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Direct Preparation of [Ru(η^2-O_2CO)(η^6-arene)(L)] Carbonate Complexes (L = Phosphane, Carbene) and Their Use as Precursors of [RuH_2(*p*-cymene)(PCy_3)] and [Ru(η^6-arene)(L)($MeCN)_2$][$BF_4]_2$: X-ray Crystal Structure Determination of [Ru(η^2-O_2CO)(*p*-cymene)(PCy_3)]·1/2CH_2Cl_2 and [Ru(η^2-O_2CO)(η^6-C_6Me_6)-(PMe_3)]·H_2O

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[$RuCl_2$(η^6-arene)(PR_3)] complexes react with K_2CO_3 in the presence of water to afford the carbonatoruthenium(II) derivatives [Ru(η^2-O_2CO)(η^6-arene)(PR_3)] (**2**; arene = *p*-cymene, R = Cy, Ph, or Me; arene = hexamethylbenzene, R = Me) involving a planar Ru(η^2-O_2CO) moiety as shown by X-ray crystal structure determination of **2a** (*p*-cymene, PCy_3) and **2d** (hexamethylbenzene, PMe_3). The complex [Ru(η^2-O_2CO)(*p*-cymene)(PCy_3)] is cleanly converted in hot methanol into the dihydride [RuH_2(*p*-cymene)(PCy_3)]. The related complexes [Ru(η^2-O_2CO)(η^6-arene)(IMes)] [arene = *p*-cymene or hexamethylbenzene, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] are straightforwardly prepared by treating [$RuCl_2$(η^6-arene)$]_2$ precursors with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride and K_2CO_3 in THF at reflux. The removal of the carbonato ligand from complexes **2** with HBF_4 in the presence of acetonitrile leads to the dicationic derivatives [Ru(η^6-arene)(L)($MeCN)_2$][$BF_4]_2$ (L = PR_3 or IMes).

Introduction

The formation of metal catalysts in situ from a metal complex and an alkali metal carbonate salt, introduced as a base, is receiving growing attention. This is the case with a variety of cross-coupling and Heck reactions catalysed by palladium complexes.[1,2] Recently, the generation of ruthenium catalysts for ring-closing enyne metathesis[3,4] or sequential alkene isomerisation/Claisen reactions,[5] by treatment of [$RuCl_2$(η^6-arene)$]_2$ with an imidazolium salt and Cs_2CO_3 in situ, has provided other useful examples. In this case, Cs_2CO_3 was expected to generate an imidazolylidene carbene by deprotonation of the imidazolium salt, as was fully demonstrated by Arduengo[6] and Çetinkaya.[7] However, the question was raised whether the carbonate anion acts solely as a proton acceptor or might additionally enter into the coordination sphere of the ruthenium centre. Indeed, there are already examples of carbonatoruthenium(II) complexes, although such complexes were most often depicted as unexpected or undesired side-products. Their formation has been observed during the course of various processes, including metathetical exchange between an alkali metal carbonate and a ruthenium halide or cationic ruthenium precursor,[8–11] reaction of carbon dioxide with an oxaruthenacyclobutane,[8] hydrolysis of carbamato ligands,[12] oxidation of coordinated carbon monoxide,[13–18] and reactions involving a formal reduction of carbon dioxide ($2\ CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$).[19,20] From a structural point of view, mononuclear carbonatoruthenium(II) complexes contain an Ru(η^2-O_2CO) fragment, whereas the carbonate dianion is a bridging ligand in the dinuclear [Ru_2(μ-$O_2CO)_4]^{3-}$ anion[21–23] and in polynuclear, heteroleptic ruthenium complexes.[9,24,25]

The involvement of carbonatoruthenium complexes in organometallic synthesis is still uncommon but, remarkably, the carbonato complex [Ru(η^2-O_2CO)(bipy)$_2$] has been shown to react with terminal alkynes under aqueous acidic conditions to conveniently produce [Ru(alkyl)(CO)(bipy)$_2]^+$ and [Ru(acyl)(CO)(bipy)$_2]^+$ derivatives.[26–28] We wish to report here the direct synthesis of [Ru(η^2-O_2CO)(η^6-arene)(PR_3)] carbonatoruthenium(II) derivatives starting from [$RuCl_2$(η^6-arene)(PR_3)] precursors and K_2CO_3, and of related [Ru(η^2-O_2CO)(η^6-arene)(IMes)] complexes, where IMes is an imidazolylidene ligand, from [$RuCl_2$(η^6-arene)$]_2$ precursors and an imidazolium salt in the presence of K_2CO_3. The present account illustrates the usefulness of the carbonato ligand as a protecting group for ruthenium centres that favours the access to valuable ruthenium hydride derivatives, such as the dihydride complex [RuH_2-

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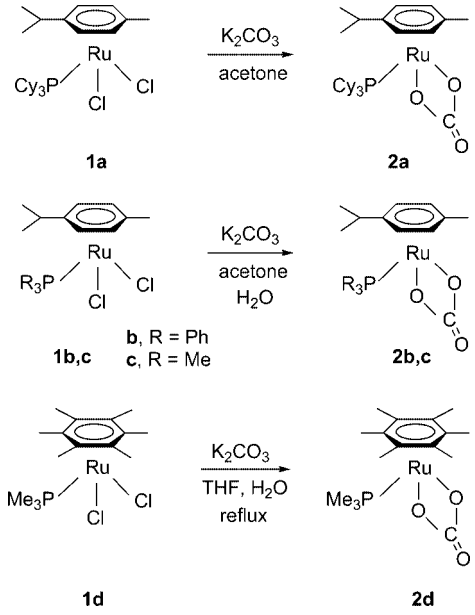
(*p*-cymene)(PCy_3)], and to dicationic [Ru(η⁶-arene)(L)-$(MeCN)_2$][BF_4]$_2$ derivatives.

Results and Discussion

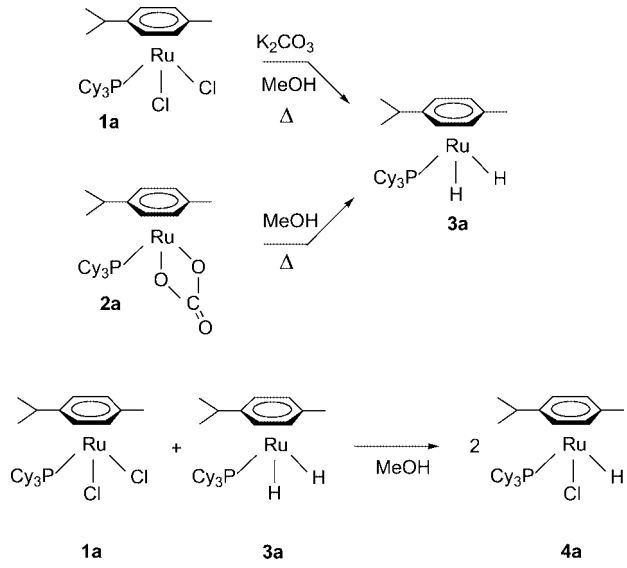
Synthesis of [Ru(η²-O_2CO)(η⁶-arene)(L)] Complexes

Upon stirring at room temperature, a red slurry consisting of [$RuCl_2$(*p*-cymene)(PCy_3)] (**1a**) and K_2CO_3 in acetone as solvent gradually (2 d) turned yellow. Subsequent workup afforded orange-yellow crystals of the new carbonato complex [Ru(η²-O_2CO)(*p*-cymene)(PCy_3)] (**2a**) in 78% yield (Scheme 1).



Scheme 1. Synthesis of the new carbonatoruthenium complexes **2a**–**d**.

No reaction was detected under similar conditions starting from [$RuCl_2$(*p*-cymene)(PR_3)] precursors **1b**,**c** (**b**: R = Ph; **c**: R = Me) without the addition of a small amount of water to the reaction mixture (ca. 2 wt.-% relative to acetone) to promote the expected reaction and the formation of complexes **2b**,**c** (Scheme 1). Complexes **2b**,**c** were isolated as orange solids in 97 and 95% yield, respectively. Since very long reaction times (10 d starting from **1c**) were required, the use of methanol (instead of acetone) as a polar solvent to facilitate the cleavage of ruthenium–chloride bonds was attempted. Starting from **1b**,**c**, an obvious decomposition was observed at room temperature, whereas **1a** still led to **2a** but also gave minor amounts of the dihydride [RuH_2(*p*-cymene)(PCy_3)] (**3a**) and the chloro hydride [RuCl(H)(*p*-cymene)(PCy_3)] (**4a**), as determined by $^{31}P\{^1H\}$ NMR spectroscopy. When the yellow reaction mixture in methanol was additionally heated at reflux for 1 h, the dihydride **3a** was obtained selectively (Scheme 2). The dihydride complex **3a** was isolated as a colourless solid in yields of up to 81%. As expected, **3a** was also obtained when a solution of pure **2a** in methanol was heated at reflux (Scheme 2).



Scheme 2. Synthesis of the ruthenium hydride complexes **3a** and **4a**.

The formation of a metal alkoxide intermediate that spontaneously undergoes a β-elimination process is among the most usual routes allowing the transformation of metal–halide into metal–hydride bonds. Evidence for such a mechanism was first obtained from the study of the reaction of [RuCl(Cp)(PPh_3)$_2$] with NaOMe,[29] and the synthesis of [RuH(Cp)(PPh_3)$_2$] has since been more conveniently achieved using K_2CO_3 in methanol.[30] The formation of the hydride derivatives **3a** and **4a** that occurs in methanol can be rationalised in the same way. The use of acetone as solvent precludes the formation of any ruthenium methoxide intermediate and thus allows selective formation of **2a**. The conversion of **2a** into the dihydride complex **3a** that occurs in methanol at reflux might result from the reaction of the carbonato ligand with two molecules of methanol to generate methoxide groups along with carbon dioxide and water. Finally, the second minor compound, identified as the chloro hydride [RuCl(H)(*p*-cymene)(PCy_3)] (**4a**), was alternatively synthesised by mixing equimolar amounts of **1a** and **3a** in methanol as solvent (Scheme 2). The synthesis of the parent complex [RuCl(H)(η⁶-benzene)(PCy_3)] has recently been achieved by treating [$RuCl_2$(η⁶-benzene)(PCy_3)] with sodium formate.[31]

As with the reaction with **1c**, the conversion of the more robust precursor [$RuCl_2$(hexamethylbenzene)(PMe_3)] (**1d**) into the corresponding carbonato complex [Ru(η²-O_2CO)(η⁶-C_6Me_6)(PMe_3)] (**2d**) needed a reaction time longer than 10 d at room temperature. The synthesis of **2d** was more rapidly (24 h) achieved by treating **1d** with K_2CO_3 in THF at reflux, although addition of a small amount of water was also required to reach completion of the reaction (Scheme 1).

The new complexes **2a**–**d**, **3a** and **4a** were characterised by ^1H, ^{13}C, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. The ^1H and $^{31}P\{^1H\}$ NMR spectra accounted for the coordination of the phosphane besides the

arene ligand. More specific and characteristic were the high-field ^{1}H NMR resonances corresponding to the RuH protons in **3a** and **4a**. The presence of the carbonato ligand in **2a**–**d** was confirmed by ^{13}C and ^{13}C{^{1}H} NMR spectroscopy as a resonance between δ = 165.6 and 166.8 ppm with a small coupling constant ($^3J_{P,C} < 2.9$ Hz). The two complexes **2a**·1/2CH_2Cl_2 and **2d**·H_2O were further characterised by an X-ray crystal structure analysis. Crystallographic data are summarised in the Exp. Sect., and ORTEP drawings of **2a** and **2d** are shown in Figures 1 and 2, respectively; selected bond lengths and angles are given in the captions.

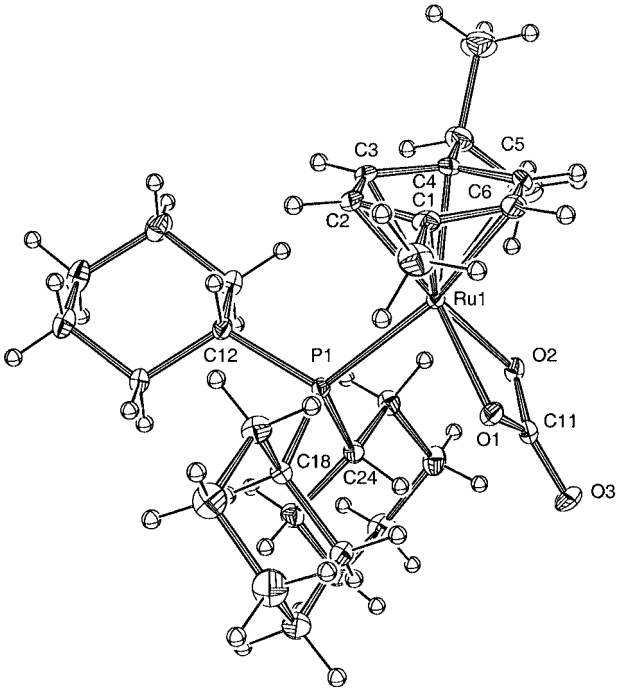


Figure 1. ORTEP drawing of **2a**·1/2CH_2Cl_2 showing 50% probability thermal ellipsoids. The CH_2Cl_2 molecule has been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–O1 2.079(2), Ru1–O2 2.087(2), O1–C11 1.323(3), O2–C11 1.315(3), O3–C11 1.232(3), Ru1–P1 2.3779(6); O1–Ru1–O2 62.90(7), C11–O1–Ru1 93.02(1), C11–O2–Ru1 92.90(1), O1–C11–O2 111.0(2), O1–C11–O3 124.5(2), O2–C11–O3 124.5(2), O1–Ru1–P1 86.92(5), O2–Ru1–P1 88.09(5).

Figures 1 and 2 show mononuclear species containing a carbonate dianion η^2-*O*,*O*-coordinated to the ruthenium centre. The two Ru–O bond lengths are almost identical, although they are slightly longer in **2d** [2.104(2) and 2.091(2) Å in **2d** vs. 2.087(2) and 2.079(2) Å in **2a**]. The two Ru–O bonds form a small angle [62.90(7)° in **2a**; 62.81(8)° in **2d**]. The exocyclic C=O bond in **2a** or **2d** [1.232(3) and 1.239(4) Å, respectively] is significantly shorter than the two endocyclic C–O bonds [1.323(3) and 1.315(3) Å in **2a**; 1.325(4) and 1.315(4) Å in **2d**]. It is worth noting the planar arrangement of the Ru(η^2-O_2CO) fragment, as indicated by the sum of the angles of the four-membered ring, and around the carbon atom, both of which are very close to 360° (359.8° and 360.0° for **2a** and 359.9° and 360.0° for **2d**, respectively). This plane is approximately perpendicular

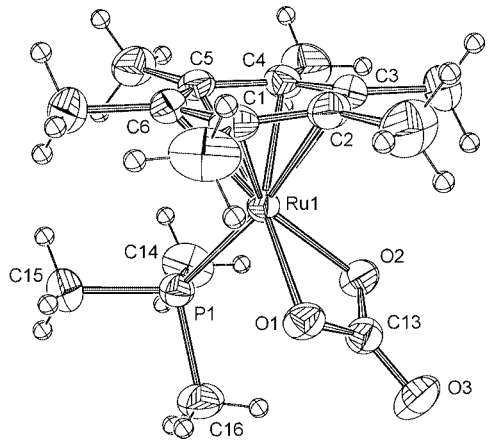


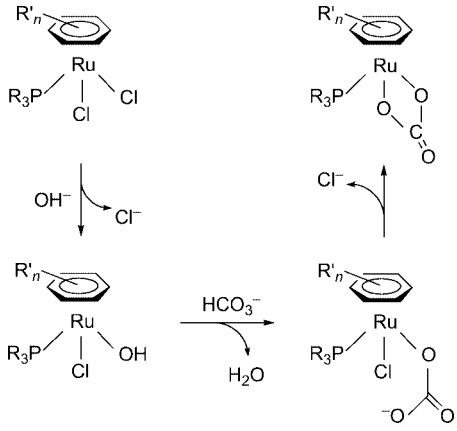
Figure 2. ORTEP drawing of **2d**·H_2O showing 50% probability thermal ellipsoids. The H_2O molecule has been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–O1 2.104(2), Ru1–O2 2.091(2), O1–C13 1.325(4), O2–C13 1.315(4), O3–C13 1.239(4), Ru1–P1 2.343(1); O1–Ru1–O2 62.81(8), C13–O1–Ru1 92.2(2), C13–O2–Ru1 93.1(2), O1–C13–O2 111.8(2), O1–C13–O3 123.7(3), O2–C13–O3 124.5(3), O1–Ru1–P1 88.61(7), O2–Ru1–P1 84.25(7).

to the Ru–P bond [**2a**: O1–Ru1–P1 = 86.92(5)°, O2–Ru1–P1 = 88.09(5)°; **2d**: O1–Ru1–P1 = 88.61(7)°, O2–Ru1–P1 = 84.25(7)°]. The Ru–P bond lengths in **2a** and **2d** are also similar [2.3779(6) and 2.343(1) Å, respectively]. Finally, these main structural features for the Ru(η^2-O_2CO) fragment in **2a** and **2d** are in good agreement with those arising from the study of the distinct complex [Ru(CO_3)(PPh_3)$_2$(CO)$_2$], obtained by hydrolysis of the carbamato ligands in [Ru(O_2CN*i*Pr$_2$)$_2$(PPh_3)$_2$(CO)$_2$].[12]

The observed need for water to generate the carbonato complexes **2** suggests a lack of reactivity of the CO_3^{2-} dianion. Furthermore, attempts to synthesise **2d** using $KHCO_3$ instead of K_2CO_3 also showed the same need for addition of water to trigger the reaction. Note that the related complex [Ru(CO_3)(η^6-C_6Me_6)(*i*Pr$_2$PCH$_2$CH$_2$OMe)] has been fortuitously synthesised from [RuCl(η^6-C_6Me_6)(η^2-*P*,*O*-*i*Pr$_2$PCH$_2$CH$_2$OMe)][PF_6] upon treatment with aqueous Na_2CO_3.[10] The addition of water might be expected to result in the additional presence of the more reactive hydroxide anion, and this suggested the formation of a Ru–OH bond in a chloride ligand substitution reaction as the first step in this reaction. As depicted in Scheme 3, subsequent reaction between the basic hydroxide intermediate and the acidic HCO_3^- anion completes the formation of the carbonato complexes.

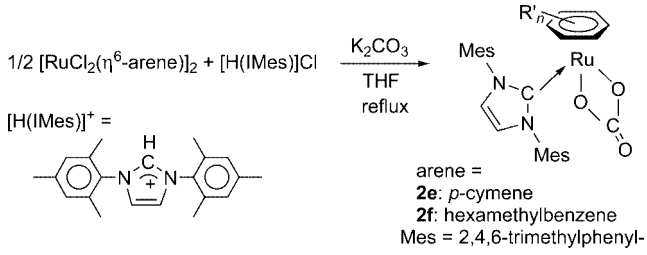
An insertion of carbon dioxide into the Ru–OH bond might also be considered. Indeed, the stable bicarbonato derivative [Ru(η^1-OCO_2H)(Me)(η^6-C_6Me_6)(PMe_3)] has been previously been obtained by treating the hydroxide complex [Ru(OH)(Me)(η^6-C_6Me_6)(PMe_3)] with carbon dioxide.[32]

The reaction between K_2CO_3 and an imidazolium salt such as 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride has been shown to generate reactive imidazol-2-ylidene species that can be trapped with sulfur.[6] This process appeared attractive to synthesise organometallic (vs. sulfide)



Scheme 3. Rationale accounting for the formation of complexes **2** catalysed by water.

derivatives under similar conditions. Thus, treatment of a 2:1 [H(IMes)]Cl/[$RuCl_2$(η⁶-arene)]$_2$ mixture with an excess of K_2CO_3 in THF at reflux led to the new carbonato complexes **2e** and **2f**, which were isolated as dark-orange solids in 79 and 46% yield, respectively (Scheme 4).



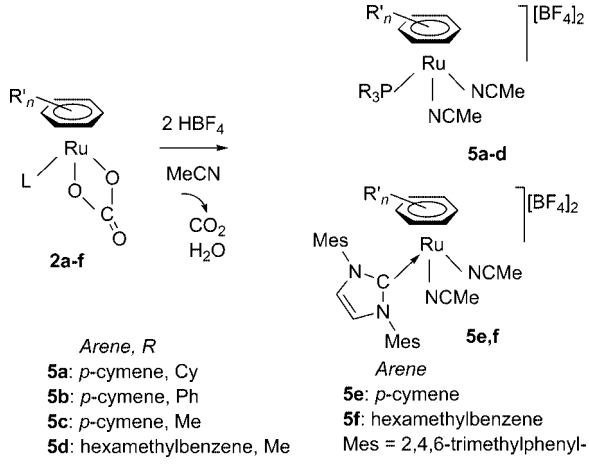
Scheme 4. Synthesis of the carbonatoruthenium complexes [Ru(η²-O_2CO)(η⁶-arene)(IMes)] (**2e** and **2f**).

Complexes **2e** and **2f**, which only differ from the carbonato complexes **2a**–**d** by the presence of the 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene ligand instead of a phosphane, were characterised by ^{1}H, ^{13}C and ^{13}C{^{1}H} NMR spectroscopy and elemental analysis. The ^{13}C NMR resonance corresponding to the carbene carbon nucleus in **2e** and **2f** is located at δ = 180.5 and 183.6 ppm, respectively. The assignment of the ^{13}C NMR resonance corresponding to the carbonato ligand in **2e** and **2f** (δ = 166.4 and 166.2 ppm, respectively) was inferred by comparison with **2a**–**d**.

The formation of the carbonato complexes [Ru(η²-O_2CO)(η⁶-arene)(IMes)] sheds new light on the preparation of catalysts for enyne metathesis and *O*-allyl isomerisation reactions, which were generated in situ by heating a mixture of [$RuCl_2$(*p*-cymene)]$_2$, imidazolium salt and an excess of Cs_2CO_3 in toluene.[3–5] The transient formation of [$RuCl_2$(*p*-cymene)(IMes)], which releases a reactive [$RuCl_2$(IMes)] moiety, was postulated. The fact that the catalytic species may arise from an [Ru(CO_3)(*p*-cymene)(IMes)] species rather than the [$RuCl_2$(*p*-cymene)(IMes)] intermediate must now be considered.

Synthesis of Dicationic [Ru(η⁶-arene)(L)(MeCN)$_2$][BF_4]$_2$ Derivatives

As previously reported for the reactivity study of the carbonato complex [Ru(η²-O_2CO)(bipy)$_2$],[26] double protonation of the carbonato ligand in complexes **2a**–**f** easily occurs under acidic conditions to generate carbon dioxide, water, and to formally release a 14-electron [Ru(η⁶-arene)(L)]$^{2+}$ fragment. The derivatives [Ru(η⁶-arene)(L)(MeCN)$_2$][BF_4]$_2$ (**5a**–**f**) were isolated in high yield (84–99%) after treating **2a**–**f** with 2 equiv. of HBF_4 (as its dimethyl ether adduct) in acetonitrile as solvent (Scheme 5).



Scheme 5. Synthesis of the dicationic derivatives [Ru(η⁶-arene)(L)(MeCN)$_2$][BF_4]$_2$ (**5a**–**f**).

Complexes **5a**–**f** are robust yellow compounds that are highly soluble in acetonitrile. They were characterised by ^{1}H, ^{13}C, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy and elemental analysis. Remarkably, the ^{13}C NMR resonance corresponding to the carbene carbon nucleus in **5e** and **5f** (δ = 163.7 and 164.1 ppm, respectively) is shifted upfield relative to **2e** and **2f** (δ = 180.5 and 183.6 ppm, respectively). This observation likely indicates a reduced back-donation from the metal atom in **5e** and **5f** as compared to **2e** and **2f**, which results in an enhanced imidazolium (vs. imidazolylidene) character.[33] A study of analogous [Ru(η⁶-benzene)(L)(MeCN)$_2$]$^{2+}$ complexes obtained by treatment of [Ru(η⁶-benzene)(MeCN)$_3$][OTf]$_2$ with a phosphane has recently been reported and emphasises the potential of such complexes.[34]

Conclusions

The easy formation of carbonatoruthenium complexes on reaction of K_2CO_3 with L_nRuCl_2 precursors in the presence of water constitutes a convenient method to remove the chloride ligands and to use the carbonato ligand as a protecting group for transition metal centres. Under acidic conditions, a clean elimination of the carbonato ligand takes place to formally generate a coordinatively unsaturated dicationic moiety. Thus, the transformation of [$RuCl_2$(η⁶-arene)(L)] precursors into dicationic [Ru(η⁶-arene)(L)(MeCN)$_2$][BF_4]$_2$ derivatives is achieved without any

involvement of strong chloride scavengers such as silver or thallium salts. The carbonato ligand also allows a convenient route to useful dihydride complexes upon reaction with methanol. Finally, the formation of carbonatoruthenium intermediates may interfere in processes where a ruthenium catalyst is generated in situ from a ruthenium dichloride complex and an alkali metal carbonate as base.

Experimental Section

General: The reactions were performed according to Schlenk-type techniques. Commercial solvents (99+% grade) were used without further purification except diethyl ether and dichloromethane, which were distilled under an inert gas after drying according to conventional methods. NMR spectra were recorded at 297 K with AC 200 FT and AC 300 Bruker instruments and referenced internally to the solvent peak. Elemental analyses were performed by the "Service de Microanalyse du CNRS", Vernaison, France. Complexes **1a**–**d** were obtained by treating the appropriate phosphane with dimeric $[RuCl_2(\eta^6\text{-arene})]_2$ ruthenium complexes in dichloromethane as solvent, as described in the literature.[35] For the convenience of this work, **1a** was prepared as its acetone adduct. The preparation of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride has been described elsewhere.[36]

$[RuCl_2(p\text{-cymene})(PCy_3)]\cdot$acetone (1a): Stoichiometric amounts of $[RuCl_2(p\text{-cymene})]_2$ (8.07 g, 13.2 mmol) and PCy_3 (7.39 g, 26.4 mmol) were mixed in dichloromethane (60 mL) as reported previously.[37] After stirring for 2 h, the mixture was concentrated to dryness and acetone (60 mL) was added to the residue. The mixture was stirred to obtain a red precipitate that was collected by filtration. Yield: 16.1 g (95%). The product retains 1 equiv. of acetone per Ru, as indicated by ^{1}H NMR spectroscopy.

$[Ru(\eta^2\text{-}O_2CO)(p\text{-cymene})(PCy_3)]\cdot 1/2CH_2Cl_2$ (2a): A mixture consisting of a sample of **1a** (6.00 g, 9.30 mmol), K_2CO_3 (2.00 g, 14.5 mmol) and acetone (50 mL) was stirred for 2 d. The volatiles were then removed under vacuum to leave a yellow solid, whicht was extracted with dichloromethane (50 mL). The solution was filtered and the filtrate was covered with acetone (20 mL) and then with diethyl ether (160 mL) to afford orange-yellow crystals. Yield: 4.51 g (78%). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 1.25 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CHMe_2), 1.16–1.89 (m, 33 H, Cy), 2.12 (s, 3 H, Me), 2.52 (m, 1 H, CHMe$_2$), 5.26 (d, $^3J_{H,H}$ = 6.2 Hz, 2 H, C_6H_4), 5.34 (d, $^3J_{H,H}$ = 6.2 Hz, 2 H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 18.7 (s, MeC$_6$H$_4$), 23.3 (s, CHMe_2), 27.0 (s, Cy, 1 C), 28.3 (d, $J_{P,C}$ = 10.2 Hz, Cy, 2 C), 29.9 (s, Cy, 2 C), 32.6 (s, CHMe$_2$), 35.4 (d, $^1J_{P,C}$ = 18.9 Hz, Cy, 1 C), 85.4 (d, $^2J_{P,C}$ = 3.8 Hz, C_6H_4, 2 CH), 86.6 (d, $^2J_{P,C}$ = 4.2 Hz, C_6H_4, 2 CH), 94.5 (s, CMe, *p*-cymene), 103.7 (s, CiPr, *p*-cymene), 165.6 (d, $^3J_{P,C}$ = 2.6 Hz, CO_3) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 37.8 ppm (s). $C_{29}H_{47}O_3PRu\cdot 1/2CH_2Cl_2$ (618.21): calcd. C 57.32, H 7.66, Cl 5.73, P 5.01; found C 57.24, H 7.82, Cl 5.52, P 5.18.

$[Ru(\eta^2\text{-}O_2CO)(p\text{-cymene})(PPh_3)]$ (2b): A mixture consisting of a sample of **1b** (2.71 g, 4.77 mmol), K_2CO_3 (1.50 g, 10.9 mmol), acetone (40 mL) and water (0.50 mL) was stirred for 3 d. The resulting yellow slurry was concentrated to dryness and the remaining solid was extracted with dichloromethane (40 mL). Acetone (10 mL) was added to the orange filtrate and this mixture was slowly concentrated to leave a crystalline orange-yellow solid, which was found to be pure by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Yield: 2.57 g (97%). Orange crystals were obtained by recrystallisation from hot acetonitrile. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 1.18 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CHMe_2), 2.00 (s, 3 H, MeC$_6$H$_4$), 2.49 (m, 1 H, CHMe$_2$), 5.12 (d, $^3J_{H,H}$ = 6.1 Hz, 2 H, C_6H_4), 5.20 (d, $^3J_{H,H}$ = 6.2 Hz, 2 H, C_6H_4), 7.37–7.54 (m, 15 H, Ph) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 18.6 (s, MeC$_6$H$_4$), 22.9 (s, CHMe_2), 31.8 (s, CHMe$_2$), 87.1 (d, $^2J_{P,C}$ = 5.4 Hz, C_6H_4, 2 CH), 87.8 (d, $^2J_{P,C}$ = 4.4 Hz, C_6H_4, 2 CH), 96.3 (s, CMe, *p*-cymene), 106.8 (s, CiPr, *p*-cymene), 128.8 (d, $^2J_{P,C}$ = 9.9 Hz, Ph, *ortho*), 131.1 (s, Ph, *para*), 131.5 (d, $^1J_{P,C}$ = 44.8 Hz, Ph, *ipso*), 134.5 (d, $^3J_{P,C}$ = 9.7 Hz, Ph, *meta*), 165.1 (s, CO_3) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 33.0 ppm (s). $C_{29}H_{29}O_3PRu$ (557.60): calcd. C 62.47, H 5.24, P 5.55; found C 62.33, H 5.30, P 5.30.

$[Ru(\eta^2\text{-}O_2CO)(p\text{-cymene})(PMe_3)]$ (2c): A mixture consisting of a sample of **1c** (1.50 g, 3.92 mmol), K_2CO_3 (1.00 g, 7.24 mmol), acetone (40 mL) and water (0.50 mL) was stirred for 10 d. The resulting yellow slurry was concentrated to dryness and the remaining solid was extracted with dichloromethane (40 mL). The solution was filtered and the orange filtrate was slowly concentrated to leave an orange, crystalline solid, which was found to be pure by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Yield: 1.38 g (95%). Recrystallisation from an acetone/acetonitrile mixture afforded dark-orange crystals. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 1.17 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CHMe_2), 1.34 (d, $^2J_{P,H}$ = 10.3 Hz, 9 H, PMe_3), 2.05 (s, 3 H, MeC$_6$H$_4$), 2.51 (m, 1 H, CHMe$_2$), 5.38 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, C_6H_4), 5.46 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 14.9 (d, $^1J_{P,C}$ = 28.4 Hz, PMe_3), 18.9 (s, MeC$_6$H$_4$), 23.2 (s, CHMe_2), 32.2 (s, CHMe$_2$), 86.1 (s, C_6H_4, 2 CH), 86.6 (s, C_6H_4, 2 CH), 94.9 (s, CMe, *p*-cymene), 103.9 (s, CiPr, *p*-cymene), 166.7 (d, $^3J_{P,C}$ = 2.9 Hz, CO_3) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 8.3 ppm (s). $C_{14}H_{23}O_3PRu$ (371.38): calcd. C 45.28, H 6.24, P 8.34; found C 45.18, H 6.29, P 8.30.

$[Ru(\eta^2\text{-}O_2CO)(\text{hexamethylbenzene})(PMe_3)]\cdot H_2O$ (2d): A mixture consisting of a sample of **1d** (2.00 g, 4.87 mmol), K_2CO_3 (1.50 g, 10.9 mmol), acetone (40 mL) and water (0.60 mL) was stirred for 10 d. The resulting yellow slurry was concentrated to dryness and the remaining solid was extracted with dichloromethane (40 mL). Acetone (10 mL) was added to the orange filtrate and this mixture was slowly concentrated to leave an orange, crystalline solid, which was found to be pure by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Yield: 1.87 g (92%). Alternatively, a mixture consisting of a sample of **1d** (1.00 g, 2.44 mmol), K_2CO_3 (1.00 g, 7.2 mmol), THF (40 mL) and water (0.50 mL) was heated at reflux for 24 h, then treated as above. Yield: 0.55 g (54%). Recrystallisation by diffusion of THF into a concentrated solution of the compound in dichloromethane afforded orange-red crystals. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 1.22 (d, $^2J_{P,H}$ = 10.2 Hz, 9 H, PMe_3), 2.04 (s, 18 H, C_6Me_6) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 13.7 (d, $^1J_{P,C}$ = 28.0 Hz, PMe_3), 16.2 (s, C_6Me_6), 95.1 (d, $^2J_{P,C}$ = 3.4 Hz, C_6Me$_6$), 166.8 (d, $^3J_{P,C}$ = 2.6 Hz, CO_3) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 4.7 ppm (s). $C_{16}H_{27}O_3PRu\cdot H_2O$ (417.45): calcd. C 46.04, H 7.00, P 7.42; found C 45.86, H 6.92, P 7.45.

$[Ru(\eta^2\text{-}O_2CO)(p\text{-cymene})(IMes)]$ (2e): A mixture consisting of a sample of $[RuCl_2(p\text{-cymene})]_2$ (2.00 g, 3.27 mmol), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (2.27 g, 6.66 mmol), K_2CO_3 (3.00 g, 21.7 mmol), THF (40 mL) and dichloromethane (10 mL) was stirred overnight then heated at reflux for 20 h. The resulting slurry was concentrated to dryness and the remaining solid was extracted with dichloromethane (30 mL). The solution was filtered and the filtrate was concentrated under vacuum to leave a brown solid, which was found to be pure by ^{1}H NMR spectroscopy. Yield: 3.60 g (79%). Recrystallisation from hot toluene afforded dark-orange crystals of **2e**·1/4C_7H_8 in 77% yield relative to crude **2e**. ^{1}H

NMR (300.13 MHz, CD_2Cl_2): δ = 0.76 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CHMe_2), 1.28 (s, 3 H, MeC$_6$H$_4$), 1.56 (m, 1 H, CHMe$_2$), 2.08 (s, 12 H, Mes, 4 Me), 2.25 (s, toluene), 2.27 (s, 6 H, Mes, 2 Me), 4.74 (d, $^3J_{H,H}$ = 6.1 Hz, 2 H, C$_6$H$_4$), 5.04 (d, $^3J_{H,H}$ = 6.2 Hz, 2 H, C$_6$H$_4$), 6.93 (s, 2 H, CH=), 6.93 (s, 2 H, Mes, 2 CH), 6.94 (s, 2 H, Mes, 2 CH), 7.04–7.15 (m, toluene) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 17.1 (s, MeC$_6$H$_4$), 18.7 (s, Mes, 4 Me), 21.2 (s, CHMe_2), 23.4 (s, Mes, 2 Me), 32.2 (s, CHMe$_2$), 84.5 (s, C$_6$H$_4$, 2 CH), 85.2 (s, C$_6$H$_4$, 2 CH), 94.7 (s, CMe, p-cymene), 100.3 (s, CiPr, p-cymene), 125.2 (s, NCH=), 129.2 (s, Mes, 4 CH), 136.9 (s, Mes, 4 CMe), 137.1 (s, Mes, 2 CN), 139.3 (s, Mes, 2 CMe), 166.4 (s, CO_3), 180.5 (s, Ru=C) ppm; the resonances of toluene have been omitted. $C_{32}H_{41}N_2O_3Ru\cdot1/4C_7H_8$ (625.80): calcd. C 64.78, H 6.60, N 4.48; found C 64.73, H 6.54, N 4.16.

[Ru(η²-O_2CO)(hexamethylbenzene)(IMes)] (2f): A mixture consisting of a sample of [RuCl$_2$(hexamethylbenzene)]$_2$ (1.50 g, 2.24 mmol), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (1.52 g, 4.46 mmol), K_2CO_3 (1.00 g, 7.24 mmol) and THF (40 mL) was stirred overnight, then heated at reflux for 24 h. The resulting slurry was concentrated to dryness and the remaining solid was extracted with dichloromethane (30 mL). The solution was filtered and the filtrate was concentrated under vacuum to leave a brown solid. Yield: 1.30 g (46%). Dark-orange crystals were obtained from hot toluene. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 1.55 (s, 18 H, C$_6$Me$_6$), 2.09 (s, 6 H, Mes, 2 Me), 2.10 (s, 6 H, Mes, 2 Me), 2.27 (s, 6 H, Mes, 2 Me), 6.83 (s, 2 H, CH=), 6.90 (s, 2 H, Mes, 2 CH), 6.92 (s, 2 H, Mes, 2 CH) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 15.6 (s, C$_6$$Me_6$), 19.1 (s, Mes, 2 Me *ortho*), 19.5 (s, Mes, 2 Me *ortho*), 21.2 (s, Mes, 2 Me *para*), 92.9 (s, C_6Me$_6$), 125.1 (s, NCH=), 128.2 (s, Mes, 2 CH), 129.5 (s, Mes, 2 CH), 135.0 (s, Mes, 2 CMe *ortho*), 137.6 (s, Mes, 2 CN), 138.7 (s, Mes, 2 CMe *para*), 139.0 (s, Mes, 2 CMe *ortho*), 166.2 (s, CO_3), 183.6 (s, Ru=C) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 125.1 ppm (dd, $^1J_{H,C}$ = 196, $^3J_{H,C}$ = 11.9 Hz, NCH=). $C_{34}H_{42}N_2O_3Ru$ (627.79): calcd. C 65.05, H 6.74, N 4.46; found C 64.72, H 6.57, N 4.56.

[RuH$_2$(p-cymene)(PCy$_3$)] (3a): A mixture consisting of a sample of **1a** (3.29 g, 5.11 mmol), K_2CO_3 (1.50 g, 10.9 mmol) and methanol (40 mL) was stirred at room temperature for 0.5 h and the resulting yellow slurry was heated at reflux for 1 h. The hot solution was immediately filtered and the brown filtrate was concentrated under vacuum to leave a solid, which was washed twice with cold methanol to give a colourless, crystalline powder. Yield: 2.13 g (81%). Similarly, a solution of **2a** in methanol was heated at reflux for 1 h and then treated as above to give **3a** in 70% yield. ^{1}H NMR (300.13 MHz, C_6D_6): δ = –11.0 (d, $^2J_{P,H}$ = 43.3 Hz, 2 H, RuH), 1.29 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CHMe_2), 1.17–2.06 (m, 33 H, Cy), 2.08 (s, 3 H, Me), 2.46 (m, 1 H, CHMe$_2$), 5.07 (d, $^3J_{H,H}$ = 5.6 Hz, 2 H, C$_6$H$_4$), 5.16 (d, $^3J_{H,H}$ = 5.6 Hz, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ = 21.7 (s, MeC$_6$H$_4$), 25.3 (s, CHMe_2), 27.7 (s, Cy, 1 C), 28.7 (d, $J_{P,C}$ = 9.8 Hz, Cy, 2 C), 31.2 (s, Cy, 2 C), 33.5 (s, CHMe$_2$), 40.0 (d, $^1J_{P,C}$ = 21.8 Hz, Cy, 1 C), 80.0 (d, $^2J_{P,C}$ = 3.8 Hz, C$_6$H$_4$, 2 CH), 85.7 (d, $^2J_{P,C}$ = 1.7 Hz, C$_6$H$_4$, 2 CH), 96.9 (s, CMe, p-cymene), 110.4 (s, CiPr, p-cymene) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6) δ = 78.1 ppm (s). $C_{28}H_{49}$PRu (517.74): calcd. C 64.96, H 9.54, P 5.98; found C 64.79, H 9.50, P 5.87.

[RuCl(H)(p-cymene)(PCy$_3$)] (4a): Equimolar amounts of **3a** (1.14 g, 2.20 mmol) and **1a** (1.42 g, 2.20 mmol) were added to methanol (30 mL) and this mixture was stirred at room temperature overnight (or heated at reflux for 1 h) to afford a yellow slurry. Concentration of the mixture and subsequent analysis of the residue by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy indicated a quantitative formation of **4a**. Recrystallisation by dissolution in dichloromethane (25 mL) and then diffusion of methanol (100 mL) afforded dark-orange crystals but in a moderate yield (0.94 g, 39%) owing to residual solubility. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = –8.0 (d, $^2J_{P,H}$ = 49.5 Hz, 1 H, RuH), 1.12 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CHMe_2), 1.26 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CHMe_2), 1.06–1.90 (m, 33 H, Cy), 1.95 (s, 3 H, Me), 2.14 (m, 1 H, CHMe$_2$), 4.28 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, C$_6$H$_4$), 4.48 (d, $^3J_{H,H}$ = 6.1 Hz, 1 H, C$_6$H$_4$), 6.05 (m, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 19.5 (s, MeC$_6$H$_4$), 21.2 (s, CHMe_2), 25.4 (s, CHMe_2), 27.3 (s, Cy, 1 C), 28.3 (d, $J_{P,C}$ = 9.9 Hz, Cy, 1 C), 28.4 (d, $J_{P,C}$ = 10.9 Hz, Cy, 1 C), 30.0 (s, Cy, 1 C), 30.1 (d, $J_{P,C}$ = 1.8 Hz, Cy, 1 C), 31.7 (s, CHMe$_2$), 36.8 (d, $^1J_{P,C}$ = 21.8 Hz, Cy, 1 C), 79.6 (d, $^2J_{P,C}$ = 2.7 Hz, C$_6$H$_4$, 1 CH), 86.7 (d, $^2J_{P,C}$ = 4.5 Hz, C$_6$H$_4$, 1 CH), 86.9 (d, $^2J_{P,C}$ = 5.4 Hz, C$_6$H$_4$, 1 CH), 91.2 (d, $^2J_{P,C}$ = 3.6 Hz, C$_6$H$_4$, 1 CH), 97.8 (s, CMe, p-cymene), 106.5 (s, CiPr, p-cymene) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 59.7 ppm (s). $C_{28}H_{48}$ClPRu (552.19): calcd. C 60.90, H 8.76, Cl 6.42, P 5.61; found C 60.89, H 9.06, Cl 6.68, P 5.74.

[Ru(p-cymene)(PCy$_3$)(MeCN)$_2$][BF$_4$]$_2$ (5a): Complexes **5a**–**f** were quantitatively formed by treating the corresponding carbonato complex in solution in cold acetonitrile with a stoichiometric amount of $HBF_4\cdot OMe_2$. In a typical procedure, a 1.2 M solution of $HBF_4\cdot OMe_2$ in methanol (7.5 mL, 9.0 mmol) was added to a stirred solution of **2a** (2.75 g, 4.45 mmol) in cold acetonitrile (30 mL, –40 °C). The mixture was allowed to reach room temperature (1 h) and then concentrated under vacuum. The resulting solution was covered with dichloromethane (20 mL) and then diethyl ether (120 mL) to afford yellow crystals. Yield: 3.26 g (95%). ^{1}H NMR (300.13 MHz, CD_3CN): δ = 1.41 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CHMe_2), 1.48–1.94 (m, broad, 33 H, Cy), 2.10 (s, 6 H, MeCN), 2.27 (s, 3 H, MeC$_6$H$_4$), 2.80 (m, 1 H, CHMe$_2$), 6.34 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, C$_6$H$_4$), 6.42 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 4.76 (s, MeCN), 18.9 (s, MeC$_6$H$_4$), 22.6 (s, CHMe_2), 26.5 (s, Cy, 1C), 27.7 (d, $J_{P,C}$ = 10.3 Hz, Cy, 2 C), 30.4 (d, $J_{P,C}$ = 1.7 Hz, Cy, 2 C), 32.2 (s, CHMe$_2$), 37.9 (d, $J_{P,C}$ = 19.8 Hz, Cy, 1 C), 90.8 (d, $^2J_{P,C}$ = 2.9 Hz, C$_6$H$_4$, 2 CH), 93.0 (d, $^2J_{P,C}$ = 1.7 Hz, C$_6$H$_4$, 2 CH), 103.9 (s, CMe, p-cymene), 114.3 (s, CiPr, p-cymene), 132.2 (s, MeCN) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 44.7 ppm (s). $C_{32}H_{53}B_2F_8N_2$PRu (771.44): calcd. C 49.82, H 6.93, N 3.63, P 4.02; found C 49.59, H 7.03, N 3.64, P 4.38.

[Ru(p-cymene)(PPh$_3$)(MeCN)$_2$][BF$_4$]$_2$ (5b): Yield: 96%, yellow crystals. ^{1}H NMR (300.13 MHz, CD_3CN): δ = 1.36 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CHMe_2), 1.94 (s, 3 H, MeC$_6$H$_4$), 2.33 (s, 6 H, MeCN), 2.94 (m, 1 H, CHMe$_2$), 5.63 (dd, $^3J_{H,H}$ = 6.7, $^3J_{P,H}$ = 1.3 Hz, 2 H, C$_6$H$_4$), 6.27 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, C$_6$H$_4$), 7.66–7.77 (m, 15 H, Ph) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_3CN): δ = 4.66 (s, MeCN), 18.7 (s, MeC$_6$H$_4$), 22.3 (s, CHMe_2), 32.3 (s, CHMe$_2$), 92.5 (s, C$_6$H$_4$, 2 CH), 93.9 (d, $^2J_{P,C}$ = 2.9 Hz, C$_6$H$_4$, 2 CH), 107.6 (s, CMe, p-cymene), 119.3 (s, CiPr, p-cymene), 129.6 (d, $^1J_{P,C}$ = 51.9 Hz, Ph, *ipso*), 130.5 (d, $^2J_{P,C}$ = 10.2 Hz, Ph, *ortho*), 132.2 (s, MeCN), 133.3 (d, $^4J_{P,C}$ = 2.9 Hz, Ph, *para*), 134.9 (d, $^3J_{P,C}$ = 10.2 Hz, Ph, *meta*) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_3CN): δ = 39.4 ppm (s). $C_{32}H_{35}B_2F_8N_2$PRu (753.30): calcd. C 51.02, H 4.68, N 3.72, P 4.11; found C 50.78, H 4.68, N 3.72, P 4.10.

[Ru(p-cymene)(PMe$_3$)(MeCN)$_2$][BF$_4$]$_2$ (5c): Yield: 88%, lemon-yellow crystals. ^{1}H NMR (300.13 MHz, CD_3CN): δ = 1.32 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CHMe_2), 1.84 (d, $^2J_{P,H}$ = 12.0 Hz, 9 H, PMe$_3$), 2.20 (s, 3 H, MeC$_6$H$_4$), 2.63 (d, $^5J_{P,H}$ = 1.3 Hz, 6 H, MeCN), 2.80 (m, 1 H, CHMe$_2$), 6.27 (m, 4 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_3CN): δ = 4.82 (s, MeCN), 16.7 (d, $^1J_{P,C}$ = 34.7 Hz, PMe$_3$), 18.6 (s, MeC$_6$H$_4$), 22.2 (s, CHMe_2), 32.0 (s,

*C*HMe$_2$), 91.7 (d, $^2J_{P,C}$ = 4.0 Hz, C_6H_4, 2 CH), 94.5 (d, $^2J_{P,C}$ = 3.3 Hz, C_6H_4, 2 CH), 102.9 (s, *C*Me, *p*-cymene), 113.0 (s, *Ci*Pr, *p*-cymene), 130.5 (s, Me*C*N) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_3CN): δ = 12.5 ppm (s). $C_{17}H_{29}B_2F_8N_2PRu$ (567.08): calcd. C 36.01, H 5.15, N 4.94, P 5.46; found C 35.74, H 5.19, N 4.95, P 5.83.

[Ru(hexamethylbenzene)(PMe$_3$)(MeCN)$_2$][BF$_4$]$_2$ (5d): Yield: 92%, lemon-yellow crystals. ^1H NMR (300.13 MHz, CD_3CN): δ = 1.55 (d, $^2J_{P,H}$ = 11.5 Hz, 9 H, PMe_3), 2.17 (s, 18 H, C_6Me_6), 2.52 (d, $^5J_{P,H}$ = 1.3 Hz, 6 H, MeCN) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ = 4.79 (s, *Me*CN), 14.8 (d, $^1J_{P,C}$ = 33.5 Hz, PMe_3), 16.6 (s, C_6Me_6), 103.6 (d, $^2J_{P,C}$ = 1.9 Hz, C_6Me_6), 129.8 (s, Me*C*N) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_3CN): δ = 8.9 ppm (s). $C_{19}H_{33}B_2F_8N_2PRu$ (595.14): calcd. C 38.35, H 5.59, N 4.71, P 5.20; found C 38.32, H 5.66, N 4.69, P 5.40.

[Ru(*p*-cymene)(IMes)(MeCN)$_2$][BF$_4$]$_2$ (5e): Yield: 99%, orange crystals. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 1.03 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH*Me$_2$*), 1.73 (s, 3 H, *Me*C_6H_4), 1.97 (m, 1 H, C*H*Me$_2$), 2.07 (s, 12 H, Mes, 4 Me), 2.34 (s, 6 H, Mes, 2 Me), 2.36 (s, 6 H, MeCN), 5.41 (d, $^3J_{H,H}$ = 6.3 Hz, 2 H, C_6H_4), 5.71 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H, C_6H_4), 7.10 (s, 4 H, Mes, CH), 7.27 (s, 2 H, CH=) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 4.74 (s, *Me*CN), 18.3 (s, Mes, 4 Me), 18.6 (s, *Me*C_6H_4), 21.2 (s, Mes, 2 Me), 22.7 (s, CH*Me$_2$*), 32.1 (s, *C*HMe$_2$), 90.6 (s, C_6H_4, 2 CH), 91.3 (s, C_6H_4, 2 CH), 104.5 (s, *C*Me, *p*-cymene), 109.0 (s, *Ci*Pr, *p*-cymene), 127.8 (s, NCH=), 129.5 (s, Me*C*N), 130.1 (s, Mes, 4 CH), 136.1 (s, Mes, 4 *C*Me), 136.4 (s, Mes, 2 CN), 141.6 (s, Mes, 2 *C*Me, Mes), 163.7 (s, Ru=C) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 127.8 ppm (dd, $^1J_{H,C}$ = 201, $^3J_{H,C}$ = 12 Hz, NCH=). $C_{35}H_{44}B_2F_8N_4Ru$ (795.44): calcd. C 52.85, H 5.58, N 7.04; found C 52.68, H 5.62, N 6.99.

[Ru(hexamethylbenzene)(IMes)(MeCN)$_2$][BF$_4$]$_2$ (5f): Yield: 84%, orange crystals. ^1H NMR (200.13 MHz, CD_3CN): δ = 1.78 (s, 18 H, C_6Me_6), 1.95 (s, 6 H, MeCN), 2.06 (s, 12 H, Mes, 4 Me), 2.35 (s, 6 H, Mes, 2 Me), 7.11 (s, Mes, 4 H), 7.25 (s, 2 H, CH=) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 5.30 (s, *Me*CN), 16.5 (s, C_6Me_6), 18.7 (s, Mes, 4 Me), 21.2 (s, Mes, 2 Me), 101.7 (s, C_6Me_6), 128.5 (s, NCH=), 129.3 (s, Me*C*N), 130.3 (s, Mes, 4 CH), 136.1 (s, Mes, 4 *C*Me), 137.1 (s, Mes, 2 CN), 141.1 (s, Mes, 2 *C*Me), 164.1 (s, Ru=C) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 128.5 ppm (dd, $^1J_{H,C}$ = 201, $^3J_{H,C}$ = 11 Hz, NCH=). $C_{37}H_{48}B_2F_8N_4Ru$ (823.49): calcd. C 53.97, H 5.88, N 6.80; found C 53.95, H 6.09, N 6.90.

X-ray Crystallography: A selected crystal of **2a**·1/2CH_2Cl_2 was studied with a NONIUS Kappa CCD diffractometer equipped with a graphite monochromator. The cell parameters were obtained with Denzo and Scalepack,[38] and data collection with NONIUS KappaCCD software.[39] Data reduction was carried out with Denzo and Scalepack.[38] A selected crystal of **2d**·H_2O was studied with a NONIUS CAD 4 automatic diffractometer equipped with a graphite monochromator.[40] After Lorenz and polarisation corrections (**2d**),[41] the structures were solved with SIR-97, which revealed the non-hydrogen atoms.[42,43] After anisotropic refinement, many hydrogen atoms might be found with Fourier difference calculations. The whole structures were refined with SHELXL-97 by full-matrix least-squares methods on F^2 (x, y, z, β_{ij} for Ru, P, Cl,

Table 1. Crystallographic data for complexes **2a**·1/2CH_2Cl_2 and **2d**·H_2O.[a]

Complex	**2a**·1/2CH_2Cl_2	**2d**·H_2O
Empirical formula	$C_{59}H_{96}Cl_2O_6P_2Ru_2$	$C_{16}H_{29}O_4PRu$
Molecular mass [g mol^{-1}]	1236.34	417.43
Crystal size [mm]	0.32 × 0.22 × 0.20	0.32 × 0.26 × 0.22
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a [Å]	14.6292(3)	12.900(4)
b [Å]	15.8474(3)	14.846(7)
c [Å]	16.0019(3)	9.764(3)
α [°]	115.050(1)	90
β [°]	114.131(1)	103.32(3)
γ [°]	94.460(1)	90
Volume [Å^3]	2922.55(10)	1819.6(12)
Z	2	4
Density [g cm^{-3}]	1.405	1.524
Temperature [K]	150(2)	293(2)
F(000)	1300	864
Mo-K_α radiation, λ [Å]	0.71073	0.71073
Absorption coefficient [mm^{-1}]	0.711	0.963
θ range [°]	1.49 to 27.51	2.12 to 27.02
Index ranges	$0 < h < 19$	$-16 < h < 16$
	$-20 < k < 20$	$0 < k < 18$
	$-20 < l < 18$	$0 < l < 12$
Reflections collected	32238	4176
Independent reflections	12228 (R_{int} = 0.0000)	3951 (R_{int} = 0.0253)
Reflections [$I > 2\sigma(I)$]	10808	3474
Data/restraints/parameters	12923/0/641	3951/0/200
Goodness-of-fit on F^2	1.088	1.018
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0328	R_1 = 0.0320
	wR_2 = 0.0759	wR_2 = 0.0858
R indices (all data)	R_1 = 0.0440	R_1 = 0.0397
	wR_2 = 0.0832	wR_2 = 0.0895
Largest diff. peak/hole [e·Å^{-3}]	0.837/–0.929	0.869/–0.840

[a] $w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 3.4483P]$ (**2a**), $1/[\sigma^2(F_o^2) + (0.0532P)^2 + 2.1077P]$ (**2d**), where $P = (F_o^2 + 2F_c^2)/3$.

O and C atoms; *x*, *y*, *z* in riding mode for H atoms).[44] ORTEP views were prepared with PLATON98,[45] and ORTEP-3 for Windows.[46] In the case of **2a**, the asymmetric unit cell consists of two molecules of complex and a dichloromethane one. The two molecules are identical, although slight differences in torsion angles were detected. Further crystallographic data are given in Table 1. CCDC-287581 (**2a**), and -287580 (**2d**) contain 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.

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