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[RuCl$_2$(η^6-*p*-cymene)] complexes bearing phosphinous acid ligands: preparation, application in C–H bond functionalization and mechanistic investigations†

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A series of [RuCl$_2$(η^6-*p*-cymene)] complexes bearing phosphinous acid (PA) ligands have been straightforwardly prepared from the dimer [RuCl$_2$(*p*-cymene)]$_2$ and secondary phosphine oxides (SPOs) and fully characterized. The steric parameter quantification of PAs, other L ligands and η^6-*p*-cymene allowed a better comprehension of the coordination chemistry of these types of complexes and explained the absence of coordination in the case of bulky SPOs such as Ad$_2$P(O)H. These complexes were tested in the C–H activation/functionalization of 2-phenylpyridine and a good activity was obtained at 80 °C for the complex exhibiting the highest steric bulk. A study on halide effects, either on the ruthenium complex or for the aryl halide partner, has also been carried out showing drastic differences. Further investigations on halide effects were performed notably by using a cationic ruthenacycle which was found to be an intermediate for the reaction. In order to rationalize the role played by the phosphinous acid, a mechanism involving a concerted metallation deprotonation favored by a phosphinito species has been proposed.

Introduction

Considered for a long time as a main challenge in organic synthesis, the C–H activation/functionalization has emerged recently as a powerful tool to prepare complex molecules starting from readily available raw materials.[1] In this quest, the use of transition metal catalysis is at the origin of groundbreaking discoveries and now various catalytic systems using palladium,[2] rhodium,[3] ruthenium,[4] copper,[5] platinum,[6] nickel,[7] cobalt,[8] f-block elements,[9] *etc.* are recognized as highly efficient for C–H bond activation. In these systems, major advances were accomplished by clear mechanistic studies which allowed for deeper understanding of the mechanism, notably the role of ligands and/or additives. For instance, Catellani developed a Pd-catalyzed regioselective C–H bond functionalization of arenes using norbornene as a covalent linker.[10] Alternatively, it was demonstrated that C–H activation could occur according to a σ-bond metathesis pathway,[11] so called concerted metallation deprotonation (CMD). In such a process, the intermolecular abstraction of the proton by acetato ligands favors the metallacycle formation.[12]

Whereas pioneering studies on catalytic C(sp^2)–H activation were carried out using Ru-based complexes,[13] catalytic systems using Pd or Rh have attracted much attention over the last decade. Nevertheless, interesting Ru-based catalytic systems have been reported in the literature mainly using the dimer [RuCl$_2$(*p*-cymene)]$_2$ in association with carboxylate additives.[4,14] During our research involving secondary phosphine oxides (SPO) and phosphinous acids (PA) as ligands in transition metal catalysis,[15] the catalytic system using [RuCl$_2$(*p*-cymene)]$_2$ and SPO developed by Ackermann in 2005 caught our attention (Scheme 1).[16] A Ru(II) complex, prepared *in situ* from [RuCl$_2$(η^6-*p*-cymene)]$_2$ and a sterically hindered di-adamantylphosphine oxide, was found to be very efficient for *ortho* C–H bond activation of the 2-phenylpyridine **1** and coupling with chlorobenzene to yield quantitatively compound **3** without any traces of monoarylated **2**. Moreover, this catalytic system showed a high efficiency for various substrates.[17] We wondered about the role played by the SPO or its tautomeric phosphinous acid form in the C–H activation process. Whereas several mechanistic hypothesis have been postulated,[4,17c] none of them was further investigated.

Therefore, we wished to investigate the mechanism of this C–H bond activation/functionalization through the synthesis of well-defined [RuCl$_2$(η^6-*p*-cymene)(PA)] complexes and to study their performances in catalysis. Control experiments

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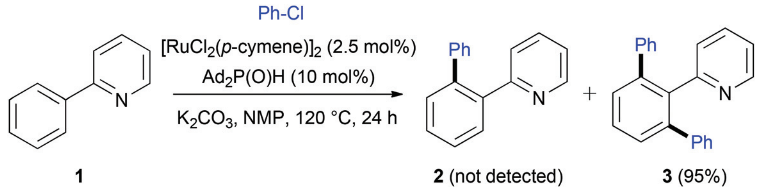


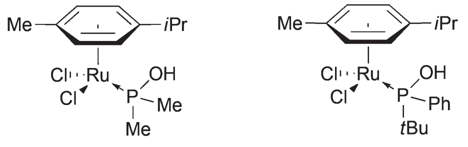
Scheme 1 C–H activation/functionalization mediated by [RuCl$_2$(*p*-cymene)]$_2$ and SPO.

have been carried out to corroborate the mechanistic proposal. The results of our study are reported herein.

Results and discussion

We started to study the coordination chemistry of SPOs with [RuCl$_2$(*p*-cymene)]$_2$. The synthesis of [RuCl$_2$(η^6-arene)(PA)] has been previously reported in the literature,[18] notably two complexes [Ru(η^6-*p*-cymene)Cl$_2$(PA)] **5a** and **5l** were already described by the groups of Tyler[19] and Leung[20] respectively (Fig. 1) and **5a** has been successfully applied to nitrile hydration.[19,21]

Following the same procedure, [RuCl$_2$(*p*-cymene)]$_2$ was treated with various secondary phosphine oxides **4** in THF at 25 °C to afford the expected complexes **5** (Table 1).[22] Of note, in dichloromethane or toluene, the reaction was sluggish compared to THF. Excepted for Cy$_2$P(O)H **4b** which required 24 h of reaction, other SPOs, either symmetrical ones (entries 2–4) or unsymmetrical ones (entries 7–11), were found very reactive. After only 2–3 h, complexes **5** were isolated in almost quantitative yields. Surprisingly, with bulky SPOs such as Ad$_2$P(O)H **4f** or *t*Bu$_2$P(O)H **4g**, we were unable to obtain the corresponding complexes **5** (entries 5 and 6). Despite prolonged reaction times and/or heating to 110 °C, their formation could not be detected by NMR spectroscopy.

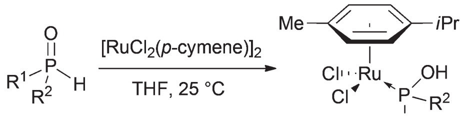


5a

5l

Fig. 1 [RuCl$_2$(η^6-*p*-cymene)(PA)] complexes described in the literature.

Table 1 Preparation of well-defined [RuCl$_2$(η^6-*p*-cymene)(PA)] complexes[a]



4b-l

5b-l

Entry	R^1	R^2	*t* (h)	Complex	Yield (%)
1	Cy	Cy	24	**5b**	89
2	Ph	Ph	2	**5c**	96
3	*p*-F-C$_6$H$_4$	*p*-F-C$_6$H$_4$	6	**5d**	84
4	3,5-Me$_2$-C$_6$H$_3$	3,5-Me$_2$-C$_6$H$_3$	3	**5e**	91
5[b]	Ad	Ad	24	**5f**	NR
6[b]	*t*Bu	*t*Bu	24	**5g**	NR
7	Me	Ph	3	**5h**	74
8	*n*Bu	Ph	3	**5i**	53
9	Bn	Ph	3	**5j**	88
10	Cy	Ph	3	**5k**	98
11	*t*Bu	Ph	3	**5l**	99

[a] Reaction conditions: [RuCl$_2$(η^6-*p*-cymene)]$_2$, SPO (2.2 equiv.), THF (0.5 M), 25 °C. [b] Reaction performed in 1,4-dioxane at 110 °C. NR = no reaction.

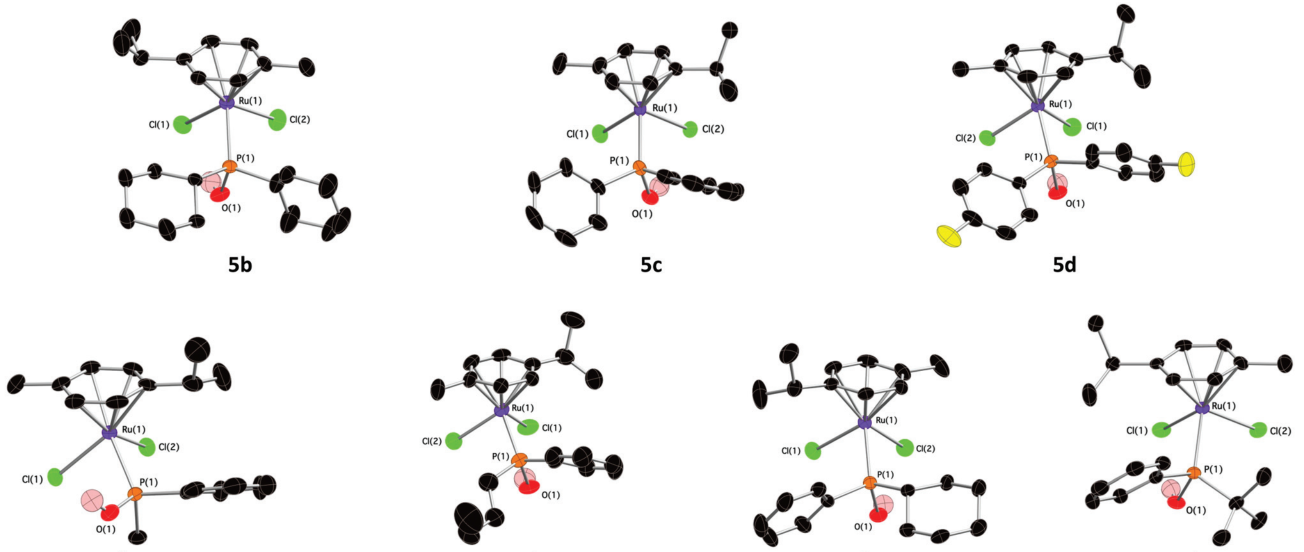
The well-defined [RuCl$_2$(η^6-*p*-cymene)(PA)] **5** were characterized by ^{1}H,[23] ^{13}C, and ^{31}P NMR spectroscopies, as well as mass spectrometry. The coordination of the phosphinous acid to the metallic center through the phosphorus atom was confirmed by NMR spectroscopy and the absence of ^1J(P,H) coupling. Moreover, ^{31}P NMR spectroscopy showed new resonances between 105–130 ppm with a significant shift to a lower field compared to SPOs ($\Delta\delta$ between 68 and 89 ppm, Table 2).

To establish unambiguously the structure of [RuCl$_2$(η^6-*p*-cymene)(PA)] complexes **5**, suitable crystals for single-crystal X-ray diffraction studies were obtained for most of the compounds. As depicted in Fig. 2, all complexes adopt a distorted octahedral structure with the expected three-legged pseudo-tetrahedral "piano-stool" geometry around the Ru atom and the η^6-coordination of the *p*-cymene. Two chlorine atoms and the phosphorus occupy the other three positions. Bond lengths are similar to those reported for analogous complexes (Table 3); the Ru–Cl bond distances range from 2.3943(10) to 2.4395(7) Å, the Ru–P bond lengths from 2.3009(8) to 2.3680(7) Å and the longest distances have been observed with cyclohexyl and *tert*-butyl *P*-substituents (entries 1, 6 and 7). This seems to be the result of a higher steric congestion of PA ligands. The P–O bond lengths (all close to 1.60 Å) are consistent with

Table 2 ^{31}P{^{1}H} NMR spectral data for SPOs **4** and Ru-complexes **5**[a]

Entry	SPO	^{31}P{^{1}H} (ppm)	Complex 5	^{31}P{^{1}H} (ppm)
1	**4b**	50.0	**5b**	129.3
2	**4c**	21.4	**5c**	107.1
3	**4d**	18.2	**5d**	105.6
4	**4e**	22.8	**5e**	107.0
5	**4h**	20.2	**5h**	109.5
6	**4i**	28.0	**5i**	113.1
7	**4j**	29.6	**5j**	109.4
8	**4k**	36.7	**5k**	114.2
9	**4l**	47.4	**5l**	115.5

[a] Measured in CDCl$_3$ at 25 °C.



5b **5c** **5d**

5h **5i** **5k** **5l**

Fig. 2 Molecular structures of complexes **5b–d**, **5h–i** and **5k–l** represented at 50% ellipsoid probability. Most of the H atoms have been omitted for clarity.

Table 3 Selected bond lengths (Å) for complexes [RuCl$_2$(*p*-cymene)(PA)] **5b–d**, **5h–i** and **5k–l**

Entry	Complex	Ru(1)–Cl(1) (Å)	Ru(1)–Cl(2) (Å)	Ru(1)–P(1) (Å)	P(1)–O(1) (Å)	O···Cl (Å)	Ru(1)–C$_{avg}$ (Å)
1	**5b**	2.4323(10)	2.3943(10)	2.3376(9)	1.600(3)	2.988(3)	2.203(4)
		2.4320(10)	2.4198(9)	2.3379(9)	1.602(3)	3.005(3)	2.214(4)
		2.4296(10)	2.4072(9)	2.3445(10)	1.612(3)	3.027(3)	2.215(4)
2	**5c**	2.4171(8)	2.4156(8)	2.3120(8)	1.602(2)	3.070(2)	2.216(3)
3	**5d**	2.4147(9)	2.3970(8)	2.3009(8)	1.605(2)	3.011(3)	2.212(3)
4	**5h**	2.4024(6)	2.4197(6)	2.3130(6)	1.6034(19)	3.175(2)	2.210(3)
5	**5i**	2.4295(11)	2.4032(11)	2.3017(10)	1.604(3)	2.988(3)	2.209(4)
6	**5k**	2.3966(8)	2.4389(9)	2.3342(8)	1.601(2)	3.009(2)	2.212(3)
7	**5l**	2.4395(7)	2.4124(7)	2.3680(7)	1.6098(19)	2.961(2)	2.214(3)

a P–O single bond. The O···Cl distances ranging from 2.961(2) to 3.070(2) Å – except for **5h**, 3.175(2) Å, entry 4 – indicate a hydrogen bonding with chlorines. Of note, with **5h**, the hydrogen bonding takes place intermolecularly.

In order to gain more insights into the coordination chemistry of [RuCl$_2$(*p*-cymene)(L)] and particularly to address the issue of the absence of reaction with bulky SPOs Ad$_2$P(O)H **4f** or *t*Bu$_2$P(O)H **4g**, we quantified the steric parameter of phosphinous acids and other ligands L (phosphine, phosphite and N-heterocyclic carbene (NHC)) through the percentage buried volume (%V_{bur}).[24,25] Selected values have been gathered in Table 4.[23] The %V_{bur} for PA ligands span from 21.9 to 24.6%. These values are significantly lower than those calculated on AuCl(PA) complexes.[15g] As expected Ph$_2$POH is more sterically demanding than Ph$_2$PH (entries 3 and 9) but less than Ph$_2$PCH$_2$OH, Ph$_2$P*n*Bu, PPh$_3$ or P(OPh)$_3$ (entries 9–13). The highest %V_{bur} calculated in [RuCl$_2$(*p*-cymene)(L)] complexes is for the NHC IMes (1,3-dimesityl-imidazol-2-ylidene) (27.9%) which is in the lower range for this ligand (entry 14).[24] These low %V_{bur} values and their narrow range attest probably that the other ligands in the coordination sphere of the Ru are

Table 4 Percentage of buried volumes of various ligands L in [RuCl$_2$(η^6-*p*-cymene)(L)] complexes[a]

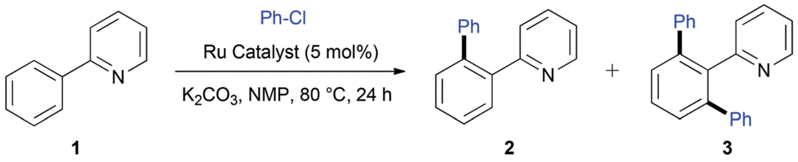
Entry	L	*d*(Ru–L) (Å)	%V_{bur} (L)
1	Me$_2$POH	2.3078(10)	21.9
2	Cy$_2$POH	2.3376(9)	24.4
3	Ph$_2$POH	2.3120(8)	24.6
4	(*p*-F-C$_6$H$_4$)$_2$POH	2.3009(8)	24.6
5	MePhPOH	2.3130(6)	22.7
6	*n*BuPhPOH	2.3017(10)	22.7
7	CyPhPOH	2.3342(8)	24.1
8	*t*BuPhPOH	2.3680(7)	24.4
9	Ph$_2$PH	2.313(2)	23.2
10	Ph$_2$PCH$_2$OH	2.3516(8)	25.1
11	Ph$_2$P*n*Bu	2.352(2)	25.6
12	PPh$_3$	2.3438(6)	26.8
13	P(OPh)$_3$	2.2642(8)	24.7
14	IMes	2.142(4)	27.9

[a] Parameters used for Samb*V*ca calculations: 3.50 Å for the sphere radius, exact distances between the ligand and the metal were considered, hydrogen atoms were omitted and bond radii scaled by 1.17.

sterically demanding and the L ligand has therefore to minimize its size. The $\%V_{bur}$ of the η^6-*p*-cymene has also been quantified in 24 X-ray structures and the size of this ligand was found to be relatively invariant with an average value of 47.5% and a standard deviation of 0.35%.[23] As intuitively expected, the η^6-*p*-cymene occupies almost half of the Ru coordination sphere and does not show any structural flexibilities. Therefore, the coordination of sterically hindered ligands, such as Ad_2POH or tBu_2POH, seems unlikely. Indeed, calculations performed on other complexes shown that $\%V_{bur}$ of tBu_2POH and Ad_2POH are around 30.5 and 31.5, respectively.[23]

Having prepared a series of well-defined $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PA)]$, we then tested their catalytic performances in C–H activation using 2-phenylpyridine **1** as the benchmark substrate using Ackermann's conditions (Table 5). A control experiment showed that at 120 °C, $[RuCl_2(p\text{-cymene})]_2$ without addition of SPO was competent for C–H functionalization since 88% of diarylated product **3** was isolated (entry 1). At 100 °C, only minute amounts of products **2** and **3** were obtained with $[RuCl_2(p\text{-cymene})]_2$ (entry 2) whereas adding either 5 or 10 mol% of Ad_2POH allowed to isolate around 80% of diarylated product **3** (entries 3 and 4). However, lowering the reaction temperature to 80 °C led to the loss of activity of the dimer $[RuCl_2(p\text{-cymene})]_2$ (entry 5). On one hand, at this temperature, $[RuCl_2(p\text{-cymene})]_2$ in association with $Ad_2P(O)H$ **4f** gave only small amounts of **2** and **3** (entry 6). On the other hand, well-defined $[RuCl_2(\eta^6\text{-cymene})(PA)]$ **5a–e** and **5i–k** were found much more competent and significant quantities of C–H functionalized products were isolated (entries 7–14). Since the reactions did not reach completion, *ca.* 1 : 1 mixtures of mono- and diarylated products were obtained. The well-defined complexes performed slightly better than *in situ*-generated complexes (entries 14 and 15) and addition of an extra quantity of SPO reduced the catalytic activity.[23] To our delight, with $RuCl_2(\eta^6\text{-}p\text{-cymene})(tBuPhPOH)]$ **5l**, only compound **3** was formed with an almost quantitative yield (entry 16). Of note, after only 2 h of the reaction, a 1 : 1 mixture of mono- and diarylated products was observed with **5l** (entry 17). The electronic properties of phosphinous acids did not influence the catalytic activities of the resulting complexes. For example Ph_2POH-containing **5c** performed better than **5b** bearing the more electron rich Cy_2POH rather than **5d** bearing electron withdrawing ligand $(p\text{-F-}C_6H_4)_2POH$ (entries 8–10). In contrast, higher activities have been obtained for more sterically demanding PA ligands, *i.e.* $tBuPhPOH$ and $(3,5\text{-Me}_2\text{-}C_6H_3)_2POH$ (entries 16 and 11, respectively). Importantly, complexes bearing phosphine or phosphite exhibited interesting activities upon C–H activation (entries 18–20). In particular, $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)]$ was found to be more selective for mono-functionalization of 2-phenylpyridine **1** (entry 18).

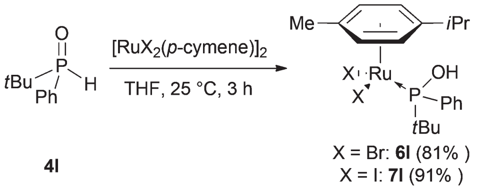
Table 5 Evaluation of catalyst performances in C–H bond activation[a]



Entry	Catalyst	Additive	Yield (%) 2	Yield (%) 3
1[b]	$[RuCl_2(p\text{-cymene})]_2$		0	88
2[c]	$RuCl_2(p\text{-cymene})]_2$		8	2
3[c]	$RuCl_2(p\text{-cymene})]_2$	$Ad_2P(O)H$ **4f** (5 mol%)	0	80
4[c]	$RuCl_2(p\text{-cymene})]_2$	$Ad_2P(O)H$ **4f** (10 mol%)	0	83
5	$[RuCl_2(p\text{-cymene})]_2$		0	0
6	$[RuCl_2(p\text{-cymene})]_2$	$Ad_2P(O)H$ **4f** (10 mol%)	7	3
7	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(Me_2POH)]$ **5a**		14	15
8	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(Cy_2POH)]$ **5b**		12	11
9	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(Ph_2POH)]$ **5c**		27	22
10	$[RuCl_2(\eta^6\text{-}p\text{-cymene})((p\text{-F-}C_6H_4)_2POH)]$ **5d**		19	11
11	$[RuCl_2(\eta^6\text{-}p\text{-cymene})((3,5\text{-Me}_2\text{-}C_6H_3)_2POH)]$ **5e**		32	32
12	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(nBuPhPOH)]$ **5i**		19	19
13	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(BnPhPOH)]$ **5j**		19	11
14	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(CyPhPOH)]$ **5k**		22	54
15	$[RuCl_2(p\text{-cymene})]_2$	$CyPhP(O)H$ **4k** (5 mol%)	21	19
16	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(tBuPhPOH)]$ **5l**		0	89
17[d]	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(tBuPhPOH)]$ **5l**		14	13
18	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)]$		58	6
19	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(PCy_3)]$		18	5
20	$[RuCl_2(\eta^6\text{-}p\text{-cymene})(P(OPh)_3)]$		19	15

[a] Reaction conditions: 2-phenylpyridine **1** (142 μL, 1 mmol), chlorobenzene (220 μL, 2.2 mmol, 2.2 equiv.), K_2CO_3 (415 mg, 3 mmol, 3 equiv.), 5 mol% of Ru complex (2.5 mol% for $[RuCl_2(p\text{-cymene})]_2$), NMP (2 mL), 80 °C, and 24 h. [b] Reaction was performed at 120 °C. [c] Reaction was performed at 100 °C. [d] Reaction time: 2 h.

In Ru-mediated C–H activation, the anionic ligands played an important role, for example carboxylate-containing complexes are extremely efficient due to chelation-assisted C–H activations.[1k,4a] Surprisingly, to the best of our knowledge, complexes bearing bromide and iodide ligands have not been investigated so far. Bromide and iodide counterparts bearing *t*BuPhPOH phosphinous acid were prepared with good yield following the same protocol than for chloride analogues (**6l** and **7l** respectively, Scheme 2). The activity of these catalysts was compared for C–H functionalization of 2-phenylpyridine **1** and as a function of the aryl halide partner (Table 6). Unexpectedly, drastic differences were observed as only low yields of C–H functionalization and with an almost equimolar mixture of mono- and diarylation were obtained (entries 2 and 3). Moreover, whereas aryl bromides are regularly used as coupling partners,[26] at 80 °C they exhibited a significantly lower activity than their chlorine counterpart (entries 1, 2 and 4).[27] We assume that this is due to an exchange of halogens between the aryl halide to the metal center occurring through the oxidative addition. Halide effects in transition metal catalysis are often difficult to rationalize,[28] however, we believe that the iodide atoms increase the congestion around the metal center and decrease its reactivity.[29]



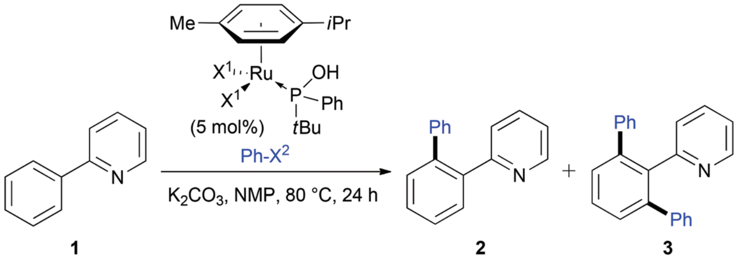
Scheme 2 Synthesis of bromide- and iodide-containing [RuX$_2$(η^6-*p*-cymene)(PA)] complexes.

From these results, a halide inhibition was suspected; the chlorine dependence was therefore investigated through the use of additives (Table 7). The addition of one equivalent of LiCl in the reaction mixture quenched indeed the C–H activation process (entries 1 and 2). A significant loss of activity was also observed with 1 equiv. of tetrabutylammonium chloride (entry 3). Nevertheless, addition of a stoichiometric amount of silver salt did not boost the catalytic performances of complexes exhibiting a moderate activity such as complexes **5a** and **5b** (entries 5 and 8). Higher quantities of silver salt led to the inhibition of the C–H functionalization (entries 6 and 9). These results suggest that chlorine atoms play a key role in the C–H activation process.

In order to gain insight into the mechanism, in particular the role of the PA ligand, and as PAs are considered as labile ligands due to a weak M–PA bond,[15d] we attempted to determine if the PA remains in the coordination sphere of the ruthenium all along the catalytic cycle. For this purpose, the ruthenium cyclometallated complex **8** was prepared[30] and tested in catalysis (Table 8). As anticipated, at 120 °C, this catalyst performed well with 91% of diarylated compound **3** isolated (entry 1). However, at 80 °C, no reaction occurred, even when the ligand *t*BuPhP(O)H **4l** was added (entries 2 and 3). On one hand, the addition of a substoichiometric amount of silver salts such as AgBF$_4$ and AgSbF$_6$ allowed the formation small quantities of products **2** and **3** (entries 4 and 5). On the other hand, the combination of the silver salt with OPS *t*BuPhP(O)H **4l** led to restore almost completely the activity of the catalytic system (entries 6 and 7).

We were also able to prepare quantitatively the cationic ruthenacycle **9c** bearing a phosphinous acid ligand by the

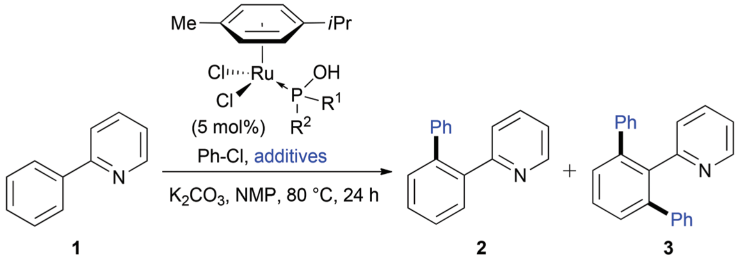
Table 6 Halogen effect in C–H activation[a]



Entry	X^1 (complex)	Ph-X^2	Yield (%) 2	Yield (%) 3
1	Cl (**5l**)	Ph-Cl	0	89
2	Br (**6l**)	Ph-Br	23	18
3	I (**7l**)	Ph-I	14	8
4	Cl (**5l**)	Ph-Br	6	21
5	Cl (**5l**)	Ph-I	3	5
6	Br (**6l**)	Ph-I	3	7

[a] Reaction conditions: 2-phenylpyridine **1** (142 μL, 1 mmol), aryl halide (2.2 mmol, 2.2 equiv.), K$_2$CO$_3$ (415 mg, 3 mmol, 3 equiv.), complex (5 mol%), NMP (2 mL), and 24 h.

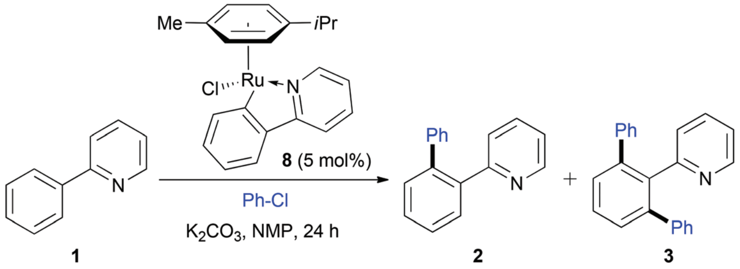
Table 7 Chlorine dependence in C–H activation[a]



Entry	Complex **5**	Additives	Yield (%)	
			2	**3**
1	**5l** (R^1, R^2 = Ph, *t*Bu)	None	0	89
2	**5l** (R^1, R^2 = Ph, *t*Bu)	LiCl (1 equiv.)	0	0
3	**5l** (R^1, R^2 = Ph, *t*Bu)	*n*Bu_4NCl (1 equiv.)	9	6
4	**5a** (R^1, R^2 = Me, Me)	None	14	15
5	**5a** (R^1, R^2 = Me, Me)	$AgBF_4$ (5 mol%)	14	16
6	**5a** (R^1, R^2 = Me, Me)	$AgBF_4$ (1 equiv.)	0	0
7	**5b** (R^1, R^2 = Cy, Cy)	None	12	11
8	**5b** (R^1, R^2 = Cy, Cy)	$AgBF_4$ (5 mol%)	9	8
9	**5b** (R^1, R^2 = Cy, Cy)	$AgBF_4$ (1 equiv.)	2	2

[a] Reaction conditions: 2-phenylpyridine **1** (142 μL, 1 mmol), chlorobenzene (220 μL, 2.2 mmol, 2.2 equiv.), K_2CO_3 (415 mg, 3 mmol, 3 equiv.), complex (5 mol%), NMP (2 mL), and 24 h.

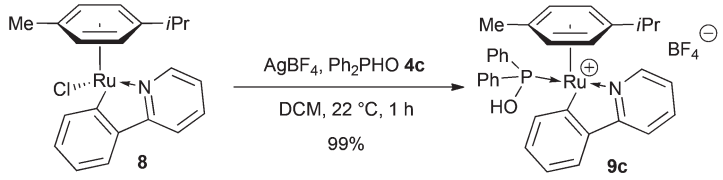
Table 8 Control experiments with ruthenacycle **8**[a]



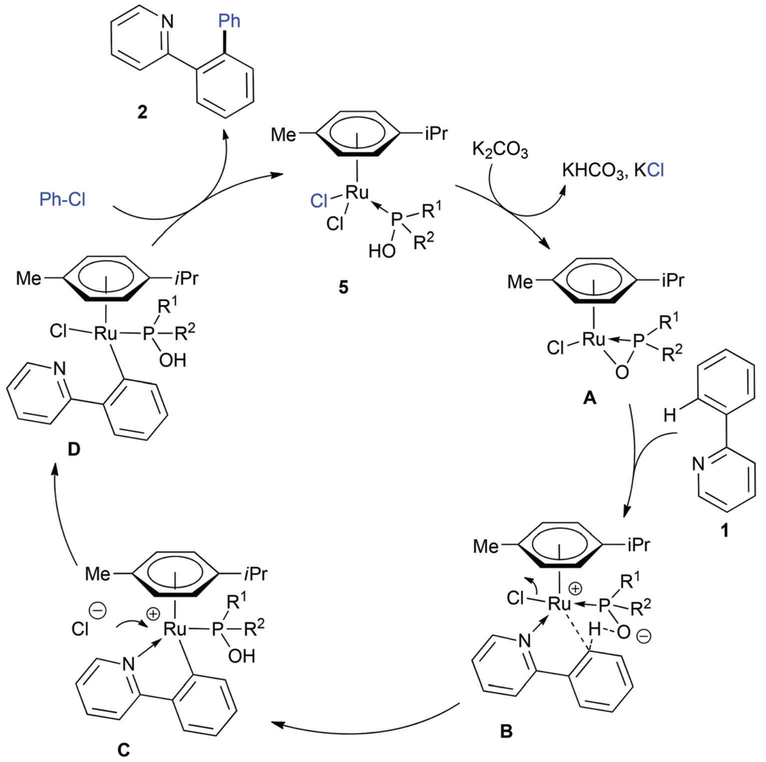
Entry	Additives	*T* (°C)	Yield (%)	
			2	**3**
1	None	120	0	91
2	None	80	0	0
3	*t*BuPhP(O)H **4l** (5 mol%)	80	0	0
4	$AgBF_4$ (6 mol%)	80	5	4
5	$AgSbF_6$ (6 mol%)	80	7	8
6	$AgBF_4$ (6 mol%), *t*BuPhP(O)H **4l** (5 mol%)	80	26	52
7	$AgSbF_6$ (6 mol%), *t*BuPhP(O)H **4l** (5 mol%)	80	26	56

[a] Reaction conditions: 2-phenylpyridine **1** (142 μL, 1 mmol), chlorobenzene (220 μL, 2.2 mmol, 2.2 equiv.), K_2CO_3 (415 mg, 3 mmol, 3 equiv.), complex **8** (21.3 mg, 5 mol%), NMP (2 mL), and 24 h.

treatment of complex **8** with OPS **4c** in the presence of silver tetrafluoroborate in a stoichiometric amount (Scheme 3). Unfortunately **9c** was found to exhibit no activity under our optimal conditions (80 °C). However, when this reaction was performed in the presence of 5 mol% of tetrabutylammonium chloride, **9c** displayed moderate activity with the formation of 11% of mono arylated product **2** and 14% of **3**. This represents only a slight decrease of the performance compared to catalyst **5c** (27% of **2** and 22% of **3**, Table 5, entry 9). To further investigate this chlorine effect, complex **9c** was treated with 5 equiv. of LiCl in $CDCl_3$ at room temperature, and rapidly ^{31}P NMR spectroscopy showed a new resonance at 108.4 ppm with



Scheme 3 Preparation of the cationic ruthenacycle **9c**.



Scheme 4 Proposed mechanism for the C–H activation mediated by $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PA)]$ complexes.

complete disappearance of the signal at 114.7 ppm after only one hour. Unfortunately, this new compound was found to be unstable and could not be isolated and fully characterized.

With these results in mind, we propose the following mechanism for C–H activation/functionalization catalyzed by $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PA)]$ complexes **5** (Scheme 4).[31] The mechanism initiates by a base-promoted loss of HCl to give the 18e ruthenium κ^2-PO-phosphinito species **A**. A transition to a κ^1 coordination frees a coordination site for the pyridine-containing substrate. At this stage, the CDM mechanism may be triggered by the phosphinito which intercepts the *ortho*-proton with a concomitant release of the chlorine atom to lead to the cationic ruthenacycle **C**. Of note, **C** corresponds to the isolated complex **9c**. According to our observations dealing with the reactivity of **9c** with LiCl, we believe that the chlorine counterattacks the metallic center and prompts to pyridine-moiety decoordination to afford species **D**. This step might be at the origin of the observed halide effect; the counterattack is probably less favored with more bulky halides such as bromide and iodide. Finally, the rate determining oxidative addition[4d,32] occurring possibly through a single electron transfer process[31] and the reductive elimination give the coupling product **2** and release complex **5**.

Conclusions

In summary, a series of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]$ complexes bearing phosphinous acid (PA) ligands has been straightforwardly prepared starting from the dimer $[RuCl_2(p\text{-cymene})]_2$ and secondary phosphine oxides. These complexes were fully characterized, notably by single-crystal X-ray diffraction which allowed us to calculate the percentage buried volumes of PAs and other phosphorus-based ligands. This quantification of the steric parameter led to a better comprehension of the coordination chemistry for these types of complexes and explained the absence of coordination in the case of bulky SPOs such as $Ad_2P(O)H$. The performances of these complexes were evaluated in C–H activation/functionalization of 2-phenylpyridine. At 80 °C, an efficient complex bearing the bulkier PA was identified. A thorough comparison of aryl halides as coupling partners revealed a sharp halide effect. Further investigations allowed us to establish a halide dependence: large quantities of chlorine inhibited the C–H activation/functionalization but stoichiometric amounts were also necessary. On the basis of these results and the isolation of a reaction intermediate, a mechanism involving successively the formation of κ^2-PO-phosphinito species, a concerted metallation deprotonation favored by the phosphinito, a chlorine counterattack and single electron transfer oxidative addition were proposed. Since the hindered Ad$_2$P(O)H does not coordinate to the metal center even though it improves the C–H activation, we believe that it participates in the CDM as an outer-sphere base. An enantioselective version of C–H activation/functionalization taking advantage of the P-stereogenic center of PA ligands is currently under investigation in our laboratory.

Experimental

All reagents were obtained from commercial sources and used as received. Secondary phosphine oxides **4c** and **4e–g** were obtained from chemical suppliers. Other SPOs were prepared according to literature procedures: **4b**,[33] **4d**,[33] **4h**,[34] **4i**,[34] **4j**,[35] **4k**[15a] and **4l**.[34] THF was purified and dried over the Braun solvent purification system (MB-SPS-800). Analytical Thin Layer Chromatography (TLC) was carried out on a Merck silica gel 60 F$_{254}$. The products were revealed by ultraviolet light (254 or 366 nm) and stained with dyeing reagents solutions. Flash chromatography was performed on a Combiflash® Companion or with Merck silica gel 60 (230–400 mesh). ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded in CDCl$_3$ at ambient temperature on Bruker Avance III 300 or 400 spectrometers operating at 300 and 400 MHz respectively for ^{1}H. ^{13}C, ^{31}P and ^{19}F nuclei were observed with ^{1}H decoupling. Solvent residual signals were used as internal standards.[36] Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz respectively. HRMS were recorded on a SYNAPT G2 HDMS (Waters) or on a QStar Elite (Applied Biosystems SGIEX) equipped with an Atmospheric Pressure Ionization (API) source. Mass spectra were obtained using a Time Of Flight (TOF) analyser. X-ray diffraction: intensity data were collected on a Bruker-Nonius KappaCCD diffractometer using MoKα radiation (0.71073 Å) at 293(2) K. Data reduction was performed using the HKL-2000 software package. The structure was resolved using the software SIR92[37] by direct methods and refined using SHELXL-97.[38] For compound **5d**, intensity data were collected on an Agilent SuperNova AtlasS2 diffractometer using MoKα radiation (0.71073 Å) at 293(2) K. Data reduction was performed using the CrysAlisPro software package (version 1.171.37.31). The structure was resolved using the software SHELXS-97 by direct methods and refined using SHELXL-2013-4. The CIF files of compounds **5b–d**, **5h**, **5i**, **5k** and **5l** have been deposited with CCDC numbers 1434226–1434232, respectively.

General procedure for the synthesis of complexes [RuCl$_2$(η^6-arene)(PA)] 5

In a Schlenk flask, a solution of ruthenium dimer [RuCl$_2$(η^6-*p*-cymene)]$_2$ (61.2 mg, 0.1 mmol, 2 equiv. of ruthenium) and secondary phosphine oxide (0.22 mmol, 2.2 equiv.) in THF (2 mL) was stirred at room temperature for 3 h. The reaction mixture was half-concentrated and *n*-hexane (10 mL) was added to initiate precipitation. The red precipitate was filtered off and washed with *n*-hexane. Recrystallisation from DCM/*n*-hexane gave crystals of the desired product.

[RuCl$_2$(η^6-*p*-cymene)(Cy$_2$POH)] 5b. According to the general procedure, complex **5b** was obtained after 24 h of reaction as a red solid (92 mg, 89%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 5.59 (d, J(H,H) = 6.0 Hz, 2H, H^{Ar}), 5.56 (d, J(H,H) = 6.0 Hz, 2H, H^{Ar}), 5.13 (br. s, 1H, PO–H), 2.81 (sept, J(H,H) = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.40–1.20 (m, 22H, CH_2 and CH), 2.10 (s, 3H, C–CH_3), 1.28 (d, J(H,H) = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 107.8 (C$^{\mathrm{Ar}}$), 94.1 (C$^{\mathrm{Ar}}$), 89.0 (C$^{\mathrm{Ar}}$–H), 84.5 (C$^{\mathrm{Ar}}$–H), 42.9 (CH, C–P), 30.9 (CH), 27.8–25.8 (10 CH$_2$), 22.3 (CH$_3$), 18.3 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 129.3 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{22}H_{37}Cl_2NaOPRu$: 543.0895 [M + Na]$^+$; found: 543.0898.

[RuCl$_2$(η^6-*p*-cymene)(Ph$_2$POH)] 5c. According to the general procedure, complex **5c** was obtained as a red solid (97 mg, 96%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.75–7.65 (m, 4H, H^{Ar}), 7.55–7.40 (m, 6H, H^{Ar}), 5.40 (d, J(H,H) = 5.9 Hz, 2H, H^{Ar}), 5.26 (d, J(H,H) = 6.0 Hz, 2H, H^{Ar}), 2.51 (sept, J(H,H) = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.01 (s, 3H, C–CH_3), 0.98 (d, J(H,H) = 7.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 137.5 (C$^{\mathrm{Ar}}$–P), 131.7 (C$^{\mathrm{Ar}}$–H), 131.3 (C$^{\mathrm{Ar}}$–H), 128.4 (C$^{\mathrm{Ar}}$–H), 108.8 (C$^{\mathrm{Ar}}$), 96.8 (C$^{\mathrm{Ar}}$), 89.7 (C$^{\mathrm{Ar}}$–H), 87.0 (C$^{\mathrm{Ar}}$–H), 30.4 (CH), 21.9 (CH$_3$), 17.9 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 107.0 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{22}H_{25}Cl_2NaOPRu$: 530.9956 [M + Na]$^+$; found: 530.9957.

[RuCl$_2$(η^6-*p*-cymene)((*p*-F-C$_6$H$_5$)$_2$POH)] 5d. According to the general procedure, complex **5d** was obtained after 6 h of reaction as a red solid (92 mg, 84%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.75–7.65 (m, 4H, H^{Ar}), 7.20–7.10 (m, 4H, H^{Ar}), 5.38 (d, J(H,H) = 5.7 Hz, 2H, H^{Ar}), 5.27 (d, J(H,H) = 5.8 Hz, 2H, H^{Ar}), 2.54 (sept, J(H,H) = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 2.00 (s, 3H, C–CH_3), 1.01 (d, J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 164.1 (C–F), 134.1 (C$^{\mathrm{Ar}}$–H), 133.2 (C$^{\mathrm{Ar}}$–P), 115.7 (C$^{\mathrm{Ar}}$–H), 109.3 (C$^{\mathrm{Ar}}$), 97.1 (C$^{\mathrm{Ar}}$), 88.7 (C$^{\mathrm{Ar}}$–H), 87.1 (C$^{\mathrm{Ar}}$–H), 30.6 (CH), 21.7 (CH$_3$), 18.0 (CH$_3$). ^{19}F{^{1}H} NMR (377 MHz, CDCl$_3$): δ (ppm) = −107.6 (s). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ (ppm) = 105.7 (s). HRMS (ESI−): *m*/*z*: calcd for $C_{22}H_{22}Cl_2OPRu$: 542.9803 [M − H]$^-$; found: 542.9792.

[RuCl$_2$(η^6-*p*-cymene)((3,5-Me$_2$-C$_6$H$_3$)$_2$POH)] 5e. According to the general procedure, complex **5e** was obtained as a red solid (103 mg, 91%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.30 (d, J(H,P) = 11.4 Hz, 4H, H^{Ar}), 7.10 (s, 2H, H^{Ar}), 6.51 (br. s, 1H, PO–H), 5.40 (d, J(H,H) = 5.8 Hz, 2H, H^{Ar}), 5.18 (d, J(H,H) = 5.8 Hz, 2H, H^{Ar}), 2.56 (sept, J(H,H) = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.35

(s, 12H, C–C*H*$_3$), 2.06 (s, 3H, C–C*H*$_3$), 0.98 (d, *J*(H,H) = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 137.8 (C^{Ar}), 137.7 (C^{Ar}), 137.3 (C^{Ar}), 136.7 (C^{Ar}), 132.82 (C^{Ar}–H), 132.80 (C^{Ar}–H), 129.1 (C^{Ar}–H), 129.0 (C^{Ar}–H), 107.9 (C^{Ar}), 95.3 (C^{Ar}), 90.21 (C^{Ar}–H), 90.16 (C^{Ar}–H), 87.72 (C^{Ar}–H), 88.66 (C^{Ar}–H), 30.3 (CH), 21.6 (CH$_3$), 21.4 (CH$_3$), 17.7 (CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ (ppm) = 105.7 (s). HRMS (ESI−): *m*/*z*: calcd for $C_{26}H_{32}Cl_2NaOPRu$: 563.0618 [M − H]$^+$; found: 563.0620.

[RuCl$_2$(η^6-*p*-cymene)(MePhPOH)] 5h. According to the general procedure, complex **5h** was obtained as a red solid (63 mg, 71%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.80–7.70 (m, 2H, *H*^{Ar}), 7.60–7.50 (m, 3H, *H*^{Ar}), 6.15 (br. s, 1H, PO–*H*), 5.24 (d, *J*(H,H) = 6.3 Hz, 1H, *H*^{Ar}), 5.21 (d, *J*(H,H) = 5.8 Hz, 1H, *H*^{Ar}), 5.08 (d, *J*(H,H) = 5.8 Hz, 1H, *H*^{Ar}), 5.04 (d, *J*(H,H) = 6.1 Hz, 1H, *H*^{Ar}), 2.65 (sept, *J*(H,H) = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.12 (d, *J*(H,P) = 10.0 Hz, 3H, P–C*H*$_3$), 1.94 (s, 3H, C–C*H*$_3$), 1.13 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.04 (d, *J*(H,H) = 7.0 Hz, 3H, C*H*(CH$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 140.9 (C^{Ar}–P), 131.1 (C^{Ar}–H), 128.9 (C^{Ar}–H), 128.8 (C^{Ar}–H), 107.6 (C^{Ar}), 96.1 (C^{Ar}), 91.3 (C^{Ar}–H), 89.3 (C^{Ar}–H), 87.6 (C^{Ar}–H), 86.1 (C^{Ar}–H), 30.5 (CH), 22.2 (CH$_3$), 21.9 (CH$_3$), 18.7 (CH$_3$), 18.3 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 109.5 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{17}H_{23}Cl_2NaOPRu$: 468.9798 [M + Na]$^+$; found: 468.9806.

[RuCl$_2$(η^6-*p*-cymene)(*n*BuPhPOH)] 5i. According to the general procedure, complex **5i** was obtained as a red solid (51 mg, 53%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.80–7.70 (m, 2H, *H*^{Ar}), 7.60–7.45 (m, 3H, *H*^{Ar}), 5.26 (d, *J*(H,H) = 6.0 Hz, 1H, *H*^{Ar}), 5.18 (d, *J*(H,H) = 5.8 Hz, 1H, *H*^{Ar}), 5.14 (d, *J*(H,H) = 6.0 Hz, 1H, *H*^{Ar}), 5.05 (d, *J*(H,H) = 5.8 Hz, 1H, *H*^{Ar}), 2.80–2.65 (m, 1H, C*H*$_2$), 2.61 (sept, *J*(H,H) = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 2.25–2.10 (m, 1H, C*H*$_2$), 1.91 (s, 3H, C–C*H*$_3$), 1.65–1.15 (m, 4H, C*H*$_2$), 1.11 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 0.97 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 0.97 (t, *J*(H,H) = 7.0 Hz, 3H, CH$_2$–C*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 138.5 (C^{Ar}–P), 130.8 (C^{Ar}–H), 129.2 (C^{Ar}–H), 128.9 (C^{Ar}–H), 107.4 (C^{Ar}), 95.7 (C^{Ar}), 92.2 (C^{Ar}–H), 88.8 (C^{Ar}–H), 87.0 (C^{Ar}–H), 86.8 (C^{Ar}–H), 31.4 (CH$_2$), 30.4 (CH), 24.6 (CH$_2$), 24.0 (CH$_2$), 22.2 (CH$_3$), 21.6 (CH$_3$), 18.2 (CH$_3$), 13.8 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 113.1 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{20}H_{29}Cl_2NaOPRu$: 511.0268 [M + Na]$^+$; found: 511.0270.

[RuCl$_2$(η^6-*p*-cymene)(BnPhPOH)] 5j. According to the general procedure, complex **5j** was obtained as a deep-red solid (92 mg, 88%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.70–7.60 (m, 2H, *H*^{Ar}), 7.50–7.40 (m, 3H, *H*^{Ar}), 7.10–7.00 (m, 3H, *H*^{Ar}), 6.85–6.75 (m, 2H, *H*^{Ar}), 5.30–5.15 (m, 3H, *H*^{Ar}), 5.10 (d, ^{3}*J*(H,H) = 5.9 Hz, 1H, *H*^{Ar}), 4.01 (m, 1H, C*H*$_2$–P), 3.54 (d, ^{2}*J*(H,P) = 15.2 Hz, 1H, C*H*$_2$–P), 2.70 (sept, ^{3}*J*(H,H) = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 1.97 (s, 3H, C–C*H*$_3$), 1.16 (d, ^{3}*J*(H,H) = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.07 (d, ^{3}*J*(H,H) = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 136.4 (C^{Ar}–P), 133.7 (C^{Ar}), 131.0 (C^{Ar}–H), 130.5 (C^{Ar}–H), 129.7 (C^{Ar}–H), 128.5 (C^{Ar}–H), 128.0 (C^{Ar}–H), 126.4 (C^{Ar}–H), 108.7 (C^{Ar}), 97.4 (C^{Ar}), 91.3 (C^{Ar}–H), 88.3 (C^{Ar}–H), 87.5 (C^{Ar}–H), 87.1 (C^{Ar}–H), 38.9 (CH$_2$), 30.4 (CH), 22.3 (CH$_3$), 21.7 (CH$_3$), 18.3 (CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ (ppm) = 109.3 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{23}H_{27}Cl_2NaOPRu$: 545.0113 [M + Na]$^+$; found: 545.0101.

[RuCl$_2$(η^6-*p*-cymene)(CyPhPOH)] 5k. According to the general procedure, complex **5k** was obtained as a red solid (100 mg, 98%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.75–7.65 (m, 2H, *H*^{Ar}), 7.55–7.45 (m, 3H, *H*^{Ar}), 5.52 (d, *J*(H,H) = 6.5 Hz, 1H, *H*^{Ar}), 5.48 (d, *J*(H,H) = 6.5 Hz, 1H, *H*^{Ar}), 5.19 (d, *J*(H,H) = 5.5 Hz, 1H, *H*^{Ar}), 4.90 (d, *J*(H,H) = 5.5 Hz, 1H, *H*^{Ar}), 2.58 (sept, *J*(H,H) = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.50–2.20 (m, 2H, C*H* and C*H*$_2$), 1.99 (s, 3H, C–C*H*$_3$), 1.90–1.10 (m, 9H, C*H*$_2$), 1.10 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 0.75 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 137.5 (C^{Ar}–P), 129.4 (C^{Ar}–H), 128.4 (C^{Ar}–H), 127.3 (C^{Ar}–H), 105.6 (C^{Ar}), 94.5 (C^{Ar}), 93.4 (C^{Ar}–H), 89.3 (C^{Ar}–H), 84.3 (C^{Ar}–H), 82.7 (C^{Ar}–H), 41.2 (*C*H–P), 29.2 (CH), 26.0–25.0 (5 CH$_2$), 21.9 (CH$_3$), 19.2 (CH$_3$), 17.0 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 114.2 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{22}H_{31}Cl_2NaOPRu$: 537.0426 [M + Na]$^+$; found: 537.0421.

[RuCl$_2$(η^6-*p*-cymene)(*t*BuPhPOH)] 5l. According to the general procedure, complex **5l** was obtained as a deep-red solid (97 mg, 99%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.80–7.70 (m, 2H, *H*^{Ar}), 7.55–7.45 (m, 3H, *H*^{Ar}), 6.20 (br. s, 1H, PO–*H*), 5.48 (d, *J*(H,H) = 5.9 Hz, 1H, *H*^{Ar}), 5.39 (d, *J*(H,H) = 6.3 Hz, 1H, *H*^{Ar}), 5.35 (d, *J*(H,H) = 6.3 Hz, 1H, *H*^{Ar}), 5.15 (d, *J*(H,H) = 6.0 Hz, 1H, *H*^{Ar}), 2.78 (sept, *J*(H,H) = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 2.01 (s, 3H, C–C*H*$_3$), 1.21 (d, *J*(H,P) = 15.0 Hz, 9H, C(C*H*$_3$)$_3$), 1.18 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.01 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 137.1 (C^{Ar}–P), 130.4 (C^{Ar}–H), 130.0 (C^{Ar}–H), 128.0 (C^{Ar}–H), 107.6 (C^{Ar}), 94.2 (C^{Ar}), 92.3 (C^{Ar}–H), 90.5 (C^{Ar}–H), 86.6 (C^{Ar}–H), 86.1 (C^{Ar}–H), 39.9 (C), 30.4 (CH), 26.3 (CH$_3$), 22.0 (CH$_3$), 21.7 (CH$_3$), 18.0 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 115.1 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{20}H_{29}Cl_2NaOPRu$: 511.0268 [M + Na]$^+$; found: 511.0272.

[RuBr$_2$(η^6-*p*-cymene)(*t*BuPhPOH)] 6l. According to the general procedure using the dimer [RuBr$_2$(η^6-*p*-cymene)]$_2$, complex **6l** was obtained as a deep-red solid (94 mg, 81%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.80–7.60 (m, 2H, *H*^{Ar}), 7.55–7.40 (m, 3H, *H*^{Ar}), 5.55 (d, *J*(H,H) = 6.1 Hz, 1H, H^{Ar}), 5.52 (br. s, 1H, PO–*H*), 5.41 (d, *J*(H,H) = 6.1 Hz, 1H, *H*^{Ar}), 5.37 (d, *J*(H,H) = 6.2 Hz, 1H, *H*^{Ar}), 5.27 (d, *J*(H,H) = 6.2 Hz, 1H, *H*^{Ar}), 2.93 (sept, *J*(H,H) = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 2.08 (s, 3H, C–C*H*$_3$), 1.23 (d, *J*(H,P) = 15.0 Hz, 9H, C(C*H*$_3$)$_3$), 1.20 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.04 (d, *J*(H,H) = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 137.6 (C^{Ar}–P), 130.3 (3 C^{Ar}–H), 127.8 (2 C^{Ar}–H), 109.6 (C^{Ar}), 94.3 (C^{Ar}), 91.8 (C^{Ar}–H), 91.2 (C^{Ar}–H), 86.6 (C^{Ar}–H), 85.0 (C^{Ar}–H), 40.7 (C), 31.1 (CH), 26.6 (CH$_3$), 22.2 (CH$_3$), 22.1 (CH$_3$), 18.7 (CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ (ppm) = 113.3 (s). HRMS (ESI+): *m*/*z*: calcd for $C_{20}H_{29}Br_2NaOPRu$: 600.9246 [M + Na]$^+$; found: 600.9247.

[RuI$_2$(η^6-*p*-cymene)(*t*BuPhPOH)] 7l. According to the general procedure using the dimer [RuI$_2$(η^6-*p*-cymene)]$_2$, complex **7l** was obtained as a deep-red solid (121 mg, 90%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.70–7.60 (m, 2H, *H*^{Ar}), 7.50–7.40 (m, 3H, *H*^{Ar}), 5.71 (d, *J*(H,H) = 6.2 Hz, 1H, *H*^{Ar}), 5.54 (d, *J*(H,H) = 6.1 Hz, 1H, *H*^{Ar}), 5.43 (d, *J*(H,H) = 6.1 Hz, 1H, *H*^{Ar}), 5.39

(d, J(H,H) = 6.3 Hz, 1H, H^{Ar}), 4.72 (br. s, 1H, PO–H), 3.21 (sept, J(H,H) = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 2.22 (s, 3H, C–CH_3), 1.24 (d, J(H,P) = 14.8 Hz, 9H, C(CH_3)$_3$), 1.23 (d, J(H,H) = 7.0 Hz, 3H, CH(CH_3)$_2$), 1.08 (d, J(H,H) = 7.0 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) = 138.9 (C^{Ar}–P), 130.6 (C^{Ar}–H), 130.1 (C^{Ar}–H), 127.5 (C^{Ar}–H), 112.9 (C^{Ar}), 95.5 (C^{Ar}), 92.8 (C^{Ar}–H), 89.8 (C^{Ar}–H), 86.3 (C^{Ar}–H), 84.0 (C^{Ar}–H), 41.3 (C), 32.4 (CH), 27.2 (CH$_3$), 23.1 (CH$_3$), 22.2 (CH$_3$), 19.9 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 113.9 (s). HRMS (ESI+): m/z: calcd for $C_{20}H_{29}I_2KOPRu$: 710.8726 [M + K]$^+$; found: 710.8737.

[Ru(η^6-*p*-cymene)(Ph$_2$POH)(2-phenylpyridine-κ^2-NC)BF$_4$] 9c. In a round-bottom flask, were introduced in turn AgBF$_4$ (56 mg, 0.29 mmol), ruthenacycle **8** (122 mg, 0.29 mmol), Ph$_2$PHO (58 mg, 0.29 mmol) and 5 mL of dry DCM. The reaction mixture was stirred at room temperature for 1 h and filtered on Celite®. The volatiles were removed to afford complex **9c** as a brown-grey solid (194 mg, 99%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 9.27 (d, J(H,H) = 5.4 Hz, 1H, H^{Ar}), 8.09 (d, J(H,H) = 7.7 Hz, 1H, H^{Ar}), 7.60–7.55 (m, 2H, H^{Ar}), 7.50 (td, J(H,H) = 7.7 and 1.1 Hz, 1H, H^{Ar}), 7.36–7.29 (m, 3H, H^{Ar}), 7.26–7.20 (m, 3H, H^{Ar}), 7.16 (d, J(H,H) = 8.2 Hz, 1H, H^{Ar}), 7.06 (t, J(H,H) = 7.7 Hz, 1H, H^{Ar}), 7.03–6.99 (m, 1H, H^{Ar}), 6.78 (dt, J(H,H) = 8.0 and 2.6 Hz, 2H, H^{Ar}), 6.50 (dd, J(H,H) = 8.4 and 1.2 Hz, 1H, H^{Ar}), 6.47 (dd, J(H,H) = 8.2 and 1.0 Hz, 1H, H^{Ar}), 6.40 (d, J(H,H) = 6.4 Hz, 1H, H^{Ar}), 6.05 (dd, J(H,H) = 6.4 and 1.4 Hz, 1H, H^{Ar}), 5.86 (dd, J(H,H) = 6.1 and 1.2 Hz, 1H, H^{Ar}), 5.33 (d, J(H,H) = 6.0 Hz, 1H, H^{Ar}), 2.24 (sept, J(H,H) = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 1.88 (s, 3H, C–CH_3), 0.80 (d, J(H,H) = 6.9 Hz, 3H, CH(CH_3)$_2$), 0.72 (d, J(H,H) = 6.9 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 171.5 (C^{Ar}), 171.3 (C^{Ar}), 165.0 (C^{Ar}), 156.49 (C^{Ar}–H), 156.47 (C^{Ar}–H), 144.9 (C^{Ar}), 141.54 (C^{Ar}–H), 141.51 (C^{Ar}–H), 137.0 (C^{Ar}–H), 136.6 (C^{Ar}), 136.0 (C^{Ar}), 132.5 (C^{Ar}), 134.7 (C^{Ar}), 130.3 (C^{Ar}–H), 130.2 (C^{Ar}–H), 130.1 (C^{Ar}–H), 130.0 (C^{Ar}–H), 129.37 (C^{Ar}–H), 129.35 (C^{Ar}–H), 129.2 (C^{Ar}–H), 129.1 (C^{Ar}–H), 129.0 (C^{Ar}–H), 127.8 (C^{Ar}–H), 127.7 (C^{Ar}–H), 127.5 (C^{Ar}–H), 127.3 (C^{Ar}–H), 125.0 (C^{Ar}–H), 123.1 (C^{Ar}–H), 122.5 (C^{Ar}–H), 119.3 (C^{Ar}–H), 113.5 (C^{Ar}), 113.4 (C^{Ar}), 108.5 (C^{Ar}), 96.61 (C^{Ar}–H), 96.59 (C^{Ar}–H), 96.56 (C^{Ar}–H), 96.4 (C^{Ar}–H), 85.3 (C^{Ar}–H), 31.0 (CH), 22.2 (CH$_3$), 22.2 (CH$_3$), 18.8 (CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ (ppm) = 114.7 (s). ^{19}F NMR (376 MHz, CDCl$_3$): δ (ppm) = −150.5 (s). HRMS (ESI+): m/z: calcd for $C_{33}H_{33}NOPRu$: 592.1347 [M − BF$_4$]$^+$; found: 592.1345.

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