



New carboalkoxybis(triphenylphosphine)palladium(II) cationic complexes: Synthesis, characterization, reactivity and role in the catalytic hydrocarboalkoxylation of ethene. X-ray structure of *trans*-[Pd(COOMe)(TsO)(PPh₃)₂] \cdot 2CHCl₃

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ABSTRACT

The cationic complexes *trans*-[Pd(COOR)(H₂O)(PPh₃)₂](TsO) have been synthesised by reacting *cis*-[Pd(H₂O)₂(PPh₃)₂](TsO) \cdot 2H₂O with CO in ROH (R=Me and Et), practically under room conditions, or by methathetical exchange of *trans*-[Pd(COOMe)Cl(PPh₃)₂] with Ag(TsO) (R=*n*-Pr, *iso*-Pr, *n*-Bu, *iso*-Bu, *sec*-Bu). They have been characterised by IR, ¹H NMR and ³¹P NMR spectroscopies.

The X-ray investigation of *trans*-[Pd(COOMe)(TsO)(PPh₃)₂] reveals that the palladium center is surrounded in a virtually square planar environment realized by two PPh₃ trans to each other, the carbon atom of the carbomethoxy ligand and an oxygen atom of the *p*-toluensulfonate anion, with two crystallization molecules of CHCl₃. The Pd–O–S angle, 151.9(3)°, is very wide, probably due to the interaction of one CHCl₃ molecule with the complex inner core. The carbomethoxy derivatives react with R'OH yielding the corresponding R' carboalkoxy derivative (R' = Et, *n*-Pr and *iso*-Pr); ethene does not insert into the Pd–COOMe bond; decarbomethoxylation occurs when treated with TsOH/H₂O in MeOH at 50 °C.

All the carboalkoxy are precursors for the catalytic carboalkoxylation of ethene if used in combination of PPh₃ and TsOH, better in the presence of some water. Experimental evidences are more in favor of the so-called “hydride” mechanism rather than the “carbomethoxy” mechanism.

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1. Introduction

Pd(II)-carboalkoxy complexes are involved as key intermediates in several catalytic carbonylation reactions, such for example the oxidative carbonylation of alkanols to carbonates and oxalates, or of olefins and alkynes to diesters or unsaturated esters [1–3], the double carbonylation of organic halides [4,5], the carbonylation of olefins to polyketones [6,7]. They have been proposed as key intermediates also in the hydroesterification of an olefin to monoesters [8–11].

Methods of synthesis are based on the reaction of Pd(II) complexes with CO and an alkanol, eventually in the presence of a tertiary amine, or an alkoxide [12–17] or on the oxidative addition of chloro or cyano formate or phenylcarbonate to Pd(0) complexes [18–22]. Most of the syntheses reported up to now are relevant to carbomethoxy derivatives. The synthesis of neutral Pd(II) com-

plexes of the type *trans*-[Pd(COOR)X(PPh₃)₂] (X=Cl and CN) with R bulkier than Me (up to cyclohexyl) has been also reported [19–24].

The cationic carbomethoxy complex *trans*-[Pd(COOMe)(H₂O)(PPh₃)₂](TsO) has been synthesised from the neutral *trans*-[Pd(COOMe)Cl(PPh₃)₂] by methathetical exchange with Ag(TsO). Its role in the catalytic hydrocarbomethylation of ethene has been investigated [25].

In the present paper we extend the study to the synthesis and characterization of the new cationic carboalkoxy complexes *trans*-Pd(COOR)(H₂O)(PPh₃)₂(TsO), with R=Et, *n*-Pr, *iso*-Pr, *n*-Bu, *iso*-Bu, *sec*-Bu, together with further studies on the reactivity of the methyl analogue in relation to the catalytic hydrocarbomethylation of ethene. We also reported the X-ray diffraction structure of *trans*-[Pd(COOMe)(TsO)(PPh₃)₂] \cdot 2CHCl₃.

2. Experimental

2.1. Materials

Carbon monoxide and ethene (purity higher than 99%) were supplied by SIAD Spa (Italy). Methanol was purchased from Baker

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(purity >99.5%, 0.01% of water) and Pd(OAc)₂, Ag(TsO), NEt₃, PPh₃ and *p*-toluenesulfonic acid were purchased from Aldrich Chemicals. NEt₃ and the solvents were commercial grade and used without further purification. [Pd(COOR)Cl(PPh₃)₂], [PdCl₂(PPh₃)₂], [Pd(H₂O)₂(PPh₃)₂](TsO)₂ and [Pd(TsO)₂(PPh₃)₂] complexes were prepared according to the methods reported in the literature [24–27].

2.2. General procedure

The IR spectra were recorded in nujol mull on a Nicolet FTIR instruments mod. Nexus. ¹H and ³¹P NMR spectra were recorded on a Bruker AMX 300 spectrometer equipped with a BB multinuclear probe operating in the FT mode at 300 and 121.5 MHz for ¹H and ³¹P, respectively. All the samples were dissolved in deuterated methanol used also as internal reference for the assignment of the chemical shifts.

2.3. Preparation of trans-[Pd(COOR)(H₂O)(PPh₃)₂](TsO) (R = Me and Et)

0.1 mmol of [Pd(H₂O)₂(PPh₃)₂](TsO)₂ was dissolved in 2 ml of MeOH or EtOH, previously saturated with CO at r.t. The solution was kept under 2 atm of CO for 5–10 min and then poured into 20 ml of cold water under vigorous stirring. A white precipitated formed immediately. The suspension was filtered, the solid was washed with cold water, *n*-pentane, and dried under vacuum (yield 77%).

2.4. Preparation of trans-[Pd(COOR)(H₂O)(PPh₃)₂](TsO) with R bulkier than Et

AgTsO was slowly added to trans-[Pd(COOR)Cl(PPh₃)₂] (0.1 mmol) suspended in 2 ml of ROH. The solution was stirred for few minutes at 15 °C till complete precipitation of AgCl and then quickly filtered using a micro-filter system. The solution was dropped directly into 20 ml of cold water, under vigorous stirring. A white solid precipitates which was separated by filtration, washed with cold water, *n*-pentane and dried under vacuum (yield 75%). This procedure gives good results also when R=Me or Et. If the filtered methanol solution is poured into warm water (50 °C), the complex trans-[Pd(COOR)(TsO)(PPh₃)₂] separates.

2.5. Reactivity

The reactivity tests under pressure higher than 2 atm were carried out by dissolving the carboalkoxy complex (0.1 mmol) in the appropriate alkanol (2 ml) in a 5–10-ml glass bottle placed in an autoclave of ca. 50 ml volume. The autoclave was first washed several times with the appropriate gas (CO or ethene), then pressurised and warmed to the desired pressure and temperature. The solution was stirred with a magnetic bar. After the desired reaction time was over the autoclave was rapidly cooled to r.t. (or even to 0 °C) and then slowly depressurised. A little sample was taken apart for GC analysis. The rest was quickly poured into water. The precipitate was collected on a filter, washed with cold water and *n*-heptane, dried under vacuum. The nature of the solid was established by IR and NMR spectroscopy.

The reactivity was tested with alkanols, acids (HCl, AcOH and TsOH), water, water/TsOH and with ethene. In order not to be redundant, the conditions of the tests are reported together with the results and the discussion in the next section.

Table 1

Crystal and refinement data.

| Complex | |
|---|---|
| Formula | C ₄₇ H ₄₂ O ₅ P ₂ SCl ₆ Pd |
| Molecular wt | 1099.9 |
| Color | colorless |
| Crystal system | monoclinic |
| Space group | P2 ₁ /n (No. 14) |
| <i>a</i> (Å) | 19.558(3) |
| <i>b</i> (Å) | 12.155(2) |
| <i>c</i> (Å) | 21.453(4) |
| β (°) | 103.87(1) |
| <i>V</i> (Å ³) | 4951(1) |
| <i>Z</i> | 4 |
| <i>D</i> _{calc} (g cm ⁻³) | 1.476 |
| <i>F</i> (000) | 2232 |
| Crystal dimens (mm) | 0.20 × 0.20 × 0.20 |
| θ limits (°) | 3.5/29.6 |
| No. of independent data | 11938 |
| No. of data with <i>I</i> > 2σ(<i>I</i>) | 3892 |
| No. of variables | 560 |
| <i>R</i> (<i>F</i>) ^a | 0.058 |
| w <i>R</i> (<i>F</i> ²) ^b | 0.110 |
| Largest peak in (<i>F</i> (e Å ⁻³)) | 0.824 |
| GOF ^c | 0.763 |

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR(F^2) = \left[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2 \right]^{1/2}$$

$$^c GOF = \left[\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p) \right]^{1/2}$$

2.6. Hydroesterification of ethene using the carboalkoxy complexes reported in Table 1 as catalyst precursors in the relevant ROH

The precursor was used as such or also in combination with PPh₃ and PPh₃/TsOH as reported in Section 3. All the experiments were carried out in a stainless steel autoclave of ca. 250 ml of capacity following the same procedure already reported, using the solvent with 800 ppm of water in order to compare the activity with that previously reported using related precursors [25,28,29].

2.7. X-ray data collection, structure solution and refinement

The X-ray data collection was performed at room temperature with a STADI 4 CCD STOE area detector diffractometer on single-crystal mounted in a thin-walled glass capillary with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were obtained by slow evaporation of a CHCl₃/*n*-hexane solution of the complex at -10 °C. A summary of the X-ray analysis is listed in Table 1.

The structure was solved by direct methods and refined by full-matrix least-squares based on *F*², where all non-hydrogen atoms were assigned anisotropic displacement parameters. As commented in Section 3.2, the solvent molecules suffer from high thermal motions. The final Fourier difference maps showed no significant features, the largest maxima (less than one electron) close to the chlorine atoms. All calculations were made with programs of the SHELXTL/PC system and SHELXL93 program [30].

3. Results and discussion

3.1. Synthesis and characterization of the carboalkoxy complexes reported in Table 2

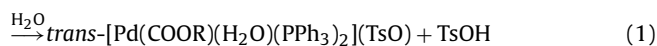
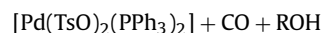
Complexes (**1a** and **1b**) have been prepared by reacting [Pd(TsO)₂(PPh₃)₂] or [Pd(H₂O)₂(PPh₃)₂](TsO)·2H₂O with CO in ROH

Table 2Selected IR, ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR data of *trans*-[Pd(COOR)(H₂O)(PPh₃)₂](TsO) (**Ia–g**), *trans*-[Pd(COOMe)(TsO)(PPh₃)₂] (**Ila**) and *trans*-[Pd(COOEt)(TsO)(PPh₃)₂] (**Ilb**).

| R | IR ^a | | $^1\text{H}^b$ | $^{31}\text{P}^c$ |
|------------------------------|------------------|------------------|--|----------------------|
| | ν | cm^{-1} | δ (ppm) | δ (ppm) |
| Me (Ia) [REF?] | H ₂ O | 3489, 3412 | 2.58 s: CH ₃ | 19.04 s ^d |
| | C=O | 1685 | 2.36 s: CH ₃ | |
| | C–O–C | 1070 | | |
| | SO ₃ | 1230, 1035, 1013 | | |
| Ila | C=O | 1668 | 2.58 s: CH ₃ | 19.04 s |
| | C–O–C | 1086 | 2.36 s: CH ₃ | |
| | SO ₃ | 1263, 1029, 1000 | | |
| Et (Ib) | H ₂ O | 3671, 3441 | 2.87 q: CH ₂ | 19.01 s |
| | C=O | 1684 | 2.36 s: CH ₃ | |
| | C–O–C | 1057 | 0.49 t: CH ₃ | |
| | SO ₃ | 1222, 1036, 1011 | | |
| Ilb | C=O | 1663 | 2.87 q: CH ₂ | 19.01 s |
| | C–O–C | 1088 | 2.36 s: CH ₃ | |
| | SO ₃ | 1268, 1029, 999 | 0.49 t: CH ₃ | |
| <i>n</i> -Pr (Ic) | H ₂ O | 3640, 3485 | 2.81 t: OCH ₃ | 19.12 s |
| | C=O | 1671 | 2.36 s: CH ₃ | |
| | C–O–C | 1083 | 0.88 m: CH ₂ | |
| | SO ₃ | 1257, 1031, 1008 | 0.51 t: CH ₃ | |
| <i>iso</i> -Pr (Id) | H ₂ O | 3220 | 3.82 m: CH | 19.08 s |
| | C=O | 1674 | 2.36 s: CH ₃ | |
| | C–O–C | 1051 | 0.31 d: CH ₃ | |
| | SO ₃ | 1223, 1038, 1014 | | |
| <i>n</i> -Bu (Ie) | H ₂ O | 3640, 3488 | 2.87 t: OCH ₂ | 19.13 s |
| | C=O | 1672 | 2.36 s: CH ₃ | |
| | C–O–C | 1081 | 0.87 m: CH ₂ | |
| | SO ₃ | 1246, 1030, 1007 | 0.68 t: CH ₃ | |
| <i>iso</i> -Bu (If) | H ₂ O | 3142 | 2.63 d: OCH ₃ | 19.27 s |
| | C=O | 1669 | 2.36 s: CH ₃ | |
| | C–O–C | 1068 | 1.08 m: CH | |
| | SO ₃ | 1218, 1036, 1012 | 0.47 d: CH ₃ | |
| <i>sec</i> -Bu (Ig) | H ₂ O | 3144 | 3.69 m: CH | 19.10 s |
| | C=O | 1671 | 2.36 s: CH ₃ | |
| | C–O–C | 1059 | 0.67 m: CH ₂ | |
| | SO ₃ | 1231, 1037, 1013 | 0.41 t: CH ₃ 0.20 d: CH ₃ | |

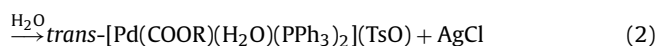
NMR spectra are recorded in CD₃OD. Abbreviations: s = singlet; t = triplet; q = quartet; m = multiplet.^a Nujol mull.^b δ (^1H) values in ppm referenced to CD₃OD.^c δ (^{31}P) values in ppm from external 85% H₃PO₄, downfield being taken as positive.^d In Ref. [25] it was erroneously reported 16.51 ppm.

(2 atm, r.t.):



The reaction with MeOH takes place in a few minutes, whereas with EtOH is significantly slower as it takes 20–30 min.

Reaction (1) with bulkier alkanols gives unsatisfactory results. An attempt to synthesise complex **If** failed. The carboalkoxy complexes (**Ic–g**) with bulkier R (Table 2) have been prepared via methathetical exchange of the corresponding neutral chloride with AgTsO, as already experienced for the synthesis of (**Ia**) [25]:



It is noteworthy to point out that the synthesis based on reaction (1) does not require the presence of a tertiary base, at difference of the analogous synthesis of the corresponding chloride *trans*-

[Pd(COOR)Cl(PPh₃)₂] starting from *trans*-[PdCl₂(PPh₃)₂], in which case the use of the base is necessary in order to neutralise HCl that forms during the reaction and that otherwise reverses the reaction [12,24].

Selected IR and NMR data are reported in Table 1. The IR spectra of (**Ia–g**) show a strong absorption band in the 1684–1670 cm⁻¹ region due to $\nu_{\text{C=O}}$ of the carboalkoxy ligand. In the corresponding neutral chloride the $\nu_{\text{C=O}}$ absorption appears at slight lower frequency [24], which might be due to a stronger π -back donation from the metal to the carboalkoxy moiety in the neutral complexes.

Absorption bands due to coordinated water are observed in the 3640–3142 cm⁻¹ region [31]. Complexes (**Ia–c** and **Ie**) show two sharp bands of low intensity; complex **If** shows one band of low intensity at 3637 cm⁻¹ and an unresolved broad absorption centered at 3142 cm⁻¹; complexes **Id** and **Ig** show a broad unresolved band centered at 3220 and at 3144 cm⁻¹, respectively. Those at lower frequency suggest the presence of a hydrogen-bond between water and TsO⁻, with consequent lowering of $\nu_{\text{O-H}}$ [31–33]. The absorptions in the ranges of 1273–1222, and 1014–1007 cm⁻¹ are identified as some of the characteristic bands of the anionic $-\text{SO}_3^-$

group [34–38]. The band in the 1037–1025 cm⁻¹ is assignable to the C–O–C stretch of the alkoxy carbonyl group [13,14,24].

The ¹H NMR spectra of (**Ia–g**) show signals in the range of 0.20–3.69 ppm assigned to the alkoxy group protons [24]. The singlets observed at 2.36 ppm is assigned to the CH₃ protons of the TsO⁻ anion. Two well separated multiplets for the aromatic protons are centered at about 7.6 and 7.3 ppm. The ³¹P NMR spectrum shows a singlet in the range of 19.01–19.27 ppm, close to that of the relevant neutral chloride complex [24].

As reported in Section 2, complexes (**Ia–g**) have been precipitated by pouring their alkanol solution into cold water. When warm water has been used to precipitate the carbomethoxy complex, a different derivative has been obtained, (**IIa**). The IR spectrum of (**IIa**) does not show absorption bands due to coordinated water. The ν_{CO} and ν_{C–O–C} are shifted from 1685 and 1036 cm⁻¹ to 1668 and 1029 cm⁻¹ and the bands of the –SO₃⁻ group are shifted from 1230 and 1013 cm⁻¹ to 1263 and 1001 cm⁻¹ and are assignable to a coordinated anion [34–38]. The ¹H and ³¹P NMR spectra of complexes (**Ia**) and (**IIa**) in CD₃OD do not differ appreciably, probably due to the fast exchange of labile water, TsO⁻, solvent. The X-ray crystal structure of the CHCl₃ clathrated of complex (**IIa**) shows that it has a *trans* geometry, in which TsO⁻ coordinates the metal (in place of H₂O) in (**Ia**) [24]; the ³¹P NMR spectrum for this complex in CDCl₃ shows a singlet at 18.51 ppm slightly lower than in CD₃OD. On the basis of these data complex (**IIa**), precipitated from MeOH/H₂O is formulated as *trans*-[Pd(COOMe)(TsO)(PPh₃)₂]. A *trans* geometry is assigned also to all the new cationic complexes (**Ib–g**).

The IR spectrum of the solid precipitated by addition of cold water to the ethanol solution of the carboethoxy derivative shows double absorptions in the ν_{CO}, ν_{C–O–C} and ν_{SO₃} regions, suggesting that this solid is a mixture of *trans*-[Pd(COOMe)(H₂O)(PPh₃)₂](TsO), (**Ib**) and *trans*-[Pd(COOMe)(TsO)(PPh₃)₂], (**IIb**).

3.2. X-ray structure analysis of [Pd(COOMe)(TsO)(PPh₃)₂]·2CHCl₃, (**IIa**)

The ORTEP [39] drawing of the complex is shown in Fig. 1, together with the numbering scheme used, while relevant bond lengths and angles are reported in Table 3. The solid state investigation revealed three sets of atoms lying in well defined planes:

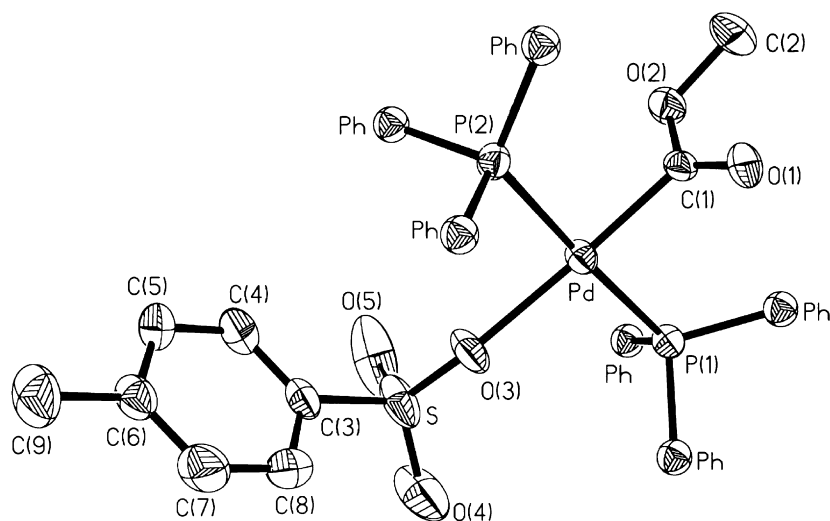


Fig. 1. A drawing of the complex with the selected numbering scheme. Ellipsoids are at the 50% level; hydrogen atoms are represented by spheres of arbitrary size. The phenyl rings and the CHCl₃ molecules have been omitted for clarity.

Table 3
Relevant bond distances (Å) and angles (°).

| | | | |
|--------------|----------|----------------|----------|
| Pd–P(1) | 2.353(2) | Pd–O(3) | 2.160(4) |
| Pd–P(2) | 2.342(2) | Pd–C(1) | 1.978(6) |
| S–O(3) | 1.452(4) | C(1)–O(1) | 1.187(7) |
| S–C(3) | 1.789(6) | C(1)–O(2) | 1.336(7) |
| | | O(2)–C(2) | 1.458(7) |
| P(1)–Pd–P(2) | 177.2(1) | C(1)–Pd–O(3) | 170.8(2) |
| P(1)–Pd–O(3) | 98.1(1) | P(2)–Pd–O(3) | 84.3(1) |
| P(1)–Pd–C(1) | 89.2(2) | P(2)–Pd–C(1) | 88.3(2) |
| Pd–O(3)–S | 151.9(3) | O(3)–S–C(3) | 104.5(3) |
| Pd–C(1)–O(1) | 124.6(5) | Pd–C(1)–O(2) | 110.0(4) |
| | | O(1)–C(1)–O(2) | 125.4(6) |

P(1)–C(1)–P(2)–O(3), C(1)–C(2)–O(1)–O(2) and O(3)–S–C(3). The atoms in the set P(1)–C(1)–P(2)–O(3) (basal plane) are virtually coplanar within 0.04 Å, with the Pd center out by 0.06 Å. The set C(1)–C(2)–O(1)–O(2) is strictly planar, and is almost orthogonal to the basal plane, the two planes making a dihedral angle of 88.9°. Instead, the O(3)–S–C(3) set is tilted from both the previous plane, being inclined of 28.6° in respect of the basal plane and of 69.8° in respect of the C₂O₂ set.

Looking at bond distances and angles, it appears worth noting that the Pd–O(3)–S angle is very wide, 151.9(3)°; this is the largest value reported to date for a mononuclear Pd(II) complex. A search in the Cambridge Structural Database (CCD) [40–42] showed that the closest values found in (trifluoromethanesulfonato) (3-(diethylamino)propionyl)(diethylamine)palladium(II) and (2-(benzene-1,1-diyl)-2-methyl-propyl)-(trifluoromethanesulfonato)trimethylphosphine-palladium(II) [43,44], were 150.5° and 146.0°, respectively. In [43], the abnormal widening of the Pd–O–S angle was attributed to van der Waals contacts between the other oxygen atoms of the sulfone with hydrogen atoms of a nearby ligands. In the present case, the large Pd–O(3)–S angle might be due to the very efficient interaction involving O(4) and the hydrogen atom of a CHCl₃ molecule, as indicated in Fig. 2 (the contact distance is 1.99 Å, and the pertinent O(4)···H–C(11) angle is 164°), and only to a limited extent to steric interactions with the PPh₃ group.

The CCD exploration returned about 20 Pd mononuclear complexes with the metal showing a Pd–O–S–C moiety and a Pd environment similar to the one found in our compound [45–55].

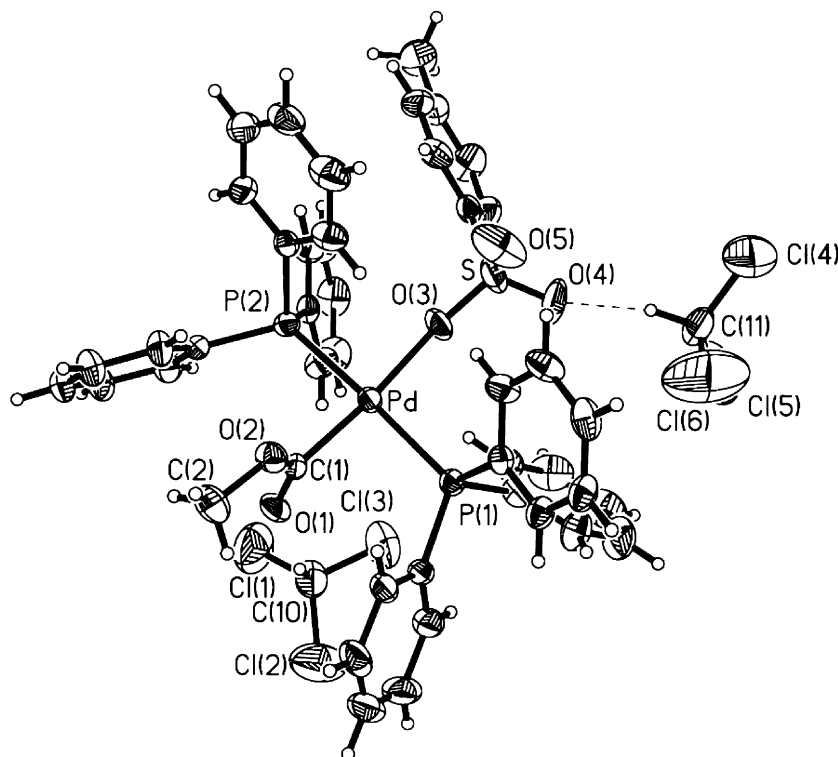


Fig. 2. The interaction between the sulfonato moiety and one of the CHCl_3 solvent molecules described in text.

The Pd–O(3) (2.160(4) Å) and O(3)–S (1.452(4) Å) distances agree reasonably with the average values found in such complexes (2.175 and 1.461 Å, respectively) [43–55]. Similar considerations also apply to other geometrical parameters involving the sulfur atom of the *p*-toluenesulfonato ligand. In fact, in the present complex the S–C(3) distance and the O(4)=S=O(5), O(3)–S–C(3) angles are 1.789(6) Å, 115.7(4) and 104.5(3)°, whereas the corresponding average parameters found in about 30 Pd square planar complexes showing at least 1 sulfonato ligand are 1.809 Å, 116.4° and 102.1°, respectively [40–42].

In the CCD there are also about 15 structures in which a mononuclear tetracoordinated Pd atom is bound by a –C(=O)–O–C moiety [14,16,17,22,25,43,56–61], most of them also showing the metal coordinated by two phosphine ligands. The average Pd–C distance and the Pd–C(=O), Pd–C–O angles in the reported structures are 1.979 Å, 126.6° and 112.9°, respectively. These values compare quite well with 1.978(6) Å, 124.6(5)° and 110.0(4)° in the complex described here. Among known structures, the complexes most closely resembling these values are *trans*-aqua-carbomethoxy-bis(triphenylphosphine)-palladium (1.975 Å, 124.5° and 111.4°) [25], *trans*-carbomethoxy-chloro-bis(triphenylphosphine)palladium (1.972 Å, 125.3° and 111.9°) [56] and chloro-(3-hydroxypropoxycarbonyl-C)-(2-(pyridin-2-yl)ethyl)diphenylphosphine-N, P)-palladium(II) (1.964 Å, 124.5° and 112.7°) [17].

The two CHCl_3 molecules in the unit cell, they are animated by high thermal motions, and only one of them, as said above, seems to interact with the complex inner core. Instead, the phenyl ring of the *p*-toluenesulfonato moiety establishes a rather long-range (4.22 Å) π -interaction with a phenyl ring bound to P(2). Other structural parameters, like the six P–C_{ph} distances (average value 1.819 Å) do not show any new feature, and the same can be said of the two Pd–PPh₃ bonds, that match quite well the average value of

2.33(3) Å found in 227 square planar Pd(II) complexes bearing two PPh₃ groups [40–42].

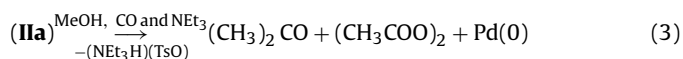
3.3. Reactivity

The reactivity has been tested with both the carbomethoxy complexes (**Ia**) and (**IIa**). They behave in the same way, therefore for the sake of simplicity here below we report the tests done with (**IIa**) only, if not otherwise indicated.

3.3.1. Reactivity with alkanols

At 80 °C, under 45 atm of CO, the carbomethoxy complex reacts with R'OH (R' = *n*-Pr, *iso*-Pr), used also as a solvent, giving complexes (**Ic–d**). These complexes react with MeOH under the same conditions giving the carbomethoxy derivative.

Under the above conditions and in the presence of a base such as triethylamine, complex (**IIa**) in MeOH is reduced to Pd(0) complexes, [Pd₃(CO)₃(PPh₃)₃] and [Pd(CO)(PPh₃)₃], the latter forms prevalently when the reaction is carried out also in the presence of 1 mol of PPh₃ per Pd atom. The reduction occurs with concomitant formation of dimethyl carbonate (DMC) and oxalate (DMO), as here below schematised:

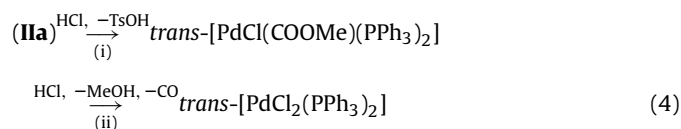


Under similar conditions the analogous complexes *trans*-[Pd(COOMe)Cl(PPh₃)₂] and *trans*-[Pd(OAc)(COOMe)(PPh₃)₂] give DMC or DMO, respectively [61–63].

3.3.2. Reactivity with acids HX (X = Cl, OAc and TsO)

The reactions have been carried in MeOH. At r.t. (**IIa**) reacts with 1 equiv. of HCl affording *trans*-[Pd(COOMe)Cl(PPh₃)₂], whereas when treated with 2 equiv. of acid the carboalkoxy moiety evolves with formation of MeOH, CO according to reaction (4) in which step

(ii) practically reverses the reaction that leads to the synthesis of *trans*-[Pd(COOMe)Cl(PPh₃)₂] from [PdCl₂(PPh₃)₂], CO and MeOH in the presence of NEt₃ [12,24]:



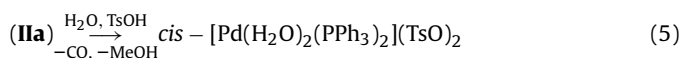
At r.t. the carboalkoxy moiety is stable when treated with AcOH or TsOH, even in excess; with the first acid, in the ratio Pd/AcOH = 1/1, (IIa) is partially converted to the corresponding acetate, *trans*-[Pd(COOMe)(OAc)(PPh₃)₂], whereas the conversion is complete using an excess of AcOH.

When treated at 50 °C with TsOH (Pd/TsOH = 1/6–1/10), complex (IIa) is unstable yielding [Pd(TsO)₂(PPh₃)₂], analogously to reaction (4), step(ii).

The complexes *trans*-[Pd(COOMe)X(PPh₃)₂] (X = Cl and AcO) are easily obtained also by adding 1 equiv. of LiX to (IIa) dissolved in MeOH.

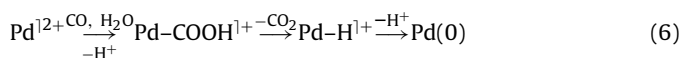
3.3.3. Reactivity with water and with water/TsOH

Complex (IIa) in MeOH/H₂O (10/1, v/v) does not react significantly in 1 h even at 50 °C, as it is recovered unreacted upon adding cold water to the solution, whereas when to this MeOH/H₂O solution TsOH is added (Pd/TsOH = 1/6) the carbomethoxy moiety is unstable and (IIa) is converted to [Pd(H₂O)₂(PPh₃)₂](TsO)₂.



Taking into consideration the reactivity of (IIa) with TsOH reported at Section 3.3.2, it appears that (i) the acid promotes the demethoxylation of the carbomethoxy moiety, probably through protonation of the oxygen atom of the methoxy group, and that (ii) water does not play a significant role in the demethoxylation step.

When the same experiment is carried out under CO pressure (20 atm), reduction to Pd(0) complexes occurs, with formation of [Pd₃(CO)₃(PPh₃)₃] or [Pd(CO)(PPh₃)₃], the latter forming when the reaction is carried out also in the presence of 1 equiv. of PPh₃. The reduction occurs with concomitant formation of CO₂, probably via a reaction closely related to the water gas shift reaction through the intermediacy of a Pd(II)–(COOH) species [64–66]:



3.3.4. Reactivity with ethene

After pressuring a methanol solution of (IIa) with ethene (1–40 atm) at r.t. for 1 h, the complex has been recovered unreacted, together with a minor amount of Pd(0) complexes (ca. 10%). In the MeOH solution no methyl propanoate was detected by GC. Nor any insertion was observed in CD₂Cl₂/MeOH from –78 °C up to 50 °C in a NMR tube pressurised with 6 atm of ethene.

In principle, ethene could insert into the Pd–(COOMe) bond with formation of a Pd–(CH₂–H₂–COOMe) moiety, which may be in equilibrium with a so-called β-esterchelate, as it has been found to occur promptly with cationic *cis*-chelated diphosphine Pd(II) complex [Pd(COOCH₃(CH₃CN)(dibpp)](TfO) (dibpp = 1,3-(*i*Bu₂P)₂C₃H₆) in CH₂Cl₂/MeOH/CH₃CN even at –30 °C at ambient pressure, as established by NMR multinuclear spectroscopy [11]. It has been also found that upon rising the temperature up to 25 °C the β-esterchelate reacts with MeOH yielding methyl propanoate and the starting carbomethoxy complex, thus the “carboalkoxy” cycle for the hydromethoxycarbonylation of ethene was demonstrated under the conditions just reported [11].

3.3.5. Catalytic properties of complexes (Ia–g) in the hydrocarboalkoxylation of ethene

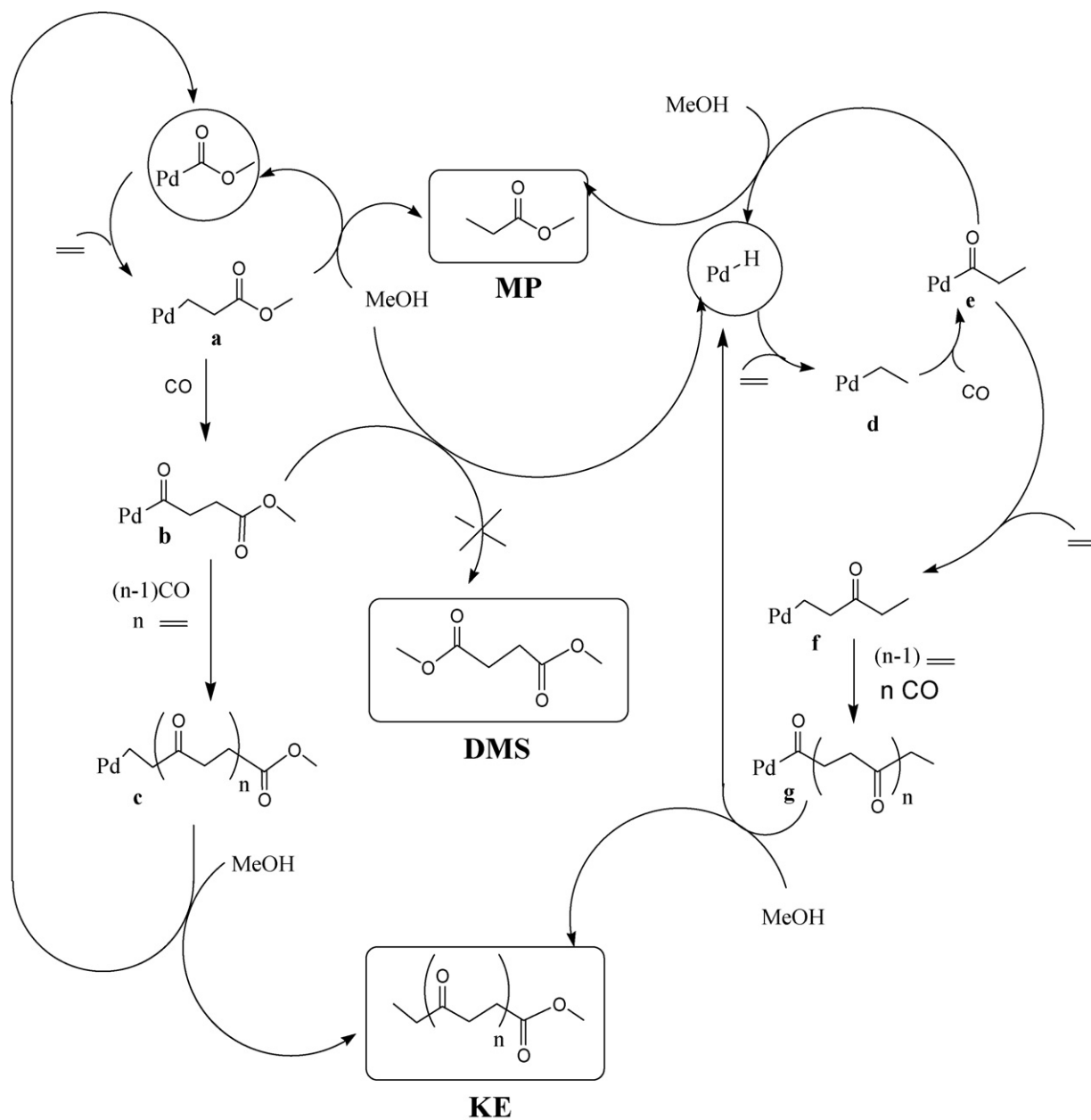
The catalytic activity of complex (Ia) in the hydroesterification of ethene in MeOH has been already reported [25,29]. Under standard conditions (40 atm, CO/ethene = 1/1, 70–100 °C) significant catalytic activity is shown only in the presence of both PPh₃ and TsOH (Pd/P/TsOH = 1/8/8). After catalysis the starting complex was recovered (65%) as *trans*-[Pd(COEt)(TsO)(PPh₃)₂], related to the “hydride” cycle (see Scheme 1) [29]. This acyl complex reacts with MeOH to give expected methyl propanoate (MP) in an almost stoichiometric amount and is a catalyst precursor for the methoxycarbonylation of a different olefin to give the expected ester and an almost stoichiometric amount of MP. This proves that the acyl complex is sufficiently stable to be isolated while being reactive enough to enter the catalytic cycle. Using [Pd(TsO)₂(PPh₃)₂] as catalyst precursor, it was found that a hydride source, such as H₂, H₂O, or TsOH, present a promoting effect on the catalysis [28]. All these experimental evidences are more in favor of the “hydride” cycle rather than of the “carbomethoxy” cycle [67]. In addition, others found that using a closely related system, derived from Pd(AcO)₂ in combination with an excess of PPh₃ and of TsOH [68], there was formation of phosphine degradation products such as MePPh₃⁺, EtPPh₃⁺ and EtCOCH₂CH₂PPh₃⁺, isolated as TsO[–] salts, thus providing further evidences for the “hydride” mechanism, the last two being Pd mediated side products of the “hydride” route [69].

In the present case, we found that also complexes (Ib–g), tested in the relevant alkanol at 100 °C, 40–50 atm, do not present any significant catalytic activity and that extensive decomposition to palladium metal occurs at 100 °C. Only in the presence of both added PPh₃ and TsOH catalytic activity is observed. Qualitative observations indicate that the activity lowers with increasing bulkiness of the alkanol.

That being said, in addition to the fact that ethene does not insert into the Pd–COOMe bond under the condition reported in Section 3.3.4, we present here further evidences that are more in favor of the “hydride” cycle. In an experiment carried out under conditions in which complex (Ia) is relatively stable, i.e., 40 °C and in the presence of 2 equiv. of added PPh₃, catalysis is not observed even under 80 atm total pressure (CO/ethene 1/1). At difference, under these conditions, but also in the presence of 10 equiv. of TsOH, there is formation of MP (TOF = 10 h^{–1}), together with minor, though significant, amounts of light CO/ethene co-oligomers having only keto–ester end groups (KE in Scheme 1), the most abundant of them being 4-oxohexanoate (*n* = 2). Even more significant, no dimethyl succinate (DMS) or higher diesters co-oligomers were detected by GC of the reaction mixture.

Both the “carbomethoxy” and the “hydride” cycles lead to the formation of MP and KE co-oligomers. Though it is well known that intermediates arising from the insertion of ethene (a), (c) and (f) are in equilibrium with the so-called β-chelates, and those arising from the insertion of CO (b) and (g) are in equilibrium with the so-called γ-chelates, the omission of these chelates do not question the validity of the reasoning that follows, therefore they are omitted for the sake of clarity.

In the “carbomethoxy” cycle, insertion of ethene into a Pd–COOMe bond gives intermediate (a), which upon protonolysis by MeOH yields MP and a Pd–OMe species, which inserts CO to continue the catalytic cycle. Protonolysis competes with the further subsequent insertion of CO and ethene, with formation of intermediates (b) and (c), which, after protonolysis with MeOH, give the KE co-oligomers and again a Pd–OMe species, that continues the catalysis. It should be noted that the copolymerization process stops after the insertion of a few molecules of monomers, i.e., the termination process competes effectively with the chain growing process. However, since it has been found that in the copolymeriza-



Scheme 1. Proposed reaction mechanism.

tion process CO insertion is faster than ethene insertion [6,7], it is hard to explain why after CO insertion into intermediate (a) (or (c)) there is no formation of dimethyl succinate (or of higher diesters). Formation of the diesters would occur *via* methanolysis with formation of a Pd-H species which can start the “hydride” cycle. The shift from one mechanism to the other has been demonstrated by multinuclear NMR spectroscopy [11]. For balance requirements of the two cycles there should be also formation of diethylketone or of co-oligomers having only keto ending groups for any molecule having only ester ending groups. However, co-oligomers of this type did not form nor diethyl ketone.

Therefore is more likely that MP and the ketoesters form through a catalytic cycle that starts from a Pd-H species and terminates *via* attack of MeOH to a Pd-acyl bond of intermediates (e) and (g), with concomitant reformation of the hydride species. The hydride would form after decarbomethoxylation of the Pd-COOMe bond promoted by TsOH/H₂O (*cf.* Section 3.3.3), followed by the inter-

action of H₂O with CO (*cf.* reaction (6): under catalytic conditions ethene would insert into the Pd-H bond before deprotonation).

These results do not exclude that, under the conditions in which catalysis occurs as just reported, ethene insertion into a Pd-COOMe bond might take place to some extent. As a matter of fact it has been found that the dibpp-based cationic complex under NMR conditions, both the acyl complex, related to the “hydride”, and the β -ester chelate, related to the “carbomethoxy” cycle, easily form at -60°C and at -30°C , respectively. In addition, it has been found that the acyl complex undergoes methanolysis at -30°C in a few minutes to give the ester as required from the “hydride” cycle, whereas methanolysis of the β -ester chelate, required to give MP from the “carbomethoxy” cycle, is slow on a timescale of days, at 25°C . It was suggested that slow methanolysis of the β -ester chelate, rather than slow insertion of an alkene into the Pd-COOMe bond, directs the catalysis towards the “hydride” mechanism [11].

However, it should be underlined that the dibpp- and the PPh₃-based systems are too different to consent a straightforward comparison. A part that dibpp acts only as *cis*-chelating ligand and that the acyl- and carbomethoxy-complexes isolated after catalysis using the PPh₃-based system have a *trans*-geometry,¹ the two systems work under different conditions. The second one requires the use of an excess of PPh₃ in order to prevent deactivation to Pd metal. When PPh₃ is added to the dibpp system the insertion of ethene into the Pd–COOMe bond is inhibited [11]. In addition, the PPh₃ system, in order to be catalytically efficient, requires also the use of an excess of TsOH and H₂O, which lead to decarbomethoxylation of the Pd–COOMe bond.

Not only, but the evidences here reported for the “hydride” mechanism, together with those reported in previous studies [25,27–29,68,69], refer to the actual catalysis conditions.

It is worth mentioning that also neutral *trans*-[Pd(COOMe)Cl(PPh₃)₂] treated at 95 °C with 1-hexene does not insert the olefin into the Pd–COOMe bond [71]. In this case the much greater coordination capacity of the chloride ligand and the bulkier 1-hexene might prevent the insertion.

References

- [1] M. Beller, A.M. Tafesh, in: B. Cornils, W.A. Hermann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, I, VCH, Weinheim, 1996, p. 187.
- [2] S. Uchiyumi, K. Ataka, T. Matsuzaki, *J. Organomet. Chem.* 576 (1999) 279.
- [3] B. Gabriele, G. Salerno, M. Costa, in: M. Beller (Ed.), *Catalytic Carbonylation Reactions*, 18, Springer, 2006, p. 239 (Top. Organomet. Chem.).
- [4] J.-T. Chen, A. Sen, *J. Am. Chem. Soc.* 106 (1984) 1506.
- [5] F. Osawa, N. Kawasaky, H. Okamoto, T. Yamamoto, A. Yamamoto, *Organometallics* 6 (1987) 1640.
- [6] A. Sen, *Acc. Chem. Res.* 26 (1993) 303.
- [7] E. Drent, P.H.M. Budzelaar, *Chem. Rev.* 96 (1996) 663.
- [8] D.M. Fenton, *J. Org. Chem.* 38 (1973) 3192.
- [9] D.E. James, L.F. Hines, J.K. Stille, *J. Am. Chem. Soc.* 98 (1982) 1806.
- [10] D. Milstein, *Acc. Chem. Res.* 21 (1988) 428.
- [11] J. Liu, B.T. Heaton, J.A. Iggo, R. Whyman, J.F. Bickley, A. Steiner, *Chem. Eur. J.* 12 (2006) 4417.
- [12] M. Hidai, M. Kokura, Y. Uchida, *J. Organomet. Chem.* 52 (1973) 431.
- [13] F. Rivetti, U. Romano, *J. Organomet. Chem.* 154 (1978) 323.
- [14] A. Sacco, G. Vasapollo, C.F. Nobile, A. Piergiovanni, M.A. Pellinghelli, M. Lanfranchi, *J. Organomet. Chem.* 356 (1988) 397.
- [15] G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, C.F. Roobeck, *J. Organomet. Chem.* 430 (1992) 357.
- [16] G.D. Smith, B.E. Hanson, J.S. Merola, F.J. Waller, *Organometallics* 12 (1993) 568.
- [17] P. Giannoccaro, D. Cornacchia, S. Doronzo, E. Mesto, E. Quaranta, M. Aresta, *Organometallics* 25 (2006) 2872.
- [18] P. Fitton, M.P. Johnson, J.E. McKeon, *Chem. Commun.* (1968) 6.
- [19] S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, K. Ataka, *J. Am. Chem. Soc.* 95 (1973) 3180.
- [20] W. Keim, J. Becker, A.M. Trzeciak, *J. Organomet. Chem.* 372 (1989) 447.
- [21] Y. Nishihara, M. Miyasaka, Y. Inoue, T. Yamaguchi, M. Kojima, K. Takagi, *Organometallics* 26 (2007) 4054.
- [22] R. Hua, H. Takeda, S. Onozawa, Y. Abe, M. Tanaka, *J. Am. Chem. Soc.* 123 (2001) 2899.
- [23] A. Derivisi, P.G. Edwards, P.D. Newman, R.P. Tooze, S.J. Coles, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* (1999) 1113.
- [24] R. Bertani, G. Cavinato, L. Toniolo, G. Vasapollo, *J. Mol. Catal.* 84 (1993) 165.
- [25] G. Cavinato, A. Vavasori, L. Toniolo, F. Benetollo, *Inorg. Chim. Acta* 343 (2003) 183.
- [26] J.M. Jenkins, J.C. Verkade, *Inorg. Synth.* 11 (1968) 108.
- [27] G. Cavinato, A. Vavasori, L. Toniolo, A. Dolmella, *Inorg. Chim. Acta* 357 (2004) 2737.
- [28] A. Vavasori, G. Cavinato, L. Toniolo, *J. Mol. Catal. A: Chem.* 176 (2001) 11.
- [29] G. Cavinato, L. Toniolo, A. Vavasori, *J. Mol. Catal. A: Chem.* 219 (2004) 233.
- [30] G.M. Sheldrick, SHELXTL/PC, Version 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994;
- [31] G.M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.
- [32] J. Vicente, A. Arcas, D. Bautista, P.G. Jones, *Organometallics* 16 (1997) 2127.
- [33] G.J. Kubas, C.J. Burns, G.R.K. Khaisa, L.S. Van Der Sluys, G. Kiss, C.D. Hoff, *Organometallics* 11 (1992) 3390.
- [34] D.M. Branan, N.W. Hoffman, E.A. McElroy, N. Prokopuk, A.B. Salazar, M.J. Robbins, W.E. Hill, T.R. Webb, *Inorg. Chem.* 30 (1991) 1200.
- [35] U. Bohner, G. Zundel, *J. Phys. Chem.* 89 (1985) 1408.
- [36] E. Horn, M.R. Snow, *Aust. J. Chem.* 37 (1984) 1375.
- [37] O.H. Bailey, A. Ludi, *Inorg. Chem.* 24 (1985) 2582.
- [38] W. Lasser, U. Thewalt, *J. Organomet. Chem.* 302 (1986) 201.
- [39] E.A. Robinson, *Can. J. Chem.* 391 (1961) 247.
- [40] C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- [41] F.H. Allen, *Acta Crystallogr. B* 58 (2002) 380.
- [42] F.H. Allen, W.D.S. Motherwell, *Acta Crystallogr. B* 58 (2002) 407.
- [43] Cambridge Crystallographic Database (Version 5.29 of November 2007).
- [44] O.P. Anderson, A.B. Packard, *Inorg. Chem.* 18 (1979) 1129.
- [45] J. Campora, J.A. Lopez, P. Palma, P. Valerga, E. Spillner, E. Carmona, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 147.
- [46] R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, P.N. Horton, M.B. Hursthouse, M.E. Light, *Organometallics* 22 (2003) 987.
- [47] A.D. Burrows, M.F. Mahon, M. Varrone, *J. Chem. Soc., Dalton Trans.* (2003) 4718.
- [48] M. Yamashita, I. Takamiya, K. Jin, K. Nozaki, *Organometallics* 25 (2006) 4588.
- [49] D.B. Grotjahn, Y. Gong, L. Zakharov, J.A. Golen, A.L. Rheingold, *J. Am. Chem. Soc.* 28 (2006) 438.
- [50] C.J. Chapman, C.G. Frost, M.F. Mahon, *J. Chem. Soc., Dalton Trans.* (2006) 2251.
- [51] T. Kochi, K. Yoshimura, K. Nozaki, *J. Chem. Soc., Dalton Trans.* (2006) 25.
- [52] D.K. Newsham, S. Borkar, A. Sen, D.M. Conner, B.L. Goodall, *Organometallics* 26 (2007) 3636.
- [53] W. Weng, C.-H. Chen, B.M. Foxman, O.V. Ozerov, *Organometallics* 26 (2007) 3315.
- [54] M. Agostinho, P. Braunstein, C. R. Chim. 10 (2007) 666.
- [55] M. Agostinho, P. Braunstein, R. Welter, *J. Chem. Soc., Dalton Trans.* (2007) 759.
- [56] M. Agostinho, P. Braunstein, *Chem. Commun.* (2007) 58.
- [57] L.N. Zhir-Lebed, L.G. Kuz'mina, Y.T. Struchkov, O.N. Temkin, V.A. Golodov, *Koord. Khim.* 4 (1978) 1046.
- [58] G. Del Piero, M. Cesari, *Acta Crystallogr. B* 35 (1979) 2411.
- [59] R. Santi, A.M. Romano, R. Garrone, R. Millini, *J. Organomet. Chem.* 566 (1998) 37.
- [60] E. Gallo, F. Ragaini, S. Cenini, F. Demartin, *J. Organomet. Chem.* 586 (1999) 190.
- [61] J. Ruiz, M.T. Martinez, F. Florenciano, V. Rodriguez, G. Lopez, J. Perez, P.A. Chaloner, P.B. Hitchcock, *Inorg. Chem.* 42 (2003) 3650.
- [62] Y. Nishihara, Y. Inoue, M. Itazaki, K. Takagi, *Org. Lett.* 7 (2005) 2639.
- [63] F. Rivetti, U. Romano, *J. Organomet. Chem.* 174 (1979) 221.
- [64] G. Cavinato, L. Toniolo, *J. Organomet. Chem.* 444 (1993) C65.
- [65] V.N. Zudin, G.N. Il'inch, V.A. Likhoholov, Y.I. Yermakov, *J. Chem. Soc. Chem. Commun.* (1984) 545.
- [66] V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Likhoholov, Yu.I. Yermakov, *J. Organomet. Chem.* 289 (1985) 425.
- [67] V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Rogov, V.A. Likhoholov, Yu.I. Yermakov, *J. Mol. Catal.* 52 (1989) 27.
- [68] G. Cavinato, L. Toniolo, A. Vavasori, in: M. Beller (Ed.), *Catalytic Carbonylation Reactions*, 18, Springer, 2006, p. 125 (Top. Organomet. Chem.).
- [69] W.G. Reman, G.B.J. De boer, S.A.J. Van Langen, A. Nahuijsen (Shell), *Eur. Pat.*, EP 411721 A3 (1991).
- [70] R.P. Tooze, K. Whiston, A.P. Malyan, M.J. Taylor, N.W. Wilson, *J. Chem. Soc., Dalton Trans.* (2000) 3441.
- [71] P.W.N.M. van Leeuwen, M.A. Zuideveld, B.H.G. Swennenhuis, Z. Freixa, P.C.J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A.L. Spek, *J. Am. Chem. Soc.* 125 (2003) 5523.
- [72] G. Cavinato, L. Toniolo, *J. Organomet. Chem.* 398 (1990) 187.

¹ This is the preferred geometry, however, in solution it is likely that *cis*-species are also present, as it is well known that this geometry favors the insertion reactions as well as the product-forming step [70].