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LETTER

New Neutral and Cationic Methylpalladium(II) Complexes Containing Tridentate Nitrogen Ligands. Synthesis, Reactivity and X-ray Crystal Structure of $\{\sigma$-*N*-2-(*N*-isopropylcarbaldimino)-6-(*N*-isopropylcarbaldimino)-σ-*N*$'$-pyridyl$\}$(chloro)methylpalladium(II) and $[\{\sigma^3$-*N*,*N*$'$,*N*$''$-2,2$'$:6$'$,2$''$-terpyridyl$\}$methylpalladium(II)] Chloride Dihydrate

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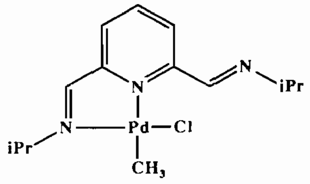
Modelling of spectator ligands in homogeneous catalytic reactions, especially those mediated by organopalladium or -platinum compounds, has thus far mainly focussed on mono- and bidentate phosphorus and nitrogen ligands [1–4]. Only a small number of organopalladium compounds containing tridentate ligands is known [5, 6]. Such tridentate ligands are interesting from the point of view of modelling intermediates in, for example, carbonylation reactions. To this end we have prepared the novel compounds **1** and **2**, which are neutral and cationic methylpalladium(II) complexes, respectively. These have been structurally characterized and their reactivity towards CO has been evaluated.



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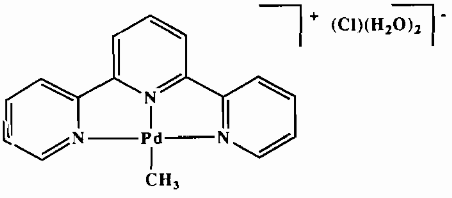

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Experimental

Materials and Apparatus

All manipulations were carried out in an atmosphere of purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. All starting chemicals were used as commercially obtained. (COD)PdCl$_2$ was prepared according to the literature [7]. The new iPr-DIP ligand (**1a**) was obtained in a way similar to ref. 8. Terpy (**2a**) was obtained from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 100 spectrometer, IR spectra on a PE 283 spectrophotometer and mass spectra were obtained on a Varian MAT 711 double-focussing mass spectrometer, fitted with a 10 μm tungsten FD-emitter. Elemental analyses were caried out by the section Elemental Analyses of the ITC/TNO, Zeist, The Netherlands.

Compounds

η^2,η^2-(Cycloocta-1,5-diene)(chloro)methylpalladium(II), (COD)Pd(Me)Cl

This compound was synthesized according to ref. 9. ^{1}H NMR (CDCl$_3$) δ 1.15 (s, 3H, CH$_3$), 2.51 (m, 8H, 4 × CH$_2$), 5.13 (m, 2H, =CH *cis* to CH$_3$), 5.88 (m, 2H, =CH *trans* to CH$_3$). Mass spectrum in agreement with simulated spectrum for $[2M - \text{Cl}]^{+\bullet}$ *m*/*z* 493 for ^{106}Pd and ^{35}Cl.

$\{\sigma$-N-2-(N-Isopropylcarbaldimino)-6-(N-isopropylcarbaldimino)-σ-N$'$-pyridyl$\}$(chloro)methylpalladium(II) (1)

A solution of 265 mg (1 mmol) (COD)Pd(Me)Cl and 250 μl (1.0 mmol) iPr-DIP (**1a**) in acetonitrile was stirred for 5 min at 20 °C. Dark red crystals of **1** formed immediately after cooling the solution to −10 °C. After decanting, these were washed with diethyl ether to give 282 mg (0.75 mmol; 75%) of dark red crystals suitable for X-ray diffraction, which were stored in the dark to avoid decomposition. *Anal.* Found (calc.) for C$_{14}$H$_{22}$ClN$_3$Pd: C, 44.65 (44.93); H, 5.94 (5.93); N, 11.12 (11.23)%. Melting point

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(m.p) 161 °C (dec). ^{1}H NMR ($CDCl_3$; 223 K): δ 1.17 (s, 3H, Pd-CH_3), 1.24 (d, 6H, $CH(CH_3)_2$, $J = 7.2$), 1.39 (d, 6H, $CH(CH_3)_2$(coord.), $J = 7.2$) 3.82 (sept, 1H, $CH(CH_3)_2$), 4.18 (sept, 1H, $CH(CH_3)_2$(coord.)), 7.75 (d, 1H, H^5, $J = 7.5$), 8.01 (t, 1H, H^4), 8.26 (d, 1H, H^3), 8.45 (s, 1H, H^7), 9.62 (s, 1H, H^8). ^{13}C NMR ($CDCl_3$; 298 K) δ 2.6 (Pd-CH_3), 23.2, 24.1 (diaster. $CH(CH_3)_2$), 55.4, 60.7 ($CH(CH_3)_2$), 126.9 (C^3, C^5), 138.7 (C^4), 152.0 (C^{12}), 158.8 (C^2, C^6), 163.2 (C^7). For numbering see Fig. 1. FD-mass: correct isotope pattern with m/z 373 $[M]^{+\cdot}$ for ^{106}Pd and ^{35}Cl.

[{σ³-N,N',N''-2,2':6',2''-Terpyridyl}methylpalladium(II)] chloride dihydrate (2)

While stirring at 20 °C, 740 mg (2.8 mmol) (COD)-Pd(Me)Cl was slowly added to a solution of 651 mg (2.8 mol) of Terpy (2a) in 25 ml of acetonitrile. A pale yellow precipitate formed instantaneously, which was filtered off, washed with acetonitrile and dried *in vacuo* at 60 °C to yield 1.05 g (2.7 mmol; 96%) of pale yellow 2. Upon dissolution in methanol, followed by slow evaporation of the solvent, a small crop of yellow needles suitable for X-ray diffraction separated. *Anal.* Found (calc.) for $C_{16}H_{18}ClN_3O_2Pd$: C, 44.91 (45.11); H, 4.29 (4.26); N, 9.88 (9.86)%. m.p. 222 °C (dec.). ^{1}H NMR (MeOH-d_4; 298 K): δ 0.83 (s, 3H, Pd-CH_3), 7.6–7.8 (m, 2H, 4',4'' protons), 8.2–8.6 (m, 9H, other py-ring protons). ^{13}C NMR (D_2O; 298 K) δ 29.0 (Pd-CH_3), 123.6 (C^3, $C^{3''}$), 125.0 C^5, $C^{5''}$), 129.2 ($C^{3'}$, $C^{5'}$), 141.8 (C^4, $C^{4''}$), 142.0 ($C^{4'}$) 150.7 (C^6, $C^{6''}$), 151.8 (C^2, $C^{2''}$) 157.4 ($C^{2'}$, $C^{6'}$). Mass: correct isotope pattern for $[M - Cl - 2H_2O]^{+\cdot}$ with m/z 354 for ^{106}Pd.

X-ray Data Collection and Structure Refinement

A crystal of 1 with dimensions 0.35 × 0.04 × 0.50 mm was measured on an Enraf Nonius CAD 4 diffractometer by employing graphite monochromated Mo Kα radiation. The crystal is triclinic, space group $P\bar{1}$ with $a = 8.723(5)$, $b = 9.422(5)$, $c = 11.292(7)$ Å, $\alpha = 113.86(7)$, $\beta = 90.23(6)$, $\gamma = 108.50(7)^\circ$, $V = 795.5(7)$ Å^3, $Z = 2$, $D_x = 1.56$ g cm^{-1}, μ(Mo Kα) = 13.1 cm^{-1}. A total of 4602 reflections were collected in the range $2.2^\circ < 2\theta < 60^\circ$ ($-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 15$) of which 3215 reflections with $I > 2.5\sigma(I)$ were used in the structure determination. The structure was solved by means of a Patterson-Minimum-Function based on the Pd and Cl positions. The remaining non-hydrogen atoms were found in subsequent difference Fourier syntheses. The hydrogen atoms of C1 were found and the positions of the other hydrogen atoms were calculated. The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were not refined. Refinement proceeded through anisotropic block-diagonal least-squares calculations employing a weighting scheme, $w = (4.74 + F_{obs} + 0.026F_{obs}^2)^{-1}$. An empirical absorption correction (DIFABS) [10] was used and an extinction correction was applied [11]. The anomalous dispersion of Pd and Cl were taken into account. Convergence to $R = 0.055$ and $R_w = 0.088$ was obtained. Calculations were carried out with XRAY 76 [12]. Scattering factors were taken from ref. 13, the dispersion corrections from ref. 14.

A crystal of compound 2, with dimensions 0.03 × 0.20 × 0.45 mm was measured in the same way as complex 1. The crystal is monoclinic, space group $P2_1/a$, with $a = 16.174(5)$, $b = 12.997(4)$, $c = 8.086(3)$ Å, $\beta = 100.56^\circ$, $V = 1671(1)$ Å^3, $D_x = 1.69$ g cm^{-1}, μ(Mo Kα) = 12.68 cm^{-1}, $Z = 4$. A total of 2927 reflections were collected in the range $2.2^\circ < 2\theta < 50^\circ$ ($-19 \leqslant h \leqslant 19$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 19$) of which 1712 reflections with $I > 2.5\sigma(I)$ were used in the structure determination. The structure was solved in a way similar to 1, except that the hydrogen atoms were refined isotropically. A weighting scheme $w = (4.14 + F_{obs} + 0.052F_{obs}^2)^{-1}$ was used. Convergence was reached at $R = 0.048$ and $R_w = 0.054$.

Results and Discussion

The compounds 1 [(σ^2-N,N'-iPr-DIP)Pd(Me)Cl] and 2 [(σ^3-N,N',N''-Terpy)Pd(Me)]$^+$Cl$^-$ have been prepared by substitution of the diene in (COD)Pd-(Me)Cl by the potentially tridentate coordinating nitrogen ligands 1a and 2a, respectively. The flexible trinitrogen ligand 1a is introduced here for the first time. The compounds 1 and 2 represent new organopalladium(II) complexes stabilized by di- and tricoordinate trinitrogen ligands. The synthesis of the iodide analogue of 2 has been briefly reported together with other compounds [6], but no spectroscopic, structural or reactivity parameters were known.

The solid state structures of 1 and 2 with the adopted numbering scheme are shown in Figs. 1 and 2. Both contain a methyl group that is σ-bonded to Pd(II). The main difference in the structural features of these compounds is the fact that the tridentate iPr-DIP ligand in 1 is σ^2-chelating, whereas in 2 the Terpy ligand is σ^3-coordinate to Pd(II); hence, a neutral Pd-entity is present in 1, whereas 2 contains a cationic [(Terpy)palladium(methyl)]$^+$ entity.

The basic geometric features around palladium in these compounds comprise a square planar configuration. In 1, the Pd–Cl vector points +14° and the Pd–Me vector +5° out of the coordination plane. Such an exceptional distortion is not found in other, similar compounds [15]. Its origin, which cannot be due to any intramolecular or intermolecular hydrogen bonding or steric interactions, remains unclear. In the cationic part of 2, the palladium centre is held in a rigid square planar environment with the three

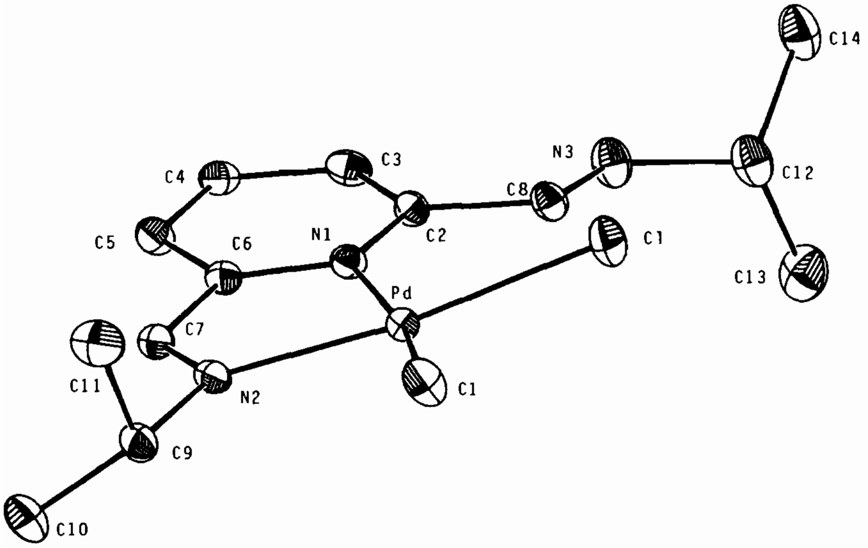

Fig. 1. ORTEP view of the molecular structure of 1. Selected bond lengths (Å) and bond angles (°): Pd–Cl, 2.324(3); Pd–C(1), 2.01(1); Pd–N(1), 2.270(7); Pd–N(2), 2.065(6); N(1)–C(6), 1.339(9); C(6)–C(7), 1.46(1); N(2)–C(7), 1.27(1); C(1)–Pd–Cl, 85.1(3); Cl–Pd–N(1), 102.2(2); N(1)–Pd–N(2), 78.2(3); N(2)–Pd–C(1), 94.2(3); Pd–N(1)–C(6), 107.7(5); N(1)–C(6)–C(7), 117.5(8); C(6)–C(7)–N(2), 121.8(7); Pd–N(2)–C(7), 114.8(5).

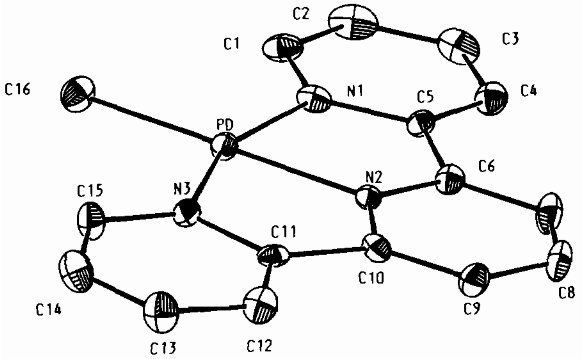

Fig. 2. ORTEP view of the molecular structure of 2. Selected bond lengths (Å) and bond angles (°): Pd–C(16), 2.041(12); Pd–N(1), 2.048(9); Pd–N(2), 2.007(7); Pd–N(3), 2.057(8); C(5)–C(6), 1.489(15); C(10)–C(11), 1.486(14); C(16)–Pd–N(1), 100.6(4); N(1)–Pd–N(2), 79.8(3); N(2)–Pd–N(3), 79.8(3); N(3)–Pd–C(16), 99.8(4); Pd–N(1)–C(5), 113.7(7); N(1)–C(5)–C(6), 114.8(8), C(5)–C(6)–N(2), 113.5(9); C(6)–N(2)–Pd, 118.1(7); Pd–N(2)–C(10), 118.3(6); N(2)–C(10)–C(11), 112.5(8); C(10)–C(11)–N(3), 116.2(9); Pd–N(3)–C(11), 113.0(6).

nitrogen atoms; the methyl-carbon atom and the palladium atom are exactly confined to one plane. The pyridine entities and methyl group make only small angles of 1.7° and 0.9°, respectively, with the coordination plane. The N–Pd–N′ angles are 80°; such a narrowing compared to the ideal value must be attributed to constraints imposed by the rigidity of the ligand, not allowing mutual perpendicular positions within the coordination plane. Further, all bond lengths and angles are within the range normally observed in comparable structural subunits (e.g. the $[(\mathrm{Terpy})\mathrm{PdCl}]^+$ cation [16]) and the Pd–C(16) distance of 2.041(12) Å in 2 represents a normal Pd–CH_3 bond. The cationic Pd(II) unit in 2 is flanked by well-defined chlorine–water strings (not shown). There are no intramolecular interactions between Pd and any other atom, minimum distances being 4.35 Å.

The fact that the Terpy ligand **2a** imposes tridentate coordination, whereas the iPr-DIP ligand **1a** coordinates in a σ^2-fashion can be explained by the relative rigidity of the Terpy molecule and the associated π-backbonding capacity of its large planar molecular π-framework when compared to that of iPr-DIP. The conformational rigidity of the Terpy system does not allow bidentate coordination of **2a** to occur, because the third nitrogen atom is held in the proximity of the metal centre once two nitrogen atoms are coordinated. Any other conformation would involve severe steric hindrance of py-ring H atoms with the Pd–Me group and/or loss of mutual conjugation of pyridine moieties. This constraint is not present in **1a**, where restricted rotation around the pyridine-to-imine C–C bond is possible.

Compound **1** is only slightly soluble in benzene, THF, acetonitrile and methanol but quite soluble in CH_2Cl_2 and $CHCl_3$. Complex **2** is insoluble in most of these solvents and dissolves to a reasonable extent only in polar solvents such as water and methanol, less in DMSO, but not in nitromethane. In water it appeared to be stable during months; even in boiling water **2** retained its structural integrity, whereas other compounds of the type $L_2Pd(Me)Cl$ (L_2 = bipy, R-DAB, iPr-DIP, etc) show limited stability toward decomposition into Pd(0) and organic compounds in solution at room temperature [17]. The solubility and stability of 2 in water provides a potential opening to homogeneous catalysis in water or to phase-transfer catalysis.

Compound 1 reacts very rapidly and quantitatively with CO at −50 °C in deuteriochloroform, yielding the acyl–palladium(II) complex (iPr-DIP)Pd(C(O)-Me)Cl, as was judged from its ^{1}H NMR (2.26 ppm s, 3H for *Me*C(O)Pd) and IR (ν(CO) 1630 and 1650 cm^{-1}) spectra. This compound is not very stable in solution and decomposes within a few hours at room temperature (within 24 h at −50 °C). When compound 1 is treated with silver triflate in CH_2Cl_2/pentane, a new compound **1b** is obtained in solution. According to its IR and ^{1}H NMR spectra this compound is $[(\sigma^3\text{-}N,N',N''\text{-iPr-DIP})PdMe]^+OTf^-$, in which the iPr-DIP ligand is coordinated to palladium in the tridentate σ^3-N_3-mode. So, a structural analogue of 2 can easily be obtained from 1 using a weakly coordinating anion instead of chloride. Attempted carbonylation of this complex in $CDCl_3$ led to immediate decomposition as judged from the rapid formation of Pd°.

Quantitative formation of the acyl complex [(Terpy)PdC(O)Me]Cl was achieved at 20 °C within a few minutes when incubating 2 with CO in MeOH or MeOH-d_4 in an NMR tube. Carbonylation of 2 could also be achieved in H_2O as the solvent. In water, fast and almost complete carbonylation was achieved within 30 min when CO was slowly bubbled into the solution. As the conformational inflexibility of the Terpy ligand precludes the creation of a free coordination site within the coordination plane at Pd(II), coordination of CO prior to the formation of the acyl–Pd species must involve a five-coordinate intermediate. The resulting Pd(II)–acyl complex is stable with regard to deinsertion of CO, i.e. passing a rapid stream of nitrogen through the solution did not cause a decrease of the acyl-CH_3 peak in the ^{1}H NMR.

Compound 1 shows fluxionality on the NMR timescale; at 298 K the ^{1}H NMR spectrum at 2.35 Tesla shows broad resonances due to intermediate exchange. The exchange process can be slowed down by cooling and at 233 K the limit of slow exchange in dichloromethane was reached; two well-resolved septets at 3.82 and 4.18 ppm emerge for each of the uncoordinated and coordinated *N*-isopropyl methine protons, respectively. The fast exchange limit was reached at 333 K in acetonitrile, a septet at 4.00 ppm being observed. Similar behaviour of the isopropyl-methyl doublets, pyridyl-H and imine N=C*H* resonances was observed. In the ^{13}C NMR, intermediate exchange has been observed at 298 K as well. Most likely, a process involving an on/off movement of the imino groups to Pd is taking place. Adding free **1a** to the solution had no influence on the dynamics, so an intramolecular exchange process is operative. Whether this process proceeds through an associative or dissociative sequence has as yet to be established.

The mechanism of the described CO-insertion reactions as well as their catalytic implications are currently being investigated.

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