Structural studies of $PdCl_2L_2$ complexes with fluorinated phosphines, phosphites, and phosphinites as precursors of benzyl bromide carbonylation catalysts, and and X-ray crystal structure of *cis*-$PdCl_2[PPh_2(OEt)]_2$

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Abstract: $PdCl_2L_2$-type complexes with phosphines (L = $PPh_x(C_6F_5)_{3-x}$ (x = 0–3)), phosphites (L = $P(OMe)_3$, $P(OPh)_3$, $P(OEt)_3$), and phosphinites (L = $PPh_2(OC_6F_5)$, $PPh_2(O\text{-}3,5\text{-}F_2C_6H_3)$, $PPh_2(OEt)$, $PPh_2(O\text{-}n\text{-}Bu)$, $PPh_2(O\text{-}t\text{-}Bu)$) were synthesized and characterized by UV–vis and ^{31}P NMR methods. $PdCl_2L_2$ complexes with less sterically demanding phosphines ($\Theta < 140°$) exist as *cis* isomers, which is confirmed by the X-ray structure of *cis*-$PdCl_2[PPh_2(OEt)]_2$. These complexes react with CO in the presence of NEt_3 forming $Pd(CO)_xL_y$ ($x + y = 4$) type carbonyls characterized by IR spectra. All $PdCl_2L_2$ complexes studied are active as precursors of benzyl bromide carbonylation catalysts at 40°C and 1 atm CO; however, the activity of the *cis* isomers is higher than that of the *trans* isomers. The highest yields of the carbonylation product, phenylacetic acid methyl ester, were obtained using *cis*-$PdCl_2[P(OMe)_3]_2$ (92%), *cis*-$PdCl_2[P(OPh)_3]_2$ (89%), and *cis*-$PdCl_2[PPh_2(O\text{-}n\text{-}Bu)]_2$ (78%) as catalyst precursors.

Key words: palladium complexes, fluorinated phosphines, benzyl bromide carbonylation.

Résumé : On a synthétisé des complexes de type $PdCl_2L_2$ comprenant des phosphines L = $PPh_x(C_6F_5)_{3-x}$ (x = 0–3), des phosphites L = $P(OMe)_3$, $P(OPh)_3$ et $P(OEt)_3$ et des phosphinites L = $PPh_2(OC_6F_5)$, $PPh_2(O\text{-}3,5\text{-}F_2C_6H_5)$, $PPh_2(OEt)$, $PPh_2(OBu)$ et $PPh_2(O\text{-}t\text{-}Bu)$ et on les a caractérisés par spectroscopie UV–vis et par RMN du ^{31}P. Les complexes $PdCl_2L_2$ comportant des phosphines stériquement moins encombrées ($\theta < 140°$) existent sous la forme d'isomères *cis*; cette situation a été confirmée par diffraction des rayons du *cis*-$PdCl_2[PPh_2(OEt)]_2$. Ces complexes réagissent avec le CO en présence de NEt_3 pour former des complexes carbonylés de type $Pd(CO)_xL_y$ ($x + y = 4$) qui ont été caractérisés par spectroscopie IR. À 40°C et 1 atm de CO, tous les complexes de type $PdCl_2L_2$ sont actifs comme précurseurs de catalyseurs pour la carbonylation du bromure de benzyle; toutefois, l'activité des isomères *cis* est supérieure à celle des isomères *trans*. Les rendements les plus élevés en produit de carbonylation, le phénylacétate de méthyle, ont été obtenus avec les *cis*-$PdCl_2[P(OMe)_3]_2$ (92%), *cis*-$PdCl_2[P(OPh)_3]_2$ (89%) et *cis*-$PdCl_2[P(OBu)_3]_2$ (78%) comme précurseurs de catalyseur.

Mots clés : complexes de palladium, phosphines fluorées, carbonylation du bromure de benzyle.

[Traduit par la Rédaction]

Introduction

The electronic and steric properties of fluorine-containing phosphorus ligands are quite different from those of their nonfluorinated analogues. The σ-electron-withdrawing character of fluorine reduces the basicity of the ligand, as has been demonstrated for *trans*-$MCl(CO)(PR_3)_2$ (M = Rh, Ir) by an increase of the ν(CO) frequency in the following series of PR_3 ligands: $PPh_3 < PPh_2(C_6F_5) < P(C_6F_5)_3$ (1). However, when only two fluorines are present in the phenyl ring of the phosphine coordinated in complexes of the same type ($PPh_x(2,6\text{-}F_2C_6H_3)_{3-x}$, x = 0–2), the ν(CO) remains constant and close to the value observed for $MCl(CO)(PPh_3)_2$ (1). On the basis of ligand displacement studies of $PtCl_2(PR_3)_2$ complexes, phosphorus ligands have been ordered according to their ligand exchange ability, which increases in the following order: $P(C_6F_5)_3 < PPh(C_6F_5)_2 < P(2,6\text{-}F_2C_6H_3)_3 < PPh_2(C_6F_5) < PPh_3$ (2). Rhodium and platinum complexes with fluorinated phosphines, diphosphines, phosphonites, and phosphinites have been studied (3–5). Examples of *ortho*-C–F bond activation in rhodium and iridium complexes with fluorinated diphosphines have been reported (6, 7).

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Dedicated to Professor Brian James on the occasion of his 65th birthday.

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Table 1. UV-vis (in $CHCl_3$) and ^{31}P NMR (in $CDCl_3$) data of $PdCl_2L_2$ complexes.

No.	L	Isomer	UV–vis (λ, nm)	^{31}P NMR $PdCl_2L_2$ (δ, ppm)	$\Delta = \delta_{compl} - \delta_L$	^{31}P NMR OPR_3 (δ, ppm)	θ (°)[a]
1	$PPh_2(O\text{-}t\text{-}Bu)$	*trans*	348	79.0	37.5	34.0	155[b]
2	PPh_3	*trans* (15)	345	23.4	29.4	28.1	145 (8)
3	PCy_3	*trans* (17)	344	24.8	13.9	50.0	170
4	$PPh_2(C_6F_5)$	*trans*	342	12.8	37.7	20.9	158 (8)
5	$PPh_2(OC_6F_5)$	*trans*	342	79.0	–3.1	27.8	145
6	$PPh_2(O\text{-}3,5\text{-}F_2C_6H_3)$	*cis*	342	79.2	–35.4	32.9	139
7	$P(OCH_2CF_3)_3$	*cis*	334	94.8	–45.1	–3.4	115
8	$PPh(C_6F_5)_2$	*trans*	333	–5.93	40.5	7.9	167 (1), 171 (8)
9	$PPh_2(OEt)$	*cis*	330	109.5	–22.5	31.0	133 (8)
10	$PPh_2(O\text{-}n\text{-}Bu)$	*cis*	326	109.3	–2.8	31.7	133
11	$P(OPh)_3$	*cis* (18)	320	83.7	–42.3	–17.0	128 (8)
12	$P(C_6F_5)_3$	*trans* (16)	317	–26.8	47.6	–8.0	184 (8), 172 (1)
13	$P(OMe)_3$	*cis*	306	94.8	–30.5	2.0 (13)	107 (8)
14	$P(OEt)_3$[c]	*cis*	305	93.1	–46.3	–1.0 (13)	109 (8)

[a] Cone angle. References are given in parentheses.
[b] Calculated from the equation $\theta = 2/3\ \Sigma\theta_i\ /2$ (8).
[c] Not isolated.

The presence of fluorines in the phosphine phenyl ring, especially in *ortho*-positions, dramatically changes the steric properties of the ligand causing an increase of the cone angle (Θ), e.g., from 145° for PPh_3 to 184° for $P(C_6F_5)_3$ (8).

Long chain alkyl fluorinated phosphines, such as $P(CH_2CH_2(CF_2)_5CF_3)_3$, are successfully applied for catalytic processes in highly fluorinated solvents (9, 10).

Looking for good modifying ligands for palladium carbonylation catalysts, we selected fluorinated phosphorus ligands such as phosphines of the form $PPh_x(C_6F_5)_{3-x}$ (x = 0–2) and phosphinites of the form $PPh_2(OC_6F_5)$ and $PPh_2(O\text{-}3,5\text{-}F_2C_6H_3)$ for systematic studies of the electronic and steric effects of ligands on the structural and catalytic properties of $PdCl_2L_2$-type palladium complexes.

It was particularly interesting to test complexes with ligands that are bulky and simultaneously have a strong acceptor character (low basicity). Recently, we found a new Pd(0)–triphenylphosphite complex formation reaction when $PdCl_2[P(OPh)_3]_2$ was treated with NEt_3 (11). Although triphenylphosphite is a stronger π-acceptor, it has relatively small cone angle (Θ = 128°), and the question arises how the same reaction with NEt_3 would proceed in the case of more bulky fluorinated phosphines. To supplement the series of complexes under study and to be able to draw more general conclusions, we prepared palladium complexes with nonfluorinated phosphites ($P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$) and phosphinites ($PPh_2(OEt)$, $PPh_2(O\text{-}n\text{-}Bu)$, $PPh_2(O\text{-}t\text{-}Bu)$) for comparison.

Results and discussion

$PdCl_2L_2$-type complexes

The palladium complexes that we used for spectroscopic and catalytic studies were prepared by substitution of cyclooctadiene (cod) in $PdCl_2$(cod) with a suitable phosphorus ligand. All complexes were isolated and characterized by spectroscopic and analytical methods (Table 1, and see *Experimental*).

Scheme 1.

Square planar complexes of the $PdCl_2L_2$ type can exist as two isomers, *cis* and *trans* (14). Some of the compounds listed in Table 1, namely $PdCl_2L_2$ (L = PPh_3, $P(C_6F_5)_3$, $P(OPh)_3$, PCy_3) had been characterized earlier by X-ray crystallography (14–18), and the presence of *trans*-isomers was confirmed for complexes with bulky ligands, e.g., *trans*-$PdCl_2(PPh_3)_2$ (15), *trans*-$PdCl_2[P(C_6F_5)_3]_2$ (14), and *trans*-$PdCl_2(PCy_3)_2$ (17). The phosphites and phosphinites, on the other hand, preferentially formed *cis*-isomers (14), as was recently confirmed by the structure of *cis*-$PdCl_2[P(OPh)_3]_2$ (8) and the structure of *cis*-$PdCl_2[PPh_2(OEt)]_2$ in this paper. On the basis of the literature data (14–18), we assigned *cis* or *trans* geometry for all complexes under study (Table 1) according to the general rule shown in Scheme 1. The only doubtful structure is that of $PdCl_2[PPh_2(OC_6F_5)]_2$, which decomposes during recrystallization thereby making it impossible to determine the structure via X-ray crystallography. The cone angle of the $PPh_2(OC_6F_5)$ ligand, calculated from the molecular structure of the platinum complex (3), is 145°, and by analogy with *trans*-$PdCl_2(PPh_3)_2$ (Θ for PPh_3 = 145°), we proposed a *trans* geometry for $PdCl_2[PPh_2(OC_6F_5)]_2$.

It is important to note that the presence of only one ^{31}P NMR signal in the spectrum of each of the palladium complexes suggested the presence of only one isomer in solution.

UV–vis spectra

Spectroscopic data for the $PdCl_2L_2$ complexes are presented in Table 1. All of the complexes display one elec-

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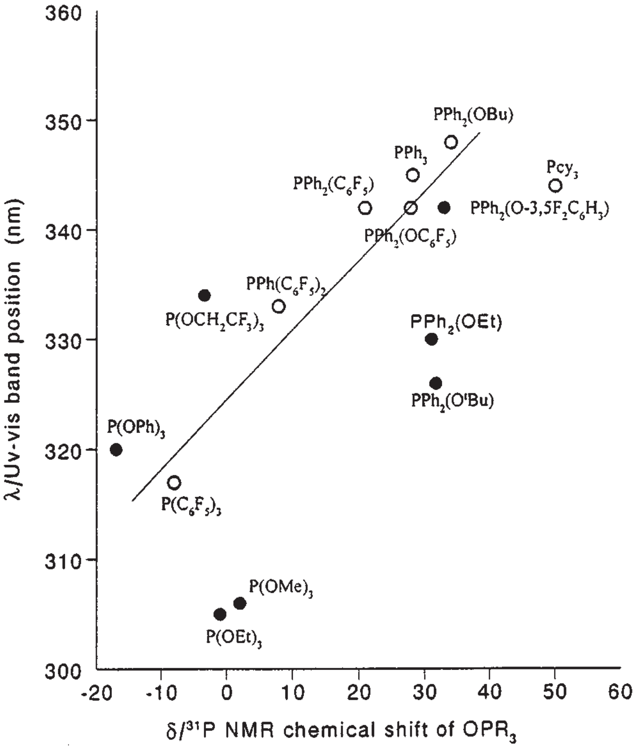
Fig. 1. Correlation between the UV–vis band position (λ, nm) of $PdCl_2L_2$ complexes in $CHCl_3$ and the ^{31}P NMR chemical shift (δ, ppm) of respective phosphine oxides OPR_3; **1** PPh_2(O-*t*-Bu), **2** PPh_3, **3** PCy_3, **4** $PPh_2(C_6F_5)$, **5** $PPh_2(OC_6F_5)$, **6** PPh_2(O-3,5-$F_2C_6H_3$), **7** $P(OCH_2CF_3)_3$, **8** $PPh(C_6F_5)_2$, **9** $PPh_2(OEt)$, **10** PPh_2(O-*n*-Bu), **11** $P(OPh)_3$, **12** $P(C_6F_5)_3$, **13** $P(OMe)_3$, **14** $P(OEt)_3$. *cis*-$PdCl_2L_2$ (●), *trans*-$PdCl_2L_2$ (○).

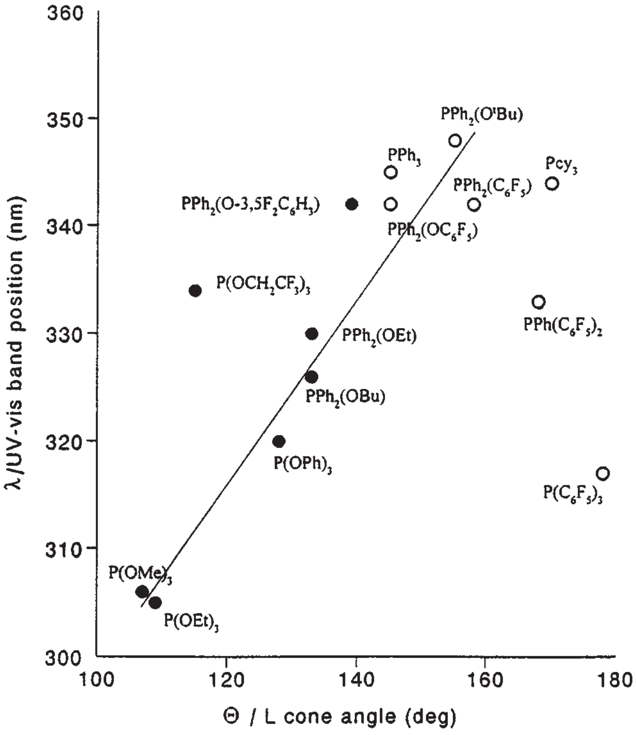


tronic transition (λ) in the 300–350 nm region of the UV–vis spectrum, as similarly reported for other palladium(II) complexes with phosphorus ligands (12). In the group of complexes studied, the band is shifted from 348 nm for $PdCl_2[PPh_2$(O-*t*-Bu)$]_3$ to 305 nm for $PdCl_2[PPh_2(OEt)]_2$, showing a dependence on the type of phosphorus ligand coordinated to palladium. The influence of the phosphorus ligand on the spectroscopic properties of metal complexes can be discussed in terms of two types of effects; electronic and steric, which could not be separated and considered as totally independent effects. In the group of palladium complexes under study, we can however, discuss the domination of electronic or steric influence of the ligand on the spectroscopic properties of the compound.

To characterize the influence of the electronic properties of the phosphorus ligand coordinated to palladium on the UV–vis spectrum of the complex, we plotted the relationship between the band position (λ) and the ^{31}P NMR chemical shift of phosphine oxides (δ_{OPR_3}) (13) (Fig. 1).

The selection of this parameter was based on Derenesceyi's demonstration (13) that the carbonyl stretching frequency (ν(CO)) of $Ni(CO)_3PR_3$, being the measure of the electronic properties of PR_3, is linearly correlated with the ^{31}P NMR chemical shift of OPR_3 (δ). The linear correlation is fairly good only for *trans*-$PdCl_2L_2$ with fluorinated phosphines (L = $PPh_x(C_6F_5)_{3-x}$ (x = 0–3)) (Fig. 1).

Fig. 2. Correlation between the UV–vis band position (λ, nm) of $PdCl_2L_2$ complexes in $CHCl_3$ and the cone angles (θ) of respective phosphines (L) **1** PPh_2(O-*t*-Bu), **2** PPh_3, **3** PCy_3, **4** $PPh_2(C_6F_5)$, **5** $PPh_2(OC_6F_5)$, **6** PPh_2(O-3,5-$F_2C_6H_3$), **7** $P(OCH_2CF_3)_3$, **8** $PPh(C_6F_5)_2$, **9** $PPh_2(OEt)$, **10** PPh_2(O-*n*-Bu), **11** $P(OPh)_3$, **12** $P(C_6F_5)_3$, **13** $P(OMe)_3$, **14** $P(OEt)_3$. *cis*-$PdCl_2L_2$ (●), *trans*-$PdCl_2L_2$ (○).



Another correlation, between the UV–vis band position (λ) and the phosphine cone angle (Θ), was plotted because of the estimation of the influence of the steric effect of the ligand on the spectroscopic properties of palladium complexes (Fig. 2). This correlation is also not satisfactory as it still shows some deviations from linearity. However, it allows one to conclude that the band position in the spectra of $PdCl_2L_2$ complexes are dependent on both the electronic and steric properties of ligand L.

^{31}P NMR spectra

The chemical shift of the ^{31}P NMR signal, being strongly dependent on the kind of phosphorus ligand, is not very informative (Table 1). However, the coordination chemical shift (Δ), defined as the difference in the ^{31}P NMR chemical shift between coordinated and free phosphine ($\Delta = \delta_{coord.} - \delta_L$), can be used to compare structurally similar complexes with different phosphorus ligands (8). The coordination chemical shift can also be used for the estimation of bond strength, as was demonstrated for $PtCl_2L_2$ complexes with fluorinated phosphines (2).

We found that the coordination chemical shift (Δ) of complexes under study increases with increase of phosphine cone angle (Θ) (Fig. 3), as was similarly reported for $RhCl(CO)(PR_3)_2$ complexes (8). The lowest (negative) values of Δ were found for complexes with less bulky phosphorus ligands (Θ < 140°), existing as *cis*-isomers. The coordination of these ligands to palladium causes an upfield shift of

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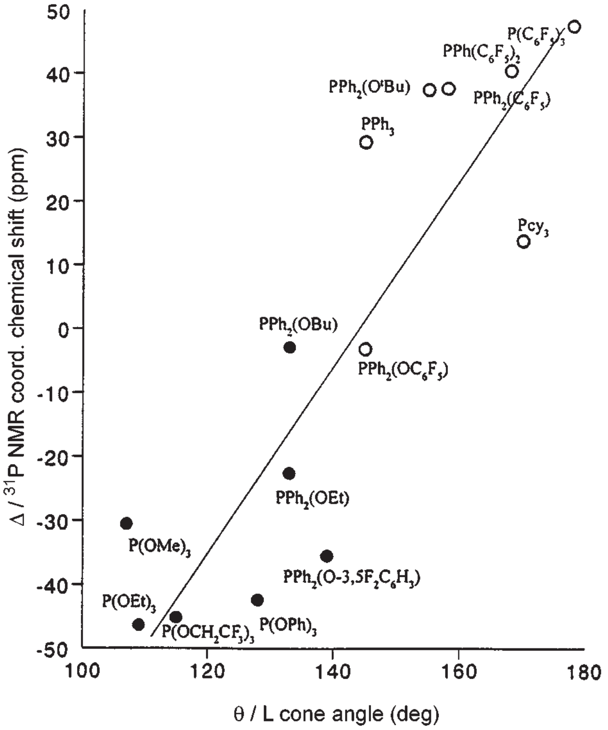
Fig. 3. Correlation between the ^{31}P NMR coordination chemical shift ($\Delta = \delta_{\text{coord.}} - \delta_L$) of $PdCl_2L_2$ complexes in $CHCl_3$ and the cone angles (θ) of the phosphorus ligand (L). **1** $PPh_2(O\text{-}t\text{-}Bu)$, **2** PPh_3, **3** PCy_3, **4** $PPh_2(C_6F_5)$, **5** $PPh_2(OC_6F_5)$, **6** $PPh_2(O\text{-}3,5\text{-}F_2C_6H_3)$, **7** $P(OCH_2CF_3)_3$, **8** $PPh(C_6F_5)_2$, **9** $PPh_2(OEt)$, **10** $PPh_2(O\text{-}n\text{-}Bu)$, **11** $P(OPh)_3$, **12** $P(C_6F_5)_3$, **13** $P(OMe)_3$, **14** $P(OEt)_3$. *cis*-$PdCl_2L_2$ (●), *trans*-$PdCl_2L_2$ (○).



the ^{31}P NMR signal as compared with the free ligand and as a consequence leads to a negative coordination shift. The highest (positive) values of Δ were noted for *trans*-complexes with bulky ligands ($\Theta > 140°$). Changes in coordination chemical shift (Δ) were explained by changes in SPS angles (angles between substituents on trivalent phosphorus upon coordination of phosphine to metal) (8).

Attempts to correlate both the ^{31}P NMR parameters; the coordination chemical shift (Δ) and the chemical shift of phosphine oxides (δ), failed.

Reactions of $PdCl_2L_2$ complexes with CO and NEt_3

A $PdCl_2L_2$ complex used as a carbonylation reaction catalyst precursor should first undergo reduction to a palladium(0) complex. We recently found that $PdCl_2[P(OPh)_3]_2$ is reduced to a Pd(0) species by NEt_3, even in aprotic solvents such as CH_2Cl_2 or C_6H_6 (11) (eq. [1]).

$$[1] \quad PdCl_2[P(OPh)_3]_2 + n NEt_3 \rightarrow Pd[(P(OPh)_3]_4 + Pd[P(OPh)_3]_x[(NEt_3)]_{4-x} \qquad x = 1\text{–}3$$

The $PdCl_2(PPh_3)_2$ complex under similar conditions exhibits different reactivity, forming a carbomethoxy complex (eq. [2]) (19):

$$[2] \quad PdCl_2(PPh_3)_2 + CO + NEt_3 + MeOH \rightarrow PdCl(C(O)OMe)(PPh_3)_2 + HNEt_3Cl$$

Table 2. ν(CO) frequencies observed for $Pd(CO)_xL_y$ ($x + y = 4$) complexes in KBr.

L	ν(CO) (cm^{-1})
$PPh_2(OEt)$	1816 (m), 1876 (vs), 1896 (s), 1916 (vs)
$PPh_2(OBu)$	1809 (m), 1846 (s), 1876 (vs), 1896 (vs), 1942 (m)
$P(OCH_2CF_3)_3$	1876 (vs), 1920 (m)
$P(OPh)_3$	1810 (m), 1849 (m), 1876 (s), 1893 (s), 1926 (m)
$P(OMe)_3$	1822 (m), 1883 (vs), 1903 (vs), 1916 (vs)

When a tertiary amine was replaced by a secondary one, a mixture of Pd(0) carbonyls, $Pd(CO)_x(PPh_3)_y$ ($x + y = 4$), was identified in the reaction product (eq. [3]) (19):

$$[3] \quad PdCl_2(PPh_3)_2 + CO + HNR^1R^2 + MeOH \rightarrow Pd(CO)(PPh_3)_3 + Pd_3(CO)_3(PPh_3)_4 + H_2NR^1R^2Cl$$

The $PdCl_2L_2$ complexes react with CO in the presence of NEt_3, giving products depending on the phosphorus ligand used.

Palladium complexes with fluorinated phosphines ($PPh_x(C_6F_5)_{3-x}$ (x = 0–2)) treated with CO (1 atm) in methanol containing an excess of NEt_3 ($[NEt_3]:[Pd] = 5$) did not give any new products, even after 24 h. In contrast, complexes with less bulky phosphines react with CO forming the respective palladium carbonyls in about 20 min (eq. [4]). The carbonyls were identified by IR spectra and showed ν(CO) bands of terminally bonded CO-ligands at ca. 1900 cm^{-1} (Table 2).

$$[4] \quad PdCl_2L_2 + CO + NEt_3 + MeOH \rightarrow Pd(CO)_x(L)_y + HNEt_3Cl$$

$$L = PPh_2(OEt),\ PPh_2(O\text{-}n\text{-}Bu),\ P(OPh)_3,\ P(OCH_2CF_3)_3,\ P(OMe)_3$$

$$x + y = 4$$

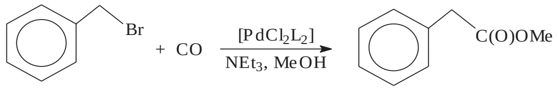
It is worth mentioning that carbomethoxy complexes were not identified during rxn. [3] nor in its final product.

It is reasonable to propose that NEt_3 acts as a reducing agent with respect to all complexes mentioned in rxn. [4], and the presence of methanol is not necessary, as palladium carbonyls were also obtained in reactions of $PdCl_2[P(OPh)_3]_2$ or $PdCl_2[PPh_2(O\text{-}n\text{-}Bu)]_2$ with CO and NEt_3 in CH_2Cl_2 as a solvent.

Catalytic activity of $PdCl_2L_2$ complexes in benzyl bromide carbonylation

A test of the catalytic activity of $PdCl_2L_2$ complexes in the carbonylation of benzyl bromide to phenylacetic acid methyl ester was performed under standard conditions of 40°C and 1 atm of CO in MeOH (eq. [5]).

[5]



The results are summarized in Fig. 4 in the form of a correlation between the yield of phenylacetic acid methyl ester and the cone angle of the phosphorus ligand (Θ). It can be

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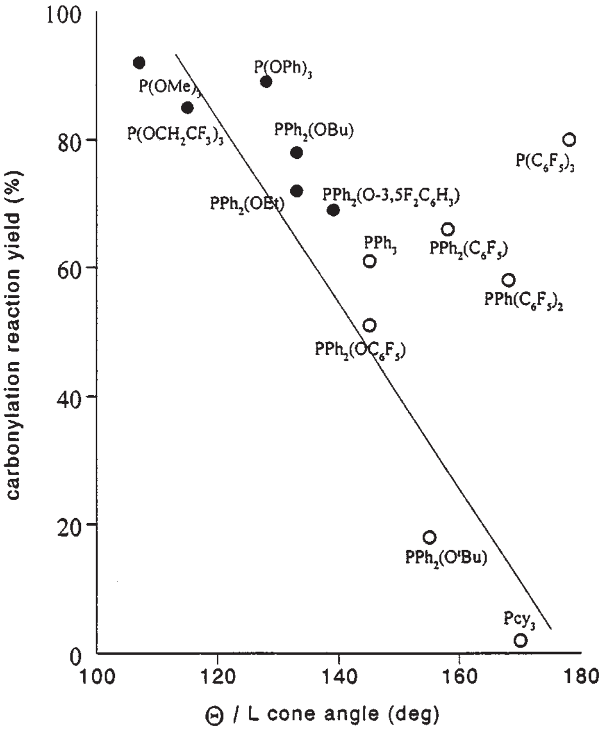
Fig. 4. Dependence of the benzyl bromide carbonylation reaction yield on the cone angle (θ) of phosphorus ligand (L) coordinated in $PDCl_2L_2$ complex. **1** PPh_2(O-*t*-Bu), **2** PPh_3, **3** PCy_3, **4** $PPh_2(C_6F_5)$, **5** $PPh_2(OC_6F_5)$, **6** PPh_2(O-3,5-$F_2C_6H_3$), **7** $P(OCH_2CF_3)_3$, **8** $PPh(C_6F_5)_2$, **9** $PPh_2(OEt)$, **10** PPh_2(O-*n*-Bu), **11** $P(OPh)_3$, **12** $P(C_6F_5)_3$, **13** $P(OMe)_3$, **14** $P(OEt)_3$. *cis*-$PdCl_2L_2$ (●), *trans*-$PdCl_2L_2$ (○).



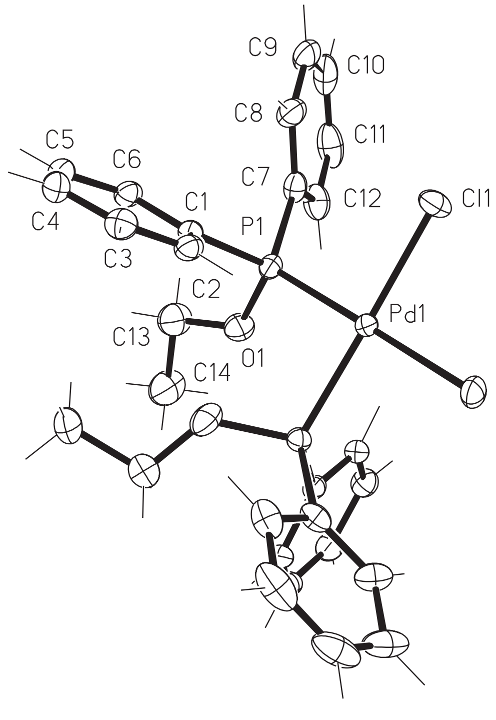
concluded that palladium complexes with less crowded phosphorus ligands ($P(OMe)_3$, $P(OPh)_3$, PPh_2(O-*n*-Bu)) exhibit higher catalytic activity, producing ca. 90% of the phenylacetic acid methyl ester. This is in agreement with the observation that these complexes undergo easier reduction to palladium(0) species when treated with CO and NEt_3 (eq. [4]). Therefore, the higher catalytic activity can be explained by the higher concentration of the active form of the catalyst, a Pd(0) complex, which activates benzyl bromide by an oxidative addition reaction. It is interesting to note that palladium complexes with fluorinated phosphines ($PPh_x(C_6F_5)_{3-x}$, x = 1 or 2) exhibit higher catalytic activity than expected on the basis of the correlation presented in Fig. 4. In these cases, the electronic effect of phosphine seems to be dominating over the steric effect.

The formation of black palladium metal at the end of some carbonylation reactions was observed, i.e., in reactions with *cis*-$PdCl_2[P(OCH_2CF_3)_3]_2$ and *cis*-$PdCl_2[P(OPh)_3]_2$. However, the good yields of carbonylation products in these reactions show that the benzyl bromide carbonylation reaction is faster than palladium reduction. It was found earlier (20) that palladium black is not catalytically active.

X-ray crystal structure of *cis*-$PdCl_2[PPh_2(OEt)]_2$

The molecular structure of the *cis*-$PdCl_2[PPh_2(OEt)]_2$ complex is shown in Fig. 5, and selected bond distances and angles are given in Table 3. The complex is of square-planar geometry with P-Pd-Cl angles of 178.54(3) and 89.40(3)°, respectively.

Fig. 5. Molecular structure of *cis*-$PdCl_2[PPh_2(OEt)]_2$ (**9**).



The Pd—P distance (2.2474(8) Å) in *cis*-$PdCl_2[PPh_2(OEt)]_2$ is significantly shorter than corresponding Pd—P distances in *trans*-$PdCl_2L_2$ complexes with L = PPh_3 (15), $P(C_6F_5)_3$ (16), PCy_3 (17). In the series of these complexes, a gradual shortening of Pd—P distances is observed as ligand's (L) basicity decreases from 2.3628(9) Å in *trans*-$PdCl_2(PCy_3)_2$ (17) to 2.3051(12) Å in *trans*-$PdCl_2[P(C_6F_5)_3]_2$ (16). The basicity of $PPh_2(OEt)$ is expected to be intermediate between that of PPh_3 and $P(C_6F_5)_3$, and therefore, the order of decreasing basicity is as follows: $PCy_3 > PPh_3 > PPh_2(OEt) > P(C_6F_5)_3$. Thus, the Pd—P bond in *cis*-$PdCl_2[PPh_2(OEt)]_2$ should be longer compared to that in *trans*-$PdCl_2[P(C_6F_5)_3]_2$, which was not observed. On the other hand, the Pd—P bond in complex *cis*-$PdCl_2[PPh_2(OEt)]_2$ is only slightly longer than that in *cis*-$PdCl_2(P(OPh)_3)_2$ (2.2299(11) and 2.2314(12) Å, respectively) (18), because of the higher basicity of the $PPh_2(OEt)$ ligand compared with that of $P(OPh)_3$. The observed shortening of the Pd—P distance in the *cis*-$PdCl_2[PPh_2(OEt)]_2$ and other *cis*-$PdCl_2L_2$ complexes with respect to *trans*-$PdCl_2L_2$ complexes is consistent with the stronger *trans* influence of a phosphorus ligand than that of a chloride ligand. The Pd—Cl bond length in *cis*-$PdCl_2[PPh_2(OEt)]_2$ (2.3430(8) Å) is similar to those found in *cis*-$PdCl_2(P(OPh)_3)_2$ (2.3273(11) and 2.3354(11) Å) (18) and *cis*-$PdCl_2[PPh_2(OMe)]_2$ (2.349(8) and 2.358(6) Å) (21). In the *trans*-$PdCl_2L_2$ complexes mentioned above the respective distances are ca. 0.04 Å longer. The conformation of $PPh_2(OEt)$ ligand is slightly different from that of $PPh_2(OEt)$, which is illustrated by smaller Pd-P-O angles, 118.6(7) and 115.5(6)° in *cis*-$PdCl_2[PPh_2(OMe)]_2$ (21) and 108.19(10)° in *cis*-$PdCl_2[PPh_2(OEt)]_2$.

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Table 3. Selected bond lengths (Å) and angles (°) for $PdCl_2[PPh_2(OEt)]_2$.

Bond lengths (Å)	
Pd(1)—P(1)	2.2474(8)
Pd(1)—P(1)′	2.2474(8)
Pd(1)—Cl(1)′	2.3430(8)
Pd(1)—Cl(1)	2.3430(8)
P(1)—O(1)	1.620(3)
P(1)—C(7)	1.804(4)
P(1)—C(1)	1.809(3)
O(1)—C(13)	1.409(5)
C(13)—C(14)	1.505(6)
Bond angles (°)	
P(1)-Pd(1)-P(1)′	89.97(4)
P(1)-Pd(1)-Cl(1)′	178.54(3)
P(1)′-Pd(1)-Cl(1)′	89.40(3)
P(1)-Pd(1)-Cl(1)	89.40(3)
P(1)′-Pd(1)-Cl(1)	178.54(3)
Cl(1)′-Pd(1)-Cl(1)	91.26(4)
O(1)-P(1)-C(7)	103.11(15)
O(1)-P(1)-C(1)	109.04(14)
C(7)-P(1)-C(1)	105.07(15)
O(1)-P(1)-Pd(1)	108.19(10)
C(7)-P(1)-Pd(1)	118.19(11)
C(1)-P(1)-Pd(1)	112.60(11)

Note: Symmetry transformations used to generate equivalent atoms (′): $-x + 1$, y, $-z + 1/2$.

Experimental

General

All syntheses were conducted under dry dinitrogen using the Schlenk technique. Ethyl ether and THF were dried prior the use by distilling over sodium. Methanol was distilled over Mg, triethylamine was dried over KOH and distilled. C_6H_6 and CH_2Cl_2 have been purified according to the standard methods (22). Compounds $C_6H_5CH_2Br$, $PClPh_2$, and PCl_2Ph were purchased from Aldrich and used without purification. $P(C_6F_5)_3$ was purchased from Strem Chemicals. $PdCl_2(cod)$ was obtained according to the literature method (23).

NMR spectra were recorded with Bruker 300 spectrometer and chemical shifts are given vs. TMS (^1H) and vs. 85% H_3PO_4 (^{31}P). Abbreviations used in multiplicities are: singlet (s), doublet (d), triplet (t), quartet (q), and virtual quartet (vq). IR spectra were measured with FT-IR Nicolet Impact 400 instrument. UV–vis spectra were measured with an HP 4852 Diode Array spectrophotometer. GC–MS analyses were carried out with HP 5890 II linked to an HP 5971 A mass detector.

Ligand syntheses

*Syntheses of fluorophenyl phosphines (**2**)*

Diphenyl pentafluorophenyl phosphine ($PPh_2(C_6F_5)$): Bromopentafluorobenzene (2.46 g, 10 mM) was added to a suspension of activated magnesium (0.3 g, 1.2 equiv) in freshly distilled THF (100 mL). The reaction mixture was stirred and heated under reflux until almost all magnesium reacted (~40 min). The reaction mixture was cooled to –30°C and distilled chlorodiphenyl phosphine (1.8 mL, 2.21 g, 10 mM) was added. The cooling bath was removed and the whole mixture was stirred overnight.

The THF was removed on rotary evaporator and the remaining oil was dissolved in methanol (30 mL) and evaporated (3 times). The oil was extracted with dry ethyl ether (3 times), the extracts were collected, and evaporated. The residue was extracted with hot petroleum ether (PE) (bp 40–60°C), the extracts were treated with charcoal, and evaporated. The crude phosphine (1.9 g, 54%) was recrystalized from PE–methanol to give 1.2 g (37.5%) of white crystals. mp 57–60°C (lit. mp (2) 65–68°C). GC–MS: single peak. MS *m/z*: 352. ^1H NMR ($CDCl_3$) δ: 7.35–7.45 (m). ^{31}P NMR ($CDCl_3$) δ: –24.9.

Phenyl di(pentafluorophenyl)phosphine ($PPh(C_6F_5)_2$): The compound was obtained in analogous manner as given above starting from bromopentafluorobenzene (20 mM) and dichlorophenylphosphine (1.38 mL, 1.82 g, 10 mM). The attempted crystallization failed so the phosphine was purified chromatographically on basic alumina with ethyl acetate – hexane (1:1 v/v) as the eluent. The obtained red oil was frozen at –10°C. A small sample of the waxy substance was dissolved in dry methanol and allowed to evaporate slowly. A few reddish crystals obtained were then used to initialize crystallization of the remaining wax. The reddish crystals were recrystallized from methanol (2 times) giving the 2.1 g of the white phosphine (38%). mp 68°C, (lit. (2) mp 68–70°C) GS–MS-MS *m/z*: 442. ^{31}P NMR ($CDCl_3$) δ: –46.4.

Syntheses of phosphinous esters and their palladium complexes ($PdCl_2L_2$)

Our attempts to synthesize pentafluorophenyl esters of (di)phenyl phosphinous acid by the literature method (applied for the synthesis of 2,6-difluorophenyldiphenyl phosphinite) (3) using pentafluorophenol, triethyl amine, and chlorodiphenyl phosphine failed. Based on NMR analysis (data not shown) we suppose that because of its acidic properties pentafluorophenol forms an adduct with the amine rather then reacting with chlorophosphine. Increasing the ratio of phenol and amine to chlorophosphine led to inhomogeneous mixture, which was very difficult to separate and purify. An additional problem of very fast hydrolysis of esters by atmospheric humidity was also observed. We, therefore, decided to use a less convenient indirect way based on the application of sodium methanolate for generation of appropriate phenolate, which in turn reacts with stoichiometric amounts of chlorodiphenyl phosphine in ethyl ether.

Preparation of sodium salts of phenols $Na(OC_6F_5)$ and $Na(O\text{-}3,5\text{-}F_2C_6H_3)$: Metallic sodium was reacted with dry methanol. When all the metal was dissolved, a stochiometric amount of appropriate phenol was added, mixed, and then the methanol was removed on rotary evaporator. To the white product was added dry ethyl ether, mixed, evaporated (3 times), and dried in vacuo.

*Preparation of pentafluorophenyl diphenylphosphinite and $PdCl_2[PPh_2(OC_6F_5)]_2$ (**5**)*: Dry sodium pentafluorophenolate (0.486 g, 2.3 mM) was dissolved in a Schlenk flask in dry ethyl ether and cooled. A solution of of chlorodiphenyl-

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phosphine (0.42 mL, 0.52 g, 2.3 mM) in ethyl ether (10 mL) of was added at once. The formation of sodium chloride occurred immediately. The mixture was stirred overnight. The NaCl was filtered off and solid $PdCl_2$(cod) (0.5 equiv) was added to the filtrate. The mixture was stirred 30 min and the yellow product was filtrated off and dried. ^{1}H NMR ($CDCl_3$) δ: 7.22 (t), 7.36 (t), 7.55 (q, Ph). Anal. calcd. for $C_{36}H_{20}Cl_2F_{10}O_2P_2Pd$: C 47.3, H 2.2; found: C 47.5, H 2.6.

Preparation of (3,5-difluorophenyl) diphenylphosphinite and $PdCl_2[PPh_2(O\text{-}3,5\text{-}F_2C_6H_3)]_2$ ***(6)***: Dry sodium 3,5-difluorophenolate (0.746 g, 5.2 mM) was allowed to react at 0°C with chlorodiphenyl phosphine (0.66 mL, 0.86 g, 3.9 mM) for 2 days. The insoluble salts were filtered off and the solution was used immediately to prepare the palladium complex (**6**) by the method given for (**5**). Yield: 78%. ^{1}H NMR ($CDCl_3$) δ: 6.1 (dd, $J_{H,F}$ = 8 Hz, $J_{H,H}$ = 2.0 Hz), 6.5 (dt, 3,5-$F_2C_6H_3$), 7.38 (t), 7.51 (vt), 7.75 (vq, Ph). Anal. calcd. for $C_{36}H_{26}Cl_2F_4O_2P_2Pd$: C 53.7, H 3.3; found: C 52.7, H 3.3.

Preparation of tert-*butyl diphenylphosphinite and* $PdCl_2[PPh_2(O\text{-t-}Bu)]_2$ ***(1)***: PPh_2(O-*t*-Bu) was prepared by reacting potassium *tert*-butanolate (0.634 g, 5.2 mM) with chlorodiphenyl phosphine (0.70 mL, 0.86 g, 3.9 mM) for 2 days. To the filtrated ether solution was added $PdCl_2$(cod) (0.5 equiv), and the complex (**1**) was isolated after 10 h of stirring of the mixture as a dark yellow powder (yield 85%). ^{1}H NMR ($CDCl_3$) δ: 0.2 (CH_3), 7.22 (t), 7.34 (d), 7.54 (q, Ph). Anal. calcd. for $C_{32}H_{48}Cl_2O_2P_2Pd$: C 54.6, H 6.9; found: C 54.7, H 6.3.

Preparation of ethyl diphenylphosphinite and $PdCl_2[PPh_2(OEt)]_2$ ***(9)***: PPh_2(OEt) was synthesized analogously to the butyl analog using sodium ethanolate (0.316 g, 4.6 mM) and chlorodiphenyl phosphine (0.83 mL, 1.03 g) in ether (30 mL) for 3 days. The addition of $PdCl_2$(cod) (0.5 equiv) and stirring of the mixture for 30 min allowed the formation of complex (**9**) with 90% yield. The crystals for X-ray studies were obtained by recrystallization of the yellow powder from CH_2Cl_2–EtOH. ^{1}H NMR ($CDCl_3$) δ: 0.96 (t, $J_{H,H}$ = 7 Hz, CH_3), 3.67 (q, CH_2), 7.38 (m), 7.48 (m), 7.76 (m, Ph). Anal. calcd. for $C_{28}H_{30}Cl_2O_2P_2Pd$: C 52.7, H 4.7; found: C 52.1, H 4.4.

Other syntheses

The other $PdCl_2L_2$ complexes have been obtained in reaction of $PdCl_2$(cod) with 2 mol equiv of phosphorus ligands in C_6H_6, CH_2Cl_2, or $(C_2H_5)_2O$. Depending on the solubility they have been isolated as precipitates or after solvent evaporation. In all cases the products have been washed by ethyl ether and dried in vacuo. The preparation and spectroscopic data of $PdCl_2[PPh_2(O\text{-}n\text{-}Bu)]_2$ (**10**) and $PdCl_2[P(OPh)_3]_2$ (**11**) are reported in ref. 11.

$PdCl_2[PPh_2(C_6F_5)]_2$ ***(4)***: ^{1}H NMR ($CDCl_3$) δ: 7.42 (t), 7.51 (t), 7.86 (q, Ph). Anal. calcd. for $C_{36}H_{20}Cl_2F_{10}P_2Pd$: C 49.0, H 2.3; found: C 49.9, H 3.0.

$PdCl_2[PPh(C_6F_5)_2]_2$ ***(8)***: ^{1}H NMR ($CDCl_3$) δ: 7.40 (t), 7.48 (t), 7.83 (q, Ph). Anal. calcd. for $C_{36}H_{10}Cl_2F_{20}P_2Pd$: C 40.7, H 1.0; found: C 40.7, H 1.0.

$PdCl_2[PCy_3]_2$ ***(3)***: ^{1}H NMR ($CDCl_3$) δ: 1.24 (s), 1.68 (m), 1.95 (d), 2.49 (m, CH_2). Anal. calcd. for $C_{36}H_{66}Cl_2P_2Pd$: C 58.6, H 9.0; found: C 58.0, H 8.5.

$PdCl_2[P(OCH_2CF_3)_3]_2$ ***(7)***: Anal. calcd. for $C_{12}H_{12}Cl_2F_{18}O_6P_2Pd$: C 17.3, H 1.5; found: C 17.1, H 1.2.

$PdCl_2[P(OMe)_3]_2$ ***(13)***: Compound **13** was obtained in reaction of $PdCl_2$(cod) with a fourfold excess of $P(OPh)_3$ in MeOH (yield 50%). ^{1}H NMR ($CDCl_3$) δ: 1.2 (s, CH_3). Anal. calcd. for $C_6H_{18}Cl_2O_6P_2Pd$: C 16.3 H 4.1; found: C 16.9, H 4.3.

Reactions of $PdCl_2L_2$ complexes with CO and NEt_3

In the typical experiment, MeOH (1 mL) and NEt_3 (ca. 0.01 mL) were added consecutively under dinitrogen to the palladium complex (0.05 g). The Schlenk tube was filled twice with CO and the solution was stirred under CO atmosphere for 30 min. The resulting precipitate of palladium carbonyl complex was filtrated off, dried, and analyzed by IR. The products decompose in the presence of air in ca. 30 min.

Carbonylation reaction of benzyl bromide

To the thermostated glass reactor (40°C), was added under a N_2 atmosphere MeOH (1.5 mL), NEt_3 (1.5 mL), and benzyl bromide (0.5 mL), the mixture was stirred for 1 min and then the catalyst (2.45×10^{-5} mol) in small teflon vessel was added. The reactor was connected with the CO-container (1 atm), flushed twice with CO, and left for 2 h with magnetic stirring. After that time, the reaction mixture was treated with HCl up to pH ca. 7. The reaction products were extracted with ethyl ether (1 mL) and analyzed by GC–MS.

X-ray crystallography

X-ray crystal data, together with refinement details, are given in Table 4. All measurements of crystal were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystal was positioned at 65 mm from the KM4CCD camera, and 612 frames were measured at 0.75° intervals with a counting time of 20 s. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw) programs. The structure was solved by direct methods (program SHELXS 97 (24)) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL 97 (25) programs. Nonhydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from geometry of molecules and $\Delta\rho$ maps but were not refined.

Conclusions

The attempts to correlate the spectroscopic (UV–vis, ^{31}P NMR) data of $PdCl_2L_2$ complexes with the steric and electronic parameters of phosphorus ligands (L) show a dominating influence of the steric over the electronic effect. Correlations between ^{31}P NMR coordination chemical shifts (Δ) and the cone angles (Θ) of L on the other are not perfect, but strong enough to show the tendency and directions

Table 4. Crystal data and structure refinement.

Empirical formula	$C_{28}H_{30}O_2Cl_2P_2Pd$
FW	318.88
T (K)	100(1)
λ (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	10.5041(6)
b (Å)	16.4709(10)
c (Å)	15.1275(11)
V (Å^3)	2617.2(3)
Z	4
D_c (Mg m^{-3})	1.619
μ (mm^{-1})	1.061
F(000)	1296
Crystal size (mm)	0.15 × 0.10 × 0.10
Diffractometer	Kuma KM4CCD
θ range for data collection (°)	3.42–28.74
h, k, and l ranges	–14–8, –21–21, –19–19
Reflections collected	17459
Independent reflections (R_{int})	3217 (0.0384)
Data/parameters	3217/160
Weighting scheme: a, b, c^a	0.0296, 9.32, 3
GoF (F^2)	1.141
Final R_1/wR_2 indices ($I > 2\sigma_I$)	0.0484/0.0975
Largest diff. peak and hole (e Å^{-3})	1.480/–1.022

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\mathrm{Max}(F_o^2, 0) + F_c^2]/c$.

of changes. The most important conclusion of the reported studies is the finding that the catalytic activity of $PdCl_2L_2$ complexes in the carbonylation of benzyl bromide also depends mainly on the steric properties of L and thus on the *cis*–*trans* geometry of the starting complex. Complexes with less sterically hindered ligands (phosphites, phosphinites) having *cis* structure are more active than those with bulky ligands ($\Theta > 140°$, e.g., PCy_3, PPh_2(O-*t*-Bu)). An exception should, however, be noted for complexes with bulky fluorinated phosphines ($PPh_x(C_6F_5)_{3-x}$, x = 0–2), which are *trans*-isomers that exhibit unexpectedly high catalytic activity.

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