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Some Studies of the Cyclopalladation Reaction

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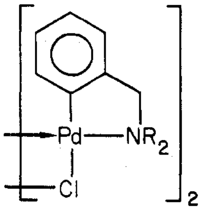
A variety of cyclic monopalladium compounds containing a Pd–Ar bond have been synthesized by the reaction of diversely substituted *N,N*-dialkylbenzylamines, *N*-benzylidene-*tert*-butylamine, and 1-phenylpyrazoles with $PdCl_4^{2-}$. 1,2- and 1,4-dipalladiobenzenes were obtained from *N,N,N',N'*-tetraalkyl-*p*-xylene-α,α'-diamine, while *N,N,N',N'*-tetraethyl-*m*-xylene-α,α'-diamine yielded the 1,3-dipalladio derivative. The 1,2-bis(chloropalladio) compound contains a relatively inert intramolecular Pd–Cl–Pd bridge. The organopalladium compounds were converted to 1,3-diketonato, tropolonato, and other neutral derivatives, to cationic pyridine complexes, and to stable, internally coordinated diarylpalladium compounds.

Following the first report that a Pd-C bond is formed directly upon the reaction of $PdCl_4^{2-}$ with azobenzene,[1] considerable interest developed in this area. The palladation reaction has subsequently been applied to systems such as *N,N*-dialkylbenzylamines,[2] *N,N*-dimethyl-1-naphthylamine,[2] 2-phenylpyridine and 2-phenylquinoline,[3] benzo[*h*]quinoline,[4] *N*-benzylidineaniline,[5] benzylidenemethylamine,[5b] and various aromatic aldoximes and ketoximes.[6] The palladation of azobenzene was found to be an electrophilic reaction,[7] and the resulting organopalladium compounds were used to synthesize other Ar-M derivatives.[8]

The dimeric, generally insoluble palladation products such as **1** were usually characterized by conversion to derivatives **2**, in which the chloride bridge has been broken and replaced by some ligand such as PR_3, AsR_3, pyridine, etc.,[9-11] or to derivatives such as **3** containing a 1,3-diketonato ligand. Another type of derivative is **4**, where the chloride bridge has been replaced by a 1,2-dihaptopyrazolide group.[12]

The structure of the bis(triethylphosphine) derivative of 2-(phenylazo)phenylpalladium(II) chloride has been established by X-ray crystallography.[13,14] Much of the above work has been summarized in a recent review.[15]



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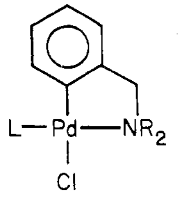

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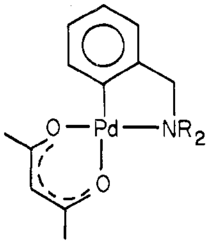

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We had investigated various aspects of the cyclopalladation reaction[16] and are presenting here those parts of our work which have not, in the interim, been reported by others.

Using methanolic Na_2PdCl_4 and running the cyclopalladation reaction at room temperature with various substrates, we have found that formation of a five-membered Pd-containing ring is a necessary but not sufficient condition for the reaction to proceed. For instance, when the donor atom was oxygen, as in methyl benzyl ether, acetophenone, or *N,N*-dimethylbenzamide (whose dipolar form has the negative charge on oxygen), no reaction took place and all palladium was recovered as $(py)_4Pd(PF_6)_2$. When the donor atom was sulfur, as in methyl benzyl sulfide, only the stable bis adduct $(C_6H_5CH_2SCH_3)_2PdCl_2$ was formed. It remained unchanged upon treatment with Na_2PdCl_4 in contrast to $(C_6H_5CH_2NMe_2)_2PdCl_2$ which was readily converted to the cyclopalladated product. A similar failure to obtain a cyclopalladation product from benzyl phenyl sulfide has been reported recently.[17]

Varying the R group in $C_6H_5CH_2NR_2$ (R = Me, Et, Pr) did not alter significantly the reaction course. Most of the resulting dimers of structure **1** were characterized directly, as was the analogous dimer derived from $C_6H_5CH{=}N\text{-}t\text{-}Bu$, the only such compound involving an aliphatic =NR group.

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(1) A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, **87**, 3272 (1965).

(2) A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, **90**, 909 (1968).

(3) A. Kasahara, *Bull. Chem. Soc. Jap.*, **41**, 1272 (1968).

(4) G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Commun.*, 912 (1970).

(5) (a) S. P. Molnar and M. Orchin, *J. Organometal. Chem.*, **16**, 196 (1969); (b) R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1787 (1972).

(6) H. Onoue, K. Minami, and K. Nakagawa, *Bull. Chem. Soc. Jap.*, 43, 3480 (1970).

(7) H. Takahashi and J. Tsuji, *J. Organometal. Chem.*, **10**, 511 (1967).

(8) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 313 (1968).

(9) M. Monoyama and K. Yamasaki, *Nippon Kagaku Zasshi*, **91**, 1058 (1970); *Chem. Abstr.*, 74, 68397 (1971).

(10) B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J. Chem. Soc. A*, 531 (1970).

(11) H. Onoue, K. Nakagawa, and I. Moritani, *J. Organometal. Chem.*, 35, 217 (1972).

(12) S. Trofimenko, *Inorg. Chem.*, 10, 1372 (1971).

(13) R. Siekman and D. L. Weaver, *Chem. Commun.*, 1021 (1968).

(14) D. L. Weaver, *Inorg. Chem.*, 9, 2250 (1970).

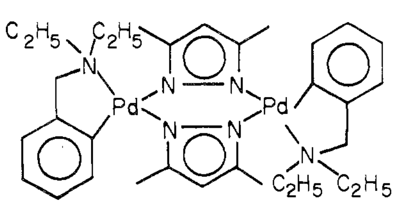
(15) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

(16) We prefer "cyclopalladation" to "ortho palladation" since this term is more general and includes cases such as *N,N*-dimethyl-1-naphthylamine.

(17) Y. Takahashi, A. Tokuda, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, 35, 415 (1972).

The products were also characterized by conversion to monomeric derivatives **3** or to analogous compounds obtained by the reaction of **1** with other uninegative bidentate ligands such as acetoacetate, 1,3-keto iminate, or tropolonate ions. These stable, organic-soluble derivatives were characterized by analytical data and nmr spectra. In the case of asymmetric derivatives (such as 1,3-keto iminates) nmr spectroscopy indicated the presence of both isomers, although one was a minor component (<10%). The major isomer is probably the sterically less hindered one. The phosphine derivatives, such as **2**, were unattractive for characterization purposes since the phosphine aryl protons interfered with the nmr study of the Pd-Ar group.

Another type of derivative with considerable diagnostic value is exemplified by the cationic pyridine adduct **5**. When dimers such as **1** react with pyridine in organic solvents, insoluble monosubstitution products of the type **2** are formed, and only chelating diamines are reported to yield cationic species.[9] However, when the reaction is carried out in water, the bis(pyridine) cations, **5**, are formed readily and can be isolated as PF_6^- salts. The formation of pyridine-based cations is of value in distinguishing chemically between compounds **1** and, *e.g.*, $(C_6H_5CH_2NR_2)_2PdCl_2$. Under these conditions pyridine will displace simply coordinated $C_6H_5CH_2NR_2$, but not the C-bonded ligand as in **1**. The proximity of the pyridine ring causes a substantial (~1.3-1.4 ppm) upfield shift of the 6 H adjacent to Pd which could be seen most clearly in the palladation product derived from the 4-methyl-substituted *N,N*-dialkylbenzylamine, where the 5H-6H coupling was eliminated. This facilitated proton assignment in the Pd-Ar derivatives.



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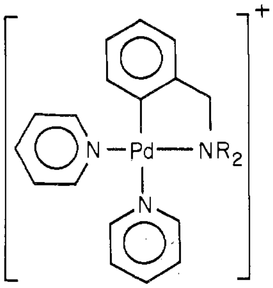
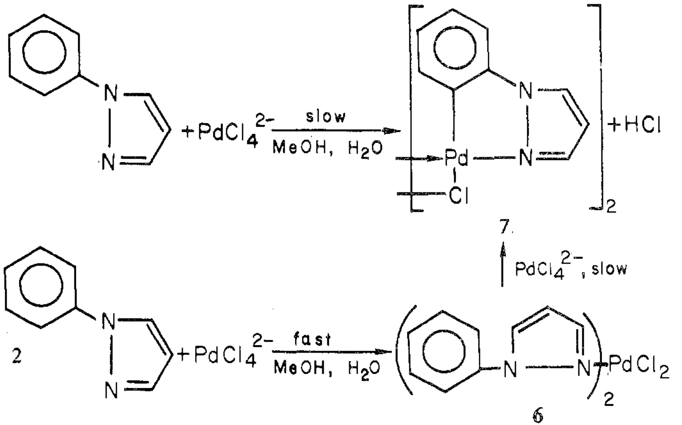
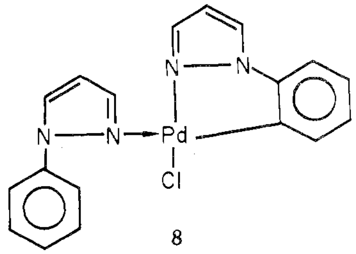


5

Interesting results were obtained with 1-phenylpyrazole, 1-C_6H_5pz. When this compound reacts with $PdCl_4^{2-}$, the bis adduct, **6**, $(1\text{-}C_6H_5pz)_2PdCl_2$, forms rapidly and can be isolated. Although analytical data on this compound were not satisfactory, because some 1-C_6H_5pz was lost on drying, its identity is not in doubt since (a) prolonged reaction with 1 equiv of $PdCl_4^{2-}$ gives **7** in excellent yield and (b) reaction with aqueous pyridine yields only $(py)_4Pd(PF_6)_2$ whereas a species such as **8** would give rise to the analog of **5**. Prolonged stirring of the original slurry gives an excellent yield of **7**. Unlike the reaction with $C_6H_5CH_2NR_2$, which requires 1 equiv of base for best results, $PdCl_4^{2-}$ reacts with 1-phenylpyrazole just as well in the absence of additional base (the pH drops continuously as the reaction proceeds), and even in the presence of excess Me_4NCl, HCl, or $HClO_4$. On the contrary, no **7** is obtained in the presence of added base. The reason for this is not clear, but perhaps the acid is necessary to remove *via* protonation one of the C_6H_5pz ligands from the rapidly formed $(C_6H_5pz)_2PdCl_2$ complex to give the intermediate $[(C_6H_5pz)PdCl_2]$ which undergoes the cyclopalladation reaction.

Similar results were obtained with 3,5-dimethyl-1-phenylpyrazole. There a simple bis adduct was formed, which did not react with aqueous pyridine (possibly for steric reasons), along with the cyclopalladation product which was converted to the cationic analog of **5**.





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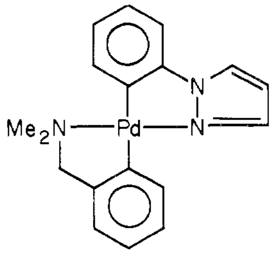
Other interesting derivatives were the internally coordinated diphenylpalladium compounds **9** and **10**, obtained by the reaction of **1** and **7** with 2-(dimethylaminomethyl)phenyllithium. These colorless, air-stable, crystalline materials which are analogs of the bis(azoaryl)palladium complexes reported by Bagga, *et al.*,[18] were soluble in organic solvents.



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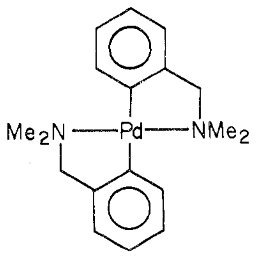

10

Their well-defined nmr spectra were in accord with the proposed structures and indicated the presence of only one isomer; it is not certain whether **9** and **10** are *cis*- or *trans*-diphenyl compounds.

Compound **10** has been reported previously by Kasahara and Izumi[19] as being yellow and possessing tetrahedral structure on the basis of the nmr spectrum where *N*-methyl and methylene protons were nonequivalent. These findings were subsequently disputed by Longoni, *et al.*,[20] who claimed that Kasahara and Izumi's compound contained benzonitrile. They, in turn described the preparation of **10**, along with other similar compounds, starting with $(Et_2S)_2PdCl_2$ and 2-(dimethylaminomethyl)phenyllithium. Their product (a) was very insoluble and (b) had a featureless nmr spectrum, being thus different from our compound **10**. On the basis of a large (6.8 D) dipole moment of the analogously prepared *N,N*-diethyl analog, Longoni, *et al.*, assigned the cis structure to their material. Assuming, then, correctness of their

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(18) M. M. Bagga, W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 1534 (1969).

(19) A. Kasahara and T. Izumi, *Bull. Chem. Soc. Jap.*, 42, 1765 (1969).

(20) G. Longoni, P. Fantucci, P. Chini, and F. Canziani, *J. Organometal. Chem.*, 39, 413 (1972).

assignment we are, very tentatively, assigning the *trans*-diphenyl configuration to our compounds **9** and **10**.

The facility with which C-Pd bonds are formed in the cyclopalladation reaction raised the question whether more than one Pd could be attached to the same benzene ring by this method. This proved to be the case, as reported in a preliminary communication.[21] By the use of suitably substituted *N,N,N',N'*-tetraalkylxylene-α,α'-diamines it was possible to synthesize *o*-, *m*- and *p*-dipalladiobenzene derivatives.

Two products, A and B, were obtained in about 7:3 ratio from the reaction of $PdCl_4{}^{2-}$ with *N,N,N',N'*-tetraethyl-*p*-xylene-α,α'-diamine. Of these, A was insoluble but could be converted to well-defined monomeric derivatives. By contrast, B had appreciable solubility in methanol and methylene chlorine for purification and analysis. The assignment of structures **11** to A and **12** to B rests on the following evidence.

1. *A priori*, structure **12**, containing one *intra*molecularly bridging Cl should have higher solubility than the extensively cross-linked **11**.

2. The presence of two different types of chlorine in **12**, one tightly bound (bridging) and the other loosely bound and reactive, was indicated by (a) X-ray photoelectron spectroscopy (ESCA) which showed a Cl peak width of 3.2 eV, a peak broadening consistent with the presence of two types of chlorine in the molecule,[22] and (b) the reaction with aqueous pyridine which resulted in replacement of only one chlorine and formation of a monocation (see **13**) containing only one pyridine per Pd, instead of two, as found customarily in monopalladio systems or dipalladiobenzenes containing nonadjacent Pd atoms.

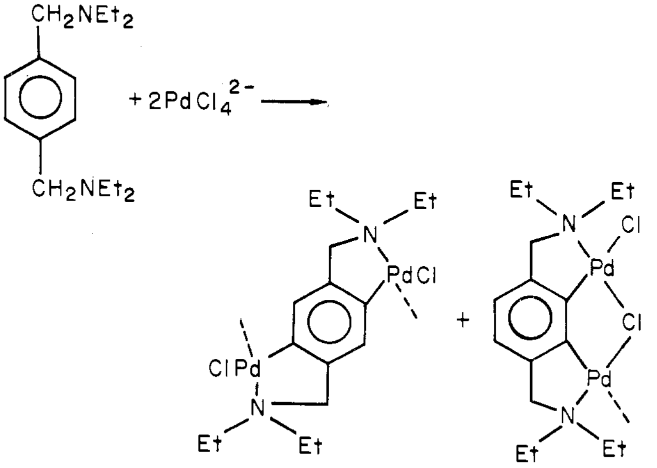
3. Isomeric 1,3-diketonato derivatives were formed from both A and B; those from B showed nonequivalence of the benzylic hydrogens and *N*-ethyl groups. This is consistent with the benzene ring and the diketonate rings not being coplanar but rather being locked in a twisted conformation with the two diketonate rings parallel to one another but tilted at an angle with respect to the phenyl plane. Molecular models show clearly the difficulty, if not impossibility, to achieve, for steric reasons, coplanarity of all three rings, as in **14**. Although no X-ray structure determination on any of these compounds has been carried out, some crystallographic data on **14** were collected (see Experimental Section).[23]

The corresponding derivatives of A had only one nmr signal for the benzylic protons, and all ethyl groups were equivalent. This would agree with coplanarity of the benzene and diketonate rings or rapid inversion of the diketonate ring through the benzene plane.

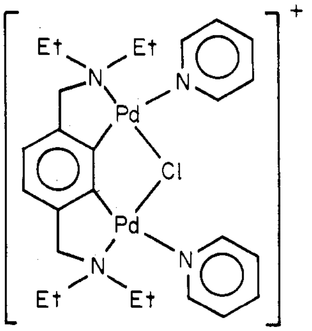
The relative proportions of 1,2- and 1,4-dipalladio isomers depended on the nature of the N substituents. While the 1,4 to 1,2 ratio was 7:3 for R = Et, it changed to 2:8 for R = *n*-Pr. When R was Me, the 1,4-dipalladation product predominated.

The 1,3-dipalladiobenzene derivatives were obtained from the reaction product of *N,N,N',N'*-tetraethyl-*m*-xylene-α,α'-diamine with $PdCl_4{}^{2-}$. This insoluble, polymeric material **15** has been converted to bis(1,3-diketonato) and bis(tropolonato) derivatives, the nmr spectra of which indicate C_{2v} symmetry of the molecule. No such symmetry would be expected in derivatives obtained from the alternative dipalladio structure,**16**.

Additional confirmation of the structure was obtained from the nmr spectrum of the tetrapyridine dication (see **17**), which, apart from indicating C_{2v} symmetry of the dication, exhibited a 2.8-ppm upfield shift of the 2 H, about twice that observed for the hydrogen ortho to Pd in dipyridine cations such as **5**.



11 **12**



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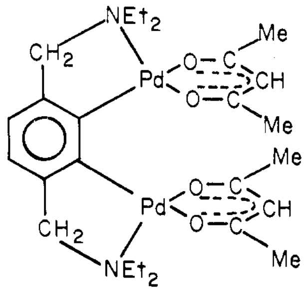

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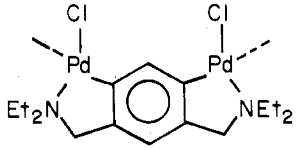

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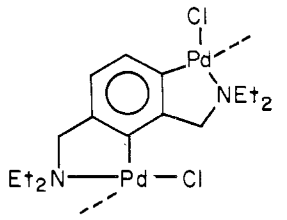

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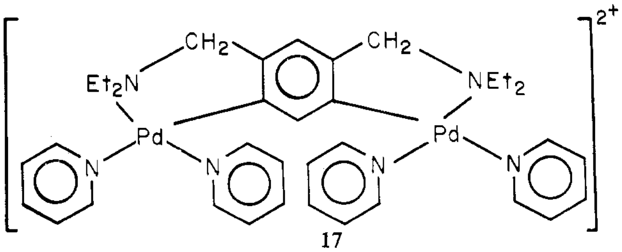


17

The presence of one Pd on the benzene ring seems to activate it toward further substitution. When *N,N,N',N'*-tetraethyl-*m*-xylene-α,α'-diamine reacted with $PdCl_4{}^{2-}$ in a 1:1 rather than 1:2 ratio, the principal product was the *m*-dipalladio derivative, **15**. This is consistent with the cyclopalladation being an electrophilic reaction.[7]

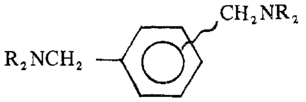
The reported 1,2-, 1,3-, and 1,4-dipalladiobenzene derivatives represent a potential entry into other dimetalloaromatic systems through the use of some reported techniques.[8] Of particular interest is the 1,2-dipalladio derivative where simultaneous interaction of both Pd atoms

[21] S. Trofimenko, *J. Amer. Chem. Soc.*, 93, 1808 (1971).

[22] This study was carried out by Dr. W. M. Riggs.

[23] These measurements were obtained by Dr. L. J. Guggenberger.

Table I. Data for *N,N,N',N'*-Tetraalkylxylene-α,α'-diamines



Isomer	R	% yield	Bp, °C (mm)	*n*D	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	Nmr, τ multiplicity [peak ratio]
Para	Et[a]	85	115 (1.3)	1.4951							
Para	R$_2$ = (CH$_2$)$_4$	61	168 (5.3)	1.4392	78.6	78.7	9.90	10.1	11.5	11.6	2.86 s, 6.58 s, 7.7 m, 8.4 m [1:1:2:2]
Meta	R$_2$ = (CH$_2$)$_4$	80	146 (2.5)	1.5340	78.6	78.5	9.90	10.0	11.5	11.5	2.8 m, 6.43 s, 7.5 m, 8.3 m [1:1:2:2]
Ortho	R$_2$ = (CH$_2$)$_4$	50	135 (1.5)	1.5342	78.6	79.0	9.90	10.4	11.5	10.6	2.8 m, 6.31 s, 7.53 m, 8.31 m [1:1:2:2]
Meta	Et	82	112 (1.4)	1.4950	77.5	77.5	11.3	11.4	11.3	11.4	3.02 m, 3.21 m, 6.86 s, 7.86 t (J = 7.0 Hz), 9.35 t (J = 7.0 Hz) [1:3:4:8:12]
Para	Me[a]	77	75 (0.9)	1.5012							3.02 m, 6.95 s, 8.15 s [1:1:3]
Para	Pr	61	147 (1.2)	1.4869	79.0	79.1	11.8	11.8	9.21	9.40	2.91 s, 6.65 s, 7.76 t (J = 7 Hz), 8.67 sextet (J = 7 Hz), 9.28 t (J = 7 Hz) [1:1:2:2:3]

[a] Known compound: R. Fusco, S. Chiavarelli, G. Palazzo, and D. Bovet, *Gazz. Chim. Ital.*, 78, 951 (1948).

with various substrates is possible.

Experimental Section

General Synthesis of *N,N,N',N'*-Tetraalkyl-α,α'-xylenediamines. To a large excess of the dialkylamine was added in small portions the appropriate α,α'-dihaloxylene. The reaction mixture was refluxed for 1 hr, cooled, and then poured into water containing alkali in excess of the amount necessary to neutralize the HX formed in the reaction. The product was extracted with ether and isolated by distillation. Properties of these compounds are shown in Table I.

Chlorine-Bridged Dimeric Arylpalladium Compounds. The arylpalladium compounds derived from *N,N*-dialkylbenzylamines and related bases were prepared by the reaction of Na$_2$PdCl$_4$ solution with the appropriate amine at room temperature in the presence of a tertiary amine. Reactions were usually complete within 1-3 days. This procedure is illustrated by the following examples.

2-(1-Pyrazolyl)phenylpalladium(II) Chloride Dimer (7). A mixture of 2 l. of 0.19 *M* Na$_2$PdCl$_4$ solution and 55 g of 1-phenylpyrazole (both 0.38 mol) was stirred with an additional 50 ml of water for 24 hr. Then another 1 g of 1-phenylpyrazole was added and the reaction mixture was stirred for another 48 hr. The slurry was filtered, and the solid was washed with water and then with methanol and ether. After air-drying there was obtained 98.8 g (91.5%) of yellow solid. An analytical sample was purified by digestion with chloroform (which removes the soluble (1-C$_6$H$_5$pz)$_2$-PdCl$_2$) and then by recrystallization from chlorobenzene. The compound darkens from about 300° and decomposes around 330°. *Anal.* Calcd for C$_9$H$_7$ClN$_2$Pd: C, 37.9; H, 2.49; N, 9.83; Pd, 37.3. Found: C, 37.8; H, 2.40; N, 9.75; Pd, 37.0.

2-(Diethylaminomethyl)-4-methylphenylpalladium(II) Chloride Dimer. To 400 ml of 0.10 *M* Na$_2$PdCl$_4$ solution was added 13.5 g of α-diethylamino-*p*-xylene and 9.8 g of diisopropylethylamine (both 0.076 mol). The mixture was stirred for 3 days at room temperature and was then filtered. The product was obtained, after washing with water and methanol and drying, in 23.8-g (99%) yield. The analytical sample was purified by chromatography on alumina, eluting with methylene chloride; mp 171-172° dec. *Anal.* Calcd for C$_{12}$H$_{18}$ClNPd: C, 45.3; H, 5.67; N, 4.42. Found: C, 45.0; H, 5.72; N, 4.50.

The nmr spectrum (τ values throughout) supported the assigned structure: 2.97 d (J = 3 Hz), 3.22 s, 6.03 s, 7.0 m (two overlapping quadruplets), 7.68 s, and 8.30 t (J = 7.0 Hz) in the correct 1:2:2:4:3:6 ratio.

Using the above method the following arylpalladium compounds were prepared.

2-(Diethylaminomethyl)phenylpalladium(II) Chloride Dimer. This compound was obtained as a bright yellow solid, mp 172-173° dec, in 72% yield. *Anal.* Calcd for C$_{11}$H$_{16}$ClNPd: C, 43.5; H, 5.27; N, 4.62. Found: C, 43.5; H, 5.39; N, 4.85.

2-(Dipropylaminomethyl)phenylpalladium(II) Chloride Dimer. This compound was obtained in 89% yield as a yellow solid, mp 174-175° dec. *Anal.* Calcd for C$_{13}$H$_{20}$ClNPd: C, 47.0; H, 6.03; N, 4.42. Found: C, 46.5; H, 6.12; N, 4.24.

The nmr spectrum was confirmatory: 2.75 m, 3.02 m, 5.96 s, 6.7-8.2 m, and 9.00 t (J = 7 Hz) in the correct 1:3:2:8:6 ratio.

2-(*N-tert*-Butylformimidoyl)phenylpalladium(II) Chloride Dimer. This compound was obtained, starting with *N*-benzylidene-*tert*-butylamine, in 33% yield as a yellow solid decomposing gradually from 230°. *Anal.* Calcd for C$_{11}$H$_{14}$ClNPd: C, 43.8; H, 4.64; N, 4.64. Found: C, 44.4; H, 4.66; N, 4.74.

The nmr spectrum was in accord with the structure: 1.97, 2.2-2.5 m, 2.6-2.9 m, and 8.35 s in the correct 1:1:3:9 ratio.

[2-(2-Pyridyl)phenyl](tri-*p*-tolylphosphine)palladium(II) Chloride. A mixture of crude 2-(2-pyridyl)phenylpalladium(II) chloride dimer and tri-*p*-tolylphosphine was dissolved with warming to 50° in dimethylformamide. The solution was cooled and poured into water. The precipitated product was purified by chromatography on alumina (packing and eluting with methylene chloride), followed by recrystallization from toluene. The complex decomposes gradually above 227°. *Anal.* Calcd for C$_{32}$H$_{29}$ClNPPd: C, 64.0; H, 4.84; Cl, 5.82; N, 2.33; P, 5.17. Found: C, 63.9; H, 4.56; Cl, 5.74; N, 2.31; P, 5.32.

Bis(benzyl methyl sulfide)palladium(II) Dichloride. To 100 ml of 0.19 *M* Na$_2$PdCl$_4$ solution was added 2.9 g of benzyl methyl sulfide and the reaction mixture was refluxed 48 hr. It was then cooled and filtered. The filtrate was stripped to dryness, the residue was stirred with water, and the mixture was filtered. Both solids had the same infrared spectrum and were obtained in a yield of 4.4 g (74%). The yellow product is soluble in halocarbons and hot benzene and sparingly soluble in heptane. It was recrystallized from 1:1 toluene-heptane and was obtained as crystals, mp 149-150°. *Anal.* Calcd for C$_{16}$H$_{20}$Cl$_2$PdS$_2$: C, 42.4; H, 4.41; Cl, 15.6; Pd, 23.4; S, 14.1. Found: C, 43.0; H, 4.51; Cl, 15.6; Pd, 23.2; S, 14.6.

The nmr spectrum is in accord with a simple 2:1 complex: 2.63 s, 5.82 s, and 7.79 s in 5:2:3 ratio.

Reaction of Halogen-Bridged Dimeric Arylpalladium Compounds with Uninegative Chelating Agents. (2,2,6,6-Tetramethyl-3,5-heptanedionato)-2-(1-pyrazolyl)phenylpalladium(II). To 11.4 g (0.04 mol) of crude 2-(1-pyrazolyl)phenylpalladium(II) chloride dimer stirred in 200 ml of dimethylformamide was added a mixture of 2,2,6,6-tetramethyl-3,5-heptanedione and triethylamine (12 g of equimolar mixture). After stirring at 50° for 1 hr the solution was added to 1 l. of water and the precipitated product was filtered and obtained in a 12-g (71%) yield. After recrystallization from ethanol this compound melts at 152-153°. It is very soluble in benzene and moderately soluble in hexane. *Anal.* Calcd for C$_{20}$H$_{26}$N$_2$O$_2$Pd: C, 55.7; H, 6.03; N, 6.49. Found: C, 55.7; H, 5.88; N, 6.69.

The nmr spectrum was confirmatory: 2.17 d (J = 2.7 Hz), 2.33 d (J = 1.8 Hz), 2.4-2.5 m, 2.9-3.0 m, 3.65 t (J = 2.5 Hz), 4.23 s, 8.72 s, and 8.76 s, in 1:1:1:3:1:1:9:9 ratio assigned, respectively, to pyrazolyl 3 and 5 H's, phenyl H's, pyrazole 4 H, dione 4 H, and the *tert*-butyl groups.

The above compound was obtained in 82% yield when thallium 2,2,6,6-tetramethyl-3,5-heptanedionate was used.

1-(Ethoxy-1,3-butanedionato)-2-(1-pyrazolyl)phenylpalladium(II). This compound was obtained in 43% yield as a colorless solid, mp 153–154° dec. *Anal.* Calcd for $C_{15}H_{16}N_2O_3Pd$: C, 47.7; H, 4.23; N, 7.41. Found: C, 47.5; H, 4.21; N, 7.49.

The nmr spectrum was confirmatory: 1.96 d ($J = 2.9$ Hz), 2.24 d ($J = 2.1$ Hz), 2.30 m, 2.77 m, 3.43 t ($J = 2.5$ Hz), 4.99 s, 5.55 q ($J = 7$ Hz), 7.81 s, and 8.55 t ($J = 7$ Hz) in the correct 1:1:1:3:1:1:2:3:3 ratio.

(2,2,6,6-Tetramethyl-3,5-heptanedionato)-2-(3,5-dimethyl-1-pyrazolyl)phenylpalladium(II). This compound was obtained in 68% yield as a pale creamy solid, mp 199–200°. *Anal.* Calcd for $C_{22}H_{30}N_2O_2Pd$: C, 57.4; H, 6.52; N, 6.09. Found: C, 58.1; H, 6.64; N, 6.43.

The nmr spectrum was confirmatory: 2.4 m, 3.03 m, 4.19 s, 4.26 s, 7.53 s, 8.76 s, and 8.84 s in 1:3:1:1:6:9:9 ratio.

(2,2,6,6-Tetramethyl-3,5-heptanedionato)-2-(2-pyridyl)phenylpalladium(II). This compound was prepared as above, using 2-(2-pyridyl)phenylpalladium(II) chloride dimer. It was obtained in 59% yield and purified by recrystallization from heptane; mp 226–227° dec. *Anal.* Calcd for $C_{22}H_{27}NO_2Pd$: C, 59.6; H, 6.06; N, 3.16. Found: C, 59.9; H, 5.98; N, 3.34.

Nmr: 1.78 d ($J = 6$ Hz), 2.1–3.1 m, 4.24 s, 8.72 s, and 8.76 s in the correct 1:7:1:9:9 ratio.

(2,2,6,6-Tetramethyl-3,5-heptanedionato)-8-(dimethylamino)-naphthylpalladium(II). This compound was obtained by the above method in 79% yield after chromatography on alumina and recrystallization from toluene–heptane; mp 206–207° dec. *Anal.* Calcd for $C_{23}H_{31}NO_2Pd$: C, 60.1; H, 6.75; N, 3.05. Found: C, 60.6; H, 7.10; N, 3.11.

Nmr: 2.3–2.9 m, 4.23 s, 6.67 s, 8.67 s, and 8.76 s in 6:1:6:9:9 ratio assigned to aromatic H's, dione 4 H, *N*-methyls, and the two *tert*-butyl groups, respectively.

For other related compounds see Table II.

Cationic Pyridine Complexes of Palladium. Tetrakis(pyridine)-palladium(II) Bis(hexafluorophosphate). This compound is obtained quantitatively on mixing a Na_2PdCl_4 solution with excess aqueous pyridine, followed by the addition of excess aqueous NH_4PF_6 solution. The precipitated product is purified by recrystallization from a mixture of acetonitrile and ethyl acetate. It darkens gradually from 250°. *Anal.* Calcd for $C_{20}H_{20}F_{12}N_4P_2Pd$: C, 33.6; H, 2.81; F, 32.1; N, 7.87. Found: C, 33.6; H, 2.82; F, 32.4; N, 7.57.

Other cationic pyridine complexes containing an aryl–Pd bond were prepared similarly, as exemplified below.

Bis(pyridine)[2-(1-pyrazolyl)phenyl]palladium(II) Hexafluorophosphate. A 2-g sample of 2-(1-pyrazolyl)phenylpalladium(II) chloride was stirred at room temperature in 75 ml of water containing about 5 ml (large excess) of pyridine. The compound dissolved rapidly, and the resulting solution was filtered and poured into aqueous KPF_6. A white solid precipitated immediately. The mixture was filtered, and the solid was washed with water and then with ether and was obtained, after air-drying, in 3.8-g (99%) yield. It was purified by dissolving it in acetonitrile, in which it is very soluble, and precipitating by the addition of ethyl acetate; sinters at 190–192°; decomposes at ~200°. *Anal.* Calcd for $C_{19}H_{17}F_6N_4PPd$: C, 41.3; H, 3.08; N, 10.1; Pd, 19.2. Found: C, 41.2; H, 3.00; N, 10.0; Pd, 19.4.

The nmr spectrum was quite complex: the pyridine 2 and 6 H's were at 1.48 (relative area 4) and the pyrazolyl H's were at 2.01 d ($J = 2.9$ Hz), 2.98 d ($J = 1.9$ Hz) and 3.73 t ($J = 2.6$ Hz) in 1:1:1 ratio while the remaining ten pyridine and phenyl H's were spread from τ 2.0 to 4.2 as a very complex peak pattern with considerable fine structure.

Bis(pyridine)[2-(diethylaminomethyl)-4-methylphenyl]palladium(II) Hexafluorophosphate. To a stirred solution of 5 ml of pyridine in 100 ml of water was added 3.18 g (0.01 mol) of 2-(diethylaminomethyl)-*p*-tolylpalladium(II) chloride. After all solid had dissolved, 20 ml of 0.65 *M* KPF_6 solution was added. The precipitate that formed was extracted with methylene chloride and the extracts were chromatographed on alumina eluting with acetone. There was obtained 3.9 g (67%) of white solid, mp 127–128°. *Anal.* Calcd for $C_{22}H_{28}F_6N_3PPd$: C, 45.2; H, 4.78; F, 19.5; N, 7.18. Found: C, 45.5; H, 5.18; F, 19.5; N, 7.16.

The nmr spectrum consisted of ~1.6 m, 2.5 m, 2.9 t ($J = 6$ Hz), 3.53 (singlet with small shoulder), 4.68 s, 6.25 s, ~7.6 m (two overlapping quadruplets), 8.38 s, and 8.85 t ($J = 7.0$ Hz) in 4:2:4:2:1:2:4:3:6 ratio assigned to pyridine 2, 4, and 3 H's, benzene 3 and 4 H's, benzene 6 H, benzyl methylene, ethyl methylene, tolyl methyl and ethyl methyls.

Dichlorobis(3,5-dimethyl-1-phenylpyrazole)palladium (A) and Bis(pyridine)[2-(3,5-dimethyl-1-pyrazolyl)phenyl]palladium(II) Hexafluorophosphate (B). The crude product which precipitated in 61% yield on stirring methanolic Na_2PdCl_4 with 3,5-dimethyl-1-phenylpyrazole at 50° for 4 hr was isolated by filtration, washed with aqueous methanol, and then stirred with excess aqueous pyridine. The insoluble solid was A. Addition of aqueous NH_4PF_6 solution to the filtrate precipitated B, which was purified by chromatography on alumina. *Anal.* Calcd for $C_{22}H_{24}Cl_2N_4Pd$ (A): C, 50.4; H, 4.58; Cl, 13.6; N, 11.1. Found: C, 50.4; H, 4.53; Cl, 14.0; N, 10.7. Calcd for $C_{21}H_{21}F_6PN_4Pd$ (B): C, 43.5; H, 3.62; F, 19.7; Pd, 18.3. Found: C, 43.8; H, 3.79; F, 19.8; Pd, 18.4.

Bis[(2-dimethylaminomethyl)phenyl]palladium(II) (10). To freshly prepared[24] 2-(dimethylaminomethyl)phenyllithium in hexane was added a THF slurry of an equimolar amount of 2-(aminomethyl)phenylpalladium chloride dimer. The reaction mixture was stirred for 2 hr; then the solvent was evaporated and the product was extracted with methylene chloride and purified by chromatography on alumina. It was obtained in 78% yield as white crystals which darken gradually from ~150° and decomposed at ~200°. *Anal.* Calcd for $C_{18}H_{24}N_2Pd$: C, 57.7; H, 6.42; N, 7.48; Pd, 28.3. Found: C, 57.4; H, 6.47; N, 7.52; Pd, 27.9.

Nmr: ~2.5 m, ~3.1 m, 6.19 s, and 7.44 s in 1:3:2:6 ratio.

(2-Dimethylaminomethylphenyl)(2-pyrazolylphenyl)palladium(II) (9). This compound was prepared as above, using 2-pyrazolylphenylpalladium chloride dimer, and was obtained in 85% yield; mp 205–207° dec. *Anal.* Calcd for $C_{18}H_{19}N_3Pd$: C, 56.4; H, 4.96; N, 11.0; Pd, 27.7; mol wt 383. Found: C, 57.0; H, 5.18; N, 11.2; Pd, 27.3; mol wt (osmometric in chloroform) 383.

Nmr: 2.09 d ($J = 2.7$ Hz), 2.3 m, 2.47 d ($J = 2.2$ Hz), ~3.0 m, 3.14 t ($J = 2.5$ Hz), 6.13 s, and 7.33 s in 1:2:1:6:1:2:6 ratio.

Dichloro-3,6-bis(diethylaminomethyl)-1,2-phenylenedipalladium(II) (A) and Dichloro-2,5-bis(diethylaminomethyl)-1,4-phenylenedipalladium(II) (B) (12 and 11). In a typical experiment, to 400 ml of 0.19 *M* Na_2PdCl_4 was added 9.4 g (0.038 mol) of *N,N,N′,N*-tetraethyl-*p*-xylene-α,α′-diamine and 9.8 g (0.076 mol) of diisopropylethylamine. The solution was stirred for 6 hr at room temperature; a considerable amount of solid separated. The mixture was filtered and the solid was washed with water and methanol. It was obtained in 16.6-g (83%) yield and was B. The crude material was used as such in subsequent experiments.

The filtrate was diluted with water to 2 l. whereupon a pale yellow solid precipitated. It was A, obtained, after drying, in 5.3-g (27%) yield. This compound is soluble in methanol and sparingly soluble in methylene chloride. *Anal.* Calcd for $C_{16}H_{26}N_2Cl_2Pd_2$: C, 36.3; H, 4.92; Cl, 13.4; N, 5.29; Pd, 40.1. Found: C, 36.5; H, 4.95; Cl, 13.5; N, 5.15; Pd, 40.3.

Nmr (CD_3CN): 3.87 s, 6.38 s, a broad multiplet (~1.2 ppm) centered around 7.5, and 8.78 t ($J = 7.0$ cps) in 1:2:4:6 ratio, assigned to the equivalent aromatic H's, benzyl CH_2's, nonequivalent ethyl CH_2's, and ethyl CH_3's.

μ-Chloro-[3,6-bis(diethylamino)-1,2-phenylene]bis(pyridine)-dipalladium(II) Hexafluorophosphate (13). A small sample of A from the above experiment was stirred with excess aqueous pyridine. To the resulting solution was added excess NH_4PF_6. The precipitate was extracted with methylene chloride and purified by chromatography on alumina, washing with methanol and ether, and drying. *Anal.* Calcd for $C_{26}H_{36}ClF_6N_4PPd$: C, 39.2; H, 4.52; Cl, 4.45; F, 14.3; N, 7.03; Pd, 26.6. Found: C, 39.2; H, 4.55; Cl, 3.90; F, 14.9; N, 7.01; Pd, 26.7.

Nmr (CD_3CN): 1.75 m, 2.6 m, 3.0 m, 3.80 s, 6.31 s, 7.6 m (two overlapping quadruplets), and 8.82 t ($J = 7.0$ Hz) in 2:1:2:2:4:6 ratio, assigned to pyridine α-H's, pyridine γ-H's, pyridine β-H's, phenyl H's, benzyl CH_2, ethyl CH_2, and ethyl CH_3, respectively.

Dichloro[3,6-bis(dipropylaminomethyl)-1,2-phenylene]-dipalladium(II) and Dichloro[2,5-bis(dipropylaminomethyl)-1,4-phenylene]dipalladium(II). To 500 ml of 0.19 *M* methanolic solution of Na_2PdCl_4 was added 14.4 g (0.048 mol) of *N,N,N′,N′*-tetrapropyl-*p*-xylene-α,α′-diamine and 12.3 g (0.095 mol) of diisopropylethylamine. After 5 hr the mixture was filtered and the solid was washed with water and methanol. It was then stirred with 400 ml of methylene chloride, filtered, washed with some more methylene chloride, and dried, to give 4.0 g (14% yield) of dichloro-[2,5-bis(dipropylaminomethyl)-1,4-phenylene]dipalladium(II).

The filtrates were combined, stirred with more water, and

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[24] R. T. Hawkins and D. B. Stroup, *J. Org. Chem.*, 34, 1173 (1969).

Table II. Data for Compounds of Structure $[2\text{-}(R_2NCH_2)C_6H_5PdL_2]^{z+},zPF_6^-$

R	L_2	z	% yield	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% F Calcd	% F Found	Nmr spectrum[a]
Me	AcAc[b]	0	74	139–140	49.6	49.4	5.61	5.81	4.13	4.07			m, 2.5–3.2; s, 4.65;s, 608; s, 7.18; s, 7.96; s, 8.03 [4:1:2:6:3:3]
Me	EAc[c]	0	79	156–158 dec	48.8	48.8	5.70	5.71	3.80	3.97			m, 2.60; m, 2.9; s, 5.12; q (7), 5.84; s, 6.02; s, 7.12; s, 7.92; t (7), 8.65 [1:3:1:2:2:6:3:3]
Me	PIP[d]	0	68	171–172	57.9	57.7	5.78	5.75	6.76	6.78			m, 2.88; m, 2.5–3.8; d (7), 4.34; s, 4.94; s, 6.10; s, 7.35; s, 7.99; s, 8.26 [5:3:1:1:2:6:3:3]
Et	$(py)_2$	1	81	161–163	44.2	44.2	4.56	4.49	7.37	7.46	19.9	19.7	m, 1.57; m, 2.50; "d" (7.0), 2.90; d (4.0), 3.33; m, 3.63; d (8.0), 4.49; s, 6.19; m, 7.5; t (7.0), 8.72 [4:2:4:2:1:1:2:4:6]
Et	DPM[e]	0	93	130–131	58.5	58.4	7.76	7.82	3.10	3.31			m, 2.7; m, 3.1; s, 4.49; s, 6.10; m, 7.13; t (7.0), 8.53; s, 8.80; s, 8.89 [1:3:1:2:4:6:9:9]
Me	$(py)_2$	1	86	204–206	42.0	42.4	4.05	3.96	7.74	7.77			"d" (5.0), 1.09; m, 2.1; m, 2.5; m, 2.9; m, 3.2; d (7.0), 3.99; s, 5.88; s, 7.35 [4:2:4:2:1:1:2:6]

[a] Listed are multiplicity (coupling constant in hertz), chemical shift in τ [relative area]. [b] 2,4-Pentanedionate. [c] 1-Ethoxy-1,3-butanedionate. Molecular weight of compound: calcd, 369; found, 372 (by osmometry in chloroform at 37°). [d] 4-Phenylimino-2-pentanonate. [e] 2,2,6,6-Tetramethyl-3,5-heptanedionate.

Table III. Data for Compounds $[m,n\text{-}(R_2NCH_2)_2\text{-}x,y\text{-}C_6H_4(PdL_2)_2]^{z+},zPF_6^-$

m,n	R	x,y	L_2	z	% yield	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% X Calcd	% X Found	Nmr spectrum[a]
3,6	Et	1,2	AcAc[b]	0	88	195–197	47.6	47.2	6.10	6.36	4.27	4.28			s, 3.20; s, 4.62; d (13.5), 5.00; d (13.5), 6.38; m, 6.3–7.6; s, 7.75; s, 7.93; m (t + t), 8.26 [1:1:1:1:4:3:3:6]
3,6	Et	1,2	DPM[c]	0	94	204–205 dec	55.4	55.4	7.79	8.29	3.40	3.46	Pd, 25.7	Pd, 25.1	s, 3.40; s, 4.53; d (13.5), 5.20; d (13), 6.60; m, ~6.7; m, ~7.4; t (7), 8.68; s, 8.78; s, 8.96 [1:1:1:1:2:2:6:9:9]
3,6	Et	1,2	TPL[d]	0	88	184–185	51.4	51.1	5.14	5.23	4.00	3.98			s, 2.98; d (1.4), 3.08; s, 3.39; m, 3.5; s, 5.92; q (7.0), 6.97; t (7.0), 8.35 [2:2:1:1:2:4:6]
3,6	Pr	1,2	DPM	0	65	185–186	57.3	57.7	8.18	8.07	3.18	2.84			s, 3.41; s, 4.52; d (13), 5.18; d (13), 6.47; m, 6.5–8.6; s, 8.75; s, 8.92; t (7.0), 9.07 [1:1:1:1:8:9:9:6]
4,6	Et	1,3	AcAc[e]	0	37	200–230 dec	47.6	47.7	6.16	6.07	4.27	4.31	Pd, 32.3	Pd, 31.3	s, 2.75; s, 3.43; s, 4.71; s, 6.12; m, 7.1; s, 8.0; s, 8.09; t (7), 8.50 [1:1:2:4:8:6:6:12]
4,6	Et	1,3	TPL	0	66	236–238	51.4	51.1	5.14	5.08	4.00	3.94			m, 2.5–2.8; m, 2.8–3.3; s, 3.38; s, 6.05; q (7.0), 6.95; t (7.0), 8.42 [5:1:1:2:4:6]
4,6	Et	1,3	$(py)_2$	2	74	205–208 dec	40.6	40.8	4.33	4.38	7.91	7.90	F, 21.5 Pd, 20.0	F, 21.9 Pd, 20.6	m, 1.8; t (8), 2.6; m, 3.1; s, 3.68; s, 5.80; s, 6.35; m, 7.6; t (7), 8.90 [8:4:8:1:1:4:8:12]
2,5	Me	1,4	AcAc	0	31	220 dec	44.0	43.2	5.33	5.37	4.67	4.63			s, 3.07; s, 4.65; s, 6.03; s, 7.13; s, 7.97; s, 8.02 [1:1:2:6:3:3]
2,5	Et	1,4	AcAc	0	58	240–242 dec	47.6	47.5	6.10	6.18	4.27	4.35			s, 3.07; s, 4.66; s, 6.00; m, 7.03; s, 7.96; s, 8.05; t (7.0), 8.47 [1:1:2:4:3:3:6]
2,5	Et	1,4	DPM	0	35	255–256 dec	55.4	55.4	7.79	8.09	3.40	3.41			s, 3.10; s, 4.43; s, 6.08; m, ~7.1; t (7.0), 8.52; s, 8.81; s, 8.90 [1:1:2:4:9:9:6]
2,5	Et	1,4	TPL	0	60	185–187	51.4	51.2	5.14	5.28	4.00	4.03			m, 2.4–2.8; m, 2.8–3.3; s, 3.35; s, 5.85; q (7), 6.93; t (7), 8.30 [2:3:1:2:4:6]
2,5	Pr	1,4	DPM	0	68	247–248 dec	57.3	57.6	8.18	8.12	3.18	3.16			s, 3.08; s, 4.39; s, 6.02; m, ~7.2; m, 7.8; s, 8.79; s, 8.87, t (7.0), 9.09 [1:1:2:4:4:9:9:6]

[a] Listed are multiplicity (coupling constant in hertz), chemical shift in τ [relative area]. [b] 2,4-Pentanedionate. Molecular weight of compound: calcd, 656; found, 661 (by osmometry in chloroform at 37°). [c] 2,2,6,6-Tetramethyl-3,5-heptanedionate. [d] Tropolonate. [e] Molecular weight of compound: calcd, 656; found, 662 (by osmometry in chloroform at 37°).

extracted with methylene chloride. The extracts were stripped to dryness, and the residue was stirred with acetone, filtered, and dried, yielding 20.7 g (74%) of dichloro[3,6-bis(dipropylaminomethyl)-1,2-phenylene]dipalladium(II).

The identities of the two products were confirmed by conversion to the isomeric 2,2,6,6-tetramethyl-3,5-heptanedionato derivatives (see Table III).

The method used for preparing these and other derivatives listed in Table III consisted, in general, of warming a solution or suspension of the chloropalladio derivative with a slight excess of the chelating ligand (either as Tl or diisopropylethylammonium salt) in DMF for several hours, diluting with water, and extracting the product with methylene chloride. The products were purified by chromatography on alumina.

Crystallographic Data on 3,6-Bis(diethylaminomethyl)phenylenebis(2,4-pentanedionatopalladium) (14). Crystals of **14** are monoclinic with $a = 13.74$ Å, $b = 11.3$ Å, $c = 20.66$ Å, and $\beta = 118.8°$. The space group is $P2_1/c$ and there are four molecules per cell. The calculated density on this basis is 1.55 g/cm^3. The observed density (flotation in a carbon tetrachloride–bromobenzene mixture) is also 1.55 g/cm^3. There is no space group imposed molecular symmetry.

Registry No. p-$(CH_2)_4NCH_2C_6H_4CH_2N(CH_2)_4$, 39022-99-6; m-$(CH_2)_4NCH_2C_6H_4CH_2N(CH_2)_4$, 39023-00-2; o-$(CH_2)_4NCH_2C_6H_4CH_2N(CH_2)_4$, 39023-01-3; m-$Et_2NCH_2C_6H_4CH_2NEt_2$, 39023-02-4; p-$Pr_2NCH_2C_6H_4CH_2NPr_2$, 39023-03-5; Na_2PdCl_4, 13820-53-6; [2-$(Me_2NCH_2)C_6H_4PdL_2$] L = AcAc, 39046-23-6; [2-$(Me_2NCH_2)C_6H_4PdL_2$] L_2 = EAc, 39046-24-7; [2-$(Me_2NCH_2)C_6H_4PdL_2$] L_2 = PIP, 39046-25-8; [2-$(Et_2NCH_2)C_6H_4PdL_2$] L_2 = (pyridine)$_2$PF$_6$, 39151-88-7; [2-$(Et_2NCH_2)C_6H_4PdL_2$] L_2 = DPM, 39046-26-9; [2-$(Me_2NCH_2)C_6H_4PdL_2$]PF$_6$ L = pyridine, 39046-30-5; [3,6-(Et_2NCH_2)-1,2-$C_6H_4(PdL_2)_2$] L = DPM, 33394-24-0; [3,6-(Et_2NCH_2)-1,2-$C_6H_4(PdL_2)_2$] L = TPL, 39046-32-7; [3,6-(Pr_2NCH_2)-1,2-$C_6H_4(PdL_2)_2$] L = DPM, 39046-33-8; [4,6-(Et_2NCH_2)-1,3-$C_6H_4(PdL_2)_2$] L = AcAc, 33394-25-1; [4,6-(Et_2NCH_2)-1,3-$C_6H_4(PdL_2)_2$] L = TPL, 39046-35-0; [4,6-(Et_2NCH_2)-1,3-$C_6H_4(PdL_2)_2$] L = pyridine, 33461-17-5; [2,5-(Me_2NCH_2)-1,4-$C_6H_4(PdL_2)_2$] L = AcAc, 39046-36-1; [2,5-(Et_2NCH_2)-1,4-$C_6H_4(PdL_2)_2$] L = AcAc, 33394-21-7; [2,5-(Et_2NCH_2)-1,4-$C_6H_4(PdL_2)_2$] L = DPM, 39046-27-0; [2,5-(Et_2NCH_2)-1,4-$C_6H_4(PdL_2)_2$] L = TPL, 39046-28-1; [2,5-(Pr_2NCH_2)-1,4-$C_6H_4(PdL_2)_2$] L = DPM, 39046-29-2; 2-(1-pyrazolyl)phenylpalladium(II) chloride dimer, 39046-05-4; 2-(diethylaminomethyl)-4-methylphenylpalladium(II) chloride dimer, 39046-06-5; 2-(diethylaminomethyl)phenylpalladium(II) chloride dimer, 33571-42-5; 2-(dipropylaminomethyl)phenylpalladium(II) chloride dimer, 39046-08-7; 2-(*N-tert*-butylformimidoyl)phenylpalladium(II) chloride dimer, 39046-09-8; [2-(2-pyridyl)phenyl](tri-*p*-tolylphosphine)palladium(II) chloride, 39046-10-1; bis(benzylmethyl sulfide)palladium(II) dichloride, 39003-76-4; (2,2,6,6-tetramethyl-3,5-heptanedionato)-2-(1-pyrazolyl)phenylpalladium(II), 29190-53-2; 1-(ethoxy-1,3-butanedionato)-2-(1-pyrazolyl)phenylpalladium(II), 39046-12-3; (2,2,6,6-tetramethyl-3,5-heptanedionato)-2-(2-pyridyl)phenylpalladium(II), 39046-13-4; (2,2,6,6-tetramethyl-3,5-heptanedionato)-2-(3,5-dimethyl-1-pyrazolyl)phenylpalladium(II), 39046-14-5; (2,2,6,6-tetramethyl-3,5-heptanedionato)-8-(dimethylamino)naphthylpalladium(II), 39046-15-6; tetrakis(pyridine)palladium(II) bis(hexafluorophosphate), 39003-77-5; bis(pyridine)[2-(1-pyrazolyl)phenyl]palladium(II) hexafluorophosphate, 39046-16-7; bis(pyridine)[2-(diethylaminomethyl)-4-methylphenyl]palladium(II) hexafluorophosphate, 39046-17-8; dichlorobis(3,5-dimethyl-1-phenylpyrazole)palladium, 39003-78-6; bis(pyridine)[2-(3,5-dimethyl-1-pyrazolyl)phenyl]palladium(II) hexafluorophosphate, 39046-18-9; bis[(2-dimethylaminomethyl)phenyl]palladium(II), 23626-48-4; (2-dimethylaminomethylphenyl)(2-pyrazolylphenyl)palladium(II), 39046-20-3; dichloro-3,6-bis(diethylaminomethyl)-1,2-phenylenedipalladium(II), 33247-34-6; dichloro-2,5-bis(diethylaminomethyl)-1,4-phenylenedipalladium(II), 33247-33-5; μ-chloro-[3,6-bis(diethylamino)-1,2-phenylene]bis(pyridine)dipalladium(II) hexafluorophosphate, 33394-22-8; dichloro[3,6-bis(dipropylaminomethyl)-1,2-phenylene]dipalladium(II), 39046-45-2; dichloro[2,5-bis(dipropylaminomethyl)-1,4-phenylene]dipalladium(II), 39046-46-3; 3,6-(diethylaminomethyl)phenylenebis(2,4-pentanedionatopalladium(II), 33394-23-9.

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2,2′-Bipyridine *N*-Oxide Chelates with Divalent 3d Metal Perchlorates

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Transition metal perchlorate chelates with the mono-*N*-oxide of 2,2′-bipyridine (*N*-bipyO) were synthesized and characterized by means of spectral (ir–electronic), magnetic, and conductance studies. The new chelates are of the types [M(*N*-bipyO)$_3$](ClO$_4$)$_2$ (M = Mn, Fe, Co, Ni, Zn) and [Cu(*N*-bipyO)$_2$](ClO$_4$)$_2$, involving respectively hexa- and tetracoordinated complex cations. *N*-bipyO acts as a bidentate O,N-chelating agent and assumes a configuration close to that of the cis form in the new complexes. Each coordinated ligand molecule involves twisting of the two aromatic rings about the 2,2′ bond. In the uv-visible spectra of the complexes, ligand, charge-transfer, and d–d bands are observed. The calculated spectrochemical parameters for the new metal chelates suggest that *N*-bipyO is a stronger ligand than 2,2′-bipyridine *N,N*-dioxide and weaker ligand than 2,2′-bipyridine. The latter ligand forms a spin-paired cationic ferrous complex of the type [FeL$_3$]$^{2+}$, but the *N*-bipyO analog is spin free; the strength of the ligand field in [Fe(*N*-bipyO)$_3$]$^{2+}$ is insufficient to produce a spin-paired Fe(II) complex. Finally, *N*-bipyO occupies a lower position than 2,2′-bipyridine in the nephelauxetic series.

Introduction

2,2′-Bipyridine (bipy) is among the most extensively studied chelating agents.[2,3] The metal complexes of this ligand (I) are characterized by five-membered chelate rings.[2,3] Metal chelates of 2,2′-bipyridine *N,N*-dioxide (*N,N*-bipyO$_2$)

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