High Reactivity of (P,N)Pd(methyl)⁺ Derivatives toward **Mixtures of CO and Norbornene**

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The reactivity of cationic $(P,N)PdMe(CO)^+$ $(P,N = Ph_2P-o-C_6H_4CH_2NMe_2, Me_2N-o-C_6H_4-$ CH₂PPh₂, 1-(dimethylamino)-8-(diphenylphosphino)naphthalene; anion, ⁻B[3,5-Ph(CF₃)₂]₄) toward CO and norbornene is described. CO and norbornene insert *slowly* into the palladium-methyl bond to yield (P,N)Pd[C(O)Me]⁺ and [-3-methyl-2-norbornyl]⁺ derivatives. Compounds (P,N)PdMe(CO)⁺ react fast with mixtures of CO and norbornene under formation of $(P,N)Pd[C_7H_{10}C(O)Me]^+$ and two isomers of $(P,N)Pd[C_7H_{10}C(O)C_7H_{10}Me]^+$. The dissimilarity in rates is explained in a kinetic model, wherein reactive intermediates are reversibly formed and trapped by norbornene in case of trans-P (P,N)Pd[C(O)Me]⁺ and CO in case of trans-P $(P,N)Pd(C_7H_{10}Me)^+$ complexes. CO insertion into the Pd–alkyl bond takes place in the trans-N Pd-alkyl complexes, and norbornene inserts into the Pd-acyl bond from the trans-P Pd-acyl complexes. Isomerization from trans-P to trans-N in (P,N)Pd[C(O)Me]⁺ is slow with respect to CO deinsertion and subsequent norbornene insertion into the trans-P (P,N)Pd⁺-acyl bond. Fast and reversible trans-N-to-P isomerization is found in compounds (P,N)Pd[C(O)-3-Me-2-C₇H₁₀]⁺.

Introduction

The formation of polyketones through the alternating insertion of CO and α -olefins into Pd-C bonds has become a major subject of both fundamental and industrial research.¹⁻⁴ Palladium(II) complexes with symmetrical P,P² and N,N³ ligands are productive catalysts for the copolymerization.¹ Group 8 complexes with P,N

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ligands and with two different donor atoms in general were found to be much less active in this regard.⁴ Vrieze and co-workers,⁵ who studied the reaction between CO and (P,N)Pd-Me complexes, attributed this fact among other factors to an additional activation energy involved with the generation of an unfavorable trans-P Pd-acyl or Pd-alkyl complex (Scheme 1, size of L represents the magnitude of the trans influence). The two possible geometrical isomers of square planar complexes with non- C_2 -symmetric cis-coordinating ligands and two nonidentical groups X and Y, (L,L')MXY, differ in energy.⁶ Since acyl and methyl groups both exert a relatively high trans influence, they tend to bind to the same coordination site in the thermodynamic moststable configuration.⁷ This implies that, after migration of an alkyl group in trans-N (P,N)PdR(CO) to coordinated CO, the most stable isomer is not formed and a driving force for a postinsertion isomerization exists. The Pd-acyl compound may adversely be formed through a preinsertion isomerization through an energetically unfavorable trans-P Pd-alkyl derivative (Scheme 1). It is an open question what role pre- or postinsertion isomerizations in palladium acyl and alkyl compounds play in the formation of polyketones with (L,L')PdR(X) complexes through consecutive CO and olefin insertion.⁵

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Van Leeuwen has shown in two elegant and convincing studies on platinum phenyl and palladium methyl compounds with P,P' bidentates (P,P': phosphine– phosphine' and/or phosphine–phosphite) that CO insertion in cationic monoalkyl CO complexes, (L,L')MR-(CO)⁺, proceeds through migration of the methyl group and is *faster* than cis–trans Pd–Me preinsertion isomerization.⁸

The cationic palladium methyl complex with the (R,S)-BINAPHOS (R,S-2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl 1,1'-binaphthalen-2,2'-diyl phosphite) ligand-phosphine and phosphite donors-was shown to be an active catalyst for the copolymerization of CO and propene. Nozaki4f,h et al. obtained polyketones from this catalyst with a high isotacticity and with a high enantioselectivity. In contrast to the post-migratory-insertion isomerization in the palladium acyl complexes documented by van Leeuwen,^{8b} it is proposed that CO insertion proceeds in the high-energy trans-phosphite (P,P')Pd-alkyl(CO) complex (preinsertion isomerization) and that the subsequent olefin insertion into the Pd-acyl bond also starts from the high energy isomer. Their arguments are based on observations also made by Van Leeuwen,⁸ who found that entities bonded trans to ligands with the higher trans-effect have an exceedingly higher aptitude for migratory insertion than those in their geometrical isomers. It was observed by Nozaki et al.4h that cis-trans isomerizations of cationic acyl and alkyl palladium species are fast with respect to olefin and CO insertion, respectively, and hence are compatible with a preinsertion isomerization.

This leaves an interesting ambiguity about the significance of cis-trans isomerizations and the relative insertion rates of the different monomers at different coordination sites in the polyketone formation with palladium complexes carrying nonsymmetrical ligands. To address this matter, we recently started a study on the reactivity of Pd-alkyl and -acyl compounds with P,N bidentate ligands toward CO and norbornene.⁹ It was found that CO insertion takes place in the trans-N Pd-alkyl isomers and that norbornene insertion into the Pd-acyl bond takes place in the trans-P Pd-acyl complex. The chemoselectivity arises from the fact that trans-N to trans-P isomerization is slow in Pd-alkyl compounds and fast in Pd-acyl complexes, relative to insertion of CO and norbornene, respectively.



Figure 1. P,N ligand systems.

Results

The P,N frameworks in this study have a more or less rigid C₃-bridge (Figure 1). Ligand **a** is N,N-dimethyl-(o-(diphenylphosphino)benzyl)amine, ligand **b** is N,Ndimethyl(2-(diphenylphosphino)methyl)aniline and. ligand c is 1-(diphenylphosphino)-8-(N,N-dimethylamino)naphthalene.⁵ Complexes $(P,N)PdMe(CO)^+$ (1a-c)were obtained by reacting the parent (P,N)PdMeCl (2a-c) with NaBAr'₄ (BAr'₄: B[3,5-Ph-(CF₃)₂]₄) in a COsaturated solution. In a slow process, the corresponding acetyl complexes, $(P,N)Pd[C(O)Me](CO)^+$ (**3a**-c), were formed.⁹ The carbonylation is easily monitored by ³¹P NMR, and during reaction no other compounds than the CO adducts of alkyl and acetyl complexes were observed. The CO stretching frequency of compounds **1a**-**c** and 3a-c is found at 2135 cm⁻¹, indicative of a weak interaction between (P,N)PdR⁺ and CO.⁵ Subsequent reactions of compounds 3a-c with norbornene yield $(P,N)Pd[C_7H_{10}C(O)Me]^+$ (**4a**-**c**, eq 1). This process is



also slow with half-lives of about 2-10 h. In these (P,N)Pd complexes, both alkyl and acetyl groups are coordinated trans to the N donor, the thermodynamically most stable isomer.

Surprising observations were made when the complexes **1a-c** were reacted with *mixtures* of CO and norbornene. A detailed study was carried for complex 1a, but similar behavior was found for the cationic Pd methyl complexes of the other ligands. Instead of the expected sluggish formation of **3a**, followed by a slow norbornene insertion into the Pd-acetyl bond to yield 4a, a fast decrease in the concentration of 1a was observed (by ¹H NMR spectroscopy). Dependent on the molar ratio and the concentration of norbornene and **1a**. three new species are formed in various ratios. These were identified as 4a and two isomers-tentatively assigned to the exo, endo and exo, exo forms-of (P,N)- $Pd[C_7H_{10}C(O)C_7H_{10}Me]^+$ (5a) (see Experimental Section). The formation of the latter compounds is the result of the consecutive insertion of norbornene (exo), CO, and insertion of a second norbornene molecule (exo or endo) into the Pd-C bond.

The identification is based on a combination of multidimensional and multinuclear NMR, IR, and MS analysis as well as independent synthesis. The reaction

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Table 1. ³¹P NMR Shifts and Signal Ratios of the Reaction Mixtures of 5 equiv of Norbornene with 1a-c under CO Atmosphere^a

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1x:	$\delta(^{31}\mathrm{P})$ (ppm)			ratios	est half-life	obsd M ⁺ (M ⁺ calc)	
х	5 (A)	5 (B)	4 (X)	B/A/X	(h)	5	4
a	33.95	34.04	34.14	1/2/1	0.3		
\mathbf{b}^{b}	44.26	44.45	44.75	1/6/2	0.3	656 (657.1)	562 (563.0)
\mathbf{C}^{a}	39.33	39.59^{b}	С	5/1/c	${\approx}5$	692 (693.2)	c (599.0)

 a (P,N)Pd[C(O)Me]+ (3c) complex is also formed. b More products are formed. c Trace amount.

mixture of **1a** and norbornene⁻¹³CO shows three C=O resonances in the $^{13}\mathrm{C}$ NMR spectrum, at δ 236.96 ppm (4a) and δ 241.3/242.2 ppm (5a). In the IR spectrum, 3 new bands of Pd-coordinated C=O entities arise around 1700 cm⁻¹, confirming the expectation of the presence of three carbonyl compounds.⁵ In the mass spectrum (FAB) of the mixture, signals for 4a and 5a are found. The ³¹P NMR spectrum shows three new signals at chemical shifts that are characteristic for palladium alkyl derivatives of ligand $\mathbf{a}^{.9}$ The acyl species $3\mathbf{a}$ is not detectable in the ³¹P NMR spectrum of the reaction mixture. Compound 4a could be synthesized and isolated from the reaction of 1 equiv of norbornene and 1a in the presence of CO. Other products were not formed under those conditions. Adversely, 5a was prepared by reacting 1a with a large excess of norbornene in a CO atmosphere (>20 eq/Pd).

The ³¹P NMR spectrum of the reaction mixtures of 1b,c and CO/norbornene (Table 1, 5-fold excess based on Pd) are reminiscent of the one obtained for 1a, and the MS (FAB) show that fragments with mass corresponding to **5b,c** and **4b,c** are formed. Although it was not possible to correlate the individual amounts of exo,endo- or exo, exo-inserted products with their signal positions in the ³¹P NMR spectrum, the relative signal intensities show that the ratios are dependent on of the type of ligand $\mathbf{a} - \mathbf{c}$ (Table 1). In case of $\mathbf{1c}$, the acetyl complex 3c is also formed in appreciable amounts (-30% of the total of Pd complexes). The increase in reactivity of the palladium complex with ligand c toward mixtures of CO and norbornene is-in comparison to carbonylation of the cationic methyl derivatives-not as pronounced as was found for complexes with ligand a or ligand **b**. The reactivity of the later two is generally higher (vide infra).

The formation of $(P,N)Pd[C_7H_{10}C(O)C_7H_{10}Me]^+$ (5a) indicates that initial insertion of norbornene into the Pd-Me bond has taken place. Norbornene insertion was also observed in the absence of CO. Treatment of complex (P,N)PdMeCl (2a) with 1 equiv of NaBAr'₄ in the presence of an excess of norbornene gives evidence for insertion into the palladium-methyl bond but at a rate that is substantially lower than the consecutive norbornene-CO-norbornene insertion. The ³¹P NMR spectrum of the reaction mixture in early stages of the reaction shows a broad resonance at about 41 ppm. Broad signals are also present in the reaction mixture of **1a**-**c** and mixtures of norbornene and CO. The broad resonances are tentatively assigned to a contact ion pair (P,N)PdMe⁺(borate)⁻ and/or CO and norbornene adducts of (P,N)PdMe⁺. The adducts may be in dynamic equilibrium with the free cation and CO or norbornene; its exact nature unknown. If the reaction mixture of (P,N)PdMeCl (**2a**), NaBAr'₄, and excess of norbornene is subsequently treated with CO, fast formation of (P,N)-Pd[C₇H₁₀C(O)C₇H₁₀Me]⁺ (**5a**) takes place.

The acetonitrile adduct of the norbornene insertion product $(P,N)Pd(C_7H_{10}Me)(NCMe)^+$ (**6a**) can be isolated from the reaction of $(P,N)PdMe^+$ with excess of norbornene after addition of 1 equiv of acetonitrile.¹⁰ This compound reacts—in contrast to **1a**—with CO in a *fast* process to give the carbonylated compound $(P,N)Pd-[C(O)C_7H_{10}Me](NCMe)^+$ (**7a**): reaction is complete within minutes at room temperature and 1 bar of CO pressure. The consecutive norbornene insertion into the Pd–acyl bond of $(P,N)Pd[C(O)C_7H_{10}Me]^+$ (to yield **5a**) is also fast, complete within 2 min under the latter conditions after the addition of norbornene.

Discussion

A couple of remarkable observations were made during the insertion reactions of the cationic (P,N)Pd methyl and acyl complexes (Scheme 2). A high rate of reaction of the methyl complexes **1a**–**c** toward a mixture of CO–norbornene is found relative to the consecutive insertion of CO into the Pd–Me and norbornene into the Pd–acyl bond, although–at least at low norbornene concentration—the same products are formed. The same is true for **5a**: its formation from the parent methyl cation is fast, but formation of **6a** through norbornene insertion into the Pd–Me bond of **1a** is slow. Second, norbornene coordination and subsequent insertion into the Pd–Me⁺ bond is competitive with that of CO.

Evidently, reactions of CO and norbornene and mixtures thereof with the (P,N)Pd compounds are not simple processes. A possible rationalization for the observations is given in Scheme 2. It contains the reaction products and feasible intermediates together with an assessment of relative rates. In the proposal, CO and norbornene compete for the fourth coordination site in the cationic palladium methyl complexes. The exclusive formation of 5a at high norbornene concentration and 1 bar CO is explained through a higher isomerization rate of the trans-P (P,N)PdC₇H₁₀Me⁺ intermediate relative to that of the analogous reaction products of CO (assuming Curtin–Hammett conditions). Carbon monoxide is not particularly strongly bonded to (P,N)PdMe⁺, as is indicated by the CO stretching frequency of 2135 cm⁻¹ in the CO adducts 1a-c, and is apparently readily displaced by norbornene. Facile decoordination of CO was also observed in (BINAPHOS)-PdMe⁺.^{4h} CO adducts with the same stretching frequency are known to be exceedingly more stable ($K \approx$ $10^{-(5-6)}$) than ethene adducts, like the ones observed for P,P and N,N systems reported by Drent^{1h} and Brookhart.^{3c} Since the rate of the consecutive reactions is here the determining factor for product formation, olefin insertion is overall a faster process than CO insertion.

The key to understanding the increased reactivity of the (P,N)PdMe⁺ compounds toward mixtures of CO and norbornene is to assume that an intermediate is fast and reversibly formed from the starting materials which

⁽¹⁰⁾ The cationic complex (L1)Pd– $C_7H_{10}Me^+$ decomposes slowly without addition of acetonitrile.

Scheme 2 $\begin{array}{c}
 & \begin{pmatrix} N \\ P \\ P \\ P \\ Me \end{array} & \overbrace{CO} \\ \downarrow P \\ Me \end{array} & \overbrace{CO} \\ \downarrow P \\ Me \end{array} & \overbrace{CO} \\ \downarrow P \\$

is subsequently trapped if CO and norbornene are present. This intermediate is trans-P Pd[C(O)Me] in the formation of compounds 4 ($Pd[C_7H_{10}C(O)Me]$) or trans-P Pd(3-methyl-2-norbornyl) for product 5 (Pd- $[C_7H_{10}C(O)C_7H_{10}Me]$) formation. They derive from the CO and the norbornene adduct of trans-N (P,N)PdMe⁺ through migratory insertion. In the absence of norbornene, the trans-P Pd[C(O)Me] compounds isomerize in a slow step to the more stable trans-N isomers. Since the trans-P Pd[C(O)Me] complex is not observed in detectable amounts during reaction of (P,N)PdMe⁺ with CO, it follows that trans-P (P,N)Pd[C(O)Me]⁺ complexes will undergo rapid decarbonylation to give back the starting materials. This was also observed in (N,N)-Pd(alkyl)⁺ compounds.^{3c} Note that the formation of the trans-P $(P,N)Pd[C(O)Me]^+$ is fast. In the presence of norbornene, the trans-P Pd[C(O)Me] is rapidly captured to give compounds 4. This accounts for the high reaction rates that are found if mixtures of CO and norbornene are reacted with the palladium methyl compounds.

Similar arguments are put forward to describe the process leading to **6a** and subsequently to **5a**. Under CO free conditions and in the presence of excess norbornene, migratory insertion of the methyl group in the norbornene adduct gives a trans-P (P,N)Pd(C_7H_{10} -Me)⁺ complex. The preferred reaction mode of this reactive intermediate is deinsertion to the starting materials, a reaction that was also described by Catellani.¹¹ Isomerization to the thermodynamically more stable trans-N Pd(C_7H_{10} Me) isomer is not very competi-

tive with norbornene deinsertion and hence, formation of **6a** is slow. Apparently, trapping of the trans-P isomer of **6a** by norbornene is not effective and polynorbornene is not formed. Steric repulsions may prevent the formation of the congested intermediate (P,N)Pd-($C_7H_{10}Me$)⁺(norbornene) adduct. This is different for the smaller CO that can trap the trans-P isomer of **6a** to yield the thermodynamically stable trans-N derivative (P,N)Pd[C(O)C₇H₁₀Me]⁺ (**7a**). It could be independently shown that the latter reacts rapidly with norbornene (<2 min) to compounds **5a**. Thus addition of CO to a mixture of the methyl compound and excess of norbornene leads to a rapid formation of compounds **5a**.

Such a kinetic scheme would account for all observations. Its feasibility is discussed below. One of the assumptions made is that the primary insertion intermediates of the methyl derivatives are formed from the ground state in a single step and that their postinsertion isomerization is relatively slow. The latter was observed before: Van Leeuwen^{8b} obtained the high-energy forms of the CO insertion into the Pd-Me bond in cations with nonsymmetric cis-coordinating bidentates as reactive products (in contrast to the mechanistic scheme proposed by Nozaki^{4h}). A direct argument in favor of the explanation given here is that if **3a** (or **6a**) alternatively would have been formed via a preinsertion isomerization in **1a** and thus that the trans-P Pd[C(O)-Me] (and Pd($C_7H_{10}Me$)) is not an intermediate, then it is hard to envision how the formation of the norbornyl acyl complex 4a (and 5a) through the action of norbornene (or CO) could be so much faster than that of **3a** (or **6a**; vide supra). Note that acyl compound **3a** was not found to undergo rapid decarbonylation (and 6a is

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stable toward norbornene deinsertion).⁹ Therefore a different, *i.e.* the trans-P, Pd[C(O)Me] (and Pd(C₇H₁₀-Me)) complex is intermediately formed. Furthermore, the trans-P (P,N)Pd[C(O)Me]⁺ and (P,N)Pd(C₇H₁₀Me)⁺ intermediates do not have the thermodynamic most stable configuration. It has been know from calculations and experiments that such compounds are significantly more reactive than the cis-P isomers.^{8b,12}

The carbonylation of **6a** is fast, contrasting that of **1a**. Since cis–trans isomerization in **6a** is slow—implied by the fact that the product is stable and its formation is slow—it is concluded that $Pd[C(O)-3-Me-2-C_7H_{10}]$ formation proceeds through postinsertion isomerization, the same pathway as for **1a**. In contrast to the acyl complex **3a**, postinsertion isomerization is fast in trans-P (P,N)Pd[C(O)-3-Me-2-C_7H_{10}] (**6a**). This may be the result of the higher steric congestion (vide infra) in trans-P (P,N)Pd[C(O)-3-Me-2-C_7H_{10}] compared to trans-P (P,N)Pd[C(O)Me] (**3a**).

It is further concluded that norbornene insertion into the $Pd-C(O)R^+$ bond of compounds **3** and **7** occurs only in the trans-P isomers. This is suggested by the geometry of the trans-N configuration of the products **4** and **5**: a preinsertion isomerization is very likely since the alternative postisomerization in the products with a chelating keto functionality is expected to be slow enough to allow the observation of the trans-P geometrical isomer. Trans-P-to-trans-N isomerization in complexes (P,N)Pd(alkyl)⁺ (methyl or C₇H₁₀Me) is generally slow.^{8b} The dissimilar ratios exo, endo- and exo, exo-5a-c that are obtained with the various P,N ligands also suggest that olefin insertion takes place cis to the phosphine where the largest changes in the sterics of the ligands are. The fact that we are not able to assign the configuration of the exo, endo- or exo, exo-5a-c products, however, thwarts further interpretation.^{4h} Another observation corroborates the assumption of norbornene insertion from the high-energy acyl isomers. Norbornene insertion into the Pd-acyl bond in **3a**, a compound with a *slow* cis-trans-P isomerization, is *slow*, whereas in compound **7a** a *fast* cis-trans isomerization and a *fast* olefin insertion is found. The faster preisomerization in 7a relative to 3a can be understood from a steric point of view. The steric bulk of the P,N ligand is the smallest cis to the amine, implying that, for sterically more demanding groups bonded cis-P to Pd, a driving force for isomerization to cis-N emanates (and decreasing the Gibbs free energy difference between trans-N and trans-P isomers). A possible lower aptitude for deinsertion of CO relative to isomerization in cis-N 7a can likewise be expected on the basis of the steric strain imposed by the P substituents in the putative product $(P,N)Pd(3-Me-2-C_7H_{10})(CO)^+$.

Concluding Remarks

The reactions of the (P,N)Pd–alkyl and –acyl complexes with CO and norbornene, and mixtures thereof, form a complex system of competing and reversible reactions. The rate of trans-P to trans-N isomerization in (P,N)Pd[C(O)Me]⁺ is the rate-determining factor in the carbonylation of (P,N)PdMe⁺ (**1a**–**c**). For (P,N)Pd-[C(O)-3-Me-2-C₇H₁₀] derivatives, the trans-N trans-P isomerization is fast in both directions. Trans-P to trans-N isomerization in $(P,N)Pd(alkyl)^+$ complexes appears to be slower than CO insertion in both the methyl and 3-methyl-2-norbornyl compounds. Norbornene insertion into the Pd–C bond in $(P,N)Pd-[C(O)R]^+$ (R = Me, C₇H₁₀Me) takes only place from the reactive trans-P isomer. In contrast, norbornene insertion proceeds from the trans-N isomer of $(P,N)PdMe^+$.

This leads to the following mechanistic scheme for the consecutive insertion of CO and olefins into the Pd-C bond in (P,N)PdR⁺ complexes: CO insertion takes place from the ground-state configuration and olefin insertion from the high-energy acyl intermediate. This leads to alternating insertions of different monomers at different sites: Migratory insertion of the olefinic monomer occurs from the coordination site with the smallest trans influence. The chemoselectivity arises from the fact that norbornene does not insert into the Pd-acyl bond of the thermodynamically more stable isomer, and Pd-alkyl preinsertion isomerization is slow relative to CO coordination and insertion. The underlying grounds for a slow trans-N-trans-P isomerization in the Pd-alkyls and a faster one for the Pd-acyl complexes may lay in the higher reactivity in general (Hammond postulate^{13,14}) or in the fact that the acyl group may become η^2 -coordinated, thereby lowering the activation energy and/or thermodynamic differences between cis and trans-P isomers. The rate-determining step in the putative polyketone formation with these complexes is CO insertion into the Pd-alkyl bond of the thermodynamically most stable isomer. This kinetic scheme contrast the one reported for (phen)PdMe⁺ cations, where olefin insertion is the rate-determining factor.^{3c}

Experimental Section

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, CCl₂H₂ over CaH₂) and distilled prior to use. CDCl₃ was vacuum transferred from CaH₂. Pd compounds were prepared as reported.^{5,9} NaBAr'₄ was prepared as published.¹⁶ Norbornene was distilled from CaH₂. CO (5N) was obtained from Messer-Griesheim and was dried over a column (2 ft, diameter 2 in.) of blue silica prior to use. 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 (CDCl₃: δ = 7.24 ppm) for ¹H NMR and to characteristic multiplets for ¹³C NMR (CDCl₃: δ = 77.0 ppm). ³¹P NMR spectra were recorded in the ¹H-decoupled mode, and ³¹P NMR shifts are reported against external H_3PO_4 at $\delta = 0$ ppm. Mass spectra were obtained with Finnigan MAT312 or Finnigan MAT 312/ AMD5000 instruments. Elemental analyses were carried out at the Micro Analytical Department of the University of Konstanz.

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 Table 2.
 ¹H NMR and ¹³C NMR Data for Compounds 5a

major iso	omer		minor isomer		
¹ H NMR	¹³ C NMR	assgnt	¹³ C NMR	¹ H NMR	
	242.2	C=O	241.3		
0.93, d, 7 Hz	18.51	Me	17.33	0.81, d, 7 Hz	
2.766	50.11	NMe	50.11	2.77	
2.38	46.44	NMe	46.31	2.37	
3.42, d, 12 Hz	65.56	PCH	65.56	3.42, d, 12 Hz	
2.98, d, 12 Hz		PCH		2.98, d, 12 Hz	
2.78	74.56	NB-CH	73.62	2.55	
3.02, d, 8 Hz	55.03	NB-CH	55.33	3.10, d, 8 Hz	
2.53, d, 10 Hz	41.56	NB-CH	43.34	2.55, br s	
2.28	43.67	NB-CH	41.3	2.33, br s	
2.17, br m	43.78	NB-CH	42.94	2.17, br m	
1.95, br s	43.23	NB-CH	43.76	1.92, br s	
1.75, br s	43.71	NB-CH	43.43	1.77, m	
1.67	55.54	NB-CH	54.6	1.67	
1.75, br s	37.58	NB-CH ₂	37.47	1.87, m	
1.27, br s				1.3, s	
1.75	34.8	$NB-CH_2$	34.8	1.67	
1.23				1.20	
1.4 - 1.6	28.75	$NB-CH_2^b$	28.66	1.4 - 1.6	
0.9 - 1.2	29.33	$NB-CH_2^b$	29.20	0.9 - 1.2	
0.3, br s	29.64	$NB-CH_2^b$	29.38	0.3, br s	
	29.87	$NB-CH_2^b$	29.91		

^a Assignments on basis of ¹H NMR, ¹³C{¹H} NMR, APT, HMQC, and/or HMBC NMR spectroscopic techniques. Phenylic resonances 7.25–7.66 ppm in ¹H NMR, 117.49, 124.59 (q, $J_{CF} = 271$ Hz, CF_3), 125.03, 127.21, 128.19, 128.79, 128.96, 129.07, 129.38, 130.12 (d, $J_{CP} = 10.7$ Hz), 131.9, 133.68 (d, $J_{CP} = 10.8$ Hz), 134.43 (d, J_{CP} = 10.8 Hz), 13 13 Hz), 134.84, 135.21 (d, $J_{CP} = 13$ Hz), 138.71 (d, $J_{CP} = 4.6$ Hz) ppm in ¹³C{¹H} NMR. ^b Correlation between ¹H and ¹³C shift not unambiguously established. HMBC spectrum of the ¹³C=O-labeled compound shows cross signals of the major isomer to NB-CH resonances at 3.02, 2.78, 2.28, 1.67 (Pd-CH) ppm and for the minor isomer at 3.1, 2.55 ppm. After decomposition of the complexes 5a through addition of Lawesson's reagent (reaction time 24 h), the resonances of the methyl groups show up as doublets at 0.79 and 0.71 ppm in the ¹H NMR spectrum, and in the ¹³C NMR APT spectrum, again 28 signals show up for the four different norbornene units, as well as two signals for the methyl groups at 17.48 and 17.11 ppm (ratio $\approx 2/1$).

Reaction of 1a–c with CO and Mixtures of Norbornene and CO. A typical experiment is described. Compound (P,N)PdMeCl (**2a**) (6.35 mg, 0.0133 mmol), NaBAr'₄ (11.8 mg, 0.0133 mmol), and norbornene (4.7 mg, 0.05 mmol) were dissolved in 0.7 mL of CO-saturated CDCl₃. The reaction was monitored by both ³¹P and ¹H NMR spectroscopy. After conversion was detected, an aliquot was removed from the sample, evaporated to dryness, and analyzed by FAB mass spectroscopy. Reactions of the acyl complexes **3a–c** with norbornene were performed in a similar way, both starting from (P,N)Pd(COMe)Cl (**8a–c**) and from the reaction products of the above experiments.

Compound 4a. (P,N)PdMeCl (2a) (84 mg, 0.18 mmol), norbornene (20 mg, 0.19 mmol), and NaBAr'₄ (160 mg, 0.18 mmol) were suspended in 15 mL of CO-saturated CH₂Cl₂. The mixture was stirred for 4 d, after which it was filtered over a short column of Na₂SO₄. The volatiles were removed in a vacuum to yield an ochre solid (203 mg, 0.14 mmol, 79%). ¹H NMR (600 MHz, CDCl₃): $\delta = -0.03$ (m, 1H, H3-exo), 0.9 (m, 1H, H3-endo), 1.03 (m, 1H, H4-exo), 1.25 (d, 1H, $J_{\rm HH} \approx$ 10 Hz, H7-endo), 1.39 (m, 1H, H4-endo), 1.63 (m, 1H, Pd-CH), 1.75 (m, 1H, H7-exo), 1.77 (m, 1H, H2), 2.30 (s, 3H, C(O)Me), 2.32 (s, 3H, NMe), 2.46 (m, 1H, H5), 2.69 (d, 1H, $J_{\rm HH} = 6.6$ Hz, H6), 2.70 (s, 3H, NMe), 2.96 (d, 1H, $J_{\rm HH} = 12$ Hz, NCH), 3.39 (d, 1H, $J_{HH} = 12$ Hz, NCH), 7.1–7.8 (m, 26H, aryl) ppm. ³¹P-{¹H} NMR (101 MHz, CDCl₃): $\delta = 34.14$ ppm. Anal. Calcd for C₆₂H₄₇BF₂₄NOPPd: C, 52.21; H, 3.32; N, 0.98. Found C, 51.73; H, 3.56; N, 0.87.



Compound 5a. Compound 2a (90 mg, 0.19 mmol), NaBAr'₄ (180 mg, 0.19 mmol), and norbornene (1.2 g, 12.7 mmol) were suspended in 5 mL of CCl₂H₂. The mixture was stirred for 1.5 h under a CO atmosphere. A black precipitate formed during this time. The reaction mixture was subsequently filtered, and the filtrate was evaporated to dryness. The oily residue solidified after the addition of 10 mL of pentane. The pentane was decanted off, and the remaining off-white solid was washed with two other portions of pentane (10 mL). An off-white solid was isolated after drying. Yield: 183 mg (0.12 mmol, 63%). The NMR (¹H, ¹³C, ³¹P) spectra show that two similar isomers are formed in a ratio A/B of about 2/1 (Table 2). Anal. Calcd for C₆₉H₅₇BF₂₄NOPPd: C, 54.51; H, 3.78; N, 0.92; Found: C, 54.17; H, 3.84; N, 1.09. Decomposition was achieved by adding Lawessons reagent to a solution of 5a in CDCl₃ after 24 h. The resulting solution was characterized by ¹H and ¹³C NMR.

Compound 6a(MeCN). Compound (P,N)PdMeCl (2a) (98 mg, 0.21 mmol), NaBAr'₄ (200 mg, 0.22 mmol), MeCN (11 μ L, 0.20 mmol), and norbornene (200 mg, 2.1 mmol) were suspended in 10 mL of CH₂Cl₂. The mixture was stirred for 24 h, after which it was filtered over a short column of Na₂SO₄. The volatiles were removed in a vacuum, and the remaining ochre solid was washed twice with 10 mL of pentane and dried. Yield: 230 mg (0.16 mmol, 77%). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.34$ (m, br, 1H, NB), 0.8–1.9 (m, 7H, NB), 1.28 (d, 3H, $J_{\rm HH} = 6.9$ Hz, NB-Me), 2.1 (m, 1H, NB), 2.20 (s, 3H, NMe/NCMe), 2.27 (s, 3H, NMe/NCMe), 2.40 (s, 3H, NMe/ NCMe), 3.18 (d, 1H, J_{HH} = 13 Hz, NCH), 3.36 (d, 1H, J_{HH} = 13 Hz, NCH), 6.9-7.7 ppm (m, 26H, aryl). ³¹P{¹H} NMR (161 MHz, CDCl₃): $\delta = 35.74$ ppm. Anal. Calcd for C₆₃H₅₀BF₂₄N₂-PPd: C, 52.57; H, 3.50; N 1.94. Found: C 53.13, H 3.77, N, 1.48.

Compound 7a. Compound **6a**(MeCN) (65 mg, 0.045 mmol) was dissolved in 5 mL of CO-saturated CHCl₃. After the solution was stirred for 15 min, the volatiles were removed in a vacuum. A brown solid resulted that was isolated. Yield: 58 mg (0.039 mmol, 87%). The compound is unstable and decomposes both in solution and the solid state. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.7-1.6$ (m, 11H, NB, NB–Me), 1.66 (d, 1H, $J_{\text{HH}} = 3.6$ Hz, NB), 1.75 (m, 1H, NB), 2.14 (s, 3H, NMe/NCMe), 2.61 (d, 1H, $J_{\text{HH}} = 4.8$ Hz, NB), 3.04 (m, 1H, NCH₂), 3.14 (m, 1H, NCH₂), 6.9–7.7 ppm (m, 26H, aryl). ³¹P{¹H} NMR (161 MHz, CDCl₃): $\delta = 20.13$ ppm. Anal. Calcd for C₆₄H₅₀BF₂₄N₂-OPPd: C, 52.39; H, 3.43; N, 1.91. Found: C, 50.33; H, 3.48; N, 1.11.

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Supporting Information Available: Text describing spectroscopic data for and/or synthetic procedures of **4a**–**c**, **6a**(MeCN), **7a**, **5a**, **1a**–**c**, and **3a**–**c** (2 pages). Ordering information is given on any current masthead page.

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