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Unprecedented eight-palladium(I) crown-cycle with metal–metal unsupported bonds

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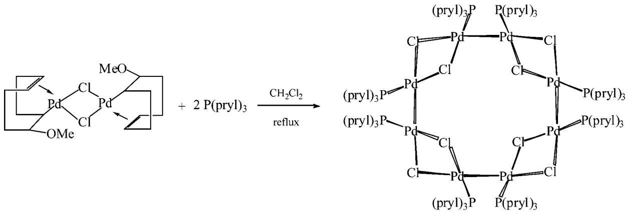
Tri(*N*-pyrrolyl)phosphine reacted with the σ/π complex [Pd(μ-Cl)(COD–MeO)]$_2$ to give the octa-cycle [Pd(μ-Cl){P(pyrl)$_3$}]$_8$ containing four Pd(I)–Pd(I) unbridged bonds.

Phosphine ligands have been widely used in coordination chemistry, organometallic chemistry, and homogeneous catalysis and the study of the limits of the donor/acceptor properties of this general class of ligands is an area of current interest.[1] Surprisingly, *N*-pyrrolylphosphines, which show exceptional π-acceptor character are an unexploited class of phosphine ligands.[2] In fact, the π-acid character of P(pyrl)$_3$ is comparable in strength to that of PF$_3$, according to a density functional study on [Fe(CO)$_4$(PR$_3$)] complexes.[3] However this contrasts with experimental studies revealing that the π-acidity of P(pyrl)$_3$ is only approximately two-thirds the π-acidity of P(OR)$_3$ and half that of P(O-*p*-XC$_6$H$_4$).[4] This electron withdrawing ability is attributed to the high electronegativity of nitrogen, enhanced by the delocalization of the nitrogen lone pair into the aromatic π-system. Only a few examples of coordination compounds of transition metals stabilized with P(pyrl)$_3$ are known,[5] but no palladium complexes of this kind have been reported to date. The fact that organophosphorus ligands with high π-acidity have been shown to be crucial in several homogeneous catalytic reactions[1] lead us to investigate the synthesis, structure and reactivity of palladium compounds containing tri(*N*-pyrrolyl)phosphine as stabilizer.

One strategy for the synthesis of phosphine palladium(0) compounds consists of the displacement of dba (dibenzylideneacetone) from palladium/dba complexes with phosphines.[6] Here, stirring a toluene solution of Pd$_2$(dba)$_3$ with P(pyrl)$_3$, gave metallic palladium along with a grayish precipitate whose IR spectrum revealed it to be polypyrrole. Despite varying the conditions (solvents, temperature, time of reaction) we were unable to successfully prepare any tri(*N*-pyrrolyl)phosphine-containing palladium(0) species. We therefore next tried the synthesis of the related palladium(II) complexes by using a well established methodology for this type of derivative: the substitution of the COD ligand from [PdCl$_2$(COD)] by the phosphine P(pyrl)$_3$. [PdCl$_2$(COD)] readily reacted with P(pyrl)$_3$ in CH$_2$Cl$_2$ at room temperature to produce a high yield of the orange complex [PdCl$_2${P(pyrl)$_3$}$_2$](**1**) and, thankfully, no polymerisation products were observed. The reaction was monitored by ^{31}P NMR spectroscopy which showed only one signal at δ 71.7 ppm. **1** was fully spectroscopically characterized.[7] Given that P(pyrl)$_3$ is able to displace the COD ligand bonded to a palladium(II) center, the question emerged as to whether this process would also occur when the three-electron ligand COD–MeO, which acts as a σ/π ligand in [Pd(μ-Cl)(COD–MeO)]$_2$, is used instead. In particular, we were interested in the possibility of isolating a palladium compound containing, along with the tri(*N*-pyrrolyl)phosphine, an alkyl group directly bonded to the palladium. It is remarkable that the only precedent in organometallic chemistry is the aryl osmium complex [OsH(*p*-tolyl)(CO){P(pyrl)$_3$}(PPh$_3$)$_2$].[8] Thus, the reaction of a solution of [Pd(μ-Cl)(COD–MeO)]$_2$ in CH$_2$Cl$_2$ with two equivalents of P(pyrl)$_3$ produced good yields of deep red crystals of [Pd(μ-Cl){P(pyrl)$_3$}]$_8$ (**2**)[9] (see Scheme 1) according to MS-MALDI TOF spectrometry (m/z = 2968 (M$^+$)) and elemental analyses. It is interesting to note that the same process carried out with triphenylphosphine gave an intractable mixture of products.

A single-crystal X-ray analysis of compound **2** demonstrated that the molecule is a cyclo-octanuclear palladium(I) complex in which four unbridged dipalladium(I) units, Pd$_2${P(pyrl)$_3$}$_2$, are linked by means of bridging chlorine atoms (Fig. 1).[10] The molecule as a whole is formed by the union of two half moieties related by a C_2 axis, but the crystallographic independent part is clearly asymmetric. In the crystal structure six CH$_2$Cl$_2$ and half a molecule of hexane solvent are present for each cycle. The eight Pd atoms are located in two almost parallel planes (dihedral angle 8.2°) and the distance between the centroids of the two sets of Pd atoms is 1.30 Å. The alternate asymmetrical Pd$_2$Cl$_2$ bridged system shows one chlorine atom tilted to the center of the cycle and the other (*trans* to



Scheme 1

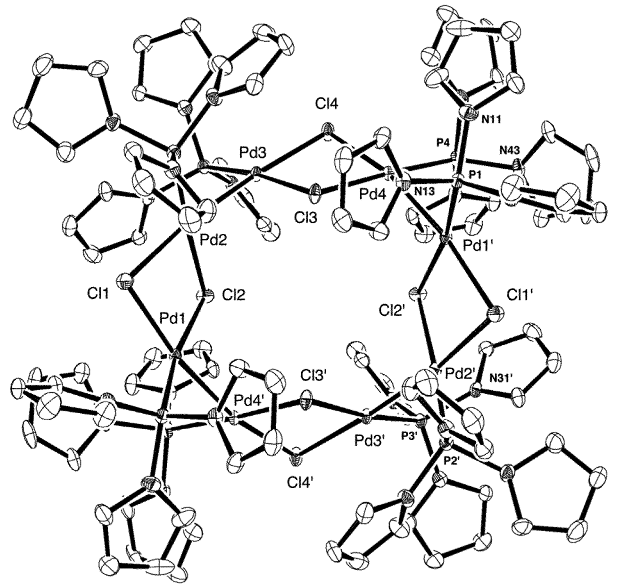


Fig. 1 Ortep drawing of compound **2**. Selected distances (Å) and angles (°): Pd(1)–Pd(4) 2.5322(7); Pd(2)–Pd(3) 2.5162(8); Pd(1)–Cl(2) 2.392(1); Pd(1)–Cl(1) 2.436(1); Pd(2)–Cl(2) 2.385(1); Pd(2)–Cl(1) 2.438(1); Pd(3)–Cl(3) 2.394(1); Pd(3)–Cl(4) 2.432(1); Pd(4)–Cl(3) 2.381(1); Pd(4)–Cl(4) 2.436(1); Pd(1)–P(1) 2.181(2); Pd(2)–P(2) 2.178(1); Pd(3)–P(3) 2.175(2); Pd(4)–P(4) 2.1860(2). Cl(2)–Pd(1)–Cl(1) 87.22(5); Cl(2)–Pd(2)–Cl(1) 87.33(5); Cl(3)–Pd(3)–Cl(4) 87.47(5); Cl(3)–Pd(4)–Cl(4) 87.67(5); Pd(1)–Cl(1)–Pd(2) 87.68(5); Pd(2)–Cl(2)–Pd(1) 89.91(5); Pd(4)–Cl(3)–Pd(3) 91.49(5); Pd(3)–Cl(4)–Pd(4) 89.24(5).

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Pd–Pd bonds) tilted out of it. The crown cycle forms a cavity of approximately 7.1 Å in diameter reduced on each face by the two inner chlorine atoms separated by 5.3 Å, and by two pyrrole rings. The cycles are staggered, thus creating some unexpected channels. It is noticeable that molecules of hexane solvent are found within these channels, although no interaction more involved than van der Waals was observed. Instead, some short interactions were found with the CH_2Cl_2. In **2**, each Pd atom supports a tri(*N*-pyrrolyl)phosphine ligand, the final geometry around the Pd being slightly distorted square-planar. The coordination planes between the directly bonded Pd atoms are staggered with the dihedral angles: plane Pd(1)–plane Pd(4) = 81.64(3)° and plane Pd(2)–plane Pd(3) = 77.59(2)°. Unbridged Pd(1)–Pd(4) and Pd(3)–Pd(2) bond lengths are 2.5322 Å and 2.5162 Å respectively, the latter being the shortest found in a dipalladium(I) system.[11] On the other hand, Pd(1)–Pd(2) and Pd(3)–Pd(4) distances, of approximately 3.4 Å, exclude the presence of metal–metal bonds.

Two sets of Pd–Cl distances can be observed: Pd–Cl *trans* to $P(pyrl)_3$ (average 2.388 Å) and Pd–Cl *trans* to the Pd–Pd bond (average 2.435 Å). The lengthening of the latter distance can be attributed to the high *trans* influence of the Pd–Pd bond as reported for the corner-sharing complex $[PdI(MeNC)_2]_2$.[12] The Pd–P bond distances, ranging from 2.175(2) to 2.186(2) Å, were shorter than that described for the unique palladium complex containing the mixed cyanopyrrolylphosphine ligand, $P(pyrl)_2(o\text{-}NC_4H_3\text{–}CN)$, $[PdCl_2\{P(pyrl)_2(o\text{-}NC_4H_3\text{–}CN)\}_2]$ (2.292 Å).[13]

It is remarkable that, in contrast with the structural features displayed by **2**, the only eight-Pd(I) cycle described up to now shows double-bridged Pd–Pd bonds.[14]

Finally, we investigated the reaction of **2** with eight equivalents of $P(pyrl)_3$ in CH_2Cl_2 at 0 °C. The solution rapidly turned orange and metallic palladium was precipitated. The ^{31}P NMR spectrum showed a clean signal at δ 71.7 ppm, which corresponds to $[PdCl_2\{P(pyrl)_3\}_2]$. From these observations we explain the formation of this compound by assuming that the first step consists of the opening of the Pd–Cl–Pd bridges by the phosphine, followed by the disproportionation of the unstable Pd(I) complex $[Pd_2Cl_2\{P(pyrl)_3\}_4]$ into Pd(0) and Pd(II).

Disproportionation is not rare in the chemistry of palladium (I).[15] When PPh_3 was used instead of $P(pyrl)_3$, a mixture of triphenyl- and tri(*N*-pyrrolyl)phosphine-complexes was detected in the ^{31}P NMR spectrum, supporting the proposed mechanism.

In conclusion, we have prepared a high nuclear Pd(I) species with unbridged Pd–Pd bonds which are stabilized by the strong π-acceptor ligand $P(pyrl)_3$. Studies to evaluate the potential use of this complex in the preparation of new Pd(I) complexes as well as in catalysis are in progress.

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7 $[PdCl_2\{P(pyrl)_3\}_2]$ (**1**): to a stirred solution of $P(pyrl)_3$ (0.323 g, 1.410 mmol) in 30 mL of dichloromethane at room temperature, the yellow solid $[PdCl_2(COD)]$ (0.201 g., 0.704 mmol) was added. Immediately the colour of the solution turned from pale yellow to smooth orange. The solution was stirred for 30 min, filtered and then dried in vacuum. The remaining residue was treated with dichloromethane (2 mL) and the product was precipitated by addition of *n*-hexane obtaining an orange powder that was isolated from the solution by filtration. Yield: 0.394 g, 88%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 71.6 ppm (s); ^1H NMR ($CDCl_3$): δ 7.04 (s_{br}, 12H), 6.42 (s_{br}, 12H); ^{13}C NMR ($CDCl_3$): δ 125.2 (s), 114.6 (s); MS (MALDI-TOF): *m/z* 282.3 $[M - 2Cl]^{2+}$; IR: 3137–3118 cm^{-1} (w), 1455 (m), 1186 (vs), 1060 (vs), 730 (vs); Anal. calcd. for $C_{24}H_{24}Cl_2N_6P_2Pd$ (635.55 g mol^{-1}): C: 45.36, H: 3.78, N: 13.22; found C:45.32, H: 3.76, N: 13.18%.

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9 $[Pd(\mu\text{–}Cl)\{P(pyrl)_3\}]_8$ (**2**): A solution of $P(pyrl)_3$ (0.170 g, 0.742 mmol) in 2 mL of dichloromethane was added to a stirred solution of $[PdCl(COD\text{–}OMe)]_2$ (0.208 g, 0.370 mmol) in 30 mL of dichloromethane at 0 °C. The mixture was stirred for a further 15 min at 0 °C and then heated to reflux for 2 h. The resulting deep red solution was concentrated to dryness. The crude was treated with 25 mL of toluene. The solution was filtered, and after addition of 20 mL of *n*-hexane a deep red solid was precipitated, which was washed with *n*-hexane and dried under vacuum. Yield: 0.173 g (62%). Crystals suitable for X-ray analyses were obtained by slow diffusion of *n*-hexane in CH_2Cl_2 solutions of **2**. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 74.6 ppm (s); ^1H NMR ($CDCl_3$): δ 6.85 (br, 48H), 6.35 (br, 48H); ^{13}C NMR ($CDCl_3$): δ 124.45 (br), 113.259 (br). MS (MALDI-TOF): *m/z* 2968 $[M\cdot]^+$, 2932 $[M - Cl]^+$. IR (KBr): 3135 cm^{-1}(w), 1455 (m), 1184 (vs), 1061 (vs), 730 (vs). Anal. calcd. for $C_{96}H_{96}Cl_8N_{24}P_8Pd_8$ C: 38.85, H: 3.23, N: 11.33; found: C: 38.76; H: 3.20; N: 11.3%.

10 Suitable red crystals of **2** were covered with mineral oil and mounted in the N_2 stream of a Bruker–Nonius Kappa CCD difractometer equiped with Mo–Kα radiation (λ = 0.71073 Å) source. The structure was solved by direct methods and refined using full matrix least squares on F^2, some solvent molecules are disordered and were refined isotropically. Crystal data for **2**: $C_{48}H_{48}Cl_4N_{12}P_4Pd_4\cdot 3\,CH_2Cl_2\cdot\frac{1}{4}\,C_6H_{14}$, M_r = 1759.58, monoclinic space group *C*2/*c*, a = 32.541(11), b = 17.474(4), c = 24.144(2) Å; β = 101.25(1)°; U = 13465(6) $Å^3$, T = 150 K, , Z = 8; d_{calc} = 1.736 g cm^{-3}, μ(Mo–Kα) = 1.588 mm^{-1}, 13853 unique reflections measured, 10142 with $I > 2\sigma(I)$ were used in all calculations. wR_2 = 0.1191, R = 0.0504. CCDC 235281. See http://www.rsc.org/suppdata/cc/b4/b405532b/ for crystallographic data in .cif or other electronic format.

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