Transition Metal Complexes of Diazenes, XXXVIII [1]  
Activation of Aromatic C-Cl Bonds in the Oxidative Addition of ortho-Chlorophenyldiazenes to Chlorotris(triphenylphosphine)rhodium  
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Refluxing a slightly acidic n-BuOH solution of RhCl(PPh₃)₃ and 2-chloro-, 2,4-dichloro-, or 2,4,6-trichloroazobenzene affords cyclometalated complexes (1) via loss of one phosphine ligand and oxidative addition of the ortho-C-Cl bond. X-ray structural analysis indicates a trans-position of the two triphenylphosphine ligands. The reaction proceeds only in polar solvents like alcohols or dimethyl sulfoxide but not in toluene. In the presence of air or oxygen a hydrido complex was formed as a by-product.

Introduction

Cyclometalation reactions are important key steps in the stoichiometric and catalytic synthesis of organic compounds [2]. Although oxidative additions of carbon-halogen bonds to square planar d⁸ metal complexes have been intensively studied [3], analogous transformations of 2-halogenoazobenzenes are relatively scarce and reaction conditions are rather stringent. As an example, 2-bromoazobenzene and IrCl(CO)(PPh₃)₂ have to be heated in boiling xylene for five days to obtain the desired product in a yield of 43% [4]. When 2-chloroazobenzene and RhCl(PPh₃)₃ are refluxed in toluene, no cyclometalated product but [RhCl(PPh₃)₂]₂ was obtained. The synthesis of only a few orthometalated diazene rhodium phosphine complexes has been reported and yields were in general rather low; furthermore, no triphenylphosphine complexes could be obtained [5]. In the course of our work on the rhodium catalyzed indole synthesis from azobenzenes and alkynes [6] we now found that 2-chloroazobenzenes and RhCl(PPh₃)₃ in boiling n-BuOH undergo a fast and clean oxidative addition. No such reaction occurs when a non-halogenated azobenzene derivative is used [7].

Results and Discussion

Synthesis and structure

Refluxing an acidic n-BuOH (6 vol% of HOAc) suspension of RhCl(PPh₃)₃ in the presence of a slight excess of 2-chloro-, 2,4-dichloro-, and 2,4,6-trichloroazobenzene for about 10 min afforded the complexes 1a - c in isolated yields of 66 - 85% (Scheme 1). Further heating was disadvantageous and produced RhCl(CO)(PPh₃)₂ and elemental rhodium [8]. Reaction progress was indicated by a color change from burgundy red to bright orange or orange-yellow. The addition of HOAc is not essential but slightly improves yield and size of the microcrystals.

The X-ray structural analysis of 1b confirms the expected octahedral geometry with the triphenylphosphine ligands in trans position (Fig. 1). Cyclometalation of 2-(chloromethyl)pyridine in refluxing toluene is also known to afford the trans-product while the cis-isomer is formed at room temperature [9].

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The angles around the central metal deviate from ideal octahedral geometry [10]. While values of 92.8° and 90.2° are found for C12-Rhl-C13 and C12-Rh1-C25, respectively, the angle of C13-Rh1-N1 is increased to 98.6°, whereas N1-Rh1-C25 is reduced to 78.4°. The non-metalated phenyl ring is twisted by 39.8° relative to the plane of the rhodacycle. These values are in accordance with structural data of analogous Rh(III) complexes [11]. The Rh1-C12 and Rh1-C13 bond lengths of 236 and 249 pm, respectively, distinctly confirm the stronger trans-bond lengthening effect of a σ-phenyl group as compared to an N-donor ligand.

Fig. 1. Crystal structure and labelling scheme of 1b; important bond lengths [pm]: Rh1-C12 236.1(1), Rh1-N1 208.0(4), Rh1-P1 239.1(2), Rh1-C13 249.3(2), Rh1-C25 199.9(5), Rh1-P2 238.6(2), N1-N2 128.0(6), N1-C10 143.7(6), N2-C20 137.6(6).

In the 1H NMR spectra of 1a - c all hydrogen atoms of the cyclometalated ring appear as distinct resonances (H2-5), whereas for the non-metalated ring this is the case only for H3 and H5, the other peaks being hidden underneath the signals of PPh3. Assignments are based on comparison of 1a - c and on 1H/1H-COSY spectra (Fig. 2). The doublet of H2 appears at lowest field, followed by the signals of H3, H5, or H3, and H4, as also reported for d6 complexes of Fe, Mo, Ru, Rh, and Ir [5, 12].

To unambiguously assign the ν(N=N) vibration, the Raman spectrum of solid 1b was measured in the range from 1300 to 1600 cm⁻¹. Only one intense line at 1357 cm⁻¹, which appeared also with medium intensity in the IR spectrum, was observed. The decreasing values of 1364, 1357 and 1350 cm⁻¹, observed for 1a, 1b, and 1c, respectively, suggest a weakening of the N=N bond upon introduction of one or two chlorine atoms into the orthometalated phenyl ring. The same trend was observed for the ν(C=C)-vibrations of the metallated phenyl ring. While in each complex the two main vibrations are separated by 26 cm⁻¹, they are shifted each times by about 9 cm⁻¹ to lower wave numbers upon proceeding from 1a to 1c. The UV-Vis spectra of 1a - 1c contain two maxima at 325 - 327 nm and 470 - 475 nm. The latter band is shifted to longer wavelength by 5 - 10 nm as compared to the n,π* transition of the free diazene ligand.

The reaction is strongly solvent dependent. In DMSO and pyridine the product did not precipitate during the reaction, but the red-orange color suggested that the reaction had occurred. Accordingly, addition of petroleum ether afforded the same complexes but in much lower yields. In toluene, no ortho-metalation but formation of [RhCl(PPh3)2]2 was observed. A similar solvent dependence was reported for oxidative addition reactions of alkyl halides to iridium complexes, where rate constants increased when more polar solvents were used [13]. Therefore a mechanism analogous to nucleophilic aromatic substitution, involving nucleophilic attack of rhodium at the halogenated ring and subsequent a rate determining chloride migration to the metal [3], is in accord with the failure of 2-fluoroazobenzene to undergo the cyclometalation. The much higher bond dissociation energy of Dc-F = 532 kJ/mol as compared to Dc-ci = 406 kJ/mol [14] supports this interpretation. When RhCp(C2H4)2, RhCl(CO)(PPh3)2, and CoBr(PPh3)3 were employed, no cyclometalation products could be detected. 2-bromoazobenzene afforded orange and yellow microcrystalline materials which had very similar physical properties as the title complexes (IR, 1H NMR, UV-Vis, and microanalysis) but were insoluble in dichloromethane.

When the reaction of 2,4-dichloroazobenzene was conducted in the presence of air or oxygen,
in addition to 1b a hydride complex precipitated in 10% yield (relative to 1b) after a reaction time of about 2 minutes. Normally rhodium hydrides are formed under reducing conditions [15]. The presence of a hydride complex is indicated by the \(^1H\) NMR spectrum which contains a doublet at -13.52 ppm (J(Rh-H) = 33 Hz, J(P-H) = 22 Hz). In an analogous rhodium complex, wherein PPh\(_3\) is substituted by P(C(\(_5\)H\(_{11}\))\(_3\)), the cis-hydrido ligand gives rise to a signal at -14.6 ppm [5]. From these data it is known that small amounts of oxygen have a beneficial effect on hydrogenation reactions catalyzed by RhCl(PPh\(_3\))\(_3\) due to a rapid conversion of a triphenylphosphine ligand to the corresponding oxide [16].

Since oxygen and RhCl(PPh\(_3\))\(_3\) afford peroxo complexes [17], their reaction with 2,4-dichloroazobenzene under nitrogen atmosphere was tested. In addition to 1b, the hydride complex was formed again but RhCl(CO)(PPh\(_3\))\(_2\) now became the major product. This suggests that the peroxo complexes oxidized \(-BuOH\) to butyraldehyde [18]. A consecutive reverse hydroformylation reaction [19] could rationalize formation of RhCl(CO)(PPh\(_3\))\(_2\) and the hydride [20].

Experimental

Unless otherwise mentioned, all reactions were carried out under nitrogen in nitrogen-saturated solvents. IR: Perkin Elmer 16 PC FT-IR. Raman: Dilor XY. UV-Vis: Shimadzu UV-3101 PC. NMR: Jeol JNM-EX 270 FT-NMR. MS: Varian Mat 212. Elemental analysis: Carlo Erba 1106 (CHN). HPLC: Knauer HPLC pump 64; column Spherisorb ODS 2 (250 x 8 mm); CH\(_2\)CN/H\(_2\)O 5/1 (v/v). RhCl(PPh\(_3\))\(_3\) [19], 2-chloro-, 2,4-dichloro-, and 2,4,6-trichloroazobenzene were prepared as described in the literature [21].

Preparation of 1a - c

Refluxing a mixture of 184 mg (0.20 mmol) of RhCl(PPh\(_3\))\(_3\) with a slight excess of the diazene (0.22 mmol) in 8 ml of \(-BuOH\) with 0.5 ml of acetic acid for about 10 min afforded 1a - c as microcrystalline powders, which were filtered off, washed three times with 10 ml of petroleum ether and dried in vacuo. The airstable complexes are soluble in dichloromethane and may be recrystallized from dichloromethane/methanol. Upon standing in aerated solutions the complexes were partly transformed into insoluble materials.

1a: Orange microcrystalline powder, 176 mg (83%). \(^1H\) NMR (CD\(_2\)Cl\(_2\); 270 MHz): 7.93 (H\(_2\), 1 H, d), 7.65 - 6.95 (34 H, m), 6.92 (H\(_3\), 1 H, t), 6.77 (H\(_3,5\), 2 H, t), 6.28 (H\(_1\), 1 H, t); \(\lambda\) (\(\varepsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 475 nm (2500), 327 nm (21500).

C\(_{48}\)H\(_{38}\)Cl\(_{3}\)N\(_2\)P\(_2\)Rh (914.1)
Calcd C 60.78 H 3.93 N 2.95%
Found C 65.41 H 4.37 N 3.17%

1b: Orange-yellow microcrystalline powder, 183 mg (85%). \(^1H\) NMR (CD\(_2\)Cl\(_2\); 270 MHz): 7.82 (H\(_2\), 1 H, d), 7.60 - 7.00 (33 H, m), 6.84 (H\(_3\), 1 H, s), 6.77 (H\(_3,5\), 2 H, t), 6.74 (H\(_1\), 1 H, d). \(^{31P}\) NMR (CD\(_2\)Cl\(_2\); 109 MHz): 8.1 (d, J(Rh-P) 95.7 Hz). UV (CH\(_2\)Cl\(_2\)); \(\lambda\) (\(\varepsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 463 nm (2900), 326 nm (19400).

C\(_{49}\)H\(_{40}\)Cl\(_{3}\)N\(_2\)P\(_2\)Rh (914.1)
Calcd C 60.37 H 4.19 N 3.06%
Found C 63.27 H 3.57 N 2.76%

1c: Orange microcrystalline powder, 190 mg (66%). \(^1H\) NMR (CD\(_2\)Cl\(_2\); 270 MHz): 7.65 - 7.00 (33 H, m), 6.86 (H\(_2\), 1 H, s), 6.82 (H\(_3\), 1 H, s), 6.79 (H\(_3,5\), 2 H, t). UV (CH\(_2\)Cl\(_2\)); \(\lambda\) (\(\varepsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 470 nm (3200), 325 nm (21000).

C\(_{45}\)H\(_{32}\)Cl\(_{6}\)N\(_2\)P\(_2\)Rh (948.5)
Calcd C 60.78 H 3.93 N 2.95%
Found C 61.00 H 3.81 N 2.63%

Formation of the hydrido complex

A) To a suspension of 46 mg (0.05 mmol) of RhCl(PPh\(_3\))\(_3\) and 13 mg (0.05 mmol) of 2,4-dichloroazobenzene 2 ml of \(-BuOH\) were added. The mixture was then heated in air for about 2 min and allowed to cool to room temp. The precipitated material (25 mg) was washed three times with petroleum ether and dried by standing in air. \(^1H\) NMR (CD\(_2\)Cl\(_2\); 270 MHz): 7.94 (H\(_2\), 1 H, d), \(J = 8\) Hz; -13.52 (Rh-H, 1 H, dt), J(Rh-H) 33 Hz, J(P-H) 22 Hz; all other signals were not assigned; \(^{31P}\) NMR (CD\(_2\)Cl\(_2\); 109 MHz): 31.4 (d, J(Rh-P) 109.3 Hz). No hydride complex was observed when the reaction was conducted under N\(_2\) in the presence of 0.2 ml of water or when 1b was heated for 2 min in refluxing aerated \(-BuOH\) suspension. 2-chloro- and 2,4,6-trichloroazobenzene did not induce formation of a hydride complex.

B) 46 mg (0.05 mmol) of RhCl(PPh\(_3\))\(_3\) was dissolved in 2 ml of dichloromethane; then oxygen was bubbled through the solution for 5 min. The solvent was removed and 13 mg (0.05 mmol) of 2,4-dichloroazobenzene in 2 ml of \(-BuOH\) was added. Thereafter the experiment was conducted in a nitrogen atmosphere as described above. \(^1H\) NMR analysis revealed that the obtained material (10 mg) contained 30% of the hydride complex relative to 1b.
but the main product was RhCl(CO)(PPh$_3$)$_2$ as indicated by the IR spectrum. The orange washing solution did not contain a hydride complex as evidenced by $^1$H NMR.

**X-ray analysis:**

Structure analysis was carried out on an automatic four-circle goniometer (Siemens P4) at 200 K using Mo-K$_\alpha$ radiation (graphite monochromator). The structure was solved by direct methods by using the SHELXTL-PLUS program [22]. For the refinement all non-hydrogen atoms were included with anisotropic temperature factors; the hydrogen positions were determined by difference Fourier analysis and included into the refinement with fixed coordinates and temperature factors.

Crystals of 1b were obtained from dichloromethane/methanol. C$_{38}$H$_{38}$Cl$_3$N$_2$P$_2$Rh $\times$ CH$_2$Cl$_2$ (1b) (99.8%), orange columns, crystal size 0.40 $\times$ 0.40 $\times$ 0.40 mm, monoclinic crystal system, space group P2$_1$/c, $a$ = 1099.5(2), $b$ = 3882.4(11), $c$ = 1053.8(2) pm, $\beta$ = 91.64$^\circ$, $V$ = 4.496(2) nm$^3$, d(calc.) = 1.48 g/cm$^3$ (Z = 4), 11854 reflections collected, 9920 independent, 5144 [F $>$ 4.0 $\sigma$(F)] observed reflections; $\mu$ = 0.785 mm$^{-1}$, $R$ = 0.040, $R_w$ = 0.033. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405453.

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[6] (a) P. Reißer, Y. Wakatsuki, H. Kisch, Monatsh. Chem. 126, 1 (1995);
[20] The initially formed Rh(II)Cl$_2$(PPh$_3$)$_2$ may undergo a PPh$_3$ assisted reductive elimination of HCl affording RhH(PPh$_3$)$_2$; subsequent oxidative addition of 2,4-dichloroazobenzene would produce the hydride complex. It is unlikely that H-abstraction from the solvent by a Rh(II) intermediate is involved since no hydride is produced when n-BuOH is replaced by iPrOH.