Synthesis and Crystal Structure of Bis(2,3-dihydro-3-methylbenzothiazole-2-ylidene)palladium(II) Diiodide: The First Palladium Complex with Benzothiazole Carbene Ligands Suitable for Homogeneous Catalysis

Vincenzo Caló,*[a] Roberta Del Sole,[a] Angelo Nacci,[a] Emanuela Schingaro,[b] and Fernando Scordari[b]

Keywords: Benzothiazole carbene / Palladium complex / Homogeneous catalysis / Heck coupling reaction

The first diiodo palladium complex with nucleophilic benzothiazole carbenes as ligands has been synthesized and characterized. The complex, which is extraordinarily stable towards heat, oxygen, and moisture, has been found to show good catalytic activity in the Heck coupling reaction.

Introduction

Phosphanes and phosphites have been used as ligands in a multitude of metal complexes that play important roles in many fields of chemistry. In view of the well-known[1] phosphane degradation through C–P bond cleavage and the sensitivity of such species to air and moisture,[2] phosphanes have recently[3–6] been substituted by nucleophilic carbenes of imidazole and triazole, these carbenes being stable and easily isolated as ligands.

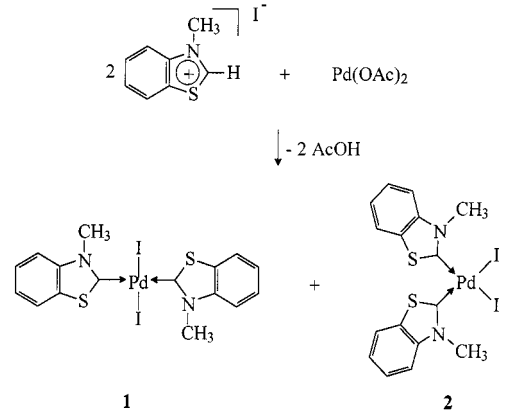
Although a great deal of effort has been devoted to the study of thiazolium (vitamin B_1) and hence to benzothiazolium-derived carbenes,[7–10] as far as we are aware no such carbenes have been incorporated as ligands at palladium. This is probably due to the known fast dimerization of these carbenes, which hampers their isolation and use as ligands.[11–14]

We report here on the first synthesis of a palladium complex with benzothiazole carbenes as ligands and its use in the Heck coupling reaction.

Results and Discussion

Reaction of two equiv. of 3-methylbenzothiazolium iodide with one equiv. of $Pd(OAc)_2$ in boiling THF leads to the dicarbenediiodopalladium(II) complexes **1** and **2** in an overall chemical yield of 90–95% (Scheme 1).

Complex **1** may be separated from **2** by column chromatography. Upon heating in DMA at 100 °C, **2**, probably the *cis* isomer,[15] is completely transformed into **1** within 1.5 h. Complex **1** (Figure 1) is obtained as a yellow fluorescent solid, which melts at temperatures of the order of 300 °C with partial decomposition. In solution in DMA, it proved to be stable to heating at 130 °C in air for several days.



Scheme 1

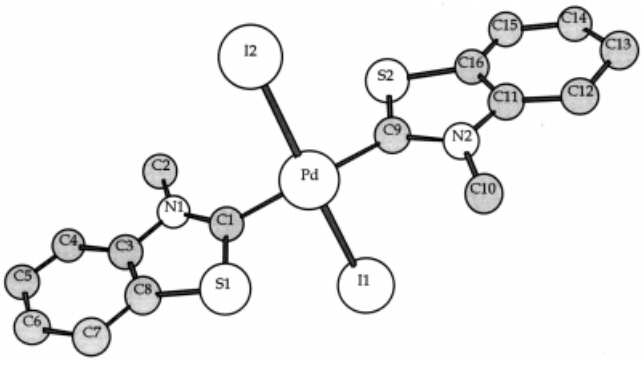


Figure 1. Crystal 6.0 representation of the crystal structure of complex **1** ($C_{16}H_{14}I_2N_2PdS_2$); H atoms are omitted for the sake of clarity; selected distances (Å) and angles (°): Pd–I1 2.587(4), Pd–I2 2.604(5), Pd–C1 2.01(4), Pd–C9 2.06(3), S1–C1 1.67(4), S1–C8 1.73(4), S2–C9 1.66(3), S2–C16 1.70(3), N1–C1 1.35(4), N1–C2 1.36(1), N1–C3 1.41(4), N2–C9 1.39(4), N2–C10 1.36(1), N2–C11 1.40(4); I1–Pd–12 178.7(2), I1–Pd–C9 89.4(9), I1–Pd–C1 89.3(11), I2–Pd–C9 90.1(9), I2–Pd–C1 91.2(11), C1–Pd–C9 178.4(17)

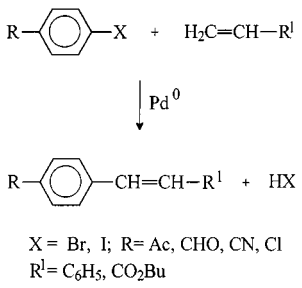
Besides the expected square-planar core geometry, a crystal structure analysis of **1** revealed that the two carbene ligands are in a *trans* arrangement and are coplanar with respect to the PdI_2 plane. The Pd–C bond lengths [2.01(4)/2.06(3) Å] lie within the established range for Pd–C(alkyl) single bonds,[16] although the ^{13}C-NMR signal of the car-

[a] Centro C.N.R. "M.I.S.O.", Dipartimento di Chimica, Università di Bari,
via Amendola 173, 70126 Bari, Italy
E-mail: calo@chimica.uniba.it
[b] Dipartimento Geomineralogico, Università di Bari,
via Orabona 4, 70125 Bari, Italy

  1434–193X/00/0306–0869 $ 17.50+.50/0

bene C appears further downfield (δ = 210.5) than the corresponding signals of imidazole and triazole carbenes (δ = 169–185);[3–5] this is in accordance with the values found for the stable *N*-diisopropylphenylthiazole carbene.[12] From an XPS analysis of **1**, a binding energy of 337.2 eV was determined, which is very close to the value of 337.0 eV typical for Pd^{II}. It may therefore be the case that benzothiazole carbenes have pronounced σ-donor properties similar to those of imidazole carbenes[3] and that π-back-bonding is probably less significant than that seen with the electron-rich phosphanes.

The Pd complexes **1** and **2** were found to efficiently catalyse the Heck coupling of aryl iodides and bromides with styrene and butyl acrylate (Scheme 2) with turnover numbers of up to one million using 10^{-4} mol-% of catalyst **1** (Table 1, run 14).



Scheme 2

considering the well-known influence of water on the rate of the Heck reaction.[17] However, both the solvents contained the same water concentration (0.1%) and differed only in their formic acid concentrations, this being twenty-five fold greater in the Carlo Erba solvent (0.0025%). Using sodium formate as the base in the Fluka DMF led to an increase in the reaction rate (Table 1, run 3). To overcome these complicating factors, we used DMA instead of DMF. This solvent has the same water concentration as DMF, but does not contain formic acid. This modification led to a dramatic reduction in the reaction rate (Table 1, run 6), but a rate enhancement was observed upon addition of sodium formate alone or of formic acid and sodium acetate as the base prior to the addition of the reagents (Table 1, run 7).

From these results, some conclusions can be drawn: if the Heck reaction takes place through a Pd^0/Pd^{II} catalytic cycle, the different rates observed must be attributed to different concentrations of formic acid in the two batches of DMF and not to the amounts of water present in the solvents. In this context, formic acid in DMF or sodium formate in DMF or DMA would behave as reducing agent for Pd. The Pd^0 carbene catalyst, probably formed upon sodium formate reduction of **1**, does indeed have a large initial activity with long-term stability in the Heck olefination (Table 1). Using only 10^{-3} mol-% catalyst, 4.5 mmol of 4-bromoacetophenone was completely converted within 12 h in DMA (Table 1, run 10) without palladium deposition; the catalyst

Table 1. Heck olefination of iodo- and bromoarenes with palladium-carbene catalyst **1**; amount of ArX, 1 mmol; alkene, 1.5 mmol; base, 2 mmol; solvent, 10 mL. Sty: styrene; bac: butyl acrylate.

Run	Substrate	Alkene	Catylist [mol-%]	Solvent	Base	*t* [h]	Yield[a] [%] (TON)
1[b]	C_6H_5I	Sty	0.01	DMF	NaOAc	4	98 (9800)
2[b]	C_6H_5I	Sty	0.01	DMF	NaOAc	18	98 (98000)
3[b]	C_6H_5I	Sty	0.001	DMF	HCO_2Na	7	95 (95000)
4[b,c]	C_6H_5I	Sty	0.01	DMF	NaOAc	4	93 (9300)
5	C_6H_5I	bac	0.01	DMF	NaOAc	1	96 (9600)
6	C_6H_5I	bac	0.01	DMA	NaOAc	24	85 (8500)
7	C_6H_5I	bac	0.01	DMA	HCO_2Na	1	95 (9500)
8	4-BrC_6H_4COMe	bac	0.01	DMF	NaOAc	2	100 (10000)
9	4-BrC_6H_4COMe	bac	0.001	DMF	NaOAc	12	100 (100000)
10	4-BrC_6H_4COMe	bac	0.001	DMA	HCO_2Na	12	93 (93000)
11	4-BrC_6H_4CN	bac	0.001	DMF	NaOAc	3	100 (100000)
12	4-BrC_6H_4CHO	bac	0.003	DMF	NaOAc	10	85 (25300)
13	4-BrC_6H_4Cl	bac	0.001	DMA	HCO_2Na	19	87 (87000)
14	C_6H_5I	bac	10^{-4}	DMA	HCO_2Na	39	90 (900000)

[a] Determined by GC analysis with diethyleneglycol di-*n*-butyl ether as internal standard. – [b] *trans*-Stilbene + 1,1-diphenylethene (15%). – [c] Catalyst **2**.

On running reactions in DMF at 130 °C in the presence of sodium acetate as a base, we did not observe an induction period as is seen for analogous reactions performed with (imidazole)Pd carbene complexes.[3] Moreover, in a kinetic study of the reaction of iodobenzene with butyl acrylate in DMF, we found that the reaction rates were affected by using solvent from different suppliers (Carlo Erba or Fluka); the rate was faster in the Carlo Erba solvent. At first, we supposed that this discrepancy was due to different water concentrations in the solvents from the two sources, remained active, as demonstrated by the fact that further olefination could be achieved upon addition of fresh reagents. Another advantage of this catalyst lies in the absence of competing Pd-catalysed hydrogenolysis of haloarenes by formate.[18,19]

In conclusion, the activity of the catalyst described here compares favourably with those of other Pd-carbene complexes. The present complex has a series of advantages over other catalysts and thus has much potential for future applications.

Experimental Section

General Procedure for the Preparation of Dicarbenediiodo-Palladium(II) Complexes 1 and 2: A solution of $Pd(OAc)_2$ (0.17 g, 0.75 mmol) and 3-methylbenzothiazolium iodide[13] (0.42 g, 1.5 mmol) in THF (30 mL) was refluxed under nitrogen for 2 h and then filtered. After concentration of the filtrate to dryness in vacuo, the products were separated and purified by column chromatography (silica gel, CH_2Cl_2).

***trans*- and *cis*-Bis(2,3-dihydro-3-methylbenzothiazole-2-ylidene)palladium(II) Diiodide (1 and 2):** After the aforementioned column chromatography, 0.34 g (80%) of *trans*-**1** and 0.05 g (12%) of *cis*-**2** were obtained. – ***trans*-1:** Yellow fluorescent solid; m.p. 308 °C (dec). – IR (KBr): $\tilde{\nu}$ = 3040, 2940, 1627, 1580, 1428, 1380, 1053, 920, 758 cm^{-1}. – ^1H NMR ($CDCl_3$, 500 MHz): δ = 4.53 (s, 6 H, CH_3), 7.40–7.45 (m, 2 H, Ar), 7.50–7.53 (m, 2 H, Ar), 7.69 (d, J = 8.3 Hz, 2 H, Ar), 7.82 (d, J = 8.0 Hz, 2 H, Ar). – ^{13}C NMR (500 MHz, $CDCl_3$): δ = 42.8, 113.4, 122.0, 124.8, 126.6, 136.7, 144.2, 210.5 (NCPd). – MS (solid probe); *m*/*z* (%); isotopomers: 662 (1), 660 (1), 658 (2), 657 (1), 656 (1), 531 (8) [M – I], 404 (13) [M – 2I], 268 (60), 254 (34), 149 (66) [carbene], 135 (100), 108 (83), 69 (64). – XPS (FAT, E_0 = 50 eV for Pd_{3d}, C_{1s}, O_{1s}, I_{3d}, S_{2p}), binding energy (B.E.) = 337.2 eV. – $C_{16}H_{14}I_2N_2PdS_2$ (658.65): calcd. C 29.17, H 2.14, N 4.25; found C 28.90, H 2.25, N 4.00. – Crystals suitable for X-ray analysis were obtained at room temperature from DMF/benzene mixtures.[20] – ***cis*-2:** Red solid, heating of which at 100 °C leads to a gradual conversion into **1**, thereby preventing a m.p. determination. – ^1H NMR ([D_7]DMF, 500 MHz): δ = 4.75 (s, 6 H, CH_3), 7.53–7.58 (m, 2 H, Ar), 7.64–7.68 (m, 2 H, Ar), 8.11 (d, 2 H, J = 8.6 Hz, Ar), 8.18 (d, 2 H, J = 7.6 Hz, Ar). – MS (solid probe); *m*/*z* (%), isotopomers: 662 (1), 660 (1), 658 (2), 657 (1), 656 (1); 531 (8) [M – I], 404 (13) [M – 2 I], 268 (60), 149 (66) [carbene], 135 (100), 108 (83), 69 (64). – $C_{16}H_{14}I_2N_2PdS_2$ (658.65): calcd. C 29.17, H 2.14, N 4.25; found C 29.05, H 2.35, N 3.90. – Crystals suitable for X-ray analysis could not be obtained for this compound.

Acknowledgments

This work was in part financially supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica, Rome, and the University of Bari (National Project: "Stereoselezione in Sintesi Organica: Metodologie ed Applicazioni"). We thank Prof. F. Palmisano for recording the mass spectra.

[1] P. E. Garrou, *Chem. Rev.* **1985**, *85*, 171–185.
[2] W. H. Herrmann, C. W. Kohlpaintner, *Angew. Chem.* **1993**, *105*, 1588–1609; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524–1544.
[3] W. H. Herrmann, M. Elison, J. Fisher, K. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2376.
[4] W. H. Herrmann, J. Fisher, K. Öfele, G. R. J. Artus, *J. Organomet. Chem.* **1997**, *530*, 259–262.
[5] D. Enders, H. Gielen, G. Raabe, J. Runsink, J. H. Teles, *Chem. Ber.* **1996**, *129*, 1483–1488.
[6] W. H. Herrmann, K. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.
[7] R. Breslow, *J. Am. Chem. Soc*. **1958**, *80*, 3719–3726.
[8] R. Kluger, *Chem. Rev.* **1987**, *87*, 863–876.
[9] H. Stetter, *Angew. Chem.* **1976**, *88*, 695; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 639–712.
[10] H. Stetter, H. Kuhlmann, *Org. React.* **1991**, *40*, 407–496.
[11] F. G. Bordwell, A. V. Satish, *J. Am. Chem. Soc.* **1991**, *113*, 985–990.
[12] A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *Liebigs Ann./Recueil* **1997**, 365–374.
[13] H.-W. Wanzlick, H.-J. Kleiner, I. Lasch, H. U. Fuldner, H. Steinmaus, *Liebigs Ann. Chem***. 1967**, *708*, 155–169.
[14] J. Metzger, H. Larivé, R. Dennilauler, R. Baralle, C. Gaurat, *Bull. Soc. Chim. Fr.* **1964**, 2857–2867.
[15] Formation of both the geometrical isomers was found in the preparation of Pd complexes of imidazole and triazole carbenes, cf. refs.[4,5]
[16] Examples: R. D. Wilson, Y. Kamitori, H. Ogoshi, Z.-I. Yoshida, J. A. Ibers, *J. Organomet. Chem.* **1979**, *173*, 199–209; A. Modinos, P. Woodward, *J. Chem. Soc., Dalton Trans.* **1974**, 2065–2069; O. P. Anderson, A. B. Packard, *Inorg. Chem.* **1978**, *17*, 1333–1337.
[17] For reviews on the Heck reaction, see: R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, **1985**; A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411; W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2–7; G. T. Crisp, *Chem. Soc. Rev.* **1998**, *27*, 427–436.
[18] I. Pri-Bar, O. Buchman, *J. Org. Chem.* **1986**, *51*, 734–736.
[19] V. V. Grushin, H. Halper, *Chem. Rev.* **1994**, *94*, 1047–1062.
[20] 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-134714. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received October 19, 1999
[O99580]