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Ligand effects in the rhodium-catalyzed carbonylation of methanol

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Contents

Abstract

The carbonylation of methanol to give acetic acid is one of the most important homogeneously catalyzed industrial processes. The original $[Rh(CO)_2I_2]^-$ catalyst, developed at the Monsanto laboratories and studied in detail by Forster and co-workers, is largely used for the industrial production of acetic acid and anhydride. The conditions used (30–60 bar pressure and 150–200 °C) have spurred the search for new catalysts which work under milder conditions. However, attempts to increase the activity of the catalyst $[Rh(CO)_2I_2]^-$ by introducing electron-donating ligands are generally hampered by the instability of the complexes formed under the harsh reaction conditions. As iridium complexes are normally more stable than the corresponding rhodium complexes, efforts have been made to find suitable iridium catalysts for the carbonylation of methanol. This resulted in the development of the Cativa process, based on $[Ir(CO)_2I_2]^-$ in combination with $Ru(CO)_4I_2$, which is presently the most efficient process for the industrial manufacture of acetic acid. On the other hand recent advances in the design of suitable ligands, mainly based on phosphorus-containing systems, allow the synthesis of highly active and stable rhodium complexes, so that a new impetus for the rhodium-catalyzed carbonylation of methanol is to be expected. In this review, attention is focused on the use of phosphine ligands in order to improve the catalytic activity of the rhodium catalysts. This review also includes our recent research results and implications in developing new multifunctional ligands for the rhodium-catalyzed carbonylation of methanol.

Keywords: Monsanto process; Rhodium complexes; Phosphine ligand

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1. Introduction

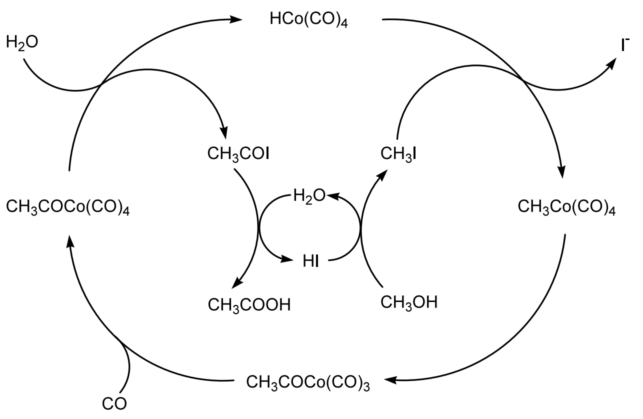
Acetic acid is an important industrial commodity chemical, with a world demand of about 6 million tons per year and many industrial uses [1]. Originally, acetic acid was produced by aerobic fermentation of ethanol, which is still the major process for the production of vinegar. The first major commercial process for the production of synthetic acetic acid was based on the oxidation of acetaldehyde, followed by oxidation of butane or naphtha.

Novel acetic acid processes and catalysts have been introduced, commercialized, and improved continuously since the 1950s. The objective of the development of new acetic acid processes has been to reduce raw material consumption, energy requirements, and investment costs. Significant cost advantages resulted from the use of carbon monoxide (derived from natural gas) and of low-priced methanol (from synthesis gas) as feedstocks. At present, industrial processes for the production of acetic acid are dominated by methanol carbonylation.

$$CH_3OH + CO \rightarrow CH_3COOH \quad (1)$$

$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O \quad (2)$$

The carbonylation of methanol is catalyzed by Group VIII transition metal complexes, especially by rhodium, iridium, cobalt, and nickel [2]. All methanol carbonylation processes need iodine compounds as essential co-catalysts, the reaction proceeding via methyl iodide, which alkylates the transition metal involved. Apart from acetic acid, the carbonylation of methanol (Eq. (1)) also gives rise to the formation of methyl acetate, according to Eq. (2). In some carbonylation processes (Cativa), methyl acetate is also used as a solvent.



Scheme 1. Catalytic cycle of the cobalt-catalyzed methanol carbonylation (BASF process).

2. Industrial methanol-to-acetic acid processes

2.1. The cobalt-based BASF process

The first methanol-to-acetic acid carbonylation process was commercialized in 1960 by BASF. It used an iodide-promoted cobalt catalyst and required very high pressures (600 atm) as well as high temperatures (230 °C), but gave acetic acid in ca. 90% selectivity [2]. By-products are methane, acetaldehyde, ethanol and ethers. $HCo(CO)_4$, formed according to Eqs. (3) and (4), is supposed to be the active species [2].

$$2CoI_2 + 2H_2O + 10CO \rightarrow Co_2(CO)_8 + 4HI + 2CO_2 \quad (3)$$

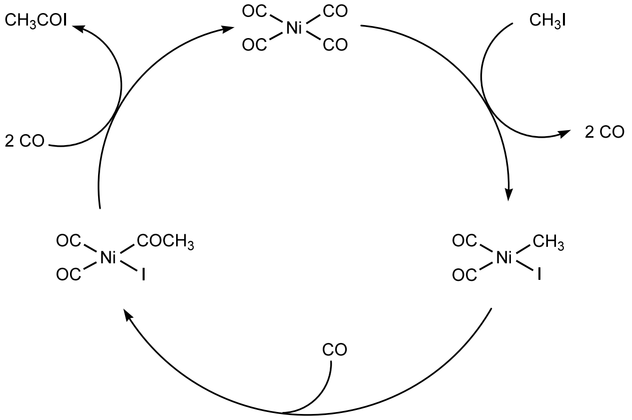
$$Co_2(CO)_8 + H_2O + CO \rightarrow 2HCo(CO)_4 + CO_2 \quad (4)$$

The assumption of hydrido cobalt carbonyl as the active species is in agreement with the observation that small amounts of H_2 enhance the catalytic activity. The mechanism of the catalytic reaction proposed is shown in Scheme 1, the intermediates postulated are, however, not well characterized [2].

Since methanol would insert CO into the O–H bond (to give methyl formate) and not into the C–O bond (to give acetic acid), the presence of iodide is necessary in order to convert methanol into methyl iodide prior to carbonylation. Thus, the actual substrate of carbonylation is methyl iodide [3]. Given that, in this process, the rate depends on the carbon monoxide pressure, high pressures of 600–700 bar are required for good conversion. Slightly lower pressures are possible in the presence of Ru, Ir, Pd, Pt, or Cu salts as activators [4,5]. Cobalt catalysts can also be used for the carbonylation of higher alcohols, such as benzyl alcohol [6].

2.2. Nickel catalysts

Nickel carbonyl, as well as a variety of nickel compounds, is also catalytically active for the carbonylation of methanol in the presence of iodine. $Ni(CO)_4$ is



Scheme 2. Catalytic cycle of the nickel-catalyzed methanol carbonylation.

formed from NiI_2 according to Eq. (5).

$$NiI_2 + H_2O + 5CO \rightarrow Ni(CO)_4 + 2HI + CO_2 \quad (5)$$

The hydrogen iodide formed in Eq. (5) is used to transform the alcohol into an alkyl halide, which adds oxidatively to nickel, as described in Scheme 2 [7]. The resulting acetyl iodide is hydrolyzed either by water or alcohols. Usually nickel catalysts require rather high pressure and temperature conditions [8]. However, with high methyl iodide concentrations, carbonylation occurs already under milder conditions [9]. If the molar ratio of CH_3I to CH_3OH is at least 1:10, pressures as low as 35 bar can be applied at 150 °C, using $Ni(OAc)_2 \cdot 4H_2O$ and Ph_4Sn as catalyst system [10]. Vapor phase carbonylation of methanol using supported nickel metal catalysts has also been reported [11].

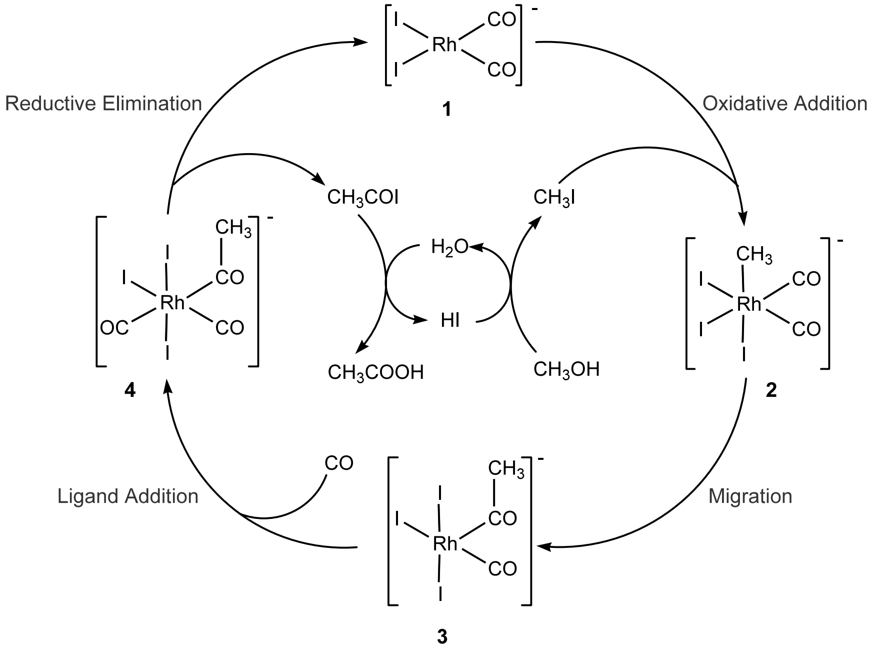
The activity of nickel catalyst systems can be increased, and the volatility of nickel carbonyl compounds can be lowered by the introduction of stabilizers such as phosphines, alkali metals, tin, and molybdenum [12–16]. The active catalysts are thought to be Ni(O) complexes. In the case of phosphine-containing nickel catalysts, 14-electron species such as $Ni(PR_3)_2$ are considered as catalysts, in addition to $Ni(CO)_4$ observed in all cases; the concentration of the latter species is reduced by strongly coordinating ligands or enhanced by weakly coordinating ligands [16].

Recent work on nickel catalyst systems shows that reaction rates and selectivities can approach those achieved in the rhodium catalyst system. Although nickel catalysts have the advantage of being much cheaper than rhodium and are easy to stabilize at low water concentrations, no commercialization has been achieved to date, since $Ni(CO)_4$ is a very toxic and volatile compound.

2.3. The rhodium-based Monsanto process

The production of acetic acid by the Monsanto process is based on a rhodium catalyst and operates at a pressure of 30–60 bar and at temperatures of 150–200 °C. The process gives selectivity of over 99% based on methanol. The catalytic cycle of this classic example of a homogeneous catalytic reaction consists of six steps (Scheme 3) [17]. The cycle includes several of the main reaction types known in organometallic chemistry [18] such as oxidative addition, ligand migration, CO insertion, and reductive elimination. These types of elementary steps have been examined separately in a number of experimental and theoretical studies. Systematic studies including a detailed inspection of full catalytic cycles are much rarer [19–24]. The catalytic cycle of methanol carbonylation was proposed [17] on the base of selected data on structures of reactants and intermediates which have been identified by X-ray crystallography [25], infrared and NMR spectroscopy (Scheme 3) [26].

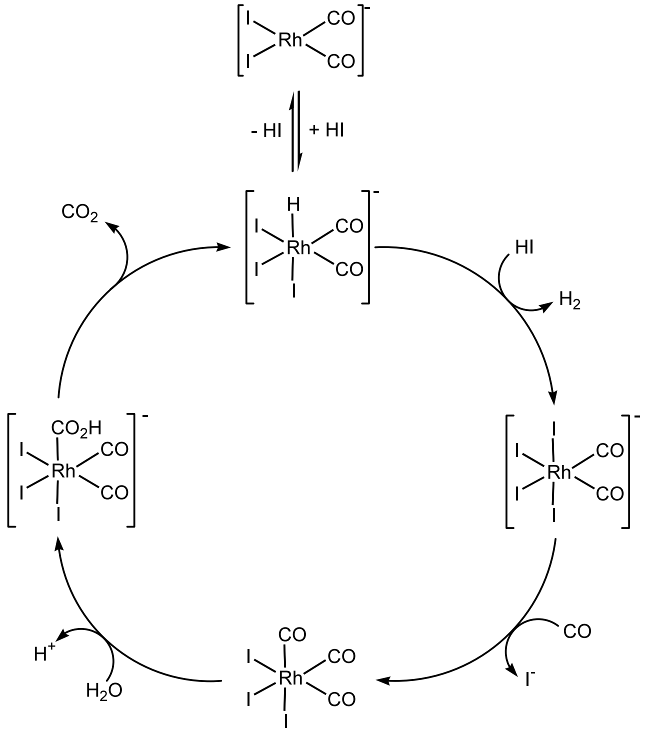
The anion *cis*-$[Rh(CO)_2I_2]^-$ (**1**) was found to be the initial catalytically active species [17]. Its interaction with the substrate CH_3I results in the formation of the hexacoordinated complex $[(CH_3)Rh(CO)_2I_3]^-$ (**2**) [26], which is kinetically unstable; it transforms into the isomeric pentacoordinated acetyl complex $[(CH_3CO)Rh(CO)I_3]^-$ (**3**) as a result of the migration of the methyl group to the CO ligand [27]. The rhodium acetyl complex **3** was isolated and characterized by X-ray crystallography [28,29]. The rhodium acetyl anion **3** was



Scheme 3. Catalytic cycle of the rhodium-catalyzed methanol carbonylation (Monsanto process).

found to form dimers through a very weak Rh–I–Rh bridge (with a rhodium–iodine distance of 3.0 Å, as compared to 2.7 Å commonly found for Rh–I bonds) [29]. Complex **3** reacts rapidly with CO to form the six-coordinated dicarbonyl complex **4** with terminal CO [29]. This species has been characterized by IR and NMR spectroscopy as a *mer* isomer [30]. An isomerization to a *fac* isomer was proposed to facilitate the subsequent elimination of CH_3COI [30]. The *fac* isomer decomposes at room temperature to yield acetyl iodide CH_3COI and $[Rh(CO)_2I_2]^-$; the latter species starts the next catalytic cycle. Finally, acetic acid is formed by acetyl iodide hydrolysis.

Kinetic investigations have confirmed the catalytic cycle depicted in Scheme 3. The rate of methanol carbonylation depends on the concentrations of both the rhodium complex and methyl iodide [31]. The reaction rate is independent of the methanol concentration and the carbon monoxide pressure. The rate-determining step is probably the oxidative addition of methyl iodide to the metal center of the rhodium complex **1**, because the reaction rate is essentially of first order in both catalyst and methyl iodide concentrations under normal reaction conditions. A substantial amount of water (14–15 wt.%) is required to achieve high catalyst activity and also to maintain good catalyst stability [26]. In fact, if the water content is less than 14–15 wt.%, the rate-determining step becomes the reductive elimination of the acetyl species, from catalyst species **4**. However, as rhodium also catalyzes the water–gas shift reaction (Scheme 4), the side reaction leading to CO_2 and H_2 is significantly affected by water and hydrogen iodide concentration in the reaction liquid [32,33].



Scheme 4. Catalytic cycle of the water–gas shift reaction as side-reaction in the rhodium-catalyzed methanol carbonylation.

Propionic acid is observed as the major liquid by-product in this process. This is produced by the carbonylation of ethanol which is often present as a minor impurity in the methanol feed. However, alternative routes to propionic acid must also be operating, since more propionic acid is observed than what can be accounted for by ethanol contamination of the feedstock. The rhodium catalyst can also generate acetaldehyde, which is supposed to undergo reduction by hydrogen to give ethanol, which subsequently yields propionic acid. One possible precursor for the generation of acetaldehyde is the rhodium–acetyl species, **4**, shown in Scheme 3 [33]. Reaction of **4** with hydrogen iodide would yield acetaldehyde and $[Rh(CO)I_4]^-$. The latter species is well known in this system and is postulated as the principal cause of catalyst loss by precipitation of inactive rhodium triiodide [33]. However, under the commercial operating conditions of the original Monsanto process, these trace compounds do not present a problem to either product yield or product purity.

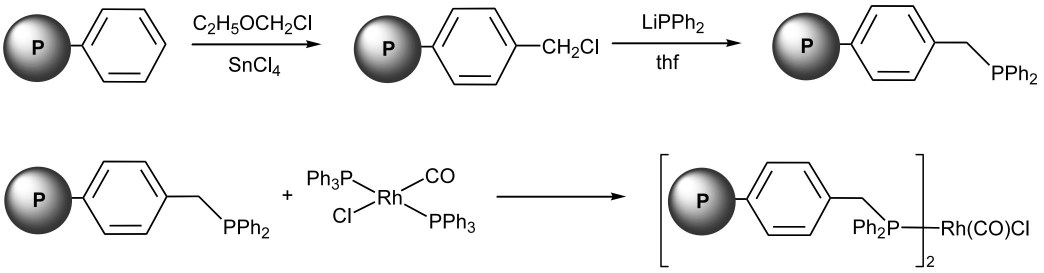
2.4. Heterogenized rhodium catalysts

An important additional requirement for all homogeneous processes is that the dissolved catalyst must be separated from the liquid product and recycled to the reactor without significant catalyst loss [34]. In order to overcome the need for a separation catalyst recycle step, the immobilization of the rhodium complex on a support has been the subject of considerable investigation. These works were reviewed by Howard et al. and include activated carbon, inorganic oxides, zeolites and a range of polymeric materials [1].

Active carbon was investigated as a possible support and proposed for vapor-phase operation. [1,35]. However, reaction rate and selectivity were poorer than with homogeneous catalysts. Inorganic oxides and zeolites were also studied as catalyst supports for use in vapor-phase operation [36,37].

For example, attaching the Rh–phosphine ligand complex to alumina by silylation was attempted [38,39]. The resultant reaction rates for these catalysts were also found to be lower than those observed for the homogeneous system. To increase catalyst activity for operation in the liquid phase, ion exchange resins based on cross-linked polystyrene and incorporating pendant phosphines, or vinyl pyridine co-polymers have been evaluated (Scheme 5) [40–42].

Although the activity of these catalysts in the liquid phase was comparable to Monsanto's homogeneous



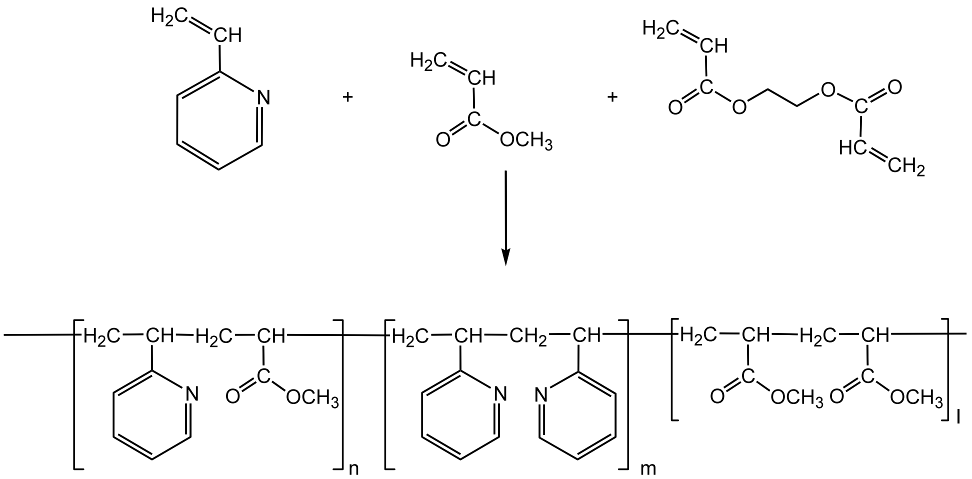
Scheme 5. Supporting the rhodium catalyst on a divinylbenzene-derived polymer.

catalyst, there were problems with rhodium metal leaching from the resins and the decomposition of the resins during operation at elevated temperature. Vinyl pyridine resin was known to be more robust and more thermostable than polystyrene resins (Schemes 6 and 7) [43].

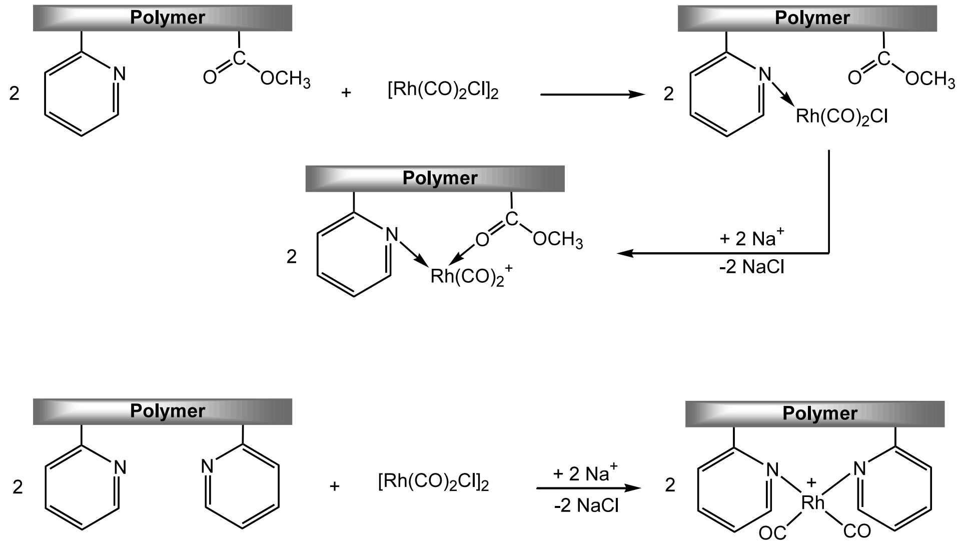
Furthermore, Chiyoda introduced novel pyridine resins and catalysts that exhibited high activity, long catalyst life, and no significant rhodium loss [44–46]. Based on this heterogeneous rhodium catalyst, Chiyoda and UOP (Universal Oil Products) have jointly developed an improved methanol carbonylation process, called 'Acetica process', for the production of acetic acid. Until the recent development of a commercial heterogeneous rhodium catalyst system by Chiyoda, no successful demonstration of such a catalyst had been known [1]. The heterogeneous catalyst commercialized for the Acetica process consists of rhodium complexed on a novel polyvinyl pyridine resin [47] which is tolerant of elevated temperatures and pressures. Under these reaction conditions, the rhodium system is converted to its catalytically active anion form $[Rh(CO)_2I_2]^-$. Furthermore, the nitrogen atoms of the resin pyridine groups become positively charged after quaternization with methyl iodide. Thus, after counterion exchange, the active anionic rhodium complex $[Rh(CO)_2I_2]^-$ is blocked in the positive polymeric matrix by strong electrostatic interactions, as shown in Scheme 8.

The concentration of rhodium on the solid phase is determined by the ion exchange equilibrium. Because equilibrium strongly favors the solid phase, virtually all the rhodium in the reaction mixture is immobilized. In the Acetica process, the methanol carbonylation reaction is conducted at moderate temperature (160–200 °C) and pressure (30–60 bar) and at low water concentration without any additives. The catalyst exhibited no deactivation after continuous operation for more than 7000 h [47].

With homogeneous methanol carbonylation routes, acetic acid productivity is directly proportional to the catalyst concentration in the reaction liquid, and as a consequence, the acetic acid production is restricted by the solubility of the active metal. Only limited success has been achieved in improving the catalyst solubility by increasing the water concentration or by adding iodide salt stabilizers [48], because both additives give rise to increased recycling costs, higher corrosion rates and separation problems. Immobilization of the catalyst significantly reduces the loss of expensive rhodium metal, because the catalyst is confined to the reactor rather than circulating downstream, where reduced pressures may cause losses of the catalyst by precipitation of rhodium or evaporation of volatile rhodium



Scheme 6. Synthesis of a copolymer derived from vinyl pyridine and vinyl acetate.



Scheme 7. Supporting the rhodium catalyst on copolymer derived from vinyl pyridine and vinyl acetate.

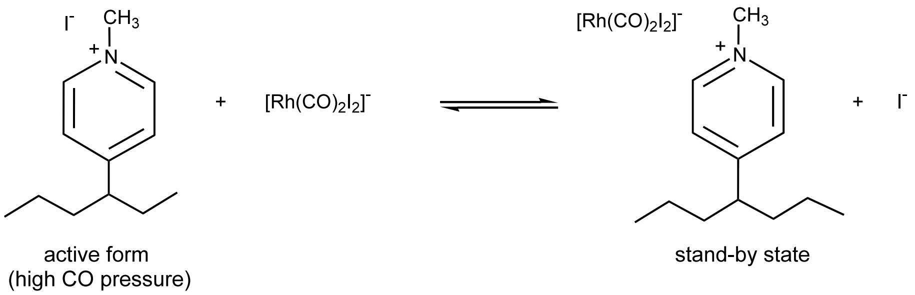
carbonyl compounds. The lower water content of 3–7 wt.%, typical of the Acetica process, results in reduced production of CO_2 and of hydrogenated by-products via the water–gas shift reaction. The lower water content also reduces the concentration of HI and thus the corrosion risk.

Very recently, Haynes et al. reported an alternative strategy for catalyst immobilisation, using ion-pair interactions between ionic catalyst complexes and polymeric ion exchange resins [34]. These results demonstrated that the same sequence of organometallic reactions occur for the polymer-supported rhodium catalyst as already established for the homogeneous system.

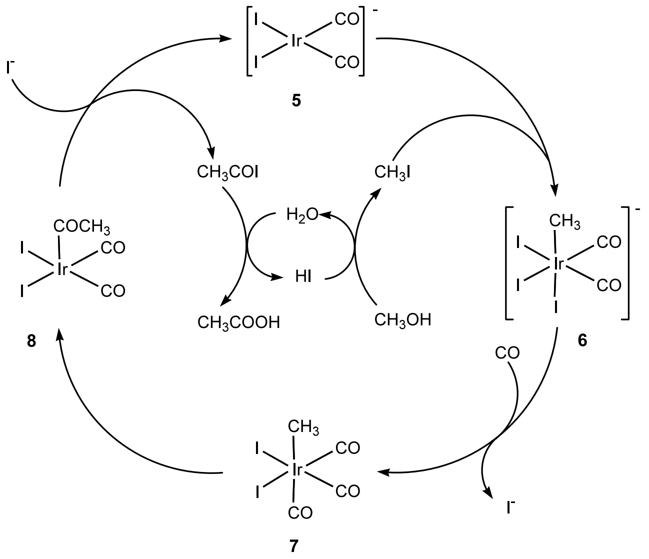
2.5. The iridium-based Cativa process

In their original work, the Monsanto group noted the effectiveness of iodide-promoted iridium catalysts [49], and this has been confirmed by other workers [25,50]. However, the reaction rate exhibited by the rhodium catalyst system was superior to that of iridium. Recently, it was disclosed that an improved iridium catalyst, in combination with a promoter metal such as ruthenium, has higher activity and selectivity than reported in previous iridium systems [51,52]. The production of acetic acid using the iridium catalyst system has been commercialized in 1996 by BP-Amoco as the 'Cativa™' process. Although much more iridium is required to achieve an activity comparable to the rhodium catalyst-based processes, the catalyst system is able to operate at reduced water levels (less than 8 wt.% for the Cativa process versus 14–15 wt.% for the conventional Monsanto process). Thus, lower by-product formation and improved carbon monoxide efficiency are achieved, and the steam consumption is decreased.

One of the major advantages of the iridium-based process was the high stability of the iridium catalyst species [52]. Its robustness at low water concentrations (0.5 wt.%) is particularly significant and ideal for optimisation of the methanol carbonylation process. The iridium catalyst was also found to remain stable under a wide range of conditions that would cause the rhodium analogues to decompose completely to inactive and largely unrecoverable rhodium salts. Besides this stability, iridium is also much more soluble than rhodium in the reaction medium, and thus higher



Scheme 8. Equilibrium between the active form and the stand-by state of the supported catalyst in the Acetica process.



Scheme 9. Catalytic cycle of the iridium-catalyzed methanol carbonylation (Cativa process).

catalyst concentrations can be obtained, making much higher reaction rates achievable.

Forster's mechanistic studies of iridium-catalyzed methanol carbonylation showed many similarities to the rhodium system but with a greater degree of complexity, due to the participation of both neutral and anionic species [53a]. The main difference between the rhodium- and iridium-based catalytic cycles has been determined by Maitlis et al. [53b]: whereas the rhodium-based cycle involves only anionic intermediates, the iridium-based cycle involves both anionic and neutral intermediates. The iridium-based cycle, shown in Scheme 9, is similar to the rhodium-based cycle, but operates with different kinetics, responsible for the advantages of the Cativa over the Monsanto process. Model studies have shown that the oxidative addition of methyl iodide to the iridium center is about 150 times faster than the analogous reaction with rhodium [53b]. This represents a dramatic improvement in the available reaction rates, as this step is now no longer rate-determining (as in the case of rhodium).

The slowest step in the iridium-based cycle is the substitution of an iodo ligand by carbon monoxide (reaction of **6** to **7**) [53b]. The inverse rate dependence upon the concentration of ionic iodide suggests that very high reaction rates should be achievable by operating at low iodide concentrations. It also suggests that the inclusion of species capable of assisting in removing iodide should promote the rate-limiting step. In fact promoters can be used to enhance the performance of the iridium catalyst. In particular, the promoters are effective at promoting the reaction at low CO partial pressures. The promoters for this system fall into two distinct groups: simple iodide complexes of zinc, cadmium, mercury, gallium and indium [54], and carbonyl–iodo complexes of tungsten, rhenium, ruthenium and osmium [55,56]. Combinations of promoters may also be used. None of these metals are effective as carbonylation catalysts in their own right, but all are effective when used in conjunction with an iridium complex.

$$[Ir(CO)_2I_2]^- + 2HI \rightarrow [Ir(CO)_2I_4]^- + H_2 \quad (6)$$

$$[Ir(CO)_2I_4]^- + CO \rightarrow [Ir(CO)_3I_3]^- + I^- \quad (7)$$

The presence of a promoter leads to a substantial increase in the proportion of 'active anionic' species $[(CH_3)Ir(CO)_2I_3]^-$ (**6**) and a substantial decrease in the loss of iridium, by the formation of inactive $[Ir(CO)_3I_3]$ and $[Ir(CO)_2I_4]^-$ species, which are intermediates in the water–gas shift reaction (Eqs. (6) and (7)).

3. Ligand design for rhodium-based catalysts

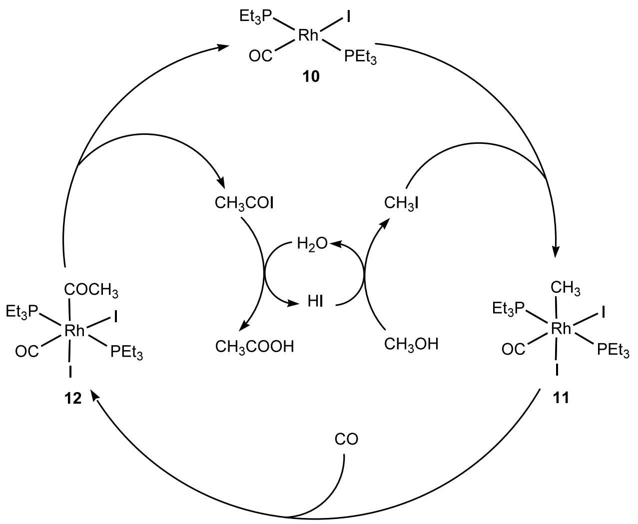
3.1. General considerations

The migratory insertion reaction of CO into metal–alkyl bonds is a fundamental step in the metal iodide-catalyzed carbonylation of methanol to acetic acid [57]. The conditions used industrially (30–60 bar pressure and 150–200 °C) [31] with the original $[Rh(CO)_2I_2]^-$ catalyst have spurred the search for new catalysts, which could work in milder conditions [58–65]. The rate-determining step of the rhodium-based catalytic cycle is the oxidative addition of CH_3I, so that catalyst design focused on the improvement of this reaction.

The basic idea was that ligands which increase the electron density at the metal should promote oxidative addition, and consequently increase the overall rate of the reaction. For this purpose, other rhodium complexes have been synthesized in the last years, and they have been shown to be active catalysts of comparable or better performance as compared to the Monsanto catalyst [60–64].

3.2. Phosphine ligands

The most important class of these rhodium complexes are those containing simple phosphine ligands such as PEt_3 [62,63]. Cole-Hamilton et al. have investigated the use of trialkylphosphines as promoters for rhodium-based carbonylation catalysts, because they are strongly electron-donating ligands. Complexes of the type $Rh(PEt_3)_2(CO)X$ (X = Cl, Br or I) have a $\nu(CO)$ absorption centered around 1960 cm^{-1}, as compared to 1988 and 2059 cm^{-1} for $[Rh(CO)_2I_2]^-$, suggesting that the rhodium center is more electron-rich in the triethylphosphine complexes. $Rh(PEt_3)_2(CO)Cl$ (**9**) turned out to be a very active catalyst precursor for acetic acid production. In the presence of 17.1 wt.% H_2O at 120–150 °C and 27 bar pressure, $Rh(PEt_3)_2(CO)I$ (**10**), formed under catalytic conditions from the pre-



Scheme 10. Catalytic cycle of the methanol carbonylation catalyzed by the neutral complex $Rh(PEt_3)_2(CO)I$.

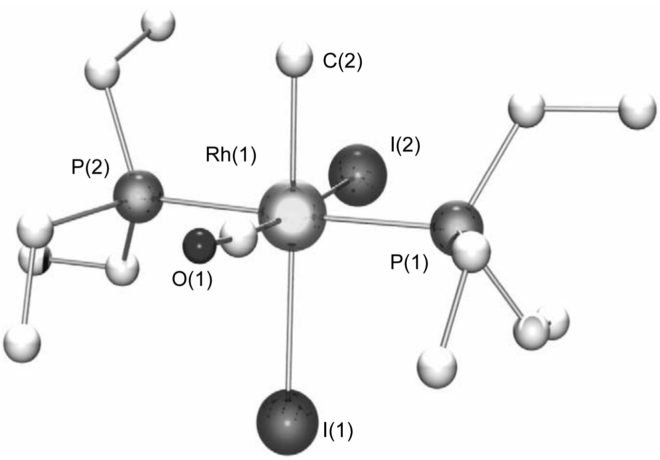
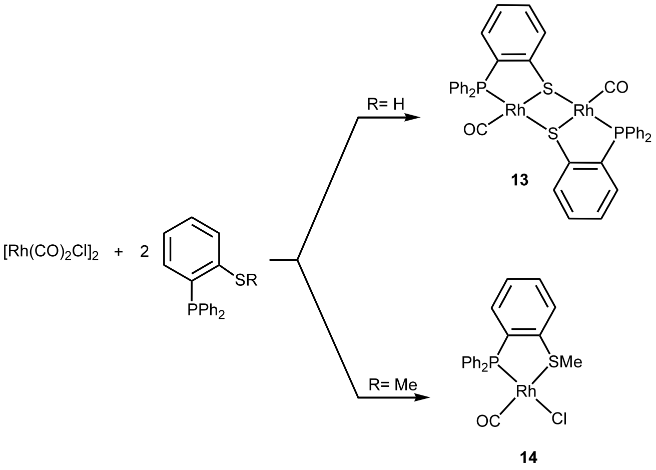


Fig. 1. Molecular structure of the complex **11**.



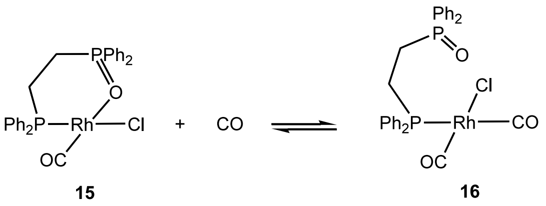
Scheme 11. Synthesis of rhodium phosphinothiolate and phosphinothioether complexes.

cursor **9**, catalyses the carbonylation of methanol at a rate nearly twice as high as that of $[Rh(CO)_2I_2]^-$. Water serves to maintain the catalyst in its active form [as rhodium(I) complex] and decreases the formation of inactive rhodium(III) complexes such as $[Rh(CO)_2I_4]^-$ or $Rh(PEt_3)_2(CO)I_3$. Thus, the rate of carbonylation is dramatically enhanced by a high water concentration. With low water concentrations, no appreciable benefit is obtained by using $Rh(PEt_3)_2(CO)Cl$ instead of $[Rh(CO)_2Cl]_2$ as catalyst precursor.

Addition of methyl iodide to $Rh(PEt_3)_2(CO)I$ in CH_2Cl_2 was shown to result in the formation of $(CH_3)Rh(PEt_3)_2(CO)I_2$ (**11**) (Scheme 10) [63]. The methyl group is *cis* with respect to the carbonyl ligand, as required for migratory insertion (Fig. 1). There is no other X-ray crystal structure analysis available for complexes of the type $(CH_3)Rh(PR_3)_2(CO)X_2$. However, there are other structurally characterized six-coordinate rhodium(III) complexes resulting from oxidative addition of CH_3I, most of them having iodide and methyl ligands in mutually *trans* positions [66–68].

The isolation of the methyl complex from a catalytically active system is rather unlikely, since the insertion of carbon monoxide into the Rh–C bond is extremely rapid. For $[Rh(CO)_2I_2]^-$, the methyl complex has a very short lifetime and was only detected as a transient species by IR spectroscopy in neat methyl iodide [26], while for the related $Rh(PPh_3)_2(CO)Cl$ the oxidative addition of methyl iodide gives the six-coordinate complex $(CH_3)Rh(PPh_3)_2(CO)(Cl)I$ in equilibrium with the five-coordinate insertion product, (CH_3CO)-$Rh(PPh_3)_2(Cl)I$ [69]. In the case of the triethylphosphine analogue, the higher electron density on the metal is responsible for the less facile methyl migration in $(CH_3)Rh(PEt_3)_2(CO)I_2$. Despite the stability of the methylrhodium(III) complex, preliminary kinetic studies suggest that the oxidative addition of CH_3I is still rate-determining.

Dilworth et al. described other methanol carbonylation catalysts which show significant improvements in absolute rates over those obtained with $[Rh(CO)_2I_2]^-$ [58]. Both, the dinuclear phosphinothiolate complex **13** and the mononuclear phosphinothioether complex **14** synthesized according to Scheme 11 efficiently catalyze the carbonylation of methanol with comparable rate.



Scheme 12. Equilibrium between $Rh[\eta^2\text{-}Ph_2P(CH_2)_2P(O)Ph_2](CO)Cl$ and $Rh[\eta^1\text{-}Ph_2P(CH_2)_2P(O)Ph_2](CO)_2Cl$.

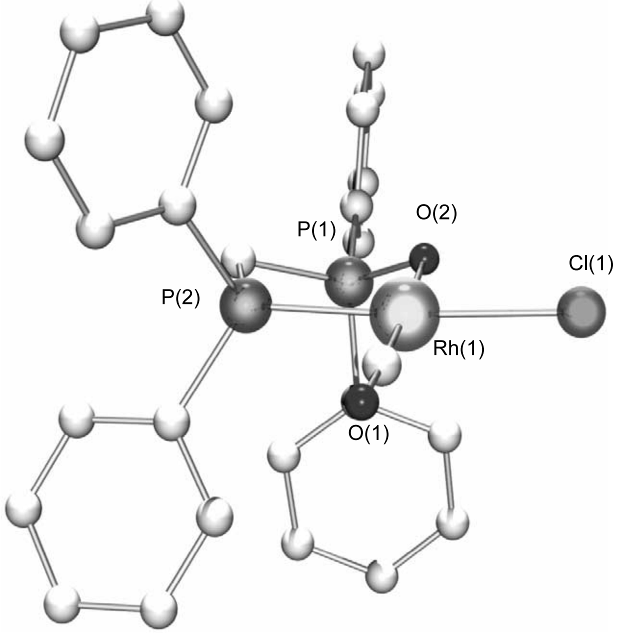


Fig. 2. Molecular structure of the complex **15**.

3.3. Hemilabile chelating ligands

Mixed bidentate ligands such as $PPh_2–CH_2–P(NPh)Ph_2$ [59], $PPh_2–CH_2–P(O)Ph_2$ [60] and $PPh_2–CH_2–P(S)Ph_2$ [64] have been also shown to be effective in rhodium-catalyzed carbonylation of methanol. Wegman et al. have found that *cis*-Rh[$Ph_2P(CH_2)_2P(O)Ph_2$](CO)Cl is a precursor to a very active catalyst for the carbonylation of methanol under mild reaction conditions [60]. Reaction of *cis*-Rh[$Ph_2P(CH_2)_2P(O)Ph_2$](CO)Cl (**15**) with CO results in the displacement of the rhodium-oxygen bond and the formation of the complex **16** (ν(CO) 2096 and 2012 cm^{-1}) according to the equilibrium shown in Scheme 12.

The ratio of the η^2- and the η^1-complexes was determined to be ca. 1:1 (at 22 °C and 1 bar CO) by infrared spectroscopy. Infrared spectroscopic studies carried out under catalytic conditions at 80 °C and 3.5 bar CO (turnover frequency 400 h^{-1}) reveal only the η^1-coordinated phosphine oxide species. Furthermore there is no indication of $[Rh(CO)_2I_2]^-$ which is the principal rhodium species present during catalysis in the classical Monsanto process [17]. In addition there is no induction period as might be expected if dissociation of $Ph_2P(CH_2)_2P(O)Ph_2$ and subsequent formation of $[Rh(CO)_2I_2]^-$ is important [25]. Hence, it can be concluded that **16** or its iodo analogue formed under catalytic conditions from **16**, act as catalytic species (Fig. 2).

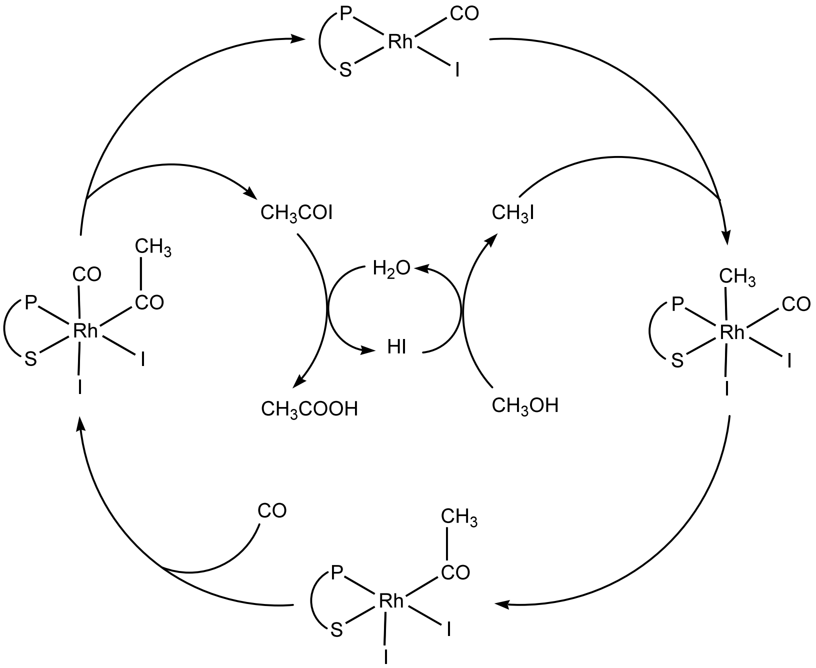
Baker et al. have found that the use of the diphosphinesulfide $Ph_2PCH_2P(S)Ph_2$ as a promoter for rhodium catalyzed carbonylation of methanol allows a substantial rate increase under industrially feasible conditions (180 °C, 70 bar CO) [64]. The initial experiments were carried out using a ligand/rhodium ratio of 4: 1, but the optimum rate enhancement was observed when the discrete complex *cis*-Rh[η^2-$Ph_2PCH_2P(S)Ph_2$](CO)Cl (**17**) was used as pre-catalyst. These authors showed that any additional phosphine quaternizes with CH_3I, and the addition of iodide inhibits the catalytic reaction (Scheme 13). Addition of three equivalents of $[(CH_3)PPh_3]I$ causes a similar retardation in rate. Rh[$Ph_2PCH_2P(S)Ph_2$](CO)Cl (**17**) is readily formed upon mixing $[Rh(CO)_2Cl]_2$ with two equivalents of $Ph_2PCH_2P(S)Ph_2$ in CH_3OH, and there is no evidence for the formation of dinuclear complexes in this reaction [70].

The X-ray crystal structure analysis of Rh[$Ph_2PCH_2P(S)Ph_2$](CO)Cl (**17**) confirms the stereochemistry at rhodium in which the phosphorus atom is *trans* with respect to the chloro ligand, while the sulfur atom is *trans* with respect to the carbonyl ligand; but the structure shows no unusual features to explain the unexpected stability of the catalyst at high temperatures. Unlike in the case of the oxygen analogue, in the case of Rh[$Ph_2PCH_2P(S)Ph_2$](CO)Cl, there is no evidence for a hemilabile behavior of the *P–S* ligand, while it has been assumed to be important for catalysis employing mixed-donor ligands [71]. These results showed for the first time that a discrete rhodium–phosphine complex can give a significant improvement in carbonylation activity over $[Rh(CO)_2I_2]^-$ under industrial conditions.

3.4. Diphosphine ligands

Recently, Pringle et al. reported that rhodium complexes of unsymmetrical ethylene diphosphine ligands are more efficient catalysts than the symmetrical dppe analogues for methanol carbonylation and longer-lived than any other reported ligand-modified catalysts under industrial conditions [65]. The catalysts were prepared by addition of diphosphines to $[Rh(CO)_2Cl]_2$ in methanol (Scheme 14).

In each case the conversion of methanol was greater than 98%, and the selectivity for acetic acid was greater than 99%; however, the carbonylation rates are lower for these diphosphine complexes than for the $[Rh(CO)_2I_2]^-$ catalyst. The following observations suggest that the catalyst is indeed a diphosphine–rhodium complex throughout the catalytic reaction and not $[Rh(CO)_2I_2]^-$. Infrared spectra obtained in situ during catalysis with $Ph_2PCH_2CH_2P(3,4,5\text{-}C_6H_2F_3)_2$ showed the absence of the intense ν(CO) bands of $[Rh(CO)_2I_2]^-$ at 2059 and 1988 cm^{-1}. At the end of the catalytic reaction, ^{31}P-NMR and IR spectra showed the presence of a mixture of diphosphine rhodium(III) carbonyl complexes. Furthermore the product *fac*-Rh[$Ph_2PCH_2CH_2P(3,4,5\text{-}C_6H_2F_3)_2$](CO)$I_3$ (**18**) was isolated from the



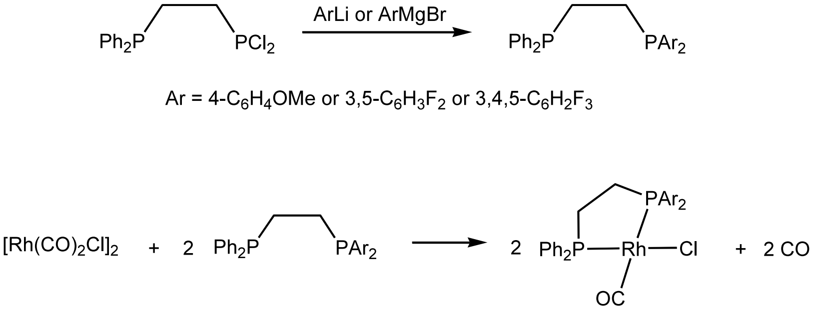
Scheme 13. Catalytic cycle of the methanol carbonylation catalyzed by the neutral complex $Rh[Ph_2PCH_2P(S)Ph_2](CO)I$.

reaction mixture, using the catalyst $Rh[Ph_2PCH_2CH_2P(3,4,5\text{-}C_6H_2F_3)_2](CO)Cl$ [65] (Fig. 3).

The rate of catalysis is constant throughout a catalytic run and, after consumption of the entire methanol, a second aliquot of methanol was injected, the rate observed was the same as in the first run. This final observation not only confirms the integrity of the catalyst, but also shows its longevity to be greater than any previous rhodium–phosphine catalyst under these conditions, since every diphosphine complex executes over 500 turnovers without noticeable diminution of activity. The rhodium–diphosphine catalysts also resemble the iridium Cativa catalyst. The amount of propionic acid reported (formed during the water–gas shift reaction) for these diphosphine catalysts is significantly less than that with $[Rh(CO)_2I_2]^-$ as catalyst under the same conditions.

The greater nucleophilicity of Rh(diphosphine)(CO)I complexes [72], as compared to $[Rh(CO)_2I_2]^-$, may partly explain the similarities between the rhodium–diphosphine and the iridium catalysts. Since the iridium catalysts are promoted by iodide-abstracting ruthenium complexes [55,56,73], Pringle et al. checked whether or not $Ru(CO)_4I_2$ also promotes the rhodium catalyst containing the $Ph_2PCH_2CH_2P(3,4,5\text{-}C_6H_2F_3)_2$ ligand. Indeed, addition of $Ru(CO)_4I_2$ more than doubles the carbonylation rate [65]. The *asymmetry* of the diphosphine is also crucial. Recent studies showed that unsymmetrical diphosphines are superior to the symmetrical analogues for hydroformylation catalysis and associated with this a preference of the better s-donor for the axial site in the trigonal bipyramidal intermediates [74]. It is noteworthy that *P*,*N*- [59], *P*,*O*- [60], and *P*,*S*-donor [64] ligands used for methanol carbonylation are all unsymmetrical with one strong and one medium or weak donor atom.

Indeed, all these new ligands enhance the oxidative addition step, but as a consequence they usually retard the subsequent CO insertion step, because the increased electron density at the metal also leads to stronger Rh–



Scheme 14. Synthesis of rhodium complexes with unsymmetrical diphosphine ligands.

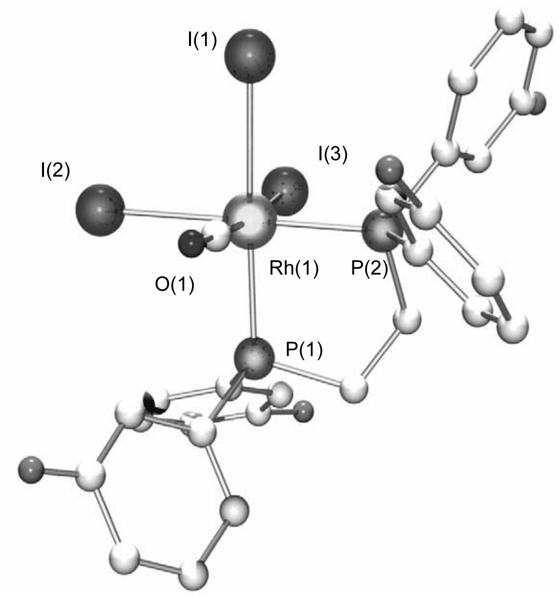


Fig. 3. Molecular structure of the complex **18**.

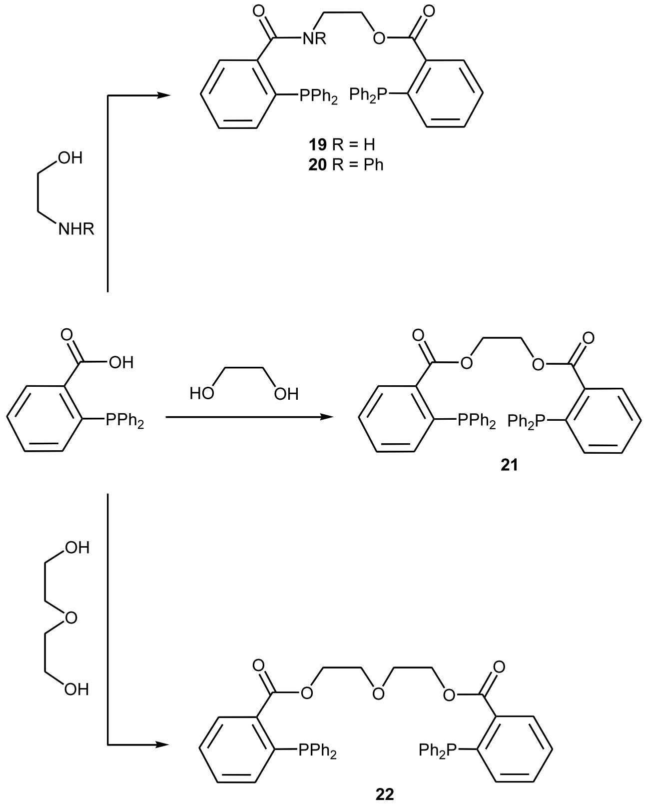
CO bonding. Optimal parameters are required to achieve the delicate balance between these two factors which will afford highly efficient catalysts. In fact, while the octahedral intermediate obtained from the square-planar precursor complex by CH_3I addition undergoes migratory insertion only under CO pressure with PEt_3 as ligands, it is relatively long-lived with the $PPh_2–CH_2–CH_2–PPh_2$ ligand. However, it is so reactive with the $PPh_2–CH_2–P(S)Ph_2$ ligand that its detection was rather difficult [72]. The fact that both, oxidative addition and CO insertion steps are accelerated with the latter ligand was quite unexpected. Therefore, it was assumed that the steric requirements of the $PPh_2–CH_2–P(S)Ph_2$ ligand destabilize the octahedral intermediate which would undergo migratory insertion to release such steric pressure [72].

Several research groups took advantage of phosphine ligand additives in the carbonylation of methanol. To summarize, square-planar rhodium complexes containing two monophosphine ligands in *trans* positions such as *trans*-$Rh(PEt_3)_2(CO)Cl$ are highly active for methanol carbonylation, but less stable than unsymmetrical diphosphine complexes such as *cis*-$Rh(Ph_2PCH_2CH_2PAr_2)(CO)Cl$ which are, however, less active catalysts.

It was anticipated that the synthesis of diphosphine ligands containing suitable spacer groups between the two phosphorus atoms, should allow *trans*-coordination in square-planar rhodium complexes which can be expected to combine high catalytic activity with thermal stability under the harsh conditions of methanol carbonylation [75].

This has led to the development of the new diphosphine ligands **19**–**22** which have been synthesized by condensation from 2-diphenyl-phosphinobenzoic acid with the corresponding aminoalcohols or diols (Scheme 15). The diphosphine ligands **19**–**22** (two equivalents) react with $[Rh(CO)_2Cl]_2$ to give the diphosphine complexes Rh(P–P)(CO)Cl (**23**: P–P = **19**; **24**: P–P = **20**; **25**: P–P = **21**) in high yields (Scheme 16).

The single-crystal X-ray structure analysis of **26** shows that the metal atoms are coordinated by the two P atoms of the two P,P-bidentate ligands. The two metal atoms are in a square-planar environment, the angles P(2)–Rh(1)–P(1), C(21)–Rh(1)–Cl(1), P(2)–Rh(1)–C(21), C(21)–Rh(1)–P(1), P(1)–Rh(1)–Cl(1), Cl(1)–Rh(1)–P(2) being 175.24(5), 174.74(10), 90.33(9), 90.78(10), 91.74(9), 86.78(12)°, respectively. The two rhodium atoms are bridged by two diphosphine ligands, maintaining the *trans*-P,P-coordination geometry of each rhodium atom (Fig. 4).

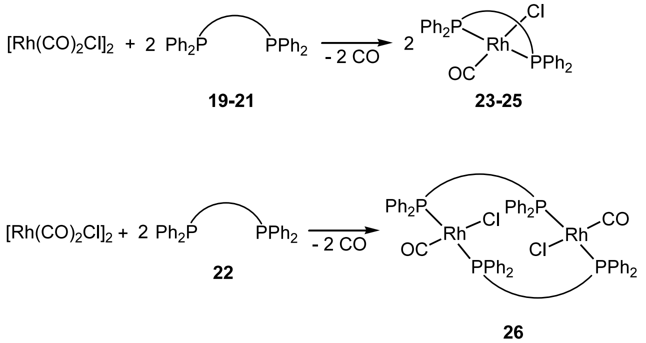


19 R = H
20 R = Ph

21

22

Scheme 15. Synthesis of ligands **19**–**22**.



19-21

23-25

22

26

Scheme 16. Synthesis of the neutral rhodium complexes **23**–**26**.

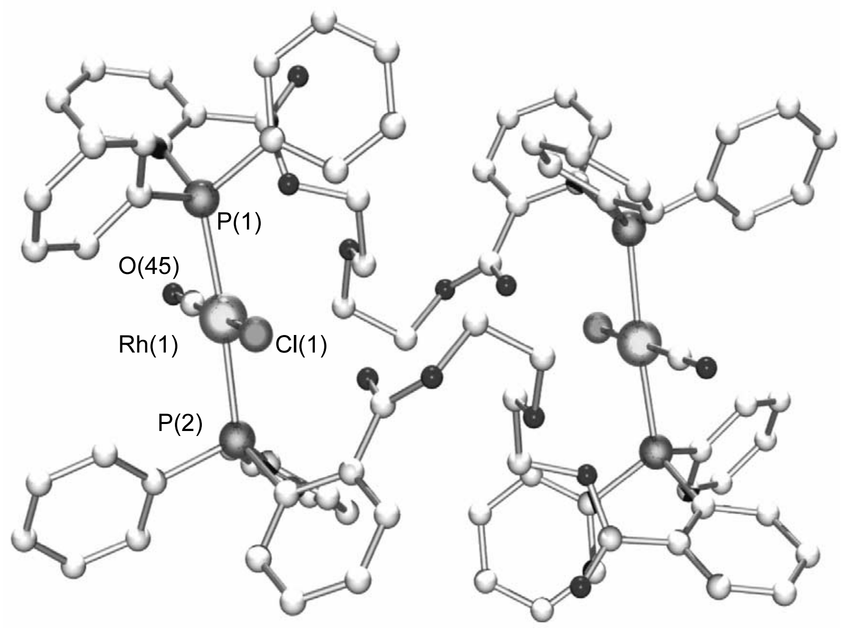
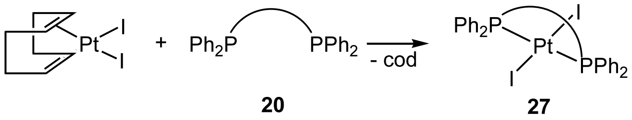


Fig. 4. Molecular structure of the dinuclear complex **26**.



Scheme 17. Synthesis of the neutral platinum complex **27**.

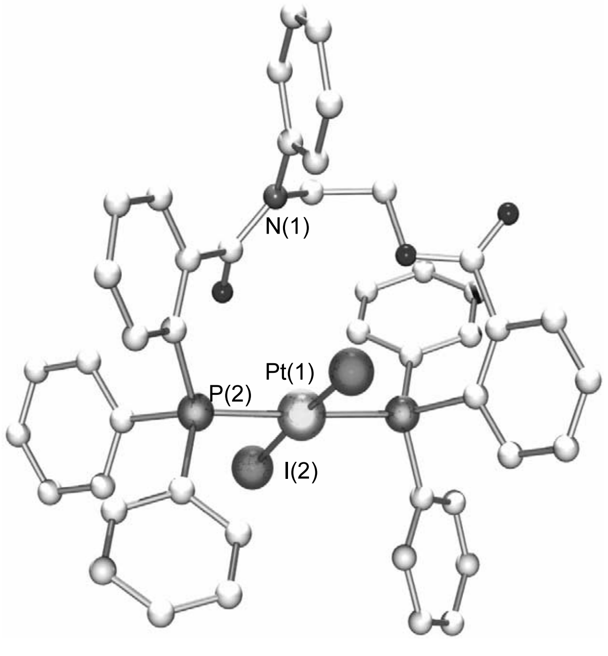


Fig. 5. Molecular structure of the mononuclear complex **27**.

The *trans* coordination of the diphosphine ligands in the mononuclear complexes, assumed for **23**–**25** on the basis of their spectroscopic data, was finally confirmed by a single-crystal X-ray structure analysis of the platinum complex Pt(**20**)I_2 (**27**). Complex **27** is obtained almost quantitatively from the reaction of Pt(cod)I_2 with the diphosphine ligand (**20**) in dichloromethane (Scheme 17).

The single-crystal X-ray structure analysis of **27** shows a square-planar coordination geometry around the platinum metal center. The Pt atom is coordinated to two I atoms and to the two P atoms of the diphosphine ligand. The molecular structure of **27** is depicted in Fig. 5. These bond distances are similar to those reported by Feringa et al. for *trans*-dichloro{bis[*N*-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}-platinum [76].

The diphosphine ligands **19**, **20**, **21** and **22** have been tested in combination with $[Rh(CO)_2Cl]_2$ for the catalytic carbonylation of methanol to give acetic acid and methylacetate in the presence of iodomethane and water. The reaction was carried out at 170 °C under a CO pressure of 22 bar, the catalyst/substrate ratio being 1:2000.

$$CH_3OH + CO \rightarrow CH_3COOH$$

$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$$

In each case the conversion of methanol was greater than 98% and the selectivity for acetic acid was greater than 99%. The complexes **23**–**26** are formed in situ on mixing $[Rh(CO)_2Cl]_2$ with two equivalents of **19**–**22** in methanol. As a control experiment, the catalytic reaction was carried out with the Monsanto catalyst $[Rh(CO)_2I_2]^-$, which was also formed in situ from $[Rh(CO)_2Cl]_2$ under the reaction conditions [64]. The catalytic activity increases considerably in the presence

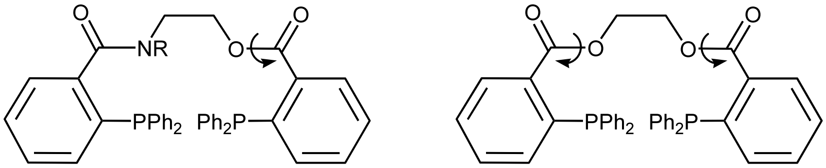


Fig. 6. Restricted rotation of amides with respect to esters.

of a rhodium precursor with the diphosphine ligands **19**, **20**, **21** and **22**, ligand **20** being the most active one. The combination $[Rh(CO)_2Cl]_2$/**20** catalyzes the carbonylation of methanol at a rate nearly double that of $[Rh(CO)_2I_2]^-$. By comparison of the system $[Rh(CO)_2Cl]_2$/**21** with the system $[Rh(CO)_2Cl]_2$/**22**, we can note that changing the distance between the two esters by modifying the length of the tether showed little variation in catalytic activity. Moreover, rhodium complexes of unsymmetrical diphosphine ligands are more efficient catalysts than their symmetrical analogues for methanol carbonylation. In the ester ligands, a source of rotational freedom may result from rotation about the acyl-oxygen bond. We rigidified this linkage by going to the analogous amide linkage as in ligands **19** and **20** (Fig. 6).

In the case of the most active combination, $[Rh(CO)_2Cl]_2$/ligand **20**, the catalyst stays active throughout several catalytic runs: an homogeneous orange–red solution is obtained after the catalytic reaction, containing two rhodium diphosphine complexes. By IR and ^{31}P-NMR analysis, one of them is identified to be the iodo analogue of the rhodium(I) complex **24**, the other one is the rhodium(III) complex **28**. This mixture is still active for further catalytic runs, showing almost the same catalytic activity.

The red complex **20** can be isolated from the organometallic residue of the catalytic reaction by crystallisation from acetone; it is also directly accessible from the reaction of **24** with methyliodide in acetone solution (Scheme 18). **28** is a dinuclear Rh(III) complex in which the rhodium atoms are bridged by one diphosphine and two iodo ligands, both rhodium atoms carrying an acetyl ligand and a terminal iodo ligand. Complex **28** exists in two isomers **28a** and **28b**, depending on the *cis* or *trans* arrangement of the two terminal iodo ligands at the two rhodium atoms. The two isomers present in solution are separated by fractional crystallization from acetone: **28a** crystallizes rapidly, while **28b** takes several hours to crystallize after elimination of **28a**. It is noteworthy that in both isomers **28a** and **28b**, the rhodium atoms do not have a square pyramidal but an octahedral coordination geometry (Figs. 7 and 8), thanks to the carbonyl oxygen atoms of the ligand chain (Rh–O 2.33 and 2.29 Å in **28a**, 2.33 and 2.38 Å in **28b**).

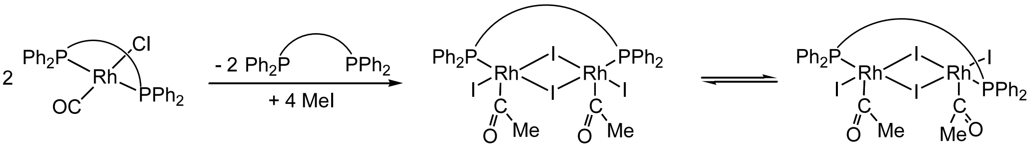
It is dangerous to assume that the species isolated from a solution is identical to the species present in the solution. It has been shown that iodo-bridged dinuclear complexes isolated in the solid state, evolved to mononuclear species such as $[Rh(CO)_2I_3]^{2-}$ or $[(COCH_3)Rh(CO)I_3]^-$ under catalytic conditions [29]. It is also known that this type of rhodium acetyl dimers is very easily cleaved with a phosphine [29]. Hence the bridge opening reaction of **28** should be facile. Thus, the highest mass ion observed in the ESI mass spectrum after a catalytic run with **24** corresponds to the mononuclear fragment $(COCH_3)Rh($**20**$)I_2$. This complex is certainly one of the species involved in the catalytic process but could not be isolated from the reaction mixture (Scheme 19).

3.5. Other ligands

Dutta et al. synthesized new $[Rh(CO)_2(Cl)L]$ complexes (where L = Ph_3PO, Ph_3PS, Ph_3PSe), which show higher activity in the carbonylation of methanol than the Monsanto catalyst [77]. Thus, interactions between the metal and the chalcogen donors were found to be operative. Furthermore these complexes undergo oxidative addition reactions with many different types of electrophiles [77].

Recently, Dutta et al. reported the synthesis of rhodium(I) complexes containing different types of nitrones (Scheme 20) and their application as catalyst precursors for the carbonylation of methanol [78].

The complex $[Rh(CO)_2Cl]_2$ undergoes bridge splitting reaction with two equivalents of nitrone ligands to



24 **28a** **28b**

Scheme 18. Formation of the neutral rhodium complexes **20a** and **20b**.

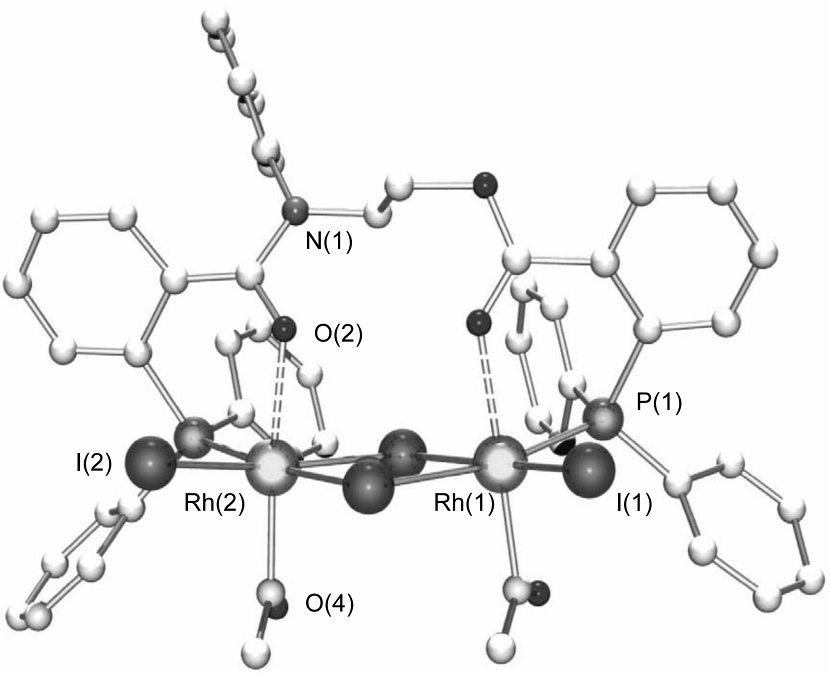


Fig. 7. Molecular structure of complex **28a**.

produce complexes of the type $[Rh(CO)_2(Cl)L]$ (**33**: L = **29**; **34**: L = **30**; **35**: L = **31**; **36**: L = **32**) (Scheme 21).

After a reaction time of 90 min, the complexes **33**–**36** show a maximum methanol conversion of 83, 91, 96 and 87% respectively, corresponding to TON of 1195, 1310, 1382 and 1252. After completion of the carbonylation reaction, the catalyst can be recovered. On recycling the catalyst for a second time, almost the same amount of conversion has been found indicating longer stability of the catalysts. It has been observed that the complexes **33**–**36** show higher TON over the species $[Rh(CO)_2I_2]^-$. The higher conversion shown by the complexes **34**–**36** over **33** may be attributed to the possible chelate formation in the complexes leading to higher stability of the intermediate complex formed during the catalytic process.

Süss-Fink et al. reported the synthesis of the multifunctional ligand thiophene-2,5-di(carboxylatomethylenebenzotriazole) (**37**) which was found to coordinate easily to rhodium through the 3-N atom of the triazole unit [79]. Thus, the reaction of **37** with $[Rh(CO)_2Cl]_2$ in toluene at room temperature gives quantitatively the

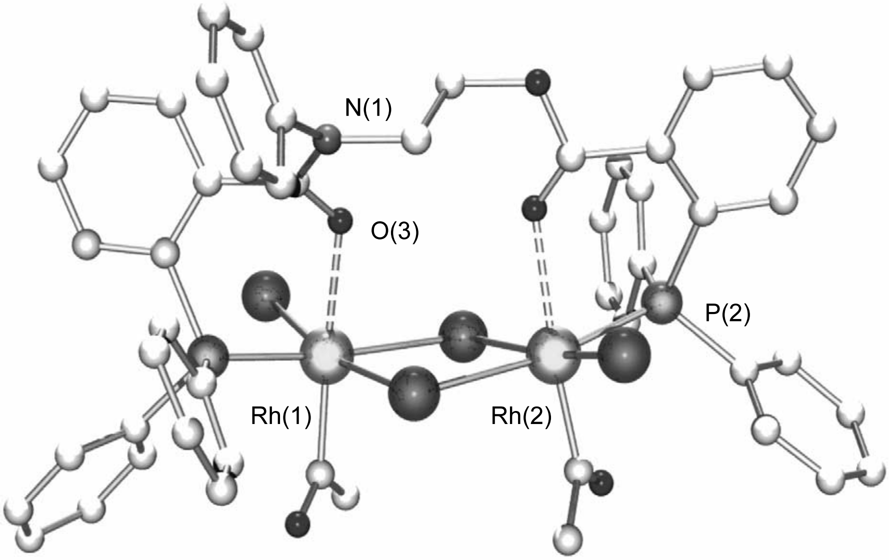
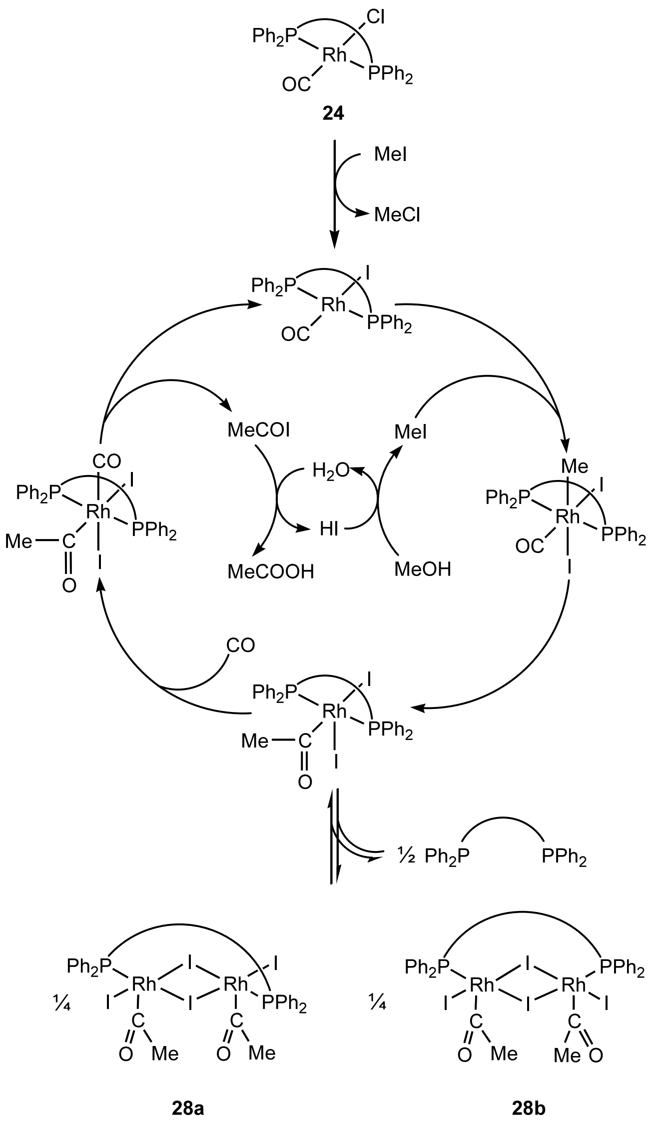
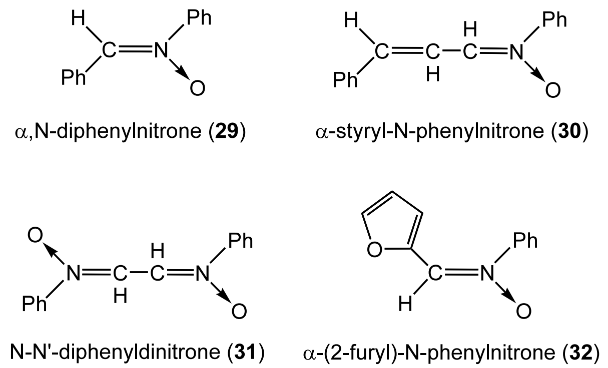


Fig. 8. Molecular structure of complex **28b**.

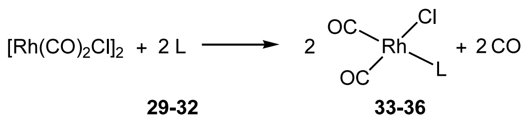


Scheme 19. Proposed mechanism for the catalytic cycle of the methanol carbonylation catalyzed by the neutral Rh(**20**)(CO)Cl (**24**).

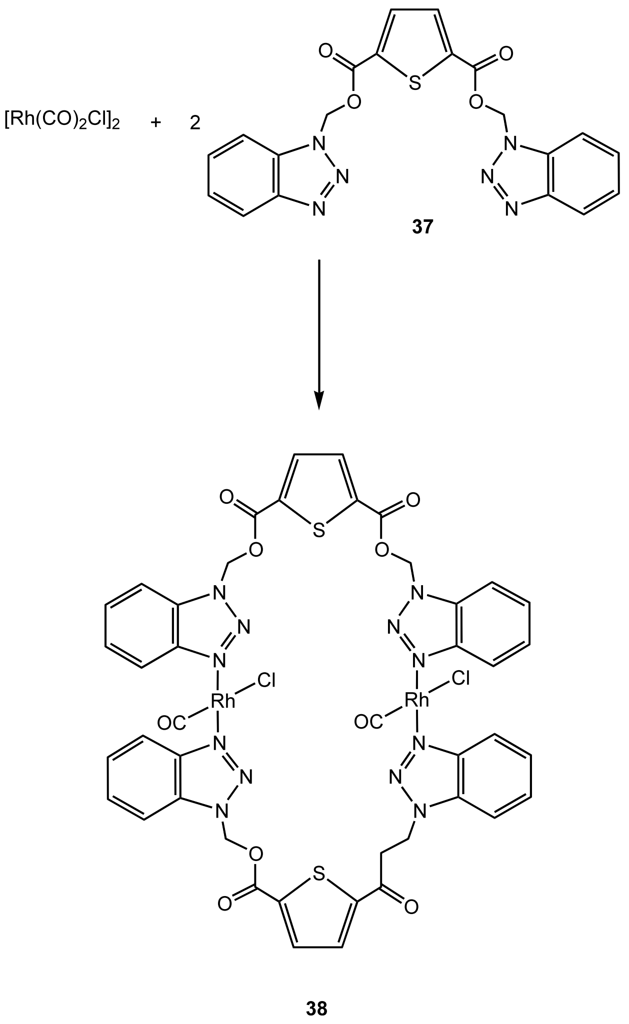


Scheme 20. Schematic representation of different nitrones used as ligands in the rhodium-catalyzed methanol carbonylation.

rhodium(I) complex [Rh(CO)Cl(**37**)]$_2$ (**38**) as an air-stable yellow solid (Scheme 22).



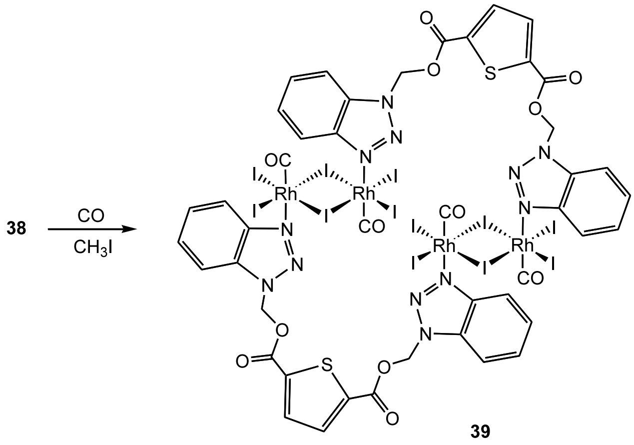
Scheme 21. Synthesis of rhodium complexes with nitrone ligands.



Scheme 22. Synthesis of the rhodium complex **38**.

Complex **38** catalyses the iodide-promoted carbonylation of methanol to give acetic acid and methyl acetate with much higher catalytic activities than that of the classical [Rh(CO)$_2$Cl]$_2$ catalyst. The catalytic reaction is performed with a methanol/methyliodide/water (58%, 26%, 16%) mixture at 170 °C under a CO pressure of 25 bar, the catalyst/substrate ratio being 1:2000. After 20 min, the catalytic turnover number (mol CH_3COOH plus mol CH_3COOCH_3 per mol **38**) is found to be 700 (catalytic turnover frequency 35 min^{-1}). [Rh(CO)$_2$Cl]$_2$ gives under the same conditions a catalytic turnover number of 400 (catalytic turnover frequency 20 min^{-1}).

From the reaction mixture the red–brown complex **39** can be isolated by crystallisation of the organometallic residue from acetone. **39** is directly accessible in high



Scheme 23. Synthesis of the rhodium complex **39**.

yield from the reaction of **38** with methyliodide and carbon monoxide (1 bar) in acetone solution (Scheme 23). **39** contains iodo ligands and a *transoid* dicarbonyl arrangement, giving rise to single ν(CO) absorption in the infrared spectrum. It was suggested for complexes containing phosphine ligands that the dissociation of the phosphine may occurred during the catalytic process. In this case there is clearly a Rh–N bond cleavage. The facile conversion of **38** into **39** under ambient conditions demonstrates that fragmentation, ligand dissociation and rearrangement are easily occurring.

In the single-crystal X-ray structure analysis, **39** turns out to be a macrocycle containing two dinuclear iodo-bridged Rh(III) units (Scheme 23). In **39**, the four rhodium atoms have a distorted octahedral coordination geometry, they are coordinated by the 3-N atoms of the benzotriazole units of **37** (Fig. 9). The four rhodium–nitrogen bonds are almost equal in length. The two planar Rh$_2$(μ_2-I)$_2$ rings are arranged perpendicular with respect to the cycle formed by the four rhodium atoms and the two ligands, Rh(1)–**37**–Rh(2)–Rh(3)–**29**–Rh(4). The bond distances and angles for each Rh$_2$I$_6$ unit are similar to those reported by Forster [28] for [Rh$_2$(MeCO)$_2$I$_6$(CO)$_2$]$^{2-}$ and by Dilworth [80] for [Rh$_2$I$_6$(Ph$_2$PC$_6$H$_4$SMe)$_2$].

In contrast to the rhodium(I) macrocycle **38**, the rhodium(III) macrocycle **39** does not catalyse itself the carbonylation of methanol: the low catalytic activity observed (TON 100 after 20 min, TOF 5 min^{-1}) when **39** is used as the catalyst precursor is due to a partial decomposition of **39** to give [Rh(CO)$_2$I$_2$]$^-$. This is in line with what has been observed for other iodo-bridged dirhodium(III) complexes [29].

To the best of our knowledge, **38** is the first macrocyclic dirhodium complex involved in the carbonylation of methanol. It is possible that the better catalytic performance of **30** with respect to that of the classical species [Rh(CO)$_2$I$_2$]$^-$ is due to its macrocyclic nature.

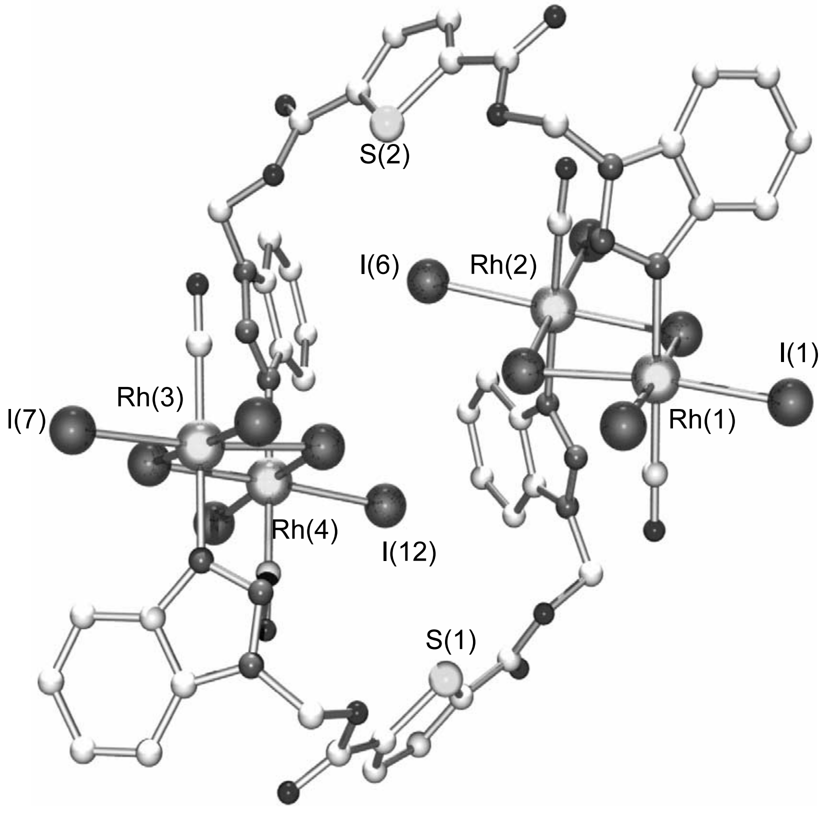


Fig. 9. Molecular structure of complex **39**.

4. Conclusions

The $[Rh(CO)_2I_2]^-$-catalyzed carbonylation of methanol is presently the most widely used commercial route to acetic acid. There have been many attempts to modify $[Rh(CO)_2I_2]^-$ by using different electron donating ligands. From the results published it appears that phosphine ligands have the most interesting perspectives for this reaction; by virtue of their good s-donor properties and their π-capability, these ligands form Rh(I) complexes, which are highly active carbonylation catalysts. It can be anticipated that this class of ligands will continue to provide new and interesting results.

Acknowledgements

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References

[1] M.J. Howard, M.D. Jones, M.S. Roberts, S.A. Taylor, Catal. Today 18 (1993) 325.
[2] (a) R.T. Eby, T.C. Singleton, in: B.E. Leach (Ed.), Applied Industrial Catalysts, vol. 1, Academic Press, 1983, p. 275;
(b) N. von Kutepow, W. Himmele, H. Hohenschutz, Chem. Ing. Technol. 37 (1965) 297.
[3] D. Forster, M. Singleton, J. Mol. Catal. 17 (1982) 299.
[4] K. Nozaki, Chem. Abstr. 81 (1974) 120023d.
[5] N. von Kutepow, F.-J. Müller, Chem. Abstr. 81 (1974) 135473z.
[6] T. Imamoto, T. Kusomoto, M. Yokoyama, Bull. Chem. Soc. Jpn 55 (1982) 643.
[7] (a) F.E. Paulik, A. Hershman, W.R. Knox, J.F. Roth, Chem. Abstr. 72 (1970) 110807y;
(b) J.S. Kanel, S.J. Okrasinski, US Patent to Eastman (1999) 5900504.
[8] R.F. Heck, J. Am. Chem. Soc. 85 (1963) 2013.
[9] J. Gauthier-Lafaye, R. Perron, European Patent to Rhone-Poulenc (1981) 35458.
[10] H.J. Hagemeyer, Chem. Abstr. 50 (1956) 16835d.
[11] A.N. Naglieri, N. Rizkalla, Chem. Abstr. 89 (1978) 42469c.
[12] K. Fujimoto, T. Shikada, K. Omata, H. Tominaga, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 429.
[13] N. Ritzkalla, Industrial chemicals via C1 processes, ACS Symposium Series 328 (1987) 61.
[14] J.D. Holmes, US Patent to Eastman (1979) 4133963.
[15] European Chemical News, 26 May-1 June 1997.
[16] (a) W.R. Moser, B.J. Marshik-Guerts, S.J. Okrasinski, J. Mol. Catal. A Chem. 143 (1999) 57;
(b) W.R. Moser, B.J. Marshik-Guerts, S.J. Okrasinski, J. Mol. Catal. A Chem. 143 (1999) 71.
[17] D. Forster, J. Am. Chem. Soc. 98 (1976) 846.
[18] B.C. Gates, Catalytic Chemistry, Wiley, New York, 1992.
[19] M. Cheong, R. Schmid, T. Ziegler, Organometallics 19 (2000) 1973.
[20] T. Kinnunen, K. Laasonen, J. Mol. Struct. (Theochem) 542 (2001) 273.
[21] T. Kinnunen, K. Laasonen, J. Mol. Struct. (Theochem) 540 (2001) 91.
[22] T. Kinnunen, K. Laasonen, J. Organomet. Chem. 628 (2001) 222.
[23] E.A. Ivanova, P. Gisdakis, V.A. Nasluzov, A.I. Rubailo, N. Rösch, Organometallics 20 (2001) 1161.
[24] T.R. Griffin, D.B. Cook, A. Haynes, J.M. Pearson, D. Monti, G.E. Morris, J. Am. Chem. Soc. 118 (1996) 3029.
[25] D. Forster, Adv. Organometal. Chem. 17 (1979) 255.
[26] A. Haynes, B.E. Mann, G.E. Morris, P.M. Maitlis, J. Am. Chem. Soc. 115 (1993) 4093.
[27] M. Bassetti, D. Monti, A. Haynes, J.M. Pearson, I.A. Stanbridge, P.M. Maitlis, Gaz. Chim. Ital. 122 (1992) 391.
[28] G.W. Adamson, J.J. Daly, D. Forster, J. Organomet. Chem. 71 (1974) C17.
[29] H. Adams, N.A. Bailey, B.E. Mann, C.P. Manuel, C.M. Spencer, A.G. Kent, J. Chem. Soc. Dalton Trans. (1988) 489.
[30] L.A. Howe, E.E. Bunel, Polyhedron 14 (1995) 167.
[31] J.F. Roth, J.H. Craddock, A. Hershman, F.E. Paulik, Chem. Technol. (1971) 600.
[32] D. Forster, T.W. Dekleva, J. Chem. Edu. 63 (1986) 204.
[33] D.J. Watson, Catalysis of Organic reactions, Marcel Dekker, New York, 1998, p. 369.
[34] A. Haynes, P.M. Maitlis, R. Quyoum, C. Pulling, H. Adams, S.E. Spey, R.W. Strange, J. Chem. Soc. Dalton Trans. (2002) 2565.
[35] R.G. Schultz, P.D. Montgromerry, J. Catal. 13 (1969) 105.
[36] A. Krzywicki, M. Marczewski, J. Mol. Catal. 6 (1979) 431.
[37] M.S. Scurrell, R.F. Howe, J. Mol. Catal. 7 (1980) 535.
[38] G. Luft, G. Ritter, US Patent to Hoechst (1987) 4657884.
[39] G. Luft, G. Ritter, US Patent to Hoechst (1988) 4776987.
[40] R.S. Drago, E.D. Nyberg, A.E. Amma, A. Zombeck, Inorg. Chem. 20 (1981) 641.
[41] M.S. Jarrel, B.C. Gates, J. Catal. 40 (1975) 255.
[42] J. Hjortkjaer, Y. Chen, B. Heinrich, Appl. Catal. 67 (1991) 269.
[43] C.R. Marston, L.G. Goe, European Patent to Reilly (1988) 277824.
[44] N. Yoneda, Y. Shiroto, K. Hamato, S. Asaoka, T. Maejima, US Patent to Chiyoda (1994) 5334755.
[45] T. Minami, K. Shimokawa, K. Hamato, Y. Shiroto, N. Yoneda, US Patent to Chiyoda (1994) 5364963.
[46] T. Minami, K. Hamato, K. Shimokawa, Y. Shiroto, US Patent to Chiyoda (1996) 5576458.
[47] N. Yoneda, T. Minami, J. Weiszmann, B. Spehlmann, Science and Technology in Catalysis, Proceedings of the Third Tokyo Conference on Advanced Catalytic Science and Technology (1998) 93.
[48] (a) M.A. Murphy, B.L. Smith, G.P. Torrence, A. Agulio, J. Organomet. Chem. 303 (1986) 257;
(b) B.L. Smith, G.P. Torrence, M.A. Murphy, A. Agulio, J. Mol. Catal. 39 (1987) 115.
[49] (a) F. Paulik, J.E. Roth, J. Chem. Soc. Chem. Commun. (1968) 1578;
(b) K.K. Robinson, A. Hershman, J.H. Craddock, J.F. Roth, J. Catal. 27 (1972) 389;
(c) A. Hershman, W.R. Knox, F.E. Paulik, J.E. Roth, Monsanto Company, US Patent (1973) 3769329.
[50] (a) T.W. Dekleva, D. Forster, Adv. Catal. 34 (1986) 81;
(b) D. Brodzki, B. Denise, G. Pannetier, J. Mol. Catal. 2 (1977) 149;
(c) T. Matsumoto, K. Mori, A. Ozaki, J. Catal. 51 (1978) 96;
(d) T. Mizoroki, T. Matsumoto, A. Ozaki, Bull. Chem. Soc. Jpn 52 (1979) 479.
[51] (a) G.J. Sunley, D.J. Watson, Catal. Today 58 (2000) 293;
(b) J.H. Jones, Platinum Metal Rev. 44 (2000) 94.
[52] K.E. Clode, D.J. Watson, C.J.E. Vercauteren, European Patent to BP Chemicals (1994) 616997.
[53a] D. Forster, J. Chem. Soc. Dalton Trans. (1979) 1639.
[53b] P.M. Maitlis, A. Haynes, G.J. Sunley, M.J. Howard, J. Chem. Soc. Dalton Trans. (1996) 2187.

[54] M.F. Giles, G. Rafeletos, M.J. Baker, C.S. Garland, European Patent to BP Chemicals (1996) 749948.

[55] J.G. Sunley, M.F. Giles, C.S. Garland, European Patent to BP Chemicals (1995) 643034.

[56] C.S. Garland, M.F. Giles, A.D. Poole, J.G. Sunley, European Patent to BP Chemicals (1996) 728726.

[57] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.

[58] J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, J. Chem. Soc. Chem. Commun. (1995) 1579.

[59] K.V. Katti, B.D. Santarsiero, A.A. Pinkerton, R.G. Cavell, Inorg. Chem. 32 (1993) 5919 (and references therein).

[60] R.W. Wegman, A.G. Abatjoglou, A.M. Harrison, J. Chem. Soc. Chem. Commun. 1 (1987) 1891 (and references therein).

[61] K.G. Moloy, R.W. Wegman, Organometallics 8 (1989) 2883.

[62] J. Rankin, A.D. Poole, A.C. Benyei, D.J. Cole-Hamilton, Chem. Commun. 19 (1997) 1835.

[63] J. Rankin, A.C. Benyei, A.D. Poole, D.J. Cole-Hamilton, J. Chem. Soc. Dalton Trans. (1999) 3771.

[64] M.J. Baker, M.F. Giles, A.G. Orpen, M.J. Taylor, R.J. Watt, J. Chem. Soc. Chem. Commun. (1995) 197.

[65] C.-A. Carraz, E.J. Ditzel, A.G. Orpen, D.D. Ellis, P.G. Pringle, G.J. Sunley, Chem. Commun. 14 (2000) 1277.

[66] T.G. Schenck, C.R.C. Milne, J.F. Sawyer, B. Bosnich, Inorg. Chem. 24 (1985) 2338.

[67] G.J. Lamprecht, G.J. Van Zyl, J.G. Leipoldt, Inorg. Chim. Acta 164 (1989) 69.

[68] M.J. Menu, P. Desrosiers, M. Darguenave, Y. Darguenave, Organometallics 6 (1987) 1822.

[69] I.C. Douek, G. Wilkinson, J. Chem. Soc. A 1 (1969) 2604.

[70] T.C. Blagborough, R. Davis, I. Ivison, J. Organomet. Chem. 467 (1994) 85.

[71] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.

[72] L. Gonsalvi, H. Adams, G.J. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 121 (1999) 11233.

[73] M.J. Howard, G.J. Sunley, A.D. Poole, R.J. Watt, B.K. Sharma, Stud. Surf. Sci. Catal. 121 (1999) 61.

[74] C.P. Casey, E.L. Paulsen, E.W. Beuttenmueller, B.R. Proft, B.A. Matter, D.R. Powell, J. Am. Chem. Soc. 121 (1999) 63 (and references therein).

[75] C.M. Thomas, R. Mafua, B. Therrien, E. Rusanov, H. Stoeckli-Evans, G. Süss-Fink, Chem. Eur. J. 8 (2002) 3343.

[76] E.K. van den Beuken, A. Meetsma, H. Kooijman, A.L. Spek, B.L. Feringa, Inorg. Chim. Acta 264 (1997) 171.

[77] P. Das, D. Konwar, P. Sengupta, D.K. Dutta, Trans. Met. Chem. 25 (2000) 426.

[78] P. Das, M. Boruah, N. Kumari, M. Sharma, D. Konwar, D.K. Dutta, J. Mol. Catal. 178 (2002) 283.

[79] C.M. Thomas, A. Neels, H. Stoeckli-Evans, G. Süss-Fink, Eur. J. Inorg. Chem. 12 (2001) 3005.

[80] J.R. Dilworth, D. Morales, Y. Zheng, J. Chem. Soc. Dalton Trans. (2000) 3007.