The unusual inhibition of a dirhodium tetraphosphine-based bimetallic hydroformylation catalyst by PPh$_3$

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This article is dedicated to the memory of John A. Osborn.

Abstract – The addition of even small amounts of PPh$_3$ to the dirhodium tetraphosphine hydroformylation catalyst generated from [rac-Rh$_2$(nbd)$_2$(et,ph-P4)](BF$_4$)$_2$ (nbd = norbornadiene; et,ph-P4 = Et$_2$CH$_2$CH$_2$(Ph)PCH$_2$P(Ph)CH$_2$CH$_2$PEt$_2$) causes a dramatic drop in the aldehyde linear-to-branched regioselectivity (25:1 to 3:1) in acetone solvent (90 °C, 6.1 bar, 1-hexene). Catalytic results are presented for differing amounts of added PPh$_3$ along with comparisons to the monometallic Rh catalyst family, HRh(CO)$_x$(PPh$_3$)$_y$ ($x = 1$–3; $y = 3 - x$), generated from PPh$_3$ and Rh(acac)(CO)$_2$ (acac = acetylacetonate). The results point to the extremely effective inhibition of the regioselective bimetallic hydroformylation mechanism and the formation of an inefficient monometallic catalyst cycle, but not fragmentation to generate free HRh(CO)(PPh$_3$)$_2$ catalysts. *To cite this article: David A. Aubry et al., C. R. Chimie 5 (2002) 473–480* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

hydroformylation / bimetallic cooperativity

Résumé – L'addition de PPh$_3$, même en faible quantité, au catalyseur d'hydroformylation dirhodium tétraphosphine généré à partir de [rac-Rh$_2$(nbd)$_2$(et,ph-P4)](BF$_4$)$_2$ (nbd = norbornadiène; et,ph-P4 = Et$_2$CH$_2$CH$_2$(Ph)PCH$_2$P(Ph)CH$_2$CH$_2$PEt$_2$) entraîne une chute spectaculaire de la régiosélectivité en aldéhyde linéaire ou branché, dont le rapport passe de 25:1 à 3:1 (90 °C, 6,1 bar, 1-héxène, acétone). Les résultats catalytiques obtenus pour différentes quantités de PPh$_3$ sont présentés, ainsi que des comparaisons avec la famille de catalyseurs de rhodium monométalliques, HRh(CO)$_x$(PPh$_3$)$_y$ ($x = 1$–3; $y = 3 - x$), générés à partir de PPh$_3$ et Rh(acac)(CO)$_2$ (acac = acetylacetonate). Les résultats indiquent l'inhibition extrêmement efficace du mécanisme d'hydroformylation régiosélective bimétallique et l'intervention d'un catalyseur monométallique inefficace, mais pas de fragmentation conduisant aux catalyseurs libres HRh(CO)(PPh$_3$)$_2$. *Pour citer cet article : David A. Aubry et al., C. R. Chimie 5 (2002) 473–480* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

hydroformylation / coopérativité bimétallique

1. Introduction

Osborn, Wilkinson and Young reported the use of Rh(PPh$_3$)$_3$Cl$_3$ (and other related complexes) as active hydroformylation (oxo) catalysts for the conversion of alkenes, H$_2$, and CO into aldehyde products under mild conditions in a very short 1965 communication

[1]. This was followed by their seminal full paper in 1968 that identified the actual catalyst as HRh(CO)$_2$(PPh$_3$)$_2$ [2]. While it had been known that rhodium was considerably more active towards hydroformylation relative to cobalt, the use of PPh$_3$ as a highly effective promoter ligand to generate a catalyst system that could perform oxo catalysis at 25 °C and

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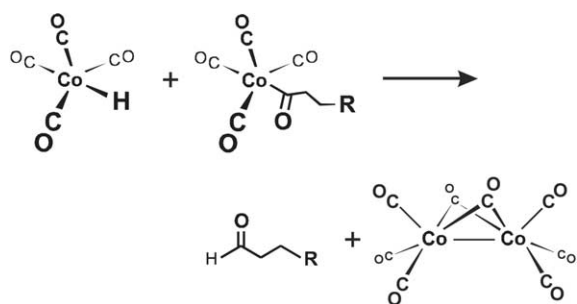   *E-mail address:* gstanley@lsu.edu (G.G. Stanley).

Fig. 1. Intermolecular hydride transfer from $HCo(CO)_4$ to $Co(acyl)(CO)_4$ leading to the reductive elimination of aldehyde and formation of $Co_2(CO)_8$.

1 bar of H_2/CO was unprecedented. In many ways, this result was more important than that of the catalyst of Osborn and Wilkinson, $RhCl(PPh_3)_3$, and its activity for the hydrogenation of alkenes [3]. Heterogeneous hydrogenation catalysts were well known and are still routinely used in most non-asymmetric hydrogenations. But for hydroformylation, homogeneous catalysts are essentially the only ones used in industry due to their higher selectivity and activity. Indeed, the exceptionally high activity of $RhH(CO)_2(PPh_3)_2$, in conjunction with Pruett's discovery [4] that excess PPh_3 is required in rhodium hydroformylation in order to stabilize the catalyst and enhance the linear aldehyde product selectivity, opened the door for low pressure hydroformylation, which currently accounts for over 70% of industrial oxo production [5].

Interest in homobimetallic cooperativity in hydroformylation catalysis goes all the way back to Heck's original 1961 mechanism for $HCo(CO)_4$-catalyzed hydroformylation where, in addition to the now commonly accepted monometallic mechanism for both Co and Rh catalysts, he proposed an intermolecular hydride transfer from $HCo(CO)_4$ to $Co(acyl)(CO)_4$ leading to the reductive elimination of aldehyde and formation of $Co_2(CO)_8$ as shown in Fig. 1 [6]. Heck, however, did not favor the bimetallic mechanism due to the low concentrations of both species involved and subsequent spectroscopic studies have effectively confirmed this [7, 8].

One strategy to enhance possible bimetallic cooperativity in the catalysis is to tether the two metal centers together using a suitable bridging ligand system. We have designed the binucleating tetraphosphine ligand $(Et_2CH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$, et,ph-P4, to strongly chelate and bridge two metal centers in order to explore bimetallic cooperativity in hydroformylation catalysis [9]. The two internal phosphines in the et,ph-P4 ligand are chiral, leading to the two diastereomers shown in Fig. 2.

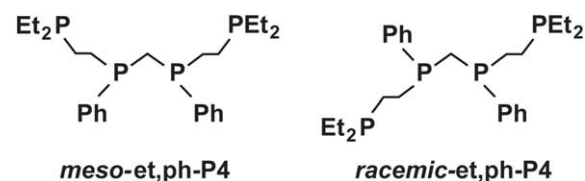The reaction of 2 equiv of $[Rh(nbd)_2](BF_4)$ (nbd = norbornadiene) with *rac*-et,ph-P4 generates the

Fig. 2. Diastereomers *meso*-et,ph-P4 and *racemic*-et,ph-P4.

homobimetallic complex $[rac\text{-}Rh_2(nbd)_2(et,ph\text{-}P4)](BF_4)_2$, **1**, which is the catalyst precursor to a highly selective and active hydroformylation catalyst for 1-alkenes (90 °C, 6.1 bar, 1 mM catalyst, 0.9 M 1-hexene, acetone solvent, initial turnover frequency = 640 h^{-1}, aldehyde linear-to-branched = 27:1, 8% alkene isomerization, 3.4% alkene hydrogenation). We have reported that this represents one of the most dramatic examples of bimetallic cooperativity in homogeneous catalysis [10]. Our in situ spectroscopic studies have indicated that the active catalyst is the unusual dicationic dirhodium complex $[rac\text{-}Rh_2H_2(\mu\text{-}CO)_2(CO)_2(et,ph\text{-}P4)]^{2+}$, **2**, shown in Fig. 3 [11]. One of the strongest and most persuasive indications that fragmentation to active monometallic catalysts is not occurring in this system was the high linear to branched (L:B) aldehyde regioselectivity of 27:1 observed for 1-hexene. Monometallic 'half' analogs of the bimetallic catalyst using chelating $R_2PCH_2CH_2PR_2$ ligands show very low activity (TOF = 1 h^{-1}), L:B regioselectivities (3:1), and considerable alkene isomerization and hydrogenation side reactions (~ 70%) [10].

Prior to our work, Kalck and coworkers also reported an active thiolate bridged dirhodium catalyst, $Rh_2(\mu\text{-}SR)_2(CO)_4$, for hydroformylation that was proposed to work via homobimetallic cooperativity [12, 13]. An unusual aspect of this catalyst was that it had no hydroformylation activity until PPh_3 was added, and then the activity and regioselectivity essentially mirrored that of $RhH(CO)_2(PPh_3)_2$. It has been subsequently demonstrated that the thiolate-bridged binuclear complex readily fragments even under mild conditions [14] and that PPh_3 simply assists in producing the active $RhH(CO)_2(PPh_3)_2$ monometallic catalyst [15].

Ongoing spectroscopic studies of our bimetallic hydroformylation catalyst $[rac\text{-}Rh_2H_2(\mu\text{-}CO)_2(CO)_2$

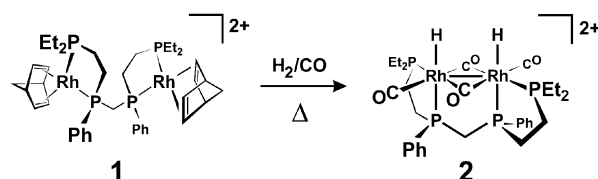Fig. 3. Synthesis of the dicationic dirhodium complex $[rac\text{-}Rh_2H_2(\mu\text{-}CO)_2(CO)_2(et,ph\text{-}P4)]^{2+}$, **2**, from **1**.

Fig. 4. Rh(III) monometallic complex [*rac*-RhH$_2$(η^4-et,ph-P4)]$^+$, **3**, and the double ligand coordinated bimetallic complex [*rac,rac*-Rh$_2$H$_2$(CO)$_2$(et,ph-P4)$_2$]$^{2+}$, **4**.

(et,ph-P4)]$^{2+}$ have clearly indicated that as the initial mixture of bimetallic carbonyl and hydrido-carbonyl complexes sits under H$_2$/CO (20 bar) that fragmentation of the catalytically active bimetallic complexes is occurring. Two of the fragmentation products that we have tentatively identified from in situ NMR studies are th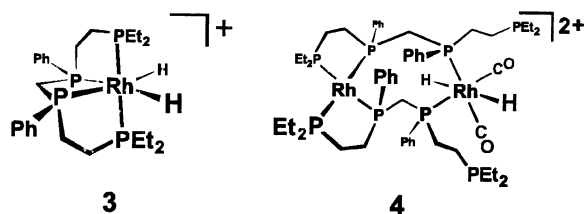e Rh(III) monometallic complex [*rac*-RhH$_2$(η^4-et,ph-P4)]$^+$, **3**, and the double ligand coordinated bimetallic complex [*rac,rac*-Rh$_2$H$_2$(CO)$_2$(et,ph-P4)$_2$]$^{2+}$, **4**, shown in Fig. 4 [16, 17]. Neither of these is believed to be catalytically active for hydroformylation and under extended 'soaking' (time spent under H$_2$/CO pressure while heating the autoclave to the reaction temperature) of the bimetallic catalyst solution under H$_2$/CO (90 °C, 6.1 bar, > 2 h), without any alkene present, we see almost complete deactivation of the catalyst towards hydroformylation. We now report the unusual effect of added PPh$_3$ on our bimetallic rhodium hydroformylation catalyst system that leads to loss of the high L:B aldehyde regioselectivity and eventually all catalyst activity.

2. Results and discussion

2.1. Addition of PPh$_3$ to bimetallic catalyst solution

The hydroformylation reaction conditions used are very similar to that previously reported [10]: 90 °C, 6.12 bar 1:1 H$_2$/CO, acetone solvent, 1 mM [*rac*-Rh$_2$(nbd)$_2$(et,ph-P4)](BF$_4$)$_2$, **1**, as the catalyst precursor, 1 M 1-hexene (1000 equiv), 160 ml Parr autoclave, and 1000 rpm stirring. The catalyst activity in acetone solvent is strongly influenced by the initial soaking under H$_2$/CO prior to the addition of the 1-hexene substrate. The catalyst precursor **1** and appropriate amount of PPh$_3$ was dissolved in 80 ml of acetone and transferred to the Parr autoclave in a glove box under inert atmosphere. The autoclave is then purged with 1:1 H$_2$/CO, pressurized to 3 bar with H$_2$/CO, and temperature ramped up as quickly as possible to 90 °C. This takes approximately 20 min and the pressure increases to about 5.4 bar. The 11 ml (1000 equiv) of 1-hexene is pressure added to the

autoclave from a small external stainless steel reservoir to initiate the hydroformylation catalysis and raise the autoclave pressure to the operating pressure of 6.12 bar.

Allowing the bimetallic catalyst solution to sit prior to alkene addition for longer periods at 90 °C under 5.4 to 6.1 bar of H$_2$/CO leads to steadily decreasing catalyst activity. For example, after 50 min, the dirhodium catalyst has only about 20% the hydroformylation activity of the 20-min system, and after 80 min, there is essentially no hydroformylation catalysis. This, in some ways, parallels the RhH(CO)$_2$(PPh$_3$)$_2$ monometallic catalyst that also deactivates on extended soaking under H$_2$/CO at 90 °C (8–12 h), even in the presence of excess PPh$_3$ (400–800 equiv) [18, 19]. The deactivation routes for the dirhodium and RhH(CO)(PPh$_3$)$_2$ monometallic catalyst, however, appear to be quite different. It has been fairly well established that RhH(CO)(PPh$_3$)$_2$ can attack and cleave a phenyl ring off the PPh$_3$ ligand to ultimately form catalytically inactive phosphido-bridged rhodium dimer and cluster complexes [20, 21] or add an alkyl group to the phosphine that is a considerably poorer ligand for hydroformylation [22, 23]. Another less serious deactivation route involves the formation of carbonyl-bridged dinuclear Rh(0) complexes like Rh$_2$(μ-CO)$_2$(CO)$_2$(PPh$_3$)$_2$, which is inhibited by excess PPh$_3$ [2, 24]. In marked contrast, we have not observed any Rh-induced fragmentations of our more alkylated et,ph-P4 ligand [11], but instead observed that the tetraphosphine does not appear to chelate the rhodium centers strongly enough leading to release of one Rh center and the formation of the catalytically inactive complexes shown in Fig. 4.

The catalytic results for the hydroformylation of 1-hexene starting with the bimetallic precursor **1** and monometallic precursor Rh(acac)(CO)$_2$ (or [Rh(nbd)$_2$]$^+$) in the presence of varying amounts of PPh$_3$ are shown in Table 1. In all runs, we observed minimal alkene hydrogenation side reactions (less than 1%). The homobimetallic catalyst [*rac*-Rh$_2$H$_2$(μ-CO)$_2$(CO)$_2$(et,ph-P4)]$^{2+}$, **2**, without any added PPh$_3$ is quite active with an initial turnover frequency (TOF) of 1200 h^{-1}, high L:B aldehyde regioselectivity of 25, and 2.5% alkene isomerization and 3.4% alkene hydrogenation side-reactions. This initial TOF is 88% faster than the 640 h^{-1} value originally reported [10] and this requires some comment.

The catalysis is first order in 1-hexene and a slightly higher alkene concentration was used (1.0 vs 0.91 M) in these studies, but this only accounts for a small amount of the increased rate. The main reason is tied into the importance of purifying the reagent grade 1-hexene by passing it through a fresh alumina column under inert atmosphere prior to each catalytic

Table 1. Hydroformylation of 1-hexene (1 M) in acetone at 90 °C and 6.12 bar 1:1 H_2/CO using the bimetallic precursors: [*rac*-$Rh_2(nbd)_2$(et,ph-P4)]$(BF_4)_2$, monometallic $Rh(acac)(CO)_2$, or cationic monometallic [$Rh(nbd)_2$](BF_4) (all 1 mM).

Precursor	Equivalents PPh_3[a]	Equivalents PEt_3[a]	Initial TOF[b] (h^{-1})	Aldehyde L:B selectivity	% Alkene isomer[c]
Bimetallic	0	0	1200	25	2.5
Bimetallic	0.5	0	660	3.4	3.0
Bimetallic	2	0	590	3.1	5.0
Bimetallic	5	0	320	2.9	3.0
Bimetallic	10	0	220	3.2	3.3
Bimetallic	100	0	0	—	0
Mono	0	0	0	—	0
Mono	2	0	2200	2.6	6.0
Mono	5	0	5300	3.2	2.9
Mono	10	0	6800	3.2	2.0
Mono	100	0	6300	5.0	< 1
Mono	400	0	780	9.1	< 1
Mono	10	1.1	3100	3.1	2.0
Mono	100	1.1	780	4.9	1.5
Mono	10	2.2	2000	3.0	< 1
Mono	100	2.2	450	3.6	< 1
Mono(+)[d]	10	0	2	1.6	80
Mono(+)[d]	100	0	300	4.2	1.8
Mono(+)[d]	10	2.2	180	3.3	1.7
Mono(+)[d]	100	2.2	180	3.1	< 1

[a] Equivalents of PPh_3 or PEt_3 added relative to the amount of rhodium catalyst precursor. [b] TOF = turnover frequency; an average of at least three consistent runs; approximately a 5% error on the rates, which have been rounded off to reflect this. [c] Isomerization (hydrogenation side reactions all considerably less than 1%, except for the first run where it is 3.4%). [d] Cationic precursor [$Rh(nbd)_2$](BF_4) (nbd = norbornadiene).

run. In our original work we degassed and stored the reagent grade 1-hexene under N_2, but did not purify it through an alumina column, which turns out to effectively remove any peroxide impurities that can lead to partial catalyst deactivation. It is this partial deactivation that produces the higher alkene isomerization (8%) and hydrogenation (4%) side reactions originally reported [10]. The difference in the L:B aldehyde regioselectivity, however, is very small (28 vs 25 here) and quite consistent within the error of our typical catalytic runs.

The addition of 2 equiv of PPh_3 to the bimetallic catalyst causes a dramatic drop in the L:B aldehyde regioselectivity from 25 to 3.1 and a considerable reduction in the initial TOF to 590 h^{-1}. Increasing amounts of PPh_3 leads to steadily decreasing catalytic rates, until at 100 equiv essentially no hydroformylation is observed. This is almost opposite behavior from Kalck's bimetallic $Rh_2(\mu$-SR$)_2(CO)_4$ system that is inactive until one adds PPh_3 and then the rate and selectivity increase with increasing amounts of added PPh_3 (up to a point). Van Leeuwen and Claver have demonstrated that Kalck's bimetallic system readily fragments and reacts with PPh_3 to generate the classic monometallic $HRh(CO)_x(PPh_3)_y$ ($x = 1$–2; $y = 3 - x$) catalyst [15].

Even the addition of only 0.5 equiv of PPh_3 causes a dramatic drop in the regioselectivity and catalyst activity as shown in Table 1. The steady deactivation and essentially constant low regioselectivity of our

bimetallic system with increasing amounts of PPh_3 is not consistent with simple fragmentation to a monometallic Wilkinson-like catalyst system. This is illustrated by the parallel runs with the monometallic precursor $Rh(acac)(CO)_2$ and PPh_3 (Table 1). At low PPh_3 ratios, one generates an extremely active, but short-lived, catalyst with relatively low selectivity. At 100 equiv of PPh_3, the catalyst starts to slow down and the aldehyde L:B regioselectivity starts to increase. At 400 equiv (0.4 M) of PPh_3, the catalyst initial TOF has deceased to 700 h^{-1}, but the L:B regioselectivity has increased to 9.1. Commercial Rh/PPh_3 hydroformylation processes are typically run with at least 0.4 M PPh_3 and up to 50% PPh_3 by solution weight when the highest L:B aldehyde regioselectivities are needed.

2.2. Mechanistic considerations

The L:B aldehyde regioselectivity data strongly indicates that the addition of even small amounts of PPh_3 strongly inhibits the highly regioselective bimetallic catalyst and generates an alternate catalyst with far lower regioselectivity. The rate and regioselectivity data, however, indicates that this alternate catalyst is not $HRh(CO)_4$, $HRh(CO)_2(PPh_3)$, or $HRh(CO)(PPh_3)_2$. Even assuming that fragmentation is generating very low concentrations of a monometallic rhodium carbonyl complex that could be intercepted by PPh_3, the rate and regioselectivity should increase as the PPh_3 concentration increases within the range studied.
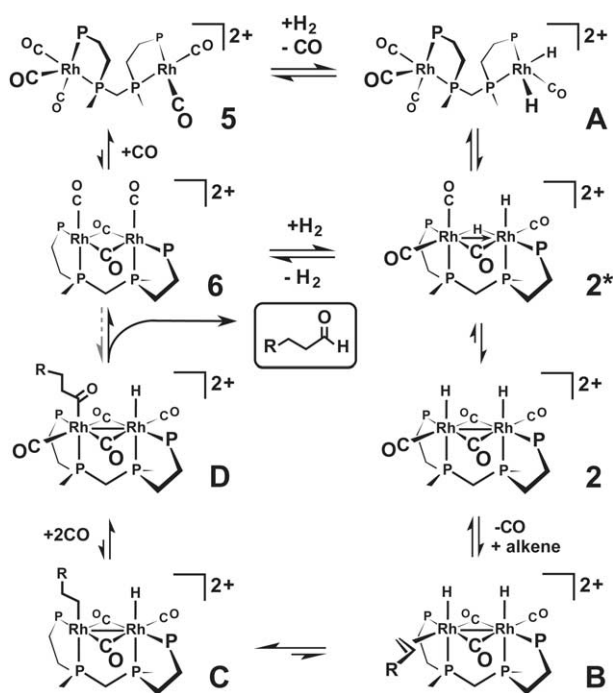
Fig. 5. Bimetallic hydroformylation catalytic cycle proposed in this article.
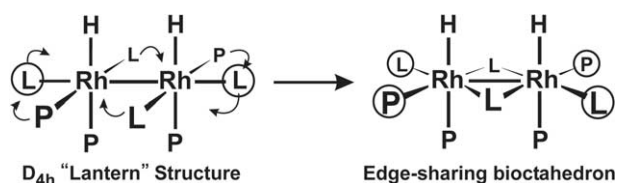

Fig. 6. Transformation of a D_{4h}-like structure into an edge-sharing bioctahedral structure.

bioctahedral structure seen for **2**, there are now two equivalent coordination sites on each metal that are roughly trans to the Rh–Rh bond and should have enhanced lability relative to the other coordination sites (Fig. 6). We will refer to these two sites, coordinated with the terminal PEt$_2$-group of the et,ph-P4 ligand and a CO, also as axial sites.

CO dissociation from **2** is followed by alkene coordination to form **B**, leading to a migratory insertion that generates the alkyl complex **C**. CO coordination is followed by a migratory insertion with the alkyl to produce the acyl complex **D**. This can then do a bimetallic reductive elimination of the aldehyde to form the bridging carbonyl Rh(I) complex **6**, that can break open to form **5** or directly react with H$_2$ to make the hydride complexes **2*** and/or **2**. Hoffmann has calculated that a direct bimetallic reductive elimination is formally symmetry forbidden and can have a high activation barrier [26]. But he also found that π-backbonding ligands like CO, along with lower symmetries, could substantially reduce the barrier for this process. We are currently performing high-level density functional theory (DFT) calculations on this dirhodium catalyst and will be studying the possibility of direct bimetallic reductive elimination.

One obvious effect of added PPh$_3$ on this catalytic cycle would be to simply block the empty axial coordination site formed when CO dissociates and prevent the alkene from coordinating. This should simply slow down the catalyst and not lower the intrinsic regioselectivity. Aside from blocking the alkene-binding site, PPh$_3$ wouldn't seem to have much impact on most of the other proposed catalytic steps. The high regioselectivity of the dirhodium catalyst is believed to arise from the Rh–Rh bond, bridging carbonyls, and Rh(II) oxidation state. These work together to create an extremely well-defined binding site that does not electronically reorganize or distort upon coordination of the alkene to the empty axial coordination site maximizing the steric directing effects of the relatively small ethyl and phenyl groups.

This is quite unlike square-planar Rh(I) monometallic catalysts that electronically distort upon coordination of the alkene to form a 5-coordinate geometry, as illustrated in Fig. 7. The electronic distortion of a square-planar complex to a 5-coordinate structure
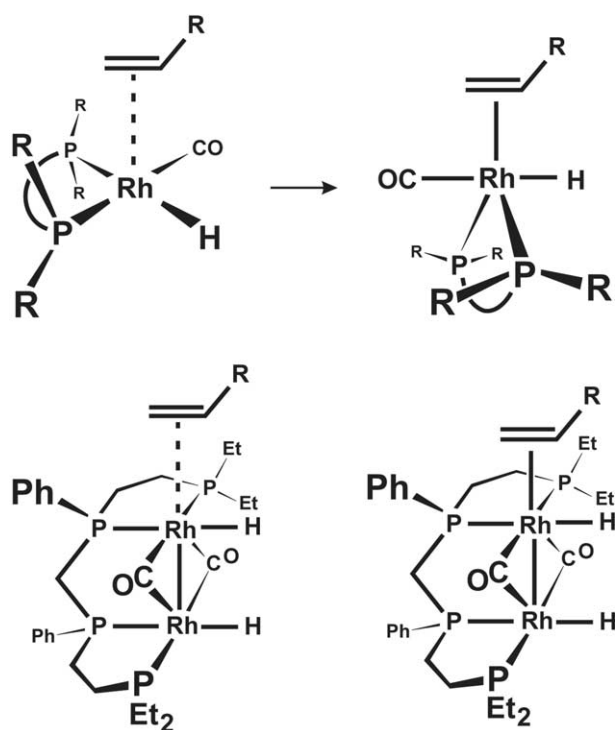
Instead, the bimetallic catalytic run with 100 equiv of PPh$_3$ is essentially inactive for hydroformylation catalysis, which is inconsistent with fragmentation to a HRh(CO)(PPh$_3$)$_2$-type catalyst.

Our proposed bimetallic hydroformylation catalytic cycle is shown in Fig. 5 with the Et and Ph groups on the et,ph-P4 ligand omitted for clarity. The in situ NMR studies indicate that the resting state of the catalyst is the simple open-mode dicationic carbonyl complex [rac-Rh$_2$(CO)$_5$(et,ph-P4)]$^{2+}$, **5**, which we have crystallographically characterized [16]. There is a very facile CO-based on-off equilibrium between the tetracarbonyl, pentacarbonyl **5**, and the transient hexacarbonyl bimetallic complexes. The localized cationic charge on each rhodium atom compensates for the strongly electron-donating nature of the et,ph-P4 ligand reducing the CO π-backbonding and enabling facile CO dissociation. Oxidative addition of H$_2$ to one of the Rh centers generates the dihydride complex **A**. This can readily rotate to form the bridged complex **2***, which can rearrange to form the symmetric Rh(II) terminal dihydride **2**.

The proposed edge-sharing bioctahedral structure for **2** is quite different from the far more common D_{4h} symmetry dirhodium tetracarboxylate-like systems that have been extensively characterized and studied [25]. Rh$_2$(O$_2$CR)$_4$ and related compounds almost always have weakly coordinated ligands in the two axial coordination sites trans to the Rh–Rh bond. When one transforms this D_{4h}-like structure into an edge-sharing

Fig. 7. Electronic distortion of a square-planar complex to a 5-coordinate structure.

Fig. 8. Opening up of the bimetallic catalyst chelate structure (**5**) to form a monometallic catalyst center with one alkylated phosphine (PEt$_3$) and a PPh$_3$ (**7**).

causes the sterically directing R groups on the phosphine ligands to be moved further away from the alkene. This minimizes the phosphine ligand steric orienting effect for the subsequent hydride–alkene migratory insertion that is the regioselectivity determining step.

While the added PPh$_3$ ligand probably inhibits the active bimetallic catalyst, it also appears to short-circuit the catalyst into another structure that has low regioselectivity and moderate activity, but one that is eventually completely inhibited by increasing amounts of PPh$_3$. The most likely entry point for disrupting the formation of the Rh–Rh bonded complex **2** involves the starting carbonyl complex **5**. PPh$_3$ coordination could easily disrupt the rotation to **2*** after H$_2$ oxidative addition. Molecular modeling studies indicate that this open- to closed-mode rotation is strongly influenced by steric effects. For example, the simple tetracarbonyl [*rac*-Rh$_2$(CO)$_4$(et,ph-P4)]$^{2+}$ (or pentacarbonyl **5**) shows no sign of rotation into a bridged-carbonyl structure like **6** (Fig. 5) in the presence of CO. Only when H$_2$ is added do we observe rhodium complexes with bridging carbonyls. Indeed, the activity of the catalyst appears to directly track with the presence and intensity of the bridging carbonyl bands in the IR spectrum. The modeling studies clearly demonstrate that it is much easier for the bimetallic complex to rotate into a closed-mode structure when there 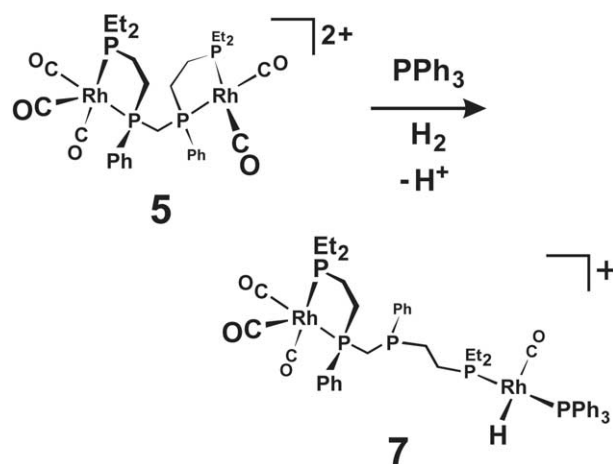are two small hydride ligands present on the one rhodium center instead of carbonyls. If a PPh$_3$ ligand was present on one or both of the Rh atoms that could easily sterically block the ability of the complex to form a closed-mode Rh–Rh bonded structure, which we believe is necessary for the high catalyst regioselectivity (and activity).

The coordination of PPh$_3$ is also proposed to open up the bimetallic catalyst chelate structure to form, in essence, a monometallic catalyst center with one alkylated phosphine (PEt$_3$) and a PPh$_3$. This is shown in Fig. 8 for one half of **5**, although it could, of course, happen to both sides of the bimetallic complex. One needs to have loss of a proton in order to generate the neutral Rh-H side of the complex. Cationic monometallic precursors like [Rh(nbd)$_2$]$^+$ (Table 1, bottom four experiments) typically generate terrible hydroformylation catalysts unless one can deprotonate the resulting saturated cationic Rh(III) dihydrides (e.g., [RhH$_2$(CO)$_2$(PPh$_3$)$_2$]$^+$) produced from the oxidative addition of H$_2$ [21]. PPh$_3$ is marginally basic enough for this, with 10 equiv giving a catalyst that is barely active for hydroformylation, but quite good at alkene isomerization. The addition of 100 equiv of PPh$_3$, however, does shift the deprotonation equilibrium enough to give modest hydroformylation activity (initial TOF = 300 h^{-1}) and dramatically reduced alkene isomerization.

Our homobimetallic catalyst normally avoids this cationic dihydride 'trap' by performing an intramolecular hydride transfer from complex **A** in Fig. 5 to ultimately form the symmetrical bimetallic dihydride **2**. This is one of the key bimetallic cooperativity steps operating in our catalyst. While PPh$_3$ can deprotonate [RhH$_2$(CO)$_2$(PPh$_3$)$_2$]$^+$ when present in high enough concentrations, it probably would not be effective for the less acidic cationic dihydride precursor that leads

to **7** due to the more strongly donating et,ph-P4 ligand. The considerably more basic et,ph-P4 ligand, however, may well be able to act as a suitable base for this deprotonation. Indeed, the internal free phosphine in **7** is well situated to act as an intramolecular deprotonating agent, although it was not drawn as such in Fig. 8.

These mechanistic proposals have been partially tested by adding 1.1 and 2.2 equiv of PEt_3 to the neutral and cationic monometallic precursor catalytic reactions. In the case of $Rh(CO)_2(acac)$, the addition of PEt_3 causes a dramatic drop in activity and a considerably smaller (sometimes negligible) drop in regioselectivity (Table 1). For example, the initial TOF with 100 equiv of PPh_3 drops from $6300\ h^{-1}$ down to $450\ h^{-1}$ when 2.2 equiv of PEt_3 are added, while the L:B aldehyde regioselectivity is reduced from 5.0 to 3.6. The deprotonating ability of 2.2 equiv of PEt_3 (one to deprotonate, one to coordinate to the Rh) was tested on the cationic $[Rh(nbd)_2]^+$ precursor system and it increased the initial rate with 10 equiv of PPh_3 from $2\ h^{-1}$ up to $180\ h^{-1}$. Comparing this to the 10 equiv of PPh_3 and 1.1 equiv of PEt_3 neutral $Rh(CO)_2(acac)$ experiment that has an initial rate of $3100\ h^{-1}$, clearly demonstrates that the PEt_3 is only partially deprotonating the cationic rhodium complex and that there is an equilibrium between the cationic and neutral catalyst species. Interestingly, with 100 equiv of PPh_3 and 2.2 equiv of PEt_3, the cationic catalyst precursor has the same initial TOF as with 10 equiv of PPh_3 and 2.2 equiv of PEt_3, but actually shows a slight decrease in the regioselectivity (3.3 down to 3.1), along with an expected drop in the alkene isomerization.

These simple model studies offer reasonable support for the proposed formation of an inefficient monometallic-like catalyst similar to **7**. The essentially complete catalytic inhibition upon addition of 100 equiv of PPh_3 is consistent with the coordination of a second PPh_3 to generate a sterically hindered $HRh(\eta^1\text{-et,ph-P4})(PPh_3)_2$ complex, which should be essentially inactive for hydroformylation catalysis. Note that the tris-PPh_3 analog of this complex only forms under considerably higher PPh_3 concentrations and has rather facile PPh_3 dissociation in order to relieve the steric strain of having three bulky PPh_3 coordinated in a square planar environment. The smaller 'PEt_2' arm of our ligand, however, should make the catalytically inactive $HRh(\eta^1\text{-et,ph-P4})(PPh_3)_2$ complex considerably more stable at lower PPh_3 concentrations. The low CO pressure being used will also help stabilize this inactive tris-phosphine complex. The inability of the simple PEt_3 model sys-

tem to mimic the zero activity with 100 equiv of PPh_3 is reasonable given that PEt_3 is certainly not the same as an η^1-et,ph-P4 ligand that has a cationic $Rh(CO)_3$ moiety coordinated to the other side, as proposed for **7**. The dramatic regioselectivity lowering effect of even a 0.5 equiv of added PPh_3 must point to the extremely efficient inhibition of the active and selective homobimetallic catalyst, which is probably only present in relatively small amounts compared to the total amount of catalyst precursor being used.

In summary, even small amounts of PPh_3 disrupt the active and regioselective bimetallic catalyst **2** through a combination of blocking effects that includes coordination to the bimetallic binding site preventing alkene coordination along with coordination to **5** that inhibits the formation of the closed-mode catalyst **2**. In concert with this, PPh_3 is also proposed to crack open **5** (with deprotonation) to form **7**, which contains the active neutral mono-hydride $HRh(CO)(\eta^1\text{-et,ph-P4})(PPh_3)$ species which is moderately active for hydroformylation, but not regioselective. Continued addition of PPh_3 rapidly leads to catalyst deactivation by 'saturating' the neutral half of **7** to form $HRh(CO)(\eta^1\text{-et,ph-P4})(PPh_3)_2$. In situ NMR and FT–IR studies will be performed to further probe the validity of these proposals. We are also designing and preparing more strongly chelating analogs of our ligand to minimize these types of side reactions.

3. In memory of John Osborn

The corresponding author (GGS) had the great privilege of working with John Osborn (Fig. 9) as a NATO and CNRS postdoctoral fellow between 1979 and 1981. Those were two of the best years of my life. John and Karen Osborn (along with their sons Michael and Nicholas) basically adopted me into their family and I was routinely invited to their apartment for dinner and to join them on weekend family trips to the surrounding area. He taught me that the quality of one's science and life is far more important than quantity. John also loved catalysis and infected me forever with that same love. Considering that John's original research is the foundation of modern rhodium hydroformylation, I'm quite pleased that my own career has ended up centered on an unusual permutation of this (homobimetallic cooperativity). John certainly lived life to the fullest and even though his life ended far too soon and on a tragic note, he certainly packed more into it than anyone I know. I will always remember him as bigger than life, with a smile on his face (although rarely for photographs), and one of the best catalytic chemists I have known.
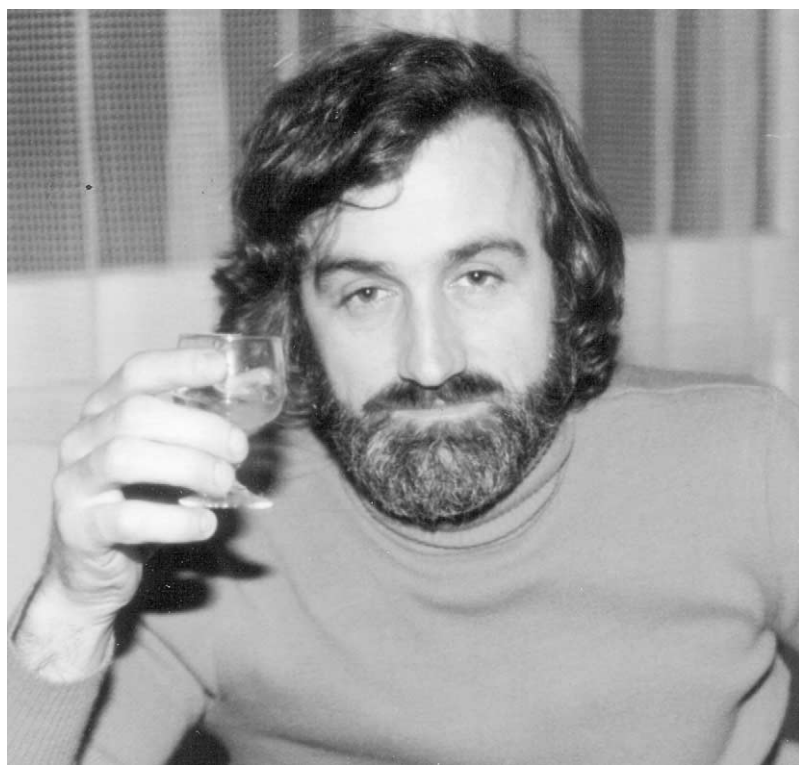
Fig. 9. John A. Osborn in 1980.

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