Ruthenium(II) N,S-heterocyclic carbene complexes and transfer hydrogenation of ketones†

Nini Ding[a] and T. S. Andy Hor*[a,b]

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A series of ruthenium(II) N,S-heterocyclic carbene (NSHC) complexes $Ru^{II}X(RCOO)(PPh_3)_2$(3-R′BzTh) (BzTh = benzothiazol-2-ylidene; R = Me, R′/X = Bz/Br (**4**), Pr^i/I (**6**), Bu^i/I (**8**); R = Et, R′/X = Bz/Br (**5**), Pr^i/I (**7**), Bu^i/I (**9**)) have been synthesized and characterized. Single-crystal X-ray structural analysis revealed that in each case the Ru(II) center adopts an essentially octahedral geometry, coordinated by two *trans*-oriented PPh_3 completed by an NSHC, chelating carboxylate and halide X (X = Br (**4–5**), X = I (**6–9**)) ligands. Although thiazol-2-ylidiene Ru(II) complexes are established and applied in metathesis, these benzothiazol-2-ylidene complexes (**4–9**) are the first of its kind. Their catalytic activities towards transfer hydrogenation of ketones have been examined and discussed.

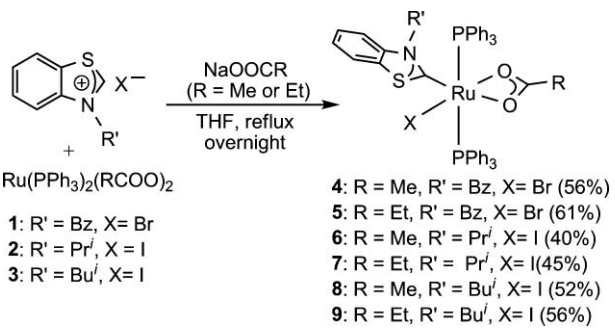
Introduction

Ruthenium(II) complexes have gained intense attention in recent years as powerful and efficient catalysts in an array of organic transformations.[1] Some of these catalysts have proven to be superior or even indispensable for given types of reactions.[2,3] Recent examples include the N,S-heterocyclic carbene-based ruthenium complexes $RuCl_2$(3-R–DMeTh)(=CH-*o*-*i*PrO–Ph) (DMeTh = 4,5-dimethylthiazol-2-ylidene; R = phenyl, 2-methylphenyl, 2,4,6-trimethylphenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl) and $RuCl_2$(3-R–DMeTh)(=CH–Ph)(PCy_3) (R = 2,4,6-trimethylphenyl, 2,6-diethylphenyl) developed by Grubbs *et al.*[2e] Different from the majority of other N-heterocyclic carbene (NHC) ligands,[4] the NSHC ligand on these Ru(II) complexes have only one exocyclic substituent. The aryl substituent tends to protect the vacant site of the metal. This is in contrast with their asymmetric NNHC counterparts which bear two exocyclic (typically aryl with alkyl) substituents.[5] Despite the lower steric protection in a single-substituent ligand, these Ru(II) catalysts are unexpectedly robust, and matching their NHC counterparts in terms of stability and activity towards metathesis.[6] Encouraged by these, and as part of our study towards metal NSHC complexes,[7] we have studied a new series of Ru–NSHC complexes, which are different from Grubbs' complexes in carrying the benzothiazol-2-ylidene carbene. It remains to be explored if these two sub-groups of NSHC ligands *viz*. thiazol-2-ylidene and benzothiazol-2-ylidene would have any significant structural or catalytic differences. The development of these heteroatomic carbenes (such as NSHC and N,O-heterocyclic carbenes (NOHC))[2e,7–10] obviously lag behind those of NHC, or precisely, NNHC, ligands. We herein also report their catalytic activites towards transfer hydrogenation, which has been applied to ketones in the preparation of alcohols under mild conditions.[11,12] Such methodology obviates the use of high hydrogen pressure and hazardous reducing agents. Although Ru(II) NHC complexes are known to be transfer hydrogenation active,[13–15] the activities of their NSHC counterparts are insofar unknown.

Results and discussion

Synthesis and characterization of the ligand precursors and complexes

The benzothiazolium salts **1–3** ([(C_6H_4)SCHNR]X (R and X = Bz and Br (**1**); Pr^i and I (**2**); Bu^i and I (**3**)) undergo a one-pot condensation reaction with $Ru(RCOO)_2(PPh_3)_2$ (R = Me, Et)[16] in the presence of NaOOCR (R = Me, Et) to give the corresponding mixed phosphine-carbene complexes $Ru^{II}X(RCOO)(PPh_3)_2$(3-R′BzTh) (BzTh = benzothiazol-2-ylidene; R = Me, R′/X = Bz/Br (**4**), Pr^i/I (**6**), Bu^i/I (**8**); R = Et, R′/X = Bz/Br (**5**), Pr^i/I (**7**), Bu^i/I (**9**)) in moderate yield (40–61%) (Scheme 1). There is no evidence of phosphine replacement by carbene. Instead, entry of the latter, and chloride, is facilitated by the carboxylate departure in form of carboxylic acid. Similar reaction of $RuCl_2(PPh_3)_3$ with **1** and NaOAc in THF, which is a method adopted in the preparation of Ru(II) NNHC complexes,[17] only gave [1,3]-benzyl migration[18] product, but not the desired complex. Preparations without addition of NaOAc also lead to incomplete reactions



Scheme 1 Synthetic route of Ru(II)-(benzothiazol-2-ylidene) complexes **4–9**.

[a]*Department of Chemistry, National University of Singapore, 3 Science Drive 3, S117543, Singapore. E-mail: andyhor@nus.edu.sg*
[b]*Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 3 Research Link, S117602, Singapore*

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Table 1 Selected bond lengths (Å) and angles (°) for **4–9**

	4	**5**	**6**	**7**	**8**	**9**
Ru(1)–C(1)	1.970(6)	1.970(3)	1.981(3)	2.003(2)	1.966(2)	1.976(2)
Ru(1)–O(1)	2.130(4)	2.163(2)	2.283(2)	2.149(2)	2.135(1)	2.134(1)
Ru(1)–O(2)	2.241(4)	2.251(2)	2.128(2)	2.242(2)	2.271(1)	2.241(2)
Ru(1)–P(1)	2.393(2)	2.3820(9)	2.3741(7)	2.3821(6)	2.3749(5)	2.3846(6)
Ru(1)–P(2)	2.374(2)	2.3825(9)	2.3898(7)	2.3949(6)	2.4112(5)	2.4031(6)
Ru(1)–X(1)[a]	2.543(1)	2.5553(4)	2.7221(3)	2.7356(3)	2.556(2)	2.7412(4)
P(1)–Ru(1)–P(2)	173.63(6)	169.03(3)	164.55(2)	171.09(2)	171.07(2)	170.09(2)
O(1)–Ru(1)–O(2)	60.2(2)	59.25(8)	59.12(7)	59.39(7)	59.29(5)	59.55(6)
S(1)–C(1)–N(1)	106.6(5)	106.5(2)	107.7(2)	106.8(2)	107.1(1)	106.6(2)
Dihedral angle[b]	3.9	9.7	27.3	4.3	24.8	26.6

[a] X = Br for **4** and **5**; X = I for **6–9**; [b] dihedral angle between the [O1O2XC1] and N,S-heterocyclic planes.

and other side products. The products prepared are probably the most stable complexes in this series because use of 2–3 fold excess of **1–3** with $Ru(RCOO)_2(PPh_3)_2$ did not yield any di-carbene or phosphine displacement products.

These NSHC complexes are generally stable as solids (under N_2) but slowly decompose in solution. They are readily soluble in CH_2Cl_2, THF and toluene and to a less extent Et_2O. Their formation is evidenced by the disappearance of the NC*H*S protons in the ^{1}H NMR spectra of **4–9** compared with their respective precursors **1–3**, as well as the appearance of the diagnostic carbenic carbon signals in the 226.0–230.1 ppm region in their ^{13}C NMR spectra.

Molecular structures of 4–9

The structures of **4–9** were unequivocally elucidated by single-crystal X-ray diffraction studies. They are invariably mononuclear with *trans*-phosphine, as well as NSHC and halide *trans* to chelating carboxylate in a distorted octahedral Ru(II) sphere (Fig. 1 and Table 1). The phosphines in $Ru(RCOO)_2(PPh_3)_2$ (R = Me, Et) are also *trans* oriented. The P–Ru–P alignments are heavily distorted from linearity [P–Ru–P: 173.63(6)° (**4**); 169.03(3)° (**5**); 164.55(2)° (**6**); 171.09(2)° (**7**); 164.55(2)° (**8**); 170.08 (2)° (**9**)] which could reflect the non-bonding contacts between the NSHC substituent with the phenyls PPh_3. For example, in **6**, there are short H...H contacts between the carbene N-substituent and phosphine phenyls, such as the methyl H9A and phenyl H6A (2.26 Å) as well as the methine H8 and phenyl H2E (1.98 Å) (Fig. 1). These complexes are static in solution, each showing only a single δ_P resonance suggesting phosphine equivalence. The Ru–C bonds (1.966(2)–2.003(2) Å) are within the range between those reported Ru–NSHC complexes such as $RuCl_2$(3-R–DMeTh)(=CH-*o*-*i*PrO–Ph) (DMeTh = 4,5-dimethylthiazol-2-ylidene; R = phenyl) (1.944(1) Å) and $RuCl_2$(3-R–DMeTh)(=CH-*o*-*i*PrO–Ph) (*R* = 2,4,6-trimethyl-phenyl) (1.953(1) Å)[2e] and Ru–NNHC complexes such as $[RuCl_3(NO)(NHC)]$[13] (NHC = 3-*tert*-butyl-1-(2-pyridyl)imidazol-2-ylidene) (2.049(5) Å), $[RuF(H)(PPh_3)_2(CO)(NHC)]$[19d] (NHC = 1,3,4,5-tetramethylimidazol-2-ylidene) (2.170(2) Å) and *mer*, *cis*-$[RuCl_2(CO)(NHC)]$[14] (NHC = 1,3-bis(2-diphenylphosphanylethyl)-3*H*-imidazol-2-ylidene) (2.038(3) Å). There is no crystallographic report on the literature phosphine containing Ru(II)–NSHC complexes. The slightly shorter Ru–C in NSHC compared to NNHC complexes could be attributed to a lower steric demand of the former and its more electron rich and nucleophilic carbenic carbon resulting from its diminished pπ-pπ interactions with the neighboring heteroatoms. The Ru–C bond lengths of the isopropyl analogues (**6** (1.981(3) Å) and **7** (2.003(2) Å)) are longest in this series, perhaps reflecting higher inter-ligand repulsions. The Ru–P lengths (2.374(2) Å to 2.411(5) Å) lie within the expected range of 2.40 ± 0.05 Å in *trans*-$Ru^{II}(PPh_3)_2$ species.[19] The chelating carboxylate oxygen, carbenic carbon and halide ligands constitute a nearly perfect equatorial plane (mean deviation, 0.0217 Å (**4**); 0.0127 Å (**5**); 0.0209 Å (**6**); 0.0058 Å (**7**); 0.0095 Å (**8**); 0.0251 Å (**9**)). Stronger *trans*-influence[20] of carbene compared to halide imparts a significant disparity between the two Ru–O lengths (Ru1–O1 (2.128(2) to 2.163(2) Å) being significantly stronger than Ru1–O2 (2.241(2) to 2.283(2) Å)). The carboxylate ligands thus adopt more an asymmetric η^2-chelating mode. The heterocyclic planes in **4**, **5**, and **7** are nearly co-planar with the equatorial coordination planes defined by O1O2XC1 (X = Br, I) whereas in **6**, **8** and **9**, they are twisted to give unequivocally dihedral angles of 27.3° (**6**), 24.8° (**8**) and 26.6° (**9**). The latter rotations help to relieve the short repulsive H...H contacts between methyl (**6** and **9**) or methine group (**8**) with the phenyl ring, *i.e.*, H9A and H6A (2.26 Å (**6**)), H9 and H2D (2.06 Å (**8**)) and H10C and H2B (1.86 Å (**9**)) (Fig. 1). The hydrogen atoms from benzyl ring in complexes **4** and **5** project to the center of phenyl ring and are therefore shielded. Accordingly, the H10 and H14 of benzyl ring in **4** are upfield shifted to 5.58 ppm. This shielding effect was confirmed by ^{1}H NMR and 2D ^{1}H–^{1}H correlation spectra (COSY). A closer examination of the packing diagrams of the crystal structures revealed that each mononuclear complex is associated with its neighboring molecule(s) to form a two dimensional structure (**4**) or dimeric species (**5–9**) (Supporting Information†).

Transfer hydrogenation

Complexes **4–9** have been screened on their activities towards transfer hydrogenation, using the reduction of *p*-methyl acetophenone to 1-(4-methylphenyl)ethanol in the presence of 2-propanol as a model (Table 2). All catalysts tested give satisfactory yields (77–91%) within 30 h at a catalyst loading of 1 mol%. Complex **4**, with benzyl substituent, generally gives better yield than the rest. It stills returns with a yield of 80% at a load down to 0.5 mol% (Table 2, Entry 5). Its effect on different alkyl and aryl ketones was hence further examined (Table 3). The results clearly show that

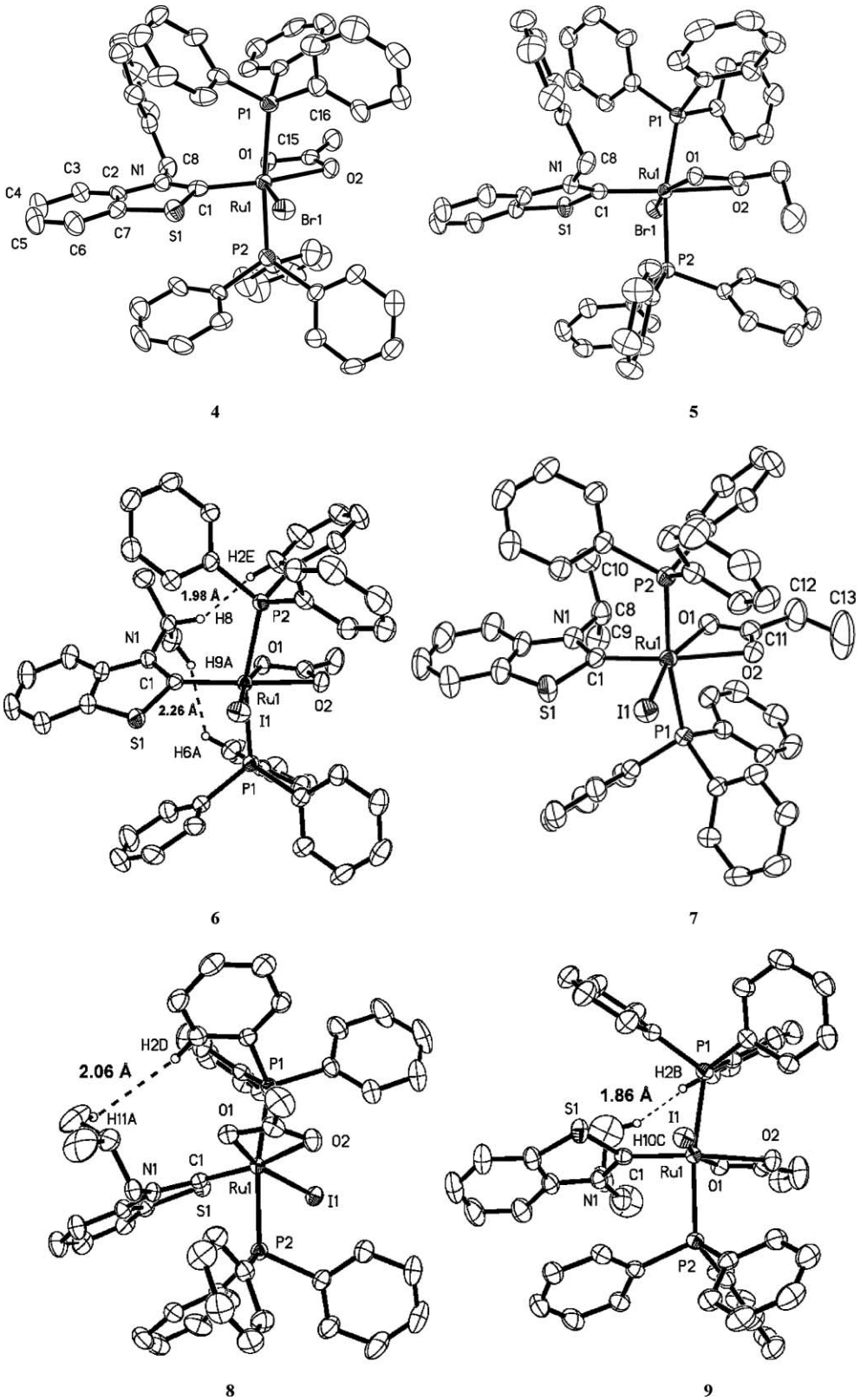
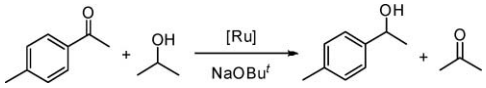


Fig. 1 Ortep diagrams of the structures of **4–9** with 50% probability ellipsoids and labelling scheme, and ortep diagrams of **6**, **8** and **9** showing short H···H contacts.

Table 2 Catalytic transfer hydrogenation of p-methyl acetophenone catalysed by **4–9**



Entry	Catalyst	Time/h	Yield (%)
1	**4**	6	49
2	**4**	18	62
3	**4**	26	84
4	**4**	30	91
5[a]	**4**	30	80
6	**5**	30	80
7	**6**	30	87
8	**7**	30	77
9	**8**	30	90
10	**9**	30	84

Experimental conditions: ketone, 1 mmol; $NaOBu^t$, 0.1 mmol; Catalyst, 0.01 mmol; 2-propanol, 15 mL; temp, 82 °C.[a] catalyst loading 0.005 mmol.

Table 3 Catalytic transfer hydrogenation of ketones catalysed by **4**

Entry	Substrate	Product	Yield (%)
1	cyclopentanone	cyclopentanol	96
2	acetophenone	1-phenylethanol	90
3	4-chloroacetophenone	1-(4-chlorophenyl)ethanol	94
4	4-bromoacetophenone	1-(4-bromophenyl)ethanol	96
5	4-methoxyacetophenone	1-(4-methoxyphenyl)ethanol	14
6	benzophenone	diphenylmethanol	3

Experimental conditions: ketone, 1 mmol; $NaOBu^t$, 0.1 mmol; Catalyst, 0.01 mmol; 2-propanol, 15 mL; temp, 82 °C; time, 30 h.

complex **4** is an efficient catalyst except towards benzophenone and 4-methoxyacetophenone (Entry 5 and 6), which is probably attributed to the electronic and steric effects of the substituent on the ketones.

The catalytic mechanism likely follows that established.[11,12b] Easy opening of the carboxylate chelate, especially through cleavage of the Ru–O bond *trans* to the carbene, would create room for entry of the ketone substrate. Exchange of halide (and carboxylate) with proton would lead to the active hydride species needed for hydrogenation transfer. These factors, coupled with the good stability of these systems under redox conditions offer possible reasons for the satisfactory catalytic activities shown. These could be further improved by using polydentate carbene ligands which tend to lend higher stability to the catalysts. For example, similar reduction of acetophenone using catalytic $[Ru(NO)(L)Cl_3]$[13] (L = 3-*tert*-butyl-1-(2-pyridyl)imidazol-2-ylidene) can achieve a yield of 96% within a shorter period of 4 h. A small catalyst loading of 0.1 mol% *fac*-$[Ru_2(\mu\text{-}Cl)_3Cl_2(PC^{NHC}P)_2]Cl$[14] ($PC^{NHC}P$ = 1,3-bis(2-diphenylphosphanylethyl)-3*H*-imidazol-2-ylidene) can also catalyze the quantitative conversion of acetophenone to 1-phenylethanol in 4.5 h.

Conclusions

Reported herein is a facile synthetic methodology that enables the introduction of a NSHC carbene ligand to the $[Ru^{II}(PPh_3)_2]$ core. The presence of potentially labile and dissociable ligands on these cores, such as carboxylate and halide, make this catalytically viable and allows further ligand replacement to alter the electronic and steric traits of the complexes. The study here suggests that these complexes may be applied to area beyond metathesis. We are actively exploring a wider catalytic scope of this and related systems.

Experimental section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Preparation of the benzothiazolium salts required treatment of freshly distilled benzothiazole and appropriate alkyl halide at room temperature (**1**) or 80 °C (**2–3**) using a solvent-free method.[8e] $Ru(RCOO)_2(PPh_3)_2$ (R = Me, Et) were prepared according to the literature method.[16] Other commercially available reagents were purchased from Sigma-Aldrich. All solvents were freshly distilled from standard drying agents. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AMX 500 spectrometer, and chemical shifts (δ) for ^1H, ^{13}C and ^{31}P were recorded in ppm relative to the residual proton of $CDCl_3$ (^1H: 500.1 MHz; ^{13}C: 125.8 MHz; ^{31}P: 202.4 MHz). Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer. The yields of hydrogenation products were determined by using Hewlett Packard Series 6890 GC (Santa Clara, CA, USA) coupled to a Hewlett Packard 5973 MS detector.

General procedures for the preparation of complexes (4–9)

A mixture of $Ru(RCOO)_2(PPh_3)_2$ (0.25 mmol), NaOOCR (0.5 mmol) (R = Me, Et) and ligands **1–3** (0.30 mmol) was stirred under vacuum at 50 °C for 1 h. Tetrahydrofuran was then added and the suspension refluxed overnight. After cooling, the solvent was removed under vacuum, leaving a dull yellow residue, which was re-dissolved in toluene (20 mL) and filtered. The filtrate was mixed with hexane (5 mL) and cooled to −20 °C to yield orange-red crystals in 1–2 weeks.

RuBr(MeCOO)(PPh$_3$)$_2$(*N*-BzBzTh) (4)

Yield: 0.14 g (0.14 mmol, 56%). ^1H NMR (500.1 MHz, $CDCl_3$): δ 7.47–7.44 (m, 12H, Ar–H), 7.27–7.23 (m, 9H, Ar–H), 7.21–7.13 (m, 13H, Ar–H), 6,98 (m, 1H, Ar–H), 6.90 (m, 1H, Ar–H), 6.58 (d, 1H, Ar–H), 6.51 (m, 2H, Ar–H), 5.58 (s, 2H, CH_2), 0.30 (s, 3H, CH_3COO). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 229.8 (N*C*S), 184.2 (CH_3COO), 143.9, 136.7, 136.5, 135.2, 135.1, 132.5, 132.4, 132.2, 129.2, 128.7, 127.5, 127.4, 126.8, 126.0, 123.8, 122.2, 120.0, 112.1 (Ar–C), 53.0 (CH_2), 22.2 (CH_3COO). ^{31}P NMR (202.4 MHz, $CDCl_3$): 36.90 (s). Anal. Calc for $C_{52}H_{44}BrNO_2P_2RuS$: C, 63.09; H, 4.48; N, 1.42. Found: C, 63.14; H, 4.71; N, 1.26.

RuBr(EtCOO)(PPh$_3$)$_2$(*N*-BzBzTh) (5)

Yield: 0.15 g (0.15 mmol, 61%). ^1H NMR (500.1 MHz, $CDCl_3$): δ 7.47–7.45 (m, 12H, Ar–H), 7.27–7.21 (m, 10H, Ar–H), 7.19–7.14 (m, 12H, Ar–H), 6.99 (m, 1H, Ar–H), 6.93 (m, 1H, Ar–H), 6.62 (d, 1H, Ar–H), 6.54 (m, 2H, Ar–H), 5.62 (s, 2H, CH_2), 0.65 (m, 2H, CH_3CH_2COO), 0.02 (t, 3H, CH_3CH_2COO). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 230.1 (N*C*S), 187.0 (CH_3CH_2COO), 143.9, 136.8, 136.6, 135.1, 135.0, 132.7, 132.5, 132.4, 129.1, 128.7, 127.4, 126.8, 126.0, 123.8, 122.2, 120.0, 112.0 (Ar–C), 53.0 (CH_2), 29.4 (CH_3CH_2COO), 7.8 (CH_3CH_2COO). ^{31}P NMR (202.4 MHz,

$CDCl_3$): 36.69 (s). Anal. Calc for $C_{53}H_{46}BrNO_2P_2RuS$: C, 63.41; H, 4.62; N, 1.39. Found: C, 63.73; H, 4.56; N, 1.34.

RuI(MeCOO)(PPh$_3$)$_2$(*N*-Pr^{i}BzTh) (6)

Yield: 0.10 g (0.10 mmol, 40%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.57–7.56 (m, 13H, Ar–H), 7.44 (d, 1H, Ar–H), 7.28, 7.21–7.14 (m, 18H, Ar–H), 7.09 (t, 1H, Ar–H), 7.03 (t, 1H, Ar–H), 5.70 (m, 1H, C*H*(CH$_3$)$_2$), 1.27 (d, 6H, CH(C*H*$_3$)$_2$), 0.50 (s, 3H, C*H*$_3$COO). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 226.0 (N*C*S), 184.5 (CH$_3$*C*OO), 142.4, 139.5, 135.4, 135.3, 135.0, 133.6, 133.5, 133.3, 129.2, 127.5, 127.4, 123.3, 121.8, 120.2, 112.8 (Ar–C), 53.7 (*C*H(CH$_3$)$_2$), 23.0 (*C*H$_3$COO), 20.8 (CH(*C*H$_3$)$_2$). ^{31}P NMR (202.4 MHz, $CDCl_3$): 37.28 (s). Anal. Calc for $C_{48}H_{44}INO_2P_2RuS$: C, 58.30; H, 4.48; N, 1.42. Found: C, 57.97; H, 4.52; N, 1.20.

RuI(EtCOO)(PPh$_3$)$_2$(*N*-Pr^{i}BzTh) (7)

Yield: 0.11 g (0.11 mmol, 45%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.58–7.51 (m, 13H, Ar–H), 7.45 (d, 1H, Ar–H), 7.28–7.26 (m, 4H, Ar–H), 7.21–7.18 (m, 13H, Ar–H), 7.14 (d, 1H, $^3J_{HH}$ = 7.55 Hz, Ar–H), 7.10 (t, 1H, Ar–H), 7.03 (t, 1H, Ar–H), 5.78 (m, 1H, C*H*(CH$_3$)$_2$), 1.27 (d, 6H, CH(C*H*$_3$)$_2$), 0.83 (m, 2H, CH$_3$C*H*$_2$COO), 0.08 (t, 3H, C*H*$_3$CH$_2$COO). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 226.6 (N*C*S), 187.2 (CH$_3$CH$_2$*C*OO), 142.5, 139.5, 137.8, 136.1, 135.4, 135.3, 133.8, 133.6, 133.5, 129.2, 129.1, 127.4, 127.3, 121.2, 120.2, 112.7 (Ar–C), 54.0 (*C*H(CH$_3$)$_2$), 30.0 (*C*H$_3$CH$_2$COO), 20.1 (CH(*C*H$_3$)$_2$), 7.7 (CH$_3$*C*H$_2$COO). ^{31}P NMR (202.4 MHz, $CDCl_3$): 37.17 (s). Anal. Calc for $C_{49}H_{46}INO_2P_2RuS$: C, 58.68; H, 4.62; N, 1.40. Found: C, 58.71; H, 4.74; N, 1.49.

RuI(MeCOO)(PPh$_3$)$_2$(*N*-Bu^{i}BzTh) (8)

Yield: 0.13 g (0.13 mmol, 52%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.60–7.56 (m, 12H, Ar–H), 7.24–7.15 (m, 19H, Ar–H), 7.09–7.01 (m, 3H, Ar–H), 4.02 (d, 2H, ^3JHH = 6.95 Hz, C*H*$_2$CH(CH$_3$)$_2$), 1.85 (m, 1H, CH$_2$C*H*(CH$_3$)$_2$), 0.87 (s, 3H, C*H*$_3$COO), 0.67 (d, 6H, ^3JHH = 6.95 Hz, CH$_2$CH(C*H*$_3$)$_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 227.3 (N*C*S), 184.8 (CH$_3$*C*OO), 144.8, 137.7, 135.6, 135.2, 135.1, 133.7, 133.6, 133.4, 129.3, 129.0, 127.5, 127.3, 127.2, 123.5, 122.1, 122.0, 111.6 (Ar–C), 55.7 (*C*H$_2$CH(CH$_3$)$_2$), 29.4 (*C*H$_2$*C*H(CH$_3$)$_2$), 24.0 (*C*H$_3$COO), 20.4 (CH$_2$CH(*C*H$_3$)$_2$). ^{31}P NMR (202.4 MHz, $CDCl_3$): 35.21 (s). Anal. Calc for $C_{49}H_{46}INO_2P_2RuS$: C, 58.68; H, 4.62; N, 1.40. Found: C, 58.45; H, 4.52; N, 1.41.

RuI(EtCOO)(PPh$_3$)$_2$(*N*-Bu^{i}BzTh) (9)

Yield: 0.14 g (0.14 mmol, 56%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.60–7.57 (m, 12H, Ar–H), 7.24–7.14 (m, 18H, Ar–H), 7.10–7.01 (m, 4H, Ar–H), 4.04 (d, 2H, ^3JHH = 7.55 Hz, C*H*$_2$CH(CH$_3$)$_2$), 1.96 (m, 1H, CH$_2$C*H*(CH$_3$)$_2$), 1.24 (m, 2H, CH$_3$C*H*$_2$COO), 0.69 (d, 6H, ^3JHH = 6.30 Hz, CH$_2$CH(C*H*$_3$)$_2$), 0.34 (t, 3H, C*H*$_3$CH$_2$COO). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 227.7 (N*C*S), 187.6 (CH$_3$CH$_2$*C*OO), 144.8, 137.7, 135.6, 135.2, 135.1, 134.8, 133.9, 133.8, 133.6, 129.2, 129.0, 127.4, 127.3, 127.2, 123.4, 122.0, 119.7, 111.6 (Ar–C), 55.8 (*C*H$_2$CH(CH$_3$)$_2$), 30.7 (CH$_3$*C*H$_2$COO), 29.2 (*C*H$_2$*C*H(CH$_3$)$_2$), 20.4 (CH$_2$CH(*C*H$_3$)$_2$), 7.9 (*C*H$_3$CH$_2$COO). ^{31}P NMR (202.4 MHz, $CDCl_3$): 35.22 (s). Anal. Calc for $C_{50}H_{48}INO_2P_2RuS$: C, 59.05; H, 4.76; N, 1.38. Found: C, 59.10; H, 5.08; N, 1.39.

Table 4 Summary of crystallographic parameters and refinement results for complexes **4–9**

	4	**5**	**6**	**7**	**8**	**9**
Formula	C62.50H56BrNO2P-2RuS	C53H46BrNO2P-2RuS	C55H52INO2P-2RuS	C63H61INO2P-2RuS	C49H46INO2P-2RuS	C50H48INO2P-2RuS
Fw	1128.06	1003.89	1080.95	1186.10	1002.84	1016.86
Cryst. syst.	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.359(4)	9.9427(4)	17.0266(6)	10.7883(5)	11.1382(5)	11.5401(16)
b/Å	14.753(5)	24.1566(10)	15.0002(6)	13.8789(7)	12.3698(6)	12.3535(17)
c/Å	17.270(6)	18.7354(7)	20.3236(7)	18.6293(9)	18.7464(8)	17.615(3)
α (°)	93.390(9)	90	90	90.8480(10)	74.5240(10)	72.444(2)
β (°)	104.451(8)	95.8130(10)	110.5390(10)	94.2400(10)	81.5730(10)	76.977(2)
γ (°)	107.960(10)	90	90	96.8600(10)	63.4010(10)	69.123(2)
V (Å^3)	2636.8(15)	4476.8(3)	4860.7(3)	2761.0(2)	2224.63(18)	2217.4(5)
Z	2	4	4	2	2	2
Dcalc$d$/g cm^{-3}	1.421	1.489	1.477	1.427	1.497	1.523
μ/mm^{-1}	1.201	1.404	1.109	0.983	1.205	1.210
F(000)	1158	2048	2192	1210	1012	1028
no. of reflns collected	28965	31658	57081	35988	28984	28850
no. of unique reflns	9311	10257	11151	12643	10201	10157
R_{int}	0.1091	0.0605	0.0357	0.0315	0.0311	0.0272
no. of observed reflns	6098	7837	10310	11067	9528	9304
Parameters	607	551	572	645	517	548
T/K	293(2)	223(2)	223(2)	223(2)	223(2)	223(2)
R_1[a] (all data)	0.1148	0.0652	0.0420	0.0417	0.0270	0.0300
wR_2[b](all data)	0.1570	0.1075	0.0861	0.0931	0.0611	0.0658
GOF[c]	1.017	0.991	1.127	1.082	1.049	1.041
$\Delta\rho$max/e Å^{-3}	0.883	1.268	0.798	1.088	0.638	0.618
$\Delta\rho$min/e Å^{-3}	–0.634	–0.381	–0.624	–0.399	–0.0611	–0.0658

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $wR_2 = \{ w\Sigma (| F_o | - | F_c |)^2 / \Sigma w | F_o |^2 \}^{1/2}$. [c] GOF = $\{ \Sigma w (| F_o | - | F_c |)^2 / (n - p) \}^{1/2}$, where n is the number of reflections and p is total number of parameters refined.

General procedure for the transfer hydrogenation reaction

The transfer hydrogenation experiments were carried out using standard Schlenk techniques. A mixture of appropriate amount of ruthenium complexes **4–9** (1 mol%), and the ketone (1 mmol) was dissolved in 2-propanol (20 mL). The solution was heated to 82 °C. When 0.1 M NaOBu^t (1 mL) was added, the reaction commenced immediately. After refluxing for about 30 h, the reaction mixture was directly passed through a pad of silica gel with Et_2O. The crude product was collected for GC-Mass chromatography analysis.

X-ray diffraction studies

Suitable crystals were mounted on quartz fibers and X-ray data were collected on a Bruker AXS APEX diffractometer equipped with a CCD detector, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART program suite and for absorption effects with SADABS. The crystal structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package.[21] In complex **4**, one of the toluene solvates lies on the inversion center and adopts a higher symmetry than the overall molecule. Such higher symmetry is suppressed in the refinement and the toluene molecule is treated by the disordered model with the occupancy factors of its atoms fixed at 0.5 each. In **9**, the isobutyl group adopts a positional disorder and the ratio of the two disordered components were refined to be 0.46/0.54. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal geometries and refined isotropically. Selected crystal data for complexes **4–9** are summarized in Table 4.

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