Methoxycarbonylation of olefins catalyzed by palladium complexes bearing *P*,*N*-donor ligands†

Pedro A. Aguirre,*[a] Carolina A. Lagos,[a] Sergio A. Moya,[b] César Zúñiga,[b] Cristian Vera-Oyarce,[b] Eduardo Sola,[c] Gabriel Peris[d] and J. Carles Bayón*[e]

Received 27th March 2007, Accepted 30th August 2007
First published as an Advance Article on the web 25th September 2007
DOI: 10.1039/b704615b

The methoxycarbonylation of alkenes catalyzed by palladium(II) complexes with *P*,*N*-donor ligands, 2-(diphenylphosphinoamino)pyridine (Ph_2PNHpy), 2-[(diphenylphosphino)methyl]pyridine (Ph_2PCH_2py), and 2-(diphenylphosphino)quinoline (Ph_2Pqn) has been investigated. The results show that the complex $[PdCl(PPh_3)(Ph_2PNHpy)]Cl$ or an equimolar mixture of $[PdCl_2(Ph_2PNHpy)]$ and PPh_3, in the presence of *p*-toluensulfonic acid (TsOH), is an efficient catalyst for this reaction. This catalytic system promotes the conversion of styrene into methyl 2-phenylpropanoate and methyl 3-phenylpropanoate with nearly complete chemoselectivity, 98% regioselectivity in the branched isomer, and high turnover frequency, even at alkene/Pd molar ratios of 1000. Best results were obtained in toluene–MeOH (3 : 1) solvent. The Pd/Ph_2PNHpy catalyst is also efficient in the methoxycarbonylation of cyclohexene and 1-hexene, although with lower rates than with styrene. Related palladium complexes $[PdCl(PPh_3)L]Cl$ (L = Ph_2PCH_2py and Ph_2Pqn) show lower activity in the methoxycarbonylation of styrene than that of the 2-(diphenylphosphinoamino)pyridine ligand. Replacement of the last ligand by (diphenylphosphino)phenylamine (Ph_2PNHPh) or 2-(diphenylphosphinoaminomethyl)pyridine ($Ph_2PNMepy$) also reduces significantly the activity of the catalyst, indicating that both the presence of the pyridine fragment as well as the NH group, are required to achieve a high performing catalyst. Isotopic labeling experiments using MeOD are consistent with a hydride mechanism for the $[PdCl(PPh_3)(Ph_2PNHpy)]Cl$ catalyst.

Introduction

Transition metal catalyzed hydrocarboxylation and hydroesterification of alkenes are attractive reactions for the synthesis of valuable products for fine chemistry.[1] In particular, a series of commercial non-steroidal anti-inflammatory agents are accessible through the reaction of vinyl aromatics with CO and H_2O or alcohols in the presence of a Pd catalyst.[2] For this process, high regioselectivities in the branched or linear product can be obtained, because the regioselectivity of the reaction is strongly dependent on the catalytic system employed, as well as the reaction conditions used.[3] Palladium–phosphine catalysts favor the formation of branched esters, while diphosphine leads to linear esters,[4] although both the bite angle of the chelate and electronic effects can strongly affect the selectivity of the reaction.[5] A significant effect on the selectivity of the counterion of the acid co-catalyst required for this reaction has been also reported.[6] Furthermore, in addition to phosphines, other ligands, such as *S*- and *N*-donor types, have been also used in Pd catalysts for these reactions.[7]

Heterobidentate *P*,*N*-donor ligands represent an important class of ligands that have been applied in various catalytic transformations,[8] but they have been scarcely used in metal catalyzed carbonylation reactions. The use of these ligands in Rh catalyzed hydroformylation is fuzzy because the N-donor fragment can be replaced by CO under reaction conditions, thus producing monodenate or hemilabile ligands.[9] As expected, in Pd(II) complexes the substitution of the *N*-donor fragment by CO is more difficult. For this reason the *P*,*N*-bonded chelate is normally preserved in the carbonylation reactions catalyzed by this metal. For instance, Pd complexes containing this type of ligand are reported to be active in the reductive carbonylation of nitroaromatics.[10] On the other hand, although CO–alkene polymerization is normally carried out with Pd species of *P*,*P*- or *N*,*N*-donor ligands,[11] there have been a number of reports dealing with the performance of Pd(II) complexes containing heterobidentate *P*,*N*-donor ligands in this reaction.[12,13] The $[PdCl_2(Ph_2PNHpy)]$ complex (Ph_2PNHpy = 2-(diphenylphosphinoamino)pyridine) has been reported to be active in the carbonylation of ethanol to ethyl propionate.[14] Palladium complexes with 2-(diphenylphosphino)pyridine (PPh_2py) have been shown to be effective catalysts in the carbonylation of alkynes to produce methyl methacrylate and related products.[15]

To the best of our knowledge, only one *P*,*N*-donor ligand has been used in the palladium hydroesterification reaction, producing mainly the branched ester derived from styrene.[16] Here we report on the methoxycarbonylation of alkenes, namely

[a]*Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Inorgánica y Analítica, Casilla 233 Santiago 1, Chile. E-mail: paguirre@ciq.uchi le.cl*
[b]*Universidad de Santiago de Chile, Facultad de Química y Biología, Departamento de Química de los Materiales, Bernardo O'Higgins 3363, Santiago, Chile*
[c]*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009, Zaragoza, Spain*
[d]*Servei Central d'Instrumentació Científica, Universitat Jaume I, 12071, Castelló de la Plana, Spain*
[e]*Departament de Química, Universitat Autònoma de Barcelona, 08193, Bellaterra, Barcelona, Spain*

† CCDC reference number 629175. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704615b

styrene, cyclohexene and 1-hexene catalyzed by Pd complexes of 2-(diphenylphosphinoamino)pyridine (Ph_2PNHpy), 2-[(diphenylphosphino)methyl]pyridine (Ph_2PCH_2py), 2-(diphenylphosphino)quinoline (Ph_2Pqn), (diphenylphosphino)phenylamine (Ph_2PNHPh) and 2-(diphenylphosphinoaminomethyl)pyridine ($Ph_2PNMepy$) (Fig. 1).

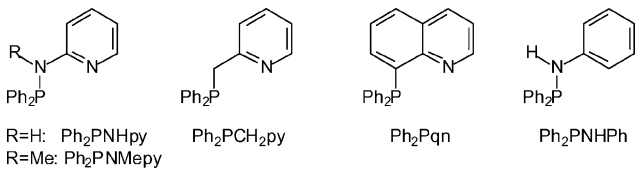


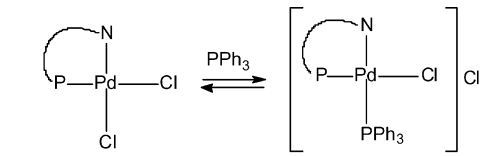
Fig. 1 *P*,*N*-Donor ligands.

Results and discussion

Synthesis of ligands and metal complexes

Ligands Ph_2PNHpy,[17] Ph_2PCH_2py,[18] Ph_2Pqn[19] and Ph_2PNHPh[20] were prepared by reported procedures, modifications of them or by alternative methods, as described in the experimental part. The ligand $Ph_2PNMepy$ was not previously reported, and it was prepared from the reaction of 2-methylaminopyridine with *n*-BuLi and PPh_2Cl.

The reaction of the four bidentate ligands with $PdCl_2$, in refluxing acetonitrile, afforded the neutral complexes $[PdCl_2L]$ (L = Ph_2PNHpy **1a**,[14,17] Ph_2PCH_2py **1b**, Ph_2Pqn **1c**,[21] and $Ph_2PNMepy$ **1d**), Scheme 1, those of Ph_2PCH_2py and $Ph_2PNMepy$ being the only ones not previously reported. When these complexes are reacted with equimolar amounts of PPh_3 in CH_2Cl_2, they produce analytically pure cationic complexes $[PdCl(PPh_3)L]Cl$ (L = Ph_2PNHpy **2a**, Ph_2Pqn **2c**, and $Ph_2PNMepy$ **2d**). The reaction proceeds readily with the complexes **1a** and **1d**. However, the complex **1c** forms only after 6 h refluxing in CH_2Cl_2. Moreover, after exhaustive reflux in this solvent, the reaction of PPh_3 with **1b** yields only a mixture of 65% of **2b**, evidenced by the two signals at 53.1 and 28.1 ppm in the ^{31}P NMR spectra, and the signal of the unreacted neutral complex **1b** at 39.8 ppm, Scheme 1.



P-, *N*-donor:
Ph_2PNHpy **1a**
Ph_2PCH_2py **1b**
Ph_2Pqn **1c**
$Ph_2PNMepy$ **1d**

P-, *N*-donor:
Ph_2PNHpy **2a**
Ph_2PCH_2py **2b**
Ph_2Pqn **2c**
$Ph_2PNMepy$ **2d**

Scheme 1

The PPh_3 substitution reaction is completely stereoselective, since only the *cis* phosphorus complexes were formed, as shown by the small J_{P-P} (*ca.* 6–10 Hz) observed in the ^{31}P NMR of the four complexes. On the other hand, the N coordination was corroborated through the downfield chemical shift (>9.50 ppm) observed for the *ortho*-H in the aromatic ring, which is characteristic of coordinated pyridine ligands.

Table 1 Crystal data for $[PdCl(PPh_3)(Ph_2PNHpy\text{-}\kappa^2P,N)]Cl\cdot(CH_2Cl_2)_2$ **2a**

Empirical formula	$C_{37}H_{34}Cl_6N_2P_2Pd$
M	887.78
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.6006(7)
b/Å	13.8728(10)
c/Å	15.8526(11)
α/°	94.061(2)
β/°	95.885(2)
γ/°	99.201(2)
V/Å^3	2065.1(3)
T/K	293(2)
Z	2
μ/mm^{-1}	0.942
Reflections collected	11899
Unique reflections, (R_{int})	7270, 0.0725
Goodness-of-fit on F^2	1.029
$R1^a$, $wR2^b$ [$I > 2\sigma(I)$]	0.0860, 0.2285
$R1^a$, $wR2^b$ (all data)	0.1777, 0.2861

^{a} $R1 = \sum|F_o| - |F_c|/\sum F_o$. ^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1a**

Pd(1)–N(1)	2.107(9)	Pd(1)–Cl(2)	2.337(3)
Pd(1)–P(2)	2.234(3)	P(2)–N(2)	1.676(9)
Pd(1)–P(3)	2.287(3)	P(2)–C(1)	1.786(12)
N(1)–Pd(1)–P(2)	82.4(3)	P(2)–Pd(1)–Cl(2)	166.89(13)
N(1)–Pd(1)–P(3)	176.7(3)	P(3)–Pd(1)–Cl(2)	86.19(12)
P(2)–Pd(1)–P(3)	99.59(11)	N(2)–P(2)–C(1)	106.2(5)
N(1)–Pd(1)–Cl(2)	92.4(3)		

The structure of complex **2a** was determined by a X-ray diffraction study (Fig. 2, Table 1). The bond lengths and angles (Table 2) around the Pd centre are very similar to those of related Pd and Pt complexes.[17] The diffraction study confirmed the *cis* phosphorus geometry. Significant distortions for ideal square

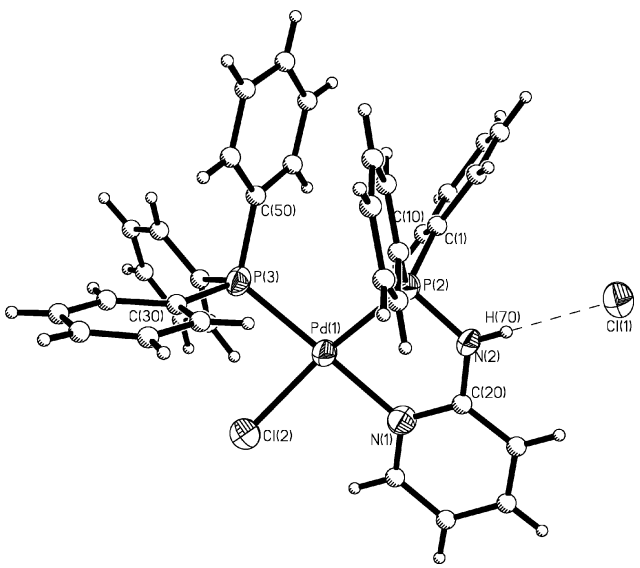
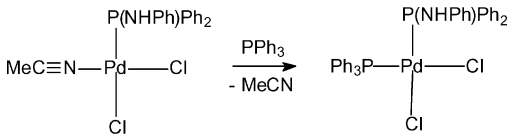


Fig. 2 Crystal structure of $[PdCl(PPh_3)(Ph_2PNHpy\text{-}\kappa^2P,N)]Cl\cdot(CH_2Cl_2)_2$ **2a**. Carbon atoms are drawn as spheres and solvent molecules are omitted for clarity.

planar geometry were evident both in N(1)–Pd(1)–P(3) 82.4(3)° and P(2)–Pd(1)–Cl(2) 99.59(11)°, arising respectively from the chelate ring restriction and the steric compression of the two adjacent phosphino fragments. The crystal structure is dominated by a pairing between the cation complex and the chloride anion through a hydrogen bond between the H of the amine and the chloride anion, with a H · · · Cl distance of 2.27(1) Å. The distance between the amine N atom and the chloride is 3.08(1) Å, with a N–H · · · Cl angle close to 160°. The stability of the *cis* phosphorus species in these compounds is also consistent with the previously reported X-ray structures of [PdCl(L)(L′)]Cl (L = Ph_2PNHpy-*P*,*N*; L′ = Ph_2PNHpy-*P*,[17] and L = Ph_2Pqn-*P*,*N*; L′ = Ph_2Pqn-*P*[22]), which show *cis* phosphine geometry.

The reaction of $[PdCl_2(CH_3CN)_2]$ with Ph_2PNHPh in CH_2Cl_2 produces the neutral complex $[PdCl_2(Ph_2PNHPh)(CH_3CN)]$ **1e**. NMR experiments reveal that **1e** reacts with PPh_3 to yield the *cis* complex **2e**, Scheme 2, as shown by the two slightly broad signals at 38.2 ppm and 22.5 ppm in the ^{31}P NMR.

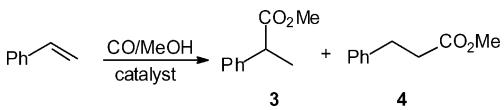


1e **2e**

Scheme 2

Catalytic results

Screening reactions were carried out in the methoxycarbonylation of styrene, Scheme 3, at 50 bar of CO, 75 °C, [Pd] = 2.0 mM in 1,2-dichloroethane, and [styrene] : TsOH : [Pd] = 400 : 10 : 1. Under these conditions, the neutral complexes $[PdCl_2L]$ **1a–c** yielded very poor conversions and selectivities, with $[PdCl_2(Ph_2PNHpy)]$ **1a** giving a slightly better performance than the other two complexes, entries 1–3, Table 3. Furthermore, extensive decomposition of the complex into Pd black was observed in all cases. However, the addition of PPh_3 to complex **1a**, entry 4, dramatically improves the conversion (99%), as well as the selectivity of the reaction. On the other hand, the addition of PPh_3 to complexes **1b** and **1c** faintly increases the output of the reaction (entries 5 and 6), although the presence of PPh_3 significantly reduces the formation Pd metal. In the case of complex **1a**, when the PPh_3/complex molar ratio was raised, entries 7 and 8, the rate of the reaction did not improve, while the selectivity decreases. As expected, the results obtained with an equimolar amount of **1a** and PPh_3 as catalysts, are very similar to those obtained with the pre-formed catalyst **2a**, entry 9, the differences being a shorter induction period, as well as better chemoselectivity for the pre-formed catalyst **2a**. Under the same screening reaction conditions as used for these catalytic systems, the classical catalyst $PdCl_2(PPh_3)_2$ only produces 56% conversion, entry 10, which indicates that the Ph_2PNHpy ligand does not behaves merely as a monodentate *P*-donor ligand. When in the solvent mixture (1,2-dichloroethane : MeOH = 15 : 5) the chlorinated solvent was replaced by toluene, the results with the **1a**/PPh_3 catalyst significantly improve, since total conversion was also reached in 6 h, but with nearly complete chemoselectivity in esters and 97% of selectivity in the branched ester **3**, entry 11. Under the same reaction conditions a mixture of $Pd_2(dba)_3$ (dba = dibenzylideneacetone), Ph_2PNHpy and PPh_3 (Pd : Ph_2PNHpy : PPh_3 = 1 : 1 : 1), entry 12, yields low conversion (32% in 24 h) and poorer regioselectivity than the chloride precursor **1a**. The replacement of 1,2-dichloroethane by toluene did not improve the catalytic properties of **1b** or **1c**, entries 13 and 14. Therefore, the catalyst **2a** or an equimolar mixture of **1a** plus PPh_3 is a better performing catalyst (99% conversion in 6 h) than the classical $PdCl_2(PPh_3)_2$ catalytic complex (56% conversion in 24 h), indicating a beneficial effect of the heterobidentate ligand for the methoxycarbonylation process.



3 **4**

Scheme 3

Table 3 Ligands and solvent effects in the methoxycarbonylation of styrene with **1a–c** catalysts.[a]

Entry	Catalyst	Solvent	PPh_3/Pd	Conversion[b] (%)	Ester[c] (%)	**3**/**4**[d]
1	**1a**	DCE	—	14	4	75/25
2	**1b**	DCE	—	5	—	—
3	**1c**	DCE	—	5	—	—
4	**1a**	DCE	1	99	93	92/8
5	**1b**	DCE	1	28	84	81/19
6	**1c**	DCE	1	9	47	78/22
7	**1a**	DCE	2	97	87	89/11
8	**1a**	DCE	3	97	95	79/21
9	**2a**	DCE	—	98 (20 h)	98	90/10
10	$[PdCl_2(PPh_3)_2]$	DCE	—	56	96	95/5
11	**1a**	PhMe	1	99 (6 h)	99	97/3
12	1/2 $Pd_2(dba)_{3+}$ PPh_2NHPy	PhMe	1	32	98	85/15
13	**1b**	PhMe	1	5	94	91/9
14	**1c**	PhMe	1	<5	—	—
15	**1d**	PhMe	1	35	95	97/3
16	**1e**	PhMe	1	54	91	93/7

[a] Reaction conditions: 4.0×10^{-2} mmol Pd in 15 mL of solvent (DCE is 1,2-dichloroethane, PhMe is toluene) and 5 mL of methanol; styrene : TsOH : Pd = 400 : 10 : 1; *P*(CO) = 50 bar; *T* = 75 °C. [b] % of styrene converted after 24 h reaction, except when indicated. [c] % of esters (**3** and **4**) of the converted substrate; (1-methoxyethyl)benzene was the only by-product. [d] Molar ratio between branched and linear ester.

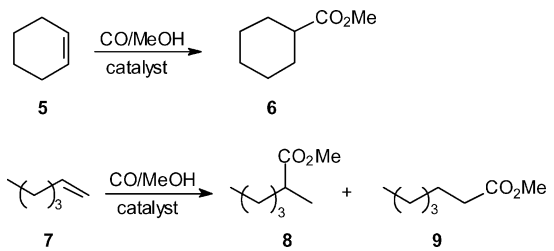
Table 4 Temperature and substrate concentration effects in the methoxycarbonylation of styrene with **1a** catalyst[a]

Entry	[substrate]/**1a**	Solvent	T(°C)	Conv.(%)[b]	tof (h^{-1})[c]	Ester(%)[d]	**3/4**[e]
17	400	DCE	60	61	10	98	94/6
18	400	DCE	70	74	12	93	94/6
4	400	DCE	75	99	17	93	92/8
19	600	DCE	75	71	18	92	93/7
20	800	DCE	75	63	21	93	94/6
11	400	PhMe	75	99 (6 h)	67	99	97/3
21	1000	PhMe	75	99	42	98	95/5
22	1000	PhMe	90	99	41	98	96/4

[a] Reaction conditions: 4.0×10^{-2} mmol of **1a** and 4.0×10^{-2} mmol PPh_3 in 15 mL of solvent (DCE is 1,2-dichloroethane, PhMe is toluene) and 5 mL of methanol; TsOH : Pd = 10 : 1; P(CO) = 50 bar. [b] % of styrene converted after 24 h reaction, except when indicated. [c] average turnover frequency at the indicated conversion. [d] % of esters (**3** and **4**) of the converted substrate; (1-methoxyethyl)-benzene was the only by-product. [e] Molar ratio between branched an linear ester.

Table 4 shows the effect of the temperature and substrate concentration on the performance of the Pd/Ph_2PNHpy catalyst. When 1,2-dichloroethane/MeOH (3/1) was used as solvent the reaction rate increases with temperature until 75 °C, entries 17 and 18 and 4. At higher temperatures, catalyst decomposition was observed and the conversion decreases. On the other hand, the reaction rate increases more than three times when the chlorinated solvent was replaced by toluene, entry 11. Consistently, in this solvent, 99% conversion was achieved in 24 h at 75 °C and styrene/Pd molar ratio equal to 1000, entry 21. In these conditions, when the temperature was raised to 90 °C, similar conversion was achieved, but a massive decomposition of the catalyst was observed at the end of the reaction, entry 22.

The complex **1a** plus PPh_3 was also assayed as catalyst for the methoxycarbonylation of cyclohexene and 1-hexene, Scheme 4. The results are collected in Table 5. Cyclohexene is converted into methyl cyclohexanecarboxylate **6** with complete chemoselectivity, although with lower reaction rates than styrene, entries 23–25. 1-Hexene is converted into methyl 2-methylhexanoate **8** and methyl heptanoate **9**, with complete chemoselectivity, but with very poor regioselectivity, entries 26–28, but with somewhat better conversions than cyclohexene. Also, with these substrates, severe decomposition of the catalyst was observed when the reaction was run at 90 °C.



Scheme 4

Catalytic species

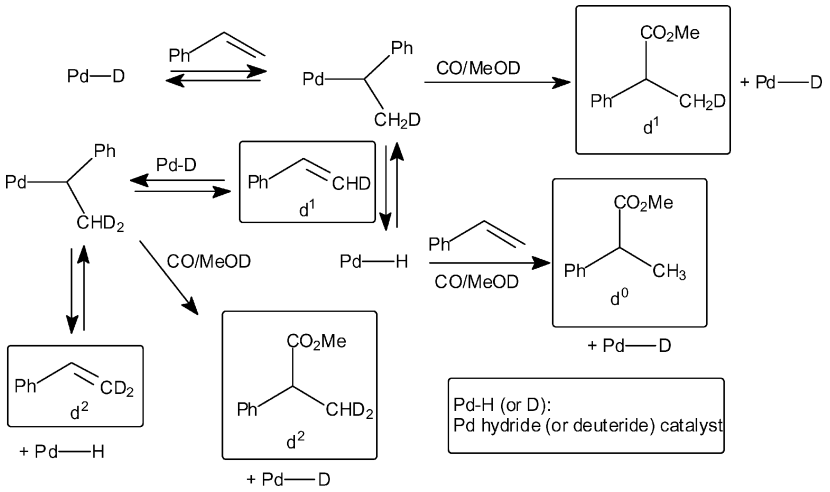
In order to investigate which is the crucial structural characteristic that makes catalyst **1a** remarkably better at performing than **1b** and **1c** in the methoxycarbonylation of styrene, complexes **1d** and **1e** were prepared and assayed in this reaction. In complex **1d**, the hydrogen of the amino group of ligand **1a** was replaced by a methyl group. This produces a very significant decrease in the rate of the reaction (35% conversion in 24 h, entry 15 in Table 3, *versus* 99% in 6 h for **1a**, entry 11). On the other hand, complex **1e**, containing the Ph_2PNHPh ligand, very similar to Ph_2PNHpy in terms of *P*-donor properties, but without the pyridine fragment, produces also a lower conversion (54% in 24 h, entry 16) than **1a**. These results suggest that in the Ph_2PNHpy, both the pyridine fragments, as well as the NH group, are crucial for its performance in the catalytic methoxycarbonylation process.

A study of the species formed by **1a** in the presence of PPh_3 under variable reaction conditions was undertaken, in order to gain some insight about the role of the heterobidentate ligand in the catalytic process. An equimolar mixture of complex **1a** and PPh_3 in toluene–MeOH in the presence of an excess of TsOH (TsOH : Pd = 10 : 1) forms **2a** as single species, as evidenced by the ^{31}P NMR spectrum. This means that pyridine coordination is robust enough to be preserved in this acidic media produced by TsOH. The catalytic mixture was pressurized with 50 bar of CO at 70 °C for 4 h and then its ^{31}P NMR was registered under

Table 5 Methoxycarbonylation of cyclohexene **5** and 1-hexene **7** with **1a** as catalyst[a]

Entry	Substrate	P_{CO}/bar	T/°C	Conversion[b] (%)	Ester[c] (%)	**9/8**[d]
23	**5**	50	75	19	>99	
24	**5**	50	90	25	>99	
25	**5**	70	75	21	>99	
26	**7**	50	75	43	>99	55/45
27	**7**	50	90	85 (12 h)	>98	57/43
28	**7**	70	75	57	>98	56/44

[a] Reaction conditions: 4.0×10^{-2} mmol **1a** and 4.0×10^{-2} mmol PPh_3 in 15 mL of toluene and 5 mL of methanol; substrate : TsOH : Pd = 400 : 10 : 1. [b] % of substrate converted after 24 h reaction. [c] % of esters (**6** for substrate **5** and **9** for substrate **7**) of the converted substrate. [d] Molar ratio between linear and branched ester for the reaction with substrate **7**.



Scheme 5

1 bar CO atmosphere. The spectrum shows that complex **2a** is still the major component of the reaction mixture. In addition, a new singlet shows at 21.8 ppm, that can be tentatively assigned to an non-coordinated P atom of the Ph_2PNHpy ligand, as well as two very minor products that appear as two doublets (113.8 and 82.2 ppm, $J_{p\text{-}p} = 25$ Hz; 92.9 and 82.1 ppm, $J_{p\text{-}p} = 19$ Hz). In summary, the catalytic results seem to indicate that the role of the PPh_3 is to stabilize the Pd(0) species, since in its absence the formation of Pd black was observed, but it is not clear if it is this ligand or the phosphorus of the bidentate ligand that produces the second vacancy required for progression of the catalytic cycle.

Two possible pathways have been proposed for the methoxycarbonylation of alkenes catalyzed by Pd phosphine and diphosphine complexes, namely the hydride and the carbomethoxy mechanisms. Isotopic labeling experiments using CH_3OD were undertaken in order to elucidate which proceeds with catalyst **2a**.[23] Analysis of the reaction products by mass spectrometry and ^2H and ^1H NMR show that $PhCH(COOMe)CH_2D$ is the major isotopomer of the branched ester **3** and its proportions remains constant (*ca.* 65%) for most of the reaction period. The presence of this isotopomer is compatible with either the hydride or the carbomethoxy mechanisms. However, both the proportion of the d^2 isotopomer of the ester $PhCH(COOMe)CHD_2$, as well as d^1 and d^2 styrene labeled at the terminal carbon, increase along the reaction, Table 6. The presence of labeled unreacted substrate and the d^2 ester arising from it are interpreted in terms of a hydride mechanism with a reversible H migration, as shown in Scheme 5. Furthermore, preliminary kinetic experiments show that the reaction is first order in the substrate. The results suggest that the rate determining step is after the formation of the alkyl complex. This seems to discard an intramolecular reaction of the Pd(0) complex with the NH group of the ligand to form the active Pd(II) hydride species, that would explain the remarkable catalytic activity of complex **2a** when compared with the rest of the catalysts here reported. A more plausible explanation for the activity of **2a** is that the NH group assists the nucleophilic attack of the MeOH, similarly to the proposed mechanism for methoxycarbonylation of alkynes catalyzed by Pd complexes of 2-pyridylphosphine.[15b] Since the basicity of the ligand Ph_2PNHpy is not expected to be too different from that of $Ph_2PNMepy$, the better performance of catalyst **2a** with respect to **2d** could be associated with the formation of a hydrogen bond between the NH group and methanol.

Table 6 Isotopomer distribution in methyl 2-phenylpropanoate and unreacted styrene at two different conversions in the methoxycarbonylation of styrene with CO and CH_3OD catalyzed by **2a**[a]

	37% conversion		61% conversion	
	Ester	Styrene	Ester	Styrene
d^0	33	89	29	73
d^1	63	10	63	20
d^2	4	1	8	7

[a] Reaction conditions: 4.0×10^{-2} mmol of **2a** in 15 mL of toluene and 5 mL of CH_3OD; styrene : TsOH : Pd = 1500 : 10 : 1; $P(CO) = 50$ bar; $T = 80$ °C.

Experimental

All manipulations were carried out under nitrogen using standard Schlenk techniques. Organic solvents and substrates were purified by distillation over standard agents and deoxygenated prior to use. The ligands Ph_2PNHpy,[17] Ph_2PCH_2py,[18] Ph_2Pqn[19] and Ph_2PNHPh[20] were synthesized by reported procedures or modifications of them. All other chemicals were commercial products and were used without further purification. NMR data were obtained on Bruker 500, 360 or 250 MHz spectrometers. GC analysis was performed on a Hewlett-Packard Agilent 5890 N chromatograph with a flame ionization detector and equipped with an HP-5 column and GC-MS were recorded on a HP-G1800A instrument.

Ph_2PNHpy

A mixture of 2-aminopyridine (1.00 g, 10.6 mmol) and triethylamine (1.50 mL, 10.6 mmol) was dissolved in THF (20 mL). The solution was cooled at 0 °C and Ph_2PCl (2.0 mL, 10.6 mmol) was slowly added. The reaction was allowed to reach room temperature and further stirred for 6 h. After this time, the ammonium salt

was separated by filtration and the solvent was removed under vacuum. The oily residue obtained was dissolved in $CHCl_3$ and precipitated with Et_2O, producing 2.8 g of white powder (96% yield). The spectroscopic data are consistent with those reported in the literature.[17]

Ph_2PCH_2py

This ligand was prepared following the procedure previously reported.[18] ^{1}H-NMR ($CDCl_3$; δ, ppm): 8.40 (H6 py, dd, 4.9 Hz, 0.7 Hz, 1H), 7.77 (*o*-H Ph and H3 py, m, 5H), 7.46 (*m*-H ph, *p*-H Ph and H4 py, m, 7H), 7.08 (H5 py, t, 6.9 Hz, 1H), 3.96 (PCH_2, d, $J_{P-H} = 16$ Hz, 2H). ^{31}P-NMR ($CDCl_3$; δ, ppm): −12.7 (s, 1P)

Ph_2Pqn

A solution of 8-chloroquinoline (0.88 g, 5 mmol) in THF (10 mL) was added dropwise to a solution of PPh_2Li (0.96, 5 mmol) in THF at −78 °C. The mixture was warmed to room temperature and stirred for 2 h. After this time, the mixture was refluxed for 12 h. The solvent was then removed and 25 mL of a water–diethyl ether (5 : 1) mixture was added. The suspension was filtered and rinsed with a few mL of a mixture of water–diethyl ether 5 : 1 and dried under vacuum producing 1.1 g (70% yield) of a white powered solid. ^{1}H-NMR ($CDCl_3$; δ, ppm): 8.89 (H2 qn, dd, 4.3 Hz, 1.8 Hz, 1H), 8.18 (H4 qn, dd, 8.1 Hz, 1.8 Hz, 1H), 7.83 (H5 qn, d, 7.1 Hz, 1H)), 7.45 (H3 qn, m, 1H), 7.40 (H6 qn, m, 1H), 7.33 (m, *o*-H Ph, *m*-H Ph, 10H), 7,15(H7 qn, m, 1H). ^{31}P-NMR ($CDCl_3$; δ, ppm): −17.0 (s, 1P).

PPh_2NMepy

A solution of 1.0 g of 2-(methylamino)pyridine (9.3 mmol) in 20 mL of diethyl ether was cooled to −70 °C, and then *n*-BuLi (9.8 mmol, 7.0 mL of a solution 1.4 M in hexane) was slowly added. The mixture was stirred for 1 h and then PPh_2Cl (2.1 g, 1.7 mL) was added dropwise. The final solution was allowed to reach room temperature and it was further stirred overnight. 3 mL of water were added and then the organic layer was extracted with diethyl ether (2 ×10 mL). The diethyl ether solution was dried over Na_2SO_4 for 30 min. After this time the solid was removed by filtration and the solvent was evaporated on a vacuum line to produce 2.7 g (65% yield) of an orange oil that becomes a pale yellow crystalline material under vacuum. ^{1}H-NMR ($CDCl_3$; δ, ppm): 8.29 (H6 py, dd, 5.5 Hz, 2.8 Hz, 1H), 7.47 (m, *o*-H Ph, *m*-H Ph, H3 py and H5 py, 12H), 6.77 (H4 py, m, 1H), 2.97 (CH_3–, d, 1.6 Hz, 3H). ^{31}P NMR ($CDCl_3$; δ, ppm): 48.7 (s, 1P).

PhPNHPh

This ligand was prepared from 360 mg of aniline, following the same procedure used for PPh_2PNHPy. The oil obtained was dissolved in $CHCl_3$ and precipitated with *n*-hexane, producing 1.5 g of white solid (75% yield). ^{1}H-NMR ($CDCl_3$; δ, ppm): 7.47 (*o*-H Ph, m, 4H), 7.40 (*m*-H Ph, *p*-H Ph, m, 6H), 7.22 (H3 aniline and H5 aniline, t, 7.3 Hz, 2H), 7.04 (H2 aniline and H6 aniline, m, 2H), 6.84 (t, H4 aniline, 7.3 Hz, 1H), 4.41 (N–H, d, 8.0 Hz,). ^{31}P-NMR ($CDCl_3$; δ, ppm): 25.9 (s, 1P).

$[PdCl_2(Ph_2PNHpy\text{-}\kappa^2P,N)]$ 1a

The product was prepared through a more direct route than that described in the literature.[14,17] A mixture of $PdCl_2$ (200 mg, 1.12 mmol) and Ph_2PNHpy (315 mg, 1.12 mmol) were dissolved in acetonitrile (30 mL) and heated to reflux for 3 h, producing a green precipitate. The suspension was cooled, and the solid was filtered off, rinsed with acetonitrile and diethyl ether, and dried under vacuum, producing 450 mg (87% yield) of a green complex. NMR and analytical data were consistent with those already reported.[17]

$[PdCl_2(Ph_2PCH_2py\text{-}\kappa^2P,N)]$ 1b

This complex was synthesized from 100 mg of $PdCl_2$, as described for **1a**, yielding 225 mg (89% yield) of a pale green solid. Found (calc. for $C_{18}H_{16}Cl_2NPPd$): C 47.55 (48.01), H 3.54(3.67), N 3.08 (2.95) %. ^{1}H-NMR (CD_2Cl_2; δ, ppm): 9.77 (H6 py, dd, 5.89 Hz, 0.9 Hz, 1H), 7.91(*o*-H Ph and H3 py, m, 5H), 7.59 (*p*-H Ph, *m*-H Ph and H4 py, m, 7H), 7.43 (H5 py, t, 6.0 Hz, 1H), 4.17 (PCH_2, d, $J_{P-H=}$ 15 Hz). ^{31}P-NMR (CD_2Cl_2; δ, ppm): 39.8 (s).

$[PdCl_2(Ph_2Pqn\text{-}\kappa^2P,N)]$ 1c

This complex was synthesized as described for **1a**, from 100 mg of $PdCl_2$, producing 205 mg of a green product (75% yield). Found (calc. for $C_{21}H_{16}Cl_2NPPd$): C 51.40 (50.95), H 3.28 (3.08), N 2.85(2.57) %. ^{1}H-NMR ($CDCl_3$; δ, ppm): 10.45 (H2 qn, dd, 5.3 Hz, 1.25 Hz, 1H), 8.54 (H4 qn, dd, 8.05 Hz, 1.25 Hz, 1H) 8.20 (H5 qn, dd, 9.6 Hz, 1,25 Hz, 1H), 8,01 (H6 qn, dd, 7.1 Hz, 1.25 Hz, 1H), 7.90 (*o*-PPh_3, H3 qn, m, 5H), 7.71 (H7 qn, dd, 8.1 Hz, $J_{P-H} =$ 5.3 Hz, 1H), 7.52 (*p*-H Ph, *m*-H Ph, m, 6H). ^{31}P-NMR ($CDCl_3$; δ, ppm): 42.4 (s, 1P).

$[PdCl_2(Ph_2PNMepy\text{-}\kappa^2P,N)]$ 1d

This complex was synthesized as described for **1a**, from 100 mg of $PdCl_2$, producing 222 mg of a green product (85% yield). Found (calc. for $C_{18}H_{17}Cl_2N_2PPd$): C 46.03 (46.20), H 3.64 (3.71), N 5.96(5.90) %. ^{1}H-NMR ($CDCl_3$; δ, ppm): 9.65 (H6 py, d, 6.1 Hz, 1H), 7.9 (*o*-H Ph, H4 py, 5H), 7.69 (*m*-H Ph, *p*-H Ph, m, 6H), 7.50 (H5 py, t, 6.0 Hz, 1H), 6.81 (H3 py, d, 8.0 Hz,3H), 2.98 (CH_3–, d, 5.9 Hz, 3H). ^{31}P-NMR ($CDCl_3$; δ, ppm): 95.7 (s, 1P).

$[PdCl_2(Ph_2PNHPh)(CH_3CN)]$ 1e

To a solution of 200 mg of $[PdCl_2(CH_3CN)_2]$ (0.78 mmol) in CH_2Cl_2 (20 mL), 108 mg (0.39 mmol) of PPh_2PNHPh in CH_2Cl_2 (5 mL) were added. The mixture was stirred for 5 h at room temperature. The resulting yellow solution was concentrated and precipitated with diethyl ether. The precipitate was collected by filtration and rinsed with diethyl ether, producing 278 mg of a bright yellow solid (72% yield). Found (calc. for $C_{20}H_{19}Cl_2N_2PPd$): C 48.46 (47.95), H 3.86 (3.79), N 5.65(5.60) %. ^{1}H-NMR ($CDCl_3$; δ, ppm): 7.92 (*o*-H Ph, m, 4H), 7.46 (*m*-H Ph, *p*-H Ph, m, 6H), 6.99 (H3 aniline and H5 aniline, t, 7.5 Hz, 2H), 6.92 (N–H, d, 7.9 Hz, 1H), 6.77 (H4 aniline, t, 7.3 Hz, 1H), 6.59 (H2 aniline and H6 aniline, d, 8.0 Hz, 2H), 2.31 (s, CH_3CN). ^{31}P-NMR ($CDCl_3$; δ, ppm): 35.0 (s, 1P).

[PdCl(Ph$_2$PNHpy-κ^2*P*,*N*)(PPh$_3$)]Cl 2a

A mixture of **1a** (200 mg, 0.45 mmol) and PPh_3 (115 mg, 045 mmol) were stirred at room temperature for 1 h in dichloromethane (30 mL). The solution obtained was concentrated and precipitated with diethyl ether. The product was filtered off and rinsed with diethyl ether (2 × 5 mL), and dried under vacuum, producing 315 mg of white powder (98% yield). Found (calc. for $C_{35}H_{30}Cl_2N_2P_2Pd$): C 58.55 (58.28), H 4.21 (4.12), N 3.90 (3.81) %. ^{1}H-NMR ($CDCl_3$; δ, ppm): 11.95 (N–H, s, 1H), 9.15 (H6 py, dd, 5.3 Hz, 4.0 Hz, 1H), 7.84 (H3 py, d, 5.2 Hz, 1H), 7.75–7.21(*m*-H Ph, *o*-H Ph, H4 py, 26H), 6.89 (H5 py, dd, 9.0 Hz, 6.5 Hz, 1H), ^{31}P-NMR ($CDCl_3$; δ, ppm): 85.1 (d, $J_{P\text{-}P} = 6$ Hz), 26.1 (d, $J_{P\text{-}P} = 6$ Hz).

[PdCl(Ph$_2$PCH$_2$py-κ^2*P*,*N*)(PPh$_3$)]Cl 2b

A mixture of **1b** (200 mg, 0.44 mmol) and PPh_3 (115 mg, 0.44 mmol) was dissolved in dichloromethane (30 mL), and heated to reflux for 6 h. After this time, a mixture of complexes **1b** and **2b** was obtained, as shown by NMR spectroscopy. The product was purified by recrystallization in chloroform–diethyl ether, producing 205 mg (65% yield) of a yellow product. Found (calc. for $C_{36}H_{31}Cl_2NP_2Pd$): C 60.31(59.90), H 4.36(4.01), N 1.95(1.87) %. ^{1}H-NMR ($CDCl_3$) (δ (ppm)): 9.48 (H6 Py, dd, 5.70 Hz, 1.9 Hz, 1H), 8.34 (H3 py, d, 7.7 Hz, 1H), 8.10–7.15 (*o*-H Ph, *m*-H Ph, *p*-H Ph, H4 py and H5 py, 27H), 5.00 (PCH_2, d, $J_{P\text{-}H} = 15$ Hz). ^{31}P-NMR ($CDCl_3$; δ, ppm): 50.8 (s br), 28.3 (s br).

[PdCl(Ph$_2$Pqn-κ^2*P*,*N*)(PPh$_3$)]Cl 2c

The procedure described above was used to prepare **2c** from 200 mg of **1c**, producing 300 mg (98% yield) of an orange solid. Found (calc. for $C_{39}H_{31}Cl_2NP_2Pd$): C 62.21 (61.17), H 4.14 (3.97), N 1.86 (1.57) %. ^{1}H-NMR: ($CDCl_3$; δ, ppm): 10.21 (H2 qn, dd, 5.3 Hz, 1.25 Hz, 1H), 9.02 (H4 qn, dd, 8.05 Hz, 1.25 Hz, 1H), 8.52 (H5 qn, d, 9.6 Hz, 1H), 7.96–7.16 (*o*-H Ph, *m*-H Ph, *p*-H Ph H3 qn, H6 qn and H7 qn, d, 28H). ^{31}P-NMR ($CDCl_3$; δ, ppm): 47.3 (d, $J_{P\text{-}P} = 9$ Hz), 26.4 (d, $J_{P\text{-}P} = 9$ Hz).

[PdCl$_2$(Ph$_2$PN(CH$_3$)py-κ^2*P*,*N*)(PPh$_3$)]Cl 2d

The same procedure described for **2a** was used to prepare **2d**. Thus, from 200 mg of **1d**, 150 mg (89% yield) of a yellow solid were obtained. Found (calc. for $C_{36}H_{32}Cl_2N_2P_2Pd$): C 59.08 (59.27), H 4.41 (4.51), N 3.83(3.91) %. ^{1}H-NMR ($CDCl_3$; δ, ppm): 10.65 (H6 py, d, 5.7 Hz, 1H), 7.90–7.67 (*o*-H Ph, *m*-H Ph, *p*-H Ph and H4 py, m, 26H), 7.60 (H5 py, t, 6.0 Hz, 1H), 6.91 (H3 py, d, 7.0 Hz,1H), 3.05 (CH_3–, d, 6.1 Hz). ^{31}P-NMR ($CDCl_3$; δ ppm) 101.7 (s, br), 26.9 (s, br).

X-Ray data collection and structure refinement

Crystals of **2a** suitable for X-ray studies were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution. A colorless prismatic crystal was mounted on the tip of a glass fiber with the use of epoxy cement. The data collection was carried out at room temperature with a Bruker SMART CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å), with a frame width of 0.3° in ω, and a counting time of 20 s per frame. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.[24,25] The structure was solved by direct methods and refined by the full-matrix method on the basis of F^2 using the SHELXTL software package.[26] All non-hydrogen atoms were refined anisotropically, whereas the positions of the hydrogen atoms were generated geometrically. Chlorine atoms of each one of the two solvating molecules of CH_2Cl_2 in the crystal were disordered among three of the four ideal tetrahedral positions. Therefore site occupancies of 2/3 were assigned to each one of the chlorine crystallographic positions. Hydrogen atoms of the CH_2Cl_2 molecules were not introduced in this disorder refinement.

Catalytic carbonylation

The catalytic methoxycarbonylation reactions were carried out in a glass-lined stainless steel autoclave fitted with temperature control unit and a sampling valve. In a typical experiment, **1a** (18.2 mg, 4.0×10^{-2} mmol), PPh_3 (10.5 mg, 4.0×10^{-2}) and TsOH (69 mg, 4.0×10^{-1} mmol) were dissolved in a mixture of 1,2-dichloroethane or toluene (15 mL) and methanol or d^1-methanol (5 mL). The solution was introduced to the reactor, which was purged three times with CO, and then charged to the required pressure and heated to the desired temperature. Samples of the reaction mixture were periodically extracted to be analyzed by GC and the pressure was adjusted if necessary.

The kinetic order of the substrate was determine by the classical logarithmic plot of the initial rate *versus* the substrate concentration.

Isotopic labeling experiments

Samples of the reaction of styrene with CO and MeOD, catalyzed by **2a** and TsOH in toluene were analyzed by GC-MS. The profile of the relevant peaks, M to M + 4 for methyl 2-phenylpropanoate and M − 4 to M + 3 for styrene, were simulated considering only the presence of d^0, d^1 and d^2 isotopomers for each species, since this model gives a good fit to the experimental data. For the simulation, it was assumed that there were not isotope effects on fragmentation. ^{2}H NMR was used to locate the deuterium atoms in the mixture of isotopomers, as well to corroborate the relative deuterium content of methyl 2-phenylpropanoate and styrene.

Conclusions

The complex **1a**, [PdCl$_2$(Ph$_2$PNHpy-κ^2*P*,*N*)] (Ph$_2$PNHpy = 2-aminophosphinopyridine), in the presence of a stochiometric amount of PPh_3, or the preformed catalyst **2a**, [PdCl(Ph$_2$PNHpy-κ^2*P*,*N*)(PPh$_3$)]Cl are reasonably active catalysts in the methoxycarbonylation of styrene, although are less active for 1-hexene and cyclohexene; under identical conditions, related complexes [PdCl$_2$(L-κ^2*P*,*N*)], L = 2-[(diphenylphosphino)methyl]pyridine, 2-(diphenylphosphino)quinoline (Ph$_2$Pqn), (diphenylphosphino)-phenylamine (Ph$_2$PNHPh) and 2-(diphenylphosphinoamino-methyl)pyridine (Ph$_2$PNMepy) show very poor conversions in this reaction. The use of (diphenylphosphino)phenylamine instead of the heterobidentate ligands renders also very low conversions, indicating that, in addition to the *P*-donor fragment, both the presence of the coordinated pyridine, as well as the N–H group are required for the good performance of the catalyst. The role of these two fragments of the ligand in the catalytic process is not fully understood, but some plausible explanations are proposed, based on a preliminary kinetic study and isotopic labelling experiments.

The last experiments are consistent with a hydride type mechanism for the catalyst **2a**. Further work is currently in progress in order to clarify the mechanism of this new type of catalyst.

Acknowledgements

The authors thank Fondecyt-Chile (Project N° 1050168), Universidad de Chile (Project CSIC19/04) and Spanish DGI (project CTQ2005-09187-C02-01 for their financial support, Cepedeq/Universidad de Chile for analytical support, and the Spanish DGI and CYTED (Project V9) for bursaries for PA and CZ.

References

1 (*a*) P. W. N. M. van Leeuwen, in *Homogenous Catalysis*, Kluwer Academic Publishers, Dordrecht, 2004, p. 239; (*b*) K. Nozaki and I. Ojima, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, Wiley, New York, 2nd edn, 2000, p. 448.
2 G. Kiss, *Chem. Rev.*, 2001, **101**, 3435.
3 (*a*) A. Seayad, A. A. Kelkar, L. Toniolo and R. V. Chaudhari, *J. Mol. Catal. A: Chem.*, 2000, **151**, 47; (*b*) J. Gironés, J. Duran, A. Polo and J. Real, *J. Mol. Catal. A: Chem.*, 2003, **198**, 77.
4 I. del Rio, N. Ruiz, C. Claver, L. A. van der Veen and P. W. N. M. van Leeuwen, *J. Mol. Catal. A: Chem.*, 2000, **161**, 39.
5 (*a*) E. Guiu, M. Caporali, B. Muñoz, C. Mueller, M. Lutz, A. L. Spek, C. Claver and P. W. N. M. van Leeuwen, *Organometallics*, 2006, **25**, 3102; (*b*) C. Bianchini, A. Meli, W. Oberhauser, P. W. N. M. van Leeuwen, M. A. Zuideveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev and A. M. Kal'sin, *Organometallics*, 2003, **22**, 2409; (*c*) H. Ooka, T. Inoue, S. Itsuno and M. Tanaka, *Chem. Commun.*, 2005, 1173.
6 I. del Rio, N. Ruiz and C. Claver, *Inorg. Chem. Commun.*, 2000, **3**, 166.
7 (*a*) N. Ruiz, I. Del Rio, I. J. J. Jiménez, C. Claver, J. Forniés-Cámer, C. C. J. Cardin and S. Gladiali, *J. Mol. Catal. A: Chem.*, 1999, **143**, 171; (*b*) J. Real, M. Pagés, A. Plo, J. F. Piniella and A. Álvarez-Larena, *Chem. Commun.*, 1999, 277; (*c*) D. Kruis, N. Ruiz, M. D. Janssen, J. Boersma, C. Claver and G. van Kotten, *Inorg. Chem. Commun.*, 1998, **1**, 295.
8 (*a*) S. Bell, B. Wuestenberg, S. Kaiser, F. Menges, T. Netscher and A. Pfaltz, *Science*, 2006, **311**, 642; (*b*) K. Kaellstroem, I. Munslow and P. G. Andersson, *Chem.–Eur. J.*, 2006, **12**, 3194; (*c*) R. J. Retz, S. Heras, Arevalo, R. de Gelder, P. W. N. M. van Leeuwen, H. Hiemstra, J. N. H. Reek and J. H. van Maarseveen, *Org. Lett.*, 2006, **8**, 3227; (*d*) Review article: P. J. Guiry and C. P. Saunders, *Adv. Synth. Catal.*, 2004, **346**, 497.
9 (*a*) A. Aghmiz, A. M. Masdeu-Bulto, C. Claver and D. J. Sinou, *J. Mol. Catal. A: Chem.*, 2002, **184**, 111; (*b*) J. Andrieu, J. M. Camus, P. Richard, R. Poli, L. Gonsalvi, F. Vizza and M. Peruzzini, *Eur. J. Inorg. Chem.*, 2006, **51**, 61; (*c*) Review article: G. Chelucci, G. Orru and G. A. Pinna, *Tetrahedron*, 2003, **59**, 9471.
10 P. Wehman, H. M. A. van Donge, A. Hagos, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Organomet. Chem.*, 1997, **535**, 187.
11 E. Drent and P. H. M. Budzeelaar, *Chem. Rev.*, 1996, **96**, 663.
12 A. D. Burrows, M. F. Mahon and M. Varrone, *Dalton Trans.*, 2003, 4718.
13 (*a*) G. P. C. M. Dekker, A. Buijs, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, W. J. J. Smeets, A. L. Spek, Y. F. Wang and C. H. Stam, *Organometallics*, 1992, **11**, 1937; (*b*) K. R. Reddy, W. W. Tsai, K. Surekha, G. H. Lee, S. M. Peng, J. T. Chen and S. T. Liu, *J. Chem. Soc., Dalton Trans.*, 2002, 1776; (*c*) K. R. Reddy, C. L. Chen, Y. H. Liu, S. M. Peng, J. T. Chen and S. T. Liu, *Organometallics*, 1999, **18**, 2574; (*d*) K. R. Reddy, K. Surekha, G. H. Lee, S. M. Peng, J. T. Chen and S. T. Liu, *Organometallics*, 2001, **20**, 1292; (*e*) P. Braunstein, M. D. Fryzuk, M. Le Dall, F. Naud, S. J. Rettig and F. Speiser, *J. Chem. Soc., Dalton Trans.*, 2000, **7**, 1067; (*f*) Y. C. Chen, C. L. Chen, J.-T. Chen and S.-T. Liu, *Organometallics*, 1994, **13**, 600.
14 X. Zhang, W. Zhao and S. Zhang, *Shiyou Huagong*, 1995, **24**, 691.
15 (*a*) E. Drent and P. H. M. Budzelaar, *J. Organomet. Chem.*, 2000, **593**, 211; (*b*) E. Drent, P. Arnoldy and P. H. M. Budzelaar, *J. Organomet. Chem.*, 1994, **475**, 57.
16 B. Jedlicka, W. Weissensteiner, T. Kégl and L. Kollár, *J. Organomet. Chem.*, 1998, **563**, 37.
17 S. M. Aucott, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2000, 2559.
18 E. de la Encarnación, J. Pons, R. Yáñez and J. Ros, *Inorg. Chim. Acta*, 2006, **359**, 745.
19 (*a*) W. Yanchun, L. Chi Wai, K. Fuk Yee, J. Wen and C. Kin Shing, *Tetrahedron*, 2004, **60**, 9433; (*b*) S. Wen-Hua, L. Zilong, H. Huaiming, W. Biao, Y. Haijian, L. Ning, L. Xuebing and W. Honggen, *New J. Chem.*, 2002, **26**, 1474.
20 D. Fenske, B. Maczek and K. Maczek, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1113.
21 (*a*) H. A. Hudali, J. V. Kingston and H. A. Tayim, *Inorg. Chem.*, 1979, **18**, 1391; (*b*) T. Suzuki, S. Kaizaki and F. Okuda, for Idemitsu Petrochemical Co., Ltd., Japan, Jpn. Kokai Tokkyo Koho, 2002, JP 2002080522.
22 T. Suzuki, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1869.
23 (*a*) G. H. Eastham, R. P. Tooze, M. Kilner, D. F. Foster and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 2002, 1613; (*b*) J. Gironés, J. Duran, A. Polo and J. Real, *Chem. Commun.*, 2003, 1776.
24 *SAINT*, Bruker Analytical X-ray Systems, Madison, WI, USA, 2001.
25 G. M. Sheldrick, *SADABS Empirical Absorption Program*, University of Göttingen, Göttingen, Germany, 2001.
26 G. M. Sheldrick, *SHELXTL*, Bruker Analytical X-ray Systems, Madison, WI, USA, 1997.

