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Syntheses and Structures of Ruthenium(II) N,S-Heterocyclic Carbene Diphosphine Complexes and their Catalytic Activity towards Transfer Hydrogenation

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Abstract: Phosphine exchange of $[Ru^{II}Br(MeCOO)(PPh_3)_2(3\text{-RBzTh})]$ (3-RBzTh = 3-benzylbenzothiazol-2-ylidene) with a series of diphosphines (bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)-ethylene (dppv), 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,4-bis(diphenylphosphino)butane (dppb), and 1,3-(diphenylphosphino)propane (dppp)) gave mononuclear and neutral octahedral complexes $[RuBr(MeCOO)(\eta^2\text{-}P_2)(3\text{-RBzTh})]$ (P_2 = dppm (**2**), dppv (**3**), dppf (**4**), dppb (**5**), or dppp (**6**)), the coordination spheres of which contained four different ligands, namely, a chelating diphosphine, carboxylate, N,S-heterocyclic carbene (NSHC), and a bromide. Two geometric isomers of **6** (**6a** and **6b**) have been isolated. The structures of these products, which have been elucidated by single-crystal X-ray crystallography, show two structural types, I and II, depending on the relative dispositions of the ligands. Type I structures contain a carbenic carbon atom *trans* to the oxygen atom, whereas two phosphorus atoms are *trans* to bromine and oxygen atoms. The type II system comprises a carbene carbon atom *trans* to one of the phosphorus atoms, whereas the other phosphorus is *trans* to the oxygen atom, with the bromine *trans* to the remaining oxygen atom. Complexes **2**, **3**, **4**, and **6a** belong to type I, whereas **5** and **6b** are of type II. The kinetic product **6b** eventually converts into **6a** upon standing. These complexes are active towards catalytic reduction of *para*-methyl acetophenone by 2-propanol at 82 °C under 1% catalyst load giving the corresponding alcohols. The dppm complex **2** shows the good yields (91–97%) towards selected ketones.

Keywords: carbenes · diphosphines · N,S-heterocycles · ruthenium · transfer hydrogenation

Introduction

Catalytic reactions utilizing ruthenium N-heterocyclic carbene (NHC) complexes have witnessed an explosive growth in the last two decades.[1,2] These species are generally robust and tolerant towards many functional groups under standard organic synthetic conditions. One of the general design principles of active ruthenium–NHC complexes requires the disposition of a labile functionality *trans* to carbene.[3] Prominent examples include the second-generation Grubbs olefin metathesis catalysts that contain coordinated tricyclohexylphosphine (PCy_3).[4] Chelating alkylidenes,[5] bidentate Schiff base ligands,[6] heterodonating P,O- and N,O-chelates[7] etc. have been introduced to improve the thermal, oxygen, and moisture tolerance. Somewhat surprising is the lack of bidentate phosphine ligands among the known ruthenium–NHC catalysts,[8] although ruthenium diphosphine complexes have been proven to be effective towards a wide range of organic transformations.[9] It is hence desirable to develop a facile synthetic methodology for ruthenium(II) NHC–diphosphine complexes for catalysis. In view of the demonstrated application of N,S-heterocyclic carbene (NSHC) in olefin metathesis,[10] and as part of our ongoing effort in NSHC research,[11] we herein report a general synthetic pathway for mixed-ligand complexes $[Ru^{II}Br(MeCOO)(\eta^2\text{-}P_2)(3\text{-RBzTh})]$ (3-RBzTh = 3-benzylbenzothiazol-2-ylidene; P_2 = diphosphine). Their structural characteristics and catalytic activities towards transfer hydrogenation are described and discussed.

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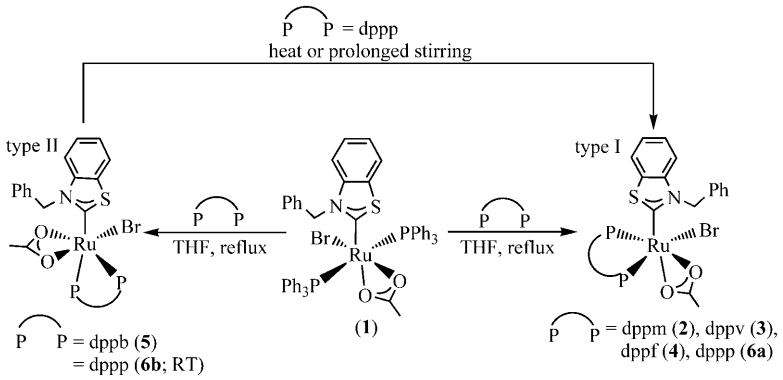
Results and Discussion

Synthesis and Characterization of Complexes 2–6

Diphosphine substitutions of [$Ru^{II}Br(MeCOO)(PPh_3)_2$(3-RBzTh)] (**1**),[11j] which can be easily prepared from [$Ru(MeCOO)_2(PPh_3)_2$], by bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethylene (dppv), 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,4-bis(diphenylphosphino)butane (dppb), and 1,3-(diphenylphosphino)propane (dppp) give new complexes [$RuBr(MeCOO)(\eta^2\text{-}P_2)$(3-RBzTh)] ($P_2$ = dppm (**2**), dppv (**3**), dppf (**4**), dppb (**5**), or dppp (**6**)) in moderate to high yields (61–95%; Scheme 1).



Scheme 1. Synthetic route to ruthenium(II)–benzothiazol-2-ylidene complexes **2**–**6**.

They are readily soluble in dichloromethane, tetrahydrofuran, and toluene and slightly soluble in diethyl ether. They can also be prepared from phosphine substitution directly with the precursor, namely [$Ru(MeCOO)_2(PPh_3)_2$], giving [$Ru(MeCOO)_2(\eta^2\text{-}P_2)$],[12] followed by acid condensation with a benzothiazolium salt. This alternative synthesis is exemplified by the successful preparation of **2** and **5** from the one-pot condensation reaction between [$Ru(MeCOO)_2(\eta^2\text{-}P_2)$] and *N*-benzylbenzothiazolium bromide [$(C_6H_4)SCHNR$]X (R and X = benzyl and Br) in the presence of NaOAc.

All products have been characterized by ESI spectral analysis. Their ^{31}P NMR spectra show downfield shifts, thus pointing to successful coordination of both phosphine sites in all cases. The most notable contrast with **1** is the presence of two discrete ^{31}P NMR resonances, implying *cis* orientation of a chelating diphosphine with different *trans* ligands across the phosphine donors. This rules out a symmetrical bridge formation or a *trans* orientation as occurred in **1**. The phosphine inequivalence and restricted rotation of the Ru–C bond differentiate the two CH_2 protons of the benzyl substituent.

The ^{31}P NMR spectrum of the reaction mixture of **1** and dppp at room temperature is unique in showing a mixture of products that are consistent with geometric isomers **6a** and **6b**. Both show mutually coupled inequivalent phosphines (**6a**: δ = 40.5 and 45.7 ppm for the phosphorus donors *trans* to bromide and oxygen atoms; **6b**: δ = 14.6 and 54.2 ppm for phosphorus *trans* to carbene and oxygen atoms, respectively). Under tetrahydrofuran reflux conditions, **6a** is formed and isolated in pure form. Complex **6b** is formed at room temperature but cannot be isolated free of **6a**. Its ^{31}P NMR resonances are fluxional, probably through an interconverting process of diastereomeric isomers in solution. Upon cooling from room temperature to −20 °C, the broad ^{31}P resonance sharpens and is then well-resolved into a pair of anticipated doublets ($^2J_{PP}$ = 40 Hz; see the Supporting Information, Figure S1). Its solution slowly changes from red to bright yellow at room temperature. Its ^{31}P NMR spectrum accordingly suggests the conversion of **6b** (^{31}P NMR spectra: δ = 54.2 and 14.6 ppm) into **6a** (^{31}P NMR spectra: δ = 45.7 and 40.5 ppm) within 66 hours at room temperature (see the Supporting Information, Figure S2) Complex **6b** is hence concluded to be a kinetic product in a reaction that drives towards **6a** as the thermodynamic outcome. Complexes **2**–**6** (except **6b**) are stable in both solid and solution states.

Molecular Structures of Complexes 2–6

All the complexes have been crystallized and their structures unequivocally elucidated by single-crystal X-ray diffraction studies (Figure 1). They are universally mononuclear and neutral, showing an octahedral ruthenium sphere with four different ligands, namely, a chelating diphosphine, carboxylate, NSHC carbene, and bromide. They can be categorized into two structural types, I and II, based on the relative dispositions of the ligands. Type I structures contain a carbenic carbon *trans* to the oxygen atom, whereas two phosphorus atoms are *trans* to the bromine and oxygen atoms. The type II system comprises a carbene carbon atom *trans* to one of the phosphorus atoms, whereas the other phosphorus atoms is *trans* to oxygen, with bromine *trans* to the remaining oxygen atom. Complexes **2**, **3**, **4**, and **6a** belong to type I, whereas **5** and **6b** are type II structures (Scheme 1). The former, with the phosphine group avoiding facing a high *trans*-ligand carbene, is more common and generally expected. Although **5** shares the same structural type as **6b**, it is thermodynamically stable and does not convert into the type I isomer under the present experimental conditions.

The heterocylic ring of the carbene tends to rotate out of the coordination plane (by 18.8–42.1° in **2**–**6**) to accommodate other secondary intra- and intermolecular interactions (see the Supporting Information, Figure S3). In **2**, the rotation (28.4°) is accompanied by intramolecular C–H···O hydrogen bonding (C8···O1: 3.03 Å; C8–H8B···O1: 138.9°) and intermolecular offset π–π interactions (3.35 Å) between the heterocyclic ring and its symmetry-generated counterpart

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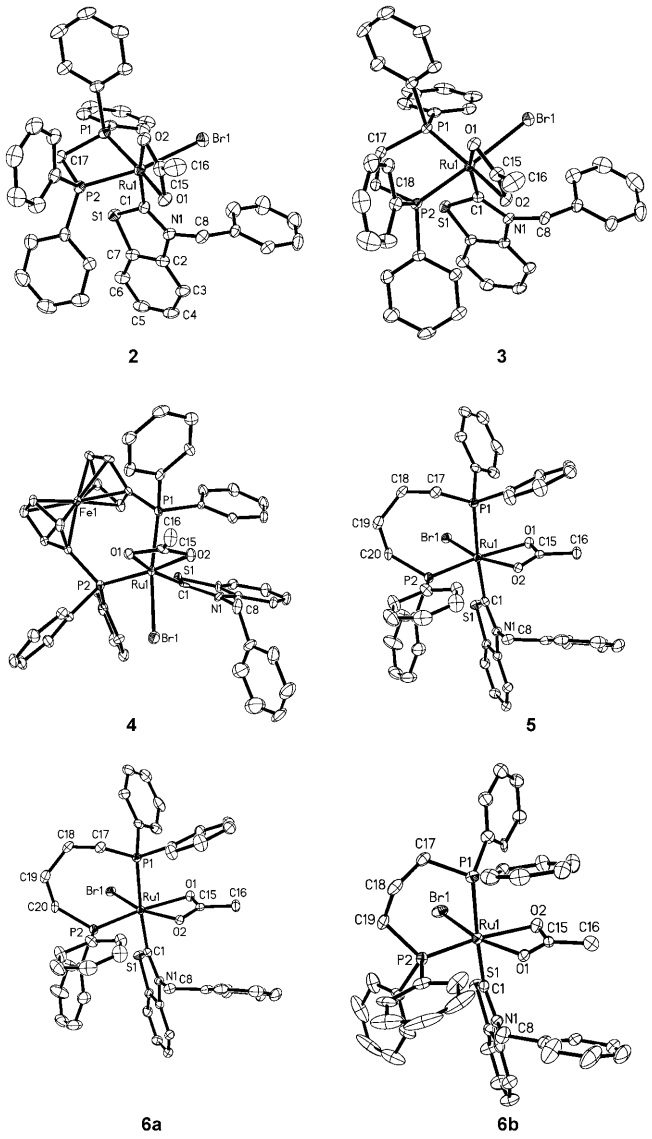


Figure 1. ORTEP of complexes **2**–**6** with 50% probability ellipsoids. All hydrogen atoms and solvent molecules are omitted for clarity.

(−*x*, −*y*+1, −*z*+1; see the Supporting Information). In **3**, similar C−H···O hydrogen bonding (C8···O2: 3.03 Å; C8−H8B···O2: 135.1°) is evident except that the rotation increases to 31.9° to alleviate the close contacts between the γ-H on the nitrogen substituent and the protons on the neighboring phenyl rings of dppv (H8A···H2C: 2.84 Å). In **4**, the rotation rises further to 32.3° to accommodate the C−H···O hydrogen bonding (C8···O2: 3.03 Å; C8−H8A···O2: 141.6°), nonbonding H···H contact (H8B···H6B: 2.48 Å), and additional intramolecular face-to-face π–π interactions between the five-membered C1-S1-C7-C2-N1 and six-membered C1B-C2B-C3B-C4B-C5B-C6B (3.45 Å between ring centroids) rings. In **5**, the intramolecular C−H···O hydrogen bonding (C8···O2: 2.89 Å; C8−H8B···O2: 121.1°) and the intramolecular face-to-face π–π interactions between the five-membered C1-S1-C7-C2-N1 and six-membered C1C-C2C-C3C-C4C-C5C-C6C (3.62 Å between ring centroids) rings possibly governs the carbene ring rotation (18.8°). The large ring rotation in **6a** (42.1°) is traced to an edge-to-face C−H···π interaction between a pair of C−H bonds of the phenyl ring of the nitrogen substituent and C=C bond of the phenyl ring of dppp (H10···C6D: 2.92 Å; C10−H10···C6D: 153.1°; H11···C5D: 3.32 Å; C11−H11···C5D: 129.9°) and the intramolecular C−H···O hydrogen bonding (C8···O2: 3.23 Å; C8−H8A···O2: 135.6°). Complex **6b** shows intermolecular hydrogen bonding within each pair of molecules. The ring rotates 23.7° out of the coordination plane to minimize interactions between the phenyl ring of the nitrogen substituent C13−H13 or C14−H14 and O2A (C13···O2A: 3.19 Å; C13−H13A···O2A: 123.9°; C14···O2A: 3.24 Å; C14−H14A···O2A: 118.2°; symmetry code to generate O2A: −*x*+2, −*y*+1, −*z*+2).

It is remarkable that these diphosphines with a diverse range of spacer lengths and skeletal properties have adapted to a common mononuclear core as chelating ligands, especially considering that ligands, such as dppf[13a] and dppb, could easily adopt the bridging mode. This feature is exemplified by the tolerance over a wide span of P-Ru-P angles (73.05(3)–101.16(7)°) and P···P distances (2.669–3.578 Å; Table 1). The metallo–diphosphine ring properties have

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2**–**6**.

	2	**3**	**4**	**5**	**6a**	**6b**
Ru(1)−C(1)	1.972(3)	1.980(4)	1.982(7)	2.056(3)	1.957(7)	2.034(6)
Ru(1)−P(1)	2.2311(9)	2.245(1)	2.335(2)	2.3751(9)	2.283(2)	2.363(2)
Ru(1)−P(2)	2.2529(9)	2.255(1)	2.297(2)	2.2580(9)	2.280(2)	2.236(1)
Ru(1)−Br(1)	2.5792(5)	2.5942(6)	2.570(1)	2.5530(4)	2.6025(9)	2.5434(7)
Ru(1)−O(1)	2.214(2)	2.217(3)	2.200(5)	2.226(2)	2.219(5)	2.127(4)
Ru(1)−O(2)	2.186(2)	2.205(3)	2.200(5)	2.135(2)	2.182(5)	2.242(4)
P(1)···P(2)	2.669	3.023	3.578	3.429	3.282	3.322
P(1)-Ru(1)-P(2)	73.05(3)	84.38(4)	101.16(7)	95.46(3)	92.00(7)	92.45(5)
O(1)-Ru(1)-O(2)	59.51(8)	59.1(1)	59.6(2)	59.84(9)	59.8(2)	59.8(2)
C(1)-Ru(1)-P(1)	95.75(9)	93.3(1)	89.7(2)	174.77(9)	93.8(2)	173.6(2)
C(1)-Ru(1)-P(2)	90.37(9)	88.8(1)	97.0(2)	89.75(9)	94.2(2)	92.9(2)
Br(1)-Ru(1)-P(1)	98.53(3)	95.71(3)	169.52(5)	90.76(2)	89.86(5)	85.95(4)
Br(1)-Ru(1)-P(2)	170.61(2)	173.36(3)	89.25(6)	89.47(2)	171.63(5)	87.79(4)
dihedral angle[a]	28.4	31.9	32.3	18.8	42.1	23.7

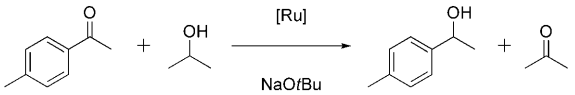
[a] Dihedral angle between the N,S-heterocyclic carbene ring and coordination plane.

been related to the catalytic behaviors of some systems.[9,13] The Ru–C bonds (1.957(7)–2.034(6) Å) for **2**–**6** are within the range reported for Ru–NSHC complexes (for example, complex **1**[11j]: 1.970(6) Å); $[RuCl_2(=CH\text{-}o\text{-}i\text{PrO-Ph})(3\text{-Ph-DMeTh})]$[10] (DMeTh = 4,5-dimethylthiazol-2-ylidene; 1.944(1) Å), $[Ru(CO)F(H)(NHC)(PPh_3)_2]$[14] (NHC = 1,3,4,5-tetramethylimidazol-2-ylidene; 2.170(2) Å), *mer*,*cis*-$[RuCl_2(CO)(NHC)]$[15] (NHC = 1,3-bis(2-diphenylphosphanylethyl)-3*H*-imidazol-2-ylidene; 2.038(3) Å). With carbene and phosphine at a mutually *trans* orientation,[16] type II structures understandably show the longest, and presumably weakest, Ru–C (2.056(3) Å for **5** and 2.034(6) Å for **6b**) and Ru–P bonds (2.3751(9) Å for **5** and 2.363(2) Å for **6b**). The acetate chelate is most distorted in **6b**, showing the highest contrast in Ru–O lengths (2.127(4) and 2.242(4) Å), the latter is also the weakest Ru–O in this series. These offer a possible explanation on the fluxionality of **6b**. A facile chelate to monodentate conversion of the acetate would readily create a fluxional 5-coordinated structure that would allow the carbene and bromide to swap positions followed by chelate reformation to give **6a**. The stability of **6a** is also exemplified by a near-ideal P1-Ru1-P2 chelate angle (92.00(7)°) and strong $^2J_{PP}$ coupling (40.9 Hz).

Transfer Hydrogenation

The catalytic performance of **2**–**6** towards the reduction of *para*-methyl acetophenone by 2-propanol to 1-(4-methylphenyl)ethanol has been compared (Table 2). Complex **2** generally gives the best yields within 24 hours at a catalyst load of 1 mol%. This result is consistent with the strength of the carbene and diphosphine chelate, as **2** has the strongest Ru–C and Ru–P bonds in this series. As this form of transfer hydrogenation typically goes through a hydride intermediate and the bromide–hydride exchange is expected to be facile, the stability of the [Ru(NSHC)(P-P)] core could be a determining factor. Complex **2** has a slight advantage over its precursor **1**, which returns with a similarly yield of approximately 90% but requires a longer reaction duration.

Table 2. Catalytic transfer hydrogenation of *para*-methyl acetophenone with complexes **2**–**6**.[a]



Entry	Catalyst	*t* [h]	Yield [%]
1	**2**	8	57
2	**2**	12	68
3	**2**	24	90
4	**1**	30	91
5	**3**	24	52
6	**4**	24	46
7	**5**	24	68
8	**6a**	24	48
9	**6b**	24	32

[a] Experimental conditions: ketone (1 mmol), NaO*t*Bu (0.1 mmol), catalyst (0.01 mmol), 2-propanol (15 mL), $T = 82$ °C.

Complex **2** was thus chosen to compare its effect on different alkyl and aryl ketones (Table 3). It returns with excellent yields (91–97%) except towards benzophenone and 4-methoxyacetophenone (Table 3, entry 5 and 6), which could be attributed to unfavorable electronic (Table 3, entry 5) and steric effects (Table 3, entry 6) of the substituent on the ketones. These are comparable with the performance of **1**.[11j] Use of phosphine-free NHC complexes,[15–17] such as $[RuCl_3(L)(NO)]$ (L = 3-*tert*-butyl-1-(2-pyridyl)imidazol-2-ylidene) provides an alternative with similar yield (96%) in similar reduction of acetophenone but within a shorter period of 4 hours. There are other effective carbene-free catalysts that are supported by [NNN] or [PNN] tridentate ligands.[18,19]

Table 3. Catalytic transfer hydrogenation of ketones with complexes **2**.[a]

Entry	Substrate	Product	Yield [%]
1	cyclopentanone	cyclopentanol	95
2	acetophenone	1-phenylethanol	91
3	4-chloroacetophenone	1-(4-chlorophenyl)ethanol	94
4	4-bromoacetophenone	1-(4-bromophenyl)ethanol	97
5	4-methoxyacetophenone	1-(4-methoxyphenyl)ethanol	8
6	benzophenone	diphenylmethanol	12

[a] Experimental conditions: ketone (1 mmol), NaO*t*Bu (0.1 mmol), catalyst (0.01 mmol), 2-propanol (15 mL), $T = 82$ °C.

Conclusions

We have developed a convenient synthetic method to ruthenium(II) complexes with all-different ligands. The formulation of these complexes are based on two stable and nondissociative (namely, NSHC carbene and diphosphine) and two dissociative and exchangeable (namely, bromide and acetate) ligands. This unique combination would potentially create a plethora of new ruthenium(II) catalysts based on the interaction of the robust [Ru(NSHC)(P-P)] core with a wide range of anions, substrates, and reactive species. Another option is to introduce chelating carbene, or dicarbene, which has been shown to be effective in catalytic transfer hydrogenation,[15,17] to this core. We are exploring the catalytic potential of this new system with reference to the rich catalytic chemistry that has been established for the $[Ru^{II}(PR_3)_{2-3}]$[9,20,21] system. A distinctive feature of this diphosphine–carbene combination is that, as demonstrated in the isolation of **5** and **6b**, alternative geometric isomers can be stabilized through adjustment of the skeletal traits of the diphsophine. Such stereochemical tuning, which is lacking among monodentate phosphines, offers a simple mechanism to examine the stereogeometrical effect on catalytic efficacy.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. Complex **1** was prepared according to the literature method.[11j] Other commercially available chemicals were purchased from Sigma–Aldrich. All solvents were freshly distilled from standard drying agents. ^{1}H (500.1), ^{31}P (202.4) and ^{13}C(125.8 MHz) NMR spectra were recorded in ppm on a Bruker AMX 500 spectrometer. The chemical shifts (δ) are referenced to TMS for ^{1}H and ^{13}C{^{1}H} and H_3PO_4 (85%) for ^{31}P{^{1}H}. ESI mass spectra were obtained by using a Finnigan LCQ. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer. The yields of transfer 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 [RuBr(MeCOO)(η^2-P2)(3-RBzTh)] Complexes (**2**–**6**)*

A mixture of [RuBr(CH_3COO)$_2$(PPh_3)$_2$(3-RBzTh)] (**1**) (0.198 g, 0.20 mmol) and diphosphorus ligands (0.22 mmol) was suspended in THF. The resultant orange solution was refluxed (**2**–**5** and **6a**) or stirred at RT (**6b**) for 3 h. Upon cooling, the solvent was removed under vacuum, leaving a yellow or orange residue, which was then washed several times with hexane. The powder product was redissolved in CH_2Cl_2 and diffused with hexane. The yellow to orange crystals of **2**–**6** were obtained within a week.

*[RuBr(η^2-dppm)(MeCOO)(3-RBzTh)] (**2**)*

Yield: 0.16 g (0.19 mmol, 94%); ^{1}H NMR ($CDCl_3$): δ = 8.25–8.22 (m, 2H; Ar-H), 8.13–8.09 (m, 2H; Ar-H), 7.48–7.32 (m, 10H; Ar-H), 7.29–7.07 (m, 10H; Ar-H), 7.07–6.94 (m, 3H; Ar-H), 6.74 (d, 1H, $^{2}J_{HH}$ = 16.4 Hz; CH_2), 6.31 (d, 1H, $^{2}J_{HH}$ = 16.4 Hz; CH_2), 5.22 (m, 1H, $^{2}J_{PH}$ = 15.1, 10.4, $^{2}J_{HH}$ = 10.7 Hz; PCH_2P), 4.93 (m, 1H, $^{2}J_{PH}$ = 14.5, 10.7, $^{2}J_{HH}$ = 10.7 Hz; PCH_2P), 1.53 ppm (s, 1H; CH_3COO); ^{13}C NMR ($CDCl_3$): δ = 231.0 (NCS), 186.1 (CH_3COO), 137.3, 136.2, 136.0, 134.2, 133.9, 133.3, 133.0, 132.9, 132.2, 132.1, 132.0, 131.9, 130.2, 130.1, 129.6, 128.7, 128.6, 128.2, 127.7, 127.0 (Ar-C), 125.1, 122.8, 119.6, 113.7 (Ar-C$_{meta/ortho,\ N/S}$), 56.4 (CH_2), 51.0 (J_{PC} = 23.0 Hz; PCH_2P), 24.6 ppm (CH_3COO); ^{31}P NMR ($CDCl_3$): δ = 14.2, 11.2 ppm (d, J_{PP} = 78.1 Hz); MS (ESI, positive mode): *m*/*z* (%): 770.03 (100) [*M*−Br]$^+$; elemental analysis calcd (%) for $C_{41}H_{36}BrNO_2P_2RuS$: C 57.95, H 4.27, N 1.65; found: C 57.71, H 4.15, N 1.64.

*[RuBr(η^2-dppv)(MeCOO)(3-RBzTh)] (**3**)*

Yield: 0.15 g (0.17 mmol, 87%); ^{1}H NMR ($CDCl_3$): δ = 8.30–8.21 (m, 3H; Ar-H), 7.96–7.78 (m, 3H; Ar-H), 7.57–7.47 (m, 3H; Ar-H, C*H*=CH, CH_2), 7.36–7.19 (m, 14H; Ar-H), 7.12–7.09 (m, 2H; Ar-H), 7.02–6.95 (m, 3H; Ar-H, C*H*=CH), 6.93–6.87 (m, 2H; Ar-H), 6.83–6.79 (m, 1H; Ar-H), 5.76 (d, 1H, $^{2}J_{HH}$ = 16.4 Hz; CH_2), 1.37 ppm (t, 3H; CH_3COO); ^{13}C NMR ($CDCl_3$): δ = 229.0 (NCS), 186.1 (CH_3COO), 153.2 (J_{CP} = 26.9, 27.9 Hz; *C*H=CH), 145.3 (J_{CP} = 24.9, 23.9 Hz; *C*H=CH), 144.3, 137.6, 136.1, 135.7, 134.5, 134.4, 133.7, 133.3, 133.1, 133.0, 132.6, 132.4, 132.3, 132.2, 132.0, 131.8, 130.2, 129.8. 129.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.0 (Ar-C), 124.7, 122.5, 119.2, 113.4 (Ar-C$_{meta/ortho,\ N/S}$), 56.6 (CH_2), 24.6 ppm (CH_3COO); ^{31}P NMR ($CDCl_3$): δ = 87.5, 84.9 ppm (d, J_{PP} = 13.6 Hz); MS (ESI, positive mode): *m*/*z* (%): 782.03 (100) [*M*−Br]$^+$; elemental analysis calcd (%) for $C_{42}H_{36}BrNO_2P_2RuS$: C 58.54, H 4.21, N 1.62; found: C 58.11, H 4.15, N 1.60.

*[RuBr(η^2-dppf)(MeCOO)(3-RBzTh)] (**4**)*

Yield: 0.16 g (0.17 mmol, 83%); ^{1}H NMR ($CDCl_3$): δ = 8.02 (m, 2H; Ar-H), 7.84 (m, 2H; Ar-H), 7.61 (m, 2H; Ar-H), 7.29–7.27 (m, 7H; Ar-H), 7.24–7.17 (m, 5H; Ar-H), 7.15–7.09 (m, 5H; Ar-H), 7.04–7.01 (m, 2H; Ar-H, CH_2), 6.98–6.94 (m, 5H; Ar-H), 6.13 (d, 1H, $^{2}J_{HH}$ = 16.4 Hz; CH_2), 5.08 (s, 1H; Cp-H), 4.79 (m, 2H; Cp-H), 4.46 (m, 2H; Cp-H), 4.36 (m, 3H; Cp-H), 1.14 ppm (s, 3H; CH_3COO); ^{13}C NMR ($CDCl_3$): δ = 230.2 (J_{CP} = 14.0, 13.0 Hz; NCS), 186.6 (CH_3COO), 145.0, 139.6, 139.2, 138.0, 136.4, 136.1, 135.8, 134.8, 134.5, 134.4, 134.3, 134.2, 134.1, 133.6, 133.5, 129.3, 128.9, 128.7, 128.1, 127.6, 127.2, 127.1, 127.0, 126.8 (Ar-C), 124.8, 122.7, 119.1, 113.5 (Ar-C$_{meta/ortho,\ N/S}$), 76.8–77.3 (Cp-C, overlapping singlets), 76.5 (d, J_{CP} = 12.0 Hz; Cp-C), 75.8 (d, J_{CP} = 10.0 Hz; Cp-C), 75.5 (dd, J_{CP} = 8.6, 7.3 Hz; Cp-C), 72.2 (d, J_{CP} = 6.0 Hz; Cp-C), 72.0 (d, J_{CP} = 7.0 Hz; Cp-C), 71.7(d, J_{CP}=6.0 Hz; Cp-C), 70.5 (d, J_{CP} = 5.0 Hz; Cp-C), 56.0 (CH_2), 24.4 ppm (CH_3COO); ^{31}P NMR ($CDCl_3$): δ = 49.4, 47.6 ppm (d, J_{PP} = 24.8 Hz); MS (ESI, positive mode): *m*/*z* (%): 940.09 (100) [*M*−Br]$^+$; elemental analysis calcd (%) for $C_{50}H_{42}BrFeNO_2P_2RuS$: C 58.89, H 4.15, N 1.37; found: C 58.89, H 4.14, N 1.48.

*[RuBr(η^2-dppb)(MeCOO)(3-RBzTh)] (**5**)*

Yield: 0.17 g (0.19 mmol, 95%); ^{1}H NMR ($CDCl_3$): δ = 8.31–8.27 (m, 2H; Ar-H), 7.99–7.96 (m, 2H; Ar-H), 7.58–7.55 (m, 2H; Ar-H), 7.38–7.29 (m, 9H; Ar-H, CH_2), 7.23 (m, 3H; Ar-H), 7.15–7.03 (m, 6H; Ar-H), 6.89–6.81 (m, 5H; Ar-H), 6.64 (d, 1H, J_{HH} = 8.2 Hz; Ar-H), 4.56 (d, 1H, J_{HH} = 4.0 Hz; CH_2), 2.95 (m, 1H; CH_2(CH_2)$_2$$CH_2$), 2.81 (m, 1H; C$H_2$($CH_2$)$_2$$CH_2$), 2.68–2.61 (m, 2H; C$H_2$($CH_2$)$_2$$CH_2$), 2.14 (m, 1H; CH_2(CH_2)$_2$$CH_2$), 2.06–1.94 (m, 2H; CH_2(CH_2)$_2$$CH_2$), 1.69 (m, 1H; CH_2(CH_2)$_2$$CH_2$), 1.46 ppm (s, 3H; C$H_3$COO); ^{13}C NMR ($CDCl_3$): δ = 229.0 (J_{CP} = 14.9, 13.0 Hz; NCS), 186.2 (CH_3COO), 144.5, 139.2, 138.9, 137.9, 137.5, 135.7, 135.3, 135.1, 134.8, 134.4, 133.8, 132.8, 132.6, 131.7, 129.4, 129.2, 129.0, 128.2, 127.9, 127.7, 127.5, 126.9 (Ar-C), 124.5, 122.4, 118.7, 113.5 (Ar-C$_{meta/ortho,\ N/S}$), 56.1 (CH_2), 27.3 (J_{CP} = 27.9 Hz; CH_2(CH_2)$_2$$CH_2$), 25.1–25.0 (m, overlapping singlets; CH_2(CH_2)$_2$$CH_2$, C$H_3$COO), 22.8 ($CH_2$(C$H_2$)$_2$$CH_2$), 20.6 ppm ($CH_2$($CH_2$)$_2$$CH_2$); ^{31}P NMR ($CDCl_3$): δ = 53.4, 37.3 ppm (d, J_{PP} = 28.5 Hz); MS (ESI, positive mode): *m*/*z* (%): 812.11 (100) [*M*−Br]$^+$; elemental analysis calcd (%) for $C_{44}H_{42}BrNO_2P_2RuS$: C 59.26, H 4.75, N 1.57; found: C 59.26, H 4.82, N 1.70.

*[RuBr(η^2-dppp)(MeCOO)(3-RBzTh)] (**6a**)*

Yield: 0.16 g (0.18 mmol, 91%); ^{1}H NMR ($CDCl_3$): δ = 8.06–8.05 (m, 2H; Ar-H), 7.85–7.82 (m, 2H; Ar-H), 7.48–7.41 (m, 5H; Ar-H), 7.38 (m, 1H; Ar-H), 7.30–7.10 (m, 13H; Ar-H), 7.05–6.95 (m, 5H; Ar-H, CH_2), 6.84 (d, 1H, J_{HH} = 8.2 Hz; Ar-H), 5.16 (d, 1H, J_{HH} = 15.8 Hz; CH_2), 3.10–2.99 (m, 2H; C$H_2$$CH_2$$CH_2$), 2.66–2.60 (m, 2H; C$H_2$$CH_2$$CH_2$), 2.45 (m, 1H; CH_2C$H_2$$CH_2$), 2.08 (m, 1H; CH_2C$H_2$$CH_2$), 1.35 ppm (s, 3H; C$H_3$COO); ^{13}C NMR ($CDCl_3$): δ = 227.9 (J_{CP} = 14.0 Hz; NCS), 185.2 (CH_3COO), 145.0, 137.4, 136.4, 136.0, 135.3, 135.2, 135.0, 134.7, 134.3, 134.1, 134.0, 133.3, 133.2, 131.8, 129.4, 129.3, 129.1, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 126.7 (Ar-C), 125.0, 122.9, 119.1, 114.0 (Ar-C$_{meta/ortho,\ N/S}$), 56.4 (CH_2), 29.0 (dd, J_{CP} = 30.9, 4.0 Hz; C$H_2$$CH_2$$CH_2$), 28.9 (d, J_{CP} = 32.9; C$H_2$$CH_2$$CH_2$), 24.5 ($CH_3COO$), 20.5 ppm ($CH_2$$CH_2$$CH_2$); ^{31}P NMR ($CDCl_3$): δ = 45.7, 40.5 ppm (d, J_{PP} = 40.9 Hz); MS (ESI, positive mode): *m*/*z* (%): 797.9 (100) [*M*−Br]$^+$; elemental analysis calcd (%) for $C_{43}H_{40}BrNO_2P_2RuS$: C 58.84, H 4.59, N 1.60; found: C 58.68, H 4.97, N 1.38.

*[RuBr(η^2-dppp)(MeCOO)(3-RBzTh)] (**6b**)*

Yield: 0.11 g (0.12 mmol, 61%); ^{1}H NMR ($CDCl_3$): δ = 8.05–8.03 (m, 2H; Ar-H), 7.69 (d, 1H; Ar-H), 7.45–7.08 (m, 21H; Ar-H), 6.82–6.60 (m, 6H; Ar-H), 5.95 (d, 1H, $^{2}J_{HH}$ = 15.8 Hz; CH_2), 5.86 (d, 1H, J_{HH} = 15.8 Hz; CH_2), 3.00 (m, 1H; C$H_2$$CH_2$$CH_2$), 2.84–2.77 (m, 2H; C$H_2$$CH_2$$CH_2$), 2.46–2.22 (m, 2H; C$H_2$$CH_2$$CH_2$), 1.77 (m, 1H; CH_2C$H_2$$CH_2$), 1.06 ppm (s, 3H; C$H_3$COO); ^{13}C NMR ($CDCl_3$): δ = 185.1 (CH_3COO), 144.3, 137.3, 136.8, 136.2, 135.9, 134.9, 134.8, 134.3, 134.1, 134.0, 133.3, 130.2, 129.9, 129.1, 128.4, 127.9, 127.8, 127.7, 127.6, 127.4, 126.8, 126.7, 125.5, 125.0, 124.8, 123.3, 121.0, 113.6 (Ar-C), 56.2 (CH_2), 27.4 ($CH_2$$CH_2$$CH_2$), 27.2 ($CH_2$$CH_2$$CH_2$), 23.7 ($CH_3COO$), 21.4 ppm ($CH_2$$CH_2$$CH_2$); ^{31}P NMR ($CDCl_3$): δ = 54.2, 14.6 ppm (m); MS (ESI, positive mode): *m*/*z* (%): 797.9 (100) [*M*−Br]$^+$.

General Procedure for the Transfer Hydrogenation Reaction

The transfer hydrogenation experiments were carried out by using standard Schlenk techniques. A mixture of an appropriate amount of **2**–**6** (1 mol%) and the ketone (1 mmol) was dissolved in 2-propanol (20 mL). The solution was heated to 82 °C. The reaction commenced immediately upon addition of 0.1 M NaO*t*Bu (1 mL). After ~24 h reflux, the mixture was passed through a small column of silica gel and eluted with Et_2O. The crude product was collected for GC-mass chromatography analysis.

Table 4. Summary of crystallographic parameters and refinement results for complexes **2**–**6**.

	2	**3**	**4**	**5**	**6a**	**6b**
formula	$C_{41}H_{36}BrNO_{2.25}P_2RuS$	$C_{42}H_{37}BrNO_{2.50}P_2RuS$	$C_{52}H_{46}BrCl_4FeNO_2P_2RuS$	$C_{44}H_{42}BrNO_2P_2RuS$	$C_{45}H_{42}BrCl_6NO_2P_2RuS$	$C_{43}H_{39}BrNO_2P_2RuS$
F_w	853.69	870.71	1189.53	891.77	1116.48	876.73
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic
space group	*P*21/*n*	*P*21/*n*	*P*21/*n*	*Pbca*	*P*−1	*P*−1
a [Å]	12.648(1)	13.2523(6)	16.771(7)	11.9272(5)	8.782(1)	10.318(1)
b [Å]	11.625(1)	10.7742(5)	16.975(7)	19.5253(8)	14.294(2)	12/481(1)
c [Å]	25.720(2)	26.924(1)	18.167(8)	32.640(1)	19.356(3)	16.283(1)
α [°]	90	90	90	90	107.130(3)	103.897(3)
β [°]	95.695(2)	99.429(1)	108.42(1)	90	98.111(3)	101.402(2)
γ [°]	90	90	90	90	95.118(3)	106.085(3)
V [Å^3]	3762.8(6)	3792.4(3)	4907(4)	7601.2(5)	2276.5(6)	1875.6(4)
Z	4	4	4	8	2	2
D_{calcd} [g cm^{-3}]	1.507	1.525	1.610	1.558	1.629	1.552
μ [mm^{-1}]	1.656	1.645	1.786	1.643	1.730	1.663
F(000)	1728	1764	2400	3632	1124	890
no. of reflns collected	26079	26039	33942	52301	29231	13429
no. of unique reflns	8633	8679	11245	8732	10458	8548
R_{int}	0.0481	0.0685	0.1131	0.0714	0.0731	0.0374
no. of observed reflns	6342	6371	7363	6898	8665	6539
parameters	477	467	587	470	533	546
T [K]	223(2)	223(2)	100(2)	100(2)	100(2)	100(2)
$R1$[a] (all data)	0.0662	0.0820	0.1259	0.0601	0.1039	0.0795
$wR2$[b](all data)	0.1027	0.1179	0.2136	0.1073	0.1802	0.1964
GOF[c]	0.991	1.018	1.045	1.043	1.171	1.049
$\Delta\rho_{max}$ [e Å^{-3}]	0.631	1.003	1.853	1.391	1.750	1.381
$\Delta\rho_{min}$ [e Å^{-3}]	−0.315	−0.542	−1.682	−0.530	−1.885	−0.854

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

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, by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ 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 by using the SHELXTL program package.[22] In **2**, the hydrogen atoms of the partially occupied free water were not located, whereas the hydrogen atoms of the water were located from the difference Fourier map and refined with restraints in bond lengths and thermal parameters in **3**. There are two phenyl rings disordered into two positions with the corresponding occupancy ratios of 0.51/0.49 and 0.47/0.53 in **6b**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal geometries and refined isotropically. Selected crystal data for complexes **2**–**6** are summarized in Table 4.

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