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$RuH_2(H_2)_2(PCy_3)_2$: a room temperature catalyst for the Murai reaction

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Abstract

$RuH_2(H_2)_2(PCy_3)_2$ (**1**) and $RuH(o\text{-}C_6H_4C(O)Me)(H_2)(PCy_3)_2$ (**2**) or, **1** and $RuH(o\text{-}C_6H_4C(O)Ph)(H_2)(PCy_3)_2$ (**3**) were shown to be efficient catalysts for the ethylene coupling reaction with acetophenone (**7a**) or benzophenone (**9**), respectively. This efficiency under such mild conditions is attributed to the facile generation of two vacancies on the ruthenium centre. Such an hypothesis is confirmed by the fact that the corresponding carbonyl complexes $RuH(o\text{-}C_6H_4C(O)Me)(CO)(PCy_3)_2$ (**4**) and $RuH(o\text{-}C_6H_4C(O)Ph)(CO)(PCy_3)_2$ (**5**) were found completely inactive for the Murai coupling under the same conditions. Furthermore, we postulate that the bis(chelate) complex $Ru(C_6H_4C(O)CH_3)_2(PCy_3)_2$ (**6**), which is the resting state of the catalyst, is responsible for the deactivation of our catalytic system.
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1. Introduction

During the past 20 years, intense research activity has been devoted to the catalytic activation of carbon–hydrogen bonds leading to the formation of new carbon–carbon bonds as an interesting and important alternative to coupling reactions involving halide derivatives. The new carbon–carbon bond can be formed via insertion of carbon monoxide, isocyanide, alkynes or alkenes into the carbon–hydrogen bond [1–4]. In 1993, Murai and co-workers reported the alkylation of aromatic ketones via the insertion of alkenes into a carbon–hydrogen bond by using ruthenium catalyst precursors, $RuH_2(CO)(PPh_3)_3$ being the most efficient [5–7]. This fairly general system, which requires reaction temperature at or above 130 °C, has been extended to a variety of aromatic and olefinic substrates [1,8–11]. The mechanism proposed by Murai and co-workers (Scheme 1) involves in a first step the formation of an intermediate 16-electron ruthenium(0) complex (**I**) produced by hydrogenation of the incoming olefin, and in a second step, the addition of the aromatic ketone leads to an *ortho*-metallated intermediate $RuH[o\text{-}C_6H_4\text{–}C(O)R]$ (**II**). Hydrogen migration and carbon–carbon coupling would lead to the organic product and regenerate the active species [Ru] (**I**). Trost and co-workers have also studied the coupling of olefinic substrates with α-unsaturated esters catalysed by $RuH_2(CO)(PPh_3)_3$ [12]. They proposed that the active species [Ru] is formed both by hydrogenation of an incoming olefin and elimination of carbon monoxide via the formation of an unsaturated species $[Ru]S(PPh_3)_3$ where S is a solvent molecule coordinated to the ruthenium centre.

In 1998, we reported briefly that the complexes $RuH_2(H_2)_2(PCy_3)_2$ (**1**) and $RuH(o\text{-}C_6H_4C(O)Me)(H_2)(PCy_3)_2$ (**2**) were efficient catalysts for the coupling between acetophenone and ethylene at room temperature [13]. A recent study using **1** as catalyst for the coupling of different *para*-substituted acetophenone derivatives with ethylene has been performed by others [14]. Deactivation of the catalyst was discussed and ligand dissociation was proposed to play an important role but without further insights into this phenomenon. We now wish to report our unpublished results [15] concerning the catalytic activity and deactivation pathways for the coupling of acetophenone (and *para*-substituted acetophenones) or benzophenone with ethylene using the ruthenium catalyst precursors **1** and

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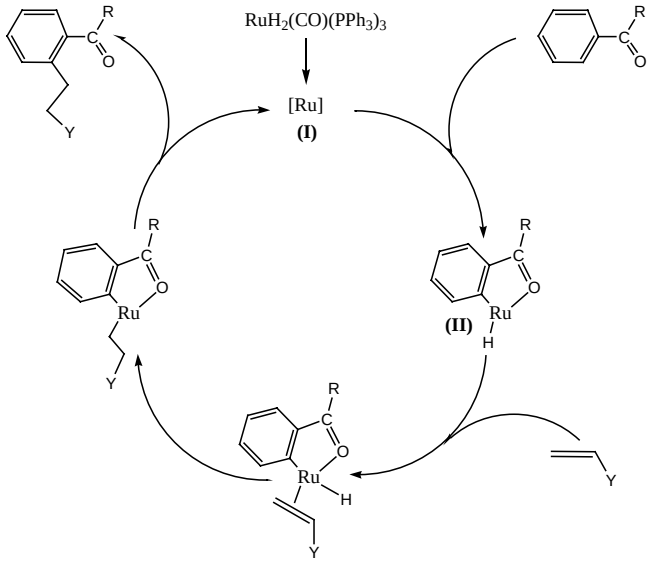
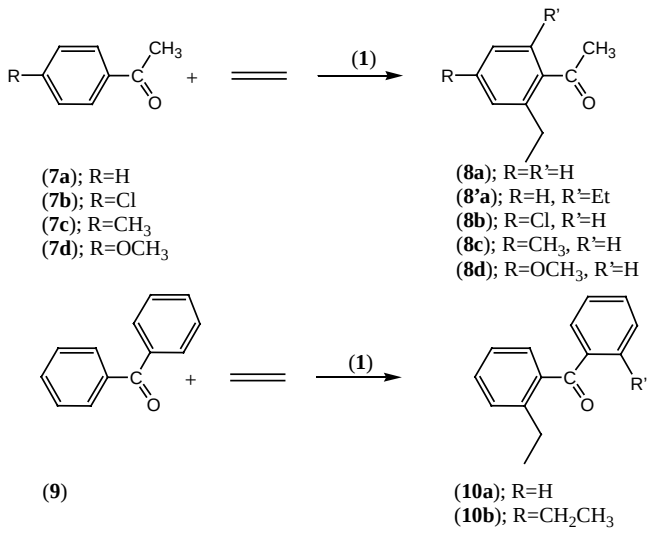


Scheme 1. Catalytic cycle proposed for the Murai reaction.

$RuH(o\text{-}C_6H_4C(O)R)(H_2)(PCy_3)_2$ (R = Me, (**2**); R = Ph, (**3**) respectively). The deactivation pathway will be discussed in details.

2. Results and discussion

We have performed a series of reactions that are depicted in Scheme 2. Total conversion of acetophenone (**7a**) was achieved after 22 h by exposing a pentane suspension of **1** to 20 bar of ethylene. The 1:1 coupling product **8a** was formed exclusively. A longer reaction time (48 h.) was necessary to observe the total conversion of 10 equivalents of benzophenone (**9**) in the same experimental conditions.



Scheme 2. Murai coupling between ethylene and *para*-substituted acetophenone or benzophenone using **1** as catalyst.

In that case, the reaction was less selective, leading to 4% of the 1:1 adduct **10a** and 96% of the 1:2 adduct **10b** (Scheme 2).

We have previously mentioned in a preliminary communication [13] the synthesis and characterization of the orthometallated complexes **2** and **3**. These hydrido(dihydrogen) complexes display unusual spectroscopic and dynamic features. At room temperature, the hydride and the dihydrogen ligands are in fast exchange, but NMR experiments at low temperatures demonstrate the presence of both quantum mechanical and classical exchange processes between these two ligands. However, due to the low solubility of **2** and **3**, this phenomenon was only fully studied with the analogous phenylpyridine complexes [15,16]. As **2** and **3** result from the direct reaction of **7a** or **9** with **1**, it was thus interesting to test their catalytic activity in the corresponding coupling reactions of **7a** and **9** with ethylene. In these cases, similar conversions were obtained when using **1** and **2** for the alkylation of **7a** or **1** and **3** for the alkylation of **9**. As mentioned in the introduction, such *ortho*-metallated complexes were proposed to be true intermediates in the catalytic cycle of the coupling of aromatic ketones with alkenes by Murai and co-workers. We were able to isolate the corresponding *ortho*-metallated carbonyl complexes $RuH(o\text{-}C_6H_4C(O)R)(CO)(PCy_3)_2$ (R = Me, **4**; R = Ph, **5**) and to test them as catalysts. Remarkably, no conversion was obtained. It is noteworthy that the analogous complexes $RuH(o\text{-}C_6H_4C(O)Ph)(CO)(dcypb)$ (with dcypb = $Cy_2P(CH_2)_4PCy_2$) [17] and $RuH(o\text{-}C_6H_4C(O)Me)(CO)(PPh_3)_2$ [18] have been reported to be respectively poorly active and completely inactive for the Murai coupling.

In order to gain more information on our catalytic system, we have performed a detailed study by varying the following parameters: temperature, solvent, catalyst/ketone ratio and substituents effects on the *para*-position of the aromatic ring of the ketone. This study was done using **1** as catalyst precursor, acetophenone and ethylene. A catalytic experiment was also carried out in cyclohexane-d_{12} and followed by ^1H NMR spectroscopy.

2.1. Influence of the temperature

Catalytic experiments were carried out at 18, 50 and 80 °C in pentane. The results are reported in Fig. 1.

As can be seen, the initial rate of the reaction slightly increases with increasing the temperature. However, the major drawback of using a higher temperature is the decrease of the conversion of **7a**–**8a** which drops to 42% at 50 °C and 25% at 80 °C. We noted that the initial colourless solution turned brown-orange as the catalysis proceeded that the activity ceased with the concomitant development of an intense purple colouring of the solution. This purple colour appeared more rapidly when increasing the temperature, which led us to the conclusion that the deactivation process was directly linked to the formation a purple coloured species.

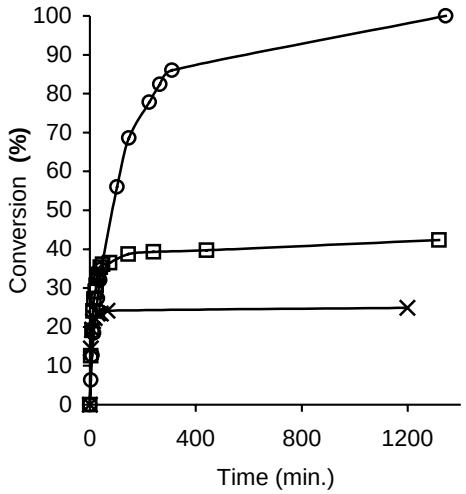


Fig. 1. Acetophenone conversion vs. time at 18 °C (○), 50 °C (□) and 80 °C (×).

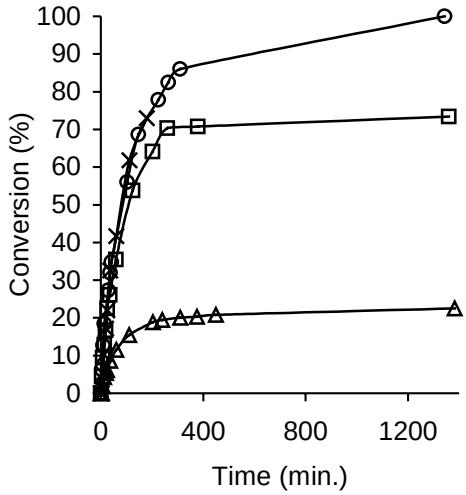


Fig. 3. *para*-substituted acetophenone conversion vs. time with R=H (○), R=Cl (×), R=Me (□) and R=MeO (△).

2.2. Influence of the solvent

We have performed several catalytic experiments using pentane, cyclohexane, toluene, tetrahydrofurane and diethyl ether as solvents at 18 °C. The results are reported in Fig. 2.

As can be seen from the Figure, the efficiency of this catalytic system is optimum when performed in cyclic or aliphatic alkanes. The initial reaction rate is not affected when performing the reaction in toluene. However, deactivation of the catalyst is observed in that case, probably as the result of the formation of an arene species. Indeed, as previously shown, **1** can react with unsaturated hydrocarbons to give π-arene complexes [19,20]. When using solvents such as tetrahydrofurane or diethyl ether that can easily coordinate to the ruthenium centre and stabilize the intermediates in the catalytic cycle, we noted a decrease in the initial rate of the catalytic reaction and a lowering of the conversion. Furthermore, when tetrahydrofurane was used as a solvent, a loss in selectivity was also observed leading to the formation of the coupling 1:2 by-product 2,6-ethylacetophenone (**8′a**) (**8a**:**8′a** in a ratio of 5.7:1). This might be attributed to the coordination of the solvent to the unsaturated fragment leading to some extent to the stabilization of an intermediate species and thus to a decrease of both the activity and the selectivity.

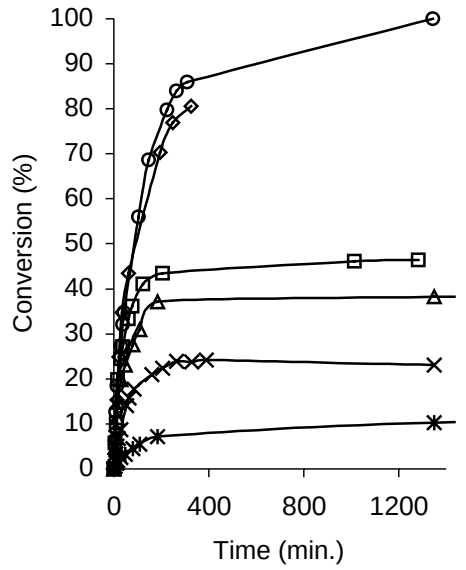


Fig. 2. Acetophenone conversion leading to **8a** vs. time in pentane (○), cyclohexane (◇), toluene (□), tetrahydrofurane (△) and diethylether (×) and acetophenone conversion leading to **8′a** vs. time in tetrahydrofurane (✱).

2.3. Influence of the substituent using para-substituted acetophenones

The catalytic experiments were done in pentane at 18 °C for all the substrates $RC_6H_4C(O)Me$ (R = H, **7a**; R = Cl, **7b**; R = Me, **7c**; R = OMe, **7d**). The results are reported in Fig. 3.

As mentioned earlier, catalytic experiments using the *para*-subtituted acetophenone substrates **7a**–**d** have been already reported by Busch and Leitner [14]. Our initial rates reflect the same order of reactivity H ≈ CH_3 > Cl > CH_3O. However, we do not observe any 1:2 coupling by-product. Furthermore, the yield determined by GC/MS after only 5 h are higher than those reported by Leitner and co-workers after 22 h which confirms the coordinating role of toluene in their system. When comparing the electron-donating substituent CH_3 and the electron-withdrawing substituent Cl, faster initial rate and higher total conversion of the substrate are observed for the latter. However, we have measured a dramatic decrease on both the conversion and the initial rate when the *para*-substituent is CH_3O instead of Cl. We thus suggest that the electron-withdrawing effect is not sufficient to explain such a behaviour and that, electronic effects including the acetyl group, which acts as a chelating assistant, should be invoked to explain such a result.

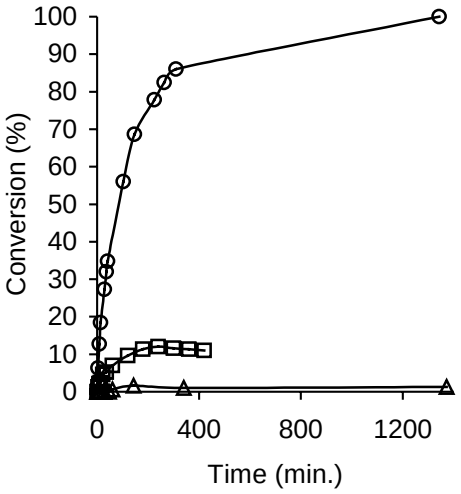


Fig. 4. Acetophenone conversion vs. time with a catalyst (**1**)/substrate (**7a**) ratio of 1/10 (○), 1/50 (□) and 1/100 (△).

2.4. Influence of the catalyst (*1*)/substrate (*7a*) ratio

The 1/10 (**1**/**7a**) ratio was chosen for direct comparison with the experiments performed by Murai and co-workers. We have also done some experiments in pentane at 18 °C with 1/50 and 1/100 ratios and a constant **1**/ethylene ratio. The results are depicted in Fig. 4.

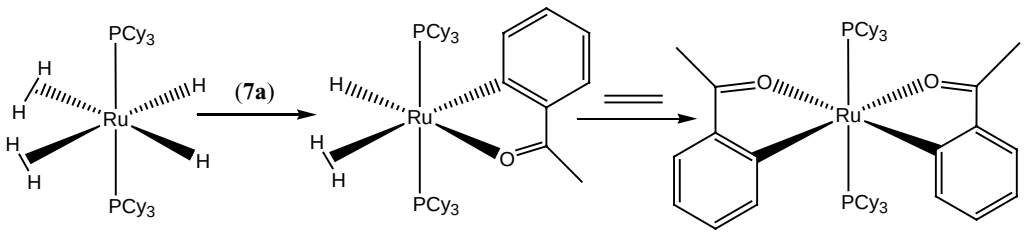
For the 1/100 ratio, almost no conversion was observed. When a sample of the catalytic mixture was taken immediately after pressurization under ethylene, we noted that the resulting solution was already purple. When a 1/50 ratio was used, only 10% of **7a** was converted to **8a**, which corresponds to only 5 catalytic cycles while in the meantime 10 catalytic cycles were obtained for the 1/10 ratio. These results suggest that the inhibition of the catalytic cycle is directly linked to the amount of the starting ketone.

2.5. Catalytic pathway

In order to gain more information on the catalytic pathway, several experiments were performed in the same experimental conditions but using cyclohexane-d_{12} as solvent (see Section 4). The catalytic reaction was stopped after 10 min and an NMR tube was filled with the resulting solution and monitored by ^{1}H NMR. The spectrum shows in addition to the signals attributed to **7a** (or **8a**), a triplet at −13.70 ppm attributed to an hydride ligand with a $^2J_{P-H}$ = 25.2 Hz. Multiplets are observed at 8.61, 7.86, 7.47 and 7.08 attributed to the aromatic ring of an *ortho*-metallated acetophenone ligand with a signal at 2.50 ppm attributed to the methyl group. Complex **1** is known to react with ethylene to give [RuH{η^3-C_6H_8)PCy_2}$(C_2H_4)(PCy_3)_2$], [21] however no signal corresponding to the partial dehydrogenation of the cyclohexyl groups of PCy_3 was observed. We proposed that this ruthenium species corresponds to a 16-electron hydride RuH(*o*-$C_6H_4C(O)CH_3)(PCy_3)_2$ (**A**) containing two tricyclohexylphosphine in a *trans* position and an *ortho*-metallated acetophenone ligand. As the presence of ethylene coordinated to the ruthenium cannot be excluded, the corresponding 18-electron species RuH(*o*-$C_6H_4C(O)CH_3)(C_2H_4)(PCy_3)_2$ with ethylene as ligand should also be considered. Our attempts to synthesize this compound by bubbling ethylene through a solution of RuH(*o*-$C_6H_4C(O)Me)(H_2)(PCy_3)_2$ (**2**) in pentane without further addition of **7a** failed, leading to complete decomposition of the starting complex. Such a 16-electron *ortho*-metallated RuH[*o*-C_6H_4-C(O)R] (**II**) complex was proposed to be the true intermediate in the catalytic cycle by Murai and co-workers [5–7]. Considering the ruthenium precursor they used, $RuH_2(CO)(PPh_3)_3$, and referring to the work of Trost and co-workers [12], decoordination of carbon monoxide is thus necessary. In our case, the formation of an unsaturated species (**A**) can be achieved via hydrogenation of a second incoming olefin. This is in agreement with the efficiency of our system at room temperature using either complexes **1**, **2** or **3**, as compared to the Murai's system operating at 135 °C with $RuH_2(CO)(PPh_3)_3$. In our system, vacancy sites on the ruthenium centre are easily available by decoordination of the H_2 ligand. This is not the case when using the carbonyl complexes **4** and **5** as catalyst precursors for the coupling of aromatic ketones with olefinic substrates at room temperature.

2.6. Deactivation pathway

Leitner and co-workers have proposed that the decoordination of a tricyclohexylphosphine is responsible for the deactivation of their catalytic system [14]. However, we have observed that the presence of free PCy_3 is detectable only after the catalytic conversion has ceased. Such an observation can be attributed to the partial decomposition of the catalyst when all the ketone substrate has been consumed. A similar behaviour was obtained when bubbling ethylene in a pentane solution of **2** without adding further **7a**. Furthermore, from the results we have obtained, it is clear that the deactivation of the system is directly correlated with the formation of a purple ruthenium species, which is strongly favoured when the temperature or the amount of **7a** have increased. It is noteworthy that such a species is formed progressively whereas the catalytic system is still active. Finally, we have observed that once the system is inactive, pressurisation under 20 bar of dihydrogen leads to the regeneration of the catalyst. The orange colour is restored and after flushing the dihydrogen atmosphere with argon and then ethylene, the catalysis proceeds. In order to clarify this deactivation pathway, we have performed the following synthesis: a large excess of **7a** was added to a pentane solution of **1**, leading after 24 h to compound **2** as characterized by NMR. Ethylene was then bubbled for 30 min and the mixture was stirred for 3 days. A purple precipitate identified as $Ru(C_6H_4C(O)CH_3)_2(PCy_3)_2$ (**6**) was obtained and isolated (see Scheme 3).



(**1**) (**2**) (**6**)

Scheme 3. Synthesis of complexes **2** and **6**.

The ^{1}H NMR spectrum of **6** displays signals at 9.20, 7.58, 7.02 and 6.80 ppm attributed to the phenyl ring and a signal at 2.53 ppm attributed to the methyl group of the orthometallated acetophenone. The ^{31}P NMR displays one signal at 21.2 ppm. It should be noticed that bubbling for 20 min dihydrogen through a C_6D_6 solution of **6** led back to a mixture of the dihydrogen complexes **1** and **2**. Moreover, when a C_6D_6 solution of **6** was pressurised under 3 bar H_2, we observed quantitative formation of **1** and free actophenone as shown by ^{1}H and ^{31}P NMR spectra. Such an observation is compatible with the possibility to regenerate the catalyst under dihydrogen atmosphere. Finally, it must be pointed out that **6** was found inactive for the coupling reaction. All these observations led us to the conclusion that, even if we cannot completely exclude partial decomposition of the catalyst by PCy_3 decoordination, complex **6** is the resting state of the catalyst and is responsible for the progressive main deactivation pathway of this catalytic system using **1** as catalyst precursor.

3. Conclusions

We have demonstrated the efficiency of complexes **1**, **2** and **3** as catalyst precursors for the regioselective coupling between aromatic ketones and ethylene at room temperature in pentane. The efficiency of our catalysts under such mild conditions compared to the use of $RuH_2(CO)(PPh_3)_3$ at 135 °C is attributed to the easier generation of two vacancies on the ruthenium centre. In our case, the unsaturated ruthenium species (**A**) can be obtained via hydrogenation of two incoming olefins while decoordination of carbon monoxide, in addition to hydrogenation of one incoming olefin, is necessary when using $RuH_2(CO)(PPh_3)_3$. Furthermore, we propose that the bis(chelate) complex **6** is the resting state of the catalyst and is responsible for the progressive main deactivation pathway when using our catalysts.

4. Experimental section

4.1. General methods

All reactions were carried out under argon by using Schlenk glassware and vacuum line techniques. All solvents were freshly distilled from standard drying agents and thoroughly degassed under argon before use. Microanalyses were performed by the Laboratoire de Chimie de Coordination Microanalytical Service. NMR Spectra were recorded on a Bruker AC 200 (at 200.13 MHz for ^{1}H, at 81.015 MHz for ^{31}P and at 50.324 MHz for ^{13}C), on a Bruker AM250 (at 250 MHz for ^{1}H, at 101.25 MHz for ^{31}P and at 62.89 MHz for ^{13}C) and on a Bruker AMX400 (at 400.13 MHz for ^{1}H, at 161.21 MHz for ^{31}P and at 100.71 MHz for ^{13}C), all these spectrometers operating on the Fourier transform mode. FT-IR spectra were collected on a Perkin-Elmer 1725 FT-IR spectrometer. $RuCl_3{\cdot}3H_2O$ was purchased form Johnson Matthey Ltd. $RuH_2(H_2)_2(PCy_3)_2$ (**1**) was made according to the procedure described in ref [22].

4.2. Ruthenium complexes

4.2.1. Synthesis of $RuH(o\text{-}C_6H_4C(O)CH_3)(H_2)(PCy_3)_2$ (2)

To a suspension of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) (120 mg, 0.18 mmol) in 20 ml pentane was added acetophenone (23 μl, 0.20 mmol) at room temperature. The reaction was allowed to react for 24 h during which a brown-orange solid precipitated. The solid was then filtered off, washed with 20 ml of pentane and dried in vacuo. Yield ca. 92%. Anal. Calcd for $RuC_{44}H_{76}P_2O$: C, 67.39; H, 9.77. Found: C, 66.68; H, 9.84. IR (cm^{-1}, nujol): 2022 (ν_{Ru-H}). ^{1}H NMR (200.13 MHz, C_6D_6, 296 K; δ, ppm): 8.60 (br), 7.68 (br), 7.08 (br), 6.90 (br)(4H, Ph); 2.54 (br, 3H, CH_3); −9.02 (br, 3H, $RuH(H_2)$). $^{31}P\{^{1}H\}$ NMR (81.01 MHz, C_6D_6, 296 K; δ, ppm): 48.0 (s). $T_{1(min)}$ (250 MHz, C_7D_8, 193 K): $\delta_{-5.6}$: 31 ms, $\delta_{-14.9}$: 85 ms.

4.2.2. Synthesis of $RuH(o\text{-}C_6H_4C(O)C_6H_5)(H_2)(PCy_3)_2$ (3)

To a suspension of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) (190 mg, 0.28 mmol) in 20 ml of pentane was added benzophenone (52 mg, 0.31 mmol) at room temperature. The reaction was allowed to react for 24 h during which a brown-orange solid precipitated. The solid was then filtered off, washed with 20 ml of pentane and dried in vacuo. Yield ca. 92%. Anal. Calcd for $RuC_{49}H_{78}P_2O$: C, 69.55; H, 9.29. Found: C, 69.59; H, 9.51. IR (cm^{-1}, nujol): 1983 (ν_{Ru-H}). ^{1}H NMR (200.13 MHz, C_6D_6, 296 K; δ, ppm): 8.08 (br), 7.15 (m)(9H, $C_6H_4C(O)C_6H_5$); −8.59 (br, 3H, $RuH(H_2)$). $^{31}P\{^{1}H\}$ NMR (81.01 MHz, C_6D_6, 296 K; δ, ppm): 48.1 (s).

*4.2.3. Synthesis of RuH(o-$C_6H_4C(O)CH_3$)(CO)(PCy_3)$_2$ (**4**)*

Carbon monoxyde was bubbled through a suspension of $RuH(C_6H_4C(O)CH_3)(H_2)(PCy_3)_2$ (**2**) (347 mg, 0.43 mmol) in 20 ml of pentane. The reaction was allowed to react for 5 min during which an orange solid precipitated. The orange precipitate was then filtered off, washed with 20 ml of pentane and dried in vacuo. Yield ca. 64%. Anal. Calcd for $RuC_{45}H_{74}P_2O_2$: C, 66.72; H, 9.21. Found: C, 66.90; H, 9.23. IR (cm^{-1}, nujol): 1879 ($\nu_{Ru–CO}$). ^1H NMR (200.13 MHz, $CDCl_3$, 296 K; δ, ppm): 7.96 (d, 1H, J_{HH} = 7.3 Hz), 7.66 (d, 1H, J_{HH} = 7.8 Hz), 7.00 (d, 1H, J_{HH} = 7.2 Hz), 6.86 (d, 1H, J_{HH} = 7.9 Hz)(C_6H_4); 2.50 (m, CH_3); −16.03 (t, 1H, J_{PH} = 23.4 Hz, Ru–H). $^{31}P\{^1H_{(PCy3)}\}$ NMR (81.01 MHz, $CDCl_3$, 296 K; δ, ppm): 41.9 (d, J_{PH} = 23 Hz). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 296 K; δ, ppm): 207.9 (s, Ru(*C*O) or Ru*C*(Ph)), 207.0 (s, Ru(*C*O) or Ru*C*(Ph)), 206.0 (s, Ru*C*(O)Me), 145.4 (s), 143.3 (s), 129.2 (s), 128.2 (s), 119.9 (s)(C6H4), 24.8 (s, CH_3).

*4.2.4. Synthesis of RuH(o-$C_6H_4C(O)C_6H_5$)(CO)(PCy_3)$_2$ (**5**)*

Carbon monoxyde was bubbled through a solution of $RuH(C_6H_4C(O)C_6H_5)(H_2)(PCy_3)_2$ (**3**) (43 mg, 0.51 mmol) in toluene (20 ml). A red solid is obtained in ca. 67% yield. Anal. Calcd for $RuC_{50}H_{76}P_2O_2$: C, 68.86; H, 8.78. Found: C, 68.84; H, 8.43. IR (cm^{-1}, nujol): 1902 ($\nu_{Ru–CO}$). ^1H NMR (400.13 MHz, $CDCl_3$, 296 K; δ, ppm): 8.05 (d, 1H, J_{HH} = 7.4 Hz), 7.72 (d, 1H, J_{HH} = 7.8 Hz), 7.59 (m, 2H), 7.48 (m, 3H), 7.04 (t, 1H, J_{HH} = 7.2 Hz), 6.86 (t, 1H, J_{HH} = 7.4 Hz)($C_6H_4C(O)C_6H_5$); −15.36 (t, 1H, J_{PH} = 23.8 Hz, RuH). $^{31}P\{^1H_{(PCy3)}\}$ NMR (81.01 MHz, C_7D_8, 296 K; δ, ppm): 42.1 (d, J_{PH} = 24 Hz). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 296 K; δ, ppm): 210.7 (t, Ru(*C*O) or Ru*C*(Ph), J_{CP} = 12.3 Hz), 206.3 (t, Ru(*C*O) or Ru*C*(Ph), J_{CP} = 12.4 Hz), 203.6 (s, Ru*C*(O)Ph), 144.3 (s), 143.4 (s), 139.6 (s), 132.7 (s), 128.9 (s), 128.5 (s), 128.0 (s), 119.7 (s) ($C_6H_4C(O)C_6H_5$). $T_{1(min)}$ (250 MHz, CD_2Cl_2, 233 K) = 139 ms.

*4.2.5. Synthesis of Ru($C_6H_4C(O)CH_3$)$_2$(PCy_3)$_2$ (**6**)*

About 37.5 equivalents of **7a** (0.65 ml, 6 mmol) were added to a solution of **1** (109.6 mg, 0.16 mmol) in pentane (15 ml) and stirred for 24 h to afford **2** as an orange precipitate. Then, ethylene was bubbled for 30 min and the solution let stirred for 3 days affording a purple precipitate identified as **6**. Anal. Calcd for $RuC_{52}H_{74}P_2O_2$: C, 69.38; H, 8.90. Found: C, 69.40; H, 8.45. ^1H NMR (200.13 MHz, C_6D_6, 296 K; δ, ppm): 9.20 (d, 7 Hz, 2H, C_6H_4), 7.58 (d, 7 Hz, 2H, C_6H_4), 7.02 (t, 7 Hz, 2H, C_6H_4), 6.80 (t, 7 Hz, 2H, C_6H_4), 2.55 (s, 6H, CH_3), 2.00–0.90 (m, 66H, PCy_3). $^{31}P\{^1H\}$ NMR (81.01 MHz, C_6D_6, 296 K; δ, ppm): 21.2 (s).

4.3. Catalytic tests

A typical experiment was done as follows: 10 equivalents of a ketone were added to a suspension of the catalyst in pentane. The mixture was then transferred via canula to an autoclave. The solution was stirred at 750 tr/min at 18 °C and pressurized under 20 bar of ethylene for 22 h. The catalyst/ketone/ethylene ratio was 1/10/800. The respective ratios reactant/monoalkylated product/dialkylated product were determined by GC analysis on a Hewlett Packard 5890 series II using a methylsilicon capillary column (30 m × 0.32 mm). GC–MS analysis was performed on a Hewlett Packard 5890 using a methylsilicon capillary column (12 m × 0.2 mm) coupled with a Hewlett Packard 5970 MSD using the electronic impact at 70 eV.

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