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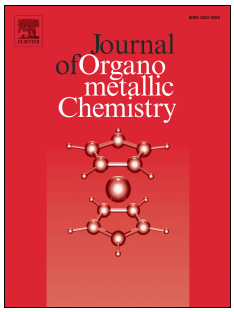

Synthesis of $RuCl_2$(xantphos)L (L = PPh_3, $P(OPh)_3$, DMSO) Complexes, and their Catalytic Activity for the Addition of Carboxylic Acids onto Olefins

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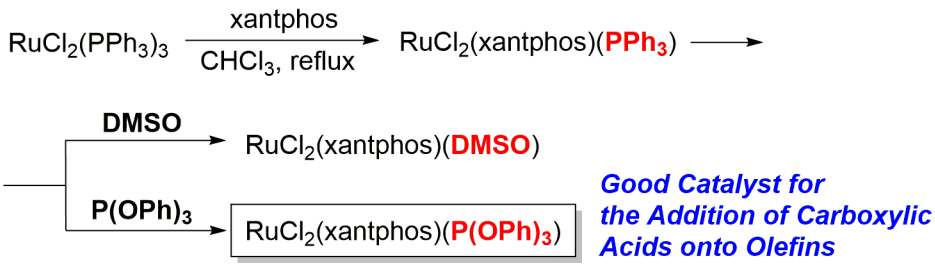
Graphical Abstract Synopsis

$RuCl_2$(xantphos)(PPh_3) was readily synthesized from $RuCl_2(PPh_3)_3$ in refluxing $CHCl_3$, which was converted into RuCl2(xantphos)($P(OPh)_3$) and $RuCl_2$(xantphos)(DMSO) by the reaction with $P(OPh)_3$ and DMSO, respectively. The catalytic activity of these complexes for the addition of carboxylic acid onto olefins is also described.



Good Catalyst for the Addition of Carboxylic Acids onto Olefins

Synthesis of $RuCl_2$(xantphos)L (L = PPh_3, $P(OPh)_3$, DMSO) Complexes, and their Catalytic Activity for the Addition of Carboxylic Acids onto Olefins

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Abstract

Readily synthesis of a series of $RuCl_2$(xantphos)L (L= PPh_3, $P(OPh)_3$, DMSO) was achieved. Thus, $RuCl_2$(xantphos)PPh_3 was synthesised by the reaction of $RuCl_2(PPh_3)_3$ with xantphos. PPh_3 in this complex is easily exchanged with $P(OPh)_3$ and Dimethylsulfoxide (DMSO) to give $RuCl_2$(xantphos){$P(OPh)_3$} and $RuCl_2$(xantphos)(DMSO), respectively.

Introduction

The ligands in transition metal complexes influence the reactivity of these complexes in homogeneous and heterogeneous catalysis. Xantphos,[1] 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene, has received much attention recently because it produces various effects in transition metal-catalysed reactions, and therefore,[2] many metal complexes such as palladium, rhodium, and iridium complexes have been synthesised and utilised.[3-5] Synthesis and characterisation of xantphos ruthenium complexes and their application to catalytic organic transformations have also been reported.[6-13] In 2001, Mol synthesised carbene ruthenium complexes containing the xantphos ligand and investigated its catalytic activity on alkene metathesis reactions.[6] Williams and Whittlesey reported that xantphos-ruthenium catalysis showed high catalytic activity for the hydrogen transfer alkylation of β–cyanoketones with alcohols.[7] They also synthesised their original ruthenium complexes containing xantphos and carbene ligands and investigated their catalytic activity in the α–alkylation reaction of cyanoacetoacetates using alcohols as alkylating reagents.[8] Dutta synthesised a $RuCl_2(CO_2)$(xantphos) complex and utilised it in the transfer hydrogenation of carbonyl compounds.[9] Whittlesey synthesised the ruthenium-xantphos complex containing a fluoride ligand.[10] In these cases, xantphos

acts as a bidentate ligand, and the $P_{xantphos}$–Ru–$P_{xantphos}$ coordination mode is defined to be *cis*. Synthesis of $RuCl_2$(xantphos)(DMSO), in which xantphos acts as a P–O–P tridentate ligand, has been reported by Kharat but with two phosphorus atoms located at the *cis*-position.[11] The pincer-type ruthenium-xantphos complex is rare. Whittlesey et al. reported preparation of Ru(xantphos)(PPh_3)HCl, in which two phosphorus atoms of xantphos were located at the *trans*-position and an oxygen atom was coordinated to the ruthenium centre like a pincer-type ligand.[12] During our ongoing study on ruthenium catalysis,[13] we have found that $RuCl_2$(xantphos)PPh_3 can readily be synthesised by the reaction of $RuCl_2(PPh_3)_3$ and xantphos and that xantphos behaves as a P–O–P pincer-type tridentate ligand.[14] Here we report the synthesis of $RuCl_2$(xantphos)PPh_3, the reaction of the complex with triphenylphosphite and DMSO, and the catalytic activity of these complexes for the addition of 2-phenylbenzoic acid onto olefins.

We hypothesised that reaction of $RuCl_2(PPh_3)_3$ (**1**) with xantphos would afford a $RuCl_2$(xantphos)(PPh_3) complex. As expected, the reaction of **1** with xantphos was performed in refluxing $CHCl_3$ for 4.5 h to afford the desired $RuCl_2$(xantphos)(PPh_3) (**2a**) in 95% yield as a red crystal (Scheme 1).

$^{31}P\{^1H\}$ NMR, FAB-MS spectra and an ORTEP structure of **2a** revealed that xantphos behaved as a pincer-type ligand. Two phosphorus signals are seen on the $^{31}P\{^1H\}$ NMR

spectrum of **2a**. One signal appears at 36 ppm as a doublet, and the other at 58 ppm as a triplet (J_{PP} = 30.6 Hz). The mass number of complex **2a** was measured by FAB-MS spectroscopy to obtain a fragment ion peak at 1012 [*m/z*]. Recrystallisation of **2a** from $CHCl_3/Et_2O$ successfully afforded a single crystal. The ORTEP diagram of **2a** is shown in Fig. 1. The xantphos in **2a** behaves as a P-O-P pincer-type ligand, and two phosphorus atoms of xantphos are located at the *trans*-positions. The oxygen, ruthenium, and phosphorus atoms in PPh_3 are nearly aligned (O-Ru-P_{PPh3} = 174.48(8)º). On the other hand, $P_{xantphos}$-Ru-$P_{xantphos}$ is apparently not linear [156.33(3)º], presumably due to the constraint of forming fused five-membered rings including oxygen, two phosphorus atoms of xantphos, and ruthenium. During our studies, Vogt et al. reported that the same complex can be prepared from another ruthenium precursor, $RuCl_2(PPh_3)_4$, and xantphos.[14]

Next, the ligand exchange reactions of PPh_3 of complex **2a** with triphenylphosphite and DMSO were next examined (Scheme 2). Initially, the reaction of **2a** with triphenylphosphite was examined. Treatment of complex **2a** with five equivalents of $P(OPh)_3$ in refluxed $CHCl_3$ afforded $RuCl_2$(xantphos){$P(OPh)_3$} (**2b**) in 85% yield as a yellow crystals. The structure of **2b** was determined from the $^{31}P\{^1H\}$ NMR spectrum and X-ray analysis just as with **2a**, indicating that PPh_3 was replaced by $P(OPh)_3$

without loss of the geometry. An ORTEP diagram of **2b** is shown in Fig. 2. Therefore, the less steric repulsion in this complex than in the similar complex **2a** leads to a shorter Ru-P bond length (Ru-$P_{P(OPh)3}$ = 2.1625(13) Å, Ru-P_{PPh3} = 2.3338(11) Å), and the xanthene ring of **2b** is almost flat while that of **2a** was slightly bent. These are presumably due to both the smaller cone angles of $P(OPh)_3$ (125°) than PPh_3 (145°) and larger π-acceptor ability of $P(OPh)_3$ compared to PPh_3.[15] The splitting pattern of **2b** on the $^{31}P\{^1H\}$ NMR spectrum was similar to that of **2a**. Thus, a doublet appeared at 40.1 ppm, and a triplet appeared at 124.4 ppm (J_{PP} = 43.4 Hz). Treatment of **2a** with DMSO afforded $RuCl_2$(xantphos)(DMSO) (**2c**) in 46% yield as a yellow precipitate. We considered that *trans*-$RuCl_2$(xantphos)(DMSO) **2c** was obtained after the reaction and that *cis*-$RuCl_2$(xantphos)(DMSO) (**2c'**) was formed during recrystallisation of the obtained complex with $CHCl_3$/DMSO/Et_2O. The chemical shifts on $^{31}P\{^1H\}$ NMR spectra of **2c** and **2c'** are apparently different: a singlet of **2c** was observed at 35.4 ppm, and that of **2c'** was obtained at 47.9 ppm. Interestingly, the reaction of *cis*-$RuCl_2(DMSO)_4$ with xantphos in refluxed toluene afforded a mixture of **2c** and **2c'**. The quantity of **2c** relative to **2c'** from $RuCl_2$(xantphos)(PPh_3) with DMSO in $CDCl_3$ was apparently higher than that from *cis*-$RuCl_2(DMSO)_4$. This phenomenon was not observed in Kharat's report of **2c'**, which described the reaction of $RuCl_2(DMSO)_4$ and xantphos in CH_2Cl_2.[11] An

ORTEP diagram of **2c'** is shown in Fig. 3. In complex **2c'**, xantphos behaves as a *cis*-chelate coordinated ligand. DMSO is coordinate to the ruthenium atom on a sulfur atom, and the S-Ru-O(xantphos) bond is close to line ($S\text{-}Ru\text{-}O_{xantphos}$ = 177.6°). The xanthene ring is apparently bent due to the cis-coordination of xantphos ligand to the ruthenium centre. The coordination strength of ligand L (PPh_3, $P(OPh)_3$, DMSO) in $RuCl_2$(xantphos)L was checked in the NMR experiments as follows, and the results are summarized in Table 1. The complex **2a** was reacted with an excess amount of DMSO to give a mixture of **2a**, **2c**, and **2c'** (**2a** : **2c** : **2c'** = 23 : 71 : 6). On the other hand, when **2c'** was treated with one equivalent of PPh_3 in refluxed $CDCl_3$ for 3 h, the complex **2a** was obtained as a main product (**2a** : **2c'** = 94 : 6). These results suggested that PPh_3 ligand was more strongly coordinated to Ru centre than DMSO. Comparing the coordination ability between PPh_3 and $P(OPh)_3$ revealed that $P(OPh)_3$ was more coordinated onto the ruthenium centre than PPh_3 ligand. Thus, the reaction of **2b** with one equivalent or even with an excess amount of PPh_3 caused no reaction. Therefore, the magnitude of bond strength of Ru-L in the present system is $P(OPh)_3$>PPh_3>DMSO in the same order as π-acidity of these ligands.[15]

With xantphos-$RuCl_2$ complexes **2a, 2b**, and **2c'** in hand, the catalytic activity of these complexes in the addition reaction of 2-phenylbenzoic acid (**3**) onto 4-allylanisole (**4a**)

was investigated, and selected results are summarised in Table 2. In the presence of 5 mol % Ru of complex **2a**, the reaction was carried out in toluene at 100ºC for 42 h to give the desired ester **5a** in 89% yield (entry 1). The use of complex **2b** enabled us to perform the reaction under milder conditions (at 80ºC), and the product yield was increased to 99% (entry 2). The use of DMSO complex **2c'** afforded **5a** in 76% yield (entry 3). Combined with the ligand exchange reactions described above, it seems that the less dissociated ligand L should be important for the high catalytic efficiency. With catalyst **2b**/2AgOTf (5 mol % Ru), some unactivated olefins were subjected to the addition of carboxylic acid **3**. As in entries 4-7, allylbenzene (**4b**), 4-phenyl-1-butene (**4c**), 1-octene (**4d**), and cyclohexene (**4e**) were good substrates to obtain the corresponding esters in 66%, 90%, 80%, and 86% yields, respectively. Catalytic activity of **2b**/2AgOTf was as high as that of our previously reported ruthenium catalysis, [(*p*-cymene)$RuCl_2$]$_2$/4AgOTf/xantphos.[13] The catalytic activity of TfOH and AgOTf was tested since a similar reaction is catalysed by TfOH[16] or AgOTf[17] (Scheme 3). The reaction of **3** with **4a** in the presence of TfOH performed under the same reaction conditions as those in Table 2 afforded no desired ester **5a**, while 62% yield of ester **5a** was obtained at room temperature.[18] On the other hand, no reaction took place when 10 mol % of AgOTf was used as a catalyst. These results suggested that the ruthenium

triflate complexes generated by the treatment of **2b** with AgOTf should show the good catalytic efficiency, probably due to a suitable quantity of TfOH for the activation of alkenes being formed by the reaction of **2b** with 2-phenylbenzoic acid.[19]

Conclusions

A facile synthetic procedure involving the $RuCl_2$(xantphos)L (L = PPh_3, DMSO, $P(OPh)_3$) family has been developed. $RuCl_2$(xantphos)(PPh_3) can be synthesised from commercially available $RuCl_2(PPh_3)_3$ and xantphos by mixing in refluxing $CHCl_3$ in high yield. Furthermore, PPh_3 can be readily exchanged with $P(OPh)_3$ and DMSO without loss of the core $RuCl_2$(xantphos) structure, though *trans*-$RuCl_2$(xantphos)DMSO was considered to be isomerised to the *cis*-coordination complex during the recrystallisation. The strong coordination of $P(OPh)_3$ to the ruthenium centre led to flat geometry of the xanthene ring and high catalytic activity for the reaction of carboxylic acid with olefins. The catalytic activities of this family for the other reactions are being investigated in our laboratory.

Acknowledgement

We would like to dedicate this article to the memory of our mentor, the late Professor

Yoshihiko Ito. This work was partially supported by Doshisha University's Research Promotion Fund, and a Grant to RCAST at Doshisha University from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This work was supported by a Grant-in-Aid for Young Scientists (Start-up: No. 20850034) from JSPS.

Experimental Section

General: All solvents are dried and distilled by means of the usual method.[20] Xantphos was perchased from Sigma Aldrich and used without further purifications. $P(OPh)_3$ was perchased from TCI and used without further purifications. $RuCl_2(PPh_3)_3$ was prepared according to the literature procedure.[21] ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian Mercury300-N plus (300.0 MHz for ^1H and 121.4 MHz for $^{31}P\{^1H\}$). FAB MS spectra were recorded on JEOL Mstation JMS-700 spectrometer. X-ray crystallography was performed by use of RIGAKU SCXmini and R-AXIS RAPID system. All calculations were performed using the Yadokari-XG, software for crystal structure analyses.[22,23]

Synthesis of $RuCl_2$(xantphos)PPh_3 (2a)[14]

A dried three-necked round bottom flask equipped with a condenser had $RuCl_2(PPh_3)_3$ (**1**) (1.156 g, 1.2 mmol), xantphos (0.7630 g, 1.32 mmol) and dry $CHCl_3$ (50 mL) added under argon atmosphere. The reaction mixture was refluxed for 3 h with stirring. After the reaction mixture was cooled to

room temperature, the solvent was removed to ca. 5 mL under reduced pressure, and Et_2O (15 mL) was then added slowly. The resulting mixture was kept until a large enough amount of crystalline solid was formed. The resulting crystalline solid was filtered, washed three times with 5 mL of benzene, and dried in vacuo to give $RuCl_2$(xantphos)PPh_3 **2a** (95%). M.p. = 215-217°C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.71 (6H, m, $C(CH_3)_2$), 6.75-6.81 (6H, m, ArH), 7.04-7.30 (33H, ArH), 7.47-7.50 (2H, m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 34.2 (2P, d, J_{pp} = 30.6 Hz, xantphos-P), 55.9 (1P, t, J_{pp} = 30.6 Hz, PPh_3-P). FAB-MS (M^++PPh_3) 1012 (m/z). HRMS (M^+–PPh_3) calcd : 1012.1260 , found : 1012.1273. Crystallographic data of **2a**: ($C_{57}H_{47}Cl_2OP_3Ru$), M = 1012.82, monoclinic, a = 10.3028(14) Å, b = 24.773(3) Å, c = 18.654(3) Å, β = 102.880(3)°, V = 4641.4(12) Å^3, space group $P2_1/n$ (No. 14), Z = 4, 46546 reflections collected, 10572 unique (R_{int} = 0.0449), R_1 (I>2σ(I)) = 0.0756, wR_2 (I>2σ(I)) = 0.1401 (all data).

Synthesis of $RuCl_2$(xantphos){P{(OPh)$_3$} (2b)

To an 80 mL schlenk tube was added $RuCl_2$(xantphos)PPh_3 **2a** (101.2 mg, 0.1 mmol), triphenylphosphite (155.2 mg, 0.5 mmol) and dry $CHCl_3$ (5 mL) in argon atmosphere. The reaction mixture was heated at 80 ºC (bath temp.) and stirred for 3 h. After the reaction mixture was cooled to room temperature, the solvent was removed to ca. 1 mL under reduced pressure, and dry Et_2O (15 mL) was then added with stirring to form yellow precipitation. The obtained solid was filtered and washed with three times of 1 mL of Et_2O. The residual solid was dried in vacuo to give

$RuCl_2$(xantphos){$P(OPh)_3$} **2b**. M.p. = 281.4-282.1°C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.79 (6H, m, $C(CH_3)_2$), 6.43-6.46 (6H, m, ArH), 6.84-6.93 (9H, m, ArH), 7.11-7.32 (16H, ArH), 7.61-7.63 (2H, m, ArH), 7.71-7.77 (8H, m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 40.1 (2P, d, J_{pp} = 43.4 Hz, 2P of xantphos), 124.4 (1P, t, J_{pp} = 43.4 Hz, $P(OPh)_3$). HRMS (FAB, M^+) calcd : 1060.1108, found : 1060.1123. Crystallographic data of **2b**: ($C_{57}H_{47}Cl_2O_4P_3Ru \cdot CHCl_3$), M = 1180.19, triclinic, a = 11.5019(3) Å, b = 13.0630(3) Å, c = 18.7270(5) Å, α = 84.429(2)°, β = 73.328(2)°, γ = 79.099(2)°, V = 2644.06(12) Å^3, space group P-1 (No.2), Z = 2, 26596 reflections collected, 9288 unique (R_{int} = 0.0779), R_1 (I>2σ(I)) = 0.0760, wR_2 (I>2σ(I)) = 0.2056 (all data).

Synthesis of $RuCl_2$(xantphos)(DMSO) (2c')[12]

To an 80 mL schlenk tube was added $RuCl_2$(xantphos)PPh_3 **2a** (101.2 mg, 0.1 mmol), dimethyl sulfoxide (1 mL) and dry $CHCl_3$ (4 mL) in argon atmosphere. The reaction mixture was heated at 80 ºC (bath temp.) and stirred for 3 h. After the reaction mixture was cooled to room temperature, the solvent was removed to ca. 1 mL under reduced pressure, and dry Et_2O (15 mL) was then added with stirring to form yellow precipitation. The obtained solid was filtered, and the residue was washed with tree times of 1 mL of Et_2O. The residual solid was dried in vacuo to give a mixture of *cis*- and *trans*-$RuCl_2$(xantphos)(DMSO) (**2c'** and **2c**), and the recrystallization of this product afforded **2c'**. M.p. = 242.3-242.8°C (dec).

2c': ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.70 (6H, s, $C(CH_3)_2$), 2.77 (6H, s, $S(CH_3)_2$), 6.59-6.64 (4H, m, ArH), 6.84-6.89 (2H, m, ArH), 6.98-7.04 (4H, m, ArH), 7.28-7.40 (10H, m, ArH), 7.42-7.57 (2H, m, ArH), 7.98-8.04 (4H, m, ArH). ^{31}P{1H} NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 47.9 (s, P of xantphos). FAB-MS (M–Cl) 793 (m/z). **2c:** ^{1}P{1H} NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 35.4 (s, P of xantphos). Crystallographic data of **2c'**: (C42H38Cl2O2P2RuS1 · CH6OS), monoclinic, M = 906.81, a = 13.8705(3) Å, b = 14.5270(4) Å, c = 21.6728(7) Å, β = 107.968(2)o, V = 4154.0(2) Å3, space group P21/c (No. 14), Z = 4, 40636 reflections collected, 7566 unique (Rint = 0.1723), R1 (I>2 σ (I)) = 0.1323, wR2 (I>2σ(I)) = 0.2777 (all data).

Notes and references

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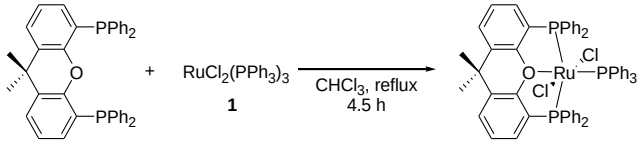
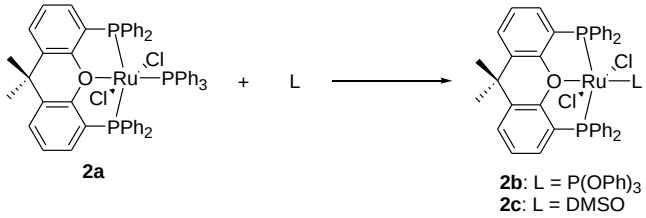
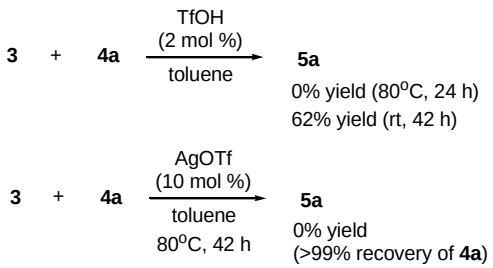
23 CCDC 1035410 (for **2a**), 1035411 (for **2b**) and 1035412 (for **2c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Scheme 1 Preparation of $RuCl_2$(xantphos)(PPh_3) (**2a**).



Scheme 2 Reaction of **2a** with $P(OPh)_3$ and DMSO.



Scheme 3 Catalytic activity of TfOH and AgOTf.

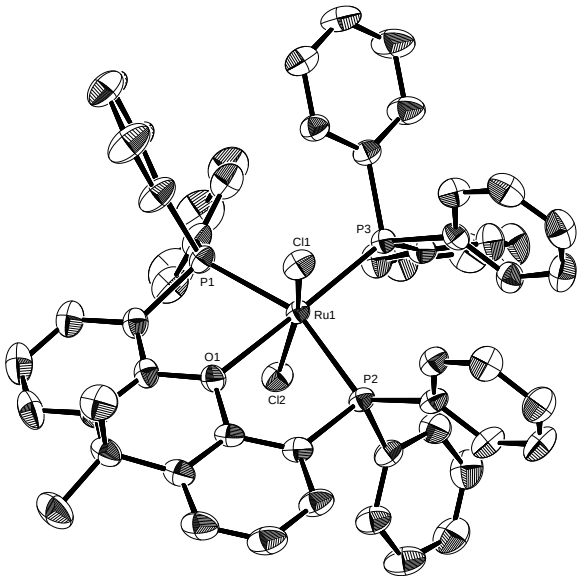


Fig.1 ORTEP diagram of **2a**. All hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond length (Å) and angles: Ru-P1 2.4088(10), Ru-P2 2.3355(10), Ru-P3 2.3338(9), Ru-O1 2.315(2), P3-Ru-O1 174.48(8), P1-Ru-P2 156.33(3).

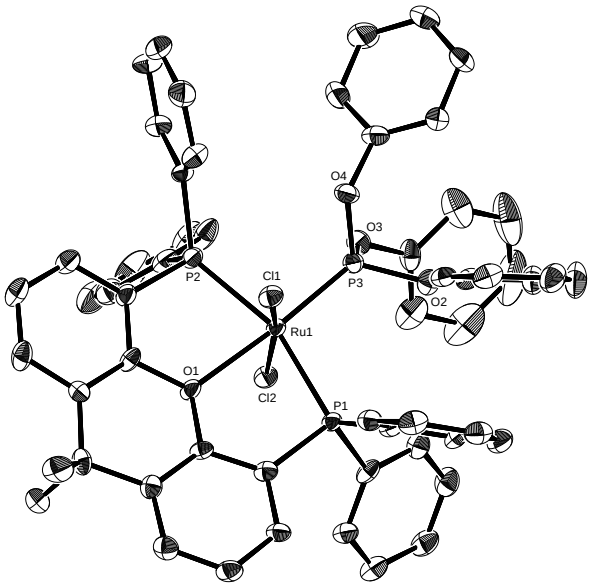


Fig.2 ORTEP diagram of **2b**. All hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond length (Å) and angles: Ru-P1 2.3381(10), Ru-P2 2.3225(11), Ru-P3 2.1625(14), Ru-O1(2.265(3),P3-Ru-O1 175.83(7), P1-Ru-P2 161.23(5), Cl1-Ru-Cl2 167.86(4).

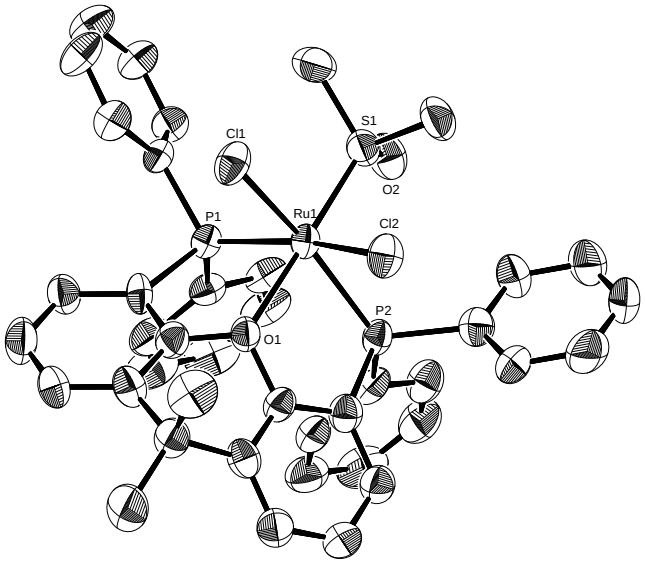
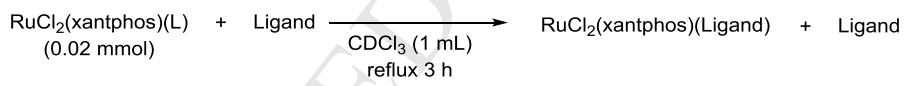


Fig.3 ORTEP diagram of **2c'**. All hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond length (Å) and angles: Ru1-S1 2.213(2), Ru1-P1 2.271(2), Ru-P2 2.339(2), Ru1-O1 2.183(5), Cl1-Ru-Cl2 85.40(8), P1-Ru-P2 103.78(8), S1-Ru1-O1 177.58(19).

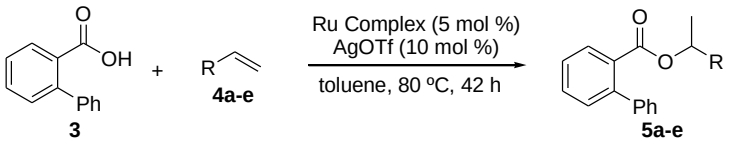
Table 1 Ligand exchange reactions of $RuCl_2$(xantphos)L with external ligands.[a]

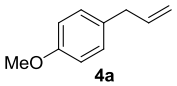
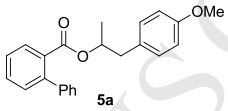
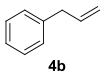
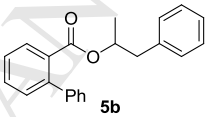
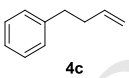
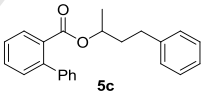
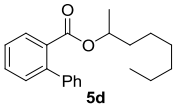
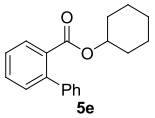


entry	complex	ligand	Yield[b]
1	**2a**	DMSO (0.2 mL)	**2a** (23%) : **2c** (71%) : **2c'** (6%)
2	**2c'**	PPh_3 (1 eq)	**2a** (94%) : **2c** (6%) : **2c'** (0%)
3	**2b**	PPh_3 (1 eq)	**2b** (100%) : **2a** (0%)
4	**2b**	PPh_3 (50 eq)	**2b** (100%) : **2a** (0%)

[a] Reaction conditions: Ru complex (0.02 mmol) and Ligand were stirred in refluxed $CDCl_3$ for 3 h, and then the reaction mixture was cooled to ambient temperature. [b] Determined by ^{31}P NMR.

Table 2 Reaction Products of 2-Phenylbenzoic Acid with Olefins in the Presence of Ruthenium Catalysis[a]



Entry	Ru Complex	Olefin	Product	Yield (%)[b]
1[c]	**2a**			89
2	**2b**	 **4a**	 **5a**	99
3[c]	**2c**			76
4	**2b**	 **4b**	 **5b**	66
5	**2b**	 **4c**	 **5c**	90
6	**2b**	 **4d**	 **5d**	80
7	**2b**	 **4e**	 **5e**	86

[a] Reaction conditions: Ru complex (0.05 mmol) and AgOTf (0.10 mmol) were stirred in refluxed toluene for 3 h, and then the reaction mixture was cooled to ambient temperature. To the reaction mixture, nucleophile (1.0 mmol) and olefin (3.0 mmol) was added and degassed by freeze-pump-thaw cycle (3 cycles). The solution was stirred at 80 ºC for 42 h. [b] Yields were determined by ^{1}H NMR by using anthracene as an internal standard. [c] at 100ºC.

Highlights

- $RuCl_2$(xantphos)(PPh_3) was readily synthesized by the mixing of $RuCl_2(PPh_3)_3$ with xantphos in refluxing $CHCl_3$.
- $RuCl_2$(xantphos)(PPh_3) was readily converted into $RuCl_2$(xantphos)($P(OPh)_3$) and $RuCl_2$(xantphos)(DMSO) through the ligand exchange reaction.
- $RuCl_2$(xantphos)($P(OPh)_3$) showed the highest catalytic activity in the addition reaction of carboxylic acids with olefins among these three complexes.

Supplementary Data for

Synthesis of $RuCl_2$(Xantphos)L (L = PPh_3, $P(OPh)_3$, DMSO) Complexes, and their Catalytic Activity for the Addition of 2-Phenylbenzoic Acid onto Olefins

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Synthesis of $RuCl_2$(xantphos)PPh_3 (2a)

A dried three-necked round bottom flask equipped with a condenser had $RuCl_2(PPh_3)_3$ (**1**) (1.156 g, 1.2 mmol), xantphos (0.7630 g, 1.32 mmol) and dry $CHCl_3$ (50 mL) added under argon atmosphere. The reaction mixture was refluxed for 3 h with stirring. After the reaction mixture was cooled to room temperature, the solvent was removed to ca. 5 mL under reduced pressure, and Et_2O (15 mL) was then added slowly. The resulting mixture was kept until a large enough amount of crystalline solid was formed. The resulting crystalline solid was filtered, washed three times with 5 mL of benzene, and dried in vacuo to give $RuCl_2$(xantphos)PPh_3 **2a** (95%). M.p. = 215-217°C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.71 (6H, m, $C(CH_3)_2$), 6.75-6.81 (6H, m, ArH), 7.04-7.30 (33H, ArH), 7.47-7.50 (2H, m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 34.2 (2P, d, J_{pp} = 30.6 Hz, xantphos-P), 55.9 (1P, t, J_{pp} = 30.6 Hz, PPh_3-P). FAB-MS (M^++PPh_3) 1012 (m/z). HRMS (M^+–PPh_3) calcd : 1012.1260 , found : 1012.1273. Crystallographic data of **2a**: ($C_{57}H_{47}Cl_2OP_3Ru$), M = 1012.82, monoclinic, *a* = 10.3028(14) Å, *b* = 24.773(3) Å, *c* = 18.654(3)

Å, β = 102.880(3)°, V = 4641.4(12) Å^3, space group $P2_1/n$ (No. 14), Z = 4, 46546 reflections collected, 10572 unique (R_{int} = 0.0449), R_1 ($I>2\sigma(I)$) = 0.0756, wR_2 ($I>2\sigma(I)$) = 0.1401 (all data).

Synthesis of $RuCl_2$(xantphos){P{(OPh)$_3$}} (2b)

To an 80 mL schlenk tube was added $RuCl_2$(xantphos)PPh_3 **2a** (101.2 mg, 0.1 mmol), triphenylphosphite (155.2 mg, 0.5 mmol) and dry $CHCl_3$ (5 mL) in argon atmosphere. The reaction mixture was heated at 80 ºC (bath temp.) and stirred for 3 h. After the reaction mixture was cooled to room temperature, the solvent was removed to ca. 1 mL under reduced pressure, and dry Et_2O (15 mL) was then added with stirring to form yellow precipitation. The obtained solid was filtered and washed with three times of 1 mL of Et_2O. The residual solid was dried in vacuo to give $RuCl_2$(xantphos){P(OPh)$_3$} **2b**. M.p. = 281.4-282.1°C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.79 (6H, m, C(CH_3)$_2$), 6.43-6.46 (6H, m, ArH), 6.84-6.93 (9H, m, ArH), 7.11-7.32 (16H, ArH), 7.61-7.63 (2H, m, ArH), 7.71-7.77 (8H, m, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 40.1 (2P, d, J_{pp} = 43.4 Hz, 2P of xantphos), 124.4 (1P, t, J_{pp} = 43.4 Hz, P(OPh)$_3$). HRMS (FAB, M^+) calcd : 1060.1108, found : 1060.1123. Crystallographic data of **2b**: ($C_{57}H_{47}Cl_2O_4P_3Ru \cdot CHCl_3$), M = 1180.19, triclinic, a = 11.5019(3) Å, b = 13.0630(3) Å, c = 18.7270(5) Å, α = 84.429(2)°, β = 73.328(2)°, γ = 79.099(2)°, V = 2644.06(12) Å^3, space group P-1 (No.2), Z = 2, 26596 reflections collected, 9288 unique (R_{int} = 0.0779), R_1 ($I>2\sigma(I)$) = 0.0760, wR_2 ($I>2\sigma(I)$) = 0.2056 (all data).

Synthesis of $RuCl_2$(xantphos)(DMSO) (2c')

To an 80 mL schlenk tube was added $RuCl_2$(xantphos)PPh_3 **2a** (101.2 mg, 0.1 mmol), dimethyl sulfoxide (1 mL) and dry $CHCl_3$ (4 mL) in argon atmosphere. The reaction mixture was heated at 80 ºC (bath temp.) and stirred for 3 h. After the reaction mixture was cooled to room temperature, the solvent was removed to ca. 1 mL under reduced pressure, and dry $E_{t2}O$ (15 mL) was then added with stirring to form yellow precipitation. The obtained solid was filtered, and the residue was washed with tree times of 1 mL of Et_2O. The residual solid was dried in vacuo to give a mixture of *cis*- and

trans-$RuCl_2$(xantphos)(DMSO) (**2c'** and **2c**), and the recrystallization of this product afforded **2c'**. M.p. = 242.3-242.8°C (dec).

2c': ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.70 (6H, s, $C(CH_3)_2$), 2.77 (6H, s, $S(CH_3)_2$), 6.59-6.64 (4H, m, ArH), 6.84-6.89 (2H, m, ArH), 6.98-7.04 (4H, m, ArH), 7.28-7.40 (10H, m, ArH), 7.42-7.57 (2H, m, ArH), 7.98-8.04 (4H, m, ArH). ^{31}P{1H} NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 47.9 (s, P of xantphos). FAB-MS (M–Cl) 793 (m/z). **2c:** ^{1}P{1H} NMR ($CDCl_3$, 121.4 MHz) δ (ppm) = 35.4 (s, P of xantphos). Crystallographic data of **2c'**: (C42H38Cl2O2P2RuS1 · CH6OS), monoclinic, M = 906.81, a = 13.8705(3) Å, b = 14.5270(4) Å, c = 21.6728(7) Å, β = 107.968(2)o, V = 4154.0(2) Å3, space group P21/c (No. 14), Z = 4, 40636 reflections collected, 7566 unique (Rint = 0.1723), R1 (I>2 σ (I)) = 0.1323, wR2 (I>2σ(I)) = 0.2777 (all data).

Typical procedure of addition Reaction of Nucleophiles onto olefins catalyzed by $RuCl_2$(xantphos){$P(OPh_3)$}/2AgOTf: To a dried 80 mL schlenk tube was added $RuCl_2$(xantphos){$P(OPh)_3$} **2b** (0.0531 g, 0.05 mmol), AgOTf (0.0257 g, 0.1 mmol) and 3.0 mL of toluene under argon atmosphere. The catalyst mixture was degassed by three times of Freeze-Pump-Thaw cycle, and then the tube was filled with argon again. The reaction mixture was stirred at 110 ºC (bath temp.) for 3 h. After cooling to ambient temperature, 2-phenylbenzoic acid **3** (0.1982 g, 1.0 mmol) and olefin (2.5 mmol) was added to the resulting mixture. The solution was degassed by three times of Freeze-Pump-Thaw cycle and then filled with argon again. The reaction mixture was stirred at 80 ºC (bath temp.) for 42 h. The product yield was determined by ^{1}H NMR spectrum in $CDCl_3$ using anthrathene as an internal standard. The product was purified through silica gel column chromatography (Hexane/Ethyl Acetate = 10/1). All products were characterized by ^{1}H and ^{13}C NMR and FAB MS spectra according to the previous our report.[S1]

1-(4-Methoxyphenyl)propan-2-yl 2-phenylbenzoate (5a). Yielded from **3** with 4-allylanisole (**4a**) as colorless viscous oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (3H, d, *J* = 6.3 Hz, CH_3), 2.84 (1H, dd, *J* = 6.9 Hz, 13.5 Hz, 1/2CH_2), 3.01 (1H, dd, *J* = 6.3 Hz, 13.8 Hz, 1/2CH_2), 3.77 (3H, s, MeO), 5.31 (1H, sextet, *J* = 6.9 Hz, OCH), 6.77-6.87 (2H, m, aromatics), 7.14-7.17 (2H, m, aromatics), 7.39-

7.44 (3H, m, aromatics), 7.51-7.56 (1H, m, aromatics), 7.99-8.02 (1H, m, aromatics). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.5, 130.2, 129.3, 128.5, 113.5, 72.2, 55.1, 41.3, 19.4. FAB-MS (*m*/*z*) = 347 [M + H^+]. CAS Registry No: 1232133-20-8.

1-Phenylpropan-2-yl 2-phenylbenzoate (5b). Yielded from **3** with allylbenzene (**4b**) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04 (3H, d, *J* = 6.3 Hz, CH_3), 2.53 (1H, dd, *J* = 6.9 Hz, 13.5 Hz, 1/2CH_2), 2.76 (1H, dd, *J* = 6.3 Hz, 13.8 Hz, 1/2CH_2), 5.13 (1H, sextet, *J* = 6.3 Hz, OCH), 7.08-7.11 (2H, m, aromatics), 7.16-7.29 (5H, m, aromatics), 7.32-7.41 (5H, m, aromatics), 7.47-7.52 (1H, m, aromatics), 7.69-7.71 (1H, m, aromatics). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.0, 142.1, 141.3, 137.3, 131.5, 130.8, 130.4, 129.4, 129.3, 128.4, 128.2, 128.0, 127.1, 126.9, 126.3, 72.4, 41.8, 18.9. FAB-MS (*m*/*z*) = 317 [M + H^+]. CAS Registry No: 1232133-21-9.

1-Phenylbutan-3-yl 2-phenylbenzoate (5c). Yielded from **3** with 4-phenyl-1-butene (**4c**) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (3H, d, *J* = 6.3 Hz, CH_3), 1.64 (2H, m, CH_2), 2.42 (2H, m, CH_2), 4.92 (1H, sextet, *J* = 6.3 Hz, OCH), 7.06-7.43 (8H, m, aromatics), 7.50-7.53 (1H, m, aromatics), 7.78 (1H, d, *J* = 6.8 Hz, aromatics). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.6, 142.4, 141.8, 132.0, 131.2, 130.9, 129.8, 128.8, 128.6, 128.5, 128.3, 127.5, 127.4, 126.1, 71.8, 37.7, 31.8, 19.8. FAB-MS (*m*/*z*) = 317 [M + H^+]. CAS Registry No: 1232133-23-1.

2-Octyl 2-phenylbenzoate (5d). Yielded from **3** with 1-octene (**4d**) as light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78 (3H, t, *J* = 7.5 Hz, CH_3), 0.84-0.96 (2H, m, CH_2), 1.05 (3H, d, *J* = 6.3 Hz, CH_3), 1.14-1.48 (9H, m, 4CH_2), 4.92 (1H, sextet, *J* = 6.3 Hz, OCH), 7.33-7.54 (8H, m, aromatics), 7.81-7.85 (1H, m, aromatics). ^{13}C NMR ($CDCl_3$, 75 MHz) δ168.6, 142.4, 141.8, 132.2, 131.1, 130.9, 130.8, 129.7, 128.7, 128.2, 128.2, 127.4, 127.3, 72.3, 35.9, 33.4, 32.1, 32.1, 29.5, 26.8, 25.5, 25.2, 23.0, 23.0, 22.9, 19.8, 14.5, 9.9. FAB-MS (*m*/*z*) = 311 [M + H^+]. CAS Registry No: 1232133-24-2.

Cyclohexyl 2-phenylbenzoate (5e). Yielded from **3** with cyclohexene (**4e**) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07-1.31 (5H, m, cyclohexyl-H), 1.41 (5H, m, cyclohexyl-H), 4.73-4.80 (1H, m, OCOCH), 7.29-7.48 (8H, m, aromatics), 7.51-7.81 (1H, m, aromatics). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.1, 142.0, 141.4, 131.8, 130.7, 130.5, 129.5, 128.3, 127.9, 127.0, 126.9, 73.4, 31.2, 25.3, 23.6. FAB-MS (*m*/*z*) = 280 [M^+]. CAS Registry No: 1232133-25-3.

References

S1. Y. Oe, T. Ohta, Y. Ito, *Tetrahedron Lett.* 2010, **51**, 2806.