Communications

Cyclometalated Compounds. XVII.[1] The First Threefold Cyclopalladation of a Single Benzene Ring

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*Summary: 1,3,5-Tris(di-2-pyridylamino)benzene (**1**) readily undergoes reaction with palladium acetate or chloride to produce the first example of a triply cyclopalladated benzene ring. The X-ray crystal structure of the trichloro derivative **2** is described.*

When Cope and Siekman, in 1965, first reported[2] the cyclopalladation of azobenzene, they opened the way to the study of a class of compounds that have attracted enormous interest in a wide variety of contexts.[3] Cyclopalladated compounds have since proved useful in organic synthesis,[4] catalysis,[5] material science,[6] and even as bioactive compounds.[7] By varying the donor atoms, ring size, and the nature of the carbon donor, a structurally diverse range of cyclopalladated compounds have been prepared.[3] In recent years, there has been much interest in multiply cyclopalladated compounds, such as those containing two different metalated phenyl rings.[1,8]

In 1971, Trofimenko[9] reported the first examples of the double cyclopalladation of a single benzene ring, but for 20 years these remained the only examples of such compounds. Since 1991 a number of other molecules have been reported that contain doubly cyclopalladated benzene rings.[10] However, to our knowledge no examples exist of the threefold cyclopalladation of a benzene derivative.[11] For some years we have been trying to effect the triple cyclopalladation of various substrates, without success. We now report the successful realization of this aim in the reaction of 1,3,5-tris(di-2-pyridylamino)benzene with palladium chloride or acetate.

Although cyclometalation reactions are known to proceed by a variety of mechanisms,[3d] cyclopalladation reactions of benzene derivatives are generally considered to occur by a simple electrophilic aromatic substitution mechanism. On this basis we hypothesized that 1,3,5-tris(di-2-pyridylamino)benzene (**1**) would be a good candidate for possible threefold cyclopalladation, because of the combined activating effects of the three electron donating amine nitrogens. Furthermore, cyclo-

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[11] A tripalladated mesitylene derivative has recently been prepared by oxidative addition to triiodomesitylene, see: Vicente, J.; Lyakhovych, M.; Bautista, D.; Jones, P. G. *Organometallics* **2001**, *20*, 4695.

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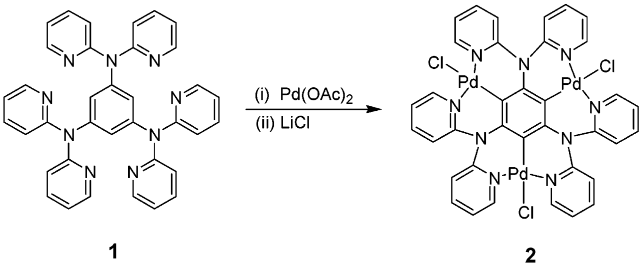
Scheme 1



metalation should be assisted by the formation of N,C,N-pincer-like subunits, which have been highly exploited by van Koten and co-workers.[12] Ligand **1** has recently been synthesized from tribromobenzene and di(2-pyridyl)amine and structurally characterized by X-ray crystallography.[13] Furthermore, zinc(II) chloride and platinum(II) chloride coordination complexes of this ligand have been prepared wherein the ligand bridges three metals with coordination via the pyridine nitrogens only, but without involvement of the central benzene ring.[14]

Undeterred by these results, we proceeded to examine the reaction of **1** with palladium chloride in the presence of 2 M HCl. Pleasingly, this led to the formation of the triply palladated product **2**, albeit in rather poor yield. Subsequently, we found that the yields could be improved by effecting the conversion in a two-step procedure with initial reaction of **1** with palladium acetate in refluxing benzene, followed by metathesis with lithium chloride. Even using this procedure the yields proved somewhat variable, ranging between 10 and 50%. The structure of **2** was initially based on elemental analysis, mass spectrometry, and NMR spectra.[15,16] In particular, the high-symmetry apparent in the ^{1}H and ^{13}C NMR spectra, combined with the absence of any signals for the central benzene ring protons in the ^{1}H NMR spectrum and the existence of four CH and three nonprotonated carbon signals in the ^{13}C NMR spectrum, strongly supported the proposed triply cyclopalladated structure. Subsequently, pale yellow crystals suitable for X-ray structure determination[17] were obtained by vapor diffusion of methanol into a DMSO solution of the crude product.

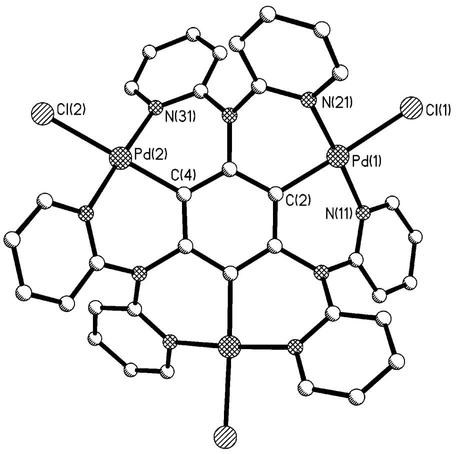


Figure 1. Structure of **2** viewed perpendicular to the tricyclometalated benzene ring. The disordered methanol solvate molecule is omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(2) 1.962(2), Pd(1)−N(11) 2.035(3), Pd(1)−N(21) 2.036(3), Pd(1)−Cl(1) 2.4017(10), Pd(1)−C(4) 1.956(4), Pd(2)−N(31) 2.036(2), Pd(2)−Cl(2) 2.4030(14), C(2)−Pd(1)−N(11) 88.05(10), C(2)−Pd(1)−N(21) 88.62(10); N(11)−Pd(1)−Cl(1) 92.26(7), N(21)−Pd(1)−Cl(1) 91.24(7), C(4)−Pd(2)−N(31) 88.89(6), N(31)−Pd(2)−Cl(2) 91.11(6).

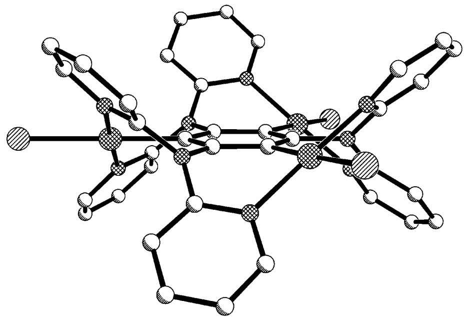


Figure 2. Perspective view of the structure of **2**, viewed from the plane of the benzene ring.

Figure 1 shows a perspective view, with selected atomic labeling, of the crystal structure of **2** which confirms that the ligand **1** has indeed yielded to threefold cyclometalation. The complex crystallizes about a crystallographic twofold rotation axis passing through the central benzene ring and one of the PdCl units. The palladium atoms have square planar geometry with relatively short Pd−C bonds (Figure 1). The threefold cyclometalation process results in the formation of six new six-membered chelate rings fused to the central benzene ring, leading to a coronene-type struc-

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[15] Preparation of **2**: The ligand **1** (20.1 mg, 0.034 mmol) and Pd(OAc)$_2$ (25.7 mg, 0.114 mmol) were refluxed in benzene for 7 days. The benzene was evaporated in vacuo, and the residue taken up in 3:2 acetone−water solution and filtered. An excess of LiCl was added and the solution stirred overnight. The resulting precipitate was collected, washed with water, then ether, and dried under vacuum. ^{1}H NMR analysis of the precipitate indicated a mixture of cyclopalladated compounds containing approximately 45% of the desired tricyclopalladated compound. Vapor diffusion of methanol into a DMSO solution of the precipitate gave pale yellow crystals suitable for X-ray crystallography. Mp: 271−273 °C. ^{1}H NMR (500 MHz, 23 °C, CDCl$_3$): δ 7.10 (t, 6H, H5), 7.49 (d, 6H, H3), 7.78 (t, 6H, H4), 9.18 (d, 6H, H6). ^{13}C NMR (CDCl$_3$): δ 154.1 (CH), 147.7 (C), 139.9 (CH), 132.6 (C), 125.1(C), 120.2 (CH), 120.0 (CH). High-resolution ES-MS: *m/z* calcd for $C_{36}H_{24}N_9Cl_2Pd_3$ ([M − Cl]$^+$) 972.8645, found 972.8638. Anal. Calcd for $C_{36}H_{24}N_9Cl_3Pd_3$·2MeOH: C 42.56, H 3.01, N 11.76. Found: C 41.79, H 2.63, N 11.83.

[16] It is our experience that cyclopalladated compounds frequently give combustion analyses that are low in the found carbon percentage. We believe that this is due to the formation of metal carbides in the combustion process, as has been previously noted for ruthenium complexes of similar ligands; see: Constable, E. C.; Cargill Thompson, A. W. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3467.

[17] Crystal data for **2**: CCD area detector, Mo Kα radiation, graphite monochromator, yellow rod with dimensions 0.60 × 0.35 × 0.29 mm^3, wavelength 0.71073 Å, *T* 168(2) K, 2θ_{max} 52.84°, formula $C_{38}H_{32}Cl_3N_9O_2Pd_3$, fw 1072.28, monoclinic, space group *C*2/*c*, *a* = 12.696(5) Å, *b* = 13.416(5) Å, *c* = 22.649(9) Å, β = 90.887(13)°, *V* 3857(2) Å^3, *Z* = 4, D_{calcd} 1.846 Mg/m^3, μ = 1.640 mm^{-1}, GoF = 1.063, R1[$I > 2\sigma(I)$] = 0.0268, wR2(all data) = 0.0653 for 3960 reflections and 263 parameters with no restraints.

ture. However, unlike coronene itself, the molecule is far from planar, as shown in the alternative view in Figure 2. To avoid steric interactions between adjacent pyridine rings, the molecule possesses internal twisting that results in the pyridine rings being positioned on alternating sides of the central benzene ring. This twisting has the effect of making each individual molecule chiral, although, of course, the crystal itself is racemic. There are no unusually short intermolecular interactions.

In summary, we are delighted to definitively describe the first example of the threefold cyclopalladation reaction of a single benzene ring. We hope that this releases access to a class of interesting new compounds with potential applications in diverse areas of organometallic chemistry.

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Supporting Information Available: Details of the X-ray crystal structure of **2**. This information is available free of charge via the Internet at http://pubs.acs.org.

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