(η^3-Allyl)palladium Complexes Bearing Diphosphinidenecyclobutene Ligands: Highly Active Catalysts for the Hydroamination of 1,3-Dienes**

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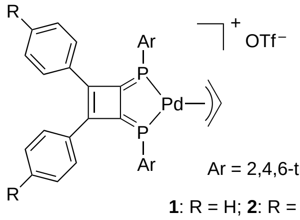
Dedicated to Prof. François Mathey
on the occasion of his 60th birthday

The catalytic hydroamination of unsaturated hydrocarbons is a useful means of synthesizing nitrogen-containing organic molecules.[1] Intramolecular cyclization of aminoalkenes is efficiently catalyzed by lanthanide complexes,[2] and amine-induced telomerization of butadienes[3] and oxidative 1,4-addition of amines to dienes[4] are successfully conducted with palladium catalysts. In contrast, simple intermolecular 1:1 addition of amines to alkenes or dienes is a rather difficult process and has been conducted at high temperature.[5, 6] Hartwig et al. recently reported a significantly improved catalyst, generated from $[Pd(PPh_3)_4]$ and CF_3CO_2H, which performs 1:1 addition of aniline to 1,3-dienes at room temperature.[7] However, even in this case, the reaction takes about a day for completion. Here we report that more efficient catalysts can be prepared by using sp^2-hybridized phosphorus ligands, namely, 1,2-diaryl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutenes.[8]

sp^2-Hybridized phosphorus compounds have a marked propensity to engage in metal-to-phosphorus π backbonding and have a strong π-acceptor property, comparable to that of the carbonyl ligand.[9] Since the catalytic addition of an amine to a 1,3-diene probably involves nucleophilic attack of the amine on an (η^3-allyl)palladium(II) or palladium(II) diene complex,[7a] we expected that diphosphinidenecyclobutene ligands may effectively enhance the electrophilicity of palladium intermediates and thus give highly active catalysts. Although transition metal complexes of sp^2-hybridized phosphorus compounds have been extensively prepared in the last decade,[9] their application to catalysis has been extremely limited,[10] except for phosphaaromatic compounds such as phosphabenzene and phosphaferrocene.[11, 12]

Complexes **1**–**3** were synthesized by treating $[\{Pd(\eta^3\text{-allyl})Cl\}_2]$[13] with the corresponding diphosphinidenecyclobutene ligand and silver trifluoromethanesulfonate (AgOTf) in CH_2Cl_2 at room temperature, and isolated as yellowish orange solids in 66–96% yields.[14] They are fairly stable towards air in solution and as solids; the solid materials can be stored at room temperature for months without notable decomposition.



Ar = 2,4,6-tri-*tert*-butylphenyl

1: R = H; **2**: R = OMe; **3**: R = CF_3

Figure 1 shows the molecular structure of **1**.[15] The diphosphinidenecyclobutene ligand chelates the (η^3-allyl)palladium moiety through two phosphorus atoms. The aryl rings C and D on the phosphorus atoms are nearly perpendicular to the main framework A, whereas the almost parallel arrangement of phenyl groups E and F and the cyclobutene ring B suggests partial π conjugation between them. The C(53)–C(54) and C(54)–C(55) bond lengths (1.383(8) and 1.376(8) Å) and the C(53)-C(54)-C(55) angle (119.9(5)°) are in the typical ranges for η^3-allyl ligands. The three Pd–C distances (2.168(5)–2.178(4) Å) are comparable to those of diphosphane analogues (2.168–2.201 Å).[16]

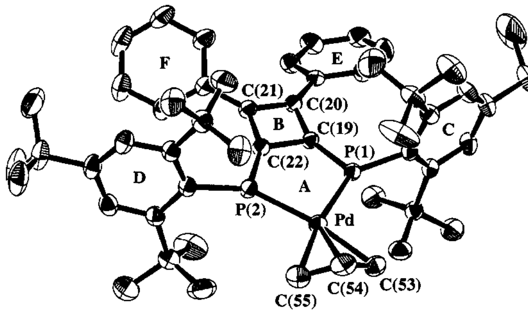
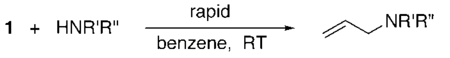


Figure 1. Molecular structure of the cation in crystals of $\mathbf{1}\cdot 2C_6H_6$. Thermal ellipsoids are drawn at the 30% probability level. Triflate anion, benzene molecules (solvent of crystallization), and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd-P(1) 2.326(1), Pd-P(2) 2.322(1), Pd-C(53) 2.168(5), Pd-C(54) 2.168(5), Pd-C(55) 2.178(4), P(1)-C(19) 1.667(4), P(2)-C(22) 1.671(4), C(19)-C(20) 1.476(5), C(19)-C(22) 1.499(5), C(20)-C(21) 1.406(5), C(21)-C(22) 1.464(5), C(53)-C(54) 1.383(8), C(54)-C(55) 1.376(8); P(1)-Pd-P(2) 85.50(4), Pd-P(1)-C(19) 107.6(1), Pd-P(2)-C(22) 107.4(1), P(1)-C(19)-C(22) 119.6(3), C(20)-C(19)-C(22) 87.8(2), P(2)-C(22)-C(19) 119.9(3), C(19)-C(22)-C(21) 88.5(3), C(19)-C(20)-C(21) 91.7(3), C(20)-C(21)-C(22) 91.9(3), C(53)-C(54)-C(55) 119.9(5). Dihedral angles between least-squares planes [°]: [A]-[B] 2.3(1), [A]-[C] 93.2(1), [A]-[D] 100.3(1), [B]-[E] 28.2(2), [B]-[F] 147.8(2).



(1)

Complex **1** is extremely reactive towards amines [Eq. (1)]. Treatment of **1** with diethylamine (10 mol equiv) in benzene at room temperature led to instant formation of 3-(*N*,*N*-diethylamino)propene in 82% yield. Similarly, the reaction with aniline afforded a 45% yield of 3-(*N*-phenylamino)pro-

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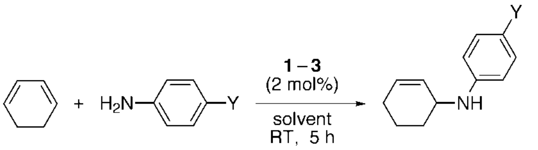
pene within a few minutes.[17] In contrast, the diphosphane analogues [Pd(η^3-allyl)(dppe)]OTf (dppe = 1,2-bis(diphenylphosphanyl)ethane) and [Pd(η^3-allyl)(dppf)]OTf (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene) were totally unreactive towards aniline under the same reaction conditions.

The high reactivity of **1** was also demonstrated in the catalytic hydroamination of 1,3-cyclohexadiene with anilines [Eq. (2)]. A typical procedure follows: Aniline (0.18 mL, 1.98 mmol) was added to a solution of **1** (21.0 mg, 0.020 mmol) and 1,3-cyclohexadiene (0.10 mL, 1.05 mmol) in toluene (2 mL) under nitrogen. The mixture was stirred at room temperature for 5 h. Analysis by GLC revealed complete consumption of the diene. The reaction mixture was concentrated to dryness by pumping, and the residue purified by column chromatography (SiO_2, hexane/AcOEt 100/1) to give 162 mg (89 % yield) of 3-(*N*-phenylamino)cyclohexene.



(2)

Representative results are listed in Table 1. The catalytic activity significantly decreased with increasing solvent polarity (entries 1–5). Toluene was among the best solvents examined. The reaction did not proceed in DMF, and precipitation of palladium black occurred. Complex **2** (R = OMe) showed catalytic activity comparable to that of **1** (entry 6), whereas CF_3-substituted **3** was less active (entry 9).[18] Hydroamination with *para*-substituted anilines was also successful (entries 7 and 8).

Table 1. Hydroamination of 1,3-cyclohexadiene with anilines catalyzed by **1**–**3** [Eq. (2)].[a]

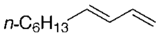
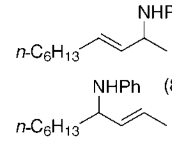
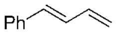
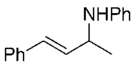
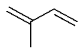
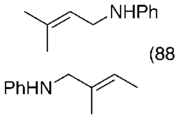
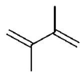
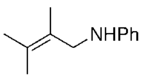
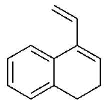
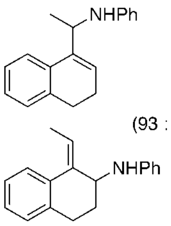
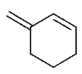
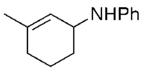
Entry	Catalyst	Y	Solvent	Yield [%][b]
1	**1**	H	toluene	89
2	**1**	H	THF	59
3	**1**	H	dioxane	30
4	**1**	H	CH_2Cl_2	2
5	**1**	H	DMF	0
6	**2**	H	toluene	91
7	**2**	F	toluene	90
8	**2**	OMe	toluene	88
9	**3**	H	toluene	58

[a] All reactions were conducted at room temperature for 5 h with diene (1.0 mmol), aniline (2.0 mmol), catalyst (0.02 mmol), and solvent (2 mL). [b] Yield of isolated product.

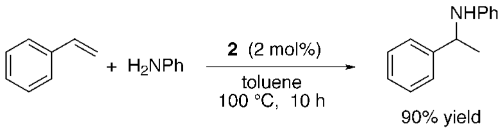
A variety of 1,3-dienes could be hydroaminated with aniline in good to excellent yields (Table 2). All reactions proceeded smoothly at room temperature, except for entry 6, in which about 30 % of unconsumed diene starting material was recovered. 1,2-Addition to a terminal vinyl group is preferred when one of the termini of the diene unit is substituted (entries 1, 2, and 5). Otherwise, 1,4-addition to the diene takes place exclusively (entries 3, 4, and 6).

The present catalysts were also effective for 1,2-addition of aniline to styrene at 100 °C [Eq. (3)]. Complex **2** gave the best result: a 90 % yield of {1-(*N*-phenylamino)ethyl}benzene.

Table 2. Hydroamination of dienes with aniline catalyzed by **2**.[a]

Entry	Diene	Time [h]	Product(s)[b]	Yield [%][c]
1		6	 (80 : 20)	80
2		5		92
3		3	 (88 : 12)	92
4		5		96
5		6	 (93 : 7)	85
6		24		68

[a] All reactions were conducted at room temperature in toluene (2 mL) with diene (1.0 mmol), aniline (2.0 mmol), and catalyst (0.02 mmol). [b] The ratio of isomers was determined by ^{1}H NMR analysis. [c] Yield of isolated product.



(3)

In conclusion, we have found highly active catalysts for the hydroamination of 1,3-dienes with aniline. The reactions readily proceed at room temperature to give the corresponding 1,2- or 1,4-addition products in high yields. The use of diphosphinidenecyclobutene ligands with sp^2-hybridized phosphorus atoms having strong π-acceptor ability is of particular importance for the catalytic activity.

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[14] Complexes **1**–**3** were characterized by NMR spectroscopy and elemental analysis: see Supporting Information.

[15] A single crystal of dimensions ca. 0.40 × 0.25 × 0.15 mm was grown by slow evaporation of the benzene solution at room temperature. Crystallographic data for **1**$\cdot 2\,C_6H_6$: $C_{68}H_{85}O_3P_2SF_3Pd$, $M_r = 1207.82$, orthorhombic, space group *Pbca* (no. 61), $a = 29.3798(4)$, $b = 27.9193(4)$, $c = 16.6779(2)$ Å, $V = 13680.3(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.173\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 3.98\ cm^{-1}$, $T = 296$ K, $2\theta_{max} = 55.0°$; of the 116497 reflections collected, 15690 were independent ($R_{int} = 0.044$) and used for the structure refinement (625 parameters); $R_1 = 0.044$, $R(F^2) = 0.073$, $R_w(F^2) = 0.133$ for 8198 data with $I > 3\sigma(I)$; $R(F^2) = 0.085$, $R_w(F^2) = 0.158$ for all data. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167652. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[17] After rapid formation in the initial phase, the reaction became significantly slower, probably due to simultaneous decomposition of palladium species (precipitation of palladium-black was noted). The yield of 3-(*N*-phenylamino)propene reached 72% after prolonged reaction time (24 h).

[18] It was confirmed that the diphosphane complexes [Pd(η^3-allyl)(dppe)]OTf and [Pd(η^3-allyl)(dppf)]OTf were inactive towards the catalytic reaction of Equation (2) at room temperature.

1433-7851/01/4023-4503 $ 17.50+.50/0