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Chelating *N*-heterocyclic carbene ligands in palladium-catalyzed heck-type reactions[1]

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Abstract

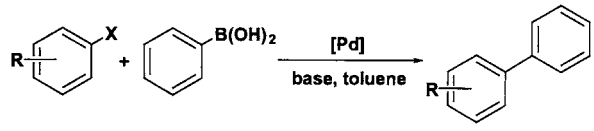
A novel synthesis of palladium complexes with chelating *N*-heterocyclic carbene ligands is reported and direct proof is presented by X-ray diffraction. These catalyst precursors are efficiently applied in palladium-catalyzed Heck-, Suzuki- and alkyne coupling reactions, demonstrating the versatility of our ligand concept in homogeneous catalysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Palladium complexes; *N*-heterocyclic; Coupling reactions

1. Introduction

Recently, we introduced 'free' carbenes derived from imidazole, pyrazole and triazole derivatives as transition metal stabilizing ligands in homogeneous catalysis. [1,2]. The corresponding complexes show usually high thermal stability and nucleophilic behaviour, because of the similarity of *N*-heterocyclic carbenes with strong Lewis-basic phosphines. In addition, the ligands are cheap, nontoxic and easily prepared as azolium salt precursors.

In recent years, we were also interested in the activation of deactivated bromo- and chloroarenes for Heck-type reactions [4]. In the present communication we report the efficient application of palladium–carbene complexes with chelating ligands in the Heck and Suzuki coupling of bromo- and chloroarenes. While the Heck reaction with non-chelating carbene ligands was already investigated by Herrmann ([2]a) and later by Enders [5], we focused our interest toward the increasing importance of unsymmetrically substituted biaryl derivatives, which are used as drug intermediates [6] and nonlinear optical materials [7]. Thus, we investigated the transferability of the catalytic properties of palladium(II) carbene complexes to the Suzuki coupling of aryl bromides with arylboronic acids (Eq. 1).



(1)

2. Results and discussion

In the beginning, we developed a more efficient route to palladium(II) complexes with chelating bis-carbene ligands, because the procedure originally published by our group gave only moderate yields. Thus, we changed the solvent from tetrahydrofuran to dimethylsulfoxide, because of the higher boiling point compared to the generated acetic acid and generally higher solubility of all reactants. This optimized salt method gave signifi-

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[1] *N*-Heterocyclic Carbenes, Part 17.-For the preceding communication of this series, see [3].

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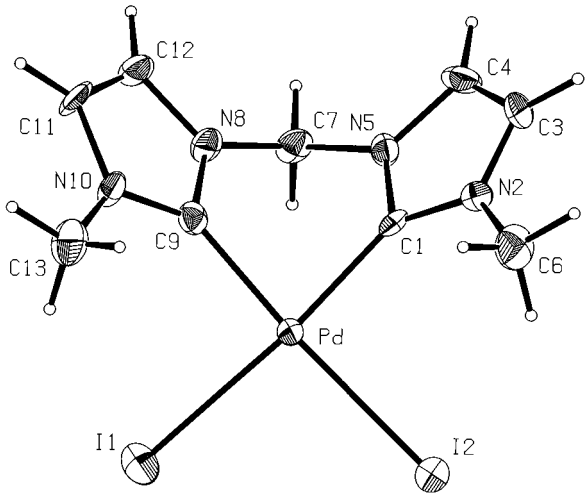
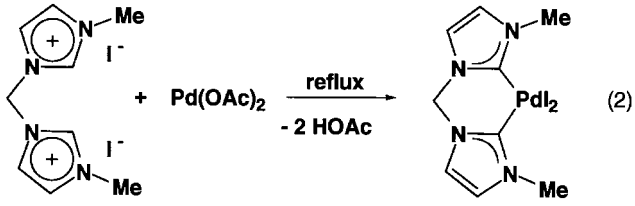


Fig. 1. Platon plot [8] of **1**. Thermal ellipsoids are at 50% probability. Selected bond distances (Å) and angles (°): I(1)–Pd 2.6450(9), I(2)–Pd 2.6573(8), Pd–C(1) 1.989(8), Pd–C(9) 1.988(7); C(1)–Pd–C(9) 83.2(3), N(2)–C(1)–N(5) 104.5(7), N(8)–C(9)–N(19) 105.3(6), N(5)–C(7)–N(8) 108.6 (6).

cantly higher yields of the corresponding complexes (Eq. 2). But more important, the chelating behavior of the ligand could also be demonstrated by X-ray diffraction for the first time.



However, NMR investigations suggested that the former published compound **1** was a dinuclear palladium(II) complex with two bridging bis-carbene ligands, resulting in an equal NMR pattern and elemental analysis, but slightly different chemical shifts. This became obvious after successful structural characterization (Fig. 1) and further mass spectrometric investigations, showing mono- and dinuclear mass peaks.

The palladacycle is fixed in a boat conformation, as reported for the analogous tetracarbene complex by Fehlhammer [9]. The two heterocyclic rings deviate from the coordination plane by $+51.3(3)$ and $-52.5(3)°$. Compared to the tetracarbene complex the Pd–C_C distances are shortened to 1.989 and 1.988 D, owing to the iodide ligand in *trans* position. Consequently the Pd–C_C distances are in the same range as bis-(1,3-dimethylimidazolin-2-yliden)diiodopalladium(II), which was reported by our group ([2]a).

In addition, the high thermal stability of complex **1** is also contradictory to our previous results, but opens the field of further catalytic applications in Heck-type reactions. Thus, we investigated the olefination of aryl halides with **1** under comparable conditions, demonstrating the superior activity of these new catalysts. Using 0.5 mol% catalyst **1** and additional 0.3 eq. tetrabutylammonium acetate, as completely dissolved base, both bromoanisole and chloroacetophenone could be converted efficiently (Entry 1–2, Table 1).

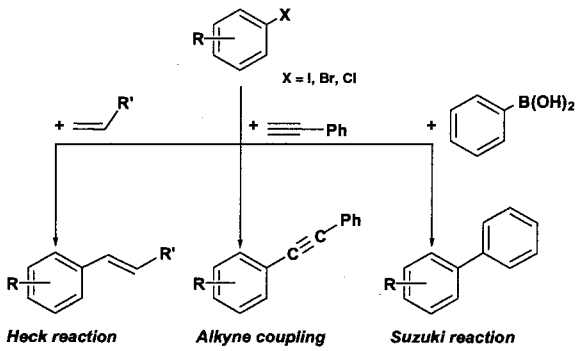
Afterwards, we investigated the catalytic applicability towards the Suzuki coupling of aryl halides with arylboronic acid, because of the increasing importance of unsymmetrically substituted biaryl derivatives in fine chemical syntheses. Here, we chose the same conditions as in our previous report about palladacycles as catalysts in cross coupling reactions [10], resulting in the successful application of a wide variety of bromo arenes and even an acceptor-substituted chloroarene (Entry 3–8, Table 1).

This new approach demonstrates the versatility of *N*-heterocyclic imidazol-2-ylidene ligands in homogeneous catalysis. However, an extension of this methodology towards terminal alkynes instead of olefins works only with activated bromo arenes and phenylacetylene (Entry 9–10, Table 1). An extremely low conversion of bromoanisole with phenylacetylene is a further example of the difference in mechanistic features behind the similarity of Heck-type reactions.

Table 1

Entry	Aryl halide	Starting material	Time (h)	T (°C)	Yield[a] (%)
1	4-Bromoanisole	*n*-Butyl acrylate	12	140	95
2	4-Chloroacetophenone	*n*-Butyl acrylate	24	140	60
3	4-Bromoacetophenone	Arylboronic acid	18	120	93
4	4-Bromonitrobenzene	Arylboronic acid	12	120	99
5	Bromobenzene	Arylboronic acid	12	120	87
6	4-Bromoaniline	Arylboronic acid	24	120	78
7	4-Bromoanisole	Arylboronic acid	22	120	80
8	4-Chloroacetophenone	Arylboronic acid	48	120	60
9	4-Bromoacetophenone	Phenylacetylene	48	90	76
10	4-Bromofluorobenzene	Phenylacetylene	48	90	71

[a] GC yield of corresponding coupling product based on aryl halide.



Scheme 1. Applications of *N*-heterocyclic palladium–carbene complexes.

3. Conclusion

It is shown, that palladium–carbene complexes are efficient catalysts in palladium(0)-catalyzed Heck-type reactions (Scheme 1). Further investigations about palladium complexes with chelating *N*-heterocyclic imidazol-2-ylidene ligands in homogeneous catalysis are under way. Especially redoxneutral palladium(II)-catalyzed applications seem to be most promising [11].

4. Experimental

Palladium(II)-acetate was purchased from DEGUSSA AG. All products were characterized by GC-MS, yields were determined by gas chromatography. Quantitative GC-analyses were performed with a Hewlett Packard 5980 A instrument using a 12.5 m HP-1 capillary column in conjunction with a flame ionization detector (GC/FID).

4.1. Catalyst preparation

Palladium acetate (200 mg, 0.89 mmol) was dissolved in 10 ml of dimethylsulfoxide. To the reddish brown solution was added imidazolium salt (385 mg, 0.89 mmol). The mixture was heated under vacuum at approx. 150°C until the solvent was completely evaporated. The orange residue was washed with 100 ml of acetonitrile in a Soxhlet apparatus. The resulting microcrystalline powder dissolved well in polar aprotic solvents, to give a yellow solution. Yield: 375 mg (78%).

^{1}H-NMR (400 MHz, 20°C, d^6-dmso): $\delta = 3.85$ (6H, s, N–CH_3); 6.28 (2H, s, CH_2); 7. 35 (2H, s, N–C*H*); 7.61 (2H, s, N–C*H*); ^{13}C{^{1}H}-NMR (100.5 MHz, 20°C, d^6-dmso): $\delta = 30.1$ (s, N–CH_3); 61.9 (s, CH_2); 121.1 (s, N–CH); 122.6 (s, N–*C*H).

4.2. Crystal-structure determination

Data for **1** were collected on an STOE- IPDS [12] at 193 K and corrected for Lorentz and polarisation effects. Preliminary positions of heavy atoms were found by direct methods [13], while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least square refinement [14]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. They were included in the structure factor calculation but not refined.

Table 2
Crystal data and details of the structure determination

Identification code	1a
Crystal data	
Formula	$C_9H_{12}I_2N_4Pd$
Crystal color, habit	orange, prism
Crystal size	0.24, 0.08, 0.08
Space group	monoclinic; $P2_1/n$ (no.:14)
Unit cell dimensions	
a (Å)	8.7889 (6)
b (Å)	16.2603 (9)
c (Å)	10.7227 (8)
α (°)	90
β (°)	113.797 (7)
γ (°)	90
V (Å^3)	1402.1 (2)
Peaks to determine cell	5000
T (K)	193
Wavelength (Å)	0.71073
Z	4
fw	536.45
D (calcd, g cm^{-3})	2.541
Abs coeff (mm^{-1})	5.708
F(000)	984
Data collection	
Diffractometer	IPDS (STOE)
Θ range for data collection (°)	$1.6 < \Theta < 25.1$
Index ranges	$-9 < h < 10$ $-18 < k < 19$ $-12 < l < 12$
Decay corr	none
Abs corr	none
No. of reflections collected	7331
No. of independent reflections	2349 ($R_{int} = 0.0479$)
No. of observed reflections [$I > 2\sigma(I)$]	1771
Solution and refinement	
Weighting scheme a, b[a]	0.0427; 0.0
Data/params	2243/145
Goodness-of-fit on F^2	0.945
Final R[b] indices [$I > 2\sigma(I)$]	$R_1(F) = 0.031$ $wR_2(F^2) = 0.0741$
Final R[b] indices [all data]	$R_1(F) = 0.049$ $wR_2(F^2) = 0.0774$
Largest diff peak and hole (eÅ^{-3})	1.142; −0.846
Largest D/esd	<0.001

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [F_o^2 + 2F_c^2]/3$.
[b] $R_1(F) = (\Sigma||F_o| - |F_c||)/S|F_o|$; $wR_2(F^2) = [\Sigma[w_i(F_o^2 - F_c^2)^2/\Sigma[w_i(F_o^2)^2]]^{1/2}$.

Crystal data, data collection and refinement parameters are presented in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (1223) 336-033, e-mail: teched@chemcrys.cam.ac.uk).

4.3. Suzuki procedure

In a 30 ml pressure tube was placed the aryl halide (10 mmol), arylboronic acid (11 mmol), potassium carbonate (20 mmol) with 1 mol% catalyst and 10 ml toluene. The reaction mixture was vigorously stirred and heated to 120°C for 12–48 h. Subsequently the cooled reaction mixture was extracted twice with water and the organic phase was separated. The solvent was removed under vacuum and the crude product was purified by chromatography on a silica gel or by recrystallization.

4.4. Heck procedure

In a 50 ml three-necked flask equipped with a septum inlet, a thermometer and a reflux condenser (Hg-bubbler) were placed aryl halide (25 mmol), anhydrous sodium acetate (2.25 g, 23 mmol), diethyleneglycol di-*n*-butylether (0.5 g, GC standard) and *N*,*N*-dimethylacetamide (20 ml). The reaction mixture was degassed under vacuum and argon was passed over the condenser for 5 min to ensure an inert reaction atmosphere. *N*-butyl acrylate (5 ml, 35 mmol) was then added last because of possible loss by evaporation. The reaction mixture was vigorously stirred and heated to the appropriate reaction temperature. After thermostating for 10 min, a preheated catalyst solution (67 mg catalyst in 10 ml solvent, 0.5 mol% Pd) was injected by syringe (start, $t = 0$). Work-up was achieved by pouring the reaction mixture at room temperature into an excess of water, extracting with dichloromethane or diethyl ether, and drying with magnesium sulphate. After removal of the extraction solvent and *N*,*N*-dimethylacetamide, the products were purified by distillation or recrystallisation.

4.5. Alkyne coupling procedure

In a 100 ml three-necked flask equipped with a septum inlet, a thermometer and a reflux condenser were placed aryl bromide (10 mmol), phenylacetylene (12 mmol), 54 mg (1 mol% Pd) catalyst, diethyleneglycol-di-*n*-butylether (0.2 g, GC standard), and triethylamine (30 ml). The reaction mixture was stirred vigorously and heated to the appropriate reaction temperature. 0.5 ml-samples were removed after every hour and sealed in GC-vials for the gas chromatographic determination of the yield. The work-up was achieved by filtering of the hot reaction mixture and subsequent cooling of the organic phase. The product was obtained by either crystallization (after several hours at room temperature) or by evaporation of the triethylamine.

Acknowledgements

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