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Stable, Chloride-Induced Monohapto-Bonding Mode for an Allyl Ligand in a Pd(II) Complex Bearing a New Bidentate Phosphonite–Oxazoline Ligand†

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Bidentate ligands can lead to stable η^1-allyl complexes of Pd(II). A novel chelating phosphonite–oxazoline P,N ligand, abbreviated NOPO^{Me2}, has been prepared by reaction of 6-chloro-6H-dibenz[c,e][1,2]oxaphosphorin with the lithium alcoholate derived from 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole. Its reaction with [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ afforded the new η^1-allyl Pd complex [PdCl(η^1-C_3H_5)(NOPO^{Me2})] **2** in 91% yield. This constitutes a still rare example of structurally characterized η^1-allyl Pd(II) complex. Chloride abstraction led to the corresponding cationic η^3-allyl complex [Pd(η^3-C_3H_5)(NOPO^{Me2})]PF_6 **3**, which has also been characterized by X-ray diffraction. CO insertion into the Pd–C σ-bond of the η^1-allyl ligand of **2** afforded the corresponding 3-butenoyl palladium complex [PdCl{C(O)C_3H_5}(NOPO^{Me2})] **4** under mild conditions, which supports the view that CO insertion into η^3-allyl palladium cationic complexes occurs via first coordination of the counterion to form a more reactive η^1-allyl intermediate.

Introduction

In addition to their intrinsic importance in inorganic and organometallic chemistry, transition metal allyl complexes are involved in numerous catalytic cycles describing key reactions in homogeneous catalysis.[1,2] It has been established that the bonding mode of an allyl fragment to a transition metal greatly influences the stereochemical course of reactions proceeding via allyl intermediates.[1] In palladium chemistry, the well-known η^3-η^1-η^3 dynamic behavior of the allyl ligand has direct implications to enantioselection, and a detailed understanding of its bonding mode to the metal is required to rationalize its reactivity. Although the η^3-bonding mode is the rule, a few Pd complexes containing η^1-allyl ligands have been previously characterized in solution,[3] and more rarely, isolated in the solid-state.[3a,b,g,4−6] This is significant owing to their considerable importance as reactive species or proposed intermediates in C−C coupling reactions.[1] We[5,6] and Kollmar and Helmchen[7] have recently established by X-ray diffraction that the occurrence of the rare η^1-bonding mode for the allyl ligand in palladium chemistry does not necessarily require the presence in the coordination sphere of Pd(II) of a strong and rigid tridentate ancillary ligand, as often believed. A suitable chelating ligand can also lead to the stabilization of η^1-allyl Pd(II) complexes,

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† Dedicated to Prof. R. J. P. Corriu on the occasion of his 70th birthday, with our sincere congratulations.

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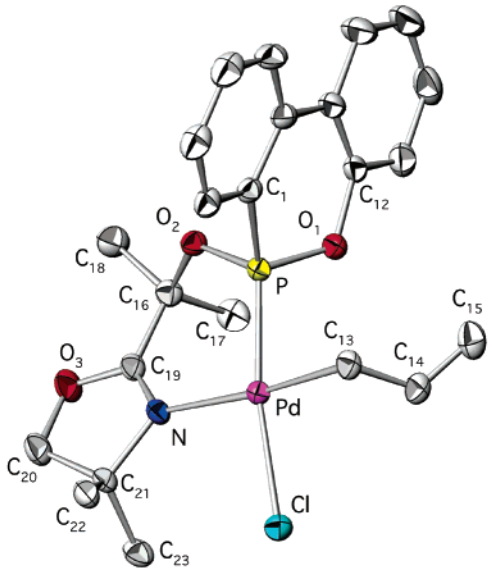
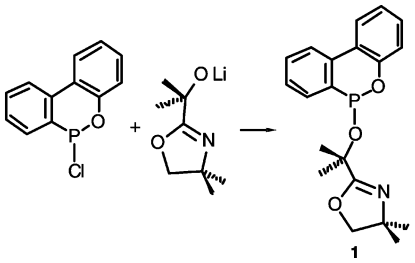


Figure 1. ORTEP view of the structure of [Pd(η^1-C_3H_5)Cl(NOPO^{Me2}-*N*,*P*)] in **2**·1/2 CH_2Cl_2. Thermal ellipsoids shown at 50% probability.

which suggests that this bonding mode for an allyl ligand might be more frequent than originally believed. Herein we report a further example of this still rare stabilization of a η^1-allyl Pd(II) complex using a new hybrid P,N chelating ligand in the presence of a chloride ligand and describe its relevance to the carbonylation of allyl complexes under mild conditions.

Results and Discussion

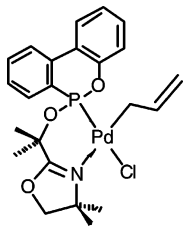
The new bidentate, racemic ligand **1**, abbreviated NOPO^{Me2}, was prepared by reaction of 6-chloro-6H-dibenz[c,e]-[1,2]oxaphosphorin with the lithium alcoholate derived from 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole (eq 1).



(1)

1

Its reaction with [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ afforded the new η^1-allyl chloro Pd(II) complex [PdCl(η^1-C_3H_5)(NOPO^{Me2})] **2** in 91% yield. This complex has been fully characterized, including by X-ray diffraction which unambiguously established the η^1-bonding mode of the allyl ligand (Figure 1).



2

Table 1. Selected Bond Distances (Å) and Angles (deg) in [PdCl(η^1-C_3H_5)(NOPO^{Me2})]·1/2CH_2Cl_2 (**2**·1/2CH_2Cl_2)

bond distances (Å)			
Pd−Cl	2.404(1)	O3−C19	1.339(3)
Pd−P	2.162(1)	O3−C20	1.458(4)
Pd−N	2.186(2)	C13−C14	1.473(4)
Pd−C13	2.071(3)	C14−C15	1.319(5)
P−O1	1.610(2)	C16−C17	1.534(4)
P−O2	1.616(2)	C16−C18	1.518(4)
P−C1	1.788(3)	C16−C19	1.524(4)
N−C19	1.276(4)	C20−C21	1.541(4)
N−C21	1.507(4)	C21−C23	1.512(4)
O1−C12	1.396(4)	C21−C22	1.526(5)
O2−C16	1.460(4)		
bond angles (deg)			
Cl−Pd−P	170.73(3)	Pd−C13−C14	110.4(2)
Cl−Pd−N	97.99(6)	Pd−P−C1	123.67(9)
Cl−Pd−C13	86.26(8)	C13−C14−C15	125.5(3)
P−Pd−N	90.63(6)	P−O1−C12	123.1(2)
P−Pd−C13	85.34(8)	P−C16−C16	122.9(2)
N−Pd−C13	174.6(1)	O2−C16−C19	108.8(2)
Pd−P−O1	110.56(8)	Pd−N−C19	126.7(2)
Pd−P−O2	114.67(8)	C19−N−C21	107.0(2)
O1−P−O2	105.3(1)	Pd−N−C21	126.3(2)
O1−P−C1	102.1(1)	O3−C19−N	118.5(2)
O2−P−C1	98.4(1)	N−C19−C16	127.1(2)

The ^{1}H NMR spectrum of **2** in CD_2Cl_2 at 177 K contains five resonances for the five allyl protons, consistent with the presence of a stereogenic center (phosphorus) in the molecule. Consistently, the diastereotopic methyl protons $OC(CH_3)_2$ and $NC(CH_3)_2$ are observed as four singlets. All the assignments for the ^{1}H and ^{13}C resonances given in the Experimental Section, including for the aromatic moiety, resulted from H−H COSY and H−C experiments. In the $^{13}C\{^1H\}$ NMR spectrum recorded at 177 K, the chemical shifts at δ 47.4, 87.8, and 123.9 ppm for the allylic Pd−CH_2, =CH_2, and −CH= carbons, respectively, are closer to the values found in η^3-allyl Pd(II) complexes, such as **3** (see below), than those found in static η^1-allyl complexes.[5,6,8] Upon raising the temperature from 177 to 298 K, the resonances of the terminal allylic carbons shift in opposite direction, from 47.4 to 39.5 ppm for the carbon cis to P and from 87.8 to 97.1 ppm for the =CH_2 carbon, and the central carbon resonance is downfield shifted from 123.9 to 130.5 ppm. The spectroscopic data suggest that an average situation is observed in solution between the neutral complex **2** and the corresponding η^3-allyl complex formed by dissociation of the chloride ligand. An independent reaction of **2** with a chloride abstractor reagent indeed led to such a complex, [Pd(η^3-C_3H_5)(NOPO^{Me2})]PF_6 **3** (see below). Although the available data do not allow quantification of the respective proportions of η^1-allyl vs η^3-allyl complex in CD_2Cl_2 solution, it is interesting to note that the chemical shifts of the allyl carbons progressively move with increasing temperature toward those of a static η^1-allyl structure.[5,6,8] A similar observation was made in the case of related Pd(II) allyl complexes with a bis(oxazoline)phenylphosphonite ligand.[5] In the solid-state structure of **2** (Figure 1), the η^1-allyl bonding mode is stabilized and occupies a position trans to the nitrogen donor, which is consistent with Pearson's antisymbiotic effect because nitrogen has a weaker trans influence than phosphorus.[9] Selected bond distances and angles are given in Table 1. The Pd−C(13) distance of

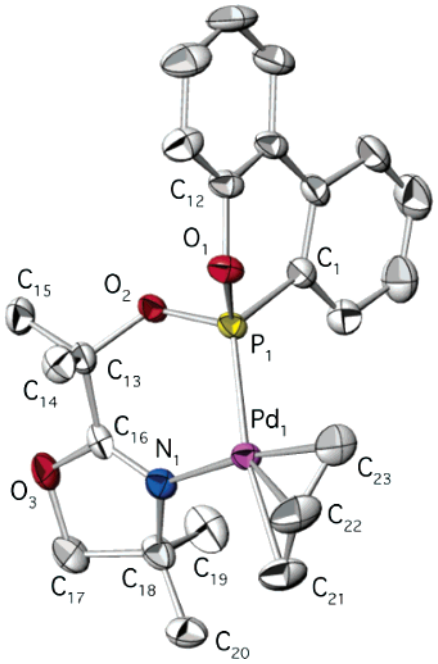
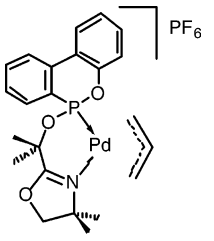


Figure 2. ORTEP view of the structure of [Pd(η^3-C_3H_5)(NOPO^{Me2}-*N*,*P*)]-PF_6 in **3**·CH_2Cl_2. Thermal ellipsoids shown at 50% probability.

2.071(3) Å is identical to the values found for this bond in our phosphonite−oxazoline η^1-allyl Pd(II) complexes.[5,6]

The cationic η^3-allyl Pd(II) complex **3** was formed by chloride abstraction from **2** and was analyzed by X-ray diffraction (Figure 2 and Tables 2 and 3). There are two different molecules in the asymmetric unit, and as their geometric parameters are not significantly different (within 3σ), only the data for one of them are presented here. The longer Pd−C(21) distance (2.215(7) Å) compared to Pd−C(23) (2.100(8) Å) reflects the larger trans influence of the P donor. The P,N ligand has structural features very similar to those in **2** but the allyl ligand is now η^3-bonded to palladium and it makes an angle of 118(1)° with the plane containing Pd, P, and N.



3

In the ^{1}H NMR spectrum of **3** in CD_2Cl_2, the signals for the NC(CH_3) and OC(CH_3) protons partly overlap and six resonances are observed for these four methyl groups. Similarly, in the ^{13}C NMR spectrum, seven resonances are observed in the methyl region. This suggests the coexistence in solution of two diastereoisomers resulting from the combined presence of the stereogenic P and two orientations for the allyl ligand, with its CH_2 termini above and below the Pd(II) square plane.

Table 2. Selected Bond Distances (Å) and Angles (deg) in [Pd(η^3-C_3H_5)(NOPO^{Me2})]PF_6·CH_2Cl_2 (**3**·CH_2Cl_2)

bond distances (Å)			
Pd1−P1	2.225(2)	N1−C16	1.274(8)
Pd1−N1	2.109(5)	N1−C18	1.510(8)
Pd1−C21	2.215(7)	P1−O2	1.613(4)
Pd1−C22	2.162(7)	C13−C15	1.520(9)
Pd1−C23	2.100(8)	C13−C16	1.520(8)
P1−O1	1.611(4)	C13−C14	1.520(8)
P1−C1	1.776(6)	C17−C18	1.526(9)
O1−C12	1.413(7)	C18−C19	1.51(1)
O2−C13	1.460(6)	C18−C20	1.522(9)
O3−C16	1.335(7)	C21−C22	1.36(1)
O3−C17	1.458(10)	C22−C23	1.37(1)
bond angles (deg)			
Pd1−P1−O2	111.6(1)	O2−P1−C1	101.1(2)
Pd1−P1−C1	121.5(2)	O3−C16−N1	117.8(5)
Pd1−P1−O1	113.8(1)	O3−C16−C13	115.5(5)
Pd1−N1−C16	124.0(4)	O3−C17−C18	103.8(5)
Pd1−N1−C18	129.7(4)	N1−Pd1−C21	105.6(2)
Pd1−C21−C22	69.8(4)	N1−Pd1−C22	136.9(3)
Pd1−C22−C21	74.1(4)	N1−Pd1−C23	172.2(2)
Pd1−C22−C23	68.8(4)	N1−C18−C20	112.7(5)
Pd1−C23−C22	73.8(5)	N1−C16−C13	126.6(5)
P1−Pd1−N1	89.6(1)	N1−C18−C17	99.6(5)
P1−Pd1−C21	164.8(2)	N1−C18−C19	108.2(5)
P1−Pd1−C22	129.8(2)	C14−C13−C16	110.6(5)
P1−O1−C12	121.2(4)	C15−C13−C16	110.5(5)
P1−O2−C13	121.6(3)	C16−O3−C17	104.5(5)
P1−Pd1−C23	97.7(2)	C16−N1−C18	106.4(5)
O1−P1−C1	102.3(2)	C17−C18−C20	111.5(6)
O1−P1−O2	104.5(2)	C17−C18−C19	113.1(6)
O1−C12−C11	115.0(5)	C21−C22−C23	122.4(7)
O1−C12−C7	121.4(5)	C21−Pd1−C22	36.1(3)
O2−C13−C14	104.4(4)	C21−Pd1−C23	67.1(3)
O2−C13−C15	112.1(4)	C22−Pd1−C23	37.4(3)
O2−C13−C16	108.0(4)		

Table 3. Selected Crystallographic Data for [PdCl(η^1-C_3H_5)-(NOPO^{Me2})]·1/2 CH_2Cl_2 (**2**·1/2 CH_2Cl_2) and [Pd(η^3-C_3H_5)(NOPO^{Me2})]-PF_6·CH_2Cl_2 (**3**·CH_2Cl_2)

	2·1/2 CH_2Cl_2	**3**·CH_2Cl_2
empirical formula	$C_{23.5}H_{28}Cl_2NO_3PPd$	$C_{24}H_{29}Cl_2F_6NO_3P_2Pd$
fw (g mol^{-1})	582.76	732.72
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	13.370(5)	30.159(5)
b (Å)	11.081(5)	12.383(5)
c (Å)	16.623(5)	16.257(5)
β (deg)	102.65(2)	104.61(1)
V (Å^3)	2402.9(2)	5875(3)
Z	4	8
ρ (calc) (g·cm^{-3})	1.611	1.657
μ (Mo Kα) (cm^{-1})	1.087	0.988
T (K)	183	183
2 Θ_{max} (deg)	33.142	30.034
no. observ. ($I > 2\sigma(I)$)	5951	11359
no. of params	289	703
GOF[a]	0.918	1.092
residuals (R; R_w)[a]	0.0452; 0.0984	0.073; 0.187
max. peak in final diff. map (e/Å^3)	0.703	1.240

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

(8) For comparison, the ^{13}C NMR resonances of the allyl carbons in *cis*-[$AuMe_2$(η^1-allyl)(PPh_3)] are 36.1 (Au−CH_2), 106.4 (=CH_2), and 143.0 (−CH=). See: Sone, T.; Ozaki, S.; Kasuga, N. C.; Fukuoka, A.; Komiya, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1523.

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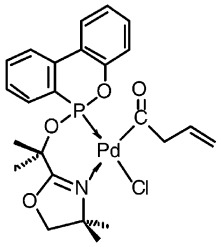
Bubbling CO through a solution of **2** in toluene led to the formation of the insertion product [PdCl{C(O)C_3H_5}-(NOPO^{Me2})] **4**.



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Its ν(C═O) band at 1703 cm^{-1} is indicative of the formation of an acyl ligand, and a resonance at $\delta = 220.9$ ppm in the ^{13}C NMR spectrum with a small ^2J(P,C) coupling of 14.9 Hz shows that the acyl group occupies a position cis to the phosphorus.[6,10] The high-field shift ($\Delta\delta = -10.9$ ppm) of the ^{31}P NMR resonance ($\delta = 114.8$), compared to that of **2** ($\delta = 125.7$), also indicates the cis arrangement of the acyl group relative to the P atom.[10a,11]

As also noted in a preliminary communication on a related system,[6] this carbonylation reaction under very mild conditions contrasts with the inactivity of [Pd(η^3-2-MeC_3H_4)PdCl-(PMe_3)][12] and further supports the view presented by Osawa, Yamamoto, et al. that CO insertion into η^3-allyl palladium cationic complexes should occur via first coordination of the counterion to form an η^1-allyl intermediate.[12] However, these authors had not succeeded in isolating such η^1-allyl intermediates.[12] In contrast to, e.g., *trans*-[Pd{C(O)CH_2CH═CH_2}Br($PMePh_2$)$_2$],[12] complex **4** exhibits sufficient stability toward decarbonylation or decomposition to be isolated pure in the solid-state, probably because of the energetically favorable *trans*-P−Pd−Cl and *trans*-N−Pd−C arrangements.[5] We note however that **4** appears slightly less stable than the other 3-butenoyl complex recently obtained by carbonylation of the η^1-allyl Pd(II) complex bearing the chelating P,N ligand NOP^{Me2}.[6] Attempts to isolate further insertion products with ethylene were unsuccessful, consistent with the lower reactivity of neutral complexes,[13] and prolonged reaction times (>1 day) led to progressive decarbonylation and formation of the corresponding η^3-allyl complex (in situ ^{1}H NMR monitoring).

In conclusion, we have added a new example which unambiguously shows that appropriate bidentate chelates are able to stabilize Pd(II) complexes containing allyl ligands in their η^1-bonding mode. These results confirm that a strong tridentate ligand is not necessarily needed to observe or isolate η^1-allyl Pd(II) complexes. The halide ligand plays a central role in stabilizing the η^1-allyl bonding mode, as noted previously,[5,6] and its abstraction immediately leads to formation of η^3-allyl palladium cationic complexes. Other strongly bound ligands, such as alkyl or aryl ligands, could lead to similar stabilization of the η^1-allyl bonding mode. Our results suggest that this still rare bonding situation may actually occur more often than expected in numerous stoichiometric or catalytic transformations and isomerization processes involving Pd(II) allyl complexes.[14a] Furthermore, our carbonylation results support the view that CO insertion into η^3-allyl palladium cationic complexes occurs via first coordination of the counterion to form an η^1-allyl intermediate. It is also noteworthy in this context that the *syn-anti* isomerization of cationic, π-allyl Pd(II) complexes is considerably enhanced in the presence of added chloride and that catalytic amounts of halide were found to beneficially influence both the regioselectivity and enantioselectivity of asymmetric allylic alkylations.[14b]

Experimental Section

General Data. All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^{1}H NMR spectra were recorded at 500.13 or 300.13 MHz, ^{31}P{^{1}H} NMR spectra were recorded at 121.5 MHz, and ^{13}C{^{1}H} NMR spectra were recorded at 125.8 or 75.4 MHz on FT Bruker AC500 or AC300 instruments.

Synthesis of the Ligand NOPO^{Me2}. The preparation of 6-chloro-6H-dibenz[c,e][1,2]oxaphosphorin was performed according to the literature.[15,16] Selected data are as follows. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ 7.27−8.06 (m). ^{31}P{^{1}H} (121.5 MHz, C_6D_6, room temp.): δ 134.6 ppm (Lit.:[15] 132 ppm). MS *m*/*z*: 234.1 (M^+).

The 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole (1.58 g, 10 mmol) was dissolved in THF (60 mL). To this colorless solution cooled to −78 °C was added BuLi (6.2 mL, 1.6 M in hexane, 10 mmol), and after stirring at −78 °C for 1 h, 6-chloro-6H-dibenz[c,e][1,2]oxaphosphorin (2.35 g, 10 mmol) in THF (5 mL) was added to the solution. The reaction mixture was allowed to slowly reach room temperature and was stirred for 24 h. Degassed water (20 mL) was added and the organic layer was separated and dried over anhydrous $MgSO_4$. The filtrate was taken to dryness under vacuum, and the colorless oil thus obtained was dried under vacuum overnight. Yield: 2.56 g (72%). ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ 1.32 [s, 3H, NC(CH_3)(CH_3)], 1.35 [s, 3H, NC(CH_3)(CH_3)], 1.42 [s, 3H, OC(CH_3)(CH_3)], 1.67 [s, 3H, OC(CH_3)(CH_3)], 4.01 and 4.03 (AB spin system, $^2J_{AB}$ = 8.1 Hz, 2H, OCH_2), 7.00−7.98 (m, 8H). ^{31}P{^{1}H} (121.5 MHz, $CDCl_3$, room temp.): δ 121.5 ppm. It was difficult to completely remove the residual 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole and a satisfactory elemental analysis could not be obtained. However, the crude product could be used for metal complexation and the resulting complexes were easier to purify.

Complex [PdCl(η^1-C_3H_5)(NOPO^{Me2})] 2. The ligand NOPO^{Me2} (0.640 g, 1.80 mmol) and [Pd(η^3-C_3H_5)(μ-Cl)]$_2$[17] (0.33 g, 0.90 mmol) were dissolved in CH_2Cl_2 (20 mL). After the yellow solution

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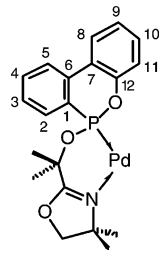
was stirred for 1 h at room temperature, the solvent was removed under vacuum. The residue was treated with pentane (30 mL) and the pale-yellow solid thus obtained was washed with a mixture of pentane/diethyl ether (1:1) (2 × 20 mL), then washed with pentane (2 × 20 mL), and dried under vacuum, to afford **2** as a pale yellow solid (0.88 g, 91%). Selected spectroscopic data (the numbering of the H and C atoms in the *P*,*N* ligand is shown below). IR (KBr): 1630 [s, ν(CN)] cm^{-1}. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 298 K): δ 1.48 [s, 3H, NC(CH$_3$)(C*H*$_3$)], 1.49 [s, 3H, NC(C*H*$_3$)(CH$_3$)], 1.52 [s, 3H, OC(CH$_3$)(C*H*$_3$)], 1.93 [s, 3H, OC(C*H*$_3$)(CH$_3$)], 3.80 (br, 4H, Pd−CH$_2$ and =CH$_2$), AB spin system: δ_A 3.98 (d, 1H, $^2J_{HH}$ = 8.3 Hz, OCH*H*), δ_B 4.01 (d, 1H, $^2J_{HH}$ = 8.3 Hz, OC*H*H), 5.97 (m, 1H, −CH=), 7.25 (dm, 1H, $^3J_{HH}$ = 8.0 Hz, H^{11}), 7.31 (m, 1H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.0 Hz, H^9), 7.43 (ddm, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.5 Hz, H^{10}), 7.55 (ddt, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 3.0 Hz, $^4J_{PH}$ = 1.5 Hz, H^3), 7.72 (ddt, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, $^5J_{PH}$ = 1.5 Hz, H^4), 8.02 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, H^5), 8.04 (ddm, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 3.0 Hz, H^8), 8.23 (ddd, 1H, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 18.0 Hz, $^4J_{HH}$ = 1.5 Hz, H^2). ^{1}H NMR (500.13 MHz, CD_2Cl_2, 177 K): δ 1.31 [s, 3H, NC(CH$_3$)(C*H*$_3$)], 1.44 [s, 3H, NC(C*H*$_3$)(CH$_3$)], 1.49 [s, 3H, OC(CH$_3$)(C*H*$_3$)], 1.92 [s, 3H, OC(C*H*$_3$)(CH$_3$)], 3.09 (d, 1H, $^3J_{HH}$ = 6.5 Hz, allylic CH$_2$), 3.19 (br, 1H, allyllic CH$_2$), 4.11 (dd, 1H, $^3J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 7.5 Hz, allylic CH$_2$), AB spin system: δ_A 4.24 (d, 1H, $^2J_{HH}$ = 9.0 Hz, OCH*H*), δ_B 4.36 (br, 1H, OC*H*H), 4.99 (dd, 1H, $^3J_{PH}$ = 7.0 Hz, $^3J_{HH}$ = 7.0 Hz, allylic CH$_2$), 5.88 (m, 1H, −CH=), 7.25 (dm, 1H, $^3J_{HH}$ = 8.0 Hz, H^{11}), 7.36 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, H^9), 7.46 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.5 Hz, H^{10}), 7.56 (m, 1H, H^3), 7.70 (d br, 1H, $^3J_{PH}$ = 12.0 Hz, H^2), 7.77 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, H^4), 8.04−8.10 (m, 2H, H^8 + H^5). ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, 298 K): δ 25.6 [d, $^3J_{PC}$ = 6.9 Hz, OC(*C*H$_3$)(CH$_3$)], 26.2 [s, NC(*C*H$_3$)(CH$_3$)], 26.8 [s, NC(CH$_3$)(*C*H$_3$)], 27.5 [d, $^3J_{PC}$ = 8.4 Hz, OC(CH$_3$)(*C*H$_3$)], 39.5 (br, allylic CH$_2$ cis to P), 68.4 [s, N*C*(CH$_3$)$_2$], 77.5 [d, $^2J_{PC}$ = 3.2 Hz, O*C*(CH$_3$)$_2$], 79.9 (s, OCH$_2$), 97.1 (v br, allylic =CH$_2$), 119.2 (d, $^3J_{PC}$ = 4.4 Hz, C^{11}), 121.1 (d, $^3J_{PC}$ = 10.4 Hz, C^7), 122.8 (d, $^3J_{PC}$ = 5.6 Hz, C^5), 123.5 (s, C^9), 124.2 (s, C^8), 125.7 (d, $^1J_{PC}$ = 63.3 Hz, C^1), 127.1 (d, $^3J_{PC}$ = 17.6 Hz, C^3), 129.3 (s, C^{10}), 130.5 (d, $^3J_{PC}$ = 6.4 Hz, allylic −CH=), 131.9−132.2 (m, C^2 + C^4 + C^6), 148.1 (d, $^2J_{PC}$ = 14.0 Hz, C^{12}), 167.7 (s, C=N). ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, 177 K): δ 25.2 [s, br, OC(*C*H$_3$)(CH$_3$)], 26.7 [s, NC(*C*H$_3$)(CH$_3$)], 27.1 [s, NC(CH$_3$)(*C*H$_3$)], 29.0 [br, OC(CH$_3$)(*C*H$_3$)], 47.4 (s, allylic CH$_2$ cis to P), 69.2 [s, N*C*(CH$_3$)$_2$], 78.2 [s, O*C*(CH$_3$)$_2$], 79.9 (s, OCH$_2$), 87.8 (v br, allylic =CH$_2$), 119.4 (s, C^{11}), 120.5 (d, $^3J_{PC}$ = 10.7 Hz, C^7), 123.5 (s, C^5), 123.9 (s, allylic −CH=), 124.4 (s, C^9), 124.9 (s, C^8), 125.7 (br, C^1), 127.7 (d, $^3J_{PC}$ = 18.3 Hz, C^3), 130.1 (s, C^{10}), 131.3 (d, $^2J_{PC}$ = 39.6 Hz, C^2), 131.9 (s, C^4), 133.5 (s, C^6), 147.5 (d, $^2J_{PC}$ = 14.3 Hz, C^{12}), 170.2 (s, C=N). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, room temp.): δ 125.7 (s). Anal. Calcd. for $C_{23.5}H_{28}Cl_2NO_3PPd$ (**2**·1/2 CH_2Cl_2): C, 48.60; H, 4.86; N, 2.41. Found: C, 48.52; H, 4.92; N, 2.42.



Complex [Pd(η^3-C$_3$H$_5$)(NOPO^{Me2})]PF$_6$ 3. The ligand NOPO^{Me2} (0.64 g, 1.80 mmol) and [Pd(η^3-C$_3$H$_5$)(μ-Cl)]2[17] (0.33 g, 0.90 mmol) were dissolved in CH_2Cl_2 (30 mL). After the yellow solution was stirred for 0.5 h at room temperature, solid NH_4PF_6 (0.30 g, 1.84 mmol) was added and the mixture was stirred for another 3 h and filtered. The filtrate was taken to dryness under vacuum and the residue was treated with pentane (30 mL), the pale yellow solid thus obtained was washed with pentane (3 × 20 mL) and dried under vacuum to afford **3** (0.95 g, 81%). Selected spectroscopic data follow. IR (CH_2Cl_2): 1624 [s, ν(CN)] cm^{-1}. ^{1}H NMR (300.13 MHz, CD_2Cl_2, room temp.): δ 1.46 [s, 4.5H, 1/2 NC(C*H*$_3$)(CH$_3$), 1/2 OC(C*H*$_3$)(CH$_3$) and 1/2 OC(CH$_3$)(C*H*$_3$)], 1.49 [s, 1.5H, 1/2 NC(CH$_3$)(C*H*$_3$)], 1.51 (s, 1.5H, 1/2 NC(C*H*$_3$)(CH$_3$)], 1.57 (s, 1.5H, 1/2 NC(CH$_3$)(C*H*$_3$)], 1.86 [s, 1.5H, 1/2 OC(CH$_3$)(C*H*$_3$)], 1.98 [s, 1.5H, 1/2 OC(CH$_3$)(C*H*$_3$)], 2.91 (dd, 1H, $^3J_{HH}$ = 12.9 Hz, $^3J_{PH}$ = 15.6 Hz, allylic H cis to P), 3.69 (dd, 1H, $^3J_{HH}$ = 6.0 Hz, $^3J_{PH}$ = 27 Hz, allylic H cis to P), 3.97 (dd, 1H, $^3J_{HH}$ = 14.4 Hz, $^3J_{PH}$ = 27 Hz, allylic H trans to P), 4.44 (m, 2H, OCH$_2$), 5.22 (m, 1H, allyl H trans to P), 5.86 (m, 1H, −CH=), 7.25−8.14 (m, 8H, aryl). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, room temp.): δ 26.5 [s, OC(*C*H$_3$)(CH$_3$)], 26.6 [s, OC(*C*H$_3$)(CH$_3$)], 27.6 [s, NC(CH$_3$)(*C*H$_3$)], 27.7 [s, NC(CH$_3$)(*C*H$_3$)], 27.9 [s, NC(*C*H$_3$)(CH$_3$)], 28.0 [s, NC(*C*H$_3$)(CH$_3$)], 29.6 [s, OC(CH$_3$)(*C*H$_3$)], 29.8 [s, OC(CH$_3$)(*C*H$_3$)], 55.6 (s br, allylic CH$_2$ cis to P), 70.1 [s, N*C*(CH$_3$)$_2$], 70.2 [s, N*C*(CH$_3$)$_2$], 79.8 (s, allylic CH$_2$ trans to P), 80.8 [s, O*C*(CH$_3$)$_2$], 80.9 [s, O*C*(CH$_3$)$_2$], 81.5 (s, OCH$_2$), 82.0 (s, OCH$_2$), 120.1 (s, allylic CH=), 121.6 (d, $^3J_{PC}$ = 10.9 Hz, C^{11}), 122.1 (d, $^3J_{PC}$ = 9.5 Hz, C^7), 124.3 (d, $^3J_{PC}$ = 5.5 Hz, C^5), 125.5 (s, C^9), 125.6 (s, C^8), 125.6−126.8 (two d for C^1, $^1J_{PC}$ = 43.2 Hz, overlaping with C^8), 128.9 (d, $^3J_{PC}$ = 17.6 Hz, C^3), 130.9 (s, C^{10}), 131.6 (d, $^2J_{PC}$ = 35.2 Hz, C^2), 133.1 (d, $^3J_{PC}$ = 14.6 Hz, C^6), 134.5 (s, C^4), 148.5 (d, $^2J_{PC}$ = 14.5 Hz, C^{12}), 172.5 (d, $^3J_{PC}$ = 12.5 Hz, C=N). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, room temp.): δ 129.3 (s), 128.6 (s), −143.2 (sept, PF_6). Anal. Calcd. for $C_{23}H_{27}F_6NO_3P_2Pd$: C, 42.64; H, 4.20; N, 2.16. Found: C, 42.12; H, 4.03; N, 2.08.

Complex [PdCl{C(O)C$_3$H$_5$}(NOPO^{Me2})] 4. CO was bubbled through a solution of **2** (0.27 g, 0.5 mmol) in toluene (50 mL) at room temperature for 1 h. After filtration and removal of the volatiles under vacuum, the residue was washed with pentane (3 × 20 mL) and dried under vacuum, to afford **4** as pale-yellow powder (0.24 g, 84.5% yield). Selected spectroscopic data follow. IR ($CHCl_3$): 1703 [s, ν(CO)], 1636 [s, ν(CN)] cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ 1.30 [s, 3H, NC(C*H*$_3$)(CH$_3$)], 1.72 [s, 3H, NC(CH$_3$)(C*H*$_3$)], 1.77 [s, 3H, OC(C*H*$_3$)(CH$_3$)], 2.17 [s, 3H, OC(CH$_3$)(C*H*$_3$)], AB spin system: δ_A 3.62 (ddt, 1H, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, C(O)C*H*H−), δ_B 3.73 (ddt, 1H, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, C(O)CH*H*−), AB spin system: δ_A 4.01 (d, 1H, $^2J_{HH}$ = 8.4 Hz, OCH*H*), δ_B 1H, 4.14 (d, 1H, $^2J_{HH}$ = 8.4 Hz, OC*H*H), 4.94 (dm, 1H, $^3J_{HH}$ = 18.1 Hz, =CH*H* trans to −CH=), 4.96 (dm, 1H, $^3J_{HH}$ = 8.7 Hz, =C*H*H cis to −CH=), 5.90 (m, 1H, −CH=), 7.23 (dm, 1H, $^3J_{HH}$ = 8.1 Hz, H^{11}), 7.29 (m, 1H, $^3J_{HH}$ = 7.5 Hz, H^9), 7.41 (dd, 1H, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.5 Hz, H^{10}), 7.59 (ddt, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 3.0 Hz, $^4J_{PH}$ = 1.2 Hz, H^3), 7.71 (ddt, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, $^5J_{PH}$ = 3.0 Hz, H^4), 7.97 (m, 2H, H^5 + H^8), 8.16 (ddd, 1H, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, H^2). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, room temp): δ 26.2 [d, $^3J_{PC}$ = 5.1 Hz, OC(*C*H$_3$)(CH$_3$)], 27.1 [s, NC(*C*H$_3$)(CH$_3$)], 27.8 [s, NC(CH$_3$)(*C*H$_3$)], 29.6 [d, $^3J_{PC}$ = 11.1 Hz, OC(CH$_3$)(*C*H$_3$)], 56.1 (d, $^3J_{PC}$ = 29.1 Hz, C(O)*C*H$_2$), 70.6 [s, N*C*(CH$_3$)$_2$], 78.2 [d, $^2J_{PC}$ = 2.7 Hz, O*C*(CH$_3$)$_2$], 81.7 (s, OCH$_2$), 117.4 (s, =CH$_2$), 120.1 (d, $^3J_{PC}$ = 4.2 Hz, C^{11}), 121.9 (d, $^3J_{PC}$ = 10.7 Hz, C^7), 124.0 (d, $^3J_{PC}$ = 5.6 Hz, C^5), 124.7 (s, C^9), 125.0 (d, $^1J_{PC}$ = 66.6 Hz, C^1), 125.3 (s, C^8), 128.1 (d, $^3J_{PC}$ = 18.0 Hz, C^3), 130.5 (s, C^{10}), 131.8 (s, −CH=), 132.8 (d, $^2J_{PC}$ = 33.9 Hz, C^2), 133.4 (d, $^2J_{PC}$ = 31.2 Hz,

C^6), 133.6 (s, C^4), 148.4 (d, $^2J_{PC}$ = 14.2 Hz, C^{12}), 170.5 (s, C═N), 220.9 (d, $^2J_{PC}$ = 14.9 Hz, C═O). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2 room temp.): δ 114.8 (s). Anal. Calcd. for $C_{24}H_{27}ClNO_4PPd$: C, 50.90; H, 4.81; N, 2.47. Found: C, 50.55; H, 4.66; N, 2.38.

Crystal Structure Determinations of 2·1/2 CH_2Cl_2 and 3·CH_2Cl_2. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The relevant data are summarized in Table 2. Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[18,19] and the refinements were conducted by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97. The appropriate disorder has been considered for the dichloromethane molecule, which is placed around the 2d position (site symmetry = −1). Full data collection parameters and structural data are available as Supporting Information. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 206450 and 206451 (this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk)).

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Supporting Information Available: Crystallographic data for **2**·1/2 CH_2Cl_2 and **3**·CH_2Cl_2 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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