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A five coordinate Pd^{II} complex stable in solution and in the solid state

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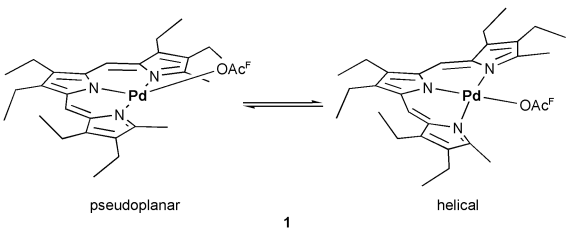
The treatment of the strained complex TrpyPdOAc^F 1 with NaBAr^F, followed by the addition of trimethylphosphine, yields the stable cationic 16VE- or 18VE-complexes 3 and 4, depending on the amount of phosphane added.

Pd^{II} ions usually form very stable square planar 16VE complexes due to a high energy non-occupied $4d_{x^2-y^2}$ orbital. Ligand exchange reactions on these tetracoordinate complexes always proceed *via* an associative mechanism, with a square-pyramidal or trigonal-bipyramidal 18VE species being the reactive intermediates.[1] Amatore and Jutand have recently shown by electrochemical methods, that anionic 18VE complexes play a major role in all important palladium catalysed C–C coupling reactions.[2] In the past, many such five-coordinate Pd^{II} species have been characterised in the solid state by X-ray diffraction. In solution, however, these compounds are mainly dissociated, and only four-coordinate 16VE species could be observed directly.

We have attempted to prepare a five-coordinate Pd^{II} complex, which is stable towards dissociation, by destabilising the respective 16VE species. Pd^{II} complexes of the new tripyrrin ligands[3] are of particular use in this regard, since the terminal functionalities at the $C_{14}N_3$ backbone are positioned directly in the donor plane of square-planar metal complexes, and effectively shield the space segment required for the binding of the fourth donor. As we have shown earlier on methyl terminated palladium tripyrrinates, the desired destabilisation of a four-coordinate Pd^{II} ion originates as a consequence of the steric interaction between the fourth ligand and the methyl termini, and becomes visible in strained, non-planar coordination modes and a fluxional behaviour (Scheme 1).[4]

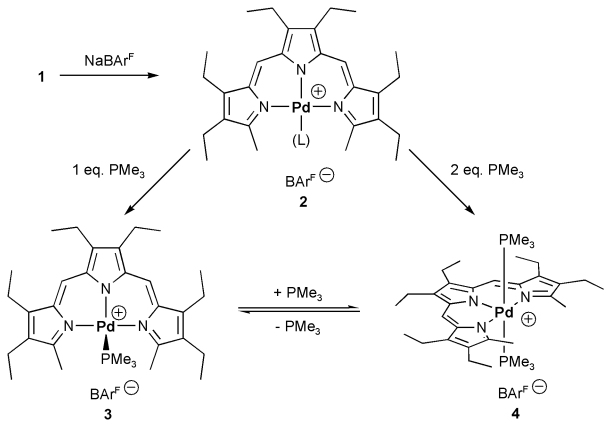
Starting from the neutral trifluoroacetate complex **1** we sought to optimize the effect of destabilisation by exchanging the trifluoroacetate ligand against the more bulky PMe_3 donor. This was performed in two steps. Salt metathesis of **1** with NaBAr^F (sodium tetrakis[3,5-bis(trifluormethyl)phenyl]borate[5]) quantitatively gave the cationic complex **2** (most likely with L = CH_2Cl_2) as a green solution. This solution of **2** was filtered from precipitated sodium trifluoroacetate and then treated with trimethylphosphine to produce the mono- and diphosphane complexes **3**[6] and **4**,[7] respectively, depending on the amount of phosphane used (Scheme 2). No excess phosphane was necessary to obtain the 18VE species **4**. Both new complexes **3** and **4** were analysed by X-ray diffraction. The molecular structures and selected data of the respective cations are shown in Figs. 1 and 2.



Scheme 1 Fluxional structure of the strained tripyrrin complex TrpyPd-OAc^F **1**.

The cationic monophosphane complex **3**[8] displays the expected pseudoplanar coordination geometry at the Pd^{II} centre. As indicated by the N(2)–Pd–P angle of 141.48°, the PdN_3P core of **3** deviates markedly from planarity. The phosphane-···tripyrrin distances C(1)···C(30) and C(16)···C(30) are as short as 3.591 and 3.450 Å, and the methyl termini of **3** are bent out of the planes of the adjacent pyrrole moieties by 7.6° [C(1)] and 9.0° [C(16)], respectively. This data accounts for a large amount of intramolecular strain, equal to a significant destabilisation of the 16VE species.

The molecular structure of the 18VE diphosphane complex **4**[9] shows a non-strained square-pyramidal coordination of the Pd^{II} ion with two equatorial P donors *trans* to each other and with the central N(2) in the apical position. Within the PdN_3P_2 polyhedron the angles deviate from the ideal 90° by a maximum of 5.1°. The deviation from the mean square plane through N(1), N(3), P(1) and P(2) is small (0.132 Å), and the Pd^{II} ion is located undistorted in the centre of this plane. Due to the antibonding interaction of the lone pair of N(2) with the filled d_{z^2} orbital at



Scheme 2 PMe_3 addition to $[TrpyPd(L)]^+BAr_F^-$ **2**.

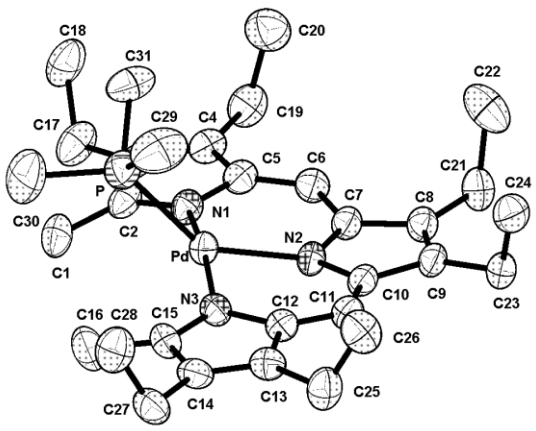


Fig. 1 ORTEP plot of the molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Pd–N1 2.020(3), Pd–N2 2.052(3), Pd–N3 2.021(3), Pd–P 2.3136(12), N1–Pd–N3 167.90(12), N2–Pd–P 141.48(8).

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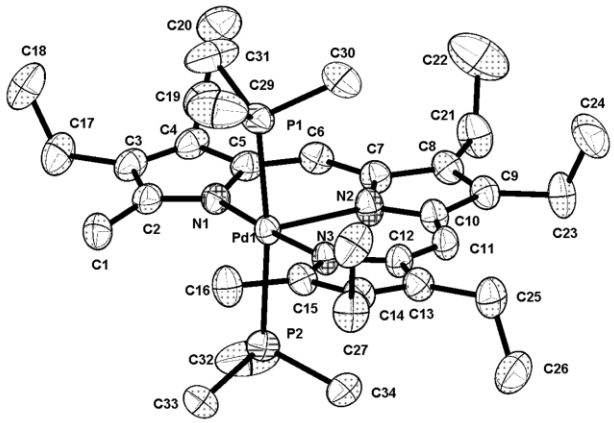

Fig. 2 ORTEP plot of the molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Pd–N1 2.0410(18), Pd–N2 2.298(2), Pd–N3 2.0354(18), Pd–P1 2.3337(7), Pd–P2 2.3207(6), N1–Pd–N3 175.97(7), P1–Pd–P2 170.15(2), N2–Pd–P1 94.44(6), N2–Pd–P2 95.10(6).

palladium the Pd–N(2) bond is elongated by ~0.3 Å to 2.298 Å.

The stepwise association of trimethylphosphine to the cation **2** in solution can easily be monitored by ^{1}H- and ^{31}P-NMR, respectively. The ^{31}P-NMR resonance shows a low-field shift from −23.1 ppm to −18.8 ppm upon going from the tetra- to the pentacoordinate species. The same process is indicated in the proton NMR by a high-field shift and change in habitus of the PMe_3-proton resonance from 1.23 ppm (doublet, **3**) to 0.71 ppm (pseudotriplet, **4**). No free phosphane was detected in either spectra. These NMR results prove the five-coordinate structure of **4** to be stable in solution.

Of particular interest is the seemingly paradoxical finding, that the coordination number of a metal ion can be *increased* by *decreasing* the number of accessible coordination sites. This aspect is the major difference to the usual approach of blocking coordination sites by large, bulky substituents, which always renders higher coordination numbers sterically impossible. The use of small, well-positioned substituents to introduce steric repulsion only at very small segments of the coordination sphere of a metal ion may be a generally applicable method for the stabilisation of "reactive" intermediates. We are currently investigating this opportunity in our laboratory.

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6 *Spectroscopic data* for **3**: mp. 160 °C (decomp.); ^{1}H NMR (CD_2Cl_2): δ = 1.09 (t, 6H, ^{3}J = 7.6 Hz, 2 × CH_2CH_3), 1.18 (t, 6H, ^{3}J = 7.6 Hz, 2 × CH_2CH_3), 1.21 (t, 6H, ^{3}J = 7.6 Hz, 2 × CH_2CH_3), 1.33 [d, 9H, $^{2}J_{PH}$ = 11.4 Hz, $P(CH_3)_3$], 2.42 (q, 4H, ^{3}J = 7.6 Hz, 2 × CH_2CH_3), 2.65 (q, 8H, ^{3}J = 7.6 Hz, 4 × CH_2CH_3), 2.69 (s, 6H, 2 × terminal CH_3), 6.92 (s, 2H, 2 × *meso*-H), 7.58 (s, 4H, 4 × *para*-H), 7.75 (s, 8H, 8 × *ortho*-H); ^{13}C NMR (CD_2Cl_2): δ = 14.7, 16.9, 17.2, 17.6, 17.9, 18.0, 18.5, 20.8 [q, $^{1}J_{CP}$ = 10.5 Hz, $P(CH_3)_3$], 117.9 (s, 4 × *para*-C), 120.9, 125.0 (q, $^{1}J_{CF}$ = 272.7 Hz, 8 × CF_3), 129.3 (qq, $^{2}J_{CF}$ = 31.5 Hz, $^{2}J_{CF}$ = 2.9 Hz, 8 × *meta*-C), 135.2 (s, 8 × *ortho*-C), 138.0, 138.8, 139.0, 140.1, 150.9, 162.1 (q, $^{1}J_{BC}$ = 49.9 Hz, 4 × *ipso*-C), 170.4; ^{19}F NMR (CD_2Cl_2): δ = −62.6; ^{31}P NMR (CD_2Cl_2): δ = −23.1; MS (FAB): *m*/*z* 598 [M − BAr^F]$^+$; calc. for $C_{63}H_{59}BF_{24}N_3PPd$ × 2 CH_2Cl_2: C 47.83, H 3.89, N 2.57; found: C 47.47, H 3.63, N 2.47%.

7 *Spectroscopic data* for **4**: mp. 129 °C (decomp.); ^{1}H NMR (CD_2Cl_2): δ = 0.71 (pseudotriplet, 18H, 6 × PCH_3), 1.08 (t, 6H, ^{3}J = 7.6 Hz, 2 × CH_2CH_3), 1.17, 1.20 (2 × t, 12H, ^{3}J = 7.6 Hz, 4 × CH_2CH_3), 2.43 (q, 4H, ^{3}J = 7.6 Hz, 2 × CH_2CH_3), 2.66, 2.69 (2 × q, 8H, 4 × CH_2CH_3), 2.80 (s, 6H, 2 × terminal CH_3), 7.06 (s, 2H, 2 × *meso*-H), 7.57 (s, 4H, 4 × *para*-H), 7.73 (s, 8H, 8 × *ortho*-H); ^{13}C NMR (CD_2Cl_2): δ = 13.6 [vt, *N* = 25.4 Hz, 2 × $P(CH_3)_3$], 15.1, 17.6, 17.7, 18.1, 18.6, 18.8, 20.2, 117.9 (s, 4 × *para*-C), 123.1, 125.0 (q, $^{1}J_{CF}$ = 272.6 Hz, 8 × CF_3), 129.4 (q, $^{2}J_{CF}$ = 31.5 Hz, 8 × *meta*-C), 135.2 (s, 8 × *ortho*-C), 135.7, 139.0, 140.1, 144.1, 152.4, 162.1 (q, $^{1}J_{BC}$ = 49.8 Hz, 4 × *ipso*-C), 168.3; ^{19}F NMR (CD_2Cl_2): δ = −62.7; ^{31}P NMR (CD_2Cl_2): δ = −18.8; MS (FAB): *m*/*z* 674 [M − BAr^F]$^+$; calc. for $C_{66}H_{68}BF_{24}N_3P_2Pd$ × CH_2Cl_2: C 48.83, H 4.22, N 2.59; found: C 49.10, H 4.16, N 2.47%.

8 *Crystal data* for $C_{63}H_{59}BF_{24}N_3PPd$ **3**: violet blocks, *M* = 1462.31, monoclinic, space group *P* $2_1/c$, *a* = 12.9944(11), *b* = 20.5527(17), *c* = 25.0962(21) Å, β = 104.331(1)°, *U* = 6493.9(9) Å^3, *Z* = 4, D_c = 1.496 g cm^{-3}, μ = 0.421 mm^{-1}, *F*(000) = 2960, 66958 reflections collected (1.30 < θ < 26.37°) at 173(2) K, 13271 independent (R_{int} = 0.0619), 10167 used in the structure refinement; R_1 = 0.0630 [$I > 2\sigma(I)$], wR_2 = 0.1456 (all data), GOF = 1.099 for 1048 parameters and 6 restraints, largest difference peak, hole = 0.847, −0.517 e Å^{-3}. CCDC 195926. See http://www.rsc.org/suppdata/cc/b3/b305547g/ for crystallographic data in .cif or other electronic format.

9 *Crystal data* for $C_{66}H_{68}BF_{24}N_3P_2Pd$ **4**: violet blocks, *M* = 1538.38, triclinic, space group *P* $\bar{1}$, *a* = 14.5341(11), *b* = 15.1714(11), *c* = 17.1442(12) Å, α = 95.9710(10), β = 97.2310(10), γ = 105.8260(10)°, *U* = 3570.0(4) Å^3, *Z* = 2, D_c = 1.431 g cm^{-3}, μ = 0.408 mm^{-1}, *F*(000) = 1564, 67837 reflections collected (1.21 < θ < 26.37°) at 173(2) K, 14572 independent (R_{int} = 0.0257), 13891 used in the structure refinement; R_1 = 0.0423 [$I > 2\sigma(I)$], wR_2 = 0.1012 (all data), GOF = 1.143 for 1056 parameters and 0 restraints, largest difference peak, hole = 0.652, −0.413 e Å^{-3}. CCDC 195925. See http://www.rsc.org/suppdata/cc/b3/b305547g/ for crystallographic data in .cif or other electronic format.