^{Te})Cl(PPh_3)_2]$  (1:1) was filtered

off, washed with EtOH, diethyl ether and hexane and charged on a column of neutral alumina ( $d = 1$  cm,  $h = 9.5$  cm). Elution with  $\text{CH}_2\text{Cl}_2$  containing 2.5 % MeOH gave a brown band of  $[\text{Re}(\text{NPhF})(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)]$ . The solvent was evaporated in vacuo, the residue was re-dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and a large excess of diethyl ether was added. The precipitated  $[\text{Re}(\text{NPhF})(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)]$  was filtered off, washed with diethyl ether and hexane and dried on air. Red-brown powder. Yield: 18.6 mg (20 %). Recrystallization can be done from  $\text{CH}_2\text{Cl}_2$ /hexane or  $\text{CH}_2\text{Cl}_2$ /diethyl ether mixtures.

Elemental analysis: Calculated for  $\text{C}_{37}\text{H}_{28}\text{ClF}_3\text{N}_2\text{OPReTe}$ : C 48.5, H 3.1, N 3.1 %; Found C 47.4, H 3.1, N 2.9 %. IR ( $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3051$  (w), 1599 (m) C=N, 1583 (m), 1566 (m), 1538 (m), 1485 (m), 1450 (m), 1434 (s), 1369 (m), 1334 (w), 1314 (w), 1290 (s), 1262 (sh), 1228 (s), 1188 (w), 1177 (m), 1162 (m), 1141 (s), 1121 (m), 1095 (s), 1028 (w), 1008 (m), 998 (m), 968 (m), 945 (w), 937 (w), 926 (m), 860 (m), 839 (s), 803 (s), 761 (s), 742 (s), 718 (m), 706 (m), 690 (vs), 648 (m), 616 (s), 603 (s), 558 (s), 546 (s). ESI+ MS ( $m/z$ ): 881.0556 (calc. 881.0527)  $[\text{M} - \text{Cl}]^+$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 8.29 (1H, d,  $^4J_{\text{H,P}} = 8.24$  Hz, HCR=NR), 7.97–7.80 (6H, m, *m*-P-ArH), 7.71–7.63 (1H, m,  $^1\text{ArH}$ ), 7.51–7.23 (12H, m, integral corrected for  $\text{CHCl}_3$ , 3  $^1\text{ArH}$ ; *o,p*-P-ArH), 7.17–7.04 (2H, m,  $^{\text{NPhF}}\text{ArH}$ ), 7.04–6.96 (1H, m,  $^1\text{ArH}$ ), 6.54–6.46 (1H, m,  $^1\text{ArH}$ ), 6.46–6.35 (4H, m, 2  $^1\text{ArH}$ ;  $^{\text{NPhF}}\text{ArH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 166.9 (s,  $\text{R}_2\text{C}_{\text{Ar-O}}$ ), 163.2 (s, RC-NR), 162.2 (d,  $^1J_{\text{C,F}} = 156$  Hz,  $^{\text{NPhF}}\text{C}_{\text{Ar-F}}$ ), 160.6 (m,  $^1\text{C}_{\text{Ar}}$ ), 153.9 (s,  $\text{R}_2\text{C}_{\text{Ar-NCR}}$ ), 136.6 (s,  $\text{R}_2\text{C}_{\text{Ar-Te}}$ ), 136.3 (s,  $^1\text{C}_{\text{Ar}}$ ), 135.5 (s,  $^{\text{NPhF}}\text{C}_{\text{Ar}}$ ), 134.5 (d,  $^3J_{\text{C,P}} = 10$  Hz, *m*-P-C<sub>Ar</sub>), 130.8 ( $^4J_{\text{C,P}} = 2$  Hz, *p*-P-C<sub>Ar</sub>), 128.4 (d,  $^2J_{\text{C,P}} = 10$  Hz, *o*-P-C<sub>Ar</sub>), 127.9 (s,  $^1\text{C}_{\text{Ar}}$ ), 126.6 (s,  $^{\text{NPhF}}\text{C}_{\text{Ar}}$ ), 126.0 (m, P-C<sub>Ar</sub>), 124.9 (s,  $^1\text{C}_{\text{Ar}}$ ), 124.9 (s,  $^1\text{C}_{\text{Ar}}$ ), 120.0 (s,  $^1\text{C}_{\text{Ar}}$ ), 118.8 (s,  $^1\text{C}_{\text{Ar}}$ ), 118.4 (s,  $^{\text{NPhF}}\text{C}_{\text{Ar}}$ ), 116.0 (s,  $^1\text{C}_{\text{Ar}}$ ), 115.8 (s,  $^1\text{C}_{\text{Ar}}$ ).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , ppm): –106.8 ppm (pseudo-ddd),  $^{19}\text{F}\{^{31}\text{P}\}$  NMR ( $\text{CDCl}_3$ , decoupled at 1.1 ppm): –106.8 (pseudo-*p*,  $^2J_{\text{F,H}} = ^3J_{\text{F,H}} = 7.16$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm): 1.1 (s).  $^{125}\text{Te}$  NMR ( $\text{CDCl}_3$ , ppm): 383 (d,  $^2J_{\text{Te,P}} = 59$  Hz).

**$[\text{Re}(\text{NPhCF}_3)_3\text{Cl}_3(\text{PPh}_3)_2]$ .**  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  (500 mg, 0.59 mmol), 4-(trifluoromethyl)aniline (0.08 mL, 0.59 mmol) and  $\text{PPh}_3$  (309 mg, 1.18 mmol) were suspended in toluene (15 mL). The mixture was heated under reflux for 4 h and filtered while hot. EtOH (10 mL) and hexane (200 mL) were added after the mixture reached room temperature. The product crystallized in the freezer overnight.

The crystals were filtered off and washed with EtOH, diethyl ether and hexane. The combined filtrates and washing solutions were left to evaporate for two days at room temperature. The remaining solvent (ca. 15 mL) was diluted with acetone. A second crop of crystals was filtered off and washed with acetone, hexane and diethyl ether. Olive-green crystals. Yield: 242 mg (42 %).

Elemental analysis: Calculated for  $\text{C}_{43}\text{H}_{34}\text{Cl}_3\text{F}_3\text{N}_2\text{P}_2\text{Re}$ : C 52.9, H 3.5, N 1.4 %; Found C 53.5, H 3.9, N 1.3 %. IR ( $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3059$  (w), 1602 (vw), 1586 (vw), 1572 (vw), 1482 (w), 1434 (m), 1406 (w), 1338 (w), 1315 (m), 1178 (m), 1122 (m), 1104 (m), 1090 (m), 1062 (m), 1029 (w), 1008 (m), 998 (w), 912 (w), 849 (m), 745 (s), 704 (sh), 691 (vs), 618 (w), 599 (w), 561 (w). ESI+ MS ( $m/z$ ): 940.1029 (calc. 940.1038)  $[\text{M} - \text{Cl}]^+$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.85–7.77 (12H, m, *m*-P-ArH), 7.35–7.20 (18H, m, integral corrected for  $\text{CHCl}_3$ , *o,p*-P-ArH), 7.03–6.83 (4H, m,  $^{\text{NPhCF}_3}\text{ArH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 158.0 (m,  $\text{R}_2\text{C}_{\text{Ar-CF}_3}$ ), 135.2 (s,  $\text{R}_2\text{C}_{\text{Ar-N=Re}}$ ), 134.2 (t,  $^3J_{\text{C,P}} = 5$  Hz, *m*-P-C<sub>Ar</sub>), 131.4 (t,  $^1J_{\text{C,P}} = 24$  Hz, P-C<sub>Ar</sub>), 130.6 (s, *o*-CF<sub>3</sub>-*m*-N=Re-C<sub>Ar</sub>), 130.3 (s, *p*-P-C<sub>Ar</sub>), 127.9 (t,  $^2J_{\text{C,P}} = 5$  Hz, *o*-P-C<sub>Ar</sub>), 125.9 (m,  $\text{R}_2\text{C}_{\text{Ar-CF}_3}$ ), 121.3 (s, *m*-CF<sub>3</sub>-*o*-N=Re-C<sub>Ar</sub>).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , ppm): –63.1 (s).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm): –23.3 (s).

**$[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)_2]$ .** A mixture of  $[\text{Re}(\text{NPhCF}_3)_3\text{Cl}_3(\text{PPh}_3)_2]$  (96 mg, 0.1 mmol) and  $\{\text{HL}^{\text{Se}}\}_2$  (44 mg, 0.08 mmol) was suspended in  $\text{CH}_3\text{CN}$  (12 mL) and heated under reflux for 5 min. The resulting

clear, dark red solution was filtered through cotton. Diethyl ether (24 mL) and hexane (52 mL) were added and the mixture was left for slow evaporation at ambient temperature for three days. The formed single crystals of  $[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Se}})\text{Cl}(\text{PPh}_3)_2]$  were filtered off, washed with hexane and dried in vacuo. Red-brown cubes. Yield: 50 mg (57 %).

Elemental analysis: Calculated for  $\text{C}_{38}\text{H}_{28}\text{ClF}_3\text{N}_2\text{OPReSe}$ : C 49.8, H 3.1, N 3.1 %; Found C 49.7, H 3.6, N 2.5 %. IR ( $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3052$  (w), 1600 (s) C=N, 1583 (m), 1569 (m), 1533 (m), 1497 (w), 1482 (m), 1454 (m), 1434 (s), 1407 (w), 1372 (sh), 1361 (m), 1335 (w), 1317 (vs), 1292 (s), 1248 (w), 1230 (w), 1177 (sh), 1159 (s), 1133 (s), 1095 (s), 1063 (s), 1029 (m), 1011 (m), 1000 (m), 962 (m), 925 (m), 847 (s), 807 (m), 752 (s), 744 (s), 719 (m), 707 (s), 690 (vs), 645 (m), 618 (m), 597 (m), 562 (m), 540 (m), 529 (vs). ESI+ MS ( $m/z$ ): 883.0608 (calc. 883.0615)  $[\text{M} - \text{Cl}]^+$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 8.36 (1H, d,  $^4J_{\text{H,P}} = 8.05$  Hz, HCR=NR), 7.90–7.82 (6H, m, *m*-P-ArH), 7.66–7.62 (1H, m,  $^1\text{ArH}$ ), 7.58–7.50 (2H, m, 2  $^1\text{ArH}$ ), 7.45–7.34 (9H, m, *o,p*-P-ArH), 7.30–7.20 (2H, m, integral corrected for  $\text{CHCl}_3$ , 2  $^1\text{ArH}$ ), 7.12–7.06 (1H, m,  $^1\text{ArH}$ ), 7.04–6.98 (3H, m,  $^1\text{ArH}$ ;  $^{\text{NPhCF}_3}\text{ArH}$ ), 6.46–6.40 (1H, m,  $^1\text{ArH}$ ), 6.46–6.40 (2H, m,  $^{\text{NPhCF}_3}\text{ArH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 166.7 (s,  $\text{R}_2\text{C}_{\text{Ar-O}}$ ), 163.5 (s, RC-NR), 158.6 (s,  $\text{R}_2\text{C}_{\text{Ar-NCR}}$ ), 158.1 (m,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 149.8 (s,  $^1\text{C}_{\text{Ar}}$ ), 136.8 (s,  $\text{R}_2\text{C}_{\text{Ar-Se}}$ ), 135.2 (m,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 134.6 (d,  $^3J_{\text{C,P}} = 10$  Hz, *m*-P-C<sub>Ar</sub>), 133.9 (s,  $^1\text{C}_{\text{Ar}}$ ), 133.4 (s,  $^1\text{C}_{\text{Ar}}$ ), 131.0 (d,  $^4J_{\text{C,P}} = 2$  Hz, *p*-P-C<sub>Ar</sub>), 131.0 (s,  $^1\text{C}_{\text{Ar}}$ ), 128.4 (d,  $^2J_{\text{C,P}} = 10$  Hz, *o*-P-C<sub>Ar</sub>), 128.2 (s,  $^1\text{C}_{\text{Ar}}$ ), 128.1 (m,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 125.7 (m, P-C<sub>Ar</sub>), 124.4 (d,  $J = 2$  Hz,  $^1\text{C}_{\text{Ar}}$ ), 122.3 (s,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 120.0 (s,  $^1\text{C}_{\text{Ar}}$ ), 118.7 (s,  $^1\text{C}_{\text{Ar}}$ ), 118.3 (s,  $^1\text{C}_{\text{Ar}}$ ), 117.9 (s,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , ppm): –63.0 (s).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm): 0.6 (s).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , ppm): 395 (d,  $^2J_{\text{Se,P}} = 24$  Hz).

**$[\text{Re}(\text{NPhCF}_3)(\text{L}^{\text{Te}})\text{Cl}(\text{PPh}_3)_2]$ .** A mixture of  $[\text{Re}(\text{NPhCF}_3)_3\text{Cl}_3(\text{PPh}_3)_2]$  (96 mg, 0.1 mmol),  $\{\text{HL}^{\text{Te}}\}_2$  (104 mg, 0.16 mmol), water (1 drop) and  $\text{NEt}_3$  (1 drop) was suspended in degassed EtOH (3 mL). Degassed  $\text{CH}_2\text{Cl}_2$  (2 mL) was added. The mixture was heated under reflux for 2.5 h. The solvents were evaporated in vacuo. The residue was re-dissolved in  $\text{CH}_2\text{Cl}_2$  and charged on a column of neutral alumina ( $d = 1$  cm,  $h = 15$  cm). Elution with  $\text{CH}_2\text{Cl}_2$  containing 0.1 % MeOH gave a brown band of the product. The solvent was evaporated in vacuo and the residue re-dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and filtered. After removal of the solvent in vacuo, a sticky product remained, which was solidified by the addition of *n*-hexane and vigorous stirring. It was filtered off, washed with hexane and dried on air. Brown powder. Yield: 16.0 mg (17 %).

Elemental analysis: Calculated for  $\text{C}_{38}\text{H}_{28}\text{ClF}_3\text{N}_2\text{OPReTe}$ : C 47.3, H 2.9, N 2.9 %; Found C 45.5, H 3.1, N 3.0 %. IR ( $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3051$  (w), 2923 (w), 2867 (w), 1600 (s) C=N, 1586 (sh), 1567 (sh), 1541 (m), 1481 (w), 1469 (m), 1452 (m), 1434 (s), 1407 (w), 1362 (m), 1381 (vs), 1287 (s), 1261 (sh), 1168 (m), 1121 (s), 1103 (s), 1063 (vs), 1029 (m), 1010 (m), 960 (w), 925 (m), 861 (sh), 845 (s), 803 (m), 744 (vs), 717 (m), 692 (vs), 645 (m), 617 (m), 603 (m), 558 (m), 541 (s). ESI+ MS ( $m/z$ ): 931.0582 (calc. 931.0495)  $[\text{M} - \text{Cl}]^+$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 8.33 (1H, d,  $^4J_{\text{H,P}} = 8.24$  Hz, HCR=NR), 7.97–7.31 (20H, 4m, *m,o,p*-P-ArH; 4  $^1\text{ArH}$ ), 7.21–6.93 (5H, 2m, 3  $^1\text{ArH}$ ; 2  $^{\text{NPhCF}_3}\text{ArH}$ ), 6.49–6.43 (1H, m,  $^1\text{ArH}$ ), 6.40–6.33 (2H, m,  $^{\text{NPhCF}_3}\text{ArH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 167.3 (s,  $\text{R}_2\text{C}_{\text{Ar-O}}$ ), 164.1 (m,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 163.0 (s, RC-NR), 162.2 (m,  $^1\text{C}_{\text{Ar}}$ ), 158.4 (s,  $\text{R}_2\text{C}_{\text{Ar-NCR}}$ ), 136.9 (s,  $\text{R}_2\text{C}_{\text{Ar-Te}}$ ), 136.4 (s,  $^1\text{C}_{\text{Ar}}$ ), 135.6 (m,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 134.6 (d,  $^3J_{\text{C,P}} = 10$  Hz, *m*-P-C<sub>Ar</sub>), 132.3 (s,  $^1\text{C}_{\text{Ar}}$ ), 132.2 (s,  $^1\text{C}_{\text{Ar}}$ ), 131.1 (s, *p*-P-C<sub>Ar</sub>), 130.8 (s,  $^1\text{C}_{\text{Ar}}$ ), 128.5 (d,  $^2J_{\text{C,P}} = 10$  Hz, *o*-P-C<sub>Ar</sub>), 128.2 (m,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 128.1 (s,  $^1\text{C}_{\text{Ar}}$ ), 125.9 (m, P-C<sub>Ar</sub>), 125.5 (s,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ), 122.8 (d,  $J = 2$  Hz,  $^1\text{C}_{\text{Ar}}$ ), 119.8 (s,  $^1\text{C}_{\text{Ar}}$ ), 118.8 (s,  $^1\text{C}_{\text{Ar}}$ ), 118.7 (s,  $^{\text{NPhCF}_3}\text{C}_{\text{Ar}}$ ).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , ppm): –63.1 (s).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm): 0.3 (s).  $^{125}\text{Te}$  NMR ( $\text{CDCl}_3$ , ppm): 486 (d,  $^2J_{\text{Te,P}} = 67$  Hz).

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