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Highly Efficient Phosphapalladacyclic Catalysts for the Hydroarylation of Norbornene

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Gérard Buono

In the last decade, organopalladium-catalyzed C–C bond formation has become one of the most important tools in the synthesis of organic molecules.[1] In particular, the Heck reaction is an important method for the preparation of aryl-functionalized alkenes in synthetic chemistry and the pharmaceutical industry.[2] Attempts to achieve industrial-scale application of this reaction proved difficult due to the need for relatively large amounts of palladium catalysts and/or expensive aryl iodides. The former problem can be overcome by more efficiently recycling the catalyst, and the latter by using catalysts of higher activity or by activating the cheaper aryl bromides and chlorides. Herrmann, Beller et al.[3] and Milstein et al.[4] described recently the synthesis of phosphapalladacycles and their use as efficient catalysts for the Heck reaction that give turnover numbers (TON)[5] one to three orders of magnitude higher than those reported before (TON > 100000). Cyclopalladated complexes, formed in situ from mixtures of Pd^{II} salts and tri-*o*-tolylphosphane were investigated.[6] More recently, it was found that fine tuning of the phosphorus ligand sphere could improve these results, and chelating diphosphanes containing P–N bonds gave higher turnover values (TON > 200000).[7] In recent years, we have studied and developed the potential of oxazaphospholidine and diazaphospholidine ligands in various catalytic reactions.[8–10] Systems in which the phosphorus atom is substituted by two nitrogen and one oxygen atom or one aromatic carbon atom proved to be excellent mediators for, inter alia, highly selective allylic substitutions,[8] copper-catalyzed Diels–Alder reactions,[9] and asymmetric cyclopropanations.[10] Here we report the synthesis of a new class of bis(alkylamino)-*p*-tolylphosphane ligands and their high efficiency in the palladium-catalyzed hydroarylation of norbornene and norbornadiene; they surpass all previously known catalysts as regards stability, lifetime, and turnover frequency (TOF).[5]

The synthesis of bis(dimethylamino)-*o*-tolylphosphane (**1**) was achieved in 78% yield from *o*-tolylmagnesium bromide and chloro-bis(dimethylamino)phosphane in THF at 0 °C (Scheme 1). Ligands **2** and **3** were synthesized from **1** by exchange reaction in refluxing toluene with two equivalents of the corresponding amine in 76 and 58% yield, respectively (Table 1).[11]

Treating palladium(II) acetate with **1**–**3** in refluxing toluene gave the expected palladacyclic complexes **4a**–**c** in high yields (90–95%) as thermally stable yellow solids insensitive to air and moisture (Scheme 2). The cyclometallated structure

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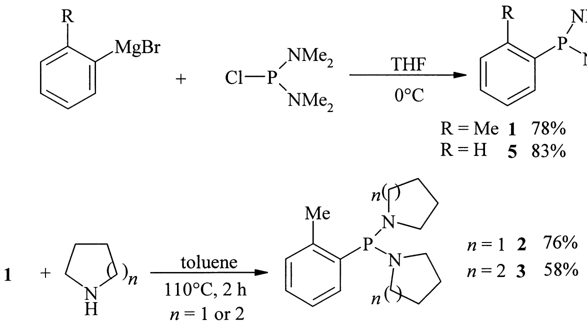


Scheme 1. Synthesis of **1**–**3** and **5**.

Table 1. Characteristic data of compounds **1**–**3**, **4a**, **5** in $CDCl_3$.

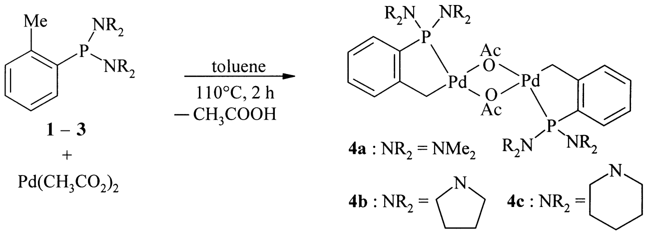
1: Purification by distillation afforded **1** in 78% yield as an oil, b.p. 80 °C (10 Pa); ^{1}H NMR (200 MHz): $\delta = 2.31$ (s, 3H), 2.69 (d, $J = 35.5$ Hz, 6H), 2.72 (d, $J = 35.5$ Hz, 6H), 7.17–7.46 (m, 4H); ^{13}C NMR (50 MHz): $\delta = 20.1$ (d, $J = 26.0$ Hz), 41.0 (s), 41.3 (s), 121.5 (s), 125.1 (s), 127.6 (s), 130.4 (s), 138.5 (s), 140.0 (d, $J = 43.6$ Hz); ^{31}P NMR (40.54 MHz): $\delta = 96.6$

2: Purification by distillation afforded **2** in 76% yield as an oil, b.p. 95 °C (3 Pa); ^{1}H NMR (200 MHz): $\delta = 1.76$ (m, 8H), 2.41 (s, 3H), 3.01 (m, 8H), 6.63–7.48 (m, 4H); ^{13}C NMR (50 MHz): $\delta = 26.4$ (d, $J = 4.8$ Hz), 36.4 (d, $J = 14.0$ Hz), 49.9 (d, $J = 13.5$ Hz), 125.3 (s), 127.7 (s), 128.7 (s), 129.8 (d, $J = 5.0$ Hz), 130.5 (s), 143.3 (d, $J = 42.0$ Hz); ^{31}P NMR (40.54 MHz, $CDCl_3$): $\delta = 89.1$

3: Purification by distillation afforded **3** in 58% yield as an oil, b.p. 130 °C (2 Pa); ^{1}H NMR (200 MHz): $\delta = 1.49$ (m, 12H), 2.46 (s, 3H), 3.0 (m, 8H), 7.0–7.42 (m, 4H); ^{13}C NMR (50 MHz): $\delta = 25.6$ (d, $J = 4.5$ Hz), 41.2 (d, $J = 35.0$ Hz), 46.2 (s), 50.4 (d, $J = 15.0$ Hz), 125.1 (s), 128.6 (s), 127.7 (s), 129.2 (s), 130.7 (s), 141.2 (d, $J = 41.0$ Hz); ^{31}P NMR (40.54 MHz): $\delta = 91.2$

4a: ^{1}H NMR (200 MHz): $\delta = 2.40$ (dd, $J = 14.0$, $J_{PH} = 1.8$ Hz, 2H), 2.55 (d, $J = 35.5$ Hz, 12H), 2.69 (d, $J = 35.5$ Hz, 12H), 2.82 (dd, $J = 14.1$, $J_{P,H} = 1.8$ Hz, 2H), 3.01 (s, 6H), 7.15–7.56 (m, 8H); ^{13}C NMR (50 MHz): $\delta = 24.7$ (d, $J = 3.1$ Hz), 30.8 (s), 41.2 (s), 41.8 (s), 121.5 (s), 125.1 (s), 127.6 (s), 131.4 (s), 138.5 (s), 148.0 (d, $J = 31.3$ Hz), 178.5 (s); ^{31}P NMR (40.54 MHz): $\delta = 89.2$; elemental analysis calcd for $C_{26}H_{42}N_4O_4P_2Pd_2$ (749.41): C 41.67, H 5.65, N 7.48, P 8.27, Pd 28.4; found C 41.8, H 5.9, N 7.45, P 8.35, Pd 28.12

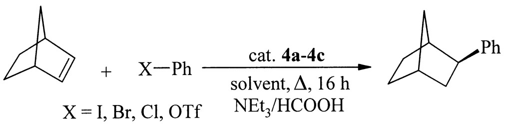
5: Purification by distillation afforded **5** in 83% yield as an oil, b.p. 60 °C (1 Pa); ^{1}H NMR (200 MHz): $\delta = 2.68$ (d, $J = 33.2$ Hz, 6H), 2.71 (d, $J = 33.2$ Hz, 6H), 7.18–7.49 (m, 5H): ^{13}C NMR (50 MHz): $\delta = 41.0$ (s), 41.5 (s), 122.5 (s), 124.1 (s), 128.6 (s), 131.4 (s), 139.5 (s), 140.2 (d, $J = 44.6$ Hz); ^{31}P NMR (40.54 MHz): $\delta = 100.7$



Scheme 2. Synthesis of **4a**–**c**.

as the result of simple C–H activation of the *ortho*-methyl group of the arylphosphane component was clearly established by NMR spectroscopy and elemental analysis (Table 1). The formulation of **4a**–**c** as μ-acetato dimeric structures was made by analogy to known palladium chemistry.[12]

We chose the arylation of norbornene as our test reaction and the reductive (NEt_3/formic acid) conditions described by Larock et al.[13] and Brunner et al.[14] (Scheme 3). Besides the simplicity and easy handling of this reaction, another reason was that the formation of chiral centers would allow enantioselective catalysis, and reaction with heteroaryl groups should lead to interesting analogues of epibatidine.[15] We initially investigated the reaction of iodobenzene with norbornene under various experimental conditions. Carbon–carbon coupling in the presence of NEt_3/formic acid as hydrogen source and catalytic amounts of **4a**–**4c**, generated in situ, led to the corresponding *exo*-phenylnorbornane in good to quantitative yield (Table 2). No other isomer was formed nor did disubstitution occur.[16]



Scheme 3. Catalytic hydroarylation of norbornene ($OTf = CF_3SO_3$).

Increasing the reaction temperature from 25 to 110 °C led to the first major improvement in the reaction yield (Table 2, entries 1 and 2; 0 and 72% yield, respectively). The acetate-bridged palladacycles **4a**–**c** become catalytically active at about 100 °C (TON of 144). Moreover, a dramatic solvent effect controls the outcome of the reaction (entries 3 and 4). Although polar solvents such as 2-(dimethylamino)ethanol (DMAE) or DMF led to excellent results (entries 6 and 8), DMSO appeared to be a much better solvent since extremely low catalyst concentrations (ca. 5×10^{-7} mol%) are fully sufficient (entry 13). Exceptional TONs of up to 196×10^6, yields of 98%, and TOFs of up to 12×10^6 were obtained with this amount of catalyst. To our knowledge, these are the highest TOFs reported to date for palladium catalysis. Furthermore, regardless of whether **4a**, **4b**, or **4c** was used in the reaction, high TONs (14×10^6 to 158×10^8 were obtained (entries 13–16). The use of Herrmann's catalyst or triphenylphosphane as ligand was less effective, and a TOF of up to 8×10^3 was obtained (entries 21–23).[17] Phenyl bromide and triflate were also successfully used and allowed the desired product to be obtained with a TOF of up to 8×10^3 (entries 19 and 20). The use of chlorobenzene instead of iodobenzene led to a marked drop in TON for the formation of phenylnorbornane (entry 17). When the catalyst concentration was decreased, no conversion occurred. We also studied the influence of the hydrogen source, and a significant effect of the nature of the reducing agent was found (Table 3, entries 1–3). Furthermore, the use of different aryl iodides led in all cases to excellent yields and high TOFs (entries 4–6). Replacement of norbonene with norbornadiene led to the formation of the expected phenylnorbornene in 98% yield with a TOF of up to 13×10^6.

The mechanism of this reaction in the presence of palladacycles **4a**–**c** and the exact nature of the palladium species involved in this highly efficient catalytic process are not fully established. Nevertheless, it is clear that the presence of a methyl group on the aromatic ring bonded to the phosphorus atom is neccessary for high reactivity. The use of the parent bis(dimethylamino)phenylphosphane **5** did not lead to any conversion when less than 0.5 mol% of palladium catalyst was used.[18]

Table 2. Catalytic hydroarylation of norbornene with palladacycles **4a**–**4c** (Scheme 3).

Entry	ArX	Catalyst (mol% Pd)	Solvent	T [°C]	Conversion [%][a]	Yield [%][b]	TON[c]
1	PhI	**4a** (0.5)	toluene	25	0	–	–
2	PhI	**4a** (0.5)	toluene	110	80	72	1.4×10^2
3	PhI	**4a** (5×10^{-4})	toluene	110	5	–	–
4	PhI	**4a** (0.5)	CH_3CN	80	12	–	–
5	PhI	**4a** (0.5)	DMF	120	100	99	1.9×10^2
6	PhI	**4a** (5×10^{-7})	DMF	120	75	62	124×10^6
7	PhI	**4a** (0.5)	DMAE	120	100	99	1.9×10^2
8	PhI	**4a** (5×10^{-7})	DMAE	120	50	42	80×10^6
9	PhI	**4a** (0.5)	DMSO	120	100	99	1.9×10^2
10	PhI	**4a** (5×10^{-2})	DMSO	120	100	99	1.9×10^2
11	PhI	**4a** (5×10^{-4})	DMSO	120	100	99	198×10^3
12	PhI	**4a** (5×10^{-6})	DMSO	120	100	98	19×10^6
13	PhI	**4a** (5×10^{-7})	DMSO	120	100	98	196×10^6
14	PhI	**4a** (5×10^{-9})	DMSO	120	100	79	158×10^8
15	PhI	**4b** (5×10^{-6})	DMSO	120	100	85	17×10^6
16	PhI	**4c** (5×10^{-6})	DMSO	120	100	71	14×10^6
17	PhCl	**4a** (0.5)	DMSO	120	100	99	1.9×10^2
18	PhCl	**4a** (5×10^{-3})	DMSO	120	5	–	–
19	PhBr	**4a** (5×10^{-4})	DMSO	120	100	98	196×10^3
20	PhOTf	**4a** (5×10^{-4})	DMSO	120	100	99	198×10^3
21[d]	PhI	5×10^{-4}	DMSO	120	100	63	126×10^3
22[d]	PhI	5×10^{-6}	DMSO	120	5	–	–
23[e]	PhI	5×10^{-6}	DMSO	120	5	–	–

[a] Conversion determined by gas chromatography. [b] Yield of isolated product. [c] Moles product per mole catalyst. [d] With Herrmann's catalyst, prepared from $Pd(OAc)_2$ and tri-*o*-tolylphosphane. [e] With catalyst prepared from $Pd(OAc)_2$ and triphenylphosphane.

Table 3. Catalytic hydroarylation of norbornene (and norbornadiene) with various aryl iodides in the presence of different hydrogen sources.

Entry	ArX	Catalyst (mol% Pd)	Hydrogen source	Conversion [%][a]	Yield [%][b]	TON[c]
1	PhI	**4a** (5×10^{-7})	NEt_3/HCOOH	100	98	196×10^6
2	PhI	**4a** (5×10^{-7})	$HCOONH_4$	100	97	194×10^6
3	PhI	**4a** (5×10^{-7})	PHMS	0	–	–
4	1-iodonaphthalene	**4a** (5×10^{-7})	NEt_3/HCOOH	100	95	190×10^6
5	2-iodoanisole	**4a** (5×10^{-7})	NEt_3/HCOOH	100	91	182×10^6
6	4-iodoanisole	**4a** (5×10^{-7})	NEt_3/HCOOH	100	96	192×10^6
7[d]	Ph-I	**4a** (5×10^{-7})	NEt_3/HCOOH	100	98	196×10^6

[a]–[c] See footnotes to Table 2. [d] Norbornadiene was used instead of norbornene.

In conclusion, we have described the synthesis of several new phosphapalladacycles and their use as catalysts in the hydroarylation of norbornene and norbornadiene. For the moment only aryl iodides are sufficiently reactive to allow TONs greater than 10^{10} to be attained. Further studies on the mechanism and the exact nature of the active species are in progress.

Experimental Section

General procedure for the hydroarylation of norbornene (Table 2, entry 13): the appropriate catalyst concentration was obtained by successive dilution of an initial catalyst solution prepared by mixing $Pd(OAc)_2$ (2.5 mg, 11×10^{-6} mol) and ligand **1** (4.8 mg, 23×10^{-6} mol) in 5 mL of DMSO under argon at 60 °C for 10 min (the mixture turned black after complete formation of the catalyst). The catalyst solution (5×10^{-7} mol%) was introduced into 10 mL of DMSO under argon. To the stirred solution were added 459 mg of iodobenzene (2.3×10^{-3} mol), 700 mg of norbornene (7.4×10^{-3} mol), 760 mg of NEt_3 (7.5×10^{-3}), and 280 mg of formic acid (6×10^{-3} mol). The mixture was heated at 120 °C for 16 h. After cooling, 15 mL of water was added, and the mixture was extracted with pentane (3 × 30 mL). The combined organic phase was dried over $MgSO_4$ and filtered, and the solvents were removed under reduced pressure. The product was purified by distillation to afford phenylnorbornane in 98% yield as a viscous oil, b.p. 124 °C (0.2 mbar); ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 1.25-1.92$ (m, 8H), 2.44 (s, 2H), 2.83 (q, $J = 8.0$ Hz, 1H), 7.20–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 29.0$ (s), 30.7 (s), 36.1 (s), 36.9 (s), 39.2 (s), 43.0 (s), 47.4 (s), 125.4 (s), 127.1 (s, 2C), 128.3 (s, 2C), 142.7 (s).

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[11] Although **1** and **2** are air- and moisture-stable, **3** should be stored under nitrogen atmosphere to avoid decomposition.

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[17] It is noteworthy that in the presence of a smaller amount of Hermann's catalyst no reaction occurs (Table 2, entry 22).

[18] The use of 0.5 mol% of Pd(OAc)$_2$/**5** led to phenylnorbornane in 83% yield (TON = 166), but no conversion occured at lower concentrations.

Synthesis and X-ray Structures of [Be(C$_5$Me$_4$H)$_2$] and [Be(C$_5$Me$_5$)$_2$]**

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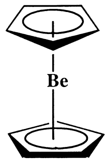
Enrique Gutiérrez-Puebla, Ángeles Monge,*
Caridad Ruiz, and Ernesto Carmona*

Dedicated to Professor José Elguero

Beryllocene, [Be(C$_5$H$_5$)$_2$], the lightest member of the alkaline earth metallocenes[1] and of the general bis(metallocene) series of compounds [MCp$_2'$], has aroused intense structural debate since its preparation by Fischer and Hofmann in 1959.[2] Structures **I**–**III** are some of the proposed models. Its unexpected dipolar nature[3] is in disagreement with the symmetrical ferrocene-like structure **I**. The most recent X-ray study,[4a] confirmed the slip-sandwich η^5/η^1 structure **II** with disordered Be atoms at −145 °C. This geometry is also in accord with electron diffraction data[5] and with molecular dynamics calculations,[6] and it has been rationalized by Beattie and co-workers, along with the structures displayed by other main-group metal cyclopentadienyls.[7] Very recent density-functional theory (DFT) calculations on structure **I** and **III** concluded that the σ-π structure **III** is lower in energy.[8]



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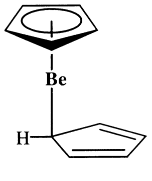
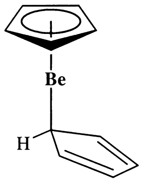


II



III

Despite this long controversy and the existence of many half-sandwich Be compounds, including [Be(η^5-C$_5$Me$_5$)Cl],[9] no other beryllocenes have been reported to date, with the exception of [Be(η^5-C$_5$Me$_5$)(η^1-C$_5$H$_5$)], which has been characterized only in solution.[10] Related dihydro-1*H*-azaboryl species have also been investigated.[11] Here we present our initial results on the synthesis and solid-state structures of the beryllocenes **1** and **2**.

[Be(η^5-C$_5$Me$_4$H)(η^1-C$_5$Me$_4$H)] **1**

[Be(η^5-C$_5$Me$_5$)$_2$] **2**

Compound **1** can be synthesized by the simple room-temperature reaction of BeCl$_2$ and K[C$_5$Me$_4$H] in diethyl ether [Eq. (1)]. Following crystallization from petroleum ether, **1** can be isolated in about 70% yield in the form of white crystals, soluble in hexane, benzene, and other nonpolar organic solvents. Both solid samples and solutions of **1** exhibit high thermal stability, but the compound is very reactive towards H$_2$O and O$_2$ and decomposes immediately in the presence of air. Similar to [Be(C$_5$H$_5$)$_2$],[12] compound **1** is highly fluxional in solution; the two rings are equivalent down to −90 °C according to the ^{1}H and ^{13}C NMR spectra (C$_7$D$_8$; see Experimental Section).

$$\mathrm{BeCl_2} + 2\,\mathrm{K[C_5Me_4H]} \xrightarrow{20\,^\circ\mathrm{C}} \underset{\mathbf{1}}{\mathrm{Be(C_5Me_4H)_2}} + 2\,\mathrm{KCl} \qquad (1)$$

Single crystals of **1** suitable for X-ray structure analysis were investigated at −160 °C and were found to be orthorhombic.[13] Figure 1a shows the molecular structure and Figure 1b a schematic representation of the Be—η^1-C$_5$Me$_4$H moiety. In contrast to the structure of [Be(C$_5$H$_5$)$_2$], in which the Be atom is disordered between two crystallographically equivalent sites, no positional or thermal disorder appears

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