Catalyst Deactivation

Dormant States of Rhodium Hydroformylation Catalysts: Carboalkoxyrhodium Complex Formed from Enones in the Alkene Feed**

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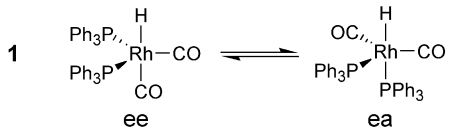
The stability, deactivation, and regeneration of the catalyst are, along with activity and selectivity, important issues in homogeneous catalysis.[1] The turnover number (TON) of a catalyst, a reflection of the catalyst stability, is one of the pivotal parameters for implementation of a process. Deactivation can occur in many ways, but sometimes deactivation is only temporary and the catalyst activity is restored. For long-term catalyst performance in the hydroformylation reaction, avoiding deactivation of the catalyst caused by reactive impurities in alkene feeds is of great importance. Such impurities may trap active rhodium catalysts either in a temporary or a permanent inactive state. Dienes and alkynes are poisons for many catalytic processes involving alkenes.[1] Since hydroformylation of dienes is much slower than that of alkenes,[2] diene impurities might thus slow down 1-alkene hydroformylation, if the resting state of the catalytic cycle of the diene is appropriate.[3] Examples of such deactivation are reported in patent literature.[4]

We have studied the deactivation of hydroformylation catalysts by controlled reaction with the most likely impurities in alkene feeds, such as dienes, alkynes, and enones. The hydrido rhodium complex, the common resting state in hydroformylation, at which the catalytic cycle starts, was prepared in a high-pressure (HP)-IR autoclave under syn gas (CO/H_2), from the catalyst precursor, $[Rh(acac)(CO)_2]$ (acac = 2,4-pentadione) and excess of PPh_3 at 80 °C. After complete conversion of $[Rh(acac)(CO)_2]$ into $[RhH(CO)_2(PPh_3)_2]$ (**1**), a substrate or a mixture of substrates was added to the reaction mixture from a separately pressurized reservoir. We have used in situ high-pressure IR spectroscopy in conjunction with (high-pressure) NMR spectroscopy to detect and characterize the catalyst under actual catalytic conditions.[5] Employing NMR spectroscopy studies Brown and Kent have shown that **1** exists as a mixture of two rapidly equilibrating trigonal-bipyramidal isomers in a diequatorial (ee) to equatorial-apical (ea) isomer ratio of 85:15 (Scheme 1).[6]

The HP-IR spectrum of **1** has four carbonyl bands (at $\tilde{\nu}$ = 2043, 1997, 1986, and 1953 cm^{-1}) that have been assigned to the two isomers.[7] HP-IR studies of the hydroformylation of 1-octene showed that, while 1-octene was present in the reaction mixture, the main species observed was **1**. Minor decomposition of **1** was due to the formation of an inactive dimer.[8] New bands, characteristic of the dimer, appeared in the IR spectrum at $\tilde{\nu}$ = 2023, 1972, and 1957 cm^{-1}.



Scheme 1. Compound **1** as a mixture of two trigonal-bipyramidal isomers.

Several linear dienes, 2,4-hexadiene, 1,5-hexadiene, and 1,3-pentadiene were tested as inhibitors of the catalyst. The addition of 2,4-hexadiene to **1** formed in situ resulted in the slow growth of two new bands in the IR spectrum (Table 1) at the cost of the four absorption bands characteristic of **1**, but these four initial bands did not disappear completely. 1,5-Hexadiene underwent fast hydroformylation and its addition to the reaction mixture did not change the nature of the resting state of the rhodium complex and it did not influence the rate of 1-octene hydroformylation either.

Table 1: Influence of poisons/inhibitors on the Rh-C=O bands of **1** under syn gas.

1 + poison/inhibitor	Rh-C=O bands [cm^{-1}]
–	1953, 1986, 1997, 2043
2,4-hexadiene	1967, 2016[a]
1,3-pentadiene	1949 (w), 1957 (s), 2016 (s)
1-octyne	1946, 1988, 2020, 2042, 2073, 2120[a]
trans-3-nonen-2-one	1946 (w), 1984 (vs)
3-buten-2-one (MVK, **2**)	1946 (w), 1984 (vs)

[a] Weak bands from **1** also present.

Addition of the conjugated 1,3-pentadiene to **1**, however, resulted in the immediate formation of new bands in the IR spectrum (Table 1). A 60-fold excess of diene gave complete conversion of **1** and new bands were observed immediately after addition of the diene (Figure 1). When the ratio of diene:Rh is 20:1, the signals of **1** did not disappear completely. After 10 min the concentration of **1** was about 50 % of its initial value. In both cases 1,3-pentadiene underwent hydroformylation to a mixture of aldehydes.

Addition of 1,3-cyclohexadiene or cyclopentadiene to **1** did not affect the IR spectrum. Both the cyclic dienes underwent fast hydroformylation and new bands characteristic of the corresponding unsaturated aldehydes appeared in the IR spectra.

Internal and terminal alkynes proved to have completely different effects on **1**. Addition of 3-hexyne did not affect the nature of **1**, whereas the addition of 1-octyne immediately caused irreversible formation of new rhodium species, as indicated by several new bands (Table 1), which remained present throughout the experiment (Figure 2). Furthermore,

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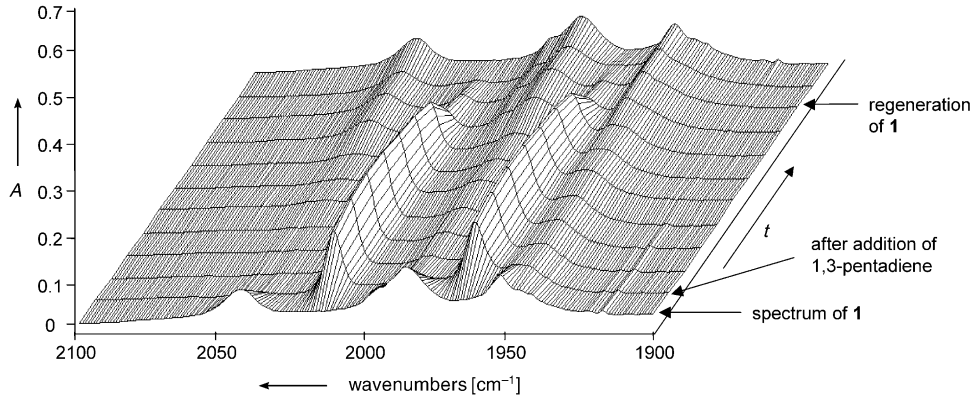


Figure 1. In situ HP-IR study of hydroformylation of 1,3-pentadiene catalyzed by **1** (1,3-pentadiene:**1** = 60:1).

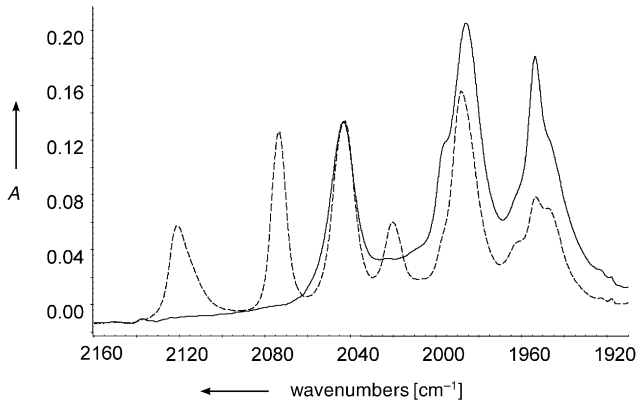


Figure 2. In situ HP-IR study of hydroformylation of 1-octyne catalyzed by **1**; —— spectrum of **1**, ----- spectrum after the addition of 1-octyne.

1-octyne underwent slow hydroformylation to a mixture of products.

Addition of unsaturated ketones, such as *trans*-3-nonen-2-one and 3-buten-2-one (MVK, **2**), to a solution of **1** immediately gave rise two new bands in the IR spectrum (Table 1) and the disappearance of the four bands characteristic of **1** (Figure 3).

Note that when most of **2** had reacted, **1** was regenerated and became again the predominant species. The addition of 2-cyclohexen-1-one to **1** had the same effect as the addition of the linear α,β unsaturated ketones. The branched unsaturated ketone, mesityl oxide (4-methyl-3-penten-2-one), did not lead to a decrease of the concentration of **1**.

The large impact of **2** on the concentration of **1** prompted us to perform a detailed study of the temporary deactivation. A high initial concentration of **2** in the reaction mixture gave a very slow initial hydroformylation of 1-octene as measured by syn-gas consumption. At low concentration of **2**, only minor inhibition occurred and the normal rates of the hydroformylation of 1-octene were observed (Figure 4).

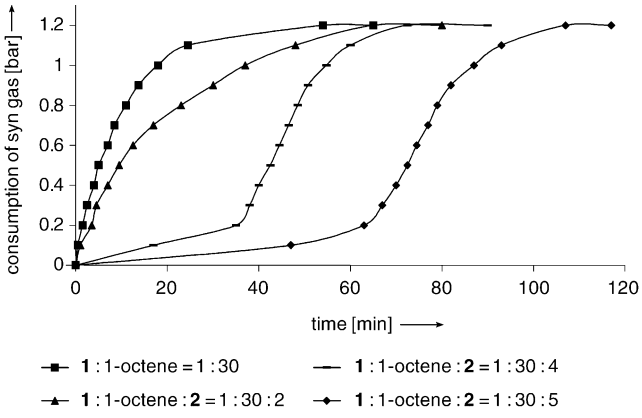


Figure 4. Comparison of the rates of hydroformylation of 1-octene and mixtures of 1-octene and **2** catalyzed by **1**.

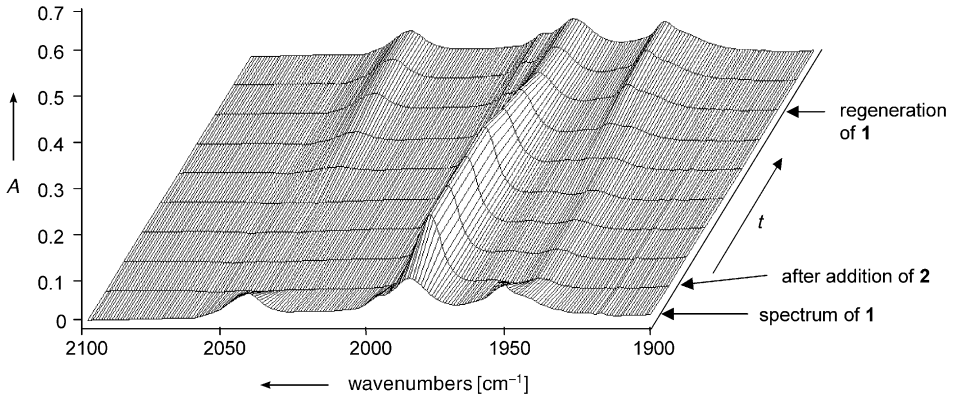


Figure 3. In situ HP-IR study of the reaction of **2** with **1**.

Similar competition experiments were carried out with the other substrates 1-octyne, 1,3-pentadiene, cyclopentadiene, and 2-cyclohexen-1-one. The substrates 1-octyne, 2-cyclohexen-1-one, and **2** changed the nature of the resting state of the rhodium species. When these new rhodium species were present in the reaction mixture, hydroformylation of 1-octene stopped or was retarded. When most of the inhibitor was converted and its concentration reached a certain lower level, the hydrido complex **1** again became the predominant species and hydroformylation of 1-octene resumed. Compounds not changing the resting state (cyclopentadiene, 2-cycloocten-1-one (not shown)) or that are converted very quickly (1,3-pentadiene) did not influence the rate of the 1-octene hydroformylation (Figure 5).

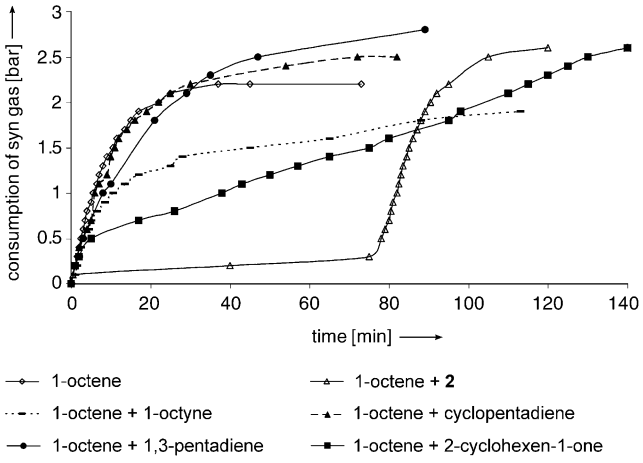
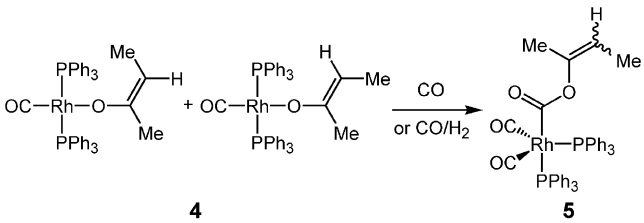


Figure 5. Comparison of the rates of hydroformylation of 1-octene and mixtures of 1-octene and other substrates catalyzed by **1**.

HP ^{1}H and ^{31}P NMR spectroscopy was employed to study the intermediate products. However, the reaction between **1** and **2** at room temperature was very fast giving a mixture containing many new compounds, which we did not attempt to identify. As a model catalyst we then used $[RhH(CO)(PPh_3)_3]$ (**3**) in the reaction with **2** in a ratio of 1:1.2. The reaction was initially monitored at −80 °C and then the reaction mixture was gradually heated to −20 °C while ^{1}H and ^{31}P NMR spectra were recorded. Subsequently, the NMR tube was cooled to −60 °C and ^{1}H, COSY, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded. ^{31}P NMR showed complete conversion of **3** and two new doublets at $\delta = 26.74$ and 29.99 ppm and a signal assigned to one equivalent of free PPh_3 at $\delta = -6.26$ ppm were observed. This result indicates formation of two isomeric insertion products, both containing two equivalent triphenylphosphane units. Because of their extremely unstable nature attempts to isolate the intermediates were not successful, but they could be identified in situ. Their structure was unambiguously determined by NMR spectroscopy.[9] Two η^1-oxygen bound rhodium enolate complexes (**4**; Scheme 2) were identified and characterized by IR spectroscopy they give a carbonyl band at $\tilde{\nu} = 1968\ cm^{-1}$. The two carbonyl bands at $\tilde{\nu} = 1690$ and $1719\ cm^{-1}$ characteristic of **2** disappear.

When the reaction of **3** with **2** was complete and a mixture of **4a** and **4b** was formed, CO/H_2 or CO was bubbled through the reaction mixture for 6 min at −60 °C. The reaction of **4** with CO was studied by NMR (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}, COSY, ^{31}P–^{31}P correlation, ^{31}P–^{13}C correlation and ^{31}P–^{103}Rh correlation) and HP-IR spectroscopy.

^{1}H and ^{31}P{^{1}H} spectra taken after the reaction showed complete conversion of **4** and formation of new species (**5**; Scheme 3) which we characterized using HP-IR and several NMR spectroscopy techniques.



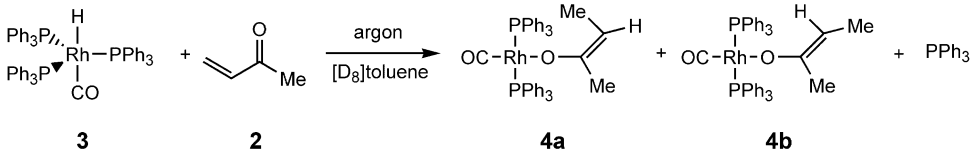
Scheme 3. Reaction of **4** with CO.

The ^{31}P{^{1}H} spectrum changed totally when CO was present in the reaction mixture. The two doublets characteristic of **4** disappeared and two new doublets of doublets at $\delta =$ 26.15 and 28.53 ppm were observed. The data were confirmed by simulation of the spectrum of **5** (Figure 6).[10]

According to the ^{31}P–^{31}P correlation spectra these two doublets of doublets belong to two inequivalent phosphorus atoms bonded to the same rhodium(I) species. This result was confirmed by ^{31}P–^{103}Rh correlation spectroscopy.

^{1}H NMR spectroscopy showed formation of two *E*/*Z* isomers that differed in the vinyl part in a ratio of 30:70. The *E* isomer (**5a**) gave three resonance signals at $\delta = 0.8$, 1.35, and 2.6 ppm. Another set of three signals at $\delta = 1.28$, 1.50, and 4.15 ppm was assigned to the *Z* isomer (**5b**). The phenyl groups of both isomers gave overlapping signals at $\delta = 6.8$–7.8 ppm. The two isomers could not be distinguished by ^{31}P NMR spectroscopy.

A more detailed examination of the structure of **5** was carried out employing ^{13}CO instead of ^{12}CO, which was bubbled through the solution of the rhodium enolate complexes **4**. The ^{13}C{^{1}H} spectrum taken at −40 °C showed one



Scheme 2. Reaction of **3** with **2** under argon.

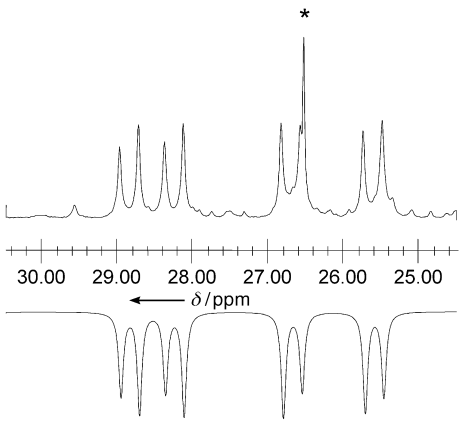
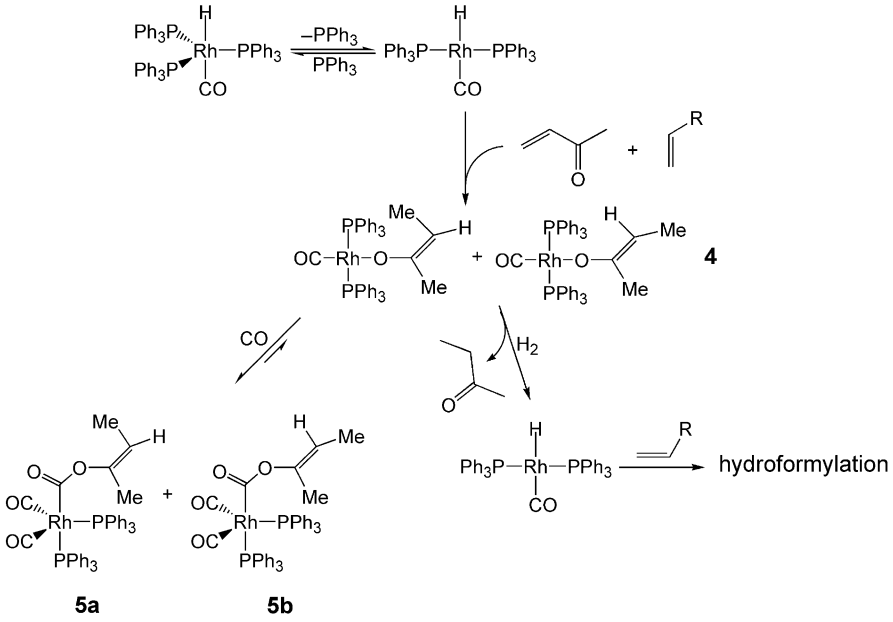


Figure 6. Top: $^{31}P\{^1H\}$ spectrum obtained after bubbling CO/H_2 through the solution containing the rhodium enolate complexes **4**, * $O{=}PPh_3$; bottom: simulation of this spectrum.

resonance for an acyl group at 235.5 ppm and one resonance for rhodium-bound carbonyl group at 198 ppm. Coupling of the acyl carbon with the rhodium ($J(Rh,C) = 22$ Hz) and phosphorus nuclei ($J(P,C) = 80$ Hz) was observed. The terminal carbonyl groups are coupled to the rhodium nucleus ($J(Rh,C) = 76$ Hz). The ^{31}P–^{13}C correlation spectrum showed strong cross-peaks for the two double doublets occurring in the $^{31}P\{^1H\}$ NMR spectrum and for the signal of a carbonyl ligand at 198 ppm and that of a rhodium-acyl resonance at 235.5 ppm. Therefore, we conclude that the two signals present in the $^{13}C\{^1H\}$ NMR spectrum and two double doublets in the $^{31}P\{^1H\}$ NMR spectrum belong to the same carboalkoxyrhodium complex, which exists as a mixture of *E*/*Z* isomers.

upon carbonylation of four-coordinate iridium alkoxides, have been reported.[12]

The formation of **5** is the cause for slow or no hydroformylation of 1-octene when **2** is present in the reaction mixture. The unsaturated ketone is much more reactive towards **1** than the alkene and forms carboalkoxy complexes with rhodium thus blocking its activity for the 1-octene hydroformylation. Catalyst **1** for the hydroformylation of 1-octene is only restored after the enone has been converted into 2-butanone. The formation of formate esters from the enone substrate was not detected by GC-MS and HP-NMR spectroscopy. The analysis of the reaction mixture confirmed that the only organic product present after the reaction was 2-butanone. The rhodium enolate complexes react very fast with CO leading to the formation of **5**, which does not react with H_2 as formate formation is apparently very slow. Instead, a de-insertion has to occur to allow for hydrogenation of **4**,



Scheme 4. Deactivation mechanism of the rhodium hydride complex by **2**.

The reaction of **4** with CO was also performed in the HP-IR autoclave. When **2** was added to a cyclohexane solution of **3** the bands in the IR spectrum characteristic of the rhodium hydride complex ($\tilde{\nu} = 2011$ and 1938 cm^{-1}) disappeared and a new band characteristic of **4** appeared at $\tilde{\nu} = 1968$ cm^{-1}. Then CO/H_2 or CO was added to the reaction mixture and the latter band disappeared and new bands at $\tilde{\nu} = 1984$ and 1946 cm^{-1} were observed, indicative of coordination of two carbonyl ligands. The positions of these bands in the IR spectrum were exactly the same as those observed after addition of **2** to the solution of **1** under CO/H_2 (Figure 3).

The NMR and IR spectroscopy studies have shown that addition of CO to the solution of **4** results in coordination of a CO molecule to the rhodium center and insertion of a second one to the rhodium–oxygen bond forming five coordinate rhodium(I) complexes (**5**; Scheme 4).[6,11] Structurally analogous carboalkoxy complexes of iridium, which are formed which results in butanone formation. In equilibrium, during a catalytic reaction, the concentration of **4** is too low to detect by HP-IR spectroscopy. When most of **2** has been converted into butanone, the hydroformylation of 1-octene can proceed. (Scheme 4).

In conclusion unsaturated impurities in the alkene feed, such as enones, dienes, and alkynes, deactivate the hydroformylation catalyst. Enones transform the "active" **1** temporarily into an inactive dormant state by formation of carboalkoxyrhodium complex. The hydroformylation catalyst is reformed by hydrogenation, which explains why the inhibiting effect can be reduced by high H_2 pressure.[3]

Experimental Section

High-pressure IR experiments were performed in an SS-316 50-mL autoclave equipped with IRTRAN windows (ZnS, transparent above

700 cm^{-1}, $\varnothing = 10$ mm, optical path length = 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure device. In a typical experiment, $[Rh(CO)_2(acac)]$ (0.008 g, 3.0×10^{-5} mol) and PPh_3 (6.0×10^{-4} mol) of were dissolved in cyclohexane (15 mL) under argon. The solution was brought into the autoclave and after flushing and pressurizing with CO/H_2, the HP-IR cell was placed into a Nicolet 510 FTIR spectrometer. Then the reaction mixture was heated to 80 °C. A substrate or a mixture of substrates were added to the reaction mixture from a separately pressurized reservoir by means of overpressure once the active catalyst, $[RhH(CO)_2(PPh_3)_2]$ (**1**), was formed. The IR spectra were recorded while the samples were stirred.

4: A solution of $[RhH(CO)(PPh_3)_3]$ (**3**; 0.05 g, 5.4×10^{-5} mol; Strem) in $[D_8]$toluene was prepared in a 5-mm NMR tube under argon. The tube was placed in a NMR machine and cooled to −60 °C. The NMR tube was then ejected and 3-butene-2-one (**2**, 5.5 μL, 6.5×10^{-5} mol) was added and the tube placed back in the precooled NMR machine and the NMR spectra were recorded. *E* isomer (**4a**): ^1H NMR (300 MHz, C_7D_8, −60 °C): $\delta = 1.49$ (s, =C(CH_3), 3H), 2.15 (d, J(H,H) = 6 Hz, 3H, =CH(CH_3)), 3.97 (q, J(H,H) = 6 Hz, 1H, =CH(CH_3)), 6.8–7.5 ppm (m, 30H, PPh_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_7D_8, −60 °C): $\delta = 26.74$ ppm (d, J(Rh,P) = 145.00 Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_7D_8, −60 °C): $\delta = 14.95$ (s, CH_3), 29.21 (s, CH_3), 92.15 (s, =CH), 159.03 (s, Rh-O-C), 191.46 ppm (dt, Rh-CO); *Z* isomer (**4b**): ^1H NMR (300 MHz, C_7D_8, −60 °C): $\delta = 1.36$ (s, 3H, =C(CH_3)), 1.53 (d, J(H,H) = 6 Hz, 3H, =CH(CH_3)), 4.63 (q, J(H,H) = 6 Hz, 1H, =CH(CH_3)), 6.8–7.5 ppm (m, 30H, PPh_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_7D_8, −60 °C): $\delta = 29.99$ ppm (d, J(Rh,P) = 146.25 Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_7D_8, −60 °C): $\delta = 14.29$ (s, CH_3), 28.95 (s, CH_3), 88.17 (s, =CH), 160.36 (s, Rh-O-C), 191.46 ppm (dt, Rh-CO); **4a** and **4b**: IR (C_5H_{12}): 1968 cm^{-1} (s).

5: First a mixture of **4** was prepared in a 5-mm NMR tube according to the description given above. Then CO or CO/H_2 was bubbled through the solution for 6 min at −60 °C and the NMR spectra were recorded. *E* isomer (**5a**): ^1H NMR (300 MHz, C_7D_8, −60 °C): $\delta = 0.8$ (d, J(H,H) = 7.2 Hz, 3H, =CH(CH_3)), 1.35 (s, 3H, =C(CH_3)), 2.6 (q, J(H,H) = 7.2 Hz, 1H, =CH(CH_3)), 6.8–7.8 ppm (m, 30H, PPh_3); *Z* isomer (**5b**): ^1H NMR (300 MHz, C_7D_8, −60 °C): $\delta =$ 1.28 (d, J(H,H) = 6.9 Hz, 3H, =CH(CH_3)), 1.50 (s, 3H, =C(CH_3)), 4.15 (q, J(H,H) = 6.9 Hz, 1H, =CH(CH_3)), 6.8–7.8 ppm (m, 30H, PPh_3); **5a** and **5b**: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_7D_8, −60 °C): $\delta = 26.15$ (dd, J(Rh,P) = 132 Hz, J(P,P) = 30 Hz), 28.53 ppm (dd, J(Rh,P) = 72 Hz, J(P,P) = 30 Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_7D_8, −40 °C): $\delta = 198$ (d, J(Rh,C) = 76 Hz, Rh-CO), $\delta = 235.5$ ppm (dd, J(Rh,C) = 22 Hz, J(P,C) = 80 Hz, Rh-COO); IR (C_5H_{12}): 1984 (vs), 1946 (w), 1652 cm^{-1} (w).

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