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Rhodium(III) complexes of N-{2-(arylseleno/telluro)ethyl} morpholine: Synthesis, structure and applications as efficient catalyst for transfer hydrogenation reaction of ketones

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ABSTRACT

N-{2-(Arylseleno/telluro)ethyl}morpholine (**L1**/**L2**) synthesized by reacting $PhSe^-$/$ArTe^-$ (generated insitu) with (2-chloroethyl)morpholine hydrochloride, reacts with $RhCl_3 \cdot 3H_2O$ resulting in complexes $[RhCl_2(\mathbf{L1}/\mathbf{L2})_4][ClO_4]$ (**1**/**2**). ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}/^{125}Te\{^1H\}$ NMR spectra of **L1**, **L2**, **1** and **2** were found characteristic. The single crystal structure of **2** has been solved. The **L2** binds with Rh in **2** as a monodentate ligand. The geometry around Rh is distorted octahedral. The Rh–Te distances are in the range 2.6509(9)–2.6688(8) Å. Both the complexes efficiently catalyze transfer hydrogenation reaction of acetophenone (TON/TOF up to $9.9\times10^4/9.9\times10^3$ h^{-1}) and benzophenone (TON up to 9.8×10^4 and TOF up to 9.8×10^3 h^{-1}).

Rhodium(III) complex with any acyclic seleno- or telluro-ether ligand characterized structurally by single X-ray diffraction, was not known up to the end of last century. The $[(\eta^5\text{-}C_5Me_5)Rh(Te(CH_2CH_2CH_2TePh)_2][PF_6]_2 \cdot MeOH$ was first such complex reported in year 2001 [1]. The $[RhCl_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]^+$, $[(\eta^5\text{-}C_5Me_5Rh\{MeS(CH_2)_3Te(CH_2)_3SMe\}][PF_6]_2$, and *mer*-$[RhCl_3\{Te(CH_2SiMe_3)_2\}_3]$ are other such rhodium(III) complexes with acyclic seleno- and telluro-ether ligands reported during the last decade [2–4], but none of them has a hybrid-organoselenium and tellurium ligand. The structurally characterized rhodium(III) complexes with cyclotelluroether ligands also, have been reported [5–7]. The applications in catalytic organic reactions (including transfer hydrogenation reaction of ketones) of any Rh(III)-seleno- and telluro-ether complex are not in our knowledge. Several Rh(III)/Rh(I) complexes with nitrogen, phosphorus and oxygen ligands have been reported for such catalytic reactions [8–25]. It was therefore thought worthwhile to explore the Rh (III) complexes of *N*-{2-(arylseleno/telluro)ethyl}morpholine (**L1**/**L2**) for their structural aspects and catalytic transfer hydrogenation reactions of ketones. The results of these investigations are the subject of present paper. These are the first examples of Rh(III) complexes in which potentially hybrid seleno- and telluro-ether ligands are present as well as of those which have been explored for catalytic transfer hydrogenation.

The ligands **L1** and **L2** were synthesized by reacting $PhSe^-$/$ArTe^-$ (generated insitu by reaction of $NaBH_4$ with diphenyldiselenide/diaryldiselluride in ethanol) with (2-chloroethyl)morpholine hydrochloride (Scheme 1) [26]. The ligand **L1** was synthesized for the first time, whereas the modified work-up procedure (based on $CHCl_3$–H_2O in place of diethyl ether–water) for synthesis of **L2** gave better yield than reported earlier [27,28]. The complexes **1** and **2** were synthesized by the reactions of $RhCl_3 \cdot 3H_2O$ with **L1** and **L2** respectively, in ethanol at room temperature (Scheme 1) [29]. Both the ligands were found soluble in common organic solvents. The complexes also showed good solubility in common organic solvents except hexane and diethyl ether in which they were found sparingly soluble. The solutions of both the complexes in DMSO showed the sign of decomposition after 30–36 h.

^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}/^{125}Te\{^1H\}$ NMR [26,29] and IR spectra (see in online supplementary material) of both the ligands and their complexes were found characteristic. The molar conductance values of both the complexes indicate their 1:1 electrolytic nature [29]. The signal in $^{77}Se\{^1H\}$ NMR spectrum of **L1** (279.5 ppm) shifts to a high frequency by ~109 ppm on complex formation. This implies the coordination of Rh through Se of **L1**. Similarly the signal in the $^{125}Te\{^1H\}$ NMR spectrum of **L2** (431.5 ppm) was found to shift to a high frequency by ~221 ppm on complex formation, implying the coordination of Rh through Te of **L2** [29]. Small splitting in the signals in $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra on complex formation appears due to coupling with ^{103}Rh [36,37]. In ^1H NMR spectra of **1** and **2** signals of H_1 appear shifted to higher frequency by 0.57 and 0.64 ppm respectively relative to those of free ligands, corroborating with the coordination of **L1**/**L2** through Se/Te donor sites as inferred from $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectral data. The insignificant shift in signals of morpholine protons on complexation, implies that nitrogen atoms

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[1] Contributed in crystallographic analysis.

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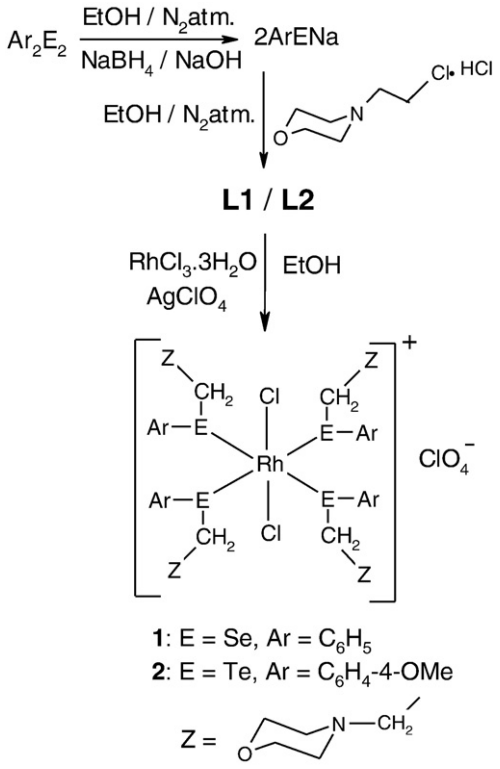
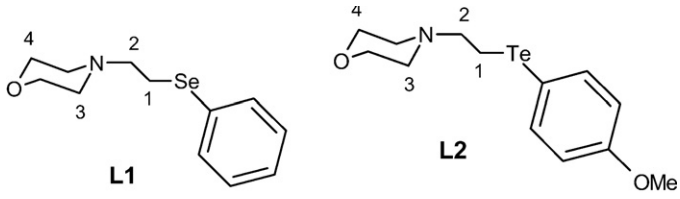


Scheme 1. Synthesis of **L1/L2** and Rh-complexes.

of **L1**/**L2** do not coordinate with Rh(III). In $^{13}C\{^1H\}$ NMR spectra of both **1** and **2** the signals of C_1 and ArC-Se/Te appear shifted to higher frequency (~2.1/1.5 and 2.4/2.9 ppm respectively) relative to those of free ligands, corroborating with the ^1H NMR spectra [29].



Single crystal structure of complex **2** (Fig. 1) [30] supports the monodentate behaviour of **L1**/**L2** as indicated by NMR spectral data. The Rh–Te bond distances (2.6509(9)–2.6688(8) Å) in **2** [31] are not identical and somewhat longer than those of $[(\eta^5\text{-}C_5Me_5)Rh(Te(CH_2CH_2CH_2TePh)_2][PF_6]_2.MeOH$, 2.6015(7)–2.6177(7) Å [1], $[(\eta^5\text{-}C_5Me_5Rh\{MeS(CH_2)_3TeCH_2)_3SMe\}][PF_6]_2$, 2.6106(7) Å [3] and *mer*-$[RhCl_3\{Te(CH_2SiMe_3)_2\}_3]$ 2.5733(7)–2.6439(7) Å [4]. Such elongation and non-equivalence of Rh–Te bonds due to steric effects of **L1** and **L2** have made geometry of rhodium distorted octahedral as indicated by bond angles [31]. The Rh–Cl bond distances 2.3531(18)–2.3645(17) Å of **2** are consistent with values 2.353(2)–2.362(2) Å reported for *trans* Rh–Cl bonds of complex *mer*-$[RhCl_3\{Te(CH_2SiMe_3)_2\}_3]$ [4].

Transfer hydrogenation reactions of ketones (Scheme 2) catalyzed with **1** and **2** were explored at 80 °C using acetophenone and benzophenone as substrates and 0.001 mol% of **1**/**2** [32]. The products were identified by ^1H NMR spectroscopy (in $CDCl_3$) and GC after

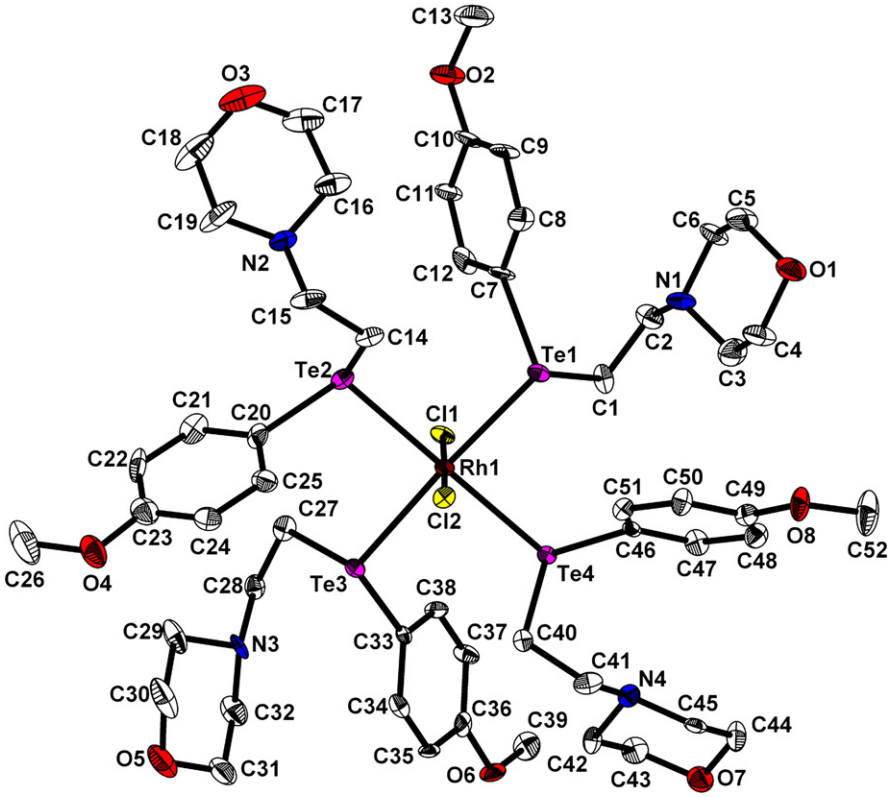
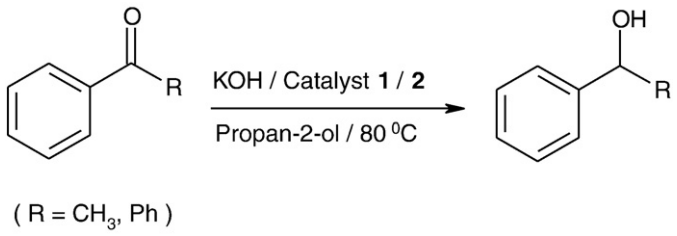


Fig. 1. ORTEP diagram of $[RhCl_2(\mathbf{L2})_4][ClO_4]$ (**2**)·C_2H_5OH·$2H_2O$ with 50% probability ellipsoids; hydrogen atoms, C_2H_5OH, H_2O and ClO_4 anion are omitted for clarity. Bond length (Å): Rh(1)–Te(1) 2.6509(9), Rh(1)–Te(2) 2.6549(8), Rh(1)–Te(3) 2.6546(9), Rh(1)–Te(4) 2.6688(8), Rh(1)–Cl(1) 2.3531(18), Rh(1)–Cl(2) 2.3645(17); bond angle (°): Cl(1)–Rh(1)–Cl(2) 178.26(7), Cl(1)–Rh(1)–Te(1) 91.27(5), Cl(1)–Rh(1)–Te(2) 86.63(5), Cl(1)–Rh(1)–Te(3) 92.03(5), Cl(1)–Rh(1)–Te(4) 90.18(5), Cl(2)–Rh(1)–Te(1) 88.53(5), Cl(2)–Rh(1)–Te(2) 91.66(5), Cl(2)–Rh(1)–Te(3) 88.25(5), Cl(2)–Rh(1)–Te(4) 91.53(5), Te(1)–Rh(1)–Te(2) 92.49(3), Te(1)–Rh(1)–Te(3) 175.85(3), Te(1)–Rh(1)–Te(4) 87.94(2), Te(2)–Rh(1)–Te(3) 90.20(2), Te(2)–Rh(1)–Te(4) 176.79(3), Te(3)–Rh(1)–Te(4) 89.54(2).



Scheme 2. Transfer hydrogenation reaction.

recovering catalyst and doing required work-up. The final conversions (reported in Table 1) were arrived by taking average of two runs of each catalytic reaction. The high efficiency was exhibited in the reduction of ketones to their corresponding alcohols by 2-propanol, which is reported to be an efficient hydrogen donor in transfer hydrogenation reactions [16,17,25] in the presence of KOH which is also reported to be best inorganic base for such reactions [17].

The rate of catalytic reaction initially was fast up to 6 h and at that time the % conversion was 90 in case of acetophenone with catalyst **1** and 92 with **2**. In case of benzophenone % conversion was 87 with catalyst **1** and 90 with **2** (Fig. 2 and Table S1 in online supplementary material). In 10 h the conversion reaches to 98–99% (Table 1) with **2**. In comparison to catalyst **1** containing Se, the performance of **2** is somewhat better particularly in the case of benzophenone. The catalytic reactions proceed probably via the hydride complex intermediate (Noyori's concerted mechanism) [33,34]. The **1** and **2** for hydrogenation reaction of ketones are better in comparison to those reported earlier [13,15–18,23–25], because they are required in less quantity and reaction time is relatively short. The cyclic voltammetric (CV) experiments performed at 298 K in CH_3CN (0.01 M NBu_4ClO_4 as supporting electrolyte) for **1** and **2** at a scan rate of 100 mV s^{-1} (anodic sweep) reveal their reversible oxidation (Figs. S1 and S2 in online supplementary material). The values of $E_{1/2}$, +1.025 and 1.065 V (vs. Ag/AgCl) (see Table S2 in online supplementary material), which are non-extreme indicate that **1** and **2** are expected to be reasonably efficient catalysts for redox process [35]. The TGA of **2** in N_2 atmosphere at heating rate 10 °C min^{-1} shows continuous weight loss (fast up to 250 °C followed by slow one up to 700 °C and fast up to 900 °C). The residue has composition Rh_2Te_5, a known phase [38,39]. The investigations on the complexes reported here and related ones are in progress, with an idea to understand their properties tunable for catalytic transfer hydrogenation of ketones and also extend their applications further.

Acknowledgements

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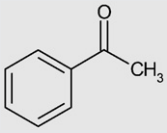
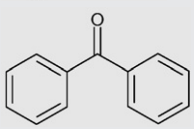
Table 1
Catalytic transfer hydrogenation of selective substrates by **1** and **2** at 80 °C.

Entry	Substrate	Catalysts	Conversion [%]	TON	TOF [h^{-1}]
1		**1**	96	9.6×10^4	9.6×10^3
		2	99	9.9×10^4	9.9×10^3
2		**1**	93	9.3×10^4	9.3×10^3
		2	98	9.8×10^4	9.8×10^3

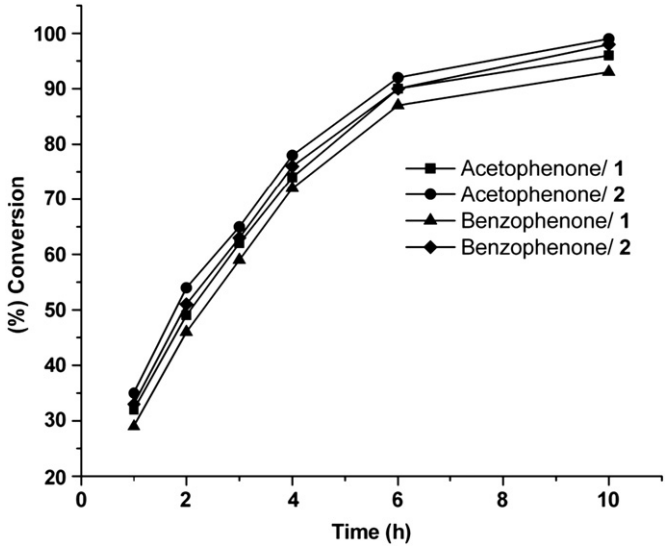


Fig. 2. Time profile of catalytic transfer hydrogenation of ketones using **1** and **2** at 80 °C.

Appendix A. Supplementary material

CCDC 772221 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.05.014.

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[26] General procedure for synthesis of ligands **L1** and **L2**: Diphenyldiselenide (0.62 g, 2.0 mmol)/bis(4-methoxyphenyl)ditelluride (0.94 g, 2 mmol) dissolved in

30 cm^3 of ethanol was reacted with solution (added drop wise) of $NaBH_4$ (0.14 g, 4.0 mmol) in NaOH (5%) under N_2 atmosphere at room temperature (for **L1**) or under refluxing (for **L2**). The resulting PhSeNa/ArTeNa. was treated with 4-(2-chloroethyl)morpholine hydrochloride (0.74 g, 4.0 mmol) dissolved in 5 cm^3 of ethanol with constant stirring. The reaction mixture further stirred for 3–4 h was poured into ice cold water (20 cm^3) containing 0.2 g of NaOH. The ligand **L1** or **L2** was extracted into $CHCl_3$ (5×40 cm^3). The extract was washed with water (3×50 cm^3) and dried over anhydrous sodium sulphate. On evaporating off chloroform under reduced pressure on rotary evaporator **L1**/**L2** was obtained as oil (**L1**: pale yellow; **L2**: white) **L1**: Yield (0.86 g, 80%). ^{1}H NMR (300.13 MHz; $CDCl_3$; 25 °C vs. Me_4Si): δ 2.44–2.46 (m, 4H, H_3), 2.68 (t, 2H, $^3J_{HH}$ 7.5 Hz, H_1), 3.02 (t, 2H, $^3J_{HH}$ 7.5 Hz, H_2), 3.66–3.69 (m, 4H, H_4), 7.19–7.24 (m, 3H, ArH-*m* + ArH-*p* to Se), 7.48 (d, 2H, $^3J_{HH}$ 6.6 Hz, ArH-*o* to Se). ^{13}C{^{1}H} NMR (75.47 MHz; $CDCl_3$; 25 °C vs. Me_4Si): δ 24.4 (C_3), 53.1 (C_1), 58.5 (C_2), 66.6 (C_4), 126.6 (ArC-*p* to Se), 128.8 (ArC-*m* to Se), 130.1 (ArC-*o* to Se), 132.2 (ArC-Se). ^{77}Se{^{1}H} NMR (57.24 MHz; $CDCl_3$; 25 °C vs. Me_2Se): δ 279.46. **L2**: Yield (0.75 g, 80%). ^{1}H NMR (300.13 MHz; $CDCl_3$; 25 °C vs. Me_4Si): δ 2.46–2.49 (m, 4H, H_3), 2.78 (t, 2H, $^3J_{HH}$ 7.5 Hz, H_1), 3.04 (t, 2H, $^3J_{HH}$ 7.5 Hz, H_2), 3.68–3.71 (m, 4H, H_4), 3.79 (s, 3H, OCH_3), 6.76 (d, 2H, $^3J_{HH}$ 6.9 Hz, ArH-*m* to Te), 7.68 (d, 2H, $^3J_{HH}$ 6.9 Hz, ArH-*o* to Te). ^{13}C{^{1}H} NMR (75.47 MHz; $CDCl_3$; 25 °C vs. Me_4Si): δ 7.8 (C_3), 53.1 (C_1), 55.1 (C_2), 59.3 (C_4), 66.9 (OCH_3), 101.3 (ArC-Te), 115.0 (ArC-*m* to Te), 140.7 (ArC-*o* to Te), 159.5 (ArC-*p* to Te). ^{125}Te{^{1}H} NMR (94.69 MHz; $CDCl_3$; 25 °C vs. Me_2Te): δ 431.52.

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[29] General procedure for synthesis of complexes $[RhCl_2(\mathbf{L1})_4][ClO_4]$ (**1**) and $[RhCl_2(\mathbf{L2})_4][ClO_4]$ (**2**)·C_2H_5OH·$2H_2O$: The mixture of ethanolic solution (20 cm^3) of $RhCl_3\cdot3H_2O$ (0.053 g, 0.2 mmol) and a solution of **L1**/**L2** (0.054/0.070 g, 0.2 mmol) made in C_2H_5OH (7 cm^3) was stirred for 3–4 h, followed by addition of $AgClO_4$ (0.042 g, 0.2 mmol) in C_2H_5OH (5 cm^3) till it became orange for **1** and red for **2**. The AgCl was filtered off. The volume of filtrate was reduced to ~7 cm^3 on a rotary evaporator. The addition of diethyl ether (15 cm^3) to the concentrate gave **1** (orange) and **2** (red) as precipitate which was filtered, washed with diethyl ether (10 cm^3) and dried in vacuo. Single crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation of its solution made in a mixture (1:4) of C_2H_5OH and CH_3CN. **1**: Yield (0.230 g, 85%). Λ_M: 140.9 S cm^2 mol^{-1}. Anal. Calcd. for $C_{48}H_{72}Cl_2N_4O_4RhSe_4.ClO_4$: C, 42.45; H, 5.34; N, 4.13%. Found: C, 42.49; H, 5.36; N, 4.15%. ^{1}H NMR (300.13 MHz; $CDCl_3$; 25 °C vs. Me_4Si): δ 2.45–2.48 (m, 16H, H_3), 3.25 (m, 8H, H_1), 3.49 (m, 8H, H_2), 3.90 (m, 16H, H_4), 7.27–7.34 (m, 12H, ArH-*m* + ArH-*p* to Se), 8.02 (m, 8H, ArH-*o* to Se). ^{13}C{^{1}H} NMR (75.47 MHz; $CDCl_3$; 25 °C vs. Me_4Si): δ 24.5 (C_3), 55.2 (C_1), 59.3 (C_2), 67.2 (C_4), 126.8 (ArC-*p* to Se), 129.3 (ArC-*m* to Se), 130.8 (ArC-*o* to Se), 134.6 (ArC-Se). ^{77}Se{^{1}H} NMR (57.24 MHz; $CDCl_3$; 25 °C vs. Me_2Se): δ 388.5 (d, $^1J(^{103}Rh$-$^{77}Se)$ 46.4 Hz). **2**: Yield (0.284 g, 85%). Λ_M: 142.5 S cm^2 mol^{-1}. Anal. Calcd. for $C_{52}H_{80}Cl_2N_4O_8RhTe_4.ClO_4$: C, 37.34; H, 4.82; N, 3.35%. Found: C, 37.34; H, 4.85; N, 3.36%. ^{1}H NMR (300.13 MHz; CD_3CN; 25 °C vs. Me_4Si): δ 2.46–2.50 (m, 16H, H_3), 3.42 (m, 8H, H_1), 3.58 (m, 8H, H_2), 3.74–3.80 (m, 16H, H_4), 3.85 (s, 12H, OCH_3), 6.99 (m, 8H, $^3J_{HH}$ 8.1 Hz, ArH-*m* to Te), 7.97 (m, 8H, $^3J_{HH}$ 8.1 Hz, ArH-*o* to Te). ^{13}C{^{1}H} NMR (75.47 MHz; $CDCl_3$; 25 °C vs. Me_4Si): δ 23.8 (C_3), 54.6 (C_1), 55.5 (C_2), 59.4 (C_4), 66.7 (OCH_3), 104.2 (ArC-Te), 116.0 (ArC-*m* to Te), 140.7 (ArC-*o* to Te), 160.2 (ArC-*p* to Te). ^{125}Te{^{1}H} NMR (94.69 MHz; $CDCl_3$; 25 °C vs. Me_2Te): δ 652.6 (d, $^1J(^{103}Rh$-$^{125}Te)$ 53.1 Hz).

[30] X-ray crystallography; Bruker AXS SMART Apex CCD diffractometer using Mo *Ka* (0.71073 Å) radiations at 100(2) K was used. Crystal data (for detail see Table S3 in online supplementary material): (**2**)·C_2H_5OH·$2H_2O$: Crystal system, monoclinic; space group, *P 21/n*; $a=15.411(3)$ Å; $b=26.282(5)$ Å; $c=17.012(4)$ Å; $b=104.126(4)$; Volume [Å^3] = 6682.0(2); $Z=2$; density (calc.) [Mg m^{-3}] 1.736; $F(000)$ 3430.0; index ranges: $-18\le h\le18$, $-31\le k\le31$, $-20\le l\le20$; absorption coeff. [mm^{-}1] 2.149; Independent reflections ($R_{int.}$) 11445 (0.0639); Max./min. Transmission; 0.704/0.574; data/restraints/parameters 11445/0/739; *R* indices (all data): $R_1=0.0748$; $wR_2=0.1182$; Largest diff. peak/hole [e Å^{-3}] 1.632/−0.977.

[31] Selected bond length(Å): (**2**)·C_2H_5OH·$2H_2O$: Rh(1)–Te(1) 2.6509(9), Rh(1)–Te(2) 2.6549(8), Rh(1)–Te(3) 2.6546(9), Rh(1)–Te(4) 2.6688(8), Rh(1)–Cl(1) 2.3531(18), Rh(1)–Cl(2) 2.3645(17); bond angle(°): Cl(1)–Rh(1)–Cl(2) 178.26(7), Cl(1)–Rh(1)–Te(1) 91.27(5), Cl(1)–Rh(1)–Te(2) 86.63(5), Cl(1)–Rh(1)–Te(3) 92.03(5), Cl(1)–Rh(1)–Te(4) 90.18(5), Cl(2)–Rh(1)–Te(1) 88.53(5), Cl(2)–Rh(1)–Te(2) 91.66(5), Cl(2)–Rh(1)–Te(3) 88.25(5), Cl(2)–Rh(1)–Te(4) 91.53(5), Te(1)–Rh(1)–Te(2) 92.49(3), Te(1)–Rh(1)–Te(3) 175.85(3), Te(1)–Rh(1)–Te(4) 87.94(2), Te(2)–Rh(1)–Te(3) 90.20(2), Te(2)–Rh(1)–Te(4) 176.79(3), Te(3)–Rh(1)–Te(4) 89.54(2).

[32] General procedure for catalytic transfer hydrogenation reaction: A mixture of the ketone (1 mmol), KOH (0.2 cm^3 of a 0.2 M solution in 2-propanol) and the catalyst complex **1**/**2** (0.001 mol%) was heated under reflux (80 °C) in 10 cm^3 of 2-propanol for 10 h. In the course of reaction an aliquot was taken at desired time intervals, extracted with diethyl ether, filtered through a short path of silica and the silica was washed with diethyl ether. The combined organic filtrates were evaporated on a rotary evaporator and analyzed by ^{1}H NMR spectroscopy (in $CDCl_3$) and GC. The final conversions are determined by average of two runs of each catalytic reaction.

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