A mechanistic investigation into the elimination of phosphonium salts from rhodium–TRIPHOS complexes under methanol carbonylation conditions†

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Phosphine modified rhodium complexes are currently the topic of considerable research as methanol carbonylation catalysts, but often suffer from poor stability. This paper reports on an investigation into how coordination mode affects the elimination of phosphonium salts from rhodium complexes, namely [*trans*-RhCl(CO)(PPh_3)$_2$] **1**, [RhCl(CO)(dppe)] **2**, [RhCl(CO)(dppb)]$_2$ **3**, [Rh(TRIPHOS)(CO)$_2$]Cl **4**. These complexes are all potential pre-catalysts for methanol carbonylation. The reaction of these complexes with methyl iodide at 140 °C under both N_2 and CO atmospheres has been studied and has revealed clear differences in the stability of the corresponding Rh(III) complexes. In contrast to both monomeric **2** and dimeric **3** that react cleanly with CH_3I to give stable Rh(III) acetyl complexes, **4** forms a novel bidentate complex after the elimination of the one arm of the ligand as a quaternised phosphonium salt. The structure of this complex has been determined spectroscopically and using X-ray crystallography. The mechanism of formation of this novel complex has been investigated using $^{13}CH_3I$ and strong evidence that supports a dissociative mechanism as the means of phosphine loss from the rhodium centre is provided.

Introduction

The carbonylation of methanol to acetic acid is one of the most important applications in homogeneous catalysis. Large scale industrial processes have typically used either $[Rh(CO)_2(I)_2]^-$ or $[Ir(CO)_2(I)_2]^-$ as catalysts with methyl iodide[1–3] and ruthenium halide scavengers as promoters.[4–6] With most of the possible variables having now been explored in 'unmodified' catalyst systems, considerable attention is now focussed on phosphine-modified rhodium catalysts[7–14] with the belief that they may offer the best opportunities for eliminating side-products or allowing the use of lower grade CO. Several BP projects have recently reported systems based on both bidentate and potentially tridentate ligands that show promise for methanol carbonylation in the presence of hydrogen.[7–9]

However, even if a suitable phosphine can be designed to deliver an improvement to selectivity and activity, the catalyst and ligand will need to show long-term stability under the forcing conditions required for industrial methanol carbonylation. It has been known for some time that rhodium complexes of monodentate phosphines are only stable for very short periods of time under industrially significant conditions. Several diphosphine systems have been reported that seem to show significantly better stability.[10–13] However, the stability of these systems has not been studied under comparable conditions making it difficult to make any conclusions on how ligand co-ordination mode, electronic and steric effects impact on stability.

Cole-Hamilton *et al.* have previously reported highly active rhodium catalysts containing electron rich phosphine PEt_3 ligands.[15,16] At temperatures exceeding 120 °C the catalyst rapidly decomposes forming the phosphorus(V) species $[Et_3PCH_3]^+I^-$ and $Et_3P{=}O$. It was suggested that such species might form directly from Rh(III) species observed in catalysis such as $[RhI(CH_3)(CO)(PEt_3)_2]$, $[Rh(I)_2(H)(PEt_3)_2]$ and $[Rh(I)_3(PEt_3)_2]$ possibly without prior dissociation of the free phosphine. An alternative mechanism involves dissociation of phosphine from the metal centre followed by quaternisation by methyl iodide.

We have recently studied the intermediates formed during methanol carbonylation using C_4 diphosphine ligands.[7] One interesting observation that prompted the investigation described here was the increased stability of the bridging bidentate complex, [RhCl(CO)(dppb)]$_2$ over that of chelate complex, [RhCl(CO)(BINAP)] to methyl iodide. This observation does not easily fit with a dissociative model for phosphine loss in these complexes, since on reaction of Rh–dppb dimer with methyl iodide, the only species present is the crystallographically characterised acetyl species, with chelating dppb ligand, $[Rh(I)_2(COCH_3)(dppb)]$. Interestingly no quaternisation occurs during this transition from a bridging to a chelating co-ordination mode, even though dissociation of one or more phosphorus atoms from the metal centre must occur in order to achieve this rearrangement.

In this paper, we report a study on how co-ordination mode affects catalyst stability under methanol carbonylation conditions, and in particular, provide evidence that supports a dissociative mechanism as the means of phosphine loss from a tridentate rhodium complex. Given that multi-dentate ligands are currently being extensively studied by several groups to deliver more stable catalyst systems, this work taken with our initial findings[7] should help guide multi-dentate ligand design for genuinely stable methanol carbonylation catalysts.

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Results and discussion

In this study, we elected to compare the stability of the known complexes that have ligands in different co-ordination modes; monodentate [*trans*-RhCl(CO)(PPh_3)$_2$], the bidentate chelate complex [RhCl(CO)(dppe)], bridging complex [RhCl(CO)(dppb)]$_2$ and the tridentate complex [Rh(TRIPHOS)(CO)$_2$]Cl (Fig. 1).[17–20] These complexes were prepared *via* literature procedures and their stability was tested by heating to 140 °C in the presence of methyl iodide under nitrogen and carbon monoxide atmospheres (Table 1).

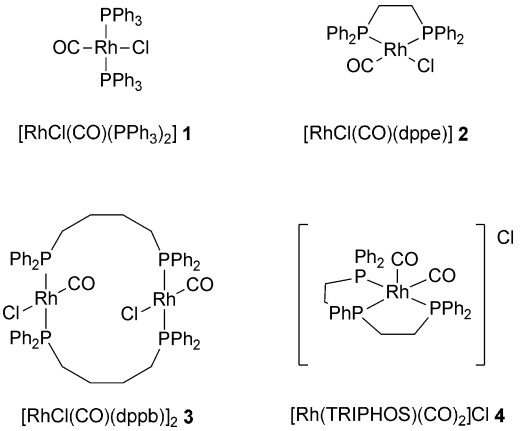


Fig. 1 The rhodium–phosphine complexes investigated in this study.

In the case of the control system [*trans*-RhCl(CO)(PPh_3)$_2$], the stability testing shows, as expected, decomposition to P(v) species at higher temperatures under both CO and N_2 atmospheres.[15]

At 140 °C, both dppe and dppb species show little to no sign of decomposition with high recovery of unquaternised rhodium acetyl complexes. Further experiments carried out at the higher temperature of 175 °C for 1 h under 5 bar CO results in the complete decomposition of dppb complexes to a mixture of unassigned P(v) species in comparison to the dppe complex that showed a much higher degree of stability (*ca.* 90% of the $^{31}P\{^1H\}$ NMR spectra can be assigned to the Rh(III) acetyl of dppe). The TRIPHOS complex however, quantitatively forms a new species, **5a** (Fig. 2) that contains two co-ordinated phosphines and one quaternised phosphine, and therefore the Rh complexes of TRIPHOS is less stable than either of the bidentate systems. However, the quaternised chelate complex was itself highly stable with no subsequent decomposition detected.

Table 1 Stability of Rh(I) carbonyl complexes under N_2 and CO atmospheres in the presence of methyl iodide

Ligand	140 °C under N_2[a]	140 °C under CO[b]
PPh_3	0	0
dppe	100[c]	75.5[c]
dppb	94.4[c]	60.2[c]
TRIPHOS	66.7[d]	66.7[d]

[a] % of Rh–P species present with respect to an external standard of tributylphosphine oxide after heating 0.0265 mmol of complex for 10 min in a CH_3OAc–CH_3I mixture (2 mL). [b] % of Rh–P complex recovered as precipitate at the end of a catalytic run at 140 °C under 26 bar CO. [c] Rh species is assigned as [Rh(I)$_2$(C(O)CH_3)(L)] by comparison of NMR and IR data with that reported in the literature.[7,21,22] [d] Quantitative conversion to complex **5a** containing a single quaternised phosphine. This has been recorded as 66.7% Rh–P species since 2 out of the 3 phosphorus atoms are unquaternised.

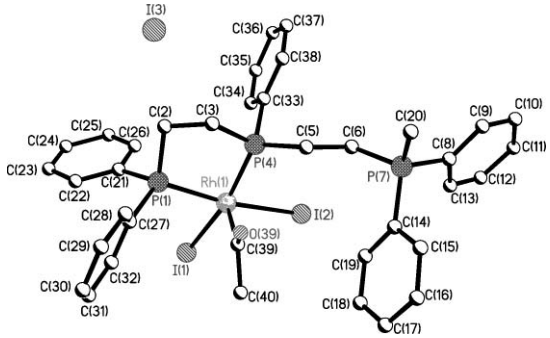


Fig. 2 X-Ray structure analysis of [Rh(I)$_2$(C(O)CH_3){$Ph_2P(CH_2)_2P(Ph)(CH_2)_2(PPh_2CH_3)$}]$^+I^-$ **5a**.

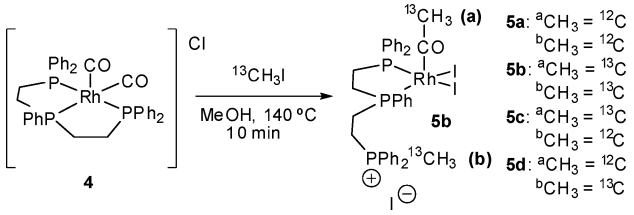
Using complex **4**, similar results were obtained under methanol carbonylation conditions with the only detectable TRIPHOS complex being **5a**, containing both quaternised and coordinated phosphines. The structure of the novel TRIPHOS complex was elucidated by spectroscopic and crystallographic methods.

The crystal structure serves to confirm the connectivity and general structural features expected in complex **5a**. The I–Rh–I bond angle [91.79(4)°] and the P–Rh–P bond angles [85.46(13)°] for the novel bidentate complex **5a** are similar to that of [Rh(I)$_2$(C(O)CH_3)(dppe)].[22]

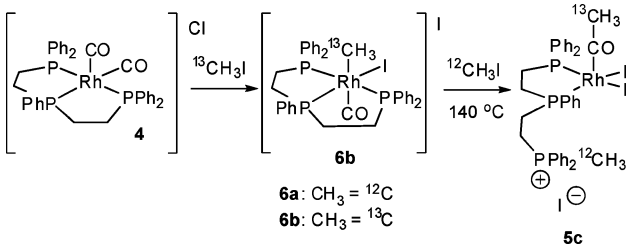
The $^{31}P\{^1H\}$ NMR spectrum of **5a** contains three different phosphorus environments, one of these being very clearly not co-ordinated to Rh (δ = 26.5, d, $^3J_{P\text{–}P}$ 47.2 Hz). The co-ordinated phosphines show significant downfield co-ordination chemical shifts as expected for 5-membered chelate rings[23] and $^1J_{P\text{–}Rh}$ coupling to Rh (see experimental).

Examining the mechanism behind the formation of this complex should lead to a greater understanding of phosphine loss in multidentate systems, which may in turn lead to the design of more stable catalysts. A number of $^{13}CH_3I$ labelled experiments were carried out in order to assess whether quaternisation of the phosphine occurs *via* direct elimination from the rhodium centre or *via* dissociation of the phosphine. The doubly labelled complex [Rh(I)$_2$($CO^{13}CH_3$){$Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2{}^{13}CH_3$}]$^+I^-$, **5b**, was prepared to aid in the characterisation of complexes **5a**–**5d**. The ^{13}C NMR ($CDCl_3$) spectrum of **5b** contained a singlet at 45 ppm associated with the $CO^{13}CH_3$ group (a) and a doublet at 9 ppm with a $^1J_{P\text{–}C}$ coupling of 54 Hz characteristic of the $^{13}CH_3$ group (b) present on the quaternised phosphine. This one step reaction gave a single species that was fully characterised (Scheme 1).

On reaction with $^{13}CH_3I$ (Scheme 2), the precursor [Rh(TRIPHOS)(CO)$_2$]Cl **4**, forms [Rh(I)($^{13}CH_3$)(TRIPHOS)(CO)] **6b** which may be isolated in good yield. The ^{13}C NMR spectra shows a clearly defined doublet of quartets relating to the labelled methyl group (Scheme 2). When complex **6b** was then dissolved in methanol and heated to 140 °C in the presence of $^{12}CH_3I$, formation of labelled **5c** took place, alongside a small amount of an unidentified product. The ^{13}C NMR ($CDCl_3$) spectra



Scheme 1 Direct formation of complex **5** and index of $^{13}C/^{12}C$ analogues.



Scheme 2 Labelled studies using $^{13}CH_3I$.

of the resulting solution, shows no evidence for the $^{13}CH_3$ label in the part of the ^{13}C spectrum where $(RPPh_2{}^{13}CH_3)^+$ would be observed. The inverse of the above experiment was also conducted by heating a sample of unlabelled $[RhI(^{12}CH_3)(TRIPHOS)(CO)]$ **6a** to 140 °C in the presence of $^{13}CH_3I$. Once again, this two-step reaction produced a side product but the ^{13}C NMR of this mixture clearly shows two doublets at 9.19 ppm and 8.13 ppm with $^{1}J_{P\text{-}C}$ couplings of 54.8 and 56.6 Hz respectively, characteristic of the $^{13}CH_3$ now being part of the quaternised phosphine for both major and minor species. All experiments in which **6b** was treated with CH_3I gave these chelate species with quaternised phosphine and no sign of tridentate species as intermediates (we were only interested in the reactivity in the presence of CH_3I, since CH_3I will be present under catalytic conditions). These results therefore point towards a dissociative mechanism in the quaternisation of this ligand.

In order to investigate this further we attempted the direct preparation of the rhodium acetyl complex by reacting the rhodium acetonitrile dimer, $[RhI(COCH_3)(CO)(CH_3CN)]_2(\mu\text{-}I)_2$,[24] with the TRIPHOS ligand. This reaction gives several species that were not separable and have therefore not been fully characterised, but this product mixture reacts cleanly with CH_3I *at room temperature* to give complex **5a** as the only species observable by $^{31}P\{^{1}H\}$ NMR spectroscopy. This latter experiment could be consistent with either mechanism (but the labelling studies demonstrate the dissociative variant). However, it does suggest that the reason behind the dissociation is the lower stability of tridentate Rh(III) acetyls of TRIPHOS in addition to, or instead of, a high energy transition state for migratory insertion in the tridentate complex, **6a/b**.

Conclusions

In summary, the reactivity of Rh(I) complexes of PPh_3, dppe, dppb and TRIPHOS has been studied. As expected, the coordination mode can have a large impact on the stability of rhodium–phosphine complexes. The use of the tridentate ligand TRIPHOS results in the loss of one of the phosphines and favours the formation of complex **5a** containing a quaternised phosphine no longer associated with the metal centre. Through a series of experiments using $^{13}CH_3I$, we have provided strong evidence that, for the TRIPHOS system, the loss of the phosphine occurs *via* a simple dissociative mechanism and not through direct elimination. This does not however, rule out the possibility that for other ligands phosphine loss could occur *via* direct elimination from the metal centre. However, we propose on the basis of these studies along with our previous observations on the Rh–BINAP system[7] that the stability of Rh–phosphine complexes to CH_3I is related to the stability of the Rh-acetyl species, rather than merely being a reflection of co-ordination mode and typical association constants of ligands to late transition metals. Given that multidentate ligands are being investigated more intensively in methanol carbonylation recently, we would suggest that a key experiment in the first stages of a study is to investigate the stability of the Rh(III) acetyl species, since multidentate systems can be less stable than those derived from diphosphines. Further studies aimed towards increasing the stability of phosphine modified rhodium carbonylation catalysts are required.

Experimental

General

All manipulations were performed using standard Schlenk line techniques under nitrogen supplied by BOC. All chemicals and solvents were obtained through commercial sources. All complexes used were prepared by standard literature procedures. Microanalyses were by the University of St. Andrews microanalytical service. NMR spectra were recorded on Bruker Avance 300 instruments. Chemical shifts are reported in ppm with ^{1}H and ^{13}C NMR spectra referenced to tetramethylsilane (external). ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. Proton and carbon signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), b (broad) or a combination of them. All spectra were recorded at room temperature and the solvent for a particular spectrum is given in the parentheses. ^{13}C and ^{31}P NMR spectra were recorded with broad-band proton decoupling. IR spectra were recorded using a Perkin Elmer Spectrum GX FT-IR system. All solids were analysed as KBr disks. Mass spectroscopy data was obtained from the EPSRC National Mass Spectroscopy Service Centre, Swansea. In addition to detecting the ions shown, all Rh complexes showed excellent agreement between calculated and expected isotope patterns. [*trans*-$RhCl(CO)(PPh_3)_2$], [RhCl(CO)(dppe)], $[RhCl(CO)(dppb)]_2$ and $[Rh(TRIPHOS)(CO)_2]Cl$ were prepared according to literature procedures.[17,18,25]

General procedures for stability testing

The majority of the stability tests run under a CO atmosphere were carried out at BP chemicals Ltd in Hull in a 300 cm^3 Hastelloy high pressure infrared (HPIR) autoclave fitted with a bursting disc, catalyst injector, overhead Magnedrive™ stirrer, impeller with gas sparging facility, gas inlet, high pressure (195 bar) carbon monoxide reservoir and thermocouple.

$[Rh(CO)_2](\mu\text{-}Cl)_2]$ (150 mg, 0.386 mmol), ligand (2 eq, 0.772 mmol) and 100 g CH_3OH were stirred together for a few minutes, which we have independently confirmed forms complexes

1–4. The relevant complex was added to the autoclave under CO. The autoclave was then sealed and pressurised with carbon monoxide (5 bar) and heated to 100 °C, controlled by the use of a thermocouple in a thermowell in the reaction solution, whilst stirring at 900 rpm. Using the catalyst injector, iodomethane (22.6 g, 0.159 mol) was then added to the autoclave with an over pressure of CO. Simultaneously, the autoclave was pressurised with CO (27 bar) from the high pressure ballast vessel. The autoclave was then heated to the desired temperature and the data collection activated. The pressure was maintained at 27 bar by a pressure regulating value which transferred CO from the high pressure ballast to the autoclave when the pressure dropped below the set-point. After the reaction, the autoclave was allowed to cool before gas, liquid and solid samples were collected.

Other stability tests carried out under CO utilised a smaller Hastelloy autoclave using isolated complexes and magnetic stirring at a range of temperatures.

For the stability tests run under a N_2 atmosphere, a Biotage™ microwave vial containing 0.0265 mmol of Rh(I)–phosphine ligand complex was charged with a solution of CH_3OAc–CH_3I (3 : 1) and heated at 140 °C for 10 min in a Biotage™ microwave. The % of Rh–P complex present was then calculated with respect to a calibrated external standard of tributylphosphine oxide using $^{31}P\{^1H\}$ NMR spectroscopy.

Safety note: These experiments were carried out using Biotage™ equipment built to withstand pressures of up to 22 bar and temperatures in excess of 200 °C. CH_3I is extremely toxic and should be used with extreme care.

X-Ray crystallography

X-Ray crystallography data were collected at 93 K by using a Rigaku MM007 High brilliance RA generator and Mercury/Saturn CCD systems using Mo K_α radiation. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. All hydrogen atoms (except the solvent water molecules which were not located) were refined as idealised riding geometries and structural refinements were obtained with full-matrix least-squares based on F^2 by using the program SHELXTL Version 6.10 (Bruker).

Crystal data†

$[Rh(I)_2(C(O)CH_3)\{Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2CH_3\}]^+I^-$ 5a. $[C_{37}H_{39}I_2O_1P_3Rh]I{\cdot}2H_2O$, M = 1112.23, monoclinic, a = 18.916(3), b = 11.4403(17), c = 20.007(4) Å, β = 115.263(8)°, V = 3915.4(12) Å^3, T = 93(2) K, space group $P2(1)/n$, Z = 4, 22382 reflections measured, 6829 unique of which 5151 were observed [$I > 2\sigma I$] (R_1 = 0.0840, wR_2 = 0.1949, R_{int} = 0.0886).

$[RhI(CH_3)(TRIPHOS)CO]^+I^-$ 6a[20]. By modification of a procedure given in ref. 20 CH_3I (1 mL, 16.06 mmol) was added to a solution of [Rh(TRIPHOS)$(CO)_2$]Cl prepared from [Rh$(CO)_2$(μ-Cl)$_2$] (30 mg, 0.077 mmol) and TRIPHOS ligand (82.5 mg, 0.154 mmol) in 5 mL of dry degassed methanol. The solution was then stirred for 24 h to obtain a bright yellow solution. The solvent was removed under vacuum and the product isolated in good yield.

Yield: 91% (113 mg, 0.140 mmol). IR (KBr), ν(CO)/cm^{-1}: 2075. LSIMS (ES) Found 779.06 [M − CO]$^+$; $C_{35}H_{36}IP_3Rh$ requires 779.01 [M − CO]$^+$. $^{31}P\{^1H\}$ NMR (CD_3OD): δ 108.73 (dt, $^1J_{Rh-P}$ 104.0 Hz, $^2J_{P-P}$ 2.97 Hz), 41.85 (dd, $^1J_{Rh-P}$ 92.1 Hz, $^2J_{P-P}$ 2.97 Hz). $^1H\{^{31}P\}$ NMR (CD_3OD): δ 7.78 (4H, C*H*-Ar, m), 7.45 (4H, C*H*-Ar, m), 7.16 (17H, C*H*-Ar, m), 3.51 (1H, CH_2, m), 2.99 (1H, CH_2, m), 2.74 (6H, CH_2, m), −0.14 (3H, CH_3, s).

$[RhI(^{13}CH_3)(TRIPHOS)CO]^+I^-$ 6b. Yield: 85% (106 mg, 0.131 mmol). IR (KBr), ν(CO)/cm^{-1}: 2076. LSIMS (ES) Found 779.77 [M − CO]$^+$; $C_{34}{}^{13}CH_{36}IP_3Rh$ requires 780.02 [M − CO]$^+$. $^{31}P\{^1H\}$ NMR (CD_3OD): δ 108.9 (m, $^1J_{Rh-P}$ 103.7 Hz), 42.0 (d (dd), $^1J_{Rh-P}$ 92.45 Hz, $^2J_{P-P}$ 2.97 Hz, $^2J_{P-^{13}C}$ 5.77 Hz). $^1H\{^{31}P\}$ NMR (CD_4OD): δ 8.12–7.31 (25H, C*H*-Ar, m), 3.82 (2H, CH_2, m), 3.05 (6H, CH_2, m), 0.17 (3H, $^{13}CH_3$, d, $^1J_{^{13}C-H}$ 135.7 Hz). ^{13}C NMR (CD_3OD): δ 7.12 ($^{13}CH_3$, dq, $^1J_{Rh-^{13}C}$ 14.4 Hz, $^1J_{P-^{13}C}$ 6.1 Hz).

$[Rh(I)_2(C(O)CH_3)\{Ph_2P(CH_2)_2P(Ph)(CH_2)_2(PPh_2CH_3)\}]^+I^-$ 5a. CH_3I (0.1 mL, 1.06 mmol) was added to a 2.0 mL Biotage™ microwave vial containing [Rh(TRIPHOS)$(CO)_2$]Cl prepared from [Rh$(CO)_2$(μ-Cl)$_2$] (15 mg, 0.039 mmol) and TRIPHOS ligand (41.3 mg, 0.077 mmol) in 2 mL of dry degassed methanol. The reaction mixture was then heated to 140 °C for 10 min. Crystals suitable for analysis by X-ray diffraction were then formed from the slow evaporation of this solution.

Yield: 75% (54 mg, 0.058 mmol). IR (KBr), ν(CO)/cm^{-1}: 1709. HRMS (ES) Found 948.9364 [M]$^+$; $C_{37}H_{39}I_2OP_3Rh$ requires 948.9353 [M]$^+$. Anal. Calc. for $C_{37}H_{39}I_3O_1P_3Rh{\cdot}2\ H_2O$ (as shown in X-ray structure of crystals): C, 39.95; H, 3.90%. Found: C, 39.85; H, 3.75%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 79.55 (dd, $^1J_{Rh-P}$ 143.7 Hz, $^3J_{P-P}$ 47.2 Hz), 70.69 (d, $^1J_{Rh-P}$ 134.1 Hz), 26.50 (d, $^3J_{P-P}$ 47.2 Hz). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 7.55 (25H, C*H*-Ar, m), 3.75 (1H, CH_2, m), 3.41 (2H, CH_2, m), 3.26 (1H, CH_2, m), 3.09 (1H, CH_2, m), 3.06 (2H, CH_2, m), 2.82 (3H, CH_3, s), 2.59 (3H, CH_3, s), 1.78 (1H, CH_2, m), 1.52 (4H, 2xH_2O, m). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 211.12 (*C*OCH$_3$, dt, $^1J_{Rh-C}$ 26.54 Hz, $^1J_{P-C}$ 4.42 Hz), 135.30–128.29 (*C*H-Ar), 118.80 (*C*-Ar, d, $^1J_{Rh-C}$ 17.14 Hz), 117.67 (*C*-Ar, d, $^1J_{Rh-C}$ 17.14 Hz), 44.99 (CO*C*H$_3$), 29.08 (*C*H$_2$, ddd, $^1J_{P-C}$ 33.17 Hz, $^2J_{P-C}$ 12.16 Hz, $^2J_{Rh-C}$ 2.21 Hz), 27.61 (*C*H$_2$, dd, $^1J_{P-C}$ 32.07 Hz, $^2J_{P-C}$ 7.74 Hz), 21.43 (*C*H$_2$, dd, $^1J_{P-C}$ 25.98 Hz, $^2J_{Rh-C}$ 2.21 Hz), 20.74 (*C*H$_2$, d, $^1J_{P-C}$ 48.65 Hz), 8.98 (*C*H$_2$, d, $^1J_{P-C}$ 54.73 Hz).

$[Rh(I)_2(C(O)^{13}CH_3)\{Ph_2P(CH_2)_2P(Ph)(CH_2)_2(PPh_2{}^{13}CH_3)\}]^+I^-$ 5c. Yield: 77% (55.6 mg, 0.059 mmol). IR (KBr), ν(CO)/cm^{-1}: 1709. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.37 (d, $^1J_{Rh-P}$ 143.8 Hz, $^3J_{P-P}$ 47.0 Hz), 69.52 (d, $^1J_{Rh-P}$ 47.0 Hz), 25.26 (dd, $^3J_{P-P}$ 47.0 Hz, $^1J_{P-C}$ 54.6 Hz). ^1H NMR ($CDCl_3$): δ 8.01–7.08 (25H, C*H*-Ar, m), 3.75 (1H, CH_2, m), 3.39 (1H, CH_2, m), 3.26 (2H, CH_2, m), 3.07 (2H, CH_2, m), 2.88 (3H, $^{13}CH_3$, d, $^1J_{C-H}$ 98.4 Hz), 2.85 (1H, CH_2, m), 2.54 (3H, CH_3, d, $^1J_{C-H}$ 97.9 Hz), 1.86 (1H, CH_2, m). ^{13}C NMR ($CDCl_3$): δ 44.97 (*C*O^{13}CH$_3$, s), 9.04 (^{13}*C*OCH$_3$, d, $^1J_{P-C}$ 54.6 Hz).

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