

On the mechanism of hydroesterification of styrene using an in situ-formed cationic palladium complex

A. Seayad^a, S. Jayasree^a, K. Damodaran^a, L. Toniolo^b, R.V. Chaudhari^{a,*}

^a Homogenous Catalysis Division, National Chemical Laboratory, Pune 411008, India

^b Dipartimento di Chimica, Università di Venezia, Calle Large-S, Marta 2137-30123, Venice, Italy

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Abstract

The mechanism of hydroesterification of styrene using in situ-formed $\text{Pd}(\text{OTs})_2(\text{PPh}_3)_2$ from $\text{Pd}(\text{OAc})_2$, PPh_3 and TsOH in methanol has been investigated by isolation and characterisation of catalytically active intermediates. From reaction mixtures, Pd–hydridocarbonyl and Pd–acyl complexes were isolated and characterised, based on which a Pd hydride mechanism has been proposed. Formation of palladium hydride species has also been confirmed by ^{31}P -NMR experiments. © 2000 Elsevier Science S.A. All rights reserved.

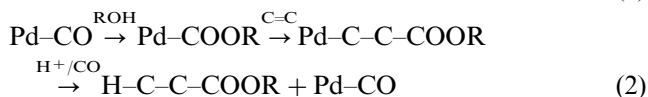
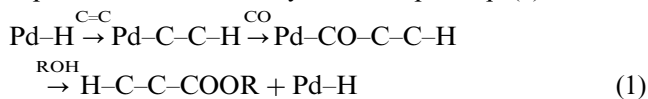
Keywords: Hydroesterification; Carbonylation; Styrene; Palladium; Mechanism; Catalytic cycle

1. Introduction

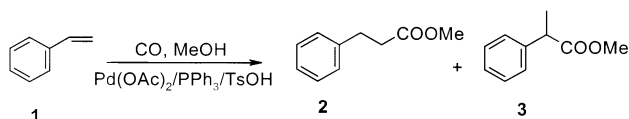
Carbonylation of vinyl aromatics [1] is an environmentally clean synthetic route [2] for the preparation of arylpropionic acids, especially 2-arylpropionic acids [3] such as Ibuprofen [4] and Naproxen [5], a class of non-steroidal anti-inflammatory agents. Palladium complexes have generally been used as catalysts along with halide promoters [6]. Formation of both branched as well as linear isomers was observed in these reactions and the regioselectivity and reaction rates vary depending on the catalyst system and the reaction conditions used [7]. The use of cationic palladium complexes provides a halogen-free catalyst system for such reactions under mild reaction conditions [8]. Recently, we have reported a detailed study on the hydroesterification of styrene using $\text{Pd}(\text{OTs})_2(\text{PPh}_3)_2$ (**I**), formed in situ from

a mixture of $\text{Pd}(\text{OAc})_2$, PPh_3 and TsOH as the catalyst precursor system [9]. Since this catalytic system is found to be promising with respect to catalytic activity and selectivity and eliminates the use of corrosive promoters, a detailed investigation on the mechanistic aspects has been carried out and presented in this paper based on the isolation and characterisation of active catalytic intermediates.

Two mechanistic pathways proposed for the hydroesterification of olefins catalysed by palladium complexes are (a) hydride mechanism [10], which is initiated by the insertion of an olefin into a palladium–hydride bond and proceeds through the formation of an acyl complex as shown in Eq. (1), and (b) alkoxy mechanism [11], which is initiated by the insertion of an olefin into a palladium–carboalkoxy bond as per Eq. (2).



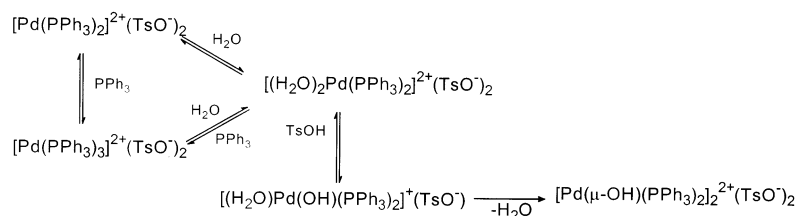
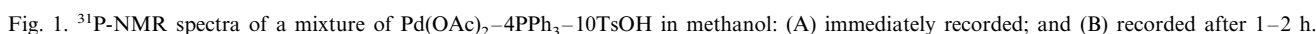
In principle, both the mechanisms can be operative for the hydroesterification of styrene (Scheme 1) using the present catalyst system consisting of $\text{Pd}(\text{OAc})_2$, PPh_3 and TsOH in methanol as a solvent. However, the



Scheme 1. Hydroesterification of styrene.

* Corresponding author. Tel.: +91-20-5893163; fax: +91-20-5893260.

E-mail address: rvc@ems.ncl.res.in (R.V. Chaudhari)



Scheme 2.

2. Results and discussion

in polar solvents like methanol as evidenced from ^{31}P -NMR analysis, which showed three signals at 37.06 (δ_1), 30.58 (δ_2) and 29.19 (δ_3) ppm. These signals are assigned to the dicationic complexes $[\text{Pd}(\text{PPh}_3)_2]^{2+}(\text{TsO}^-)_2$, $[(\text{H}_2\text{O})_2\text{Pd}(\text{PPh}_3)_2]^{2+}(\text{TsO}^-)_2$ and $[\text{Pd}(\text{PPh}_3)_3]^{2+}(\text{TsO}^-)_2$, respectively, according to the values reported in the literature for similar palladium dicationic complexes [13]. This solution showed a different spectrum after standing for 1–2 h. Two new signals at 38.35 (δ_4) and 33.82 (δ_5) ppm developed at the expense of δ_1 , δ_2 and δ_3 as shown in Fig. 1. This change in the spectrum is due to the degradation of the above-mentioned Pd-dicationic species in the presence of residual water present in the solvent (ca. 1000 ppm). The signal at δ_4 corresponds to a dicationic species $[\text{Pd}(\mu\text{-OH})(\text{PPh}_3)_2]^{2+}(\text{TsO}^-)_2$ [14], which can be formed as shown in Scheme 2. Our earlier studies [9]

also showed that the isolated $\text{Pd}(\text{OTs})_2(\text{PPh}_3)_2$ was highly moisture sensitive and changed to a sticky mass in the solid state when exposed to air for 10–15 min. The signal at δ_5 is assigned to triphenylphosphine oxide, $\text{O}=\text{PPh}_3$, in comparison with a standard sample in methanol¹.

When the catalyst precursor system ($\text{Pd}(\text{OAc})_2-4\text{PPh}_3-10\text{TsOH}$) was treated with CO (500 psig) at 75°C for 30 min, shining white flakes of a complex were observed on cooling the reactor contents to room temperature. The supernatant solution was light yellow in colour, which changed to black slowly on exposure to air showing the precipitation of palladium metal. The white complex was found to be highly unstable and changed immediately to a light yellow and then to a brown complex and finally to Pd metal. IR and ^1H -NMR spectra of the white complex were taken immediately. IR spectra showed absorption at 2154 cm^{-1} corresponding to Pd–H [15] in addition to a carbonyl absorption at 1955.7 cm^{-1} . ^1H -NMR spectra showed a weak Pd–H signal at -5.9 ppm . This Pd–H signal was found to be different from that observed from a mixture of $\text{Pd}(\text{PPh}_3)_4$ with excess TsOH in CDCl_3 , which showed two Pd–H signals at -6.7 and -7.3 ppm , corresponding to $[\text{HPd}(\text{PPh}_3)_2\text{S}]^+(\text{TsO}^-)$ and $[\text{HPd}(\text{PPh}_3)_3]^+(\text{TsO}^-)$, respectively, where S is a solvent molecule. The in situ formation of palladium hydride species from a mixture of Pd(0) complexes and acidic promoters has also been reported earlier [16]. The yellow flakes that formed from the white complex showed only the carbonyl absorption at 1955.5 cm^{-1} and no signal corresponding to Pd–H was observed in IR or in ^1H -NMR spectra. Elemental analysis of this complex showed the presence of phosphorus and sulfur. Further characterisations were difficult due to its instability even under inert atmosphere and at lower temperature. From the decomposed solution of the complex in CDCl_3 , transparent faint yellow crystals were obtained in addition to palladium metal. The crystal was identified as $\text{PdCl}_2(\text{PPh}_3)_2 \cdot \text{CDCl}_3$ (by crystallography) and may form by the interaction of palladium hydride with the residual HCl present in CDCl_3 . With these evidences, it is proposed that the isolated palladium hydride complex has a formula $[\text{HPd}(\text{CO})(\text{PPh}_3)_2]^+(\text{TsO}^-)$ (VI). Palladium hydrides are generally quite unstable for isolation [17] and have been fully characterised only in a few cases [18]. Even though the bridged binuclear palladium hydridocarbonyl species has been well characterised [19], no mononuclear analogue has been isolated and characterised though it has been proposed [20]. A platinum analogue of VI was reported earlier [21].

¹ 26.5 ppm in DMF as the solvent, $\text{PPh}_3=\text{O}$ can be formed by the interaction of H_2O with Pd–phosphine complexes as explained by Amatore et al. [13a].

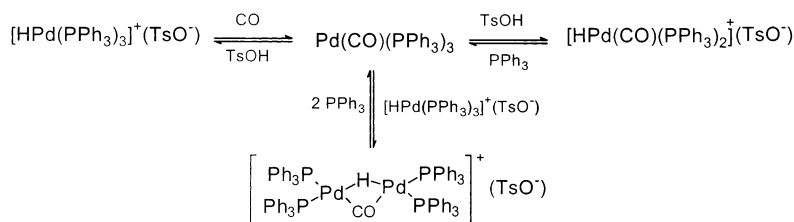
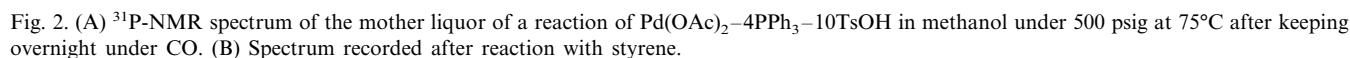
No Pd–methoxy complexes were isolated in the above case in the presence of excess TsOH. But when the same reaction was carried out in the absence of TsOH, a yellow microcrystalline complex, which turned to red, was obtained on cooling the reactor contents to room temperature. IR spectra of this complex showed two characteristic strong carbonyl absorptions at 1955 and 1860 cm^{-1} corresponding to $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ and $[\text{Pd}(\text{CO})(\text{PPh}_3)]_n$, respectively [22]. ^{31}P -NMR spectra of this mixture of complexes showed three signals at 27.43 (δ_6), 22.19 (δ_7) and 20.12 (δ_8) ppm in DMF as a solvent. The ^{31}P -NMR spectrum of the mother liquor after isolating the above complex showed three weak signals at 19.02 (δ_9), 19.62 (δ_{10}) and 19.92 (δ_{11}) ppm in addition to a sharp signal at -4.13 ppm corresponding to free PPh_3 . A pale yellow complex was isolated on evaporation of the solvent, the IR spectrum of which showed strong carbonyl absorptions at 1671 and 1654 cm^{-1} and at 1304 and 1060 cm^{-1} corresponding to $\text{Pd}(\text{COOMe})(\text{OAc})(\text{PPh}_3)_2$ as well as very weak absorptions at 1630 and 1010 cm^{-1} corresponding to $\text{Pd}(\text{COOMe})_2(\text{PPh}_3)_2$ [23].

When the same reaction was carried out with two equivalents of TsOH, pale yellow shining flakes of a complex were obtained, which showed a carbonyl absorption at 1955 cm^{-1} corresponding to $\text{Pd}(\text{CO})(\text{PPh}_3)_3$. Evaporation of the mother liquor gave a yellow complex, which also showed strong absorption at 1955 cm^{-1} along with weak carbonyl absorptions at 1751 and 1625 cm^{-1} . No carbonyl absorption corresponding to the carbomethoxy complex was observed in this case. This suggests that formation of palladium–carbomethoxy complexes is quite unlikely in the presence of TsOH. The instability of carbomethoxy species in acidic medium has also been reported earlier [24].

In order to further investigate the nature of the species formed in solution in the presence of CO under reaction conditions (75°C and 500 psig of CO), experiments were performed in which intermediate liquid samples were taken under CO atmosphere followed by ^{31}P -NMR analysis. An intermediate sample from the reaction of $\text{Pd}(\text{OAc})_2-4\text{PPh}_3$ with excess of TsOH (ten equivalents) under 500 psig of CO at 75°C showed a signal at 30.52 ppm (δ_{12}) and a broad signal between 18 and 25 ppm (δ_{13}) along with a small signal at δ_5 (that of $\text{O}=\text{PPh}_3$). The broad signal can be assigned to Pd(0) carbonyls in fast equilibrium with free PPh_3 as per Eq. (3).



When the spectrum was recorded with styrene immediately added to a fresh intermediate sample of the above reaction, two new signals were found to develop at 23.65 (δ_{14}) and 24.09 (δ_{15}) ppm at the expense of the signal at δ_{12} . The broad signal at δ_{13} also disappeared



Scheme 3.

$$\text{Pd}(\text{PPh}_3)_4 \xrightleftharpoons{\text{PPh}_3} \text{Pd}(\text{PPh}_3)_3 \xrightleftharpoons{\text{PPh}_3} \text{Pd}(\text{PPh}_3)_2 \quad (4)$$

reaction was carried out under similar conditions to those in which **VI** was isolated. The supernatant liquid after keeping overnight under CO showed a signal at δ_{12} along with signals at δ_5 , δ_{16} and δ_{17} . A new signal at 23.34 (δ_{19}) was also observed in this case. Styrene was added to this reaction mixture (containing the white flakes and the mother liquor) and stirred under CO atmosphere at 40°C for 10 min. The intermediate sample of this reaction also showed the development of signals δ_{14} and δ_{15} at the expense of the signals at δ_{12} and δ_{19} , in addition to a broad signal at δ_4 (Fig. 2). This further confirms that the signal at δ_{12} corresponds to the palladium hydride species **VI**. The signal at δ_{19} can be assigned to a bridged hydrido-carbonyl species $[\text{Pd}(\mu\text{-H})(\mu\text{-CO})(\text{PPh}_3)_2]_2^+(\text{TsO}^-)$ (in comparison with the value reported in the literature for similar complexes) [27], which may form an equilibrium as shown in Scheme 3.



The isolation of Pd–H as well as Pd–acyl complexes under reaction conditions confirms the involvement of the hydride mechanism for the hydroesterification of styrene using Pd(OAc)₂–PPh₃–TsOH as the catalyst system. As shown in Scheme 5, the catalytic cycle starts with the insertion of styrene into the Pd–H bond [33] of the active palladium hydrido carbonyl species **VI** forming the Pd–alkyl complex (**VIII** or **X**), which on migratory insertion of CO gives the Pd–acyl complex (**XI** or **XII**). The formation of product esters from the palladium–acyl complex is the final step in the catalytic cycle, which generates the active palladium hydride for further catalysis. Methanol can attack the palladium–acyl complex in two ways, i.e. through coordination to the acyl complex or by the direct nucleophilic attack as explained by Lin and Yamamoto [34] for the hydroesterification of benzylic halides. Though both the modes of attack may be operating in the present system, most

The mechanism of hydroesterification of styrene using in situ-formed $\text{Pd}(\text{OTs})_2(\text{PPh}_3)_2$ complex from $\text{Pd}(\text{OAc})_2\text{-PPh}_3\text{-TsOH}$ as the catalyst precursor system was investigated. The catalytic cycle was found to proceed through a hydride mechanism rather than a methoxy mechanism. The hydride mechanism was confirmed by characterisation of isolated active palladium hydride and palladium-acyl complexes, which are the key intermediates in the catalytic cycle. ^{31}P -NMR experiments carried out to investigate the nature of species formed in solution in the presence of CO under reaction conditions also confirmed the formation of Pd-H as well as the Pd-alkyl species.

Styrene, Pd(OAc)₂, PdCl₂, *p*-toluenesulphonic acid monohydrate (Aldrich, USA), PPh₃ (Loba Chemie, India), and CO (Matheson, USA) were used as received without further purification. Methanol was distilled and degassed with argon before use and the water content was analysed to be ca. 1000 ppm. Other solvents were also distilled and degassed before use. Gas chromatographic analysis was done on a Hewlett Packard 5890 Series GC, controlled by the HP Chemstation software, by using an FFAP megabore column (30 m × 0.53 mm × 0.1 µm film thickness, on a poly ethyleneglycol

stationary phase). Elemental analysis of the complexes was carried out on a CHNS-O EA1108 Elemental Analyser of Carlo Erba Instruments, Italy, and the ion chromatography on a Waters Ion Chromatograph, Austria, having Waters 432 Conductivity Detector, Waters 600S Controller and Waters 626 Pump. ^1H -, ^{13}C - and ^{31}P -NMR spectra were recorded by Bruker MSL-300 and Bruker AC-200 spectrometers. The ^1H - and ^{13}C -NMR chemical shift values are given relative to TMS and those of ^{31}P -NMR (121.19 MHz) are given relative to external 85% H_3PO_4 . The IR spectra in DRS mode were obtained from a Shimadzu Hyper IR by mixing samples with KBr and in transition mode using a Perkin–Elmer Spectrum-2000 IR spectrometer.

4.1. Hydroesterification experiments

The hydroesterification reactions were performed in a 50 ml Parr autoclave, the details of which were given in Refs. [8b,9]. In a typical experiment, known quantities of styrene, $\text{Pd}(\text{OAc})_2$, PPh_3 , TsOH and methanol were charged into the autoclave, and the contents were flushed with nitrogen and then with CO. The autoclave was heated to 75°C , and after attaining the temperature, the system was pressurised with CO to 500 psig. The reaction was initiated by agitation (900 rpm). In order to maintain pressure in the reactor, CO was fed through a constant pressure regulator from a reservoir vessel. After the reaction, the liquid samples were analysed by gas chromatography.

4.2. Isolation of $[\text{HPd}(\text{CO})(\text{PPh}_3)_2]^+(\text{TsO}^-)$ (VI)

A mixture of $\text{Pd}(\text{OAc})_2$ (0.223 mmol), PPh_3 (0.892 mmol), and TsOH (2.23 mmol) was charged to the autoclave, flushed with nitrogen and subsequently with CO, heated to 75°C , charged with 500 psig of CO and stirred for 0.5–1 h. The reaction mixture was then cooled to room temperature (r.t.) and kept under CO atmosphere for 2–6 h. After depressurising CO and flushing with argon, the white flake-like complex obtained was transferred to a Schlenk flask under argon atmosphere and the complex was allowed to settle down. The mother liquor was decanted³ and the complex washed with degassed methanol and *n*-hexane successively and dried under vacuum to obtain the complex VI, which is highly air sensitive and becomes reddish brown within a few minutes of exposure to air and was only moderately stable under argon atmosphere. IR and NMR spectra were taken immediately. IR (DRS, KBr): 2154 (ν , Pd–H), 1955.7 (ν , Pd–CO) cm^{-1} . ^1H -NMR (CDCl_3), δ –5.90 (s, Pd–H), 2.10 (s, 3H, CH_3 of TsOH), 7.50–8.10 (m, 35H, Ph of PPh_3 and

TsO^-). The complex VI changed to a light yellow complex within a few minutes under argon atmosphere and the IR spectrum of the resulting complex showed no Pd–H signal at 2154 cm^{-1} and δ –5.9 ppm (^1H -NMR), while the carbonyl peak at 1955.7 cm^{-1} in the IR spectrum was retained.

4.3. Isolation of palladium–acyl complexes (XI and XII)

Hydroesterification of styrene (7.2 mmol) was carried out using a mixture of $\text{Pd}(\text{OAc})_2$ (0.223 mmol), PPh_3 (0.892 mmol) and TsOH (2.23 mmol) in methanol with low water content (200–500 ppm) at 55°C and 500 psig of CO for 1–2 h. The contents in the reactor were cooled to r.t. and kept for 2 days under CO atmosphere. The yellow needle-shaped air-sensitive crystals obtained were transferred to a Schlenk flask under argon atmosphere and isolated as per the procedure given for the isolation of VI. IR and NMR spectra of the complex were taken immediately. IR (DRS, KBr): 1687 (Pd–CO–St), 1463, 1377, cm^{-1} . ^1H -NMR⁴ (CDCl_3): δ 1.05 (s, CH_3), 1.60 (Pd–CO– CH_2 – CH_2), 2.20 (Pd–CO– CH_2), 2.30 (s, CH_3 of TsO^-), 3.60 (Pd–CO–CH), 7.10–7.70 (m, Ph of PPh_3 and TsO^-), 7.70–8.10 (m, Ph of acyl).

The complex changed immediately to reddish brown on exposure to air in solid state and also decomposed within a few minutes to palladium metal. ^1H -NMR spectroscopy showed that the isolated complex was a mixture of iso (XI) and linear (XII) coordinated palladium acyl complex.

4.4. Preparation of $\text{PdCl}(\text{PPh}_3)_2(\text{COCH}_2\text{CH}_2\text{Ph})$ (XIII)

Hydroesterification of styrene (7.2 mmol) was carried out with PdCl_2 (0.565 mmol), PPh_3 (2.29 mmol), and TsOH (5.65 mmol) in methanol under 75°C and 500 psig of CO for 2–3 h. The contents in the reactor were cooled to r.t., CO depressurised and the reaction mixture kept in a freezer below 0°C for 2 days. The white crystals formed were transferred to a Schlenk flask under argon atmosphere and isolated as per the procedure given for the isolation of complex VI. IR (DRS, KBr): 1685.7 cm^{-1} (Pd–CO–St). ^1H -NMR (CDCl_3): δ 1.60 (t, 2H, Pd–CO– CH_2 – CH_2), 2.50 (t, 2H, Pd–CO– CH_2), 7.40–7.70 (m, 30H, Ph of PPh_3), 7.70–7.90 (m, 5H, Ph of acyl ligand). ^{13}C -NMR (CDCl_3): δ 234 (Pd–CO–St), 59.84 (Pd–CO– CH_2), 32.92 (Pd–CO– CH_2 – CH_2), 125–141 (Ph of PPh_3 and acyl ligand). ^{31}P -NMR (CDCl_3): δ 19.98 s. Anal. Calc.⁵ for

³ Decantation was done because the complex decomposes to a brownish mass on filtration.

⁴ The NMR spectrum was poorly developed because of the decomposition of the compound.

⁵ The difference in calculated and experimental values is due to the presence of a small amount of the linear ester product adhering to the complex.

C₄₅H₃₉ClOP₂Pd: C, 67.59; H, 4.91; Cl, 4.43; P, 7.74. Found: C, 66.36; H, 5.07; Cl, 4.10; P, 6.23%.

4.5. ³¹P-NMR experiments

Samples for ³¹P-NMR experiments were prepared by mixing Pd(OAc)₂ (0.022 mmol), PPh₃ (0.088 mmol) and TsOH (0.22 mmol) in 2.5 ml of degassed methanol in a 10 mm NMR tube flushed with argon. The spectra were recorded at 121.1 MHz by using 85% H₃PO₄ as the external standard and internal D₂O (added in a capillary tube) as the deuterium source. For preparation of samples under CO pressure, Pd(OAc)₂ (0.112 mmol), PPh₃ (0.448 mmol) and TsOH (1.12 mmol) in 15 ml of degassed methanol were charged to the 50 ml autoclave, flushed with argon followed by CO, heated to 75°C, pressurised to 500 psig with CO and kept under stirring for 30 min. Intermediate samples were directly taken under CO atmosphere to the NMR tube with the help of a sampling device and the spectra recorded as stated above.

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References

- [1] (a) A. Mullen, in: J. Falbe (Ed.), *New Synthesis with Carbon Monoxide*, Springer, Berlin, 1980, p. 243. (b) B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 1, VCH, Weinheim, 1996. (c) H.M. Colquhoun, D.J. Thompson, M.V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum, New York, 1991.
- [2] (a) R.A. Sheldon, *Chem. Ind.* (1992) 903. (b) R.A. Sheldon, *J. Chem. Tech. Biotechnol.* 68 (1997) 381. (c) C.B. Dartt, M.E. Davis, *Ind. Eng. Chem. Res.* 33 (1994) 2887.
- [3] (a) J.P. Rieu, A. Boucherle, H. Cousse, G. Mouzin, *Tetrahedron* 42 (1986) 4095. (b) H.R. Sonawane, N.S. Bellur, J.R. Ahuja, D.G. Kulkarni, *Tetrahedron: Asymmetry* 3 (1992) 163.
- [4] V. Elango, M.A. Murphy, G.N. Mott, E.G. Zey, B.L. Smith, G.L. Moss, *EP* 400 892, 1990.
- [5] (a) H. Zhou, J. Cheng, S. Lu, H. Fu, H. Wang, *J. Organomet. Chem.* 556 (1998) 239. (b) A. Seayad, S. Jayasree, R.V. Chaudhari, *Catal. Lett.* 61 (1999) 99.
- [6] (a) J. Tsuji, *Palladium Reagents and Catalysis: Innovations in Organic Synthesis*, Wiley, New York, 1997. (b) E. Billig, R.L. Pruet, in: J.J. Zuckerman, A.D. Norman (Eds.), *Inorganic Reactions and Methods*, vol. 16, VCH, New York, 1993, pp. 364.
- [7] (a) D.M. Fenton, *J. Org. Chem.* 38 (1973) 3192. (b) T. Hiyama, N. Wakasa, T. Kusumoto, *Synlett* (1991) 569. (c) J.Y. Yoon, E.J. Jang, K.H. Lee, J.S. Lee, *J. Mol. Catal. A: Chem.* 118 (1997) 181. (d) K. Nozaki, M.L. Kantam, T. Horiuchi, H. Takaya, *J. Mol. Catal. A: Chem.* 118 (1997) 247. (e) K. Bittler, N.V. Kutepow, D. Neubauer, H. Reis, *Angew. Chem. Int. Ed. Engl.* 7 (1968) 329. (f) Y. Sugi, K. Bando, S. Shin, *Chem. Ind.* (1975) 397. (g) Y. Sugi, K. Bando, *Chem. Lett.* (1976) 727. (h) A. Seayad, S. Jayasree, R.V. Chaudhari, *Org. Lett.* 1 (1999) 459.
- [8] (a) S. Oi, M. Nomura, T. Aiko, Y. Inoue, *J. Mol. Catal. A: Chem.* 115 (1997) 289. (b) A. Seayad, A.A. Kelkar, R.V. Chaudhari, L. Toniolo, *Ind. Eng. Chem. Res.* 37 (1998) 2180.
- [9] A. Seayad, A.A. Kelkar, L. Toniolo, R.V. Chaudhari, *J. Mol. Catal. A: Chem.* 151 (2000) 47.
- [10] (a) J.F. Knifton, *J. Org. Chem.* 41 (1976) 793. (b) J.F. Knifton, *J. Org. Chem.* 41 (1976) 2885. (c) G. Cavinato, L. Toniolo, *J. Organomet. Chem.* 398 (1990) 187. (d) M. Sperrle, G. Consiglio, *Chem. Ber.* 130 (1997) 1557.
- [11] (a) D. Milstein, *Acc. Chem. Res.* 21 (1988) 428. (b) D.M. Fenton, *J. Org. Chem.* 38 (1973) 3192. (c) R.F. Heck, *J. Am. Chem. Soc.* 94 (1972) 2712. (d) A. Schoenberg, I. Bartoletti, R.F. Heck, *J. Org. Chem.* 39 (1974) 3318.
- [12] R. Bertani, G. Cavinato, L. Toniolo, G. Vasapollo, *J. Mol. Catal.* 84 (1993) 165.
- [13] (a) C. Amatore, A. Jutand, M.J. Medeiros, *New J. Chem.* 20 (1996) 1143. (b) V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Rogov, V.A. Likhonolov, Yu.I. Yermakov, *J. Mol. Catal.* 52 (1989) 27.
- [14] S. Ganguly, J.T. Mague, D.M. Roundhill, *Inorg. Chem.* 31 (1992) 3831.
- [15] P. Leoni, M. Sommovigo, M. Pasquali, S. Midollini, D. Braga, P. Sabatino, *Organometallics* 10 (1991) 1038.
- [16] Y. Kushino, K. Itoh, M. Miura, M. Nomura, *J. Mol. Catal.* 89 (1994) 151.
- [17] (a) V.V. Grushin, *Chem. Rev.* 96 (1996) 2011. (b) D.L. Reger, D.G. Garza, *Organometallics* 12 (1993) 554.
- [18] (a) H. Munakata, M.L.H. Green, *Chem. Commun.* (1971) 881. (b) M.L.H. Green, H. Munakata, *J. Chem. Soc. A.* (1971) 469. (c) E.H. Brooks, F. Glockling, *J. Chem. Soc. A.* (1967) 1030. (d) A.L. Seligson, R.L. Cowan, W.C. Troglor, *Inorg. Chem.* 30 (1991) 3371.
- [19] (a) M. Portnoy, F. Frolow, D. Milstein, *Organometallics* 10 (1991) 3960. (b) I. Tóth, C.J. Elsevier, *Organometallics* 13 (1994) 2118. (c) A.R. Siedle, R.A. Newmark, W.B. Gleason, *Inorg. Chem.* 30 (1991) 2005. (d) M. Portnoy, D. Milstein, *Organometallics* 13 (1994) 600.
- [20] (a) B.El. Ali, H. Alper, *J. Mol. Catal.* 33 (1992) 7. (b) N. Koga, K. Morokuma, *J. Am. Chem. Soc.* 107 (1985) 7230.
- [21] H.C. Clark, K.R. Dixon, *J. Am. Chem. Soc.* 91 (1969) 596.
- [22] (a) A. Misono, Y. Uchida, M. Hidai, K. Kudo, *J. Organomet. Chem.* 20 (1969) P7. (b) K. Kudo, M. Hidai, Y. Uchida, *J. Organomet. Chem.* 33 (1971) 393.
- [23] F. Rivetti, U. Romano, *J. Organomet. Chem.* 154 (1978) 323.
- [24] A. Dervisi, P.G. Edwards, P.D. Newman, R.P. Tooe, S.J. Coles, M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.* (1999) 1113.
- [25] C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, G. Meyer, *Organometallics* 14 (1995) 5605. (b) C. Amatore, A. Jutand, M.A. M'Barki, *Organometallics* 11 (1992) 3009. (c) C. Amatore, A. Jutand, F. Khalil, M.A. M'Barki, L. Mottier, *Organometallics* 12 (1993) 3168.
- [26] (a) V.V. Grushin, H. Alper, *Organometallics* 15 (1996) 5242. (b) A. Jutand, A. Mosleh, *Organometallics* 14 (1995) 1810.
- [27] (a) V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Likhonolov, Yu.I. Ermakov, *J. Organomet. Chem.* 289 (1985) 425. (b) R.M. Laine, E.J. Crawford, *J. Mol. Catal.* 44 (1988) 357.
- [28] A. Vavasori, L. Toniolo, *J. Mol. Catal. A: Chem.* 110 (1996) 13.
- [29] (a) T. Yoshida, Y. Ueda, S. Otsuka, *J. Am. Chem. Soc.* 100 (1978) 3941. (b) E. Drent, *Pure. Appl. Chem.* 62 (1990) 661.
- [30] G. Cavinato, L. Toniolo, *J. Mol. Catal.* 10 (1981) 161.
- [31] R. Bardi, A. Del Pra, A.M. Piazzesi, L. Toniolo, *Inorg. Chem. Acta* 35 (1979) L345.
- [32] R. Bardi, A.M. Piazzesi, A. Del Pra, G. Cavinato, L. Toniolo, *Inorg. Chem. Acta* 102 (1985) 99.
- [33] Cs. Benedek, Sz. Törös, B. Heil, *J. Organomet. Chem.* 586 (1999) 85.
- [34] Y. Lin, A. Yamamoto, *Organometallics* 17 (1998) 3466.