DALTON COMMUNICATION

Use of amido Grignard reagents in inorganic chemistry. Synthesis and crystal structure of *anti*-[Pd(Cl)(py)(μ-2,6-$Pr^i_2C_6H_3NH$)]$_2$

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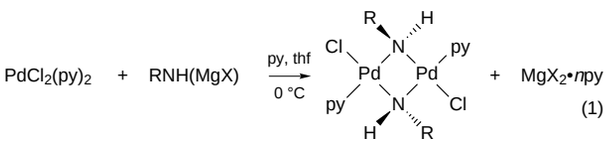
Treating a pyridine (py) solution of $PdCl_2(py)_2$ with a tetrahydrofuran or diethyl ether solution of the amido Grignard reagent 2,6-$Pr^i_2C_6H_3NH(MgCl)$ afforded a dimeric palladium complex, containing two bridging amido groups, which has been structurally characterised.

Late-transition-metal amido and imido complexes, especially those in a low oxidation state, have attracted much attention during the last ten years since their high reactivity may render them reactive reagents or intermediates in catalytic cycles.[1] Several approaches have been used for the synthesis of these complexes, but the use of the 'Grignard' amido reagents RNH(MgX) (X = halogen, R = aryl) does not appear to have been investigated before. However, the analogous reagent $[(thf)MgNPh]_6$ (thf = tetrahydrofuran) has been recently reported as an imido-transfer reagent for the synthesis of imido complexes of titanium, zirconium and manganese.[2]

Aryl-amido and -imido Grignard reagents have been known for a long time and their use in organic synthesis has been extensively investigated by Okubo *et al.*[3] Since palladium is probably the most widely used metal in homogeneous catalysis, we decided to start our investigation from a simple precursor, $PdCl_2(py)_2$ (py = pyridine), in the hope that following substitution of the labile pyridine ligands the product may represent a versatile entry into a wide class of complexes.

Treating a pyridine solution of $PdCl_2(py)_2$ with a thf solution of 2,6-$Pr^i_2C_6H_3NH(MgBr)$, generated from the corresponding aniline and EtMgBr, afforded an orange solution and a white precipitate, which was shown by ^{1}H NMR spectroscopy to contain a mixture of pyridine-containing complexes, but no residue deriving from the anilido fragment. The filtered solution was further treated with *n*-hexane affording a yellow precipitate that, upon standing in the mother-liquor for 2 weeks, separated into a white microcrystalline powder and some orange crystals.† The orange crystals were suitable for X-ray diffraction studies and were shown to be made up of the dimeric amido complex *anti*-[Pd(Cl)(py)(μ-2,6-$Pr^i_2C_6H_3NH$)]$_2$, the structure of which is shown in Fig. 1 [equation (1)].



(R = 2,6-$Pr^i_2C_6H_3$; X = Cl or Br)

Palladium amido complexes have attracted much attention as possible intermediates in various reactions and their involvement in the interesting amination of halogenoarenes[5,6] has been recently proven. Most of the reported complexes are mononuclear and only a few dinuclear amido-bridged palladium complexes are known.[7–11] To the best of our knowledge, only in three cases has the crystal structure of a dinuclear palladium amido complex been reported,[8,9,11] although the crystal structure of a trinuclear complex bearing both amido and imido bridging groups has also been reported.[12]

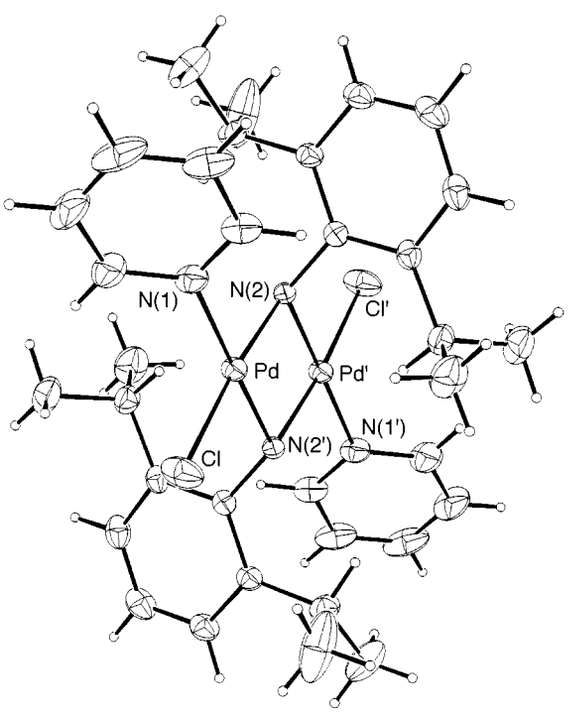


Fig. 1 An ORTEP[4] drawing of *anti*-[Pd(Cl)(py)(μ-2,6-$Pr^i_2C_6H_3NH$)]$_2$. Thermal ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (°): Pd–N(1) 2.060(3), Pd–N(2) 2.078(3), Pd–N(2′) 2.047(3), Pd–Cl 2.379(1); N(1)–Pd–N(2) 95.3(1), N(1)–Pd–Cl 89.5(1), Cl–Pd–N(2′) 93.6(1), N(2)–Pd–N(2′) 81.8(1), N(1)–Pd–N(2′) 176.7(1), N(2)–Pd–Cl 174.5(1)

† A thf (5 cm^3) solution of EtMgBr was prepared from Mg (24.3 mg, 1.0 mmol) and EtBr (0.715 mmol, 78 mg, 53 μl) in a standard way. To this was added 2,6-$Pr^i_2C_6H_3NH_2$ (0.77 mmol, 126.8 mg, 135 μl) at 0 °C followed by heating at 50–55 °C for 1.5 h. The resulting solution was slowly added to a pyridine (15 cm^3) solution of $PdCl_2(py)_2$ (0.350 mmol, 117.4 mg) at 0 °C. A small amount of an off-white solid precipitated and the initially yellow solution became orange. The solution was allowed to reach room temperature and, after 30 min, was filtered through a frit and the residue washed with hexane (60 cm^3). The crystals (see text) were separated taking advantage of their much higher sedimentation rate with respect to the powder when the solution (or the following hexane washings, 2 × 20 cm^3) is stirred.

In the crystal, the dimeric complex is located about a crystallographic inversion centre.‡ Both palladium atoms display an almost square-planar geometry and are bridged by the two amido ligands and bound to a chlorine atom and to a pyridine molecule. The phenyl ring of the amido ligand is almost normal to the plane defined by its nitrogen atoms and by the palladium atoms, for steric reasons. During the structure refinement, the chlorine atom showed an anomalous thermal parameter. A subsequent refinement of its multiplicity revealed that in the crystal used for the structure solution chlorine is partially replaced by bromine (about 20%), derived from the preparation of the Grignard reagent. This replacement has been confirmed by analysing the crystal used with an energy dispersive X-ray microprobe, which revealed the presence of both chlorine and bromine.

Note that the mutual disposition of the chloride and the pyridine ligands on the two palladium atoms renders the two tetrahedral nitrogen atoms chiral. The two stereogenic centres have the opposite configuration in any single molecule. Thus the obtained product is the *meso* form.

The observed geometry is the one generally found to be more stable even in the case of other bis-bridging amido complexes, although in some cases it is even possible to observe in solution the corresponding *syn* isomer. In the present case, this last isomer is probably highly disfavoured because of the steric interaction between the *o*-isopropyl groups.

The ^{1}H NMR spectrum (in $CDCl_3$) of the dissolved crystals showed the presence of at least six different methyl groups, but signals were not well resolved and it was not clear how many of the signals were due to the bromide substitution in the complex. When the same synthesis was repeated employing the Grignard reagent derived from benzyl chloride instead of the one from ethyl bromide a cleaner spectrum was obtained, in which four doublets of equal intensity were clearly observed [δ 0.44, J(H–H) = 6.76; 1.18, J = 6.81; 2.27, J = 6.90, 2.50; J = 6.90 Hz]. These are attributable to the eight methyl groups of the isopropyl groups, upon considering that rotation around the $C–N_{amido}$ bonds is hindered. Indeed, chirality at nitrogen is sufficient to render the two methyl groups of each isopropyl group magnetically inequivalent even if rotation around the $C_{aromatic}–C_{Pr^i}$ bond was fast.

Three doublets of much weaker intensity (integrated as ≈5% of the preceding ones) were also observed [δ 0.24, J(H–H) = 6.74; 1.39, J = 6.78; 2.44, J = 6.63 Hz] which are attributable to a minor product, possibly the *syn* isomer (the fourth signal is probably obscured by the more intense signals of the *anti* isomer), although data are not sufficient to prove this attribution. The signal of the protons bound to the tertiary carbon atom of the isopropyl groups could not be located. However they should appear as two signals with a very high multiplicity (the two methyl groups are not magnetically equivalent) and this renders them very weak.

The use of a chloride-containing reagent for the generation of the Grignard reagent also allowed us to identify the white by-product as $MgCl_2·n$py since exactly the same signals in the ^{1}H NMR spectrum [δ 8.68 (br) and 8.62 (br), in $CDCl_3$] could be obtained by dissolving $MgCl_2·nH_2O$ in pyridine, drying *in vacuo*, and redissolving the solid thus obtained in $CDCl_3$.

The dimeric amido complex reported here is indefinitely stable in air as a solid or in solution under dinitrogen and can thus represent a suitable starting material for the synthesis of more complex products.

‡ Crystal data: $C_{34}H_{46}Cl_2N_4Pd_2$, M 794.48, monoclinic, space group $P2_1/c$, a = 10.866(1), b = 14.453(2), c = 11.680(2) Å, β = 105.79(1)°, U = 1765.1(4) Å^3, Z = 2, D_c = 1.49 g cm^{-3}, μ = 11.9 cm^{-1}, T = 22(2) °C. The structure was solved by Patterson and Fourier methods and refined using 2121 observed reflections [$I > 3\sigma(I)$] to R = 0.025 and R' = 0.036. CCDC reference number 186/668.

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