still partially hydrated or in strong interaction with the anion. Similar structural features are present in the Ba^{2+} salt of antibiotic X-537A[10] in which, however, the hydrophobic exterior is large in comparison with that of ligands I and II.

The structure of A shows that ligand I can only partially remove the hydration sphere of barium whereas it generally replaces completely the hydration spheres of the alkali metal ions. In the solid-state structures of the alkali metal cryptates of ligand I, the cation is located within the molecular cage and is surrounded only by the eight heteroatoms. The metal ion does not interact appreciably with the anion or with water molecules when the latter are present. In all the compounds studied so far, metal–anion or metal–H_2O distances are greater than 3.5 Å.[4,11]

The structural data suggest also that the selectivity of ligand I for the Ba^{2+} ion is higher than that of ligand II. A higher coordination number is observed for the cation in B but as a result of the geometrical constraints the distances between the cation and the heteroatoms are greater and hence the energy contribution per dipole is smaller (see the mean values given for the barium–oxygen and barium–nitrogen distances).

Acknowledgment. We thank Professor J. M. Lehn for supplying the compounds.

(11) B. Metz, D. Moras, and R. Weiss, to be published.

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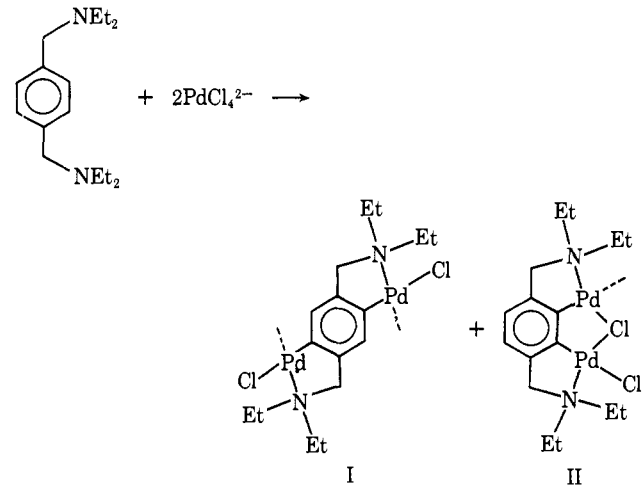
Dipalladiobenzenes

Sir:

Numerous compounds containing a transition metal σ bonded to an aromatic ring have been reported in recent years.[1] These compounds encompass a variety of transition metals and also different types of substitution on the benzene ring. However, in no instance has the bonding of more than one transition metal to the same benzene ring been accomplished. We now wish to report the synthesis and characterization of 1,2-, 1,3-, and 1,4-dipalladiobenzenes which constitute the first such examples. These compounds were prepared by the ortho-palladation reaction[2-4] and characterized by elemental analysis, nmr spectroscopy, and conversion to diverse 1,3-diketonato and pyridine derivatives.

The reaction of *N,N,N′,N′*-tetraethyl-*p*-xylylenediamine with tetrachloropalladate ion in 95% aqueous methanol in the presence of 1 equiv of a hindered tertiary amine readily gave a mixture of dimetalated products. Of these, the insoluble polymeric 1,4-dipalladio derivative I was isolated by filtration, while the soluble 1,2-dipalladio derivative II was precipitated by diluting the filtrate with water. The I:II ratio was about 7:3.



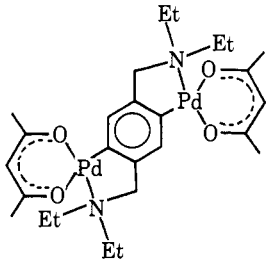
The 1,4-dipalladio compound, I, was converted to the monomeric bisacetylacetonato derivative,[5] III, mp 240–242° dec, the nmr spectrum of which indicated substitution of two aromatic hydrogens and the presence of two acetylacetonato ligands per molecule: τ 3.07 (s, aromatic H), 4.66 (s, acetylacetonato CH), 6.00 (s, benzylic CH_2), 7.03 (m, two overlapping quadruplets, J = 7.0) (ethyl CH_2), 7.96 (s), 8.05 (s, both acetylacetonato CH_3), and 8.47 (t, ethyl CH_3, J = 7.0) in a 1:1:2:4:3:3:6 ratio.

The 1,2-dipalladio derivative II was sufficiently soluble in halocarbons to permit purification and analysis.[5] Its nmr spectrum indicated substitution of two aromatic hydrogens and C_{2v} symmetry for the molecule: τ 3.87 (s, aromatic H), 6.38 (s, benzylic CH_2), ~7.5 (center of complex multiplet, ethyl CH_2), and (t, ethyl CH_3, J = 7.0) in a 1:2:4:6 ratio. The assignment of structure II rather than I for this compound rests not only on its higher solubility[6] but also on chemical evidence which indicates one of the chlorines to be less reactive than the other. Thus, the reaction of II with aqueous pyridine gave the cation IV, isolated as the hexafluorophosphate,[5] mp 220–225° dec. Compound IV still contained one bridging chlorine and its nmr spectrum was consistent with C_{2v} symmetry: τ 1.75 (m, pyridine 2-H), 2.6 (m, pyridine 4-H), 3.0 (m, pyridine 3-H), 3.80 (s, aromatic H), 6.31 (s, benzylic CH_2), (m, two overlapping quadruplets), 7.6 (ethyl CH_2), and 8.82 (t, J = 7.0, ethyl CH_3) in the correct 2:1:2:1:2:4:6 ratio. Simple 2-(dialkylaminomethyl)-phenylpalladium(II) chlorides, as well as their 1,4- and 1,3-dipalladio analogs, react with aqueous pyridine, invariably giving cations containing two pyridines per palladium.

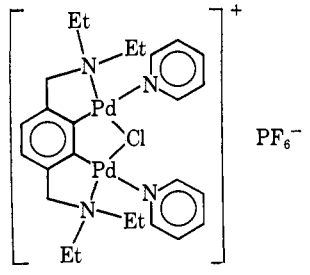
While the distance between the two palladium atoms in II is too great for a Pd–Pd bond,[7] the two atoms are close enough so that 1,3-diketonate substituents interfere with each other, causing distortion of the

(1) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, 7, 157 (1968).
(2) A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, **90**, 909 (1968).
(3) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).
(4) G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Commun.*, 912 (1970).

(5) Satisfactory elemental analyses and molecular weights were obtained for this and other compounds reported here.
(6) A compound such as II with one rather than two *intermolecular* chlorine bridges would be expected to be more soluble.
(7) Taking the Pd–C distance found in the 2-phenylazophenylpalladium analog [D. L. Weaver, *Inorg. Chem.*, **9**, 2250 (1970)] and assuming normal bond distances and angles in the phenyl ring, the Pd–Pd distance turns out to be abut 3.4 Å, considerably greater than the bonding distance of 2.64 Å based on covalent radii.

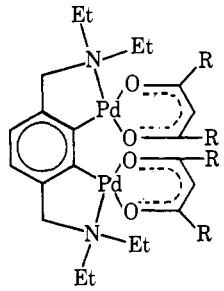


III

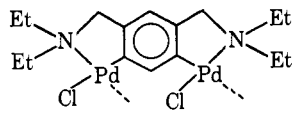


IV

molecule from C_{2v} symmetry. For instance, the nmr spectrum of the bisacetylacetonato derivative, Va, mp 195–197°, while confirming the presence of all ligands shown, indicated nonequivalence of the ethyl groups and of benzylic methylenes: τ 3.20 (s, aromatic CH), 4.62 (s, acetylacetonato CH), 5.00 (d, J = 13.5) and 6.38 (d, J = 13.5, nonequivalent benzylic H's), 6.3–7.6 (complex, unresolved multiplet, ethyl CH_2),



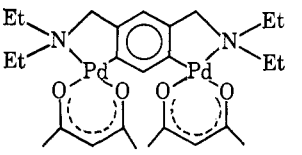
Va, R = Me
b, R = *t*-Bu



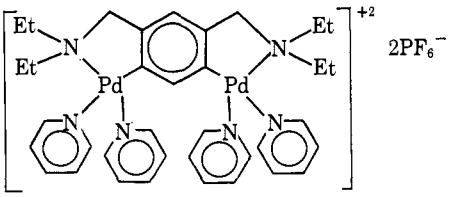
VI

7.75 and 7.93 (singlets, both acetylacetonate CH_3), and 8.26 (m, overlapping triplets, ethyl CH_3) in a 1:1:1:1:4:3:3:6 ratio. Molecular models suggest that coplanarity of the acetylacetonate rings with the benzene ring would entail prohibitive steric crowding. This can be relieved by tilting of both rings so that the coordination planes for both palladium atoms are fixed parallel to each other, but at an angle with regard to the benzene ring. This would make the ethyl groups and the benzylic hydrogens nonequivalent. The same effect was observed with the 2,2,6,6-tetramethyl-3,5-heptanedionato derivative, Vb, mp 204–205° dec.

A representative of 1,3-dipalladiobenzenes, VI, was obtained as an insoluble, polymeric solid by the reaction of tetrachloropalladate ion with *N,N,N',N'*-tetraethyl-*m*-xylylenediamine. It was characterized by conversion to the bisacetylacetonato derivative VII, the nmr spectrum of which was confirmatory: τ 2.75 (s, aromatic 2-H), 3.43 (s, aromatic 5-H), 4.71 (s, acetylacetonato CH), 6.12 (s, benzylic CH_2), 7.1 (m, two overlapping quadruplets, J = 7.0, ethyl CH_2), 8.00 and 8.09 (singlets, both acetylacetonato CH_3), and 8.50 (t, J = 7.0, ethyl CH_3) in a 1:1:2:4:8:6:6:12 ratio. The assignment of the τ-2.75 singlet to the 2-H is based on its large upfield shift (2.8 ppm, relative to the benzyl CH_2, with the τ-3.43 singlet remaining unshifted) in the nmr spectrum of the tetrapyridine cation VIII, isolated as the hexafluorophosphate salt, mp 205–208° dec: τ 1.8 (m, pyridine 2-H), 2.6 (t, J = 8, pyridine 4-H), 3.1 (m, pyridine 3-H), 3.68 (s, aromatic 5-H), 5.80 (s, aromatic 2-H), 6.35 (s, benzyl CH_2), 7.58 (m, two overlapping quadruplets, J = 7.0, ethyl CH_2), and 8.90 (t, J = 7.0) in the correct 8:4:8:1:1:4:8:12 ratio. The shift is



VII



VIII

presumably a consequence of the pyridine ring current and it is almost twice as large as that in analogous monopalladio systems.[8]

(8) An upfield shift of 1.3–1.4 ppm for the aromatic H adjacent to Pd has been observed in 2-(dialkylaminomethyl)phenylpalladium(II) derivatives and in analogous systems upon formation of the bispyridine cation: S. Trofimenko, unpublished results.

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Determination of Iron Coordination in Nonheme Iron Proteins Using Laser–Raman Spectroscopy. II. *Clostridium pasteurianum* Rubredoxin in Aqueous Solution[1]

Sir:

Three-dimensional X-ray techniques can provide structural data of the highest information content for crystalline proteins and enzymes. The extent to which the structures displayed by these complex molecules in the crystalline phases resemble those adopted in the aqueous solutions that are presumably their physiological environments is generally an open question. Here we present evidence that bears on this important point for the nonheme iron protein rubredoxin, isolated from *Clostridium pasteurianum*.[2]

The biological functions of the rubredoxins are obscure, although it is known that they can substitute for ferredoxins in some electron-transfer reactions[2] and that rubredoxin from *Pseudomonas oleovorans* is a component of the ω-hydroxylation system of that aerobe.[3] This participation in oxidation–reduction processes focuses attention on the iron atom and the residues to which it binds to the protein. In an X-ray study of crystalline rubredoxin, Herriott, Sieker, Jensen, and Lovenberg[4] conclude that an electron density map based on 2.5-Å resolution data shows that the single iron is tetrahedrally coordinated to four cysteinyl sulfur atoms. Recently, we suggested the possibility of characterizing the mode of binding of iron in nonheme

(1) Paper I: T. V. Long, II, and T. M. Loehr, *J. Amer. Chem. Soc.*, **92**, 6384 (1970).
(2) W. Lovenberg and B. E. Sobel, *Proc. Nat. Acad. Sci. U. S.*, **54**, 193 (1965).
(3) J. A. Peterson and M. J. Coon, *J. Biol. Chem.*, **243**, 329 (1968).
(4) J. R. Herriott, L. C. Sieker, L. H. Jensen, and W. Lovenberg, *J. Mol. Biol.*, **50**, 391 (1970).