

Preliminary communication

N-heterocyclic carbene complexes of palladium and rhodium:
cis/trans-isomers¹

Wolfgang A. Herrmann*, Jakob Fischer, Karl Öfele, Georg R.J. Artus

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Received 10 October 1996

Abstract

Stable carbene complexes of palladium or rhodium are readily accessible by (i) reaction of imidazolium or triazolium salts with palladium complexes bearing basic ligands or rhodium alkoxide complexes, (ii) adduct formation of the free carbene, e.g. 1,3-dimethylimidazoline-2-ylidene, with metal compounds. In the case of palladium(II) and rhodium(I), the resulting complexes show *cis/trans*-isomerization and can be compared to analogous phosphine complexes.

Keywords: *N*-Heterocyclic carbenes; Palladium complexes; Rhodium complexes; *cis/trans*-Isomerism

1. Introduction

Free carbenes were discovered by Arduengo et al. as remarkably stable compounds in 1991 [2]. It was shown in our research group that the standard ligand 1,3-dimethylimidazoline-2-ylidene coordinates to both low and high oxidation state transition metals [3], such as zero-valent iron, chromium, molybdenum and tungsten, tetravalent titanium, zirconium, hafnium, vanadium, niobium and tantalum, hexavalent molybdenum, and heptavalent rhenium. Several carbene complexes of metals relevant for catalysis (e.g. palladium, rhodium, ruthenium, osmium, iridium) have also been prepared [4]. It was discovered that metal complexes of *N*-heterocyclic carbenes catalyze a number of coupling reactions [5]. Furthermore, carbene complexes with O-, N-, P-heteroatom functionalized side chains, chiral carbenes, water-soluble and polymer-supportable carbenes

have been prepared [6]. The σ -donor/ π -acceptor characteristics of these ligands are similar to those of trimethyl- or tricyclohexylphosphine. Another striking similarity is the *cis/trans*-isomerization reported as follows.

2. Results and discussion

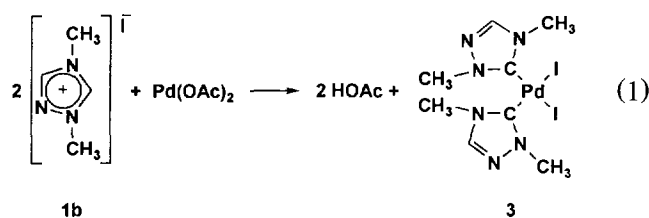
Imidazolium and triazolium salts were prepared from cheap starting materials (e.g. imidazole, 1,2,4-triazole) and methyl iodide. 1,3-Dimethylimidazolium iodide **1a** is deprotonated in liquid ammonia/thf by sodium hydride. The free monomeric carbene **2** is thus obtained in high purity [4].

The triazolium salt **1b** is more soluble in thf and more acidic than the corresponding imidazolium salt 1,3-dimethylimidazolium iodide. As shown in Eq. (1), the reaction of palladium(II) acetate with 1,4-dimethyl-1,2,4-triazolium iodide **1b** in thf cleanly yields diiodobis(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene)palladium(II) **3**, a yellow solid of extraordinary thermal stability: m.p. 308 °C! The compound is obtained after removal of the solvent and acetic acid in vacuo. The precipitate is washed with toluene and *n*-pentane. The triazole-derived complex **3** is soluble in polar organic solvents like methylene chloride, chloroform and particularly nitromethane. The ¹H NMR spectrum shows four signals for the methyl groups whereas

* Corresponding author.

¹ Communication 14 of the series *Heterocyclic Carbenes*. This work is part of the Ph.D. Thesis of J. Fischer, Technische Universität München, February 1996. Preceding Paper 13 of this series: W.A. Herrmann, J. Fischer, K. Öfele and G.R.J. Artus, submitted to *Organometallics*. The term 'carbene', conceived by Doering, Winstein and Woodward, seems suitable to describe the class of compounds under concern but conflicts with established rules of the International Union of Pure and Applied Chemistry (IUPAC). The metal-carbene nomenclature was introduced by Fischer [1] and became common in the organometallic literature.

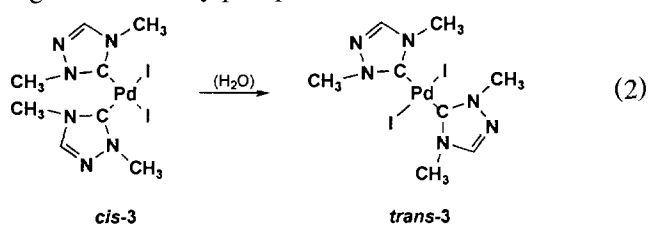
the ^{13}C NMR spectrum shows only one signal for the quarternary carbon atom at 169.8 ppm. This can be explained by assuming a *cis*-configuration together with a rather high rotation barrier at room temperature at the Pd–C bonds. This leads to two different geometries of *cis*-configured complexes where either both nitrogen atoms N2 of the triazole ring are on the same side of the plane of the coordination sphere or the two nitrogens are on different sides. No side-products occur. When washing **3** with water to remove traces of the triazolium salt, the colour darkens to deep grey. Interestingly, elemental analyses confirm an unchanged composition; however, the ^{13}C NMR spectra now show two signals for the quarternary carbon atoms at 166.3 (major signal, *trans*-configuration) and 169.8 ppm. A partial rearrangement to the *trans*-configuration obviously has taken place. The two signals for the methyl groups in the *trans*-complex do not split in the ^1H NMR spectrum at room temperature. It seems that the rotation barrier is much lower than in the *cis*-configured complex.



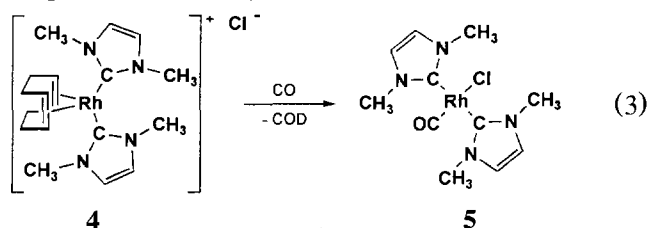
The ^{13}C and ^1H NMR spectra show the *cis*- and *trans*-compounds in a 1:6 ratio; the data of the *trans*-product are given in brackets in Section 3. No side-products were detected.

We note that a *cis/trans*-isomerization has taken place without dissociation of the ligand (Eq. (2)). This

is known in the literature from phosphine complexes, e.g. with trimethylphosphine.



A *cis/trans*-isomerization was observed in the case of rhodium too. Thus, when *cis*-[(η^4 -1,5-cyclooctadiene)bis(1,3-dimethylimidazoline-2-ylidene)rhodium(I)]chloride **4** (configuration confirmed by spectroscopic data and X-ray analysis) was dissolved in methylene chloride and treated with carbon monoxide, *trans*-carbonylchlorobis(1,3-dimethylimidazoline-2-ylidene)rhodium(I) **5** was formed in almost quantitative yield (*trans*-configuration established by spectroscopic data and X-ray analysis) (Eq. (3)).



The crystal and molecular structure of the carbene–rhodium complex **5** was determined by means of a single-crystal X-ray diffraction analysis [7]. Apart from the expected square-planar coordination of the metal, this study reveals the *trans*-configuration of the five-

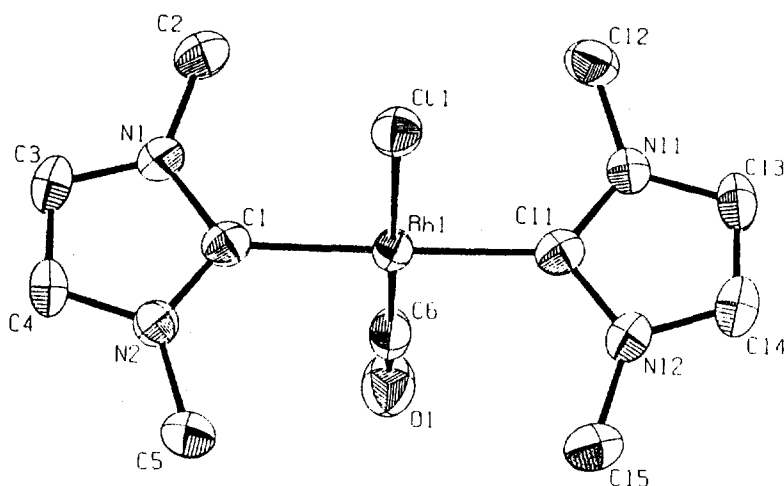


Fig. 1. PLATON plot [12] of the carbene–rhodium complex **5**. Hydrogen atoms omitted for clarity, thermal ellipsoids at 50% probability level. Selected bond lengths (Å) and angles (°): Rh1–Cl1 2.407(1), Rh1–C1 2.049(4), Rh1–C11 2.047(4); C11–Rh1–Cl1 89.6(1), Cl1–Rh1–C6 177.7(1).

membered carbene ligands. The rhodium–carbene distances in **5** are 2.049(4) and 2.047(4) Å respectively (Fig. 1). The *cis*-isomers of type-**5** compounds are accessible from the free carbenes and $[(\text{CO})_2\text{RhCl}]_2$ in kinetically controlled reactions [13].

3. Experimental section

All reactions were performed with standard Schlenk techniques in oxygen free nitrogen atmosphere. Solvents were dried with standard methods and distilled under N_2 . Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer, the ^1H and ^{13}C spectra at 400 and 100.54 MHz respectively on an FT Jeol GX 400 instrument. Elemental analyses were performed in the Microanalytical Laboratory of our institute.

3.1. Diiodobis(1,4-dimethyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)palladium(II) (**3**)

Powdered 1,4-dimethyl-1,2,4-triazolium iodide **1b** (10 mmol) and palladium(II) acetate (5 mmol) were partly dissolved in 300 ml of thf (not necessarily anhydrous). The mixture was refluxed for 10 min. The oil bath was removed and the metal complex **3** began to precipitate as a yellow solid. The compound was obtained by removal of the solvent and the acetic acid in vacuo. The precipitate was washed with toluene and water. The compound is soluble in polar organic solvents like methylene chloride, chloroform and especially nitromethane.

Yield 100% raw material.

3.1.1. Spectroscopic data of **3**

^1H NMR (400 MHz, $\text{DMSO}-d_6$, 20 °C, ppm): δ 8.81 (8.76) (s, 2H, NCH), 4.17, 4.16 (4.12) (s, 6H, NCH_3), 3.98, 3.97 (3.96) (s, 6H, NCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 100.1 MHz, 20 °C, ppm): δ 169.8 (166.3) (carbene-C), 145.2 (144.5) (NCH), 35.5, 35.4 (35.0, 34.9) (NCH_3). IR [KBr ν (cm^{-1})]: 3116, 3058, 2941, 1547, 1483, 1349, 1220, 1127, 1050, 969, 856, 768, 648, 462. Anal. Found: C, 17.26; H, 2.22; N, 15.50. $\text{C}_8\text{H}_{14}\text{N}_6\text{I}_2\text{Pd}$ (554.47) Calc.: C, 17.33; H, 2.55; N, 15.16%. M.p. 308 °C (without dec.).

3.2. Carbonylchlorobis(1,3-dimethylimidazoline-2-ylidene)rhodium(I) (**5**)

Carbon monoxide was bubbled through a solution of $[(\eta^4-1,5\text{-cyclooctadiene})\text{bis}(1,3\text{-dimethylimidazoline-2-ylidene})\text{rhodium(I)}]\text{chloride}$ **4** in methylene chloride. After stirring for another 15 min at room temperature, the solvent and 1,5-cyclooctadiene were removed in vacuo. The precipitate was washed with two portions of

ether and *n*-pentane. The obtained yellow-coloured compound is best soluble in chloroform and methylene chloride, good in thf and toluene, less in ether and *n*-pentane.

3.2.1. Spectroscopic data of **4**

^1H NMR (400 MHz, CDCl_3 , 20 °C, ppm): δ 7.0 (s, 4H, NCH_3) and 4.0 (s, 12H, NCH_3), 4.2 (m, 4H), 2.3 (4H), 2.1 (4H) cyclooctadiene. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.1 MHz, 20 °C, ppm): δ 180.5 (d, $^1J(\text{C}-\text{Rh}) = 52.4$ Hz), 123.1, 38.3 carbene, 88.8, 30.4 cyclooctadiene. IR [KBr ν (cm^{-1})]: 3450, 3154, 3094, 2920, 2977, 2828, 1634, 1574, 1458, 1380, 1230, 1115, 1084, 991, 823, 744, 695, 668, 461. Anal. Found: C, 50.26; H, 6.44; N, 12.66. $\text{C}_{18}\text{H}_{28}\text{ClN}_4\text{Rh}$ (438.81 g mol^{-1}) Calc.: C, 49.27; H, 6.43; N, 12.77%. X-ray crystal structure.

3.2.2. Spectroscopic data of **5**

^1H NMR (400 MHz, CDCl_3 , 20 °C, ppm): δ 3.95 (s, 12H, NCH_3), 6.94 (s, 4H, NCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.1 MHz, 20 °C): δ 38.3 (NCH_3), 121.6 (NCH), 183.6 (d, $^1J_{\text{CRh}} = 39.1$ Hz, C-carbene), 185.9 (d, $^1J_{\text{CRh}} = 86.6$ Hz, CO). IR [KBr ν (cm^{-1})]: 1924 (s, $\nu(\text{CO})$).

3.3. X-ray CSD of rhodium complex **5** [7]

Formula $\text{C}_{11}\text{H}_{16}\text{ClN}_4\text{ORh}$, formula weight 358.63 g mol^{-1} , F_{000} 720, μ 13.8 cm^{-1} , orange platelet of size $0.08 \times 0.15 \times 0.23$ mm^3 , ρ_{calc} 1.69 g cm^{-3} , $Z = 4$, space group monoclinic, $P2_1/c$ (No. 14), final lattice parameters were obtained by least-squares refinement of 194 reflections with $I/\sigma(I) > 6.0$ out of four images measured at φ -angles of 0°, 50°, 100°, 150° with $\Delta\varphi = 0.2^\circ$: $a = 7.340(4)$, $b = 13.684(5)$, $c = 14.176(7)$ Å, $\beta = 98.31(3)^\circ$, $V = 1408.9$ Å³. All data were measured at -50 ± 0.3 °C on an IPDS (STOE) diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). 240 images were measured at a crystal-to-detector distance of 80 mm ($2.86^\circ < 2\theta < 48.4^\circ$) with a rotating angle of 1.5° and an exposure time of 300 s per image. 16413 data measured, 44 overflows, 0 overlapping, 446 systematically absent, 2234 unique, 64 with negative intensity, 1925 reflections with $I > 1.0\sigma(I)$ used for refinement. Corrections for Lorentz and polarisation terms and empirical absorption correction performed with the IPDS operating software [8]. Structure solution with the Patterson method [9] and difference Fourier techniques [10]. All non-hydrogen atoms were refined anisotropically, all hydrogen atoms could be found by difference maps and were refined isotropically. 227 parameters, Chebyshev weighting scheme [11], shift/esd < 0.01 in the last cycle, residual density $+0.41$ e Å⁻³, -0.51 e Å⁻³, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.031$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.036$, GOF 1.088.

For further details regarding this crystal structure

determination, the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-76344 Eggenstein Leopoldshafen (Germany) may be contacted, quoting the reference to this paper, the names of the authors, and the registration number CSD-406506.

Acknowledgements

This work received generous support from the Deutsche Forschungsgemeinschaft (carbene- and germylene-metal complexes), the Fonds der Chemischen Industrie and Degussa AG.

References

- [1] E.O. Fischer and A. Maasböl, *Chem. Ber.*, **100** (1967) 2445; R. Aumann and E.O. Fischer, *Chem. Ber.*, **101** (1968) 954; E.O. Fischer, *Pure Appl. Chem.*, **24** (1970) 407; **30** (1972) 353.
- [2] A.J. Arduengo III, R.L. Harlow and M. Kline, *J. Am. Chem. Soc.*, **113** (1991) 361; A.J. Arduengo III, H.V. Rasika Dias, R.L. Harlow and M. Kline, *J. Am. Chem. Soc.*, **114** (1992) 5530; M. Regitz, *Angew. Chem.*, **108** (1996) 791; *Angew. Chem., Int. Ed. Engl.* (1996).
- [3] K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer and J. Mink, *J. Organomet. Chem.*, **459** (1993) 177; M. Regitz, *Angew. Chem.*, **103** (1991) 691; W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn and P.W. Roesky, *J. Organomet. Chem.*, **480** (1994) C7; W.A. Herrmann, O. Runte and G.R.J. Artus, *J. Organomet. Chem.*, **501** (1995) C1; W.A. Herrmann, K. Öfele, D. Mihalios, M. Elison, E. Herdtweck, T. Priemeier and P. Kiprof, *J. Organomet. Chem.*, **498** (1995) 1.
- [4] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher and G.R.J. Artus, *J. Eur. Chem.*, **2**(7) (1996) 772; W.A. Herrmann, M. Elison, J. Fischer and C. Köcher, *DE-447066*, Hoechst AG, 1994.
- [5] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher and G.R.J. Artus, *Angew. Chem.*, **107** (1995) 2602; *Angew. Chem., Int. Ed. Engl.*, **34** (1995) 3005; W.A. Herrmann, M. Elison, J. Fischer and C. Köcher, *DE-4447068*, Hoechst AG, 1994; B. Cornils and W.A. Herrmann (eds.), *Applied Homogeneous Catalysis with Organometallic Complexes*, VCH, Weinheim, 1996.
- [6] W.A. Herrmann, C. Köcher, L. Gooßen and G.R.J. Artus, *J. Eur. Chem.*, **2** (1996) 1627.
- [7] G.R.J. Artus, *Ph.D. Thesis*, Technische Universität München, 1996.
- [8] STOE-IPDS operating system 1995.
- [9] G.M. Sheldrick, SHELXS-86, *Acta Crystallogr.*, **A46** (1990) 467.
- [10] D.J. Watkin, P.W. Betteridge and J.R. Carruthers, CRYSTALS, Oxford University Computing Laboratory, 1986–1996.
- [11] J.R. Carruthers and D.J. Watkin, *Acta Crystallogr.*, **A35** (1979) 698.
- [12] A.L. Spek, PLATON, *Acta Crystallogr.*, **A46** (1990) C34.
- [13] W.A. Herrmann et al., unpublished results; M. Prinz, *Diploma Thesis*, Technische Universität München, in preparation (1997).