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Effects of phosphine substituents on CO and norbornene insertion rates into (P,N)–Pd–alkyl and –acyl bonds

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Abstract

The synthesis is described of (P,N)–PdMe(X) (P,N = R_2P-*o*-$C_6H_4CH_2NMe_2$ (**L1**), Me_2N-*o*-$C_6H_4CH_2$–PR_2 (**L2**), 1-(dimethylamino)-8-(R_2phosphino)naphthalene (**L3**) with $R_2 = Ph_2$ (**a**), Cy_2 (**b**), Me,Ph (**c**, for **L1** only); X = Cl, OTf) and cationic (P,N)–PdMe(L)$^+$ (L, MeCN, CO; anion, $^-$B[3,5-Ph–$(CF_3)_2]_4$). The complexes react with CO to give (P,N)–Pd{C(O)Me}(X/L$^+$) derivatives. Carbonylation is faster in complexes with the more basic phosphines of type **1**, but slower in ligand type **2** and **3**. Norbornene inserts slowly into the (P,N)–Pd–acetyl bond of the cationic borate complexes with **L1**–**3**, and for **L2** with X = Cl, OTf. Cationic palladium complexes with phenyl substituted phosphine ligands are more reactive toward CO/norbornene mixtures than those with cyclohexyl and complexes of **L2** and **L1** react faster than that of **L3**. The observed reactivity is described in terms of differences in CO insertion rates and a rate determining isomerization or trapping by norbornene of the intermediates, *trans*-P (P,N)–Pd{C(O)Me}$^+$ complexes.

Keywords: Palladium; Carbonylation; CO; Kinetics; Olefin insertion

1. Introduction

Olefin polymerization and copolymerization with Pd(II) or Ni(II) catalysts [1–14] has recently become a major field of catalysis research. The facile co- and terpolymerization of CO and 1-olefins to perfectly alternating polyketones is part of this research [2–11]. The majority of metal complexes that are productive catalysts for this polymerization contain *cis*-chelating ligands with either two phosphorus- or two nitrogen-donor atoms, for example, the series of diphenyldiphosphines with C_1 through C_4 bridges first exploited by Drent and coworkers [12], and bipy and phen compounds utilized by a number of groups [13–16].

Mixed (P,N)–Pd(II)-systems, received very minor attention as polymerization catalysts [17,18] and are generally less active. Consecutive insertion of CO and olefins in the palladium carbon bond in square planar complexes with non-C_2-symmetrical bidentate ligands is complicated by possible pre- or post-insertion *cis*–*trans*-isomerization (Scheme 1) [18–21]. We recently reported that in (P,N)–PdR$^+$ complexes, CO insertion takes place in the *trans*-N Pd-alkyl isomers, and norbornene insertion in the *trans*-P Pd-acyl derivatives [22]. The chemoselectivity of the coordination sites for both monomers results from two factors: CO insertion into the Pd–Me bond is faster than *trans*-N to *trans*-P pre-insertion isomerization and, norbornene insertion occurs only in the reactive *trans*-P Pd{C(O)Me}$^+$ isomer [22–24]. Methyl migration in the *trans*-N (P,N)–PdMe(CO)$^+$ complex to yield the *trans*-P (P,N)–Pd{C(O)Me}$^+$ insertion product is fast and reversible, and is followed by a rate-determining isomerization to the *trans*-N (P,N)–Pd{C(O)Me}(CO)$^+$ complex (Scheme 1) [22]. The *trans*-P (P,N)–Pd{C(O)Me}$^+$ complex is very reactive and may be trapped by norbor-

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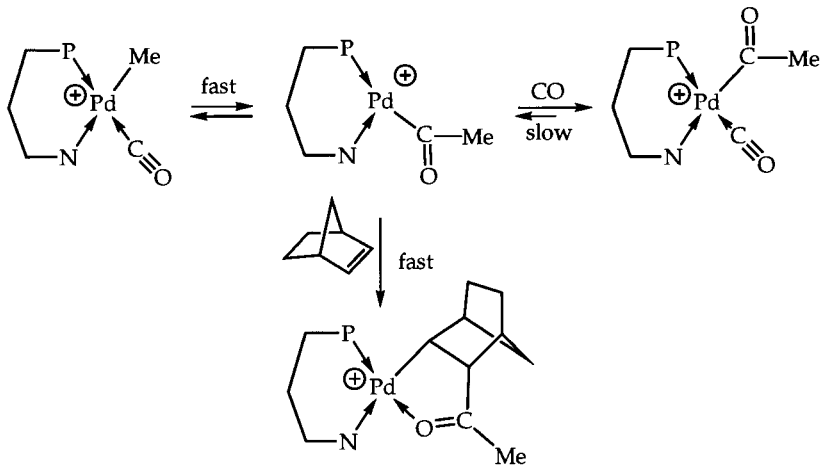


Scheme 1. Reaction pathways for the reaction of (P,N)–PdMe(CO)$^+$ with CO and norbornene.

nene to give the *trans*-N (P,N)–Pd{-2-C_7H_{10}-3-{C(O)Me}}$^+$ complex in a fast reaction. Reaction of the *trans*-N (P,N)–Pd{C(O)Me}$^+$ complex with norbornene is slow. Norbornene insertion into the (P,N)–Pd–{C(O)Me}$^+$ bond proceeds most likely through a pre-insertion isomerization to a configuration with a *trans*-P Pd–{C(O)Me} group.

Palladium complexes with P,N ligands form a very interesting class of potential copolymerization catalysts: The different coordination sites *trans* to the ligand donor atoms have different affinities and reactivity toward (dissimilar) substrates [25,26]. Both features are desirable properties for the synthesis of alternating copolymers through coordination polymerization [27,28]. Based on the insight that CO and norbornene insertion take place (independently) at different coordination sites, we started an investigation on the ligand effects on both type of insertion rates with the objective to prepare active CO–olefin copolymerization catalysts through individually tailoring the phosphine and the nitrogen donors [22]. It was therefore decided to determine the effects of substituent variation of the phosphine and the bridge of rigid C_3-bridged ligands on the individual steps of the CO/olefin insertion pathways of Scheme 1. The reaction of the (P,N)–PdMe(X/L$^+$) complexes with CO, (P,N)–Pd{C(O)Me}(X/L$^+$) with norbornene as well as reaction of (P,N)–PdMe(L)$^+$ with mixtures of CO and norbornene were studied (X = Cl, OTf; L = CO, MeCN). Relative reaction rates were determined from competition experiments and the results were interpreted in terms of the steps in Scheme 1.

2. Results

2.1. Synthesis and characterization of (P,N)–PdMeX and -PdMe$^+$(L) compounds

P,N ligands with a C_3-bridge were chosen in this study (Fig. 1). Ligands of type **L1** have an *N*,*N*-dimethyl-*o*-phosphino-benzylamine frame [29,30]. In type **L2**, the frame has the 'opposite' constitution with *N*,*N*-dimethyl-2-(phosphinomethylene) aniline as a backbone [31]. In type **L3**, a 1,8-substituted naphthalene forms the bridge between the phosphine and the amine [19]. In ligands of type **1**–**3**, the phosphorus atom is substituted with either two phenyl (**a** type) or two cyclohexyl substituents (**b** type), of type **1**, the mixed methyl phenyl substituted phosphine derivative (**L1c**) was also included. Palladium methyl chloride complexes, (P,N)–PdMe(Cl) (**1a**–**3b**, with **L1a**–**L3b** respectively) were obtained from the reaction of the P,N ligands with (COD)PdMe(Cl) [19,32]. CO insertion into the palladium carbon bond in complexes with 1-diphenylphosphino-8-dimethylamino-naphthalene (**L3a**) was studied in depth before by Vrieze and coworkers and forms one of the starting points of this study [19].

$$\underset{}{(COD)PdMeCl} + \underset{\textbf{L1a-3b}}{P,N} \xrightarrow[-\,COD]{} \underset{\textbf{1a-3b}}{(P,N)PdMeCl} \xrightarrow{AgOTf} \underset{\textbf{T1a-3 b}}{(P,N)PdMeOTf} \qquad ((1))$$

The corresponding triflate derivatives (P,N)–PdMe(OTf) (**T1a**–**3b**; OTf: OSO_2CF_3)[1] were prepared through reaction of **1a**–**3b** with AgOTf (Eq. (1)). One

[1] The following codes are used to allow an easy identification of the complexes: prefix **T** is used for triflate, **C** for the CO complex of the cations, **A** for CO insertion, **N** for norbornene insertion, and order of **A** or **N** is such that the first character relates to the first insertion process. Thus **AN** indicates subsequent insertion of CO and norbornene.

Table 1
^{31}P-NMR (ppm) in $CDCl_3$ at 298 K and IR (cm^{-1}) data of complexes containing **L1a–3b**

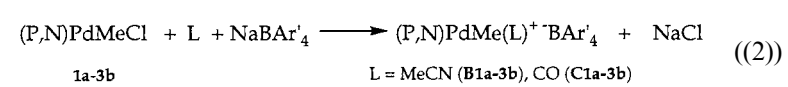
Compound/Ligand	**1a**	**1b**	**1c**	**2a**	**2b**	**3a**	**3b**
Ligand (**L**)	−14.6	−17.3	−37.6	−8.8	6.9	0.5	6.6
PdMeCl	37.7	30.9	15.1	45.7	57.2	40.2	44.5
PdCOMe(Cl) (**A**)	19.3	23.6	4.6	25.7	42.8	20.4	36.8
IR (ν(C=O))	1684	1702	1701	1686	1704	1691	1695
PdMe(OTf) (**T**)	37.7	39.8	21.0	50.6	64.9	42.7	51.2
PdCOMe(OTf) (**TA**)	19.6	31.3	9.9	22.8	50.6	20.6	38.3
IR (ν(C=O))	1696	1701	1695	1704	1695	1691	1695
PdMe(MeCN)$^+$ (**B**)	36.1	35.2	17.9	49.4	60.6	41.7	49.0
IR (ν(C≡N))	2317	2317	2319	2316	2315	2318	2317
(ν(C≡N))	2290	2288	2293	2289	2287	2291	2289
PdCOMe(MeCN)$^+$ (**BA**)	18.2	27.2	6.9	29.5	45.0	22.2	40.7
PdMe(CO)$^+$ (**C**)	34.2	34.6	16.7	48.4	59.8	39.0	43.3
PdCOMe(CO)$^+$ (**CA**)	18.2	27.3	5.2	27.8	42.7	21.9	39.3
$\Delta\delta(^{31}P)^a$ mean	18.1	7.8	11.0	22.1	15.3	19.4	8.2
Standard deviation	1.6	0.6	0.4	3.8	1.3	1.7	3.7

[a] $\delta(^{31}P)$: Difference in ^{31}P-NMR chemical shift between acyl and methyl derivatives of (P,N)–Pd(R)(X/L$^+$).

set of signals is observed in the ^{1}H-, ^{13}C- and ^{31}P-NMR spectrum for both the chloride and the triflate derivatives, demonstrating that only one isomer is present in solution [17,33,34]. The methyl group is bonded *trans* to the nitrogen donor as indicated by a small scalar coupling of the methyl hydrogens to P (J(H–P) ≈ 3 Hz) [35], as expected by the different *trans* influences of the ligands in the coordination sphere of Pd [36].

Cationic complexes of the type (P,N)–PdMe(N≡CMe)$^+$ $^-$B[3,5-Ph-$(CF_3)_2$]$_4$ (**B1–3b**) were prepared in situ by reaction of the respective chlorides with one equivalent of NaB[3,5-Ph–$(CF_3)_2$]$_4$(NaBAr′$_4$) in the presence of one equivalent of acetonitrile (Eq. (2)) [13,37]. Compared to free acetonitrile, it was found that the C≡N stretching frequency is shifted about 35 cm^{-1} to higher wavenumbers in the cationic complexes. The shift is not dependent on the ligand **L1a–3b**. It is about twice as large as was observed for *trans* $(PPh_3)_2$PdMe$^+$(N≡CMe) [38], indicating that the Lewis acidity of the (P,N)–Pd compounds is higher than that of the bisphosphine analogs.

The carbonyl complexes, (P,N)–PdMe(CO)$^+$ (**C1a–3b**) were obtained through reaction of **1a–3b** with the borate anion sodium salt, NaBAr′$_4$, in a CO saturated chloroform solution. The carbonyl stretching frequency is found at 2135 cm^{-1} for all compounds **C1a–3b**, close to that of free CO in solution [19]. In a cationic bisphosphine palladium alkyl CO complex, the stretching frequency was found at 2077 cm^{-1}, again indicating the relative increase in Lewis acidity in the (P,N)Pd-systems [39].



((2))

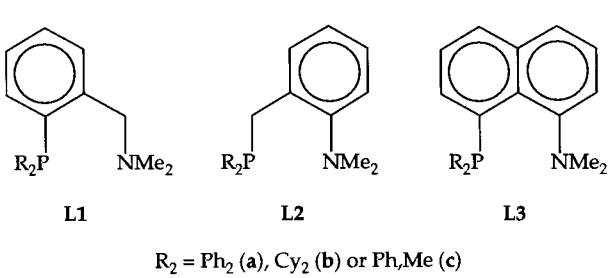


Fig. 1. (P,N)-Ligand systems.

2.2. CO insertion

Treatment of chloride complexes **1a–3b** with CO at 1 bar results in the formation of the acyl complexes (**A1a–3b**), reaction times range from 1 to 50 h for completion. The triflates **T1a–3b** react likewise with CO to the acyl compounds (**TA1a–3b**). Carbonylation of the triflate complexes is about ten times faster than of the chloro compounds [19,40–42]. The IR absorption for the C=O group in palladium acyl chloride compounds appears between 1685 and 1705 cm^{-1}, which compares nicely to the 1693 cm^{-1} reported for **A3a** [19] (Table 1). The acyl group coordinates *trans* to the nitrogen donor as was inferred from the ^{31}P-NMR shift and the absence of a coupling between P and the acyl carbon atom [19].

It is revealing to compare the difference of the ^{31}P-NMR chemical shift ($\Delta\delta(^{31}P)$) between the acyl and

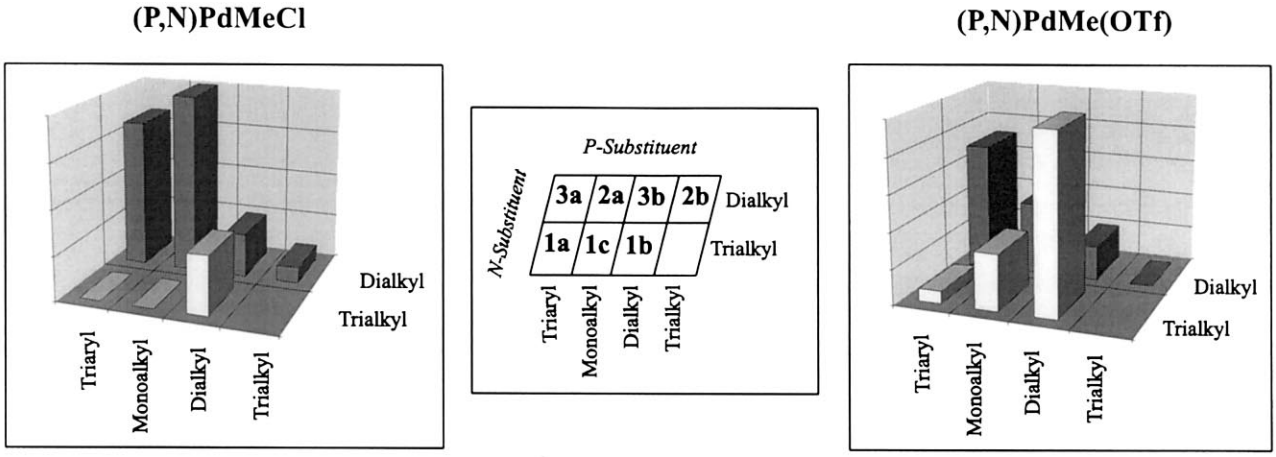


Fig. 2. 2-D Representation of the carbonylation rate of **1a**–**3b** (A) and **T1a**–**3b** (B), axis according to the number of aryl substituents on the phosphine and alkyl on the amine donor.

methyl complexes. In the carbonylated products, an upfield shift is found with a magnitude that is characteristic for the P,N ligand (Table 1), but hardly dependent of the anion X or the neutral donor L. Large upfield shift changes of 15–20 ppm are found for the phenyl phosphino derivatives (with **L1a**, **L2a** and **L3a**).[2] An upfield shift of 18 ppm was also reported for the (1,3-bis(diphenylphoshino)propane)PdMe(X/L) system [19], indicating that such a number is characteristic for PPh_2 donors [40,42]. For the electron richer cyclohexyl phosphine groups (**L1b**, **L2b** and **L3b**), a change of about half that magnitude is observed. The differences $\Delta\delta(^{31}P)$ between phenyl and cyclohexyl derivatives can be attributed to the basicity of the phosphine ligation. The smaller change in chemical shift in the cyclohexyl phosphine derivatives demonstrates that the change in charge density on the electron richer alkyl phosphine is smaller than in the phenyl derivatives. The ^{31}P-NMR shift change between acyl and alkyl derivatives is thus characteristic for a ligand frame and may be used to detect CO insertion (Table 1, vide infra).[3]

2.3. Relative CO insertion rates

Relative carbonylation rates of chloro **1a**–**3b** and the triflate derivatives **T1a**–**3b** were determined from competition experiments in order to obtain insight into the influence of the bridge and phosphine substituents on the CO insertion. Equimolar amounts of two methyl complexes (P,N)–PdMe(X) (X = Cl, OTf) were dissolved in $CDCl_3$. The solution was saturated with CO and the decrease in the concentration of the two methyl complexes was determined by ^{1}H-NMR spectroscopy. The following series were established for the chloride and the triflate derivatives:

$$\mathbf{2a} \overset{1.5}{>} \mathbf{3a} \overset{10}{>} \mathbf{1b} \overset{1.5}{>} \mathbf{3b} \overset{2}{>} \mathbf{2b} \overset{1.5}{>} \mathbf{1c} \overset{1.5}{>} \mathbf{1}$$

$$\mathbf{T1b} \overset{5}{>} \mathbf{T4a} \overset{5}{>} \mathbf{T2} \overset{2}{>} \mathbf{T1c} \overset{2}{>} \mathbf{T4b} \overset{2}{>} \mathbf{T1a} \overset{1.5}{>} \mathbf{T2b}.$$

The numbers above the inequality sign indicate the relative enhancement in rate between two adjacent compounds. The same competition experiments were performed for in situ prepared palladium methyl CO complexes **C1a**–**3b** (Eq. (2)):

$$\mathbf{C1b} > \mathbf{C4a} \overset{2-3}{>} \mathbf{C2a} \overset{4}{>} \mathbf{C1c} \overset{2}{>} \mathbf{C4b} \overset{2}{>} \mathbf{C1a} \overset{1.5}{>} \mathbf{C2b}.$$

The relative rates of carbonylation of **C1a**–**3b** coincide with that of the triflate series. It may thus be assumed that the dissociation of the triflate anion does not significantly affect the relative carbonylation rates and that the observed trends are characteristic for the P,N-ligand frame. Treatment of the acetonitrile adducts **B1a**–**3b** with CO yields the acyl derivatives (**BA1a**–**3b**). The reactivity order of CO insertion was not measured by competition experiments for these complexes, but qualitatively follows the one established for the triflate (**T1a**–**3b**) and cationic CO complexes (**C1a**–**3b**). This was concluded from reaction rate of in situ prepared **B1a**–**3b** with CO.

A more informative overview of the relative carbonylation rates is obtained by a simple two dimensional representation, where the axes are categorized according to the number of aryl substituents on phosphine and alkyl substituents on nitrogen, respectively (Fig. 2). From Fig. 2, the influence of the phosphine substituents on the carbonylation rate can be extracted. In compounds with ligand of type **1**, we observe an increase in the rate of Pd-acyl formation with the electron richer

[2] The $\delta(^{31}P)$ can, like in ^{13}C-NMR, be described through substituent increments [43], with the restriction that no major changes in the geometry around P occurs. These are probably small here: the difference between two structurally alike compounds is considered.

[3] The change of $\Delta\delta(^{31}P)$ between the free ligand and coordinated to (P,N)–PdMeX(/L) (X = Cl, OTf; L = MeC + N) shows a lesser dependence on the phosphine substituents and a much larger shift difference (ca. 50 ppm for type **L1**–**3** and 40 ppm for **L4**).

Table 2
^{31}P-NMR shifts and signal ratios of the reaction mixtures of five equivalents norbornene with **C1a**–**3b** under a CO atmosphere

Cx	δ^{31}P (ppm)			Ratios	Estimated half-life (h)	Observed M^+ (M^+ calculated)	
x	NAN(A)	NAN(B)	AN(X)	B/A/X		NAN	AN
1a	33.95	34.04	34.14	1/2/1	0.3		
1b[a]			32.64[b]		2	668 (669.2)	574 (575.1)
1c[a,c]	18.10	18.33	18.53	3/2/4	$\gg$5	500 (500.9)	594 (595.1)
2a[c]	44.26	44.45	44.7	1/6/2	0.3	656 (657.1)	562 (563.0)
2b	52.68	53.39	53.39	3/1/5	3	668 (669.2)	574 (575.1)
3a[a]	39.33	39.59[b]	[d]	5/1/–	>5	692 (693.2)	(599.0)[d]
3b[a]	45.11	45.44	45.69	4/3/2	>10	704 (705.3)	610 (611.1)

[a] (P,N)–Pd{C(O)R}$^+$ complex (R = Me (**L3a**,**b**), $C_7H_{10}COC_7H_{10}Me$ (**L1b**,**c**)) is also formed.
[b] Less than three signals observed, but the proton NMR spectrum and mass spectrum indicate that all three products are formed.
[c] More products are formed.
[d] Trace amount.

phosphines **b** and **c**, whereas in both types **2** and **3** the opposite effect is found.[4]

2.4. Norbornene insertion into the Pd–acyl bond

The (**L1a**–**3b**)–Pd{C(O)Me}(X) (X = Cl, OTf) derivatives have a low reactivity toward norbornene; insertion was only found for ligand **L2a** and **L2b**. Sen has shown in compounds of the type $\{(PPh_3)_2Pd\{C(O)R\}(MeCN)^+\}^-BF_4$ (R = Me, Ph) that the insertion rate of norbornene is significantly faster than in the corresponding chlorides [38]. Similar observations were made by others [44]. Exchange of the chloride for the non-coordinating BAr'_4 anion in the acyl complexes **A1** and **A3** resulted in insertion of norbornene at an observable rate. Apparently, if a free coordination site is available through the application of non-coordinating anions, olefin insertion occurs readily [22]. This is evident from the appearance of signals of diastereotopic methyl groups for the NMe_2 group in the ^{1}H-NMR spectrum, and a characteristic ^{31}P-NMR signal. An IR absorption in the range of 1620–1635 cm^{-1} indicates that the carbonyl of the norbornyl acyl entity is coordinating to palladium. Competition experiments as for the CO insertion were not performed because of the low rates. Qualitatively, the order is **CA2** $\approx$ **CA1** > **CA3**. For cyclohexyl phosphine derivatives **b** norbornene insertion is generally slower than for the phenyl derivatives **a**, but formation of (P,N)–Pd[3-{C(O)Me}-2-C_7H_{10}]$^+$ (**AN1a**–**3b**) is observed for the complexes with the P,N ligands of Fig. 1.

2.5. Reaction of Pd methyl derivatives with mixtures of CO and norbornene

Reaction of (P,N)–PdMe$^+$ compounds with mixtures of CO and norbornene results in the formation of three major products, **AN1a**–**3b** and the *exo*,*endo* and *exo*,*exo* isomers of (P,N)–Pd{C_7H_{10}–CO–C_7H_{10}Me}$^+$, **NAN1a**–**3b**, the product of consecutive norbornene–CO–norbornene insertion [22]. Formation of the latter two becomes dominant at high norbornene concentrations. The ratio of *exo*,*exo*- to *exo*,*endo*-inserted isomers of **NAN** is dependent on ligand **L1a**–**3b** (Table 2). For compound **C1b**, a ^{31}P-NMR signal was observed at a characteristic position for an acyl derivative (ca. 10% of Σ (**AN1b**, **NAN1b**)) and is assigned to **NANA1b**. Its formation is corroborated by the FAB-MS spectrum of the reaction mixture. For complexes **C3a** and **C3b**, the acyl complexes **CA3a**(**b**) are formed in appreciable amounts (ca. 30% of the total of Pd-complexes). This is explained by the generally lower activity of complexes with ligands **L3** toward mixtures of CO and norbornene (Table 2) [22].

Several competition experiments were carried out to establish the differences in reactivity of cationic complexes with **L1a**–**3b** toward mixtures of CO and norbornene. Equimolar amounts of compounds **1a** and **1b** were activated with $NaBAr'_4$ and reacted with a mixture of CO and about one equivalent of norbornene. It was observed that formation of **AN1a** is faster than that of **AN1b**, contrary to formation of the respective acetyl derivatives **CA1a** and **CA1b**. A similar competition experiment with excess of norbornene analogously shows that formation of **NAN1a** is faster than that of **NAN1b**. Phenyl phosphine derivatives of **L2** and **L3**

[4] Note that geometry is of particular importance. A swap of aryl-phosphine-benzyl-amine **1** to benzyl-phosphine-aryl-amine **2** takes us from the slowest to the fastest CO insertion rates in the chloro derivatives, and in the cyclohexyl triflate derivatives **T1b** and **T2b** from the fastest to the slowest carbonylation rate. The individual type ligand frames respond with a different sensitivity to anion substitution. The ratio of carbonylation rates between **1a**/**1b** over **T1a**/**T1b** increases by a factor of 30, whereas for ligand type **2** the ratio is 0.3 and about 1 for **L3**. As a consequence, the absolute reactivity order changes, but the order within one type of ligand remains the same. Probably, (a preequilibrium) substitution of the anion plays a role in the overall rate of carbonylation [19,40].

also react faster with CO/norbornene mixtures than their cyclohexyl derivatives. Relative reaction rates of the three compounds with diphenyl substituted phosphines (**a**), (**L1a**–**3a**)–$PdMe^+$ with mixtures of CO and norbornene were measured for formation of **AN** in reactions with about one equivalent per Pd as well as for **NAN** in reactions with excess (five equivalents per Pd) norbornene. For methyl complexes with ligands **L** the order was found to be **L2a** ≈ **L1a** ≫ **L3a** in both cases.

3. Discussion and conclusions

An elaborate study was performed on the CO and norbornene insertion chemistry of cationic palladium complexes; the details are discussed below [45]. Complexes with more basic phosphines (**b**,**c**) undergo a faster carbonylation with ligands of type **1**, and a slower one for those of types **2** and **3**. These differences in carbonylation rate between **L1** and **L2**,**3** can be rationalized based on the model given in Scheme 1. CO insertion into the Pd–Me bond of (P,N)–$PdMe^+$ occurs through reversible formation of the *trans*-P $Pd\{C(O)Me\}^+$ followed by a slow isomerization to the stable *trans*-N $Pd\{C(O)Me\}^+$ compound. The overall rate constant is hence a function of the forward and reverse rate constants for formation of the *trans*-P and its isomerization rate to the *trans*-N $Pd\{C(O)Me\}^+$ complex. It may be inferred from the known *trans* influences and effects that with increasing basicity of the phosphine [46], the Gibbs energy and activation energy for formation of the *trans*-P $Pd\{C(O)Me\}^+$ species is increased. Thus, its concentration is lower in complexes with more basic phosphines. *Trans*-P $Pd\{C(O)Me\}^+$ derivatives that have a higher Gibbs free energy on the other hand, may isomerize faster by virtue of the Hammond Postulate [47]. Assuming Curtin–Hammett conditions, it follows that the higher rate of carbonylation of **C1b** over **C1a** results from a negative $\Delta\Delta G^{\ddagger}_{iso}$ for ligand type **1**, and a positive one for ligands of types **2** and **3** ($\Delta\Delta G^{\ddagger}_{iso} = \Delta G_{iso}$ (cyclohexyl) $- \Delta G^{\ddagger}_{iso}$ (phenyl)).

In the above explanation, it is assumed that the (steady state) concentration of the reactive *trans*-P $Pd\{C(O)Me\}^+$ complex is effectively lower in all complexes with cyclohexyl phosphines. This was substantiated for complexes with **L1b** and **L1a** through the competition experiment with mixtures of norbornene and CO. Indeed, (**L1a**)–$PdMe^+$ reacts faster than (**L1b**)–$PdMe^+$, *indicative* of a higher equilibrium concentration of the *trans*-P $Pd\{C(O)Me\}^+$ species or a faster migration of the methyl group to CO.[5] The fact that the order of rates for the formation of the *trans*-N (P,N)–$Pd\{C(O)Me\}(X/L^+)$ is the same within one type of ligand, irrespective whether chloride, triflate, MeCN or CO are coordinating *trans* to the phosphine suggests that the rate determining step is the *trans*-P to *trans*-N isomerization and that other possible reactions steps—e.g. anion/donor displacements by CO, methyl migration, (partial) decoordination of the chelate—are of kinetically less importance for the carbonylation rate.

Norbornene insertion into the (P,N)–Pd–$\{C(O)Me\}^+$ bond is faster for the phenyl substituted derivatives of all ligand types. Insertion proceeds through pre-insertion *trans*-N to *trans*-P isomerization of the acetyl group, which is expected to be more difficult in the cyclohexyl phosphines. It is assumed that the *trans*-N to *trans*-P isomerization in Pd–acetyl derivatives is the rate determining factor and not the subsequent trapping by norbornene (vide infra, Fig. 3). The order of reactivity thus corresponds to the concentration of the *trans*-P $Pd\{C(O)Me\}^+$ intermediates.

The order of reaction rate of palladium methyl cations toward mixtures of CO and norbornene is the same as for the rate of the palladium acetyl compounds with norbornene with respect to phosphine substituents as well as the ligand frames: complexes of **L2** and **L1** react faster than those with **L3**. This again relates to the formation of the *trans*-P $Pd\{C(O)Me\}$ intermediates. The order of rates suggests that a partly flexible backbone in the ligand is favorable for isomerization and migratory insertion of methyl to coordinated CO [19].

Finally, the experimental data and the analysis of the insertion chemistry of cationic P,N-ligated palladium complexes allow the following conclusions for consecutive CO–olefin insertions. Migration of the methyl group to coordinated CO is retarded by large electronic differences between donor atoms [19,23], and has become the rate determining factor in the reaction of the (**L1a**–**3b**)–Pd complexes with mixtures of norbornene and CO. The high rate of reaction of the highly reactive *trans*-P $Pd\{C(O)Me\}^+$ complexes with olefins is thereby outweighed. It is an intriguing question whether it would be possible to change this to a situation with comparable rates of CO and olefin insertion. We are currently investigating this matter.

4. Experimental section

4.1. General considerations

All operations were performed in an inert atmosphere with rigorous exclusion of oxygen and moisture using Schlenk, vacuum-line or glovebox techniques. Solvents were thoroughly dried (ether and THF over Na/benzophenone, pentane over Na/K alloy, toluene over Na, CCl_2H_2 over CaH_2) and distilled prior to use. Norbor-

[5] This does not constitute a conclusive proof, since no data are available on the relative rates of trapping of the reactive *trans*-P $Pd\{C(O)Me\}^+$ intermediates by norbornene.

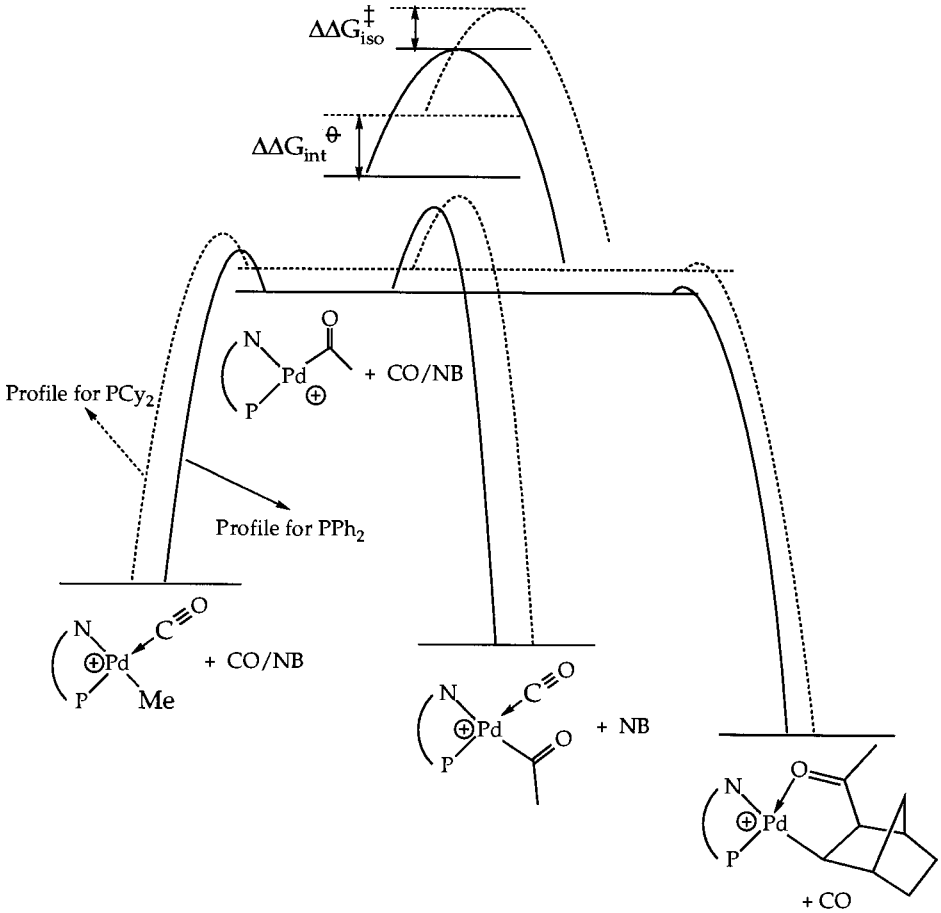


Fig. 3. Qualitative energy diagram for formation of (P,N)–Pd(COMe)$^+$.

nene was distilled from CaH_2. $CDCl_3$ was vacuum transferred from CaH_2. AgOTf was recrystallized through diffusion of pentane into a concentrated toluene solution. CO (5 N) was obtained from Messer-Griesheim and was passed over blue silica prior to use. PMePhCl [48], PCy_2Cl [49], $NaPPh_2$ [50], *o*-lithio-*N*,*N*-dimethylbenzylamine [51], 1-dimethylamino-8-lithionaphthalene [52] and $NaBAr'_4$ [53] and (COD)PdMeCl [54], **L1a** [26], **L1b** [27], **L2a** [28] and **L3a** [26] were prepared as published.

IR spectra were recorded on a Mattson Galaxy spectrometer as Nujol mulls between KBr disks. NMR spectra were recorded on Bruker WM250, AC250, DXR 600 Avance or JEOL FX-90Q, JNM GX400 spectrometers. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents ($CDCl_3$: $\delta = 7.24$ ppm) for ^{1}H-NMR and to characteristic multiplets for ^{13}C-NMR ($CDCl_3$: $\delta = 77.0$ ppm). ^{31}P shifts are reported against external H_3PO_4 at 0 ppm. Mass spectra were obtained with Finnigan MAT 312 or Finnigan MAT 312/AMD5000 instruments. Elemental analyses were carried out at the Micro Analytical Department of the University of Konstanz.

4.2. *L1c*

A solution of ClPMePh (310 mg, 1.96 mmol) in 20 ml of THF was added to solid *o*-lithio-*N*,*N*-dimethylbenzylamine (0276 mg, 1.96 mmol) at room temperature. The mixture turned yellow within minutes. After 20 min, the solvent was exchanged for ether (30 ml) and the resulting suspension was filtered. The ether was removed in vacuum to leave a colorless oil that was pure enough for further reaction. Yield 290 mg (1.08 mmol, 55%). ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.53$ (d, J(H–P) = 4.3 Hz, 3H, P–Me), 2.14 (s, 6H, NMe_2), 3.42 (dd, J(H–P) = 2.9 Hz, J(H–H) = 13.1 Hz, 1H, N–CH), 3.74 (dd, J(H–P) = 2.9 Hz, J(H–H) = 13.1 Hz, 1H, N–CH), 7.2–7.45 (m, 9H, aryl) ppm.

4.3. *L2b*

2-Methyl-*N*,*N*-dimethylaniline (4.8 ml, 0.03 mol) was added to a mixture of 6 ml TMEDA (0.04 mol) and 24 ml of a 1.6 N solution of BuLi (0.038 mol) in hexane. After refluxing for 3 h, the yellow reaction mixture was cooled to -60°C and $ClPCy_2$ (7.66 g, 0.033 mol) was

added. The mixture was slowly warmed to room temperature. Water (50 ml) was added (exothermic reaction). The organic layer was separated and the water phase was extracted twice with ether. The ether and the organic phase were combined and dried over Na_2SO_4. The solvents were removed in vacuum to yield a yellowish crystalline material that was not further purified. Yield: 6.0 g (0.018 mol, 55%). Anal. Found: C, 75.81; H, 10.61; N. 4.42. Calc. for $C_{21}H_{34}NP$: C, 76.09; H, 10.34; N, 4.22%. ^{1}H-NMR (90 MHz, $CDCl_3$): $\delta = 0.8$–2.0 (m, 22H, Cy), 2.87 (d, 2H, J(H–P) = 2.4 Hz, CH_2), 2.65 (s, 6H, NMe_2), 6.91–7.25 (m, 3H, aryl), 7.40 (d, J(H–H) = 7 Hz, 1H, aryl) ppm.

4.4. *L3b*

A THF (50 ml) solution of 8-lithium-(1-*N*,*N*-dimethyl)naphthylamine etherate (1.3 g, 5.04 mmol) was treated with dicyclohexylphosphine chloride (1.17 g, 5.04 mmol). The solution first became yellow and subsequently brown. After stirring for 48 h, the volatiles were removed in vacuum and the residue extracted with 50 ml of ether. The ether was removed and the residue was washed several times with pentane. Yield: 0.82 g (2.2 mmol, 44%). Anal. Found: C, 78.68; H, 9.15; N, 3.52. Calc. for $C_{24}H_{34}NP$: C, 78.43; H, 9.32; N, 3.81%. ^{1}H-NMR (600 MHz, $CDCl_3$): $\delta = 1.1$–1.3 (m, 10H, Cy), 1.63 (m, 2H, Cy), 1.69 (m, 6H, Cy), 1.79 (m, 2H, Cy), 1.88 (m, 2H, Cy), 2.68 (s, 6H, NMe_2), 7.28 (d, J(H–H/P) = 0.9 Hz, 1H, aryl-H7), 7.37 (m, 2H, aryl-H3/6), 7.56 (m, 2H, aryl-H4/5), 7.73 (d, J(H–H) = 7 Hz, 1H, aryl-H2) ppm.

4.5. Compound *1a*

Pd(COD)MeCl (150 mg, 0.56 mmol) was added to a solution of **L1a** (180 mg, 0.56 mmol) in 15 ml of ether. The color changed to faintly yellow, and after stirring for 1 h, the volatiles were removed in vacuum. The off-white residue was washed three times with 20 ml of ether and dried. Yield: 170 mg (0.36 mmol, 64%). Anal. Found: C, 55.65; H, 5.42; N, 2.96. Calc. for $C_{22}H_{25}ClNPPd$: C, 55.48; H, 5.29; N, 2.94%. ^{1}H-NMR (600 MHz, $CDCl_3$): $\delta = 0.58$ (d, 3H, J(H–P) = 3.4 Hz, Pd–Me), 2.59 (s, br, 6H, NMe_2), 3.12 (s, br, 2H, CH_2), 6.86 (ps. t, J(H–H) = 9 Hz, 1H, aryl-H6), 7.19 (dd, J(H–H/P) = 7 and 4.1 Hz, 1H, aryl-H3), 7.30 (ps. t, J(H–H) = 8 Hz, 1H, aryl-H5), 7.40 (m, 1H, aryl-H4), 7.4–7.5 (m, 10H, aryl) ppm. Compounds **1b**–**3b** were prepared analogously.

4.6. Compound *1b*

Scale 2.63 mmol, yield 78%. The color of the solution becomes faintly yellow, the solid is white. Anal. Found: C, 53.93; H, 7.68; N, 3.16. Calc. for $C_{22}H_{37}ClNPPd$: C, 54.10; H, 7.63; N, 2.87%. ^{1}H-NMR (90 MHz, $CDCl_3$): $\delta = 0.73$ (d, J(H–P) = 2.9 Hz, 3H, Pd–Me), 1.0-2.5 (m, 22H, Cy), 2.47 (s, br, 6H, NMe_2), 3.85 (s, br, 2H, NCH_2), 7.17 (m, 1H, aryl), 7.4 (m, 2H, aryl), 7.64 (m, 1H, aryl) ppm.

4.7. Compound *1c*

Scale 0.76 mmol, yield 71%. The color of the solution becomes brown, the solid is brown. Anal. Found: C, 48.08; H, 5.37; N, 2.90. Calc. for $C_{17}H_{23}ClNPPd$: C, 49.29; H, 5.59; N, 3.38%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.80$ (d, J(H–P) = 3.6 Hz, 3H, Me–Pd), 1.83 (d, J(H–P) = 10 Hz, 3H, Me–P), 2.30 and 2.74 (s, 3H, NMe_2), 2.94 (d, br, J(H–H) = 12 Hz, 1H, NCH), 3.46 (d, J(H–H) = 12 Hz, 1H, NCH), 7.2–7.75 (m, 9H, aryl) ppm.

4.8. Compound *2a*

Scale 8.15 mmol, yield 82%. The color of the solution becomes dark-red, the solid is ochre. Anal. Found: C, 54.48; H, 5.14; N, 3.27. Calc. for $C_{22}H_{25}ClNPPd$: C, 55.48; H, 5.29; N, 2.94%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.65$ (d, J(H–P) = 3.3 Hz, 3H, Pd–Me), 3.22 (s, 6H, NMe_2), 3.75 (d, J(H–P) = 11.1 Hz, 2H, P–CH_2), 6.81 (m, 1H, aryl), 6.85 (m, 1H, aryl), 7.17 (m, 1H, aryl), 7.27 (m, 1H, aryl), 7.33–7.41 (m, 6H, aryl), 7.54 (m, 4H, aryl) ppm.

4.9. Compound *2b*

Scale 3.55 mmol, yield 95%. The solution becomes brown, reaction time is 2 h, the solid is grayish. Anal. Found: C, 54.49; H, 7.64; N, 2.90. Calc. for $C_{22}H_{37}ClNPPd$: C, 54.15; H, 7.67; N, 2.87%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.72$ (d, J(H–P) = 2.5 Hz, 3H, Pd–Me), 1.03–2.02 (m, 22H, Cy), 3.08 (s, 6H, NMe_2), 3.14 (d, J(H–P) = 10.8 Hz, 2H, P–CH_2), 7.09–7.51 (m, 4H, aryl) ppm.

4.10. Compound *3b*

Scale 0.84 mmol, 74%. The color of the solution becomes yellowish, reaction time is 48h and the solid is white. Anal. Found: C, 57.82; H, 7.52; N, 3.27. Calc. for $C_{25}H_{37}ClNPPd$: C, 57.26; H, 7.11; N, 2.67%. ^{1}H-NMR (600 MHz, $CDCl_3$): $\delta = 0.81$ (d, J(H–P) = 2.3 Hz, 3H, Pd–Me), 0.44–2.34 (m, 22H, Cy), 3.0 (s, 6H, NMe_2), 7.32 (d, J(H–H) = 7.5 Hz, 1H, aryl), 7.44 (t, J(H–H) = 7.5 Hz, 1H), 7.51 (t, J(H–H) = 7.5 Hz, 1H, aryl), 7.60 (d, J(H–H) = 7.5 Hz, 1H, aryl), 7.75 (t, J(H–H) = 7.5 Hz, 1H, aryl), 7.94 (d, J(H–H) = 7.5 Hz, 1H) ppm.

4.11. Compound *A1a*

CO was admitted to a dichloromethane solution (15 ml) of (*o*-diphenylphosphino–dimethylbenzylamine)PdMeCl (**1a**) (100 mg, 0.21 mmol). The mixture was stirred for 2 days. The solution was evaporated to dryness to give an ochre solid (95 mg, 0.19 mmol, 89%). Anal. Found: C, 52.57; H, 4.99; N, 3.51. Calc. for $C_{23}H_{25}ClNOPPd$: C, 54.77; H, 4.99; N, 2.37%. ^{1}H-NMR (250 MHz, $CDCl_3$): 2.08 (s, 3H, Pd–COMe), 2.46 (s, br, 6H, NMe_2), 3.18 (s, br, 2H, NCH_2), 7.06–7.62 (m, 14H, aryl) ppm. Other derivatives were prepared analogously.

4.12. Compound *A1b*

Scale 0.39 mmol, yield 91%, reaction time 2 days, ochre. Anal. Found: C, 53.25; H, 7.32; N, 3.06. Calc. for $C_{23}H_{37}ClNOPPd$: C, 53.49; H, 7.22; N, 2.71%. ^{1}H-NMR (90 MHz, $CDCl_3$): $\delta = 0.8$–2.4 (m, 22H, Cy), 2.37 (s, 3H, COMe), 2.91 (s, 6H, NMe_2), 3.72 (s, br, 2H, NCH_2), 7.1–7.7 (m, 14H, aryl) ppm.

4.13. Compound *A1c*

Scale 0.15 mmol, yield 89%, reaction time 4 days, ochre. Anal. Found: C, 47.10; H, 5.16; N, 3.29. Calc. for $C_{18}H_{29}ClNPPd$: C, 48.88; H, 5.24; N, 3.17%. ^{1}H-NMR (250 MHz, $CDCl_3$): 1.75 (d, J(H–P) = 9.3 Hz, 3H, PMe), 2.18 (s, 3H, COMe), 2.18 and 2.58 (s, 3H, NMe_2), 2.83 (d, br, J(H–H) = 12 Hz, 1H, NCH), 3.38 (d, J(H–H) = 12 Hz, 1H, NCH), 7.2–7.8 (m, 9H, aryl) ppm.

4.14. Compound *A2a*

Scale 0.63 mmol, yield 98%, reaction time 1 day, yellow-orange. Anal. Found: C, 54.10; H, 5.11; N, 3.13. Calc. for $C_{23}H_{25}ClNOPPd$: C, 54.77; H, 4.99; N, 2.77%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.94$ (s, 3H, COMe), 3.08 (s, 6H, NMe_2), 3.82 (d, J(H–P) = 10.8 Hz), 6.71 (d, J(H–H) = 8.0 Hz, 1H, aryl), 6.78 (t, J(H–H) = 8.0 Hz, 1H, aryl), 7.18-7.55 (m, 12H, aryl) ppm.

4.15. Compound *A2b*

Scale 0.8 mmol, yield 96%, reaction time 1 day, gold. Anal. Found: C, 52.12; H, 7.25; N, 2.72. Calc. for $C_{23}H_{37}ClNOPPd$: C, 53.49; H, 7.22; N, 2.71%. ^{1}H-NMR (600 MHz, $CDCl_3$): $\delta = 0.85$–2.15 (m, 22H, Cy), 2.54 (s, br, 3H, COMe), 2.94 (s, 6H, NMe_2), 3.09 (d, J(H–P) = 11 Hz, 2H, P–CH_2), 7.05 (t, J(H–H) = 7.5 Hz, 1H, aryl), 7.10 (d, J(H–H) = 7.5 Hz, 1H, aryl), 7.25 (m, 2H, aryl) ppm.

4.16. Compound *A3a*

Scale 0.9 mmol, yield 48%, reaction time 12 h, ochre. Anal. Found: C, 56.47; H, 4.31; N, 3.04. Calc. for $C_{26}H_{25}NOPPd$: C, 57.79; H, 4.66; N, 2.59%. ^{1}H-NMR (600 MHz, $CDCl_3$): $\delta = 2.21$ (s, 3H, COMe), 3.21 (s, 6H, NMe_2), 7.36–7.74 (m, 14H, aryl), 7.90 (d, J(H–H) = 7 Hz, 1H, aryl), 8.13 (d, J(H–H) = 7 Hz, 1H, aryl) ppm.

4.17. Compound *A3b*

Scale 0.44 mmol, yield 58%, reaction time 30 h, white. Anal. Found: C, 55.22; H, 6.84; N, 2.75. Calc. for $C_{26}H_{37}ClNOPPd$: C, 56.55; H, 6.75; N, 2.53%. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.2–2.5 (m, 20H, Cy), 2.27 (m, 2H, Cy), 2.70 (s, 3H, COMe), 2.92 (s, 6H, NMe_2), 7.25 (d, J(H–H) = 8 Hz, 1H, aryl), 7.43 (t, J(H–H) = 8 Hz, 1H, aryl), 7.60 (d, J(H–H) = 8 Hz, 1H, aryl), 7.92 (d, J(H–H) = 8 Hz, 1H, aryl), 7.49 (t, J(H–H) = 8 Hz, 1H, aryl), 7.76 (t, J(H–H) = 8 Hz, 1H, aryl) ppm.

4.18. Compound *T1a*

Compound **1a** (0.89 g, 1.87 mmol) was dissolved in 15 ml of CH_2Cl_2 and AgOTf (0.41 g, 0.61 mmol) was added. After stirring for 48 h, a yellow solution had formed that was filtered and evaporated to dryness. Yield: 0.85 g (1.38 mmol, 74%). Anal. Found: C, 47.05; H, 4.41; N, 2.69. Calc. for $C_{22}H_{25}F_3NO_3PPdS$: C, 46.62; H, 4.59; N, 2.36%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.65$ (d, J(H–P) = 1.8 Hz, 3H, Pd–Me), 2.53 (s, br, 6H, NMe_2), 3.32 (s, br, 2H, NCH_2), 7.15–7.56 (m, 13H, aryl), 6.84 (ps. dt, J(H–H) = 1.2 and 6.5 Hz, 1H, aryl) ppm. Other derivatives were prepared analogously.

4.19. Compound *T1b*

Scale 0.76 mmol, yield 84%, reaction time 2 h, faintly yellow. Anal. Found: C, 44.15; H, 5.93; N, 2.04. Calc. for $C_{23}H_{37}F_3NO_3PPdS$: C, 45.89; H, 6.19 N, 2.32%. ^{1}H-NMR (90 MHz, $CDCl_3$): $\delta = 0.78$ (d, J(H-P) = 0.9 Hz, 3H, Pd–Me), 1.0–2.1 (m, 22H, Cy), 2.41 (s, br, 6H, NMe_2), 3.85 (s, br, 2H, NCH_2), 7.1–7.9 (m, 4H, aryl) ppm.

4.20. Compound *T1c*

Scale 0.24 mmol, yield 76%, reaction time 24 h, the brown product was washed three times with 20 ml of ether. Anal. Found: C, 40.22; H, 4.26; N, 2.10; S, 5.68. Calc. for $C_{18}H_{23}F_3NO_3PPdS$ (527.83): C, 40.96; H, 4.39; N, 2.65; S, 6.07%. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.84 (d, J(H–P) = 1 Hz, 3H, Pd–Me), 1.89 (d, J(H–P) = 10.9 Hz, 3H, PMe), 2.25 and 2.62 (s, 3H, NMe_2),

2.99 (d, br, J(H–H) = 12 Hz, 1H, NCH), 3.47 (d, J(H–H) = 12 Hz, 1H, NCH), 7.2–7.75 (m, 9H, aryl) ppm.

4.21. Compound *T2a*

Scale 1.12 mmol, yield 89%, reaction time 24 h, the red-brown product was washed three times with 20 ml of ether. Anal. Found: C, 47.39; H, 4.48; N, 2.63. Calc. for $C_{23}H_{25}F_3NO_3PPdS$: C, 46.83; H, 4.27; N, 2.37%. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.65 (s, br, 3H, Pd–Me), 3.12 (s, 6H, NMe_2), 3.73 (d, J(H–P) = 11.8 Hz, 2H, PCH_2), 6.81 (d, J(H–H) = 7 Hz, 1H, aryl), 6.88 (t, J(H–H) = 7 Hz, 1H, aryl), 7.2–7.54 (m, 12H, aryl) ppm.

4.22. Compound *T2b*

Scale 1.54 mmol, yield 88%, reaction time 24 h, greyish. Anal. Found: C, 46.33; H, 6.29; N, 2.47. Calc. for $C_{23}H_{37}F_3NO_3PPdS$: C, 45.89; H, 6.79; N, 2.32%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.69 (s, br, 3H, Pd–Me), 1.02–1.99 (m, 22H, Cy), 2.98 (s, 6H, NMe_2), 3.15 (d, J(H–P) = 11.6 Hz, 2H, PCH_2), 7.11–7.73 (m, 4H, aryl) ppm.

4.23. Compound *T3a*

Scale 1.8 mmol, yield 39%, reaction time 12 h, brown-orange. Anal. Found: C, 50.52; H, 4.27; N, 2.56. Calc. for $C_{26}H_{25}F_3NO_3PPdS$: C, 49.89; H, 4.03; N, 2.24%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.63 (d, J(H–P) = 3.1 Hz, 3H, Pd–Me), 2.92 (s, 6H, NMe_2), 7.21–7.72 (m, 14H, aryl), 7.90 (m, 1H, aryl), 8.13 (m, 1H, aryl) ppm.

4.24. Compound *T3*

Scale 1.1 mmol, yield 52%, reaction time 48 h, the yellow solid was washed three times with 20 ml of ether). Anal. Found: C, 48.58, H, 6.04; N, 2.63. Calc. for $C_{26}H_{37}F_3NO_3PPdS$: C, 48.94; H, 5.84; N, 2.19%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.45 (m, 2H, Cy), 0.82 (s, 3H, Pd–Me), 0.75–2.05 (m, 18H, Cy), 2.3 (m, 2H, Cy), 2.90 (s, 6H, NMe_2), 7.35 (d, J(H–H) = 7 Hz, 1H, aryl), 7.46 (m, 2H, aryl), 7.65 (d, J(H–H) = 7 Hz, 1H, aryl), 7.74 (t, J(H–H) = 7 Hz, 1H, aryl), 7.96 (d, J(H–H) = 7 Hz, 1H, aryl) ppm.

4.25. Compound *TA1a*

Compound **T1a** (610 mg, 1.1 mmol) was stirred for 2 days in 15 ml of CH_2Cl_2 in a CO atmosphere. The solution was filtered from Pd and evaporated to dryness. A brown-yellow solid resulted. Yield: 0.61 g (1.0 mmol, 96%). Anal. Found: C, 46.52; H, 4.60; N, 2.29. Calc. for $C_{24}H_{25}F_3NO_4PPdS$: C, 46.65; H, 4.07; N, 2.66%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.12 (d, J(H–P) = 0.8 Hz, 3H, COMe), 2.44 (s, br, 6H, NMe_2), 3.18 (s, br, 2H, CH_2), 7.06–7.62 (m, 14H, aryl) ppm. Other derivatives were prepared analogously.

4.26. Compound *TA1b*

Scale 0.24 mmol, yield 67%, reaction time 24 h, brown-yellow. Anal. Found: C, 44.59; H, 6.21; N, 2.16; S, 5.03. Calc. for $C_{24}H_{37}F_3NO_4PPdS$: C, 45.75; H, 5.92; N, 2.22; S, 5.09%. ^{1}H-NMR (90 MHz, $CDCl_3$): δ = 1.0–2.5 (m, 22H, Cy), 2.34 (s, br, 6H, NMe_2), 2.65 (s, 3H, COMe), 3.75 (s, br, 2H, NCH_2), 7.1 (m, 1H, aryl), 7.4 (m, 2H, aryl), 7.6 (m, 1H, aryl) ppm.

4.27. Compound *TA1c*

Scale 0.07 mmol, yield 94%, reaction time 24 h, brown). Anal. Found: C, 40.81; H, 4.79; N, 2.07; S, 5.01%. Calc. for $C_{19}H_{23}F_3NO_4PPdS$: C, 41.06; H, 4.17; N, 2.52; S, 5.76%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.79 (d, J(H–P) = 9.9 Hz, 3H, PMe), 2.15 and 2.56 (s, 3H, NMe_2), 2.58 (d, J(H–P) = 0.9 Hz, 3H, COMe), 2.87 and 3.42 (d, J(H–H) = 11.5 Hz, 1H, NCH_2), 7.2–7.9 (m, 9H, aryl) ppm.

4.28. Compound *TA2a*

Scale 0.93 mmol, yield 94%, reaction time 48 h, dark-ochre. Anal. Found: C, 46.17; H, 4.00; N, 2.41. Calc. for $C_{24}H_{25}F_3NO_4PPdS$: C, 46.65, H, 4.07; N, 2.26%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.97 (s, 3H, COMe), 3.04 (s, 6H, NMe_2), 3.82 (d, J(H–P) = 11.6 Hz, 2H, P–CH_2), 6.69 (d, J(H–H) = 7.5 Hz, 1H, aryl), 6.81 (t, J(H–H) = 7.5 Hz, 1H), 7.10–7.60 (m, 12H, aryl) ppm.

4.29. Compound *TA2b*

Scale 0.8 mmol, yield 96%, reaction time 24 h, gold. Anal. Found: C, 46.28; H, 6.19; N, 2.26. Calc. for $C_{24}H_{37}F_3NO_4PPdS$: C, 45.75 H, 5.91; N, 2.22%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.8–2.1 (m, 22H, Cy), 2.54 (s, 3H, COMe), 2.91 (s, 6H, NMe_2), 3.12 (d, J(H–P) = 11.6 Hz, 2H, PCH_2), 7.05–7.4 (m, 4H, aryl) ppm.

4.30. Compound *TA3a*

Scale 0.9 mmol, yield 83%, reaction time 12 h, yellow-brown. Anal. Found: C, 50.72; H, 3.88; N, 1.99. Calc. for $C_{27}H_{25}F_3NO_4PPdS$: C, 49.59; H, 3.85; N, 2.14% ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.88 (s, 2H, COMe), 2.76 (s, 6H, NMe_2), 7.36–7.76 (m, 15H, aryl), 8.04 (d, J(H–H) = 8.2 Hz, 1H, aryl) ppm.

4.31. Compound *TA3b*

Scale 0.5 mmol, yield 96%, reaction time 24 h, white). Anal. Found: C, 53.89; H, 4.15; N, 3.15. Calc. for $C_{27}H_{37}F_3NO_4PPdS$: C, 53.24; H, 6.12; N, 2.29%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.35$ (m, 2H, Cy), 0.8–2.1 (m, 18H, Cy), 2.33 (m, 2H, Cy), 2.70 (s, 3H, COMe), 2.88 (s, 6H, NMe_2), 7.29 (d, J(H–H) = 7 Hz, 1H, aryl), 7.4–7.55 (m, 2H, aryl), 7.64 (d, J(H–H) = 8 Hz, 1H, aryl), 7.78 (t, J(H–H) ≈ 7 Hz, 1H, aryl), 7.97 (d, J(H–H) = 8 Hz, 1H, aryl) ppm.

4.32. Compounds *B1a–3b*, *BA1a–3b*, *C1a–3b*, *CA1a–3b* and *B1a*

Compound **1a** (P,N)PdMeCl (6.35 mg, 0.0133 mmol), 11.8 mg $NaBAr'_4$ (0.0133 mmol) and 0.72 μl MeCN (0.0133 mmol) were mixed in 0.5 ml $CDCl_3$ to yield a yellow-brown solution and a dark precipitate. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.36$ (d, J(H–P) = 1.5 Hz, Pd–Me), 1.98 (s, 3H, NC<u>Me</u>), 2.30 (s, 6H, NMe_2), 3.20 (s, br, 2H, N–CH_2), 6.8–7.6 (m, 16H, aryl) ppm. Other borate complexes were prepared in the same way. The respective acyl compounds (**BA1a–3b**) were obtained by saturating thus prepared solutions with CO. Reaction times are 2–8 h. The same procedure was used to obtain **C1a–3b** and **CA1a–3b**, respectively, but no MeCN was present and reactions were performed in a CO atmosphere with CO saturated solvent.

4.33. Compound *AN2a*

Compound **A2a** (150 mg, 0.3 mmol) was dissolved in 30 ml of CCl_2H_2 and norbornene (50 mg, 0.6 mmol) was added at room temperature. After stirring for 5 days, the volatiles were removed in vacuum. A brown solid resulted which was isolated. Yield: 160 mg (0.28 mmol, 93%). Anal. Found: C, 57.54; H, 5.55; N, 2.13. Calc. for $C_{30}H_{35}ClNOPPd$: C, 60.21; H, 5.89; N, 2.34%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = -0.21$ (m, 1H, NB), 0.67 (m, 1H, NB), 0.92 (d, J(H–H) = 9.4 Hz, 2H, NB), 1.1–1.45 (m, 3H, NB), 1.71 (d, J(H–H) = 9.7 Hz, 1H, NB), 2.31 (s, 6H, NMe_2/COMe), 2.34 (s, 3H, NMe), 2.57 (d, J(H-H) = 6.5 Hz, 1H, NB), 4.22 and 4.33 (dd, J(H–H)/J(H–P) = 14 Hz, 1H, PCH_2), 6.8–7.6 ppm (m, 11H, aryl), 7.85 (ps. t, J(H–H) = 8 Hz, 2H, aryl), 8.17 (d, J(H–H) = 8 Hz, 1H, aryl) ppm. ^{31}P{^{1}H}-NMR (101 MHz, $CDCl_3$): $\delta = 40.21$ ppm.

4.34. Compound *AN2b*

Compound **A2b** (200 mg, 0.32 mmol) and 60 mg norbornene (0.64 mmol) were dissolved in 30 ml of CH_2Cl_2 and the mixture was stirred for 2 days. The solvent was removed in vacuum to yield a gray solid (172 mg, 0.28 mmol, 89%). Anal. Found: C, 55.29; H, 7.50; N, 2.27. Calc. for $C_{30}H_{45}ClNOPPd$: C, 59.21; H, 7.45; N, 2.30%. ^{1}H-NMR (600 MHz, $CDCl_3$): $\delta = 0.2$ (m, 1H, NB), 0.8–2.2 (m, 29H, NB, Cy), 2.48 (s, 3H, COMe), 2.84 and 3.25 (s, br, 3H, NMe_2), 3.13 and 3.24 (dd, J(H–P) = 20 Hz, J(H–H) = 12.7 Hz, 2H, PCH_2), 7.18–7.65 (m, 4H, aryl) ppm. ^{31}P{^{1}H}-NMR (242.9 MHz, $CDCl_3$): $\delta = 53.21$ ppm.

4.35. Compound *TAN2a*

Compound **T2a** (200 mg, 0.34 mmol) and norbornene (40 mg, 0.43 mmol) were stirred for 2.5 days in 30 ml of CH_2Cl_2. The solvent was removed in vacuum and the resulting solid was washed several times with 20 ml portions of ether to give a brown product. Yield: 220 mg (0.31 mmol, 91%). Anal. Found: C, 55.98; H, 5.37; N, 2.06; S, 4.07. Calc. for $C_{31}H_{35}F_3NO_4PPdS$: C, 52.29; H, 4.95; N, 1.97; S, 4.50%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.3$ (m, 1H, NB), 0.9–1.75 (m, 8H, NB), 2.43 (s, 3H, COMe), 2.86 (d, J(H–H) = 6.5 Hz, 1H, NB), 3.09 (s, br, 6H, NMe_2), 3.64 (ps. t, J(H–H) /J(H–P) = 14 and 13 Hz, 1H, PCH), 4.31 (dd, J(H–H)/J(H–P) = 14 and 8.1 Hz, 1H, PCH), 6.8–7.6 (m, 14H, aryl) ppm. ^{31}P{^{1}H}-NMR (101 MHz, $CDCl_3$): $\delta = 45.35$ ppm.

4.36. Compound *TAN2b*

As **TAN2a** starting from **TA2b** (scale 0.15 mmol, reaction time 3 days, yield 55%, color brown). Anal. Found: C, 51.30; H, 6.71; N, 2.14. Calc. for $C_{31}H_{43}F_3NO_4PPdS$: C, 51.52; H, 6.27; N, 1.94%. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.2$ (m, 1H, NB), 0.75–2.05 (m, 29H, NB, Cy), 2.49 (s, 3H, COMe), 2.86 and 3.25 (s, 3H, NMe_2), 3.25 (m, 2H, PCH_2), 7.20–7.36 (m, 4H, aryl) ppm. ^{31}P{^{1}H}-NMR (242.9 MHz, $CDCl_3$): $\delta = 56.21$ ppm.

4.37. Reactions of *CA1a–3b* with norbornene

A typical experiment is described. Compound **AN1b**. Complex **A1b** (7.5 mg, 0.012 mmol), $NaBAr'_4$ (10.6 mg, 0.012 mmol) and 2-norbornene (2 mg, 0.021 mmol) were dissolved in $CDCl_3$. After 4 h, the following spectrum was recorded. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.68$ (m, 1H, norbornyl), 0.8–2.2 (m, 29H, Cy/NB), 2.05 (s, 3H, COMe), 2.32 (s, br, 3H, NMe), 2.52 (m, 1H, NB), 2.75 (s, 3H, N–Me), 2.93 (m, 1H, NB), 3.17 (d, J(H–H) = 13.2 Hz, 1H, NCH), 4.46 (d, J(H–H) = 13.2 Hz, 1H, NCH), 7.1–7.7 (m, 16H, aryl) ppm. ^{31}P{^{1}H}-NMR (161 MHz, $CDCl_3$): $\delta = 32.62$ ppm.

4.38. Competition experiments for determination of relative carbonylation rates

A typical experiment is described for **T2a** and **T3a**. Compound **T2a** (5.53 mg, 0.01 mmol) and **T3a** (6.3 mg,

0.01 mmol) were dissolved in 0.5 ml of $CDCl_3$. The solution was saturated with CO, and the decrease in concentration of the methyl complexes was monitored by integrating the ^{1}H-NMR signals of the methyl groups against silicon grease as internal standard, and by appearance of the respective acyl signals. The competition experiments were performed for various combinations of both the chlorides **1a**–**3b** and triflates **T1a**–**3b**. Two arbitrary compounds were mixed and the one with the faster carbonylation rate was identified. Then, the fastest was run against another. If it was still the fastest the other was also run against the slower. This procedure was repeated until the order of all compounds was established. The absolute rates allow for a convenient monitoring at room temperature.

4.39. Competition experiments with mixtures of norbornene and CO

A typical procedure is described. Compound **1a** (5.9 mg, 0.0124 mmol), compound **3a** (6.4 mg, 0.0124 mmol), norbornene (2.2 mg, 0.023 mmol) and $NaBAr'_4$ (22 mg, 0.0242 mmol) were dissolved in 0.5 ml of $CDCl_3$. A brown suspension forms, which was analyzed by ^{31}P- and ^{1}H-NMR spectroscopy. It was found that the resonances assigned to **C1a** disappear and of **AN1a** appear considerably faster than the corresponding ones of **C3a** and **AN3a**. Similar experiments were performed to establish the order of reactivity of **1a**/**2a** and **2a**/**3a** toward mixtures of norbornene and CO. It was also found that **1a** and **2a** react at about the same rate with a mixture of excess norbornene (ca. ten equivalents/ ΣPd); both are faster than **3**.

5. Supplementary material available

Spectroscopic properties (^{13}C-NMR shifts, IR) of compounds **L2b**, **L3b**, **1a**–**3b**, **A1a**–**3b**, **T1a**–**3b**, **TA1a**–**3b**, **AN2a**,**b**, **TAN2a**,**b**, **B1a**–**3b**, **BA1a**–**3b**, **C1a**–**3b**, **CA1a**–**3b**, **AN1c**–**3b**, and the data on the statistical analysis of $\Delta\delta(^{31}P)$ (11 pages).

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