Palladium(0) Complexes with Unsymmetric Bidentate Nitrogen Ligands for the Stereoselective Hydrogenation of 1-Phenyl-1-propyne to (*Z*)-1-Phenyl-1-propene

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A series of zerovalent palladium complexes Pd(NN)(alkene) of bi- or tridentate nitrogen ligands of the general formula 6-R″-C_5H_3N-(C(R′)═NR)-2 (R″ = H, Me, CH═NR′; R′ = H, Me; R = alkyl, aryl, or amino group) and dimethylfumarate (dmfu) have been prepared and were subsequently employed as precatalysts in the homogeneous stereoselective semihydrogenation of 1-phenyl-1-propyne. An X-ray structure of Pd(C_5H_4N-(C(Me)═N*i*-Pr)-2)(dmfu) was obtained. Whereas only relative small changes in substituents apply, the various complexes show very different stabilities under hydrogenation conditions. The complex Pd(C_5H_4N-(C(H)═N$(CH_2)_2$OH)-2)(dmfu) exhibits a good selectivity for the (*Z*)-alkene but decomposes just before full conversion of the alkyne, whereas the complex Pd(C_5H_4N-(C(H)═N*i*-Pr)-2)(dmfu) exhibits a good selectivity and stability under hydrogenation conditions and is a suitable catalyst for the stereoselective hydrogenation of 1-phenyl-1-propyne to (*Z*)-1-phenyl-1-propene.

Introduction

The catalytic hydrogenation of unsaturated hydrocarbons has been extensively studied.[1] In recent years chemo- and stereoselective hydrogenations of unsaturated carbon−carbon double and triple bonds have taken a fundamental role in organic synthesis, both in laboratory as well as in industry.[2] The hydrogenation of carbon−carbon double bonds has been mostly described. Although the selective hydrogenation of internal alkynes to (*Z*)-alkenes is a very desirable tool, the hydrogenation of triple bonds has received much less attention. Various catalysts are suitable for this semihydrogenation reaction, many of which are heterogeneous, such as the Lindlar catalyst,[3] nickel boride,[4] and the "P2Ni" catalyst.[5] There are also examples of homogeneous systems with various metals and ligands, but only a few exhibit a good selectivity toward a variety of alkynes with different functional groups. Examples of homogeneous catalysts with a high selectivity for the (*Z*)-alkene are the cationic Rh(I) systems of Schrock and Osborn[6] and the Cr(arene)$(CO)_3$ complexes by Sodeoka and Shibasaki.[7] Surprisingly little is known about the effect of the ligands on this reaction, and very few systematic studies concerning this aspect have been reported in the literature. Recently, some of us reported the selective homogeneous Pd(0)-catalyzed hydrogenation of alkynes to (*Z*)-alkenes,[8] a reaction tolerant of functional groups that proceeds under very mild conditions (25 °C, 1 bar of H_2 pressure). The precatalysts employed are the Pd(Arbian)(alkene) compounds,[9] which had previously been used in the homogeneous hydrogenation of electron-poor alkenes[10] and in carbon−element bond formation reactions.[11] This type of Pd(0) complex is able to hydrogenate a wide variety of alkynes to the corresponding (*Z*)-alkenes, with good to excellent selectivities (Scheme 1). Moreover, the complexes are completely stable under hydrogen until the substrate has been semihydrogenated to the alkene. It was observed that the selectivity in the hydrogenation of 1-phenyl-1-propyne strongly depends on the nature of the substituents attached to the imine nitrogens of the bian ligand.

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(1) For example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(2) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (b) Mashima, K.; Kusano, K.; Ohta, T.; Notori, R.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1989**, 1208.
(3) (a) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446. (b) Lindlar, H.; Dubuis, R. *Org. Synth.* **1966**, *46*, 89.
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Scheme 1

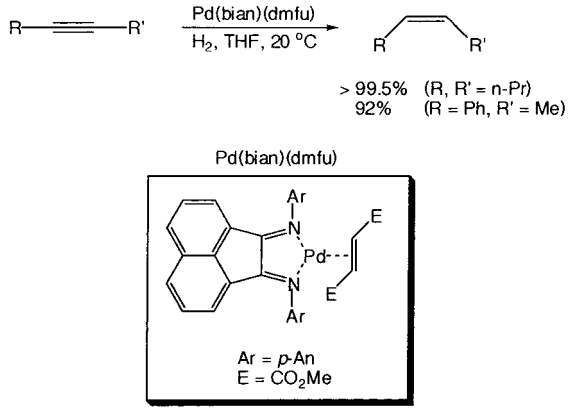
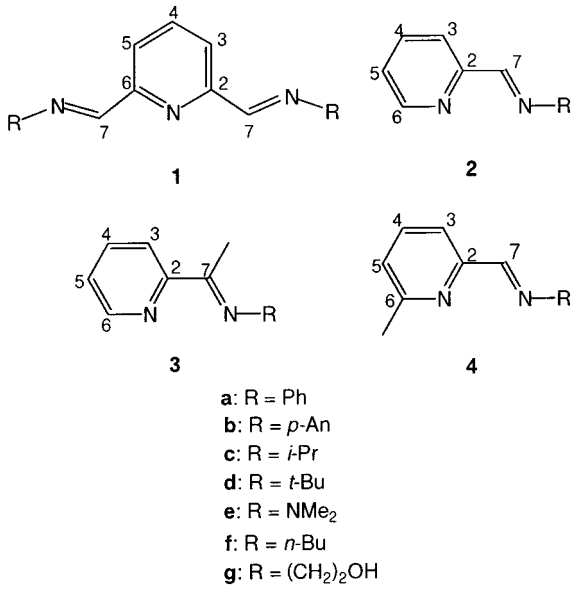


Chart 1



Also, the suitability of other bidentate nitrogen ligands in the selective hydrogenation of 1-phenyl-1-propyne has been briefly addressed by some of us.[8] It was found that, in contrast to bian, bidentate ligands of the bipyridine (bipy) and 1,4-diazabutadiene (dab) type were not able to stabilize the homogeneous $Pd^0(NN)$ species under hydrogenation conditions, leading to extensive decomposition of the catalysts prior to full conversion of the substrate. Some of us have reported that the homogeneous hydrogenation of alkenes and alkynes can be also accomplished, under mild conditions, by using Pd(II) complexes containing potentially tridentate ligands as precatalysts;[12] for the acetylenic substrates a good chemoselectivity to the corresponding alkenes was found.

We here wish to report on the use of bidentate and tridentate nitrogen ligands of the pyridine-2-carbaldimine (pyca) type in the synthesis of a series of Pd(0) complexes of the type Pd(NN)(η^2-alkene) and on their use as catalysts in the homogeneous stereoselective semihydrogenation of alkynes. These pyca ligands have already been applied before in the synthesis of Pd(0) complexes stabilized by electron-poor alkenes,[13,14] and the equilibrium constants of the alkene exchange have been studied.[15] The only example known of homogeneous hydrogenation catalyzed by Pd(NN)(η^2-alkene) complexes where NN is a diimine or a pyridyl−imine ligand, apart from those reported,[8] has been reported by Ruffo, employing diimines containing carbohydrate substituents as catalyst for the hydrogenation of several alkenes in water.[16] It was found that the homogeneity of this process is strongly dependent on the pH of the reactant solution.

The pyca type ligands may, due to their expected hemilability, more or less readily promote an open coordination position for activation of hydrogen. Also the presence of two different donor sites allows for variable coordination of the two donor sites to incipient Pd species dependent on the type of donor atom required for a stable intermediate and might therefore lead to a more stable and active catalyst. Therefore, we synthesized a variety of bidentate ligands and their palladium(0) complexes with dimethylfumarate (dmfu) as ancillary ligand (Chart 1).

Furthermore, the effect of a third nitrogen donor atom was studied (ligands **1**), since these tridentate ligands might stabilize the incipient zerovalent Pd species by forming tricoordinate 16-electron Pd(NNN) complexes. The ligands investigated were chosen so that the influence of steric and electronic effects of the substituents could be examined.

Results and Discussion

Ligand and Complex Synthesis. The ligands have been prepared by condensation of the pyridyl-2-carbonyl system with the appropriate amine, in the presence of molecular sieves and, where necessary, a catalytic amount of *p*-toluenesulfonic acid.

Palladium complexes were obtained by reaction of $Pd(dba)_2$ (dba = dibenzylideneacetone) with the appropriate ligand, in the presence of dimethyl fumarate (dmfu) as ancillary ligand in a 1:1.1:1.1 molar ratio, according to Scheme 2. Three different methodologies were followed: (i) stirring all reactants at room temperature in dry acetone for 8−36 h, (ii) stirring the solution of the NN ligand and dmfu in dry acetone while small portions of $Pd(dba)_2$ are added at 45 °C over several hours, or (iii) stirring all reagents in dry tetrahydrofuran (THF) for 2 h.

Most complexes could be obtained by the first method, except **6d**, for which an extensive release of palladium black was observed without any formation of the complex. This was thought to arise from steric repul-

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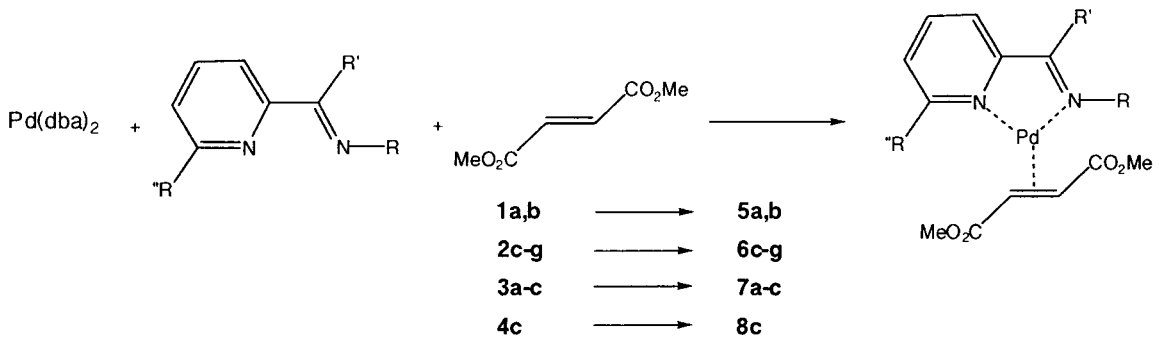
Scheme 2



	R	R'	R"		R	R'	R"
5a	Ph	H	HC=NPh	**6g**	$(CH_2)_2OH$	H	H
5b	*p*-An	H	HC=N*p*-An	**7a**	Ph	Me	H
6c	*i*-Pr	H	H	**7b**	*p*-An	Me	H
6d	*t*-Bu	H	H	**7c**	*i*-Pr	Me	H
6e	NMe_2	H	H	**8c**	*i*-Pr	H	Me
6f	*n*-Bu	H	H				

Table 1. ^{1}H NMR Data of Compounds 5a, 6c−g, 7a−c, and 8c[a]

	R	6	5	4	3	7	=C*H* (alkene)	CO_2CH_3 (alkene)
5a	Ph[b]		7.84 d [8]	8.05 pst	8.57 d [8]	9.27 s	4.04−3.92 br	3.40−3.00 br
6c	*i*-Pr[c]	8.85 d [5]	7.55 m, 2H		7.55 m, 2H	8.41 s	3.95 d	3.61 s
								3.60 s
6d	*t*-Bu[d]	8.83 d [4.8]	7.51 pst	7.91 pst	7.58 d [7.8]	8.27 s	3.96 d	3.59 s
							3.78 d [10.2]	3.58 s
6e	NMe_2[e]	8.60 d [5]	7.24 m [2]	7.72 pst	7.24 m [2]	7.08 s	4.01−3.72 br	3.61 br
6f	*n*-Bu[f]	8.79 d [4.2]	7.51 m	7.92 pst	7.57 d [7.8]	8.32 s	4.00−3.90 br	3.62 br
6g	$(CH_2)_{2-OH}$[g]	8.80 d [4.2]	7.56 pst	7.94 pst	7.61 d [7.8]	8.42 s	4.12−3.94 br	3.65 br
7a	Ph[h]	8.88 d [5]	7.64 pst	8.05 pst	7.91 d [7.8]	2.33 s	3.84−3.45 br	3.60 br
7b	*p*-An[i]	8.88 d [4.2]	7.55 pst	7.96 pst	7.82 d [8.1]	2.33 s	3.61−3.38 br	3.82 br
7c	*i*-Pr[j]	8.90 d [4.2]	7.49 pst	7.91 pst	7.73 d [5.4]	2.40 s	3.91 d	3.61 s
							3.79 d [9.6]	3.59 s
8c	*i*-Pr[k]	2.84 s	7.32 pst	7.76 pst	7.45 d [8.1]	8.40 s	3.88 m	3.60 s
							3.78 d [9.3]	3.58 s

[a] The coupling constants (in Hz) are given in brackets. [b] *H*C=N, δ 8.68 (s, 1H); Ph, δ 7.40 (m, 5H). [c] C*H*(Me)$_2$ + 1H alkene, δ 3.87 (m, 2H); CH_3, δ 1.46 (d, 3H, 6 Hz), 1.24 (d, 3H, 6 Hz). [d] *t*-Bu, δ 1.42 (s, 9H). [e] N(CH_3)$_2$, δ 3.31 (s, 6H). [f] N−CH_2, δ 3.90−3.70 (br, 2H); NCH$_2$CH_2, δ 1.88 (m, 2H); CH_2CH$_3$, δ 1.38 (m, 2H); CH$_2$CH_3, δ 0.97 (t, 3H, 7.5 Hz). [g] CH_2CH_2OH, δ 4.10−3.70 (br, 4H). [h] Ph, δ 7.44 (d, 2H, 7.4 Hz), 7.38 (pst, 1H, 7.4 Hz), 7.41 (d, 2H, 7.4 Hz). [i] *p*-An, δ 7.05 (d, 2H, 8.7 Hz), 6.92 (d, 2H, 8.7 Hz). [j] C*H*(Me)$_2$, δ 4.10 (sep, 1H, 6.3 Hz), CH_3 1.49 (d, 3H, 6.0 Hz), 1.17 (d, 3H, 6.0 Hz). [k] C*H*(Me)$_2$, δ 3.86 (m); CH(CH_3)$_2$, δ 1.49 (d, 3H, 6.3 Hz), 1.24 (d, 3H, 6.3 Hz).

sions between the demanding *t*-Bu group bonded to the imine nitrogen and the ester groups of the dmfu; then the synthesis was attempted using the less steric maleic anhydride as ancillary ligand, but also here palladium black was formed and no product formation could be detected. However, when the second method was applied, complex **6d** was obtained in 58% yield, without extensive formation of palladium black. Also, **7c** could not be obtained using the first method, but it was successfully synthesized using the second method. Later on during the investigation the third method, which involves the use of THF as solvent at room temperature, was adopted. This procedure proved to be superior to the former methods, since the reactions were complete within 2 h, higher yields were obtained, and the workup was much easier. It was therefore extended to the synthesis of all complexes and also gave good results for **6d** and **7c**. However, the complex containing ligand **3d** could not be obtained with any of the aforementioned methods; in this case extensive precipitation of palladium was observed (vide infra).

NMR Spectroscopy. The ^{1}H NMR spectra of the complexes (Table 1) all show similar characteristics. There is a noticeable, but not uncommon, low-frequency shift of the alkene resonances of the dmfu, caused by the π-back-donation of palladium into the alkene π^* orbital. The halves of the alkene are not equivalent; they either show a broadened signal, indicating slow alkene rotation on the NMR time scale, as in **5a**,**b, 6e**−**g**, and **7a**,**b**, or two signals, as in **6c**,**d, 7c**, and **8c**, that couple with each other to give doublets. The latter can only be explained by assuming a rigid coordination of the dmfu to the palladium in these complexes: i.e., no or very slow rotation around the Pd−alkene axis occurs on the NMR time scale. The $^3J_{HH}$ coupling of about 9−10 Hz can be determined for the alkene protons of **6c**,**d, 7c**, and **8c**, whereas for the complexes **5a**, **6e**−**g**, and **7a**,**b** the severe broadening of the same signals does not allow determination of any coupling constant in those cases. The dmfu in complexes **6c**,**d, 7c**, and **8c** experience hindrance from the sterically demanding *i*-Pr or *t*-Bu group, preventing the dmfu from freely rotating around

the Pd−alkene bond. This leads to the nonequivalence of the alkene protons and thus to two anisochronous resonances and the $^3J_{HH}$ coupling observed. In the case of complexes **5a**,**b, 6e**−**g**, and **7a**,**b**, with the less sterically demanding R groups on the imine, the rotation is less hindered, leading to a severe broadening of the alkene signals. As described in X-ray Crystal Structure (vide infra), in the complex **7c** the methyls of the *i*-Pr group are placed so as to reduce the steric repulsions with the methoxy group of the dmfu and the methyl group of the imine carbon, and the rotation around the N(imine)−$CH(CH_3)_2$ bond is consequently hampered. This rigidity does not allow a free rotation of the coordinated alkene around the Pd−π(C=C) bond, thus leading to a high resolution of the alkene protons.

The ^{1}H NMR spectrum of the complex with the potentially tridentate ligand **1a** clearly shows that the ligand is coordinated in a bidentate fashion via one of the imines and the pyridine function. The signals are somewhat broadened, indicating that the process is probably due to a flipping motion of the two imine arms on palladium. Complex **1b** shows this fluxional behavior to such an extent that the ^{1}H NMR signals become too broadened to warrant their correct attribution. Since the complexes **1a** and **1b** are not stable under hydrogenation conditions (vide infra), their dynamic behavior was not further investigated. In the case of complexes **6c**, **7c**, and **8c**, containing an *i*-Pr group on the imine, the *i*-Pr methyl groups become diastereotopic upon coordination of the ligand, and indeed two signals are observed for these methyl groups.

Due to the low solubility of the complexes in most common nonchlorinated NMR solvents and to their extensive decomposition in chlorinated solvents, within the time required to obtain ^{13}C NMR spectra (usually more than 1 h), high-quality ^{13}C NMR data have been obtained only for **6c**,**d**,**g**. At low temperatures (−20 °C), the solubility dropped so considerably that decent ^{13}C NMR signals were not observed even after measuring for 18 h.

X-ray Crystal Structure. Single crystals of **7c**·$0.5CH_2Cl_2$ suitable for X-ray diffraction were obtained from a refrigerated dichloromethane solution. The compound crystallizes with two independent complex molecules and one dichloromethane molecule in the asymmetric unit. The solid-state structure of one complex molecule is depicted in Figure 1; selected bond lengths and angles for the structure are given in Table 2. The pair of complex molecules, which do not display significant geometric differences, is related by a noncrystallographic 2-fold axis parallel to *z*, simulating a orthorhombic *Pnca* space group, perturbed by distortion of β to 93.369(2)°. The coordination sphere around the 16-electron Pd(0) center is formally square planar, on the basis of the NN chelation of ligand **3c** and on a η^2 interaction with the alkene, with the N,N,C−C,Pd system planar within 0.08 Å in both cases. However, the coordination may be conveniently described also as trigonal planar, by taking the midpoint *M* of the alkenic C−C bond as the third coordination position: the ligand bite angles are 76.4(1) and 76.0(1)°, respectively, for the two complexes, and the Pd−*M* directions form angles ranging from 137.9(1) to 145.9(1)° with the Pd−N bonds. The geometry of ligand **3c** can be compared with that

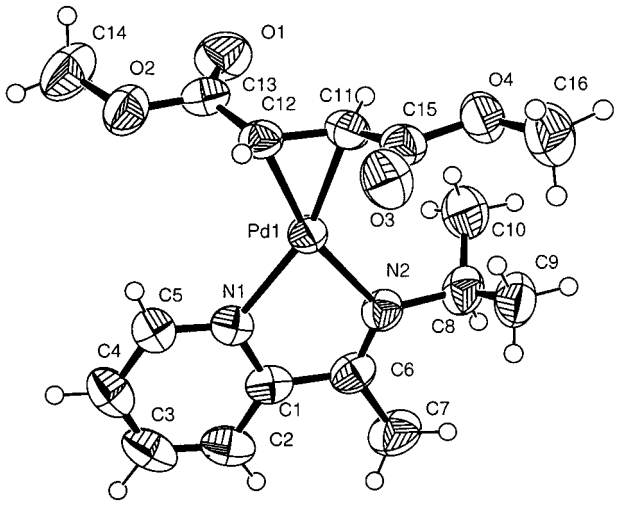


Figure 1. ORTEP plot of **7c**·$0.5CH_2Cl_2$ with ellipsoids drawn at the 50% probability level.

Table 2. Selected Bond Distances and Bond Angles of 7c·$0.5CH_2Cl_2$

Pd(1)−C(12)	2.055(3)	Pd(2)−C(27)	2.055(4)
Pd(1)−C(11)	2.072(3)	Pd(2)−C(28)	2.077(4)
Pd(1)−N(1)	2.120(3)	Pd(2)−N(3)	2.122(3)
Pd(1)−N(2)	2.143(3)	Pd(2)−N(4)	2.165(3)
Pd(1)−*M1*	1.937(3)	Pd(2)−*M2*	1.939(4)
N(1)−C(1)	1.362(4)	N(3)−C(17)	1.353(4)
N(2)−C(6)	1.282(4)	N(4)−C(22)	1.281(4)
N(2)−C(8)	1.483(5)	N(4)−C(24)	1.485(5)
C(1)−C(6)	1.489(5)	C(17)−C(22)	1.485(5)
C(11)−C(12)	1.422(5)	C(27)−C(28)	1.423(5)
C(11)−C(15)	1.445(5)	C(27)−C(31)	1.466(5)
C(12)−C(13)	1.467(5)	C(28)−C(29)	1.462(5)
C(12)−Pd(1)−C(11)	40.3(1)	C(27)−Pd(2)−C(28)	40.3(1)
C(12)−Pd(1)−N(1)	119.3(1)	C(27)−Pd(2)−N(3)	117.7(1)
C(11)−Pd(1)−N(1)	159.4(1)	C(28)−Pd(2)−N(3)	157.8(1)
C(12)−Pd(1)−N(2)	164.2(1)	C(27)−Pd(2)−N(4)	166.0(1)
C(11)−Pd(1)−N(2)	123.9(1)	C(28)−Pd(2)−N(4)	125.9(1)
N(1)−Pd(1)−N(2)	76.4(1)	N(3)−Pd(2)−N(4)	75.9(1)
M1−Pd(1)−N(1)	139.5(1)	*M2*−Pd(2)−N(3)	137.9(1)
M1−Pd(1)−N(2)	144.0(1)	*M2*−Pd(2)−N(4)	145.9(1)

observed for the analogous aldimine[17] and cycloketimine complexes (pyridineketimine)Pd^{II}(Cl)(CH_3C(O))[18] and Pd^0(aldimine)(fn) (fn = fumaronitrile = (*E*)-1,2-dicyanoethene).[19] In our system, the bond lengths C(Ar)−C(CH_3) = 1.489(5), 1.485(5) Å, C(CH_3)=N = 1.282(5), 1.282(5) Å, and N−C(*i*-Pr) = 1.483(5), 1.486(5) Å are perfectly comparable with those observed for the above-mentioned Pd(II) and Pd(0) compounds (ranges 1.418−1.484, 1.262−1.286, and 1.473−1.497 Å for the three bonds), showing that the metal oxidation state does not greatly influence either the electron distribution on the ligand conjugate system or the Pd−N bond lengths, which in the Pd(0)−alkene systems (2.115, 2.160 Å in the Pd(aldimine)(fn) complex, 2.120−2.165 Å in the present compound) are comparable to the average of those shown by the Pd(II) complexes (ranges: 2.062−2.081 Å for trans-Cl and 2.171−2.275 Å for trans-C bonds). This is accomplished by the above two Pd(0) systems by extensive back-donation into the

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highly electron withdrawing π^* orbitals of the alkenes fn and dmfu. The C═C bond in the alkene ligands is remarkably weakened, being 1.427 Å for fn[19] and 1.422(5) and 1.423(5) Å in the present dmfu complex. The latter C═C bond is significantly weaker than that observed in the only other Pd^0(dmfu) complex structurally known (Pd(dmfu)[((dimethylamino)ethyl)(diphenylphosphino)ferrocene];[20] 1.409 Å), while the Pd−C bonds are correspondently stronger (2.055, 2.077 Å for **7c** and 2.083, 2.154 Å for the phosphine-containing system). The dmfu molecule is in this case slightly twisted around the C═C bond: C15−C11−C12−C13 = 154.8(3)°, C31−C27−C28−C29 = 154.6(4)°. The comparison of Pd−N distances between **7c** and the above similar Pd^0(aldimine)(fn) compound suggests that the replacement of the aldimine *H*C═N with a methyl group affects the strength of the Pd−N(imine) bond, which is stronger in Pd^0(aldimine)(fn)) (2.115 Å) than in **7c** (2.143(3) and 2.165(3) Å) respectively, whereas the reverse is observed for the Pd−N(pyridine) bond (2.160 Å in Pd^0(aldimine)(fn) and 2.120(3) and 2.123(3) Å in **7c**). Regarding the intramolecular arrangement of ligand **3c** and dmfu around Pd in **7c**, the shortest contact observed is between *i*-Pr and the nearest methoxy oxygen of dmfu: C9···O4 = 3.622(5) Å and C25···O6 = 3.622(6) Å for the two independent molecules, and in both cases the pair of *i*-Pr methyl groups point toward the oxygen atom, rather than being pushed away from it. This is a consequence of the steric hindrance of the CH_3C═N methyl group, which restricts the freedom of rotation of the *i*-Pr around N−C in the range Pd−N−C(H)−CH_3 = 25−90° for a minimum repulsive contact of 3.4 Å (observed value 74° for both molecules). The oscillation of the *i*-Pr group is further reduced between 65 and 90° by the presence of the CH_3O− group of the dmfu ligand (a rotation of the *i*-Pr group below 65° implies a close contact between *i*-Pr and CH_3O− of less than 3.4 Å). This could explain the fact that obtaining a stable complex containing the steric demanding ligand **3d** is not possible. The equivalence of Pd−N−C−CH_3 torsion angles in the two independent molecules (73.6(4) and 74.2(4)°) suggests that the shape and the moderately positive charge distributions on the methyls of the *i*-Pr group are capable of interacting with the local partial negative charge on the methoxy oxygen, by means of a medium-range favorable electrostatic interaction. This would explain why in both molecules one *i*-Pr···dmfu distance is shorter than the other (3.622, 4.077 Å and 3.62, 3.992 Å for C(*i*-Pr)···O(dmfu) in the two molecules). A displacement from the arrangement found in the solid state would decrease the electrostatic attraction and increase the repulsive effect. This also explains why the rotation of the alkene around the bond to Pd is hindered in solution on the NMR time scale.

Hydrogenation. The Pd(NN)(dmfu) complexes have been used in the hydrogenation of 1-phenyl-1-propyne as the substrate (Scheme 3). This substrate was chosen because it gave, in the corresponding Pd(Ar-bian)(dmfu)-catalyzed hydrogenations,[8] a high but not complete selectivity to (*Z*)-1-phenylpropene with concomitant formation of some of the *E* isomer and 1-phenylpropane. Hence, comparison would be relevant for this substrate.

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Scheme 3

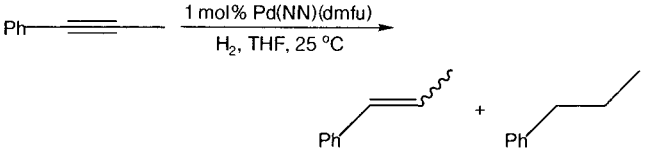

Table 3.[a] Product Distribution in the Hydrogenation of 1-Phenyl-1-propyne

complex	% (*Z*)-alkene	% (*E*)-alkene	% alkane	% conversion[a]
5a[b]		immediate decomp		
5b[c]		immediate decomp		
6c	87	3	10	100
6d	78	3	6	87
6e	50	-	3	53
6f	68	2	7	77
6g	85	4	7	96
7a[c]		immediate decomp		
7b	28	3	46	77
7c	76	4	6	86
8c	50	3	6	59

[a] Referenced to the catalyst decomposition. [b] Decomposed immediately when the substrate was added. [c] Decomposed when subjected to a hydrogen atmosphere.

The results have been collected in Table 3. The hydrogenations were carried out under mild conditions, 1 bar of H_2 pressure and 25 °C, using 1 mol % of catalyst.[8]

The substituents on the imine nitrogen range from the slightly electron-withdrawing phenyl and the weakly donating *p*-anisyl group to the very electron-donating dimethylamino group. The different ligands show a markedly diverse behavior in catalysis, especially concerning the stability of the catalyst during the hydrogenation. At first, the complexes **5a** and **5b** were tested. As mentioned, the tridentate ligands could potentially stabilize the corresponding Pd(0) complexes under hydrogenation conditions, thanks to their chelating effect. However, we observed that complex **5a** decomposes immediately upon addition of the alkyne, even before being subjected to a hydrogen atmosphere, whereas **5b** decomposes within a few seconds after the introduction of hydrogen into the system. The most similar bidentate analogues, complexes **7a** and **7b,** show a higher stability during the hydrogenation: the complex **7a** remains stable when the substrate is added, as compared to **5a**, which decomposes after addition of the substrate, and **7b** is stable for some time under hydrogention conditions, as compared to **7b**, which decomposes immediately when subjected to hydrogenation conditions. Hence, it can be concluded that the tridentate ligands exhibit no additional stabilizing effects. Therefore, the use of the tridentate ligands was not further pursued, and the investigation was directed to the complexes containing the pyridinecarboxaldimine (pyca) type ligands.

The most stable catalyst proved to be **6c**, which decomposes only after the complete conversion of the alkyne. The selectivity observed is high, with 87% of the (*Z*)-alkene formed, the main side product being 1-phenylpropane resulting from the overreduction of the alkene. All other catalysts decompose prior to reaching total conversion of the alkyne, either at a very high conversion, as in the case of the complexes **6d**,**g** and **7c**, or almost immediately after the start of the reaction,

as in the case of **6e** or **8c**. From these results it can be concluded that the stability of the catalysts strongly depends on the nature of the imine substituents, which must be the result of a delicate balance between steric and electronic effects. The four most stable catalysts, **6c**,**d**,**g** and **7c**, all have a good σ-donating alkyl group on the imine nitrogen. This can be considered beneficial for its coordinating capability. When **6c** is compared to **7c**, it is obvious that the additional inductive effect of the CH_3 does not have any positive effect on the stability, since **7c** decomposes before full conversion of the alkyne (86% conversion). This might stem from the increased steric requirements of the ligand, as inferred by X-ray and NMR data. Also **6d** is inferior to **6c** with respect to the stability under hydrogenation conditions, as it decomposes before the full conversion of the substrate (decomposition at 87% of conversion); in this case it is obvious to invoke steric factors, which then seem more important than the inductive ones. When a methyl group is added at the 6-position of the pyridine moiety as in **8c**, the augmented electron-donating capability of the heteroaromatic ring is not sufficient to overcome the encumbrance generated in the coordination plane, and a decreased stability is observed. Complex **8c**, in fact, decomposes at low (59%) conversion. In the case of **6e**, with the very electron donating NMe_2 group on the imine nitrogen, a high selectivity is observed, but palladium precipitation occurs in an early stage of the reaction (53% conversion). When the catalysts **7a**,**b** are compared, the drastic effect of the electronic features of the ligand becomes apparent. With a relatively small change in electron-withdrawing capability, a rather large difference in stability is observed. The catalyst with the phenyl group (**7a**) decomposes immediately when subjected to hydrogenation conditions, whereas the catalyst with the *p*-anisyl group (**7b**) remains stable for a longer time during the hydrogenation, leading to a 77% conversion. Since the steric requirements are the same, it seems apparent that the more electron-donating capacity of the *p*-anisyl group has a beneficial effect on the lifetime of the catalyst. Worth noticing is the fact that complex **7b** leads to the lowest chemoselectivity observed with the employed complexes (46% of alkane). This can be explained by considering the absence of a partial steric crowding (for **7a**,**b**) created in the coordination plane when alkyl groups are bound to the imine nitrogen (as in **6c**,**d**,**g** and **7c**), which allows only the coordination of the alkyne, excluding the poorer coordinating alkene. None of these Pd(NN)(alkene) complexes are as stable as the Pd(Ar-bian)(alkene) type complexes during the hydrogenations, although their stereoselectivity in alkyne hydrogenation (i.e. the selectivity toward the (*Z*)-alkene) is comparable.[8] Several of the complexes are more stable than the previously studied complexes with the bidentate nitrogen ligands bipy and dab.[8] From these results it can be concluded that, to obtain a stable and active catalyst containing a pyca type ligand, a not too bulky and good σ-donor group on the imine nitrogen is required; excessive steric encumbrance in the coordination plane must be avoided. With regard to the imine carbon substituent, the proton is preferred to the methyl, due to torsion within the five-membered palladacycle in the case of the latter, decreasing the complex stability.

Conclusions

The nature of the substituent on the imine nitrogen seems to be the most determining factor regarding the stability of the various precatalysts under hydrogenation conditions; the better the σ-donating capacity of the substituent, the higher the stability of the complex. Furthermore, it was shown that increasing the steric bulk of the ligand results in lower stability, even when these substituents might have beneficial inductive effects. The inherent selectivities of these complexes in the hydrogenation of 1-phenyl-1-propyne, except for **7b**, are all comparable with each other and also with the known Pd(Ar-bian) system.[8] Only their stability, with the exception of **6c**, is poorer when compared to that of the Pd(Ar-bian) systems, but they are certainly better than the complexes containing bipy or dab.

Experimental Section

General Methods. Chemicals were obtained from Acros Chimica and Aldrich Chemical Co. All syntheses of ligands and complexes and hydrogenations were carried out in dried glasswork, using standard Schlenk techniques under an atmosphere of purified nitrogen. THF and Et_2O were distilled from sodium/benzophenone, acetone was distilled from K_2CO_3, and dichloromethane was distilled from CaH_2. Primary alkylamines were distilled before use and stored under nitrogen on molecular sieves (4 Å). The aldehydes and ketones were distilled prior to use and stored under nitrogen. Other chemicals were used as received. The starting materials dba[21] and $Pd(dba)_2$[22] were prepared according to literature procedures. ^1H and ^{13}C NMR data were recorded on a Bruker AMX300 or a Varian Mercury300 spectrometer (^1H, 300.13 MHz; ^{13}C, 75.47 MHz), using either $CDCl_3$ as a solvent and as an external reference (^1H, 7.26 ppm; ^{13}C, 77.0 ppm) or CD_2Cl_2 (^1H, 5.32 ppm; ^{13}C, 54.0 ppm). IR spectra were recorded on a Nicolet 5PC FT-IR or a Bio-Rad FTS-7 using a KBr pellet. The gas chromatographic analyses were performed on a Dani HP 3800 flame-ionization gas chromatograph (OV 101 on a CHP capillary column).

Syntheses of the Ligands. Most of the ligands described below have been reported before and usually well characterized. For the ligand see the references cited: **1a**,[23a] **2c,d**,[23b,c] **2e**,[23d] **2f**,[23b] **2g**,[23e] **3a**,[23f] **4c**.[23c,g] The ligands were synthesized using methods somewhat different from those reported before, and these methods are described below.

2,6-Bis(*N*-phenylcarbaldimino)pyridine (1a). A solution of 2,6-pyridinedicarbaldehyde (0.71 g, 5 mmol) and aniline (1.14 g, 12.5 mmol) in 50 mL of absolute ethanol was refluxed for $^1/_2$ h. When the mixture was cooled, a white powder precipitated. The solution was filtered, and the powder was recrystallized from absolute ethanol and dried in vacuo.

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Yield: 0.57 g (40%) of a white powder. ^{1}H NMR: δ 8.69 (s, 2H, H_7), 8.32 (d, 2H, H_3-H_5, $^3J_{HH}$ = 7 Hz), 7.96 (pst, 1H, H_4, $^3J_{HH}$ = 7 Hz), 7.34 (m, 10H, Ph). IR (cm^{-1}): ν(C=N) 1567 w. Mp (°C): 134. Anal. Calcd for $C_{19}H_{15}N_3$: C, 80.07; H, 5.26; N, 14.73. Found: C, 79.55; H, 5.27; N, 14.52.

2,6-Bis(*N*-4-methoxyphenylcarbaldimino)pyridine (1b). The same procedure was used as for compound **1a**, but in this case a white solid precipitated immediately; this was filtered, washed with diethyl ether, and dried in vacuo.

Yield: 0.35 g (72%) of a white powder. ^{1}H NMR: δ 8.71 (s, 2H, H_7), 8.25 (d, 2H, H_3-H_5, $^3J_{HH}$ = 8 Hz), 7.91 (pst, 1H, H_4, $^3J_{HH}$ = 8 Hz), 7.37 (d, 4H, *p*-An, $^3J_{HH}$ = 9 Hz), 6.97 (d, 4H, *p*-An, $^3J_{HH}$ = 9 Hz), 3.85 (s, 6H, OCH_3). IR (cm^{-1}): ν(C=N) 1596 w. Mp (°C): 156. Anal. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.11; H, 5.55; N, 12.17. Found: C, 72.99; H, 5.40; N, 11.96.

2-(*N*-2-Propanecarbaldimino)pyridine (2c). A solution of 2-pyridinecarbaldehyde (0.55 g, 5 mmol) and 2-isopropylamine (3.0 g, 50 mmol) was stirred in 50 mL of dry diethyl ether in the presence of activated molecular sieves (4 Å) for 30 min. The solution was filtered, the collected molecular sieves were washed with dry diethyl ether, and the solvent was removed in vacuo. Yield: 0.14 g (97%) of a yellow oil. ^{1}H NMR: δ 8.57 (d, 1H, H_6, $^3J_{HH}$ = 5 Hz), 8.33 (s, 1H, H_7), 7.92 (d, 1H, H_3, $^3J_{HH}$ = 8 Hz), 7.65 (pst, 1H, H_4, $^3J_{HH}$ = 8 Hz), 7.22 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 3.60 (sept, 1H, C*H*$(CH_3)_2$, $^3J_{HH}$ = 6 Hz), 1.21 (d, 6H, CH(C*H*$_3)_2$, $^3J_{HH}$ = 6 Hz). IR (cm^{-1}): ν(C=N) 1526 w.

2-(*N*-*tert*-Butylcarbaldimino)pyridine (2d), 2-(*N*-(Dimethylamino)carbaldimino)pyridine (2e), 2-(*N*-Butylcarbaldimino)pyridine (2f), 2-(*N*-(2-Hydroxyethyl)carbaldimino)pyridine (2g), and 2-(*N*-(2-Propyl)carbaldimino)-6-methylpyridine (4c). The same procedure was used as for compound **2c**. For compound **4c**, 6-methyl-2-pyridinecarbaldehyde was used. The excess of amine was varied between 1.1 and 10 equiv. For compound **2g** the resulting oil was washed with ethanol to remove the excess of the high-boiling amine. Yields were in all cases almost quantitative (97−100%) except for **2g** (75%). ^{1}H NMR: **2d**, δ 8.55 (d, 1H, H_6, $^3J_{HH}$ = 5 Hz), 8.29 (s, 1H, H_7), 7.94 (d, 1H, H_3, $^3J_{HH}$ = 9 Hz), 7.63 (pst, 1H, H_4, $^3J_{HH}$ = 9 Hz), 7.20 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 1.24 (s, 9H, CH_3); **2e**, δ 7.92 (d, 1H, H_6, $^3J_{HH}$ = 5 Hz), 7.24 (d, 1H, H_3, $^3J_{HH}$ = 8 Hz), 7.08 (pst, 1H, H_4, $^3J_{HH}$ = 5 Hz), 6.72 (s, 1H, H_7), 6.55 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 2.48 (s, 6H, CH_3); **2f**, δ 8.47 (d, 1H, H_6, $^3J_{HH}$ = 4 Hz), 8.21 (s, 1H, H_7), 7.83 (d, 1H, H_3, $^3J_{HH}$ = 9 Hz), 7.54 (pst, 1H, H_4, $^3J_{HH}$ = 9 Hz), 7.11 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 3.51 (t, 2H, CH_2-N, $^3J_{HH}$ = 6 Hz), 1.56 (m, 2H, CH_2), 1.27 (m, 2H, CH_2), 0.78 (t, 3H, CH_3, $^3J_{HH}$ = 7 Hz); **2g**, δ 8.63 (d, 1H, H_6, $^3J_{HH}$ = 5 Hz), 8.41 (s, 1H, H_7), 7.92 (d, 1H, H_3, $^3J_{HH}$ = 9 Hz), 7.70 (pst, 1H, H_4, $^3J_{HH}$ = 9 Hz), 7.30 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 3.95 (t, 2H, C*H*$_2$OH, $^3J_{HH}$ = 6 Hz), 3.81 (t, 2H, *CH*$_2-$N, $^3J_{HH}$ = 6 Hz), 2.75 (br, 1H, OH); **4c**, δ 8.35 (s, 1H, H_7), 7.79 (d, 1H, H_3, $^3J_{HH}$ = 8 Hz), 7.59 (pst, 1H, H_4, $^3J_{HH}$ = 8 Hz), 7.14 (d, 1H, H_5, $^3J_{HH}$ = 7 Hz), 3.60 (sept, 1H, C*H*$(CH_3)_2$, $^3J_{HH}$ = 6 Hz), 2.56 (s, 3H, CH_3(py)), 1.25 (d, 6H, CH(C*H*$_3)_2$, $^3J_{HH}$ = 6 Hz).

2-(*N*-Phenylacetimino)pyridine (3a) and 2-(*N*-(4-Methoxyphenyl)acetimino)pyridine (3b). A solution of 2-acetylpyridine (0.61 g, 5 mmol) and a slight excess (5.5 mmol) of the appropriate amine (**3a**, aniline (0.51 g); **3b**, *p*-anisidine (0.62 g)) in 15 mL of dry toluene was heated in the presence of activated molecular sieves (4 Å) to 120 °C in an Ace pressure tube for 72 h. The reaction mixture was filtered and the solvent evaporated. The remaining oil was washed with ethanol and dried in vacuo. Yields: **3a**, 0.82 g (83%) as a yellow oil; **3b**, 0.58 g (84%) as a red oil. ^{1}H NMR: **3a**, δ 8.67 (d, 1H, H_6, $^3J_{HH}$ = 5 Hz), 8.27 (d, 1H, H_3, $^3J_{HH}$ = 8 Hz), 7.78 (pst, 1H, H_4, $^3J_{HH}$ = 8 Hz), 7.36 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 2.36 (s, 3H, CH_3); **3b**, δ 8.64 (d, 1H, H_6, $^3J_{HH}$ = 5 Hz), 8.24 (d, 1H, H_3, $^3J_{HH}$ = 8 Hz), 7.76 (pst, 1H, H_4, $^3J_{HH}$ = 8 Hz), 7.34 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 6.91 (d, 2H, *p*-An, $^3J_{HH}$ = 7 Hz), 6.79 (d, 2H, *p*-An, $^3J_{HH}$ = 7 Hz), 3.81 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3).

2-(*N*-(2-Propyl)acetimino)pyridine (3c) and 2-(*N*-*tert*-Butylacetimino)pyridine (3d). The procedure was identical with that reported for **3a**,**b**, except for the reaction time, which was 48 h. Yields: **3c**, 0.58 g (79%) as a yellow oil; **3d**, 0.58 g (65%) as an orange oil. ^{1}H NMR: **3c**, δ 8.52 (d, 1H, H_6, $^3J_{HH}$ = 6 Hz), 7.99 (d, 1H, H_3, $^3J_{HH}$ = 8 Hz), 7.50 (pst, 1H, H_4, $^3J_{HH}$ = 8 Hz), 7.22 (pst, 1H, H_5, $^3J_{HH}$ = 6 Hz), 3.86 (sept, 1H, C*H*$(CH_3)_2$, $^3J_{HH}$ = 6 Hz), 2.31 (s, 3H, CH_3), 1.18 (d, 6H, CH_3); **3d**, δ 8.58 (d, 1H, H_6, $^3J_{HH}$ = 5 Hz), 7.94 (d, 1H, H_3, $^3J_{HH}$ = 9 Hz), 7.74 (pst, 1H, H_4, $^3J_{HH}$ = 9 Hz), 7.40 (pst, 1H, H_5, $^3J_{HH}$ = 5 Hz), 2.66 (s, 3H, C(CH_3)=N), 1.31 (s, 9H, *t*-Bu).

Syntheses of the Complexes. Pd(2,6-bis(*N*-phenylcarbaldimino)pyridine)(dmfu) (5a). A solution of $Pd(dba)_2$ (0.57 g, 1 mmol), **1a** (0.31 g, 1.1 mmol), and dmfu (0.16 g, 1.1 mmol) in 50 mL of dry acetone was stirred for 8 h at room temperature. A brown solid formed, which was filtered and washed repeatedly with diethyl ether to remove dba. The resulting solid was dissolved in dichloromethane and filtered over Celite to remove traces of Pd(0). The resulting solution was concentrated and the product precipitated by addition of *n*-hexane, filtered, and dried in vacuo. Yield: 0.42 g of a brown powder, (78%). IR (cm^{-1}): ν(C=C + C=O) 1678 s; ν(C=N) 1581 w. Dec pt (°C): 154. Anal. Calcd for $C_{25}H_{23}N_3O_4Pd$: C, 56.03; H, 4.29; N, 7.84. Found: C, 55.59; H, 4.09; N, 7.59.

Pd(2,6-bis(*N*-(4-methoxyphenyl)carbaldimino)pyridine)(dmfu) (5b), Pd(2-(*N*-(2-propyl)carbaldimino)pyridine)(dmfu) (6c), Pd(2-(*N*-(dimethylamino)carbaldimino)pyridine)(dmfu) (6e), and Pd(2-(*N*-(2-propyl)carbaldimino)-6-methylpyridine)(dmfu) (8c). The procedure was similar to that of **5a.** In the case of **6e**, the reaction required 16 h to go to completion, whereas in the case of **8c** 36 h was required.

Data for **5b** are as follows.Yield: 0.16 g (75%) of a brown powder. Dec pt (°C): 154. Anal. Calcd for $C_{27}H_{27}N_3O_6Pd$: C, 54.46; H, 4.57; N, 7.05. Found: C, 53.90; H, 4.34; N 6.88. ^{1}H NMR: owing to dynamic processes it was not possible to unambiguously attribute the signals. IR (cm^{-1}): ν(C=C + C=O) 1693 s; ν(C=N) 1558 w. Data for **6c** are as follows. Yield: 0.34 g (85%) as a yellow solid. Anal. Calcd for $C_{15}H_{20}N_2O_4Pd$: C, 42.06; H, 4.75; N, 10.51. Found: C, 42.35; H, 4.78; N, 10.32. ^{13}C NMR: δ 160.29 (C7), 153.87 (C2), 152.45 (C6), 138.84 (C4), 128.50 (C5), 126.50 (C3), 62.81 (CH_3 ester), 51.20 + 50.86 (CH *i*-Pr), 42.13 + 41.14 (CH alkene), 24.00 + 23.64 (CH_3 *i*-Pr), the carbonyl signal was not observed. IR (cm^{-1}): ν(C=C + C=O) 1671 s; ν(C=N) = 1592 w. Data for **6e** are as follows. Yield: 0.56 g (82%) as a yellow solid. Anal. Calcd for $C_{14}H_{19}N_3O_4Pd$: C, 42.06; H, 4.75; N, 10.51. Found: C, 42.35; H, 4.78; N, 10.32. IR (cm^{-1}): ν(C=O) 1674 w; ν(C=N) 1596 w. Data for **8c** are as follows. Yield: 0.04 g (35%) as a brown solid. Anal. Calcd for $C_{16}H_{22}N_2O_4Pd$: C, 46.56; H, 5.37; N, 6.79. Found: C, 47.03; H, 4.94; N, 6.80. IR (cm^{-1}): ν(C=C + C=O) 1671 s; ν(C=N) 1592 w.

Pd(2-(*N*-*tert*-butylcarbaldimino)pyridine)(dmfu) (6d), Pd(2-(*N*-phenylacetimino)pyridine) (7a), Pd(2-(*N*-(4-methoxyphenyl)acetimino)pyridine)(dmfu) (7b), and Pd-(2-(*N*-(2-propyl)acetimino)pyridine)(dmfu) (7c). A 3.00 mmol portion of **2d** (0.31 g) or 0.33 mmol of **3a**,**b** (0.07 g) or **3c** (0.05 g) was dissolved in 40 mL of acetone at 45 °C in the presence of 0.33 mmol (0.05 g) of dmfu. A 0.17 g (0.30 mmol) amount of $Pd(dba)_2$ was added in small portions within 2 h, with care taken to observe the disappearance of the purple color of the $Pd(DBA)_2$ between every addition. The solvent was then removed under reduced pressure andthe residue dissolved in dichloromethane and filtered through Celite. The product was precipitated by addition of diethyl ether.

Data for **6d** are as follows. Yield: 0.24 g (58%). ^{13}C NMR: δ 175.14 + 174.38 (C=O), 157.74 (C7), 154.77 (C2), 152.18 (C6), 138.81 (C4), 128.38 (C5), 126.93 (C3), 61.33 (CH_3 ester), 51.20 + 50.83 (C *t*-Bu), 42.16 + 41.41 (CH alkene), 29.60 (CH_3 *t*-Bu). Anal. Calcd for $C_{16}H_{22}N_2O_4Pd$: C, 46.56; H, 5.37; N, 6.79. Found: C, 46.31; H, 5.40; N, 6.46. IR (cm^{-1}): ν(C=C + C=O)

Table 4. Crystal Data and Structure Refinement for 7c·0.5CH_2Cl_2

empirical formula	$C_{16.50}H_{23}ClN_2O_4Pd$
fw	455.22
temp	293(2) K
wavelength	0.710 69 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	$a = 13.629(2)$ Å $b = 20.363(2)$ Å $c = 14.169(2)$ Å $\beta = 93.369(2)°$
V	3925.5(9) Å^3
Z	8
density (calcd)	1.541 Mg/m^3
abs coeff	1.103 mm^{-1}
$F(000)$	1848
cryst size	0.5 × 0.3 × 0.3 mm^3
θ range for data collection	1.50−26.36°
index ranges	$-17 \le h \le 16$, $-25 \le k \le 25$, $-17 \le l \le 17$
no. of rflns collected	40 678
no. of indep rflns	8001 (R(int) = 0.0347)
no. of obsd rflns ($I > 2\sigma(I)$)	5907
no. of data/restraints/params	8001/0/508
goodness of fit on F^2	0.973
final R indices ($I > 2\sigma(I)$)	R1 = 0.0318, wR2 = 0.0835
R indices (all data)	R1 = 0.0494, wR2 = 0.0908
largest final F max/min	0.955/−0.766 e Å^{-3}

1685 s; ν(C═N) 1591 w. Data for **7a** are as follows. Yield: 0.05 g (35%) as a red powder. Anal. Calcd for $C_{19}H_{20}N_2O_4Pd$: C, 51.08; H, 4.48; N, 6.27. Found: C, 51.21; H, 4.40; N, 6.48. Data for **7b** are as follows. Yield: 30% of a brown powder. Anal. Calcd for $C_{20}H_{22}N_2O_5Pd$: C, 50.38; H, 4.65; N, 5.87. Found: C, 50.12; H, 4.22; N 5.68. IR (cm^{-1}): ν(C═C + C═O) 1685−1666 s; ν(C═N) 1590 w. Data for **7c** are as follows. Yield: 0.17 g (40%). Anal. Calcd for $C_{16}H_{22}N_2O_4Pd$: C, 46.56; H, 5.37; N, 6.79. Found: C, 46.62; H, 5.40; N, 6.46. IR (cm^{-1}): ν(C═C + C═O) 1676 s; ν(C═N) not visible.

Pd(2-(*N*-butylcarbaldimino)pyridine)(dmfu) (6f) and Pd(2-(*N*-(2-hydroxyethyl)carbaldimino)pyridine)-(dmfu) (6g). A solution of $Pd(dba)_2$ (0.57 g, 1 mmol), **2f** (0.18 g, 1.1 mmol) or **2g** (0.17 g, 1.1 mmol), and dmfu (0.16 g, 1.1 mmol) in 50 mL of dry THF was stirred for 2 h at 20 °C. A clear yellow solution was obtained, which was concentrated until a precipitate formed. The product was further precipitated by addition of diethyl ether. The solid was filtered, washed with diethyl ether, and redissolved in dichloromethane, and then this solution was filtered over Celite. The product was precipitated with *n*-hexane, filtered, and dried in vacuo. Data for **6f** are as follows. Yield: 0.32 g (77%) of a yellow powder. Data for **6g** are as follows. Yield: 0.30 g (75%) of a yellow powder. ^{13}C NMR: δ 164.42 (C7), 152.62 (C6), 139.03 (C4), 128.81 (C5), 126.77 (C3), 66.24 (CH_3 ester), 64.91 (CH_2-OH), 62.05 (CH_2N); the carbonyl, C2, and alkene signals were not observed.

Crystal Structure Determination of 6c. A red irregular prismatic single crystal of **6c** was mounted on a glass fiber, and X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with a CCD detector, using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Data collection details are: crystal to detector distance 5.0 cm, 2424 frames collected (complete sphere mode), time per frame 30 s, oscillation $\Delta\omega = 0.300°$. Crystal decay was negligible. Data reduction was performed up to $d = 0.80$ Å by the SAINT package,[24] and data were corrected for absorption effects by the SADABS[25] procedure (T_{max} = 1.000, T_{min} = 0.857). The phase problem was solved by direct methods[26] and refined by full-matrix least squares on all F^2,[27] implemented in the WinGX package.[28] Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were located from Fourier maps and refined isotropically, except for methyl and CH_2Cl_2 hydrogens, which were introduced in calculated positions. The Cambridge Crystallographic Database[29] facility was used for the discussion of the structure. The final map was featureless. Data collection and refinement results are summarized in Table 4.

Hydrogenation Experiments. The hydrogenation reactions were performed by dissolving, in a Schlenk tube, 0.04 mmol of the appropriate palladium complex in 40 mL of dry THF, under a nitrogen atmosphere. Subsequently, 4 mmol of 1-phenyl-1-propyne was added and the Schlenk tube was connected to a standard gas buret filled with hydrogen. The solution was then vigorously stirred at 25 °C; micro samples were withdrawn at regular intervals to monitor the reaction, and the samples were analyzed by means of a gas chromatograph.

Supporting Information Available: Listings of atomic fractional coordinates, hydrogen atom fractional coordinates, anisotropic displacement parameters, and all bond distances and angles, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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