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Transfer Hydrogenation of Ketones and Catalytic Oxidation of Alcohols with Half-Sandwich Complexes of Ruthenium(II) Designed Using Benzene and Tridentate (S, N, E) Type Ligands (E = S, Se, Te)

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The complexes of composition *fac*-[(η^6-C_6H_6)Ru(**L**)][PF_6][X] (**1**−**6**; X = PF_6 or Cl), formed by reacting 2-$MeSC_6H_4CH{=}NCH_2CH_2E$-C_6H_4-4−R (**L1**−**L3**) and 2-$MeSC_6H_4CH_2$-$NHCH_2CH_2E$-C_6H_4-4−R (**L4**−**L6**) (where E = S or Se, R = H; E = Te, R = OMe) with [{(η^6-C_6H_6)RuCl(μ-Cl)}$_2$] and NH_4PF_6, have been characterized by ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H}, and ^{125}Te{^{1}H} NMR spectroscopy and X-ray crystallography. The Ru−Se and Ru−Te bond lengths are in the ranges 2.4837(14)−2.4848(14) and 2.6234(6)−2.6333(7) Å, respectively. Complexes **1**−**6** have been found to be efficient catalysts for catalytic oxidation of alcohols with *N*-methylmorpholine-*N*-oxide, *t*BuOOH, NaOCl, and $NaIO_4$ and transfer hydrogenation reaction of ketones with 2-propanol. The TON values are up to 9.9×10^4 and 9.8×10^4 for two catalytic processes, respectively. The oxidation probably involves the formation of intermediate species having Ru(IV)=O. Complexes **1**−**3** are as efficient as **4**−**6** for transfer hydrogenation of ketones. In transfer hydrogenation, the mechanism does not appear to be dependent on the availability of hydrogen on nitrogen and probably involves Ru−H bond formation. The catalytic efficiency for both processes follows the order Te > Se > S, which may be due to the presence of a MeO group on Te.

Introduction

Half-sandwich complexes of Ru(II) are of current interest due to their diverse catalytic activities. The transfer hydrogenation of ketones is one of them.[1] The species of type [(η^6-arene)RuCl(N,N)]$^+$ have been found suitable for transfer hydrogenation of ketones even in aqueous medium.[2] Ogo[3] and Süss-Fink[4] have reported transfer hydrogenation reactions of ketones with sodium formate or formic acid, catalyzed in aqueous solution by [(η^6-arene)Ru(bipy)(OH_2)]$^{2+}$. The base-free transfer hydrogenation of ketones is reported[5] with [(η^6-benzene/*p*-cymene)RuCl(N,N)][BPh_4] ((N,N) = 2-hydroxyphenylbis(pyrazol-1-yl)methane or 2-hydroxyphenylbis(3,5-dimethylpyrazol-1-yl)methane). Ruthenium-arene-sulfonated diamine complexes being soluble in water catalyze transfer hydrogenation of α-aryl ketones in aqueous medium.[6] The catalytic transfer hydrogenation of ketones with η^6-arene-ruthenium(II) complexes containing bis(pyrazolyl)methane[7] or bis(imidazolin-2-imine)[8] ligands has been found to be efficient. The complex is a 16-electron species in the case of bis(imidazolin-2-imine). The ternary system consisting of [{(η^6-benzene)RuCl(μ-Cl)}$_2$], *N*-tosylethylenediamine or ethanolamine, and KOH (1:1:2 molar ratio) catalyzes the transfer hydrogenation of ketones[9] including the asymmetric one. This has been shown to occur via a nonclassical metal−ligand bifunctional mechanism.[10,11] Half-sandwich complexes of Ru(II) have been found to be good catalysts for the oxidation of alcohols too. [η^5-Cp*Ru-(μ-Cl)$_3$RuCl(PPh_3)$_2$] has been reported to be efficient for catalytic oxidation of secondary alcohols with 2-butanone.[12] Nonactivated secondary alcohols are oxidized to ketones by MnO_2 in the presence of a catalytic system consisting of [{(η^6-*p*-cymene)RuCl(μ-Cl)}$_2$] and 2,6-di-*tert*-butylbenzoquinone.[13] [{(η^6-*p*-cymene)RuCl(μ-Cl)}$_2$] with bis(diphenylphosphino)butane catalyzes the oxidation of alcohols to amides.[14] Half-sandwich complexes of Ru have been used

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(1) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300.
(2) Romain, C.; Gaillard, S.; Elmkaddem, M. K.; Toupet, L.; Fischmeister, C.; Thomas, C. M.; Renaud, J.-L. *Organometallics* **2010**, *29*, 1992.
(3) (a) Ogo, S.; Abura, T.; Watanabe, Y. *Organometallics* **2002**, *21*, 2964. (b) Ogo, S.; Uehara, K.; Abura, T.; Watanabe, Y.; Fukuzumi, S. *Organometallics* **2004**, *23*, 3047.
(4) (a) Canivet, J.; Labat, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2005**, 4493. (b) Canivet, J.; Süss-Fink, G.; Stepnicka, P. *Eur. J. Inorg. Chem.* **2007**, 4736.
(5) Carrión, M. C.; Sepúlveda, F.; Jalón, F. A.; Manzano, B. R. *Organometallics* **2009**, *28*, 3822.
(6) Canivet, J.; Süss-Fink, G. *Green Chem.* **2007**, *B*, 391.
(7) Carrión, M. C.; Jalón, F. A.; Manzano, B. R.; Rodríguez, M.; Sepúlveda, F.; Maestro, M. *Eur. J. Inorg. Chem.* **2007**, 3961.
(8) Glöge, T.; Petrovic, D.; Hrib, C.; Jones, P. G.; Tamm, M. *Eur. J. Inorg. Chem.* **2009**, 4462.
(9) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.
(10) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466.
(11) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931.
(12) da Silva, A. C.; Piotrowski, H.; Mayer, P.; Polborn, K.; Severin, K. *Eur. J. Inorg. Chem.* **2001**, 685.
(13) Karlsson, U.; Wang, G.-Z.; Bäckvall, J.-E. *J. Org. Chem.* **1994**, *59*, 1196.
(14) Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. *Org. Lett.* **2009**, *11*, 2667.

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in a biomimetic coupled catalytic system for alcohol oxidation.[15] A variety of other catalytic reactions of half-sandwich compounds of ruthenium are also known. Hydrogenation of benzene using clusters having (η^6-arene)Ru units[16] was reported by Süss-Fink et al. Arene-ruthenium-salicyloxazolines complexes were found to be suitable as asymmetric catalysts for Diels−Alder reactions.[17] The compounds [(η^6-arene)Ru=C=C=CR_2(**L**)(Cl)][PF_6] (**L** = PCy_3, $PiPr_3$), are reported as excellent catalyst precursors for ring-closing olefin metathesis.[18] The atom transfer radical polymerization of methyl methacrylate has been catalyzed with [(η^6-*p*-cymene)$RuCl_2(PCy_3)$].[19] [{(η^6-*p*-Cymene)RuCl(μ-Cl)}$_2$], the pyrimidinium or benzimidazolium salt, and Cs_2CO_3 constitute a catalytic system that selectively promotes the diarylation of 2-pyridylbenzene with aryl bromides.[20] Acetate-assisted C−H activation of 2-substituted pyridines with [{(η^6-*p*-cymene)RuCl(μ-Cl)}$_2$] has been reported.[21] A variety of neutral ruthenium-carbene complexes, [$RuCl_2$(carbene)-(arene)], have been used in the catalytic synthesis of furans.[22] Kharasch additions are catalyzed with [(η^6-*p*-cymene)$RuCl_2$ (PAr_3)].[23] The exceptional efficacy of [(η^6-*p*-cymene)$RuCl_2$-(PR_3)] complexes as a catalyst precursor for the ring-opening metathesis polymerization of low-strain cyclo-olefins[24] is reported. Chiral cationic (η^6-arene)(pyridylamino)ruthenium(II) complexes act as enantioselective catalysts for Diels−Alder reactions with good *exo*:*endo* selectivity.[25]

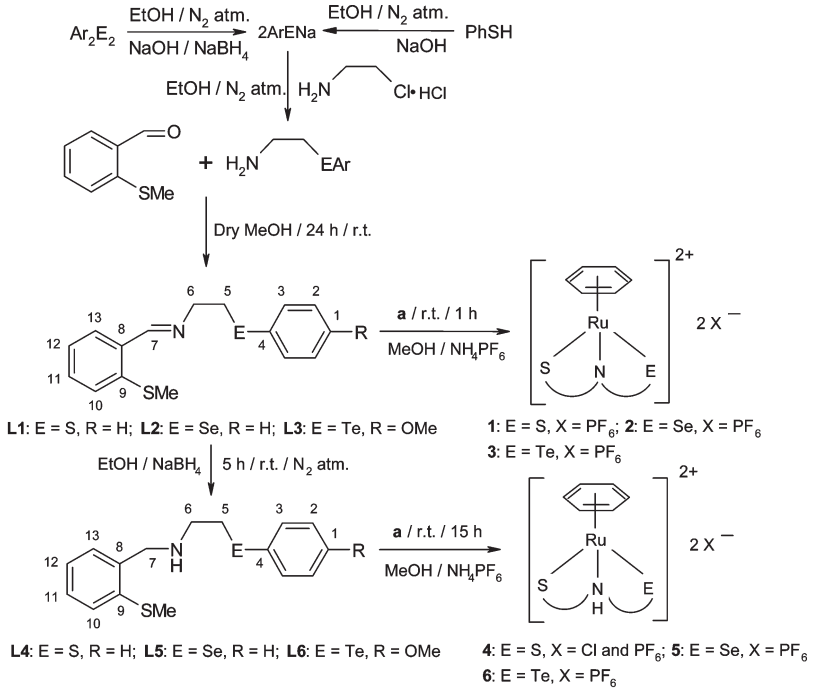
Several half-sandwich Ru(II) compounds show promising anticancer activity.[26−30] Consequently related chemistry has also gotten attention. Thiolate ligand oxygenation is believed to activate cytotoxic [(η^6-arene)Ru(en)(SR)]$^+$ complexes toward DNA binding.[31] (η^6-Arene)Ru(II) complexes with pyrone-derived ligands are rendered active against cancer cells by replacement of the coordinated O,O donor with a S, O donor.[32] The promising cytotoxic effects of water-soluble dinuclear (η^6-arene)Ru(II) complexes in human cancer cells increase[33] with an increase in spacer length between the metal centers. The interaction of [(η^6-*p*-cymene)$RuCl_2$(pta)] (pta = phosphatriazaadamantane), reported to be an effective anticancer and antimetastatic agent, with biological nucleophiles, important with respect to its mechanism of action, has been studied.[34] The anticancer activity of organometallic (η^6-arene)ruthenium(II) complexes coordinated to maltol-derived ligands, against human tumor cell lines has been noticed.[35] The water-soluble (η^6-arene)ruthenium(II) complexes containing pyridinethiolato ligands show cytotoxicity toward ovarian cancer cells.[36] In vitro studies have revealed that (3,5,6-bicyclophosphite-α-*d*-glucofuranoside)-(η^6-*p*-cymene)dihalogenidoruthenium(II) is the most cytotoxic compound for human cancer cell lines.[37] It was therefore thought worthwhile to understand the chemistry of half-sandwich Ru(II) compounds that have tridentate organochalcogen ligands, as they are scantly studied and may be efficient catalysts. The biological activity of such resulting species may also be of interest due to the presence of Se or S in the molecule. Thus ligands **L1**−**L6** (Scheme 1) and their complexes having a (η^6-C_6H_6)Ru(II) unit have been synthesized. They are explored for catalytic oxidation of alcohols with *N*-methylmorpholine-*N*-oxide (NMO), *tert*-butylhydroperoxide (*t*BuOOH), sodium oxychloride (NaOCl), and sodium periodate ($NaIO_4$) and for transfer hydrogenation of ketones. The results of these investigations constitute this paper.

Experimental Section

Physical Measurement. A Perkin-Elmer 2400 Series II C, H, N analyzer was used for elemental analysis. The ^{1}H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, and $^{125}Te\{^1H\}$NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, 57.24, and 94.69 MHz, respectively. IR spectra in the range 4000−400 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The UV−vis spectra were recorded on a Lambda Bio-20 (Perkin-Elmer, USA; model 330). The conductivity measurements were carried out in CH_3CN (concentration ca. 1 mM) using an ORION conductivity meter, model 162. Single-crystal diffraction studies were carried out with a Bruker AXS SMART Apex CCD diffractometer using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements.[38,39] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The least-squares refinement cycles on F^2 were

(15) Csjernyik, G.; Éll, A H.; Fadini, L.; Pugin, B.; Bäckvall, J.-E. *J. Org. Chem.* **2002**, *67*, 1657.
(16) Süss-Fink, G.; Faure, M.; Ward, T. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 99.
(17) Davenport, A. J.; Davies, D. L.; Fawcett, J.; Russell, D. R. *Dalton Trans.* **2004**, 1481.
(18) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315.
(19) Delfosse, S.; Borguet, Y.; Delaude, L.; Demonceau, A. *Macromol. Rapid Commun.* **2007**, *28*, 492.
(20) Özdemir, I.; Demir, S.; Çetinkaya, B.; Gourlaouen, C.; Maseras, F.; Bruneau, C.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2008**, *130*, 1156.
(21) Boutadla, Y.; Al-Duaij, O.; Davies, D. L.; Griffith, G. A.; Singh, K. *Organometallics* **2009**, *28*, 433, and references therein.
(22) Kücükbay, H.; Çetinkaya, B.; Guesmi, S.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2434.
(23) Richel, A.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2006**, *47*, 2077.
(24) Jan, D.; Delaude, L.; Simal, F.; Demonceau, A.; Noels, A. F. *J. Organomet. Chem.* **2000**, *606*, 55.
(25) Carmona, D.; Lamata, M. P.; Viguri, F.; Rodŕguez, R.; Lahoz, F. J.; Dobrinovitch, I. T.; Oro, L. A. *Dalton Trans.* **2008**, 3328.
(26) (a) Süss-Fink, G. *Dalton Trans.* **2010**, *39*, 1673. (b) Chen, H. M.; Parkinson, J. A.; Parsons, S.; Coxall, R. A.; Gould, R. O.; Sadler, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 3064.
(27) Chen, H. M.; Parkinson, J. A.; Morris, R. E.; Sadler, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 173.
(28) Wang, F.; Chen, H. M.; Parsons, S.; Ostwald, I. D. H.; Davidson, J. E.; Sadler, P. J. *Chem.—Eur. J.* **2003**, *9*, 5810.
(29) Fernandez, R.; Melchart, M.; Habtemariam, A.; Parsons, S.; Sadler, P. J. *Chem.—Eur. J.* **2004**, *10*, 5173.
(30) Yan, Y. K.; Melchart, M.; Habtemariam, A.; Sadler, P. J. *Chem. Commun.* **2005**, 4764.
(31) Sriskandakumar, T.; Petzold, H.; Bruijnincx, P. C. A.; Habtemariam, A.; Sadler, P. J.; Kennepohl, P. *J. Am. Chem. Soc.* **2009**, *131*, 13355.
(32) Kandioller, W.; Hartinger, C. G.; Nazarov, A. A.; Kuznetsov, M. L.; John, R. O.; Bartel, C.; Jakupec, M. A.; Arion, V. B.; Keppler, B. K. *Organometallics* **2009**, *28*, 4249.
(33) Mendoza-Ferri, M. G.; Hartinger, C. G.; Eichinger, R. E.; Stolyarova, N.; Severin, K.; Jakupec, M. A.; Nazarov, A. A.; Keppler, B. K. *Organometallics* **2008**, *27*, 2405.
(34) Hartinger, C. G.; Casini, A.; Duhot, C.; Tsybin, Y. O.; Messori, L.; Dyson, P. J. *J. Inorg. Biochem.* **2008**, *102*, 2136.
(35) Kandioller, W.; Hartinger, C. G.; Nazarov, A. A.; Kasser, J.; John, R.; Jakupec, M. A.; V Arion, B. P.; Dyson, J.; Keppler, B. K. *J. Organomet. Chem.* **2009**, *694*, 922.
(36) Gras, M.; Therrien, B.; S.-Fink, G.; Štěnička, P.; Renfrew, A. K.; Dyson, P. J. *J. Organomet. Chem.* **2008**, *693*, 3419.
(37) Berger, I.; Hanif, M.; Nazarov, A. A.; Hartinger, C. G.; John, R. O.; Kuznetsov, M. L.; Groessl, M.; Schmitt, F.; Zava, O.; Biba, F.; Arion, V. B.; Galanski, M.; Jakupec, M. A.; J.-Jeanneret, P. L.; Dyson, J.; Keppler, B. K. *Chem.—Eur. J.* **2008**, *14*, 9046.
(38) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(39) Sheldrick, G. M. *SHELXL-NT* Version 6.12; University of Gottingen: Germany, 2000.

Scheme 1. Synthesis of L1−L6 and Their Ru(II) Complexes, 1−6



a: $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$

performed until the converged model. The highly distorted solvent molecule in the crystal of complex **4** was omitted using the SQUEEZE algorithm. The resulting new data set after this omission was generated, and the structure was refined to convergence. The molecular structures of complexes were drawn using ORTEP-3 for Windows, version 2.02.[40] The catalytic conversions were determined with a NUCON Engineers (New Delhi, India) gas chromatograph (with FID detecter), model 5765, equipped with an Alltech ($Ec^{TM\text{-}1}$) column of 30 m length, 0.25 mm diameter and having a liquid film of 0.25 μm thickness. The cyclic voltammetric studies were performed on a BAS CV 50 W instrument at University of Delhi (Department of Chemistry), India. A three-electrode configuration composed of a Pt disk working electrode (3.1 mm^2 area), a Pt wire counter electrode, and an Ag/AgCl reference electrode was used for the measurements. Ferrocene was used as an internal standard ($E_{1/2}$ = 0.500 V vs Ag/AgCl), and all the potentials are expressed with reference to Ag/AgCl. Melting points determined in an open capillary are reported as such.

Chemicals and Reagents. $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$, 2-(phenylsulfanyl)ethylamine, 2-(phenylseleno)ethylamine, 2-(4-methoxyphenyltelluro)ethylamine, and bis(4-methoxyphenyl) ditelluride were synthesized by reported methods.[41−45] Thiophenol, diphenyldiselenide, 2-chloroethylamine hydrochloride, 2-methylthiobenzaldehyde, NH_4PF_6, KOH, and all the alcohols and ketones were procured from Sigma-Aldrich (USA) and used as received. The solvents were dried and distilled before use by standard procedures.[46]

General Procedure for Synthesis of Ligands L1, L2, and L3. 2-Methylthiobenzeldehyde (0.76 g, 5 mmol) dissolved in 15 cm^3 of dry CH_3OH stirred at room temperature for 0.5 h was mixed with a solution of 2-(phenylsulfanyl)ethylamine (0.77 g, 5 mmol), 2-(phenylseleno)ethylamine (1.00 g, 5 mmol), or 2-(4-methoxyphenyltelluro)ethylamine (1.40 g, 5 mmol) (respectively for **L1**, **L2**, and **L3**) made in 10 cm^3 of dry CH_3OH with constant stirring. The mixture was further stirred at room temperature for 24 h. The solvent was evaporated on a rotary evaporator to obtain ligands **L1**, **L2**, or **L3** as an oil.

L1: Yellow oil. Yield: 1.26 g, 90%. ^1H NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 2.47 (s, 3H, SCH_3), 3.29 (t, ^3J = 6.9 Hz, 2H, H_5), 3.88 (t, ^3J = 6.9 Hz, 2H, H_6), 7.18−7.42 (m, 8H, H_{1-3}, H_{11-13}), 7.81 (d, ^3J = 7.8 Hz, 1H, H_{10}), 8.72 (s, 1H, H_7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 16.8 (SCH_3), 34.5 (C_5), 60.6 (C_6), 125.5−134.0 (C_{1-4}, C_{10-13}), 136.0 (C_8), 139.3 (C_9), 160.6 (C_7). IR (KBr, cm^{-1}): 3046 (m; $\nu_{C-H\ (aromatic)}$), 2929 (s; $\nu_{C-H\ (aliphatic)}$), 1642, 1586 (s; $\nu_{C=N}$), 1232 (m; ν_{C-N}), 751 (m; $\nu_{C-H\ (aromatic)}$).

L2: Yellow oil. Yield: 1.48 g, 90%. ^1H NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 2.46 (s, 3H, SCH_3), 3.25 (t, ^3J = 6.9 Hz, 2H, H_5), 3.95 (t, ^3J = 6.9 Hz, 2H, H_6), 7.16−7.39 (m, 6H, $H_{1-2,}$ H_{11-13}), 7.52−7.56 (m, 2H, H_3), 7.80 (d, ^3J = 7.8 Hz, 1H, H_{10}), 8.72 (s, 1H, H_7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 16.9 (SCH_3), 28.5 (C_5), 61.5 (C_6), 125.5−132.8 (C_{1-4}, C_{10-13}), 134.1 (C_8), 139.3 (C_9), 160.3 (C_7). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_2Se; δ, ppm): 278.3. IR (KBr, cm^{-1}): 3059 (m; $\nu_{C-H\ (aromatic)}$), 2921 (s; $\nu_{C-H\ (aliphatic)}$), 1637, 1585 (s; $\nu_{C=N}$), 1197 (m; ν_{C-N}), 746 (m; $\nu_{C-H\ (aromatic)}$).

L3: Red oil. Yield: 1.86 g, 90%. ^1H NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 2.47 (s, 3H, SCH_3), 3.15 (t, ^3J = 7.2 Hz, 2H, H_5), 3.79 (s, 3H, OCH_3), 4.04 (t, ^3J = 7.2 Hz, 2H, H_6), 6.75 (d, ^3J = 8.7 Hz, 2H, H_2), 7.19−7.37 (m, 3H, H_{11-13}), 7.71 (d, ^3J = 8.7 Hz, 2H, H_3), 7.79 (d, ^3J = 7.8 Hz, 1H, H_{10}), 8.71 (s, 1H, H_7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 10.2 (C_5), 16.9 (SCH_3), 55.1 (OCH_3), 62.8 (C_6), 100.6(C_4), 115.1 (C_2), 125.5−130.7 (C_{10-13}), 134.1 (C_8), 139.3 (C_9), 141.0 (C_3), 159.5

(40) *ORTEP-3 for Windows*. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(41) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063.
(42) Katritzky, A. R.; Xu, Y.-J.; He, H.-Y.; Mehta, S. *J. Org. Chem.* **2001**, *66*, 5590.
(43) Khanna, A.; Bala, A.; Khandelwal, B. L. *J. Organomet. Chem.* **1995**, *494*, 199.
(44) Singh, A. K.; Srivastava, V. *Phosphorus Sulfur Silicon* **1990**, *47*, 471.
(45) Irgolic, K. J.; Zingaro, R. A. Reactions of Organotellurium Compounds. In *Organometallic Synthesis*; Becker, E.; Tsutsui, M., Eds.; John Wiley and Sons, Inc.: New York, 1971; Vol. *2*.
(46) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; ELBS, Longman Group U K Ltd., 1989.

(C_1), 159.7 (C_7). $^{125}Te\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_2Te; δ, ppm): 438.3. IR (KBr, cm^{-1}): 3052 (m; $\nu_{C-H\ (aromatic)}$), 2930 (s; $\nu_{C-H\ (aliphatic)}$), 1639, 1588 (s; $\nu_{C=N}$), 1209 (m; ν_{C-N}), 747 (m; $\nu_{C-H\ (aromatic)}$).

General Procedure for Synthesis of Ligands L4, L5, and L6. They were synthesized from **L1**, **L2**, and **L3**, respectively. **L1** (0.58 g, 2 mmol), **L2** (0.67 g, 2 mmol), or **L3** (0.82 g, 2 mmol) was dissolved in 20 cm^3 of dry ethanol, and the solution cooled in an ice bath for 0.5 h. $NaBH_4$ (0.18 g, 5 mmol) was added to it in small lots with stirring within 15 min. The reaction mixture was further stirred at room temperature for 10 h. On a rotary evaporator solvent was removed, resulting in a semisolid, which was redissolved in diethyl ether (30 cm^3) and stirred for 10 min. Distilled water (20 cm^3) was added, and the mixture further stirred until both phases became clear. The diethyl ether layer was separated, washed with distilled water (2×50 cm^3), and dried over anhydrous sodium sulfate. Its solvent was evaporated off on a rotary evaporator to obtain ligands **L4**, **L5**, and **L6** as an oil.

L4: Red oil. Yield: 0.51 g, 88%. ^1H NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 1.84 (s, 1H, NH), 2.47 (s, 3H, SCH_3), 2.86 (t, $^3J = 6.6$ Hz, 2H, H_5), 3.10 (t, $^3J = 6.6$ Hz, 2H, H_6), 3.86 (s, 2H, H_7), 7.09−7.13 (s, 1H, H_1), 7.14−7.35 (m, 8H, H_{2-3}, H_{10-13}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 15.7 (SCH_3), 34.2 (C_5), 47.5 (C_6), 51.3 (C_7), 124.9−129.8 (C_{1-4}, C_{11-13}), 135.7 (C_{10}), 137.4 (C_8), 137.6 (C_9). IR (KBr, cm^{-1}): 3054 (m; $\nu_{C-H\ (aromatic)}$), 2930 (s; $\nu_{C-H\ (aliphatic)}$), 1191 (m; ν_{C-N}), 746 (m; $\nu_{C-H\ (aromatic)}$).

L5: Red oil. Yield: 0.59 g, 88%. ^1H NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 1.90 (s, 1H, NH), 2.47 (s, 3H, SCH_3), 2.89 (t, $^3J = 6.6$ Hz, 2H, H_5), 3.07 (t, $^3J = 6.6$ Hz, 2H, H_6), 3.85 (s, 2H, H_7), 7.08−7.13 (s, 1H, H_1), 7.20−7.50 (m, 8H, H_{2-3}, H_{10-13}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 15.7 (SCH_3), 28.5 (C_5), 48.2 (C_6), 51.1 (C_7), 124.8−129.6 (C_{1-4}, C_{11-13}), 132.9 (C_{10}), 137.3 (C_8), 137.6 (C_9). $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_2Se; δ, ppm): 265.0. IR (KBr, cm^{-1}): 3052 (m; $\nu_{C-H\ (aromatic)}$), 2927 (s; $\nu_{C-H\ (aliphatic)}$), 1188 (m; ν_{C-N}), 744 (m; $\nu_{C-H\ (aromatic)}$).

L6: Red oil. Yield: 0.74 g, 90%. ^1H NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 1.90 (s, 1H, NH), 2.47 (s, 3H, SCH_3), 2.93−3.03 (m, 4H, H_{5-6}), 3.79 (s, 3H, OCH_3), 3.85 (s, 2H, H_7), 6.72 (d, $^3J = 8.7$ Hz, 2H, H_2), 7.10−7.28 (m, 4H, H_{10-13}), 7.65 (d, $^3J = 8.7$ Hz, 2H, H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C vs TMS; δ, ppm): 10.5 (C_5), 15.7 (SCH_3), 49.6 (C_6), 51.0 (C_7), 55.1 (OCH_3), 100.4 (C_4), 115.1 (C_2), 124.8−128.9 (C_{10-13}), 137.3 (C_8), 137.7 (C_9), 141.0 (C_3), 159.7 (C_1). $^{125}Te\{^1H\}$ NMR ($CDCl_3$, 25 °C vs Me_2Te; δ, ppm): 414.3. IR (KBr, cm^{-1}): 3049 (m; $\nu_{C-H\ (aromatic)}$), 2923 (s; $\nu_{C-H\ (aliphatic)}$), 1184 (m; ν_{C-N}), 745 (m; $\nu_{C-H\ (aromatic)}$).

General Method of Synthesis of Half-Sandwich Ru Complexes 1 and 3−6. The solid $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ (0.05 g, 0.1 mmol) was added to the solution of **L** (0.2 mmol) (**L** = **L1**, **L3** to **L6**) made in CH_3OH (15 cm^3). The mixture was stirred for 1 h in the case of Schiff bases and 15 h in the case of reduced Schiff bases at room temperature. The resulting yellow solution was filtered, and the volume of the filtrate was reduced (∼7 cm^3) with a rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol), and the resulting yellow or orange microcrystalline solid (**1** and **3** to **6**) was filtered, washed with 10 cm^3 of cold (∼5 °C) CH_3OH, and dried in vacuo. Single crystals of the complex (**1** and **3** to **6**) suitable for X-ray diffraction were obtained by diffusion of diethyl ether into its solution (1 cm^3) made in a mixture of CH_3OH and CH_3CN (v/v, 1:4).

1: Yield: 0.12 g, 76%. Anal. Calcd for $C_{22}H_{23}NRuS_2\cdot[PF_6]_2$: C, 34.93; H, 3.06; N, 1.85. Found: C, 34.96; H, 3.03; N, 1.87. Mp: 252 °C. Mol. cond. (Λ_M): 251.9 S cm^2 mol^{-1}. ^1H NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 3.22 (s, 3H, SCH_3), 3.57−4.23 (m, 2H, H_5), 4.36−4.77 (m, 2H, H_6), 5.63 (s, 6H, Ru-ArH), 7.40−7.84 (m, 6H, H_{1-2}, H_{11-13}), 8.01 (m, 2H, H_3), 8.47 (m, 1H, H_{10}), 8.92 (m, 1H, H_7). $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 22.1 (SCH_3), 35.8 (C_5), 72.8 (C_6), 79.7 (Ru-ArC), 129.6−132.4 (C_{1-3}, C_{10-13}), 136.2 (C_4), 136.6 (C_8), 172.9 (C_9), 173.8 (C_7). IR (KBr, cm^{-1}): 3068 (m; $\nu_{C-H\ (aromatic)}$), 2922 (s; $\nu_{C-H\ (aliphatic)}$), 1615 (s; $\nu_{C=N}$), 1136 (m; ν_{C-N}), 842 (s; ν_{P-F}), 745 (m; $\nu_{C-H\ (aromatic)}$).

[3·CH$_3$CN]: Yield: 0.15 g, 85%. Anal. Calcd for $C_{23}H_{25}NORuSTe\cdot[PF_6]_2$: C, 31.32; H, 2.86; N, 1.59. Found: C, 31.36; H, 2.89; N, 1.58. Mp: 256 °C. Mol. cond. (Λ_M): 244.5 S cm^2 mol^{-1}. ^1H NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 3.15 (s, 3H, SCH_3), 3.31−3.43 (m, 2H, H_5), 3.93 (s, 3H, OCH_3), 4.27−4.38 (m, 2H, H_6), 5.67 (s, 6H, Ru-ArH), 6.98 (d, $^3J = 8.7$ Hz, 2H, H_2), 7.21−7.39 (m, 3H, H_{11-13}), 7.84 (d, $^3J = 8.7$ Hz, 2H, H_3), 8.67 (d, $^3J = 7.5$ Hz, 1H, H_{10}), 8.74 (s, 1H, H_7). $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 16.4 (C_5), 22.4 (SCH_3), 56.2 (OCH_3), 75.5 (C_6), 77.2 (Ru-ArC), 116.4 (C_4), 117.8 (C_2), 129.2−133.1 (C_{10-13}), 135.8 (C_8), 140.3 (C_9), 162.0 (C_3), 163.2 (C_1), 173.4 (C_7). $^{125}Te\{^1H\}$ NMR (CD_3CN, 25 °C vs Me_2Te; δ, ppm): 692.0. IR (KBr, cm^{-1}): 3048 (m; $\nu_{C-H\ (aromatic)}$), 2926 (s; $\nu_{C-H\ (aliphatic)}$), 1633, 1585 (s; $\nu_{C=N}$), 1209 (m; ν_{C-N}), 842 (s; ν_{P-F}), 746 (m; $\nu_{C-H\ (aromatic)}$).

[4·H$_2$O]: Yield: 0.10 g, 80%. Anal. Calcd for $C_{22}H_{25}NRuS_2\cdot[PF_6][Cl]$: C, 40.71; H, 3.88; N, 2.16. Found: C, 40.72; H, 3.88; N, 2.14. Mp: 254 °C. Mol. cond. (Λ_M): 255.1 S cm^2 mol^{-1}. ^1H NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 2.19 (s, 1H, NH), 3.01 (s, 3H, SCH_3), 3.75−4.22 (m, 2H, H_5), 4.41−4.81 (m, 2H, H_6), 5.29 (s, 2H, H_7), 5.73 (s, 6H, Ru-ArH), 7.42−7.80 (m, 7H, H_{1-2}, H_{10-13}), 7.85−7.93 (m, 2H, H_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 24.4 (SCH_3), 38.9 (C_5), 59.1(C_6), 61.2 (C_7), 87.0 (Ru-ArC), 128.3−132.5 (C_{1-4}, C_{10-13}), 139.2 (C_8), 141.6 (C_9). IR (KBr, cm^{-1}): 3052 (m; $\nu_{C-H\ (aromatic)}$), 2925 (s; $\nu_{C-H\ (aliphatic)}$), 1188 (m; ν_{C-N}), 844 (s; ν_{P-F}), 747 (m; $\nu_{C-H\ (aromatic)}$).

5: Yield: 0.14 g, 87%. Anal. Calcd for $C_{22}H_{25}NRuSSe.[PF_6]_2$: C, 31.32; H, 2.86; N, 1.59. Found: C, 31.36; H, 2.89; N, 1.58. Mp: 252 °C. Mol. cond. (Λ_M): 253.1 S cm^2 mol^{-1}. ^1H NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 2.22 (s, 1H, NH), 3.12 (s, 3H, SCH_3), 3.34−3.93 (m, 2H, H_5), 4.26−4.51 (m, 2H, H_6), 5.17 (s, 2H, H_7), 5.72 (s, 6H, Ru-ArH), 7.30−7.68 (m, 7H, H_{1-2}, H_{10-13}), 7.82−7.92 (m, 2H, H_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 26.0 (SCH_3), 33.8 (C_5), 57.2(C_6), 61.5 (C_7), 87.1 (Ru-ArC), 128.1−132.6 (C_{1-4}, C_{10-13}), 135.3 (C_8), 136.5 (C_9). $^{77}Se\{^1H\}$ NMR (CD_3CN, 25 °C vs Me_2Se; δ, ppm): 338.3. IR (KBr, cm^{-1}): 3054 (m; $\nu_{C-H\ (aromatic)}$), 2923 (s; $\nu_{C-H\ (aliphatic)}$), 1185 (m; ν_{C-N}), 842 (s; ν_{P-F}), 746 (m; $\nu_{C-H\ (aromatic)}$).

[6·CH$_3$CN]: Yield: 0.14 g, 87%. Anal. Calcd for $C_{23}H_{27}NORuSTe\cdot[PF_6]_2$: C, 31.25; H, 3.08; N, 1.58. Found: C, 31.26; H, 3.08; N, 1.61. Mp: 250 °C. Mol. cond. (Λ_M): 245.5 S cm^2 mol^{-1}. ^1H NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 2.19 (s, 1H, NH), 3.03 (s, 3H, SCH_3), 3.17−3.60 (m, 2H, H_5), 3.86 (s, 3H, OCH_3), 3.90−4.12 (m, 2H, H_6), 5.10 (s, 2H, H_7), 5.77 (s, 6H, Ru-ArH), 7.00 (d, $^3J = 8.5$ Hz, 2H, H_2), 7.30−7.82 (m, 4H, H_{10-13}), 7.99 (d, $^3J = 8.5$ Hz, 2H, H_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C vs TMS; δ, ppm): 16.2 (C_5), 26.3 (SCH_3), 56.2 (OCH_3), 56.4 (C_6), 59.6 (C_7), 87.1 (Ru-ArC), 116.9 (C_4), 117.5 (C_2), 127.6−133.5 (C_{10-13}), 136.5 (C_8), 138.3 (C_9), 162.6 (C_3), 163.2 (C_1). $^{125}Te\{^1H\}$ NMR (CD_3CN, 25 °C vs Me_2Te; δ, ppm): 672.6. IR (KBr, cm^{-1}): 3047 (m; $\nu_{C-H\ (aromatic)}$), 2920 (s; $\nu_{C-H\ (aliphatic)}$), 1180 (m; ν_{C-N}), 843 (s; ν_{P-F}), 746 (m; $\nu_{C-H\ (aromatic)}$).

2. This was synthesized by a procedure reported earlier by us.[47] IR spectrum and ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** given in the Supporting Information are consistent with an earlier report. $^{77}Se\{^1H\}$ NMR (CD_3CN, 25 °C vs Me_2Se; δ, ppm): 381.5.

Catalytic Oxidation of Alcohols with NMO. A typical reaction carried out for catalytic oxidations of primary alcohols to corresponding aldehydes and secondary ones to ketones with *N*-methylmorpholine-*N*-oxide and complexes **1−6** is as follows. A solution of a complex among **1−6** (0.001 mol %) in 20 cm^3 of CH_2Cl_2 was mixed with neat alcohol substrate (1 mmol) and solid NMO (3 mmol). The mixture was refluxed for 2 h with

(47) Singh, P.; Das, D.; Singh, M.; Singh, A. K. *Inorg. Chem. Commun.* **2010**, *13*, 223.

catalyst **1**−**3** and 3 h with catalyst **4**−**6**. Thereafter solvent was evaporated off using a rotary evaporator. The residue having an oxidized product was extracted with 20 cm^3 of petroleum ether (60−80 °C). The complex−catalyst undissolved in petroleum ether was recovered almost quantitatively for the next catalytic cycle. The oxidized product present in petroleum ether was analyzed by GC.

Catalytic Oxidation of Alcohols with *t*BuOOH. A mixture of a complex among **1**−**6** (0.001 mol %) dissolved in 20 cm^3 of CH_2Cl_2 and neat alcohol substrate (1 mmol) was made. *t*BuOOH (4 mmol) was added to the mixture with a dropping funnel over 0.5 h, and the resulting mixture was stirred for 2 h with catalyst **1**−**3** and 3 h with catalyst **4**−**6** at room temperature. The solvent from the reaction mixture was mostly evaporated off with a rotary evaporator, resulting in a semisolid, containing the complex−catalyst and the oxidized alcohol. It was extracted with 20 cm^3 of petroleum ether (60−80 °C). The extract containing oxidized product was analyzed by GC, and the residue containing complex−catalyst in nearly quantitative amount was preserved for the next catalytic cycle.

Catalytic Oxidation of Alcohols with NaOCl and $NaIO_4$. The solution of a ruthenium complex among **1**−**6** (0.001 mol %) made in 10 cm^3 of CH_2Cl_2 was added to a 5 cm^3 solution of $NaHCO_3$−Na_2CO_3 (1.0 M, pH = 9.5) buffer. A few drops of aqueous NaOCl/$NaIO_4$ (0.7 M/1.0 M) were added at 0 °C, and the mixture was stirred vigorously until the organic phase became yellow or orange in color, leaving the aqueous phase colorless. The solution of alcohol substrate (1 mmol) made in 5 cm^3 of CH_2Cl_2 was added in one lot to the reaction mixture with stirring. The aqueous solution of 0.7 M NaOCl (5.7 cm^3)/ 1.0 M $NaIO_4$ (4 cm^3) was added to the reaction mixture dropwise with a dropping funnel over a period of 1 h. The resulting reaction mixture was stirred for 2 h with catalyst **1**−**3** and 3 h with catalyst **4**−**6** at room temperature, maintaining its pH at ∼9.5 and shaken thereafter with 30 cm^3 of CH_2Cl_2. The organic layer was separated, and its solvent was mostly evaporated off with a rotary evaporator, resulting in a semisolid, which was extracted with petroleum ether (60−80 °C) (20 cm^3). The complex−catalyst left as a solid residue was recovered almost quantitatively for other catalytic cycle. The resulting products extracted into petroleum ether were analyzed by GC.

General Procedure for Catalytic Transfer Hydrogenation Reaction. A solution of the ketone (1 mmol), KOH (0.2 cm^3 of a 0.2 M solution in 2-propanol), and the catalyst complexes **1**−**6** (0.001 mol %) was heated under reflux (80 °C) in 10 cm^3 of 2-propanol for 5 h with catalysts **1**−**3** and 7 h with catalysts **4**−**6**. 2-Propanol was removed under vacuum, and an aliquot of the remaining product was extracted with diethyl ether, filtered through a short column of silica gel. The column was washed with diethyl ether. The filtrate and washings of the column were mixed and evaporated on a rotary evaporator and analyzed by GC. The final conversions are reported as an average of two runs of each catalytic reaction.

Results and Discussions

Scheme 1 summarizes the syntheses of **L1**−**L6** and their ruthenium(II) complexes **1**−**6**. The ligands **L1**, **L4**, and **L5** have been synthesized for the first time. **L2** has been prepared by a synthetic procedure reported earlier.[47] Similarly **L3** and **L6** have been synthesized in better yield than reported earlier[48] using longer reaction time (24 h) in the case of **L3** and a different workup procedure for **L6** (diethyl ether−water). The molar conductance values in acetonitrile (see Experimental Section) indicate a 1:2 electrolyte nature of all complexes **1**−**6**. The solubility of each ligand was good in common organic solvents, while complexes showed good solubility in CH_3OH, CH_3CN, CH_2Cl_2, and $CHCl_3$. In diethyl and petroleum ether complexes **1**−**6** were almost insoluble. However, solutions of complexes in DMSO showed signs of decomposition within a few hours.

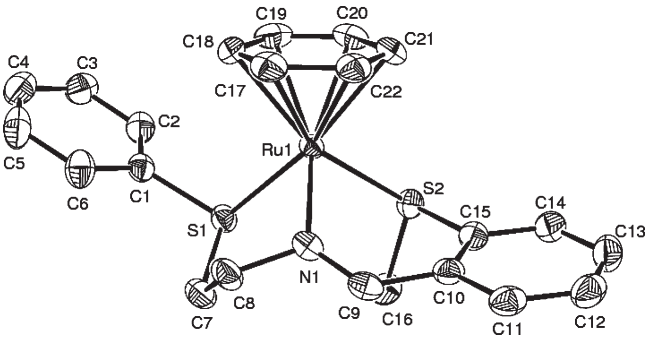


Figure 1. ORTEP diagram of the cation of **1** with 30% probability ellipsoids. Hydrogen atoms and PF_6 are omitted for clarity. Bond lengths (Å): Ru(1)−S(1) 2.3921(19), Ru(1)−S(2) 2.3465(19), Ru(1)−N(1) 2.073(6), Ru(1)−C 2.197(7)−2.224(7). Bond angles (deg): S(1)−Ru(1)−S(2) 91.56(7), N(1)−Ru(1)−S(1) 79.72(16), N(1)−Ru(1)−S(2) 86.21(17).

NMR Spectra. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **L1**−**L6** and their complexes **1**−**6** were in agreement with their molecular structures. The $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra of ligands **L2**, **L3**, **L5**, and **L6** and their corresponding complexes **2**, **3**, **5**, and **6** are given in the Supporting Information (Figures S1 to S8). The signals in the $^{77}Se\{^1H\}$ NMR spectra of **2** and **5** appear shifted to higher frequencies by 103.2 and 73.3 ppm with respect to those of free **L2** and **L5**, respectively, as Se is coordinated to the ruthenium center. Similarly in the $^{125}Te\{^1H\}$ NMR spectra of **3** and **6** the signals appear at frequencies higher by 253.7 and 258.3 ppm relative to those of free **L3** and **L6**, respectively, which are coordinated to ruthenium through Te. In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**−**6** signals of protons and carbon atoms generally appear at higher frequency relative to those of free ligands which coordinate with ruthenium in a tridentate mode. However, the magnitude of the shift to higher frequency is high for C_5 to C_7 (up to 12.2 ppm in $^{13}C\{^1H\}$ NMR) and protons attached to them (up to 1.43 ppm in ^1H NMR). The signals of SCH_3 in the $^{13}C\{^1H\}$ and ^1H NMR spectra of **1**−**6** also appear at higher frequency (up to 10.6 and 0.75 ppm, respectively). The signals of NH in the ^1H NMR spectra of **4**−**6** shift to higher frequencies (up to 1.35 ppm) with respect to those of free **L4**−**L6**.

Crystal Structures. The crystal structures of **1**−**6** have been solved. The results of **2** have been reported earlier,[47] and those of the remaining five complexes are described here. The ORTEP diagrams of **1** and **3**−**6** are given in Figures 1 to 5 with selected bond distances and angles. In the cations of these five complexes, there is a pseudo-octahedral half-sandwich "piano-stool" disposition of donor atoms around ruthenium. The benzene ring occupies one face of octahedron, and a tridentae ligand among **L1** and **L3**−**L6** the opposite one. In the cation of **1** the Ru−S(1) bond distance, 2.3921(19) Å, is greater than its Ru−S(2) distance, 2.3465(19) Å. The Ru−S(1) and Ru−S(2) bond lengths of the cation of **4** are not much different. The Ru−S bond lengths of cations of **1** and **3**−**6** are also within the range 2.3548(15)−2.4156(9) Å, in which the Ru−S bond distances of $[(\eta^6\text{-}C_6H_6)RuCl(N\text{-}\{2\text{-(phenylthio)ethyl}\}pyrrolidine)]^+$,

(48) Kumar, P. R.; Upreti, S.; Singh, A. K. *Inorg. Chim. Acta* **2008**, *361*, 1426.

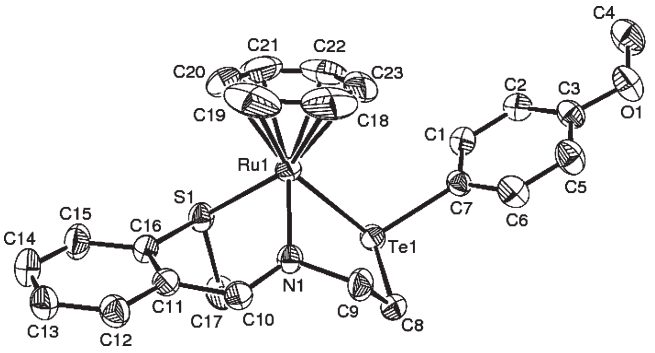


Figure 2. ORTEP diagram of cation of **3** with 30% probability ellipsoids. Hydrogen atoms, CH_3CN, and PF_6 are omitted for clarity. Bond lengths (Å): Ru(1)−Te(1) 2.6234(6), Ru(1)−S(1) 2.3484(15), Ru(1)−N(1) 2.077(4), Ru(1)−C 2.183(8)−2.205(7). Bond angles (deg): Te(1)−Ru(1)−S(1) 91.01(4), N(1)−Ru(1)−Te(1) 80.72(12), N(1)−Ru(1)−S(1) 86.74(12).

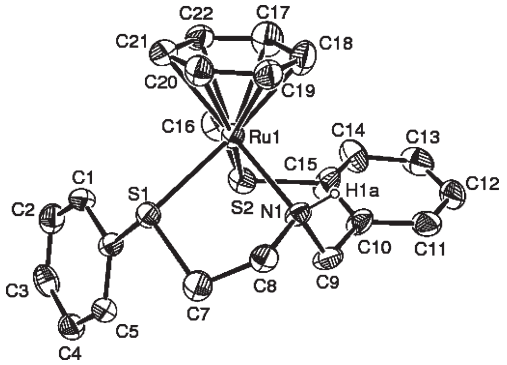


Figure 3. ORTEP diagram of cation of **4** with 30% probability ellipsoids. Hydrogen atoms (except NH), H_2O, Cl, and PF_6 are omitted for clarity. Bond lengths (Å): Ru(1)−S(1) 2.374(3), Ru(1)−S(2) 2.379(2), Ru(1)−N(1) 2.135(5), Ru(1)−C 2.146(15)−2.218(9). Bond angles (deg): S(1)−Ru(1)−S(2) 90.75(10), N(1)−Ru(1)−S(1) 83.0(2), N(1)−Ru(1)−S(2) 86.51(18).

$[(\eta^6\text{-}C_6H_6)RuCl(N\text{-}\{2\text{-(phenylthio)ethyl}\}morpholine)]^+$, $[Cp^*Ru(PMe_3)_2(SC_6F_4H)]$, and $[Cp^*Ru(NO)(SC_6F_4H)_2]$ have been reported.[49−51] The Ru−Se bond length of the cation of **5** (2.4848(14) Å) is consistent with the Ru−Se bond length of the cation of **2** (2.4837(14) Å)[47] and the value reported for half-sandwich complexes of Ru(II) with *N*-{2-(phenylseleno)ethyl}-pyrrolidine[49] (2.4770(5)−2.480(11) Å). The Ru−Se bond lengths of **2** and **5** fall within the range 2.4756(10)−2.5240(9) Å, reported for such bond lengths in clusters $[Ru_3(\mu_3\text{-Se})(CO)_7(\mu_3\text{-CO})(\mu\text{-dppm})]$ and $[Ru_3(\mu_3\text{-Se})(\mu_3\text{-S})(CO)_7(\mu\text{-dppm})]$.[52] For the Ru(IV) complex $[RuCp^*\{\eta^2\text{-}Se_2P(i\text{Pr})_2\}\{\eta^2\text{-}SeP(i\text{Pr})_2\}][PF_6]$ the Ru−Se bond lengths[51] are reported in the range 2.538(2)−2.590(2) Å, longer than those of cations of **2** and **5** due to steric crowding. The Ru−Se bond distance in $[RuCp(CO)(C{\equiv}CPh)(\mu\text{-Se})ZrCp_2]$, 2.494(1) Å,[53] is closer to that of cations of **2** and **5**.

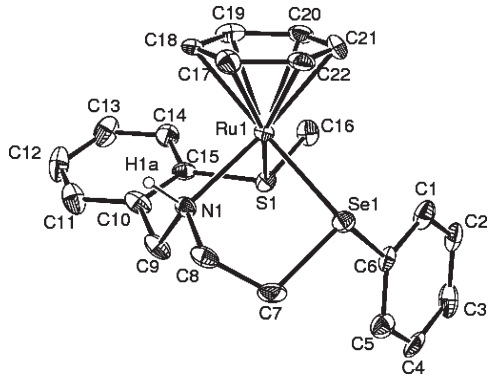


Figure 4. ORTEP diagram of cation of **5** with 50% probability ellipsoids. Hydrogen atoms (except NH) and PF_6 are omitted for clarity. Bond lengths (Å): Ru(1)−Se(1) 2.4848(8), Ru(1)−S(1) 2.3742(17), Ru(1)−N(1) 2.169(5), Ru(1)−C 2.217(7)−2.233(7). Bond angles (deg): Se(1)−Ru(1)−S(1) 91.37(5), N(1)−Ru(1)−Se(1) 84.05(15), N(1)−Ru(1)−S(1) 85.25(16).

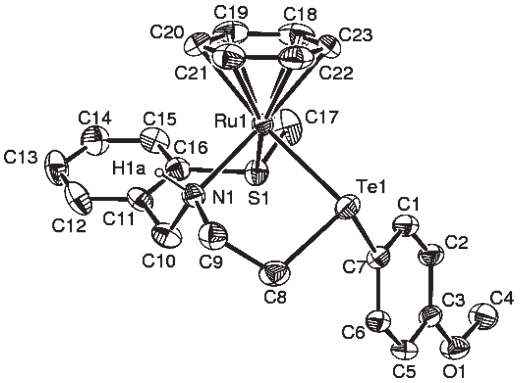


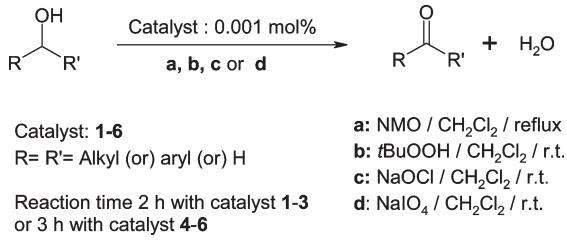
Figure 5. ORTEP diagram of cation of **6** with 30% probability ellipsoids. Hydrogen atoms (except NH), CH_3CN, and PF_6 are omitted for clarity. Bond lengths (Å): Ru(1)−Te(1) 2.6333(7), Ru(1)−S(1) 2.3853(17), Ru(1)−N(1) 2.175(5), Ru(1)−C 2.204(6)−2.226(7). Bond angles (deg): Te(1)−Ru(1)−S(1) 90.0(2), N(1)−Ru(1)−Te(1) 84.41(14), N(1)−Ru(1)−S(1) 85.30(14).

The Ru−Se bond distances of $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-SeR})_3(\eta^5\text{-}C_5Me_5)Ru]Cl$ (R = tolyl) (2.446(4)−2.466(4) Å)[54] are shorter than those of cations of **2** and **5**, because RSe^- is expected to be bonded strongly in comparison to selenated Schiff bases and their reduced analogues. In $[Ru(MeCp)(PPh_3)]_2(\mu\text{-}Se_2)_2(Otf)_2$, Ru−Se bond distances are 2.518(1) and 2.556(1) Å,[55] somewhat longer than those of cations of **2** and **5**.

The Ru−Te bond length (2.6234(6) Å) of the cation of **3** is shorter than that of the cation of **6** (2.6333(7) Å). Both the values are longer than earlier reported[50] values, 2.6143(7) Å for $[(\eta^6\text{-}C_6H_6)Ru(II)Cl(N\text{-}\{2\text{-(4-methoxyphenyltelluro)ethyl}\}morpholine)]^+$ and 2.619(8) Å for $[(\eta^6\text{-}p\text{-cymene})RuCl_2(2\text{-(4-ethoxyphenyltelluromethyl)tetrahydro-}2H\text{-pyran})]$,[56] but consistent with the value 2.6371(4) Å reported for $[(\eta^6\text{-}p\text{-cymene})RuCl(H_2NCH_2CH_2TeC_6H_4\text{-4-OMe})Cl\cdot H_2O]$.[57] The present Ru−Te distances are shorter than the reported values

(49) Singh, P.; Singh, M.; Singh, A. K. *J. Organomet. Chem.* **2009**, *694*, 3872.
(50) Singh, P.; Singh, A. K. *Eur. J. Inorg. Chem.* **2010**, 4187.
(51) Zhang, Q.-F.; Cheung, F. K. M.; Wong, W;-Y.; Williams, I. D.; Leung, W.-H. *Organometallics* **2001**, *20*, 3777.
(52) Ahmed, S. J.; Hyder, M. I.; Kabir, S. E.; Miah, M. A.; Deeming, A. J.; Nordlander, E. *J. Organomet. Chem.* **2006**, *691*, 309.
(53) Sunada, Y.; Hayashi, Y.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **2001**, *40*, 7072.
(54) Matsuzaka, H.; Ogino, T.; Nishio, M.; Hidai, M.; Nishibayashi, Y.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1994**, *2*, 223.
(55) Amarasekera, J.; Houser, E. J.; Rauchfuss, T. B.; Stern, C. L. *Inorg. Chem.* **1992**, *31*, 1614.
(56) Singh, A. K.; Kadarkaraisamy, M.; Misra, M.; Sooriyakumar, J.; Drake, J. E.; Hursthouse, M. B.; Light, M. E.; Jasinski, J. P. *Inorg. Chim. Acta* **2001**, *320*, 133.
(57) Kumar, P. R.; Singh, A. K.; Butcher, R. J.; Sharma, P.; Toscano, R. A. *Eur. J. Inorg. Chem.* **2004**, 1107.

Scheme 2. Catalytic Oxidation of Alcohols



of 2.6528(9) Å for [(η^6-*p*-cymene)$RuCl_2$bis{2-(2-thienyl)ethyl} telluride],[58] 2.651(5) Å for [(η^6-*p*-cymene)$RuCl_2${bis(1,3-dioxan-2-yl)}ethyl telluride}],[59] and 2.6559(9) Å for [(η^6-*p*-cymene)$RuCl_2${*N*-[2-(4-methoxyphenyltelluro)ethyl]phthalimide}],[60] in which hybrid organotellurium ligands bind in a monodentate mode via Te with (η^6-*p*-cymene)Ru(II).

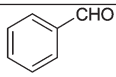
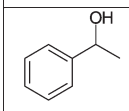
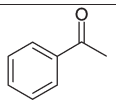
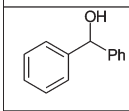
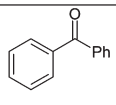
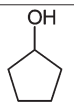
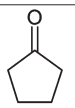
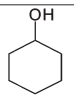
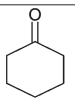
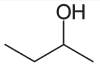
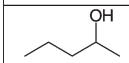
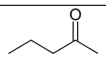
The Ru−N bond lengths (sum of covalent radii ca. 1.95 Å) of cations of **1** and **3**−**6** are between 2.073(6) and 2.175(5) Å. They are shorter than the values of the half-sandwich complex of Ru(II) with *N*-{2-(phenylseleno)ethyl}pyrrolidine (2.190(3)−2.201(5) Å).[49] The Ru−N bond distances of **5** and **6** are longer in comparison to the values reported recently (2.0511(17)−2.163(10) Å).[48,52] In half-sandwich complexes of (η^6-*p*-cymene)RuCl[61−65] with several nitrogen ligands, Ru−N bond lengths have been reported generally between 2.060(5) and 2.156(2) Å, which are less than the present values. The Ru−C bond lengths (2.146(15)−2.233(7) Å) and C−Ru−C bond angles of cations of **1** and **3**−**6** are in the normal range.[47−49,52,56,58−60,66−70] The solvent molecules CH_3CN and MeOH respectively in the crystal structures of **3** and **4** were found distorted. In the case of **4**, using the SQUEEZE algorithm, the solvent molecule (MeOH) is removed. In the case of **3**, due to disorder, the false impression of two methyl groups appears in the structure. However in the program ORTEP-3 for Windows, version 2.02, CH_3CN appears as a linear molecule (Supporting Information Figure S15).

Catalytic Applications. Complexes **1**−**6** have been used for catalytic oxidation of primary and secondary alcohols. Maximum conversions were reached in 2 h with catalysts **1**−**3** and in 3 h with catalysts **4**−**6** (Scheme 2). The oxidation of alcohols with NaOCl and $NaIO_4$ has been carried out at pH 9−10 because of the earlier reports[71,72] that suggest that in this pH range conversions are optimum. A series of blank experiments were carried out under identical conditions (see Experimental Section), which suggest that neither ruthenium(II) complexes nor oxidants (NMO, *t*BuOOH, NaOCl, or $NaIO_4$) alone result in catalytic oxidation to any significant level.

The cyclic voltammetric experiments performed at 298 K in CH_3CN (0.01 M n-Bu_4ClO_4 as supporting electrolyte) on **1**−**6** at a scan rate of 100 mV s^{-1} (anodic sweep) reveal a one-electron irreversible oxidation with $E_{1/2}$ values between 0.557 and 0.689 V (vs Ag/AgCl) (see Table S4 and Figures S9 to S14 in the Supporting Information for details), which are not extreme, implying that both species Ru(II) and Ru(III) are equally stabilized by the same set of ligands. The $E_{1/2}$ in such a range has been reported to be favorable for a catalytic oxidation process earlier;[73,74] of course no one-to-one relationship has been unequivocally established. The TON values are given in Table 1 for oxidation (catalyzed by **1**−**6**) of various alcohols by four oxidants, viz., NMO, *tert*-butyl hydroperoxide (*t*BuOOH), sodium oxychloride (NaOCl), and sodium periodate ($NaIO_4$). **3** appears to be the most efficient among all six Ru species with all four oxidants. The ruthenium complexes of chalcogenated Schiff base ligands show better catalytic efficiency than their reduced counterparts (Table 1). The azomethine group, >C=N, is a better donor than NH, which in turn facilitates the formation of Ru(IV)=O containing intermediate species, which is believed to carry out oxidation of substrates.The catalytic efficiency varies with chalcogen ligands in the order of Te > Se > S, which is also the order of "softness" of these donor sites. However, further increase in softness of Te due to a strong electron-donating methoxy group cannot be ignored and may be responsible for generating this order. The softer ligand makes easier the formation of Ru(IV)=O species, which are believed to be intermediates in the oxidation process on the basis of several observations mentioned below. Undoubtedly determining the mechanism of these oxidative transformations unambiguously is not straightforward, as intermediate species are of low stability. On the basis of earlier work[71,72,75−82] and some observations made by us, the mechanism of catalytic oxidation appears to involve Ru(IV)=O species, which appear to be formed by free radicals (generated by heterolytic cleavage of oxidants). The addition of AIBN [a free radical initiator, azobis(isobutyronitrile)] to the benzyl alcohol oxidation in the presence **3** (most efficient catalyst) with any one of the four oxidants

(58) Bali, S.; Singh, A. K.; Sharma, P.; Toscano, R. A.; Drake, J. E.; Hursthouse, M. B.; Light, M. E. *J. Organomet. Chem.* **2004**, *689*, 2346.
(59) Singh, A. K.; Sooriyakumar, J.; Drake, J. E.; Hursthouse, M. B.; Light, M. E. *J. Organomet. Chem.* **2000**, *613*, 244.
(60) Singh, A. K.; Kadarkaraisamy, M.; Murthy, G. S.; Srinivas, J.; Varghese, B.; Butcher, R. J. *J. Organomet. Chem.* **2000**, *605*, 39.
(61) Bugarcic, T.; Habtemariam, A.; Deeth, R. J.; Fabbiani, F. P. A.; Parsons, S.; Sadler, P. J. *Inorg. Chem.* **2009**, *48*, 9444.
(62) Soriano, M. L.; Jalón, F. A.; Manzano, B. R.; Maestro, M. *Inorg. Chim. Acta* **2009**, *362*, 4486.
(63) Bacchi, A.; Pelagatti, P.; Pelizzi, C.; Rogolino, D. *J. Organomet. Chem.* **2009**, *694*, 3200.
(64) Singh, A.; Singh, N.; Pandey, D. S. *J. Organomet. Chem.* **2002**, *642*, 48.
(65) Cabeza, J. A.; da Silva, I.; del Río, I.; Gossage, R. A.; Martínez-Méndez, L.; Miguel, D. *J. Organomet. Chem.* **2007**, *692*, 4346.
(66) Mishra, H.; Mukherjee, R. *J. Organomet. Chem.* **2006**, *691*, 3545.
(67) Mishra, H.; Mukherjee, R. *J. Organomet. Chem.* **2007**, *692*, 3248.
(68) Bali, S.; Singh, A. K.; Drake, J. E.; Hursthouse, M. B.; Light, M. E. *J. Organomet. Chem.* **2006**, *691*, 3788.
(69) Singh, A. K.; Sooriyakumar, J.; Husebye, S.; Tornroos, K. W. *J. Organomet. Chem.* **2000**, *612*, 46.
(70) Singh, A. K.; Amburose, C. V.; Misra, M.; Butcher, R. J. *J. Chem. Res., Synop.* **1999**, 716–717.
(71) Gonsalvi, L.; Arends, I. W. C. E.; Moilanen, P.; Sheldon, R. A. *Adv. Synth. Catal.* **2003**, *345*, 1321.
(72) Gonsalvi, L.; Arends, I. W. C. E.; Sheldon, R. A. *Org. Lett.* **2002**, *4*, 1659.
(73) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, 11830.
(74) Delaude, L.; Demonceau, A.; Noels, A. F. *Top. Organomet. Chem.* **2004**, *11*, 155, and reference therein..
(75) Drago, R. S. *Coord. Chem. Rev.* **1992**, *117*, 185.
(76) Cundari, T. R.; Drago, R. S. *Inorg. Chem.* **1990**, *29*, 3904.
(77) Fung, W.-H.; Yu, W.-Y.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 2873, and refrences therein..
(78) Che, C.-M.; Lai, T.-F.; Wong, K.-Y. *Inorg. Chem.* **1987**, *26*, 2289.
(79) Catalano, V. J.; Heck, R. A.; Immoos, C. E.; Öhman, A.; Hill, M. G. *Inorg. Chem.* **1998**, *37*, 2150.
(80) Kumar, K. N.; Venkatachalam, G.; Ramesh, R.; Liu, Y. *Polyhedron* **2008**, *27*, 157.
(81) EI-Hendawy, A. M.; Alkubaisi, A. H.; Koarashy, A. E.; Shanab, M. M. *Polyhedron* **1993**, *12*, 2343.
(82) Goldstein, A. S.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1991**, 21.

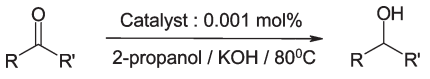
Table 1. Catalytic Oxidation of Primary and Secondary Alcohols Using Complexes 1−6 As Catalyst[a]

Substrate	Product			TON (% Conversion)					
			Absence of catalysts	1	2	3	4	5	6
		a		7.7×10^4 (77)	8.3×10^4 (83)	8.7×10^4 (87)	7.7×10^4 (77)	8.1×10^4 (81)	8.6×10^4 (86)
		b	Product	7.5×10^4 (75)	8.0×10^4 (80)	8.3×10^4 (83)	7.3×10^4 (73)	7.8×10^4 (78)	8.4×10^4 (84)
		c	not	7.1×10^4 (71)	7.8×10^4 (78)	8.1×10^4 (81)	7.0×10^4 (70)	7.5×10^4 (75)	8.0×10^4 (80)
		d	detected	7.0×10^4 (70)	7.5×10^4 (75)	7.9×10^4 (79)	6.8×10^4 (68)	7.4×10^4 (74)	7.8×10^4 (78)
		a		8.4×10^4 (84)	9.0×10^4 (90)	9.3×10^4 (93)	8.5×10^4 (85)	9.0×10^4 (90)	9.3×10^4 (93)
		b	Product	8.1×10^4 (81)	8.8×10^4 (88)	9.0×10^4 (90)	8.1×10^4 (81)	8.8×10^4 (88)	8.9×10^4 (89)
		c	not	7.6×10^4 (76)	8.5×10^4 (85)	8.8×10^4 (88)	7.5×10^4 (75)	8.5×10^4 (85)	8.7×10^4 (87)
		d	detected	7.4×10^4 (74)	8.3×10^4 (83)	8.7×10^4 (87)	7.4×10^4 (74)	8.3×10^4 (83)	8.6×10^4 (86)
		a		8.8×10^4 (88)	9.3×10^4 (93)	9.6×10^4 (96)	8.7×10^4 (87)	9.3×10^4 (93)	9.5×10^4 (95)
		b	Product	8.4×10^4 (84)	9.0×10^4 (90)	9.2×10^4 (92)	8.5×10^4 (85)	8.9×10^4 (89)	9.3×10^4 (93)
		c	not	7.8×10^4 (78)	8.6×10^4 (86)	8.8×10^4 (88)	7.8×10^4 (78)	8.6×10^4 (86)	8.9×10^4 (89)
		d	detected	7.7×10^4 (77)	8.5×10^4 (85)	8.6×10^4 (86)	7.6×10^4 (76)	8.6×10^4 (86)	8.7×10^4 (87)
		a		8.6×10^4 (86)	9.1×10^4 (91)	9.4×10^4 (94)	8.6×10^4 (86)	9.0×10^4 (90)	9.3×10^4 (93)
		b	Product	8.2×10^4 (82)	8.7×10^4 (87)	9.0×10^4 (90)	8.1×10^4 (81)	8.7×10^4 (87)	9.1×10^4 (91)
		c	not	7.7×10^4 (77)	8.5×10^4 (85)	8.7×10^4 (87)	7.5×10^4 (75)	8.4×10^4 (84)	8.8×10^4 (88)
		d	detected	7.5×10^4 (75)	8.3×10^4 (83)	8.7×10^4 (87)	7.4×10^4 (74)	8.3×10^4 (83)	8.8×10^4 (88)
		a		8.8×10^4 (88)	9.2×10^4 (92)	9.6×10^4 (96)	8.6×10^4 (86)	9.2×10^4 (92)	9.5×10^4 (95)
		b	Product	8.4×10^4 (84)	9.0×10^4 (90)	9.3×10^4 (93)	8.4×10^4 (84)	8.8×10^4 (88)	9.3×10^4 (93)
		c	not	7.9×10^4 (79)	8.7×10^4 (87)	9.0×10^4 (90)	7.8×10^4 (78)	8.5×10^4 (85)	8.9×10^4 (89)
		d	detected	7.8×10^4 (78)	8.6×10^4 (86)	8.9×10^4 (89)	7.7×10^4 (77)	8.5×10^4 (85)	8.8×10^4 (88)
		a		9.0×10^4 (90)	9.4×10^4 (94)	9.7×10^4 (97)	8.9×10^4 (89)	9.4×10^4 (94)	9.7×10^4 (97)
		b	Product	8.6×10^4 (86)	9.2×10^4 (92)	9.4×10^4 (94)	8.4×10^4 (84)	9.1×10^4 (91)	9.3×10^4 (93)
		c	not	8.3×10^4 (83)	8.9×10^4 (89)	9.1×10^4 (91)	8.2×10^4 (82)	8.8×10^4 (88)	9.1×10^4 (91)
		d	detected	8.3×10^4 (83)	8.8×10^4 (88)	9.0×10^4 (90)	8.1×10^4 (81)	8.6×10^4 (86)	8.9×10^4 (89)
		a		9.1×10^4 (91)	9.6×10^4 (96)	9.9×10^4 (99)	9.0×10^4 (90)	9.5×10^4 (95)	9.8×10^4 (98)
		b	Product	8.8×10^4 (88)	9.4×10^4 (94)	9.6×10^4 (96)	8.7×10^4 (87)	9.2×10^4 (92)	9.5×10^4 (95)
		c	not	8.4×10^4 (84)	9.0×10^4 (90)	9.3×10^4 (93)	8.3×10^4 (83)	9.0×10^4 (90)	9.2×10^4 (92)
		d	detected	8.2×10^4 (82)	8.8×10^4 (88)	9.1×10^4 (91)	8.3×10^4 (83)	8.9×10^4 (89)	9.2×10^4 (92)

[a] Reaction time 2 h for **1**−**3** and 3 h for **4**−**6**. Oxidant: a = NMO; b = *t*BuOOH; c = $NaIO_4$; d = NaOCl.

under the same reaction conditions resulted in enhanced conversion (85−96%). Further addition of AIBN in the same oxidation reaction in the absence of **3** did not result in any oxidation. In the presence of benzoquinone [a free radical inhibitor] the conversion was in trace amounts. These observations are consistent with those made by Drago and co-workers in the oxidation of alkanes[82] with H_2O_2 and OCl. On adding NMO, *t*BuOOH, $NaIO_4$, or NaOCl to the solutions of complexes **2** and **5**, the signals in their $^{77}Se\{^1H\}$ NMR spectra shift to higher frequencies by ≥485 ppm. The signals in the $^{125}Te\{^1H\}$ NMR spectra of **3** and **6** shift to higher frequencies by ≥305 ppm in the presence of any of the present four oxidants. The signals in the $^{77}Se\{^1H\}$NMR spectra of **L2** and **L5** and in the $^{125}Te\{^1H\}$NMR spectra of **L3** and **L6** remain unshifted on addition of any of the four oxidants. Therefore, ruthenium is most probably oxidized to Ru(IV)═O. On addition of any one of these oxidants to a dichloromethane solution of **1**−**6**, a new shoulder at 390−395 nm appears in their UV−visible spectrum, which is believed[79−84] to be due to Ru(IV)═O, species reported to be responsible for transfer of the oxygen to alcohol substrates, resulting in their catalytic oxidation. The solvent from a mixture of any of these four oxidants with a complex among **1**−**6** was evaporated off, and the IR spectra of the remaining residue was found to exhibit a very strong band at 845−848 cm^{-1} (ν_{P-F} at 842−844 cm^{-1} is of medium intensity only), which further supports the formation of Ru(IV)═O species[75,80,83−86] responsible for catalytic oxidation of alcohols. The ^{18}O-labeling experiments further supported

Scheme 3. Catalytic Transfer Hydrogenation Reaction of Ketone



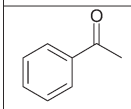
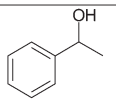
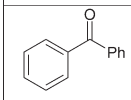
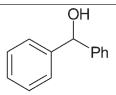
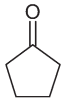
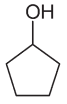
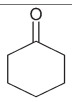
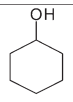
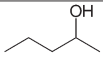
Catalyst: **1-6**
R= R'= Alkyl (or) aryl

Reaction time 5-7 h

the formation of Ru(IV)═O species. *t*BuOOH (70% aqueous solution) was mixed with excess $H_2{}^{18}O$ (∼95%) and kept for 5 days. Thereafter the mixture was used as an oxidant for alcohols (Table 1) using complexes **2**, **3**, **5**, and **6** as catalysts. IR spectra of the intermediate isolated by the procedure mentioned earlier were found to exhibit an additional band at 820−826 cm^{-1} due to the formation[87] of Ru(IV)═^{18}O. It is red-shifted 22−25 cm^{-1} with respect to that of unlabeled Ru(IV)═O species. Moreover, the catalytic activities of Ru(IV)═O species for oxidation reported earlier[78−82,88] further strengthens our proposition. The short lifetime of Ru(IV)═O transient species restricted us from acquiring evidence of mass spectra. The ^1H NMR spectra of ruthenium complexes recorded after adding oxidants become broad, indicating the formation of paramagnetic species as intermediates. On the basis of these observations and literature knowledge a detailed mechanism is difficult to assign, but a gross one is mentioned in the Supporting Information (Figure S16). The advantages of **1**−**6** in comparison to recently reported good

(83) Raja, M. U.; Gowri, N.; Ramesh, R. *Polyhedron* **2010**, *29*, 1175.
(84) Leung, W. H.; Chem, C. M. *Inorg. Chem.* **1989**, *28*, 4619.
(85) EI-Shahawi, M. S.; Shoir, A. F. *Spectrochim. Acta A* **2004**, *60*, 121.
(86) Chatterjeea, D.; Mitra, A.; Roy, B. C. *J. Mol. Catal. A* **2000**, *161*, 17.
(87) (a) Seok, W. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7358. (b) Aoyagi, K.; Nagao, H.; Yukawa, Y.; Ogura, M.; Kuwayama, A.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Chem. Lett.* **1986**, 2135.
(88) Khan, M. M. T.; Chatterjee, D.; Merchant, R .R.; Paul, P.; Abdi, H. S. R.; Srinivas, D.; Siddiqui, M. R. H.; Moiz, M. A.; Bhadbhade, M. M.; Venkatasubramanian, K. *Inorg. Chem.* **1992**, *31*, 2711.

Table 2. Catalytic Hydrogen Transfer Reaction of Ketones Using Complexes 1−6 As Catalyst[a]

Substrate	Product	TON (% Conversion)						
		Absence of catalysts	**1**	**2**	**3**	**4**	**5**	**6**
		Product not detected	9.3×10^4 (93)	9.5×10^4 (95)	9.7×10^4 (97)	9.2×10^4 (92)	9.5×10^4 (95)	9.8×10^4 (98)
		Product not detected	8.9×10^4 (89)	9.2×10^4 (92)	9.5×10^4 (95)	9.0×10^4 (90)	9.1×10^4 (91)	9.6×10^4 (96)
		Product not detected	8.7×10^4 (87)	9.0×10^4 (90)	9.3×10^4 (93)	8.8×10^4 (88)	8.9×10^4 (89)	9.3×10^4 (93)
		Product not detected	8.6×10^4 (86)	8.9×10^4 (89)	9.0×10^4 (90)	8.6×10^4 (86)	8.8×10^4 (88)	9.2×10^4 (92)
		Product not detected	8.5×10^4 (85)	8.8×10^4 (88)	8.8×10^4 (88)	8.4×10^4 (84)	8.7×10^4 (87)	9.0×10^4 (90)
		Product not detected	8.3×10^4 (83)	8.5×10^4 (85)	8.7×10^4 (87)	8.1×10^4 (81)	8.5×10^4 (85)	8.8×10^4 (88)

[a] Reaction time 5 h for **1**−**3** and 7 h for **4**−**6**.

Ru-based catalytic species[77,80,83,89−93] for oxidation of alcohols are (i) high efficiency/yield, as they are needed in less quantity, (ii) short reaction time, and (iii) flexibility regarding oxidant. The half-sandwich Ru(II) complexes containing chalcogenated pyrrolidine, morpholine, and benzotriazole known to catalyze the oxidation of alcohols efficiently[49,50,94] (TON up to 9.8×10^4) are comparable with the present complexes (TON up to 9.9×10^4).

Transfer hydrogenation reaction in which hydrogen is transferred from one organic molecule to another is of great importance in organic synthesis since one can avoid the use of molecular hydrogen.[95] Transfer hydrogenation reactions of ketones (Scheme 3) were explored at 80 °C using catalysts **1**−**6** (0.001 mol %). The most efficient conversions are found in the case of acetophenone with all catalysts **1**−**6** (up to 98%), while in the case of aliphatic secondary ketones the conversions were up to 90%. The details of percent conversions and TONs are given in Table 2. The products were identified by GC after recovering the catalyst and doing required workup. The conversions reported are averages of two runs in the case of all catalytic reactions (Table 2). The high efficiency was exhibited in the reduction of ketones to their corresponding alcohols with 2-propanol as hydrogen donor in the presence of KOH, which is reported to be the best inorganic base for such reactions.[96]

The catalytic efficiency varies with chalcogen ligands in the order of Te > Se > S, which may be tailored by a strong electron-donating methoxy group present on tellurium. The complex catalysts **3** and **6** are the most efficient catalyst among all. The complexes of Schiff bases and their reduced analogues do not differ significantly in catalytic efficiency. This implies that a nonclassical metal−ligand bifunctional mechanism[10,11] for which hydrogen on nitrogen is essential is not operative in our case. On monitoring the transfer hydrogenation reactions catalyzed with **2**, **5**, **3**, and **6** by $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectroscopy, it is observed that the signals in the spectra shift to higher frequency (20−25 ppm), indicating that probably the Ru−S(methyl) bond is cleaved[97] or weakened very significantly to make a coordination site on ruthenium available so that formation of an intermediate having a Ru−H bond takes place. The transfer hydrogenation reaction catalyzed with **3** and **6** was monitored by ^1H NMR. After 1 h a broad singlet was noticed around −10 to −11 ppm. These signals are characteristic of hydrides and indicate the formation of Ru−H.[98] As Ru complexes of Schiff bases and their reduced derivatives are equally efficient as catalysts, the transfer of hydrogen to ketone via a classical mechanism appears to be most plausible (For details

(89) Do, Y.; Ko, S.-B.; Hwang, I.-C.; Lee, K.-E.; Lee, S. W.; Park, J. *Organometallics* **2009**, *28*, 4624.
(90) Cheung, W. M.; Ng, H.-Y.; Williams, I. D.; Leung, W.-H. *Inorg. Chem.* **2008**, *47*, 4383.
(91) Hornstein, B. J.; Dattelbaum, D. M.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **2007**, *46*, 8139.
(92) Mizoguchi, H.; Uchida, T.; Ishida, K.; Katsuki, T. *Tetrahedron Lett.* **2009**, *50*, 3432.
(93) Ganesamoorthy, S.; Shanmugasundaram, K.; Karvembu, R. *Catal. Commun.* **2009**, *10*, 1835.
(94) Das, D.; Singh, P.; Singh, A. K. *J. Organomet. Chem.* **2010**, *695*, 955.
(95) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, 2045. Gladiali, S.; Mestroni, G. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; p 97.
(96) Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. *Organometallics* **2008**, *27*, 571.
(97) Bacchi, A.; Balordi, M.; Cammi, R.; Elviri, L.; Pelizzi, C.; Picchioni, F.; Verdolino, V.; Goubitz, K.; Peschar, R.; Pelagatti, P. *Eur. J. Inorg. Chem.* **2008**, 4462.
(98) Deb, B.; Sarmah, P. P.; Dutta, D. K. *Eur. J. Inorg. Chem.* **2010**, 1710.

see Supporting Information Figure S17). It is interesting to compare recently reported transfer hydrogenation reactions of ketones catalyzed with ruthenium species with those of **1**−**6**. Ru(II) complexes of 2-(aminomethyl)pyridine-phosphine[99] were found among the most efficient catalysts for transfer hydrogenation (TOF up to 10^5 h^{-1} and conversion up to 97%) in 2-propanol using NaOH as base. The percent conversion values for **1**−**6** are also in the same order. The yield of catalytic transfer hydrogenation of ketones with [(η^6-arene)RuCl(N,N)]BF_4 (arene = benzene, *p*-cymene; N,N = bis(pyrazolyl)methane)[7] has been reported to be up to 97%, but the amount of catalyst used in the presence of refluxing 2-propanol and KOH is almost double in comparison to those of **1**−**6**. The Ru(II) complexes of (N,N,N) unsymmetrical pincer ligand 2-(benzoimidazol-2-yl)-6-(pyrazol-1-yl)-pyridine[100] are needed in 0.05 mol % (50 times more than the amount of **1**−**6** used) in refluxing 2-propanol to obtain conversions on the order similar to those of **1**−**6**. The NHC−carbene-based[101] (η^6-arene)Ru(II) complexes have been found to reduce ketones up to 97% in refluxing 2-propanol but only when the amount of catalyst used is 100 times more than the required amounts of **1**−**6**. Recently the [(η^6-arene)Ru(L)Cl][PF_6] complex (L = dipyridylamine) was reported[2] to catalyze the transfer hydrogenation reaction of ketones in the presence of water, but a high amount of catalyst (5 mol %) is required, resulting in a TON of only up to 100. These comparisons indicate the promising performance of **1**−**6** as transfer hydrogenation catalysts. In comparison to Ru(II) complexes of bidentate ligands,[2,7] complexes **1**−**6** of Ru(II) containing tridentate ligands are more efficient catalysts for the transfer hydrogenation reaction of ketones, as the amount of catalyst used and reaction time are lower.

Conclusion

The complexes *fac*-[(η^6-C_6H_6)Ru(**L**)][PF_6]X (**1**−**6**; X = PF_6 or Cl) of 2-$MeSC_6H_4CH$=N-CH_2CH_2E-C_6H_4-4−R (**L1**−**L3**) and 2-$MeSC_6H_4CH_2$-$NHCH_2CH_2$E-C_6H_4-4−R (**L4**−**L6**) (where E = S or Se, R = H; E = Te, R = OMe), synthesized and structurally characterized by single-crystal X-ray diffraction, are very efficient catalysts for the oxidation of primary and secondary alcohols (TON up to 9.9×10^4) and transfer hydrogenation reactions of ketones (TON up to 9.8×10^4). The oxidation appears to occur through Ru(IV)=O-containing species and hydrogen transfer through a classical mechanism involving Ru−H formation. The short reaction time and flexibility regarding the oxidant are among the advantages of **1**−**6** as oxidation catalysts. The catalytic efficiency appears to vary with chalcogen ligands in the order of Te > Se > S. However, tellurium ligands have a strong electron-donating methoxy group, which may also be responsible for tailoring this order.

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Supporting Information Available: Crystal data and refinements table and detailed bond lengths and angles for complexes **1** and **3**−**6**. $^{77}Se\{^1H\}$ NMR spectra of ligands **L2** and **L5** and complexes **2** and **5**. $^{125}Te\{^1H\}$ NMR spectra of ligands **L3** and **L6** and complexes **3** and **6**. ^1H and $^{77}Se\{^1H\}$ NMR spectra of **2**. Cyclic voltammetric values table and figures of **1**−**6**. ORTEP diagram of complex **3** with solvated CH_3CN. Proposed mechanism for oxidation and transfer hydrogenation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

(99) Baratta, W.; Herdtweck, E.; Siega, K.; Toniutti, M.; Rigo, P. *Organometallics* **2005**, *24*, 1660.

(100) Zeng, F.; Yu, Z. *Organometallics* **2009**, *28*, 1855.

(101) Gürbüz, N.; Yaşar, S.; Özcan, Ö. E.; Özdemir, İ.; Çetinkaya, B. *Eur. J. Inorg. Chem.* **2010**, 3051.