

Quinone Complexes of Palladium: Synthesis and Characterisation of the Dimer $[\text{Pd}_2\{\text{Pd}(\text{dbsq})_2\}_2]$ ($\text{dbsq} = 3,5\text{-di-}t\text{-butyl-1,2-benzoquinone}$) formed by the Reaction between 3,5-Di-*t*-butyl-1,2-benzoquinone and Palladium(0)

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The dimer $[\text{Pd}_2\{\text{Pd}(\text{dbsq})_2\}_2]$ has been prepared by treating a Pd^0 -alkene complex, $[\text{Pd}_2(\text{dba})_3]$ ($\text{dba} = \text{dibenzylideneacetone}$), with 3,5-di-*t*-butyl-1,2-benzoquinone; it has been characterized spectroscopically and by X-ray crystallography.

The co-ordination chemistry of catecholates and semiquinones has been developed extensively with metals of the first transition series.¹⁻⁷ Related complexes prepared with the larger atoms of the second and third row metals have shown marked differences in chemistry and charge distribution.⁸⁻¹⁵ We have been interested in extending this chemistry to the platinum group elements, and particularly to palladium and platinum. The quinone complexes of these metals may be of biological interest as anticancer agents in view of their intercalation properties and support of electron transfer,¹⁶ and as selective spectroscopic probes.¹⁷ Complexes of the metal atoms¹⁸ and the planar quinones¹⁹ separately are known to form stacked one-dimensional conducting systems; this property might be expected to occur in the planar quinone complexes of platinum and palladium.

Catecholates and hydroquinones serve as reducing agents for the divalent platinum and palladium ions giving the neutral metal and free benzoquinone. The reaction between $[\text{PdCl}_4]^{2-}$ and 3,5-di-*t*-butylcatechol in the presence of mild base results in 3,5-di-*t*-butyl-1,2-benzoquinone (dbbq) and Pd metal. In past studies, metal carbonyl complexes have provided convenient synthetic routes to the neutral bis- and tris-quinone complexes by reaction with the benzoquinone form of the ligand. The reaction between $\text{Ni}(\text{CO})_4$ and dbbq gave the Ni^{II} -semiquinone tetramer $[\text{Ni}(\text{dbsq})_2]_4$.⁵ Carbonyl complexes of Pd and Pt are not readily accessible, and a different synthetic procedure had to be designed. The tris(dibenzylideneacetone)dipalladium complex $[\text{Pd}_2(\text{dba})_3]$ ²⁰ and its platinum analogue²¹ can be conveniently prepared as tris(alkene) complexes of the zerovalent metal and may serve in the capacity of a metal carbonyl. The reaction between $[\text{Pd}_2(\text{dba})_3]$ and dbbq produced the solvated $\text{Pd}(\text{dbbq})$ complex in high yield. Magnetic susceptibility measurements at room temperature indicate that the complex is diamagnetic, and in toluene solution it shows no e.p.r. signals. The dark blue complex shows intense bands in the u.v.-visible spectrum at 238 (ϵ 30 000 $\text{l mol}^{-1} \text{cm}^{-1}$), 296 (11 432), 382 (2 500), and 840 nm (6 500). Crystals of the dichloromethane solvate have been investigated crystallographically.[†] The molecule is shown to consist of four palladium atoms and four quinone ligands in the arrangement shown in Figure 1. Two square planar $\text{Pd}(\text{dbsq})_2$ units are bridged by two additional palladium atoms, each bonded to allylic regions of the semiquinone ligands. Within the unit cell there are two crystallographically independent $\text{Pd}_2[\text{Pd}(\text{dbsq})_2]_2$ units, located about inversion

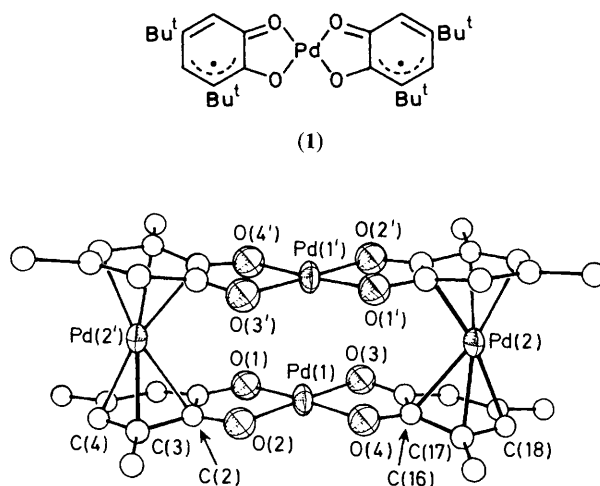


Figure 1. View of one centrosymmetric $[\text{Pd}_2\{\text{Pd}(\text{dbsq})_2\}_2]$ molecule with *t*-butyl methyl carbon atoms omitted; planes of the two $\text{Pd}(\text{dbsq})_2$ units are slipped so that the bis(η^3 -allyl)palladium regions of the dimer are in the form of the *trans*-isomer.

centres, and one molecule of dichloromethane. The square planar geometry of the metal ions and the average Pd-O bond length of 1.99(2) Å are strongly suggestive of Pd^{II} , requiring the semiquinone formulation (1) for the quinone ligands. Bond distances within the ligand rings reflect the allylic character resulting from interaction with the additional palladium atoms. In all four independent quinone ligands, the carbonyl bond to the carbon atom at the 1-position of the 3,5-di-*t*-butyl-1,2-semiquinone ring is shorter [1.28(2) Å] than the C-O bond to C-2 [1.35(2) Å]. A sharp, intense i.r. band at 1580 cm^{-1} may be associated with this carbonyl group. The ring carbon atoms C-2, -3, and -4 bond with the bridging palladium atoms as allylic groups with Pd-C bond lengths ranging from 2.20 to 2.42 Å. These values are relatively large for allylic complexes of Pd^{II} but compare well with Pd(0)-C lengths found for $[\text{Pd}(\text{dba})_3]$ ²² and $[\text{Pd}_2(\text{dba})_3]$.²⁰ The most appropriate charge distribution for the complex appears to be one with paramagnetic semiquinone ligands chelated to Pd^{II} , with neutral Pd^0 atoms bonded to the allylic regions of the ligands in the bonding manner found in bis(η^3 -allyl)palladium.²³ In accord with this assignment, the n.m.r. spectrum of the complex shows paramagnetically broadened and shifted *t*-butyl and ring proton resonances. $[\text{Pd}_2\{\text{Pd}(\text{dbsq})_2\}_2]$ is effectively diamagnetic, owing to semiquinone-semiquinone spin-spin coupling either through the chelated metal ion or through the metal atom bridges. However, n.m.r. is more sensitive to residual paramagnetism at the semiquinone ligands than the magnetic susceptibility measurement. At -80°C in toluene solution $[\text{Pd}_2\{\text{Pd}(\text{dbsq})_2\}_2]$ shows *t*-butyl resonances at 1.43 p.p.m., with half-height width ($w_{1/2}$) 0.15

† Crystal data: $\text{C}_{57}\text{H}_{82}\text{Pd}_4\text{Cl}_2\text{O}_8$, monoclinic, space group $P2_1/c$, $a = 15.534(3)$, $b = 19.978(4)$, $c = 19.604(4)$ Å, $\beta = 91.52(3)^\circ$, $U = 6082(2)$ Å³, $D_c = 1.520$ g cm^{-3} , $Z = 4$, Mo- K_α radiation ($\lambda = 0.71069$ Å). The structure was solved by heavy-atom techniques and refined using 1954 unique, observed [$I > 6\sigma(I)$] reflections; $R = 0.071$, $R_w = 0.085$, goodness of fit = 1.36. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

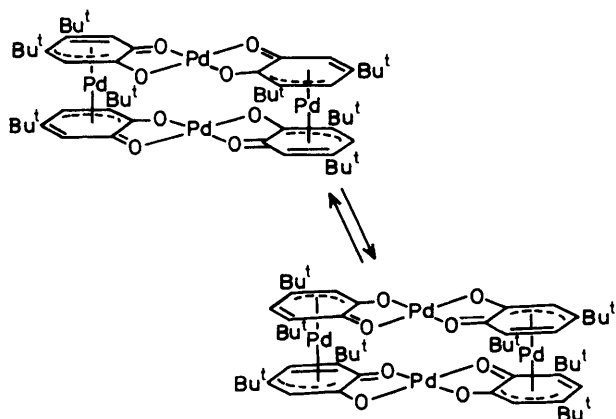


Figure 2

p.p.m., and at 1.14 p.p.m. with $w_{\frac{1}{2}}$ 0.16 p.p.m. As temperature is increased the 1.43 p.p.m. resonance remains essentially unchanged but the 1.14 p.p.m. resonance moves to lower field, across the second resonance. At 100 °C the 1.14 p.p.m. resonance has moved to 3.4 p.p.m. ($w_{\frac{1}{2}}$ 0.25 p.p.m.). A dynamic process where planar complex units move in a direction perpendicular to the bridging atoms to shift the allylic region from the C-2, -3, and -4 to the C-1, -6, and -5 may affect the resolution of the n.m.r. spectrum (Figure 2). However, both forms of the complex should exhibit two t-butyl resonances, and there is no spectral evidence for such a process or for the presence of other isomeric forms of the complex, even at low temperature.

Features of this complex demonstrate a mode of bridged co-ordination which may prove significant in the study of stacked, planar quinone complexes. Also, antiferromagnetic coupling of paramagnetic organic ligands, propagated through a diamagnetic metal, exists as an interesting reversal of the more usual magnetic exchange between ligand-bridged paramagnetic metal ions.

This research was supported by the National Science Foundation (grant CHE 85-03222).

Received, 22nd December 1987; Com. 1833

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