Cyclometalated Compounds. XI.[1] Single and Double Cyclometalations of Poly(pyrazolylmethyl)benzenes

Chris M. Hartshorn and Peter J. Steel*

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Received February 9, 1998

Six ligands containing 1,3-bis(pyrazol-1-ylmethyl)benzene subunits are shown to readily undergo cyclometalation reactions. 1,3-Bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene (**1**) is cyclopalladated to form the complex PdCl[$C_6HMe_2(CH_2pz)_2$-*N*,*C*,*N*] (**3**), containing two fused-ring six-membered metallocycles, for which the X-ray crystal structure of the DMSO solvate is described. The tetramethyl-substituted derivative $C_6H_2Me_2(CH_2Me_2pz)_2$ (**2**) and the 1,3,5-tris(pyrazol-1-ylmethyl)benzenes $C_6HMe_2(CH_2pz)_3$ (**7**) and $C_6HMe_2(CH_2Me_2pz)_3$ (**8**) behave similarly. Reaction of **1** with a (terpyridine)ruthenium reagent ultimately produces the cycloruthenated derivative (tpy)Ru[$C_6HMe_2(CH_2pz)_2$-*N*,*C*,*N*]$^+$ (**6**), the hexafluorophosphate salt of which is also crystallographically characterized. This reaction proceeds by way of a novel intermediate dication (tpy)Ru[$C_6H_2Me_2(CH_2pz)_2$-*N*,*N*]$^{2+}$ (**5**) that is shown, by detailed NMR studies, to contain an aryl C−H···Ru interaction. The 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzenes $C_6H_2(CH_2pz)_4$ (**12**) and $C_6H_2(CH_2Me_2pz)_4$ (**13**) undergo single and double cyclopalladation reactions. The X-ray crystal structure of the doubly palladated derivative of **13** is described. In all cases, the six-membered metallocycles exist in boat conformations, which leads to interesting dynamic behavior in their ^{1}H NMR spectra.

Introduction

Cyclometalated compounds have been much studied over the last three decades,[2] with such compounds having found numerous applications in organic synthesis,[3] in material science,[4] and as biologically active compounds.[5] Cyclometalated compounds are usually classified according to the metal incorporated, the heteroatom donor, and the chelate ring size.[2] By far the most well-studied examples are five-membered palladocycles with nitrogen or phosphorus donors.[2] Examples of six-membered chelate ring-sized metallocycles have become more common in recent years[6] but still remain relatively rare. The incorporation of a second chelating donor atom to produce fused ring metallocycles is also known, and, in this context, cyclometalated analogues of 2,2′:6′,2″-terpyridine (tpy) have generated much recent interest.[7,8]

Double cyclometalation of certain ligands is also possible,[1] and such compounds have attracted interest as potential components of molecular electronic devices due to the significant metal−metal intereactions in these compounds.[9] While many compounds containing two palladated phenyl rings have been reported,[10] relatively few are known wherein two sites in the same benzene ring are cyclometalated.[11]

We have previously described syntheses of a series of poly(pyrazolylmethyl)benzenes.[12] These compounds exhibit a variety of modes of coordination to transition

* To whom correspondence should be addressed. E-mail: p.steel@chem.canterbury.ac.nz.

(1) Part X: O'Keefe, B. J.; Steel, P. J. *Organometallics*, in press.

(2) (a) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (b) Omae, I. *J. Organomet. Chem. Libr.* **1986**, *18*, 1. (c) Omae, I. *Coord. Chem. Rev.* **1988**, *83*, 137. (d) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(3) Ryabov, A. D. *Synthesis* **1985**, 233.

(4) Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1993**, 2983. Buey, J.; Espinet, P. *J. Organomet. Chem.* **1996**, *507*, 137 and references therein.

(5) Navarro-Ranninger, C.; Lopez-Solera, I.; Rodriguez, J.; Garcia-Ruano, J. L.; Raithby, P. R.; Masaguer, J. R.; Alonso, C. *J. Med. Chem.* **1993**, *36*, 3795. Navarro-Ranninger, C.; Lopez-Solera, I.; Gonzalez, V. M.; Perez, J. M.; Alvarez-Valdes, A.; Martin, A.; Raithby, P. R.; Masaguer, J. R.; Alonso, C. *Inorg. Chem.* **1996**, *35*, 5181.

(6) (a) Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1477. (b) Albert, J.; Ceder, R. M.; Gomez, M.; Granell, J.; Sales, J. *Organometallics* **1992**, *11*, 1536. (c) Hiraki, K.; Nakashima, M.; Uchiyama, T.; Fuchita, Y. *J. Organomet. Chem.* **1992**, *428*, 249. (d) Barro, J.; Granell, J.; Sainz, D.; Sales, J.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **1993**, *456*, 147. (e) Alonso, M. T.; Juanes, O.; de Mendoza, J.; Rodriguez-Ubis, J. C. *J. Organomet. Chem.* **1994**, *484*, 19. (f) Krylova, L. F.; Dulepova, N. V. *Zh. Neorg. Khim.* **1994**, *39*, 2022. (g) Tollari, S.; Palmisano, G.; Demartin, F.; Grassi, M.; Magnaghi, S.; Cenini, S. *J. Organomet. Chem.* **1995**, *488*, 79. (h) Fuchita, Y.; Yoshinaga, K.; Kusaba, H.; Mori, M.; Hiraki, K.; Takehara, K. *Inorg. Chim. Acta* **1995**, *239*, 125.

(7) Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1990**, 443. Constable, E. C.; Dunne, S. J.; Rees, D. G.; Schmitt, C. X. *J. Chem. Soc., Chem. Commun.* **1996**, 1169. Constable, E. C.; Cargill Thompson, A. M. W. *New J. Chem.* **1996**, *20*, 65.

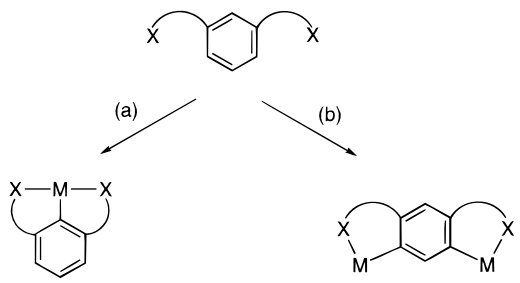
(8) Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831. Garcia-Herbosa, G.; Munoz, A.; Miguel, D.; Garcia-Granda, S. *Organometallics* **1994**, *13*, 1775. Lucena, N.; Casabo, J.; Escriche, L.; Sanchez-Castello, G.; Teixidor, F.; Kivekas, R.; Sillanpaa, R. *Polyhedron* **1996**, *15*, 3009. Jouaiti, A.; Geoffroy, M.; Collin, J.-P. *Inorg. Chim. Acta* **1996**, *245*, 69 and references therein.

(9) Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1993**, *32*, 4539. Barigelletti, F.; Flamigni, L.; Guadigli, M.; Juris, A.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1996**, *35*, 136 and references therein.

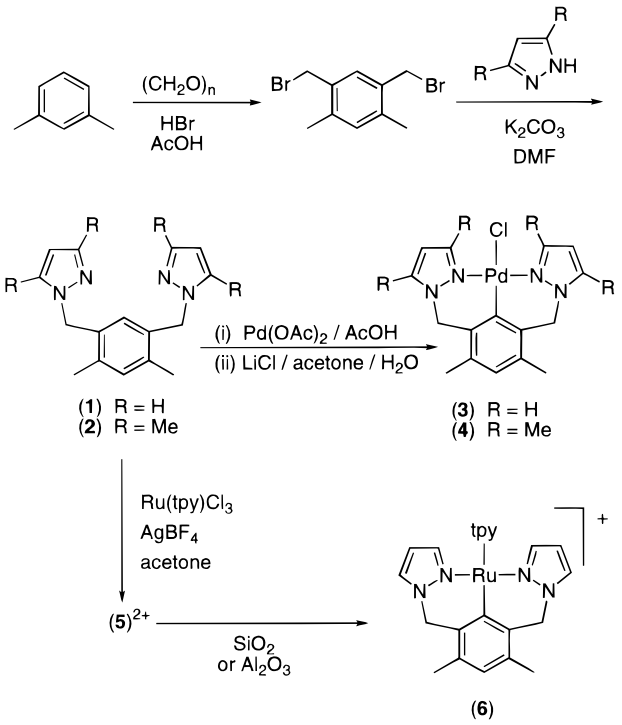
(10) (a) Izumi, T.; Kasahara, A. *Bull. Yamagata Univ., Eng.* **1979**, *15*, 213. (b) Espinet, P.; Garcia, G.; Herrero, F. J.; Jeannin, Y.; Philoche-Levisalles, M. *Inorg. Chem.* **1989**, *28*, 4207. (c) Caygill, G. B.; Hartshorn, R. M.; Steel, P. J. *J. Organomet. Chem.* **1990**, *382*, 455. (d) Caygill, G. B.; Steel, P. J. *J. Organomet. Chem.* **1990**, *395*, 359 (e) Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *Tetrahedron Lett.* **1993**, *34*, 3413. (f) Selvakumar, K.; Vancheesan, S. *Polyhedron* **1996**, *15*, 2535. (g) Vila, J. M.; Gayoso, M.; Lopez Torres, M.; Fernandez, J. J.; Fernandez, A.; Ortigueira, J. M.; Bailey, N. A.; Adams, H. *J. Organomet. Chem.* **1996**, *511*, 129. (h) Lopez, C.; Bosque, R. *J. Organomet. Chem.* **1996**, *524*, 247.

S0276-7333(98)00085-5 CCC: $15.00
Publication on Web 07/03/1998

Scheme 1



Scheme 2



metals. For example, we have reported their ability to encapsulate metal ions[13] and to form large nanoscale metallosupramolecular cages.[14] We now describe cyclometalation reactions of some of these compounds. The ligands employed in the present study all incorporate 1,3-bis(pyrazolylmethyl)benzene subunits which, upon cyclometalation, result in the formation of products that contain two fused six-membered metallocycles. Furthermore, the use of tetrasubstituted benzenes leads to novel compounds in which a single benzene is doubly metalated, with each metal incorporated into two fused metallocycles.

Results and Discussion

1,3-Bis(pyrazolylmethyl)benzenes. 1,3-Disubstituted benzenes can undergo two modes of cyclometalation (Scheme 1). Single metalation in the 2-position leads to two fused chelate rings (path a). Alternatively, reaction in the 4- and 6-positions leads to a doubly cyclometalated product (path b). Examples of both modes of reaction are known.[10f,11,15] 1,3-Bis(pyrazolylmethyl)benzene has previously been reported to undergo cyclopalladation via path a.[16]

To restrict reaction to this desired pathway (a), it was decided to block the 4- and 6-positions by substitution with methyl groups. Thus, the two new ligands $C_6H_2Me_2(CH_2pz)_2$ (**1**) and $C_6H_2Me_2(CH_2Me_2pz)_2$ (**2**) were prepared, as shown in Scheme 2. Extension of a recently reported method[17] for the bromomethylation of tri- and tetramethylbenzenes to reaction with *m*-xylene gave a 3:1 mixture of regioisomers, from which the desired major isomer was readily purified by recrystallization. This was then used for the alkylation of pyrazole and 3,5-dimethylpyrazole to give **1** and **2**, respectively, in satisfactory yields.

While assignment of the ^{1}H NMR spectrum of **1** was trivial, that of **2** was more complicated. Unambiguous assignments were made by a series of difference NOE experiments. Irradiation of H4′ resulted in enhancements for the adjacent 3′-CH_3 and 5′-CH_3 groups. Irradiation of the methylene proton signal gave enhancements of the 5′-CH_3 signal (1.7%), the xylyl-CH_3 signal (2.6%), and that of the adjacent benzene proton (12.6%). This proton resonates at a remarkably high-field chemical shift of 5.43 ppm, which we attribute to shielding from the ring currents of the adjacent pyrazole groups, which are forced to adopt conformations perpendicular to the plane of the central benzene ring.

Cyclopalladation of these compounds proceeded smoothly by reaction with palladium acetate in refluxing glacial acetic acid, to give acetato complexes that were transformed to the chloro complexes $PdCl[C_6HMe_2(CH_2pz)_2$-*N*,*C*,*N*] (**3**) and $PdCl[C_6HMe_2(CH_2Me_2pz)_2$-*N*,*C*,*N*] (**4**) using lithium chloride (Scheme 2). These compounds were characterized by microanalysis and ^{1}H and ^{13}C NMR spectroscopy. The number of signals in the ^{1}H spectra, along with observed downfield shifts for the palladated carbon in **2** (143.97 ppm) and **3** (147.33 ppm), consistent with those in known cyclopalladated systems,[10f] confirmed the palladated structures. Again, complete assignment of the ^{1}H NMR spectrum of **4** required difference NOE experiments to assign signals in the methyl region. As for **2**, irradiation of the signals for the methylene and H4′ protons allowed for the unambiguous assignment of the signals for the three different methyl environments.

Only one previous report (with two examples) has described X-ray crystal structures of orthopalladated complexes in which coordination of the metal gives two fused six-membered palladocycles.[6a] Hence, and in order to confirm the cyclopalladated structures, a single-

(11) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1971**, *93*, 1808. (b) Phillips, I. G.; Steel, P. J. *J. Organomet. Chem.* **1991**, *410*, 247. (c) Chakladar, S.; Paul, P.; Venkatsubramanian, K.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1991**, 2669. (d) Chakladar, S.; Paul, P.; Nag, K. *Polyhedron* **1991**, *10*, 1513. (e) Chakladar, S.; Paul, P.; Mukherjee, A. K.; Dutta, S. K.; Nanda, K. K.; Podder, D.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1992**, 3119. (f) Loeb, S. J.; Shimizu, G. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1395. (g) Vila, J. M.; Gayoso, M.; Pereira, M. T.; Torres, M. L.; Fernandez, J. J.; Fernandez, A.; Ortigueira, J. M. *J. Organomet. Chem.* **1996**, *506*, 165. (h) Steenwinkel, P.; James, S. L.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 513. (i) Lydon, D. P.; Rourke, J. P. *Chem. Commun.* **1997**, 1741.

(12) Hartshorn, C. M.; Steel, P. J. *Aust. J. Chem.* **1995**, *48*, 1587.

(13) Hartshorn, C. M.; Steel, P. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2655.

(14) Hartshorn, C. M.; Steel, P. J. *Chem. Commun.* **1997**, 541.

(15) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681 and references therein. Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **1995**, *1*, 343. Djukic, J.-P.; Maisse, A.; Pfeffer, M.; de Cian, A.; Fischer, J. *Organometallics* **1997**, *16*, 657.

(16) Canty, A. J.; Honeyman, R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1990**, *389*, 277.

(17) van der Made, A. W.; van der Made, R. H. *J. Org. Chem.* **1993**, *58*, 1262.

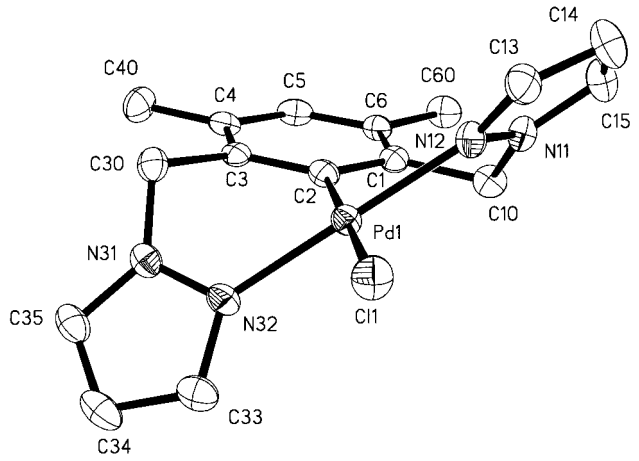


Figure 1. Perspective view and atom labeling of the X-ray structure of **3**·DMSO. The hydrogen atoms and disordered solvate are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C2 1.993(4), Pd1−N12 2.008(3), Pd1−N32 2.007(3), Pd1−Cl1 2.429(1); C2−Pd1−N12 88.8-(1), C2−Pd1−N32 88.7(1), Cl1−Pd1−N12 91.2(1), Cl1−Pd1−N32 91.4(1), C2−Pd1−Cl1 176.0(1), N12−Pd1−N32 177.3(1).

crystal X-ray structure determination was carried out on a sample of **3** after recrystallization from DMSO.

The complex crystallizes in the monoclinic space group $P2_1/c$ and contains one cyclopalladated molecule and a disordered dimethyl sulfoxide solvate in the asymmetric unit. A perspective view and atom labeling of the metalated unit is shown in Figure 1, along with a list of selected bond lengths and angles. The palladium atom has approximately square planar coordination to the N, C, N, Cl donor set.[18] The plane of coordination is twisted 37.1(3)° out of the plane of the benzene, placing the two pyrazole rings on opposite sides of the extended plane of the benzene ring. The palladium atom is 0.067(2)−0.108(2) Å out of the planes of the three donor rings, but there is minimal distortion of the planarity of the rings themselves (maximum displacement from a ring mean plane = 0.008(5) Å for N31). While the Pd1−C2, Pd1−N12, and Pd1−N32 bond lengths are within the range of lengths found in related structures, the Pd1−Cl1 distance (2.429(1) Å) is relatively long. However, it is consistent with those of other structures with a chlorine trans to a σ-bonded carbon. Such Pd−Cl bond lengthening has previously been attributed to the trans influence of the C-donor, due to its low electronegativity.[11d,19]

The fused six-membered metallocycles each exist in a boat conformation: Pd1 and C10 are 0.734(2) and 0.592(5) Å, respectively, above the mean plane defined by C1, C2, N11, N12, and Pd1 and C30 are 0.813(2) and 0.594(5) Å below the mean plane defined by C2, C3, N31, N32. This conformation allows for a weak interaction between the palladium and a hydrogen from each methylene group (Pd1−H10A 3.14(2) Å, Pd1−H30A 3.05(2) Å), as has been observed in other six-membered palladocycles.[20] The existence of the chelate rings in boat conformations has interesting effects in the ^{1}H NMR spectra, which are discussed in more detail below.

Having demonstrated that **1** and **2** readily undergo cyclopalladation reactions, attempts were made to prepare a cyclometalated ruthenium complex of **1**, with interesting results. Following a methodology previously employed for the preparation of other cycloruthenated complexes containing tridentate heterocyclic ligands,[9] the ligand **1** was reacted with a (terpyridine)tris-(acetone)ruthenium complex, generated by treatment of the trichloro analogue with silver tetrafluoroborate. NMR analysis of the crude product, isolated as the hexafluorophosphate salt, showed that this was not the expected product (tpy)Ru[$C_6HMe_2(CH_2pz)_2$-*N*,*C*,*N*]$^+$ (**6**), but rather a cation (**5**) containing an unsymmetrical tpy ligand and the intact ligand **1** in a symmetrical environment, with both benzenoid hydrogens present. Attempts to purify this brown solid by chromatography on either silica gel or alumina resulted in conversion to a purple compound. Such a color is characteristic of Ru-(II) in a C,N_5-cyclometalated coordination environment.[21] Indeed, isolation and NMR analysis showed that this was the originally expected cycloruthenated complex **6**, having a symmetrical tpy ligand and only one benzene proton signal.

Thus, cycloruthenation of **1** proceeds through an intermediate dication **5**, whose conversion to **6** is catalyzed by silica or alumina. To isolate and identify this intermediate, various attempts were made to purify it. This was finally achieved by chromatography on Sephadex, and FAB mass spectrometry of the isolated hexafluorophosphate salt showed a highest mass peak corresponding to the stoichiometry [Ru(tpy)(**1**)](PF$_6$)$^+$. A variety of NMR techniques were used both to assign the ^{1}H NMR spectrum and to assist with the structure elucidation of **5**. COSY and 1D-TOCSY experiments readily located the different ring systems of the complex. Selected signals were then irradiated in NOE experiments in order to assist with the complete assignment of the spectrum of **5** and to examine the relative spacial arrangement of the tpy and ligand **1** within the complex.

Figure 2 shows some relevant difference NOE spectra for the dication **5**. Irradiation (Figure 2b) of the methyl group signal (2.74 ppm) gives the expected enhancement of one of the benzene protons (13.3%), which can thus be assigned as H5. Additional enhancements are observed for one of the pair of geminally coupled methylene hydrogens (3.9%) and one of the pyrazole group hydrogens (1.3%). Irradiation of one of the two methylene hydrogen signals (Figure 2c) shows that it lies close in space to a pyrazole ring hydrogen (H5′, 7.1% enhancement), while the other (Figure 2d) is close to H2. Finally, (Figure 2e), irradiation of H2 results in enhancements of one of the methylene hydrogens (4.3%) and each of the two terminal pyridine hydrogens in the 6-position, but to very different extents (3.1% and 18.9%).

(18) There is evidence of a slight tetrahedral distortion from square planarity around the palladium, as the mean plane defined by Pd1 (deviation from the plane of 0.023(2) Å), Cl1 (−0.046(3)), C2 (−0.058-(5)), N12 (0.040(5)), and N32 (0.040(5)) shows alternating displacement of the donor atoms above and below the plane.

(19) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.

(20) Watson, A. A.; House, D. A.; Steel, P. J. *Aust. J. Chem.* **1995**, *48*, 1549 and references therein.

(21) Collin, J.-P.; Beley, M.; Sauvage, J.-P.; Barigelletti. F. *Inorg. Chim. Acta* **1991**, *186*, 91. Constable, E. C.; Hannon, M. J. *Inorg. Chim. Acta* **1993**, *211*, 101. Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1994**, 3095. Bardwell, D. A.; Jeffrey, J. C.; Schatz, E.; Tilley, E. E.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 825.

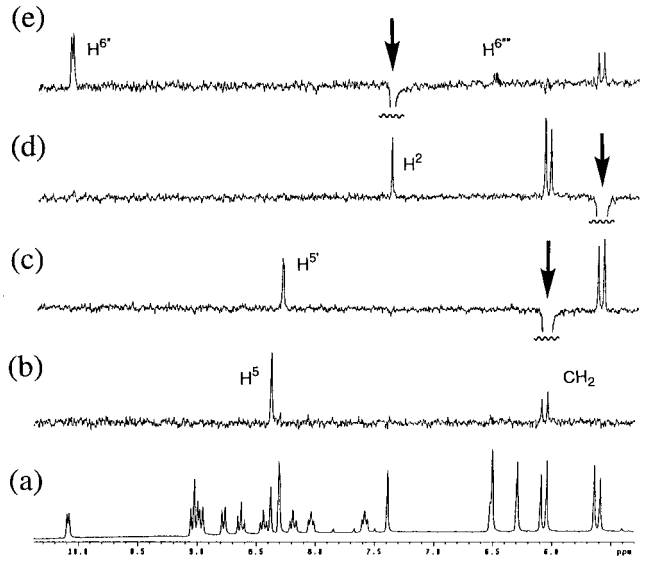


Figure 2. ^{1}H NMR spectrum of the intermediate dication **5** (a) and difference NOE spectra, resulting from irradiation of the CH_3 (b), CH_2 (c and d), and H2 (e) signals, respectively.

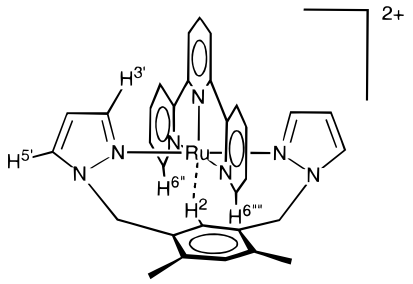


Figure 3. Proposed structure for the intermediate dication **5**.

On the basis of these results, we propose the structure (tpy)Ru[$C_6H_2Me_2(CH_2pz)_2$-*N,N*]$^{2+}$, shown in Figure 3, for the intermediate dication **5**. This has C_s symmetry passing through the plane of the tpy ligand, which in turn makes the two pyrazole rings equivalent but the two terminal tpy pyridines inequivalent. We believe that, in this complex, the benzene ring is locked into the conformation shown by an aryl C−H···Ru interaction. Such an interaction is exactly what is required for subsequent CH activation and cyclometalation.[22] Furthermore, some remarkable chemical shift values support this structure for **5**. The low-field shift for H6″ (10.09 ppm) is consistent with it being deshielded by the ring current of the benzene ring. Conversely, H6′′′′, which lies over the shielding region of the benzene ring, has an exceptionally high-field shift (6.52 ppm). The H3′ signal (6.51 ppm) also has a chemical shift higher than is typical, due to the shielding effect of the nearby central pyridine ring of the tpy ligand. Strong support for this proposed structure for the dication **5** has very recently been provided by van Koten and co-workers, who isolated and crystallographically characterized a structurally related intermediate having such an aryl C−H···Ru interaction, supported by two adjacent phosphine donors.[23]

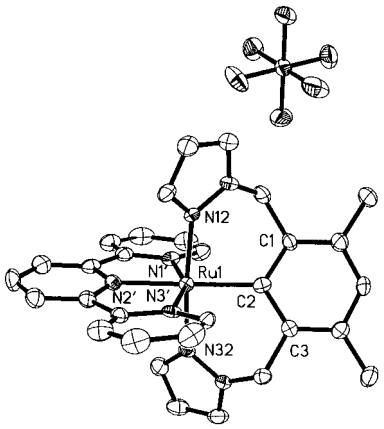


Figure 4. Perspective view and partial atom labeling of the X-ray structure of the hexafluorophosphate salt of **6**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−C2 2.073(4), Ru1−N12 2.073(4), Ru1−N32 2.079(4), Ru1−N1′ 2.062(4), Ru1−N2′ 2.000(4), Ru1−N3′ 2.081(4); C2−Ru1−N12 87.6(2), C2−Ru1−N32 87.8(2), C2−Ru1−N1′ 100.1(2), C2−Ru1−N3′ 103.0(2), N12−Ru1−N1′ 96.0(2), N12−Ru1−N2′ 92.5(1), N12−Ru1−N3′ 84.9(1), N32−Ru1−N1′ 96.0(2), N32−Ru1−N2′ 92.1(1), N32−Ru1−N3′ 96.3(1), N1′-Ru1−N2′ 78.3(2); N3′-Ru1−N2′ 78.6(2), C2−Ru1−N2′ 178.4(2), N12−Ru1−N32 175.4(1), N1′-Ru1−N3′ 156.9(2).

The structure of the cycloruthenated complex (tpy)Ru[$C_6HMe_2(CH_2pz)_2$-*N,C,N*]$^+$ (**6**) was deduced from a combination of NMR and mass spectrometry. The ^{1}H NMR spectrum of **6** showed significant broadening of several of the peaks at room temperature. To confirm this structure, and to examine the geometry of the complex, a single-crystal X-ray structure determination was carried on crystals obtained by vapor diffusion of pentane into an acetone solution of **6**. The complex crystallizes in the orthorhombic space group *Pbca*, the asymmetric unit of which contains one cycloruthenated cation and a hexafluorophosphate anion. A perspective view and atom labeling of the contents of the asymmetric unit is shown in Figure 4, along with a list of selected bond lengths and angles.

The coordination geometry around the ruthenium is distorted octahedral. The largest deviations from this geometry are due to the geometrical constraints imposed by the tpy ligand, with the shortest bond being to the nitrogen of the central ring. These features are typical for tpy complexes.[24] The ruthenium atom lies 0.014(4)−0.285(4) Å out of the planes of the six donor rings, with the largest of these distances being out of the planes of the pyrazole rings (0.285(4) and 0.226(4) Å). The mean plane of the terpyridine ligand is inclined at an angle of 65.5(4)° to the plane of the benzene ring. Within the terpyridine ligand, the three pyridine rings are not coplanar, with the two terminal rings being 7.8(4) and 8.9(4)° out of the plane of the central ring. As shown in Figure 5, this situation occurs to relieve the

(22) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. Kawamoto, T.; Nagasawa, I.; Kuma, H.; Kushi, Y. *Inorg. Chem.* **1996**, *35*, 2427.

(23) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317.

(24) See, for example: Rasmussen, S. C.; Ronco, S. E.; Mlsna, D. A.; Billadeau, M. A.; Pennington, W. T.; Kolis, J. W.; Petersen, J. D. *Inorg. Chem.* **1995**, *34*, 821. Gerli, A.; Reedijk, J.; Lakin, M. T.; Spek, A. L. *Inorg. Chem.* **1995**, *34*, 1836.

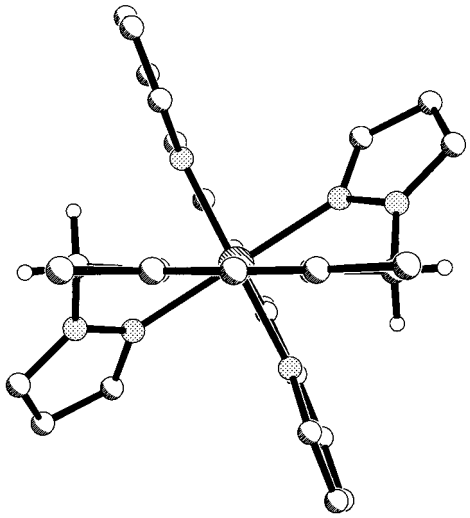


Figure 5. Perspective view of **6** showing the distortion of the terminal pyridine rings away from the methylene hydrogens. All hydrogens, except those of the methylenes, are omitted for clarity.

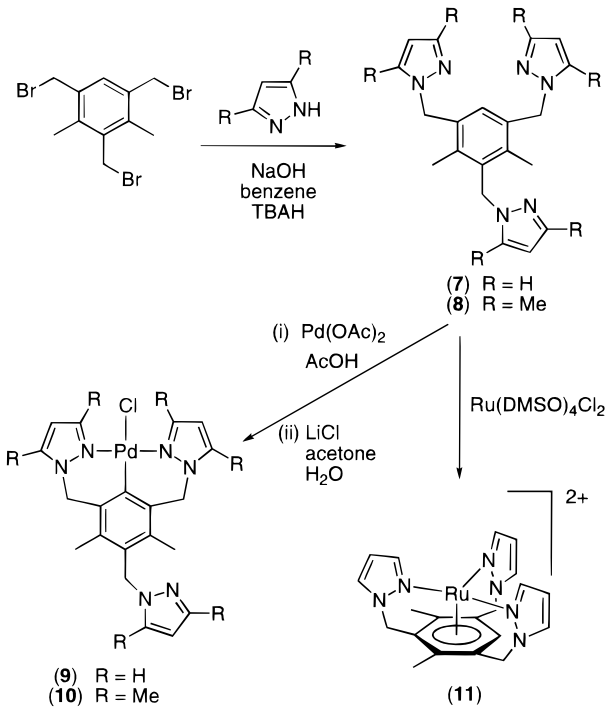
steric compression between the terminal pyridines and the nearby methylene hydrogens. Once again, boat conformations are observed for the fused metallocycles, with 0.605(7)−0.679(4) Å displacements of the Ru and CH_2 groups out of the plane of the respective boat. The smaller average displacement from the plane of the boat, relative to the palladocycle **3**, may be due to the fact that agostic interactions are not available to the six-coordinate ruthenium.

Having demonstrated that 1,3-bis(pyrazol-1-ylmethyl)benzenes readily undergo cyclometalation reactions, we then proceeded to investigate the cyclometalation chemistry of more highly substituted poly(pyrazolylmethyl)benzenes.

1,3,5-Tris(pyrazolylmethyl)benzenes. The two new 1,3,5-tris(pyrazol-1-ylmethyl)benzenes, $C_6HMe_2(CH_2pz)_3$ (**7**) and $C_6HMe_2(CH_2Me_2pz)_3$ (**8**), were synthesized as shown in Scheme 3. The required precursor, 1,3,5-tris(bromomethyl)-2,4-dimethylbenzene, was obtained by more exhaustive bromomethylation of *m*-xylene and then reacted with pyrazole and 3,5-dimethylpyrazole under phase-transfer-catalyzed conditions[12] to give **7** and **8**, respectively. ^{1}H and ^{13}C NMR assignments of these ligands were made by comparison with the spectra of related ligands.[12] Once again, the benzenoid proton in **8** appears at an unusually high-field position of 5.28 ppm, due to shielding by the twisted pyrazole rings, while that in **7** appears at a more normal position of 6.64 ppm.

The cyclopalladated compounds PdCl[$C_6Me_2(CH_2pz)_3$-*N*,*C*,*N*] (**9**) and PdCl[$C_6Me_2(CH_2Me_2pz)_3$-*N*,*C*,*N*] (**10**) were synthesized, in good yields, using reaction conditions similar to those employed above. These compounds were characterized by microanalysis and ^{1}H and ^{13}C NMR spectroscopy. As for the previous palladocycles, the number of signals in the ^{1}H spectra, along with observed downfield shifts for the palladated carbon in **9** (144.85 ppm) and **10** (147.83 ppm), served to confirm the structures. The presence of the noncoordinated (hypodentate[25]) pendant pyrazole groups in these two compounds suggests the potential for further coordination to a second metal. Work in this area will be presented elsewhere.

Scheme 3



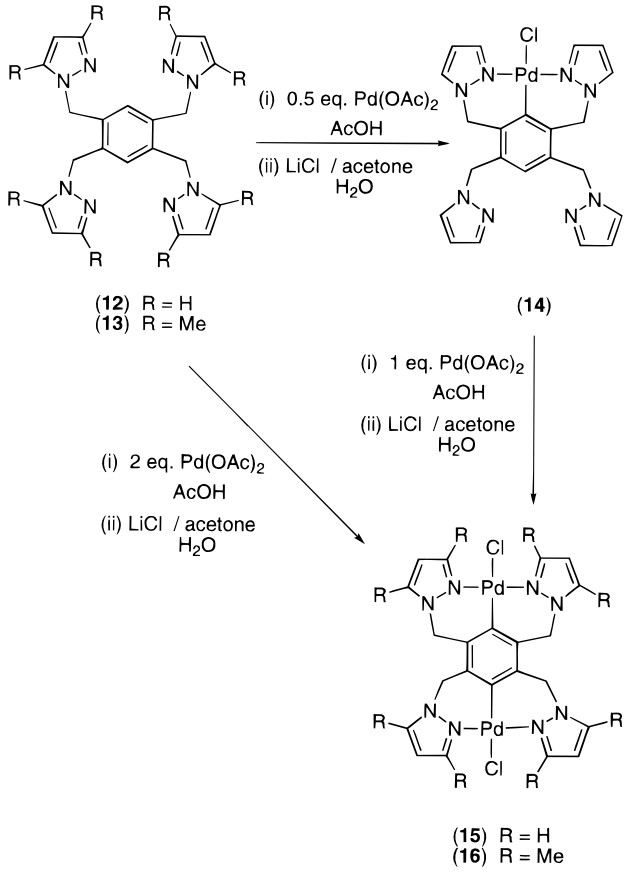
No attempt was made to cycloruthenate these ligands. Instead, a ruthenium derivative was prepared by reaction with $Ru(DMSO)_4Cl_2$. We have previously described the ability of 1,3,5-tris(pyrazol-1-ylmethyl)benzenes to encapsulate metal atoms.[13] Such a species (**11**) was obtained as the chloride salt which, after metathesis to the more soluble hexafluorophosphate salt, showed physical and spectroscopic properties consistent with the proposed structure **11** (Scheme 3). In particular, the ^{1}H NMR spectrum showed the required mirror symmetry, with coordination-induced shifts ranging between −0.06 and +0.89 ppm, with similar induced shifts for each of the pyrazole rings. The methylene protons give rise to a singlet for the 3-substituent and a pair of geminally coupled doublets for the 1,5-substituents, which requires that these hydrogens are locked in inequivalent environments. Such properties are consistent with those reported for analogous ruthenium complexes of related ligands.[13] We anticipate that this compound will show interesting reaction chemistry, since the single unsubstituted position of the benzene ring should be susceptible to attack by a variety of nucleophiles with conversion to the corresponding η^5-cyclohexadienyl adduct.[26] Work in this area is in progress.

1,2,4,5-Tetrakis(pyrazolylmethyl)benzenes. The preparations of the tetrapodal ligands $C_6H_2(CH_2pz)_4$ (**12**) and $C_6H_2(CH_2Me_2pz)_4$ (**13**) have been described elsewhere.[12] These are potentially capable of undergoing double cyclometalation reactions. However, the synthesis and isolation of the bis-cyclopalladated complexes of **12** and **13** proved to be more difficult. Although the

(25) Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67.

(26) Shirin, Z.; Pramanik, A.; Ghost, P.; Mukherjee, R. *Inorg. Chem.* **1996**, *35*, 3431. Bhambri, S.; Tocher, D. A. *J. Organomet. Chem.* **1996**, *507*, 291.

Scheme 4



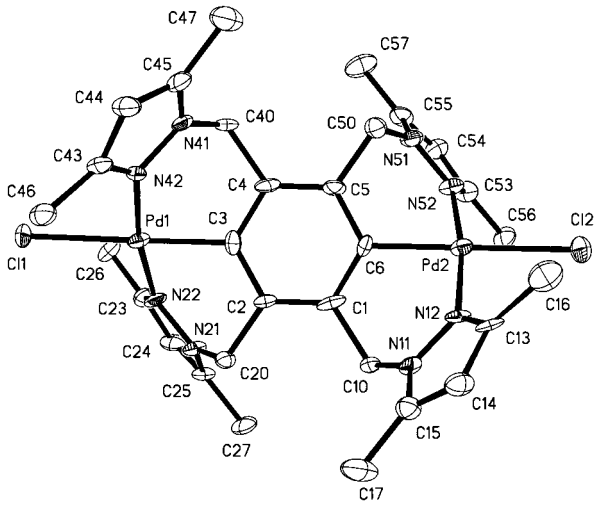


Figure 6. Perspective view and atom labeling of one of the two independent molecules of **16**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for each of the two independent molecules: Pd1−C3 1.969(8), 1.984(8); Pd1−N22 2.023(7), 2.027(7); Pd1−N42 2.037(7), 2.041(7); Pd1−Cl1 2.461(2), 2.460(2); Pd2−C6 1.973(8), 2.002(8); Pd2−N12 2.037(7), 2.045(7); Pd2−N52 2.018(6), 2.031(7); Pd2−Cl2 2.473(2), 2.458(2); C3−Pd1−N22 85.5(3), 85.1(3); C3−Pd1−N42 85.2(3), 85.9(3); Cl1−Pd1−N22 94.8(2), 94.9(2); Cl1−Pd1−N42 94.5(2), 94.1(2); C3−Pd1−Cl1 179.3(3), 178.7(2); N22−Pd1−N42 170.5(2), 171.0(3); C6−Pd2−N12 85.4(3), 86.3(3); C6−Pd2−N52 86.0(3), 85.4(3); Cl2−Pd2−N12 94.6(2), 94.3(2); Cl2−Pd2−N52 94.1(2), 94.0(2); C6−Pd2−Cl2 176.7(3), 179.1(2); N12−Pd2−N52 171.3(2), 171.6(3).

bis-cyclopalladated complex $[C_6(CH_2pz)_4(PdCl)_2$-*N*,*C*,*N*] (**15**) (Scheme 4) can be synthesized directly using two or more equivalents of palladium acetate, it proved awkward to isolate this compound from impurities formed during the extended period of reflux in acetic acid. Instead, the monocyclopalladated complex PdCl-$[C_6H(CH_2pz)_4$-*N*,*C*,*N*] (**14**) was efficiently synthesized using 1 equiv of the ligand to 0.5 equiv of palladium acetate.[27] The monocyclopalladated complex **14** was then reacted with a further equivalent of palladium acetate and, after conversion to the chloride, gave **15** as a white solid, in excellent yield.

The more soluble doubly cyclopalladated complex $[C_6(CH_2Me_2pz)_4(PdCl)_2$-*N*,*C*,*N*] (**16**) was able to be prepared and purified, directly from **13**, by reaction with 2 equiv of palladium acetate, albeit in modest yield. The structure of each of the cyclopalladated compounds **14**−**16** was supported by microanalysis and ^{1}H and ^{13}C NMR spectroscopy. To confirm the structure and to examine the relative orientations of the fused chelate rings, a single-crystal X-ray structure determination was carried out on **16**, using crystals obtained by vapor diffusion of methanol into a DMSO solution of the complex.

The complex crystallizes in the triclinic space group $P\bar{1}$, the asymmetric unit of which contains two doubly cyclopalladated molecules along with four methanol solvate molecules, two of which are disordered. One of the two cyclometalated molecules in the asymmetric unit is shown with atom labeling in Figure 6. Selected bond lengths and angles for both molecules are also listed. Hitherto, only two examples of 1,4-bis-palladated aromatic rings have been crystallographically characterized, each of which contains tridentate, fused-ring donor sets, with additional N-donors trans to the C-donors.[11e,g] However, these structures are topologically quite different, as they contain only five-membered, planar palladocycles.

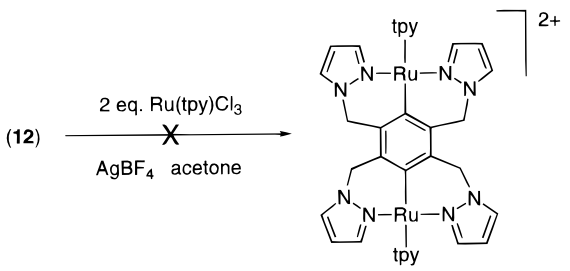
The four independent palladium−carbon bond lengths of **16** range between 1.969(8) and 2.002(8) Å (average = 1.982(8) Å), which are comparable to the length observed in the mononuclear complex **3** (1.993(4) Å). This suggests that the Pd−C bond strength is not affected by the presence of the second, para-substituted palladium atom. The intramolecular Pd···Pd separations for **16** are 6.730(1) and 6.734(1) Å, somewhat longer than the corresponding values in the two previously reported 1,4-dipalladated compounds (6.567(2) and 6.547(1) Å).[11e,g]

The Pd coordination planes[28] are twisted by 49.1−49.9(4)° with respect to the planes of the attached benzene rings. Within each molecule, the two such twists are in opposite directions, which results in an alternating pattern of the pyrazole rings above and below the plane of the benzene ring, to give an overall saddle-shaped structure. This twisting is significantly

(27) The unreacted excess ligand was recovered with good efficiency from the reaction mixture.

(28) The palladium atoms each have approximately square planar coordination to the N, C, N, Cl donor set, with a slight tetrahedral distortion from this geometry. This can again be seen in the alternating pattern above and below the plane defined by Pd and the four coordinated atoms. The trans coordination angles for the four C−Pd−Cl sets (average angle 178.5(3)°) are less distorted from linearity than the N−Pd−N sets (average angle 171.1(3)°).

Scheme 5



(**17**)

greater than that observed in **3** (vide supra) and presumably occurs to relieve steric interactions between the chloro substituents and the nearby methyl groups. These interactions are also reflected in the long palladium−chlorine distances (2.458(2)−2.473(2) Å), there being few structurally characterized examples with longer bond lengths from a palladium to a nonbridging chlorine.[29] This twisting further results in a slight twist-boat distortion of the central benzene rings, which is most dramatically seen in the fact that the attached methylene carbons lie between 0.17(1) and 0.26(1) Å away from coplanarity with their benzene rings. Boat conformations are again observed for the metallocycles, with the distances of the palladiums and methylene carbons from the plane of their boats averaging 0.939 and 0.649 Å, respectively.

Finally, attempts were made to synthesize {$C_6(CH_2$-pz)$_4$[Ru(tpy)]$_2$-*N,C,N*} (**17**), the doubly cycloruthenated complex of 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene (**12**) (Scheme 5). Despite numerous attempts using a variety of modifications (solvent, concentration, reaction times, and workup procedures) to the reaction conditions used to prepare **6**, only mixtures of complexes were obtained, none of which resembled the desired product **17**. We have shown previously that a variety of modes of coordination are possible for 1,2-, 1,3- and 1,4-bis(pyrazol-1-ylmethyl)benzene ligands.[30] All of these substituent relationships are present in **12**, and, consequently, a wide range of complexes could form on reaction with ruthenium. Only in one of these cases, where there is trans coordination of the 1,5-substituents to a first ruthenium and trans coordination of the 2,4-substituents to a second ruthenium, will double cycloruthenation of **12** be possible. This is only one of many modes of coordination, and formation of some of the others may be more favored, which probably accounts for our failure to observe or isolate **17**.

Variable-Temperature NMR Studies. The X-ray crystal structures described above show that the metallocyclic rings exist in boat conformations. This has interesting effects in the ^{1}H NMR spectra of these compounds. In a boat conformation, the two hydrogens attached to each methylene carbon are diastereotopic and give rise to different signals in the ^{1}H NMR spectrum. However, in solution, the possibility exists for inversion of the boat conformers, which has the effect of interchanging the environments of the two hydrogens, which, if rapid on the NMR time scale, leads to a single signal for the two hydrogens. In all the cyclopalladated compounds bearing 3,5-dimethylpyrazolyl substituents (viz. **4**, **10**, and **16**), this inversion process is slow on the NMR time scale, and two signals are observed for the methylene protons, with no broadening of the signals on increasing the temperature to 80 °C. The presence of the methyl groups clearly slows the inversion process, since the transition structure for inversion requires the 3′-methyl groups to come into close proximity to the coordinated chlorine atom. This barrier to inversion is obvious from inspection of the X-ray crystal structure of **16** (Figure 6).

In contrast, for the four cyclopalladated compounds with unsubstituted pyrazole rings (viz. **3**, **9**, **14**, and **15**), the coalescence temperature for the inversion process is at or near room temperature. By means of variable-temperature NMR studies of DMSO solutions of these four compounds, it was possible to estimate $\Delta G^{\ddagger}$ for the inversion process as 58 ± 4 kJ mol^{-1} for these compounds. These values are similar to those reported for inversion of other six-membered palladocycles.[6h,31] We also believe that the inversions are correlated, such that, in the doubly palladated compound **15**, all four rings undergo inversion simultaneously, thereby maintaining the saddle-shaped structure observed in the solid state, with an alternating pattern of pyrazole rings on either side of the plane of the central benzene ring.

Conclusion. Ligands containing 1,3-bis(pyrazol-1-ylmethyl)benzene subunits have been shown to readily undergo cyclopalladation reactions to produce fused-ring, six-membered metallocyles with *N,C,N* donor sets that show interesting dynamic behavior in their ^{1}H NMR spectra. 1,2,4,5-Tetrakis(pyrazol-1-ylmethyl)benzenes undergo double cyclopalladation reactions to produce complexes incorporating 1,4-dipalladated benzene rings. Such compounds have recently been shown to possess interesting mesogenic properties.[11i] 1,3-Bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene undergoes cycloruthenation via an interesting intermediate containing an aryl C−H···Ru interaction. X-ray crystal structures of both singly and doubly palladated products and a cycloruthenated compound have been determined.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian 300 Unity spectrometer with a 3-mm probe and operating at 300 MHz. ^{13}C NMR spectra were recorded on a Varian 300 Unity spectrometer or a Varian XL-300 spectrometer with a 3- or 5-mm probe, respectively, and operating at 75 MHz. Spectra recorded in $CDCl_3$ were referenced relative to internal Me_4Si, and those recorded in $(CD_3)_2SO$, $(CD_3)_2CO$, CD_2Cl_2, and CD_3CN were referenced against the solvent signals. When required, NOE, 1D-TOCSY, and COSY experiments were performed using standard pulse sequences and parameters available with the Unity 300 system.

UV/visible absorption spectra were recorded using a Perkin-Elmer Lambda 2 spectrophotometer. Mass spectra were recorded using a Kratos MS80RFA spectrometer with a Mac 3 data system. Electron impact spectra of ligands were obtained at 70 eV with a source temperature of 150 °C. Fast

(29) Intille, G. M.; Pfluger, C. E.; Baker, W. A. *Cryst. Struct. Commun.* **1973**, *2*, 217. Arack, R.; Zetterberg, K. *Organometallics* **1987**, *6*, 1230. Davies, J. A.; Pinkerton, A. A.; Syed, R.; Vilmer, V. *J. Chem. Soc., Chem. Commun.* **1988**, 47. Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269. Perreault, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1992**, *31*, 2740.

(30) Hartshorn, C. M. Ph.D. Thesis, University of Canterbury, 1996.

(31) Polyakov, V. A.; Ryabov, A. D. *J. Chem. Soc., Dalton Trans.* **1986**, 589.

atom bombardment (FAB) spectra of complexes were acquired in a nitrobenzyl alcohol matrix using an Iontech ZN1FW FAB gun operated at 8 kV and 2 mA.

Melting points were determined using an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed at the University of Otago, Dunedin, New Zealand. Column chromatography was performed with silica gel (grade 923 100−200 mesh) or Sephadex-SP C-25 ion-exchange resin (40−120 μm).

Solvents were purified according to literature procedures. Unless otherwise stated, reagents were obtained from commercial sources and used as supplied. 1,2,4,5-Tetrakis(pyrazol-1-ylmethyl)benzene (**12**),[12] 1,2,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene (**13**),[12] dichlorotetrakis(dimethyl sulfoxide)ruthenium(II),[32] and trichloro(terpyridine)ruthenium(III)[33] were prepared according to literature procedures.

Synthesis of 1,3-Bis(bromomethyl)-4,6-dimethylbenzene. A mixture of 1,3-dimethylbenzene (3.19 g, 30.0 mmol), paraformaldehyde (1.85 g, 60.0 mmol), and hydrobromic acid (40% solution in acetic acid, 12 mL) was heated in acetic acid (15 mL) at 85 °C for 24 h. The resulting solution was poured into water (40 mL) and the solid filtered and recrystallized from petroleum ether (3 × 50 mL) to give 1,3-bis(bromomethyl)-4,6-dimethylbenzene (2.72 g, 31%), mp 109 °C (lit.[34] 111 °C). ^{1}H NMR ($CDCl_3$): δ 2.37, 6H, s, CH_3; 4.48, 4H, s, CH_2; 7.02, 1H, s, H5; 7.25, 1H, s, H2. ^{13}C NMR ($CDCl_3$): δ 18.39, CH_3; 31.78, CH_2; 131.43, C5; 133.35, C2; 133.74, C4,6; 138.04, C1,3.

Synthesis of 1,3-Bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene (1). A mixture of 1,3-bis(bromomethyl)-4,6-dimethylbenzene (0.49 g, 1.7 mmol), pyrazole (0.25 g, 3.7 mmol), and potassium carbonate (0.93, 6.7 mmol) was refluxed in dimethylformamide (5 mL) for 24 h. The solvent was removed and the residue covered with water (15 mL) and extracted with chloroform. The extracts were concentrated to give the crude product as a brown solid. Recrystallization from petroleum ether gave **1** (0.29 g, 66%) as a white solid, mp 86 °C. Anal. Calcd for $C_{16}H_{18}N_4$: C, 72.15; H, 6.81; N, 21.04. Found: C, 72.34; H, 6.67; N, 20.90. ^{1}H NMR ($CDCl_3$): δ 2.21, 6H, s, CH_3; 5.25, 4H, s, CH_2; 6.23, 2H, t, H4′; 6.75, 1H, s, H2; 7.03, 1H, s, H5; 7.23, 2H, d, H5′; 7.52, 2H, d, H3′. ^{13}C NMR ($CDCl_3$): δ 18.45, CH_3; 53.62, CH_2; 105.62, C4′; 128.81, C5′; 129.75, C2; 132.28, C4,6; 133.03, C5; 136.66, C1,3; 139.22, C3′.

Synthesis of 1,3-Bis(3,5-dimethylpyrazol-1-ylmethyl)-4,6-dimethylbenzene (2). Reaction of 1,3-bis(bromomethyl)-4,6-dimethylbenzene (0.52 g, 1.8 mmol), 3,5-dimethylpyrazole (0.37 g, 3.9 mmol), and potassium carbonate (0.98, 7.1 mmol), as above, gave the crude product as a brown solid. Recrystallization from petroleum ether gave **2** (0.30 g, 52%) as a white solid, mp 115 °C. Anal. Calcd for $C_{20}H_{26}N_4$: C, 74.50; H, 8.13; N, 17.37. Found: C, 74.41; H, 8.01; N, 17.42. ^{1}H NMR ($CDCl_3$): δ 1.99, 6H, s, 5′-CH_3; 2.20, 6H, s, 3′-CH_3; 2.25, 6H, s, 4,6-CH_3; 5.04, 4H, s, CH_2; 5.43, 1H, s, H2; 5.76, 2H, s, H4′; 6.93, 1H, s, H5. ^{13}C NMR ($CDCl_3$): δ 10.45, 5′-CH_3; 13.13, 3′-CH_3; 18.07, 4,6-CH_3; 49.61, CH_2; 104.93, C4′; 123.22, C2; 131.67, C5; 133.04, C4,6; 133.14, C1,3; 139.01, C5′; 146.90, C3′.

Cyclopalladation of 1. Preparation of PdCl[C_6HMe_2-($CH_2Me_2pz)_2$-*N,C,N*] (3). A mixture of **1** (50 mg, 0.19 mmol) and palladium acetate (42 mg, 0.19 mmol) was refluxed in glacial acetic acid (5 mL) for 16 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>5 equiv), and this was stirred in acetone/water (3:2, 5 mL) for 2 days and then filtered to give **3** (44 mg, 56%), mp > 285 °C dec. Anal. Calcd for $C_{16}H_{17}N_4ClPd\cdot0.5H_2O$: C, 46.17; H, 4.36; N, 13.46; Cl, 8.51. Found: C, 45.87; H, 4.34; N, 13.26; Cl, 8.69. ^{1}H NMR (DMSO): δ 2.42, 6H, s, CH_3; 5.53, 4H, s, CH_2; 6.52, 2H, t, H4′; 6.81, 1H, s, H5; 7.92, 2H, d, H5′; 8.39, 2H, d, H3′. ^{13}C NMR (DMSO): δ 19.60, CH_3; 53.17, CH_2; 106.57, C4′; 129.05, C5; 132.48, C4,6; 132.77, C1,3; 133.02, C5′; 142.74, C3′; 143.97, C2. Recrystallization of **3** from DMSO yielded crystals suitable for single-crystal X-ray structure determination.

Cyclopalladation of 2. Preparation of PdCl[C_6HMe_2-($CH_2Me_2pz)_2$-*N,C,N*] (4). A mixture of **2** (60 mg, 0.19 mmol) and palladium acetate (42 mg, 0.19 mmol) was refluxed in glacial acetic acid (5 mL) for 6 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>5 equiv), and this was stirred in acetone/water (3:2, 5 mL) for 2 days and then filtered to give **4** (68 mg, 79%), mp > 240 °C dec. Anal. Calcd for $C_{20}H_{25}N_4ClPd$: C, 51.85; H, 5.44; N, 12.09; Cl, 7.65. Found: C, 52.08; H, 5.34; N, 12.04; Cl, 7.62. ^{1}H NMR (DMSO): δ 2.35, 6H, s, 4,6-CH_3; 2.47, 6H, s, 5′-CH_3; 2.54, 6H, s, 3′-CH_3; 5.39 and 5.41, 4H, AB-q, CH_2; 6.06, 2H, t, H4′; 6.69, 1H, s, H5. ^{13}C NMR (DMSO): δ 11.35, 5′-CH_3; 14.85, 3′-CH_3; 18.79, 4,6-CH_3; 49.97, CH_2; 106.47, C4′; 127.89, C5; 131.90, C4,6; 133.27, C1,3; 140.69, C5′; 147.33, C2; 150.55, C3′.

Cycloruthenation of 1. Preparation of (tpy)Ru[$C_6H_2Me_2(CH_2pz)_2$-*N,N*]$^{2+}$ (5) and (tpy)Ru[$C_6HMe_2(CH_2pz)_2$-*N,C,N*]$^+$ (6). A mixture of trichloro(terpyridine)ruthenium(III) (60 mg, 0.14 mmol) and silver tetrafluoroborate (85 mg, 0.44 mmol) was refluxed in acetone (15 mL) for 2 h. This mixture was then filtered and the solvent removed under reduced pressure. The ligand **1** (36 mg, 0.14 mmol) was added, and this mixture was refluxed in 1-butanol (10 mL) for 19 h and then filtered. The residue was washed repeatedly with water.

(a) The aqueous washings were concentrated and then subjected to ion-exchange chromatography (Sephadex, 50:50 aqueous NaCl (0.1 M)/acetone). The first fraction collected was concentrated and redissolved in water, and excess ammonium hexafluorophosphate was added to give pure **5** (40 mg, 33%), mp > 210 °C dec. For $C_{31}H_{29}N_7RuPF_6$: calcd $M^{\bullet+}$ 746.1170, found $M^{\bullet+}$ 746.1172. ^{1}H NMR ($(CD_3)_2CO$): δ 2.74, 6H, s, CH_3; 5.62, 2H, d, CH_2; 6.07, 2H, d, CH_2; 6.29, 2H, t, H4′; 6.51, 2H, d, H3′; 6.52, 1H, d, H6‴; 7.39, 1H, s, H2; 7.58, 1H, t, H5‴; 8.03, 1H, t, H5″; 8.19, 1H, t, H4‴; 8.31, 2H, d, H5′; 8.38, 1H, s, H5; 8.44, 1H, t, H4″; 8.63, 1H, t, H4‴; 8.78, 1H, d, H3‴; 8.97, 1H, d, H3″; 9.01, 1H, d, H5‴; 9.04, 1H, d, H3‴; 10.09, 1H, d, H6″.

(b) Alternatively, to the aqueous washings was added excess ammonium hexafluorophosphate, which gave a mixture of **5** and another terpyridineruthenium complex, not containing the pyrazolyl ligand. Upon subjecting this mixture to column chromatography (silica gel, acetone), an intense purple band developed in the column. This fraction was collected and the solvent removed under reduced pressure to give **6** (33 mg, 33%), mp > 300 °C. For $C_{31}H_{28}N_7Ru$: calcd $M^{\bullet+}$ 600.1450, found $M^{\bullet+}$ 600.1447. UV/vis (CH_3CN) λ/nm (ϵ/M^{-1} cm^{-1}): 230 (31 300), 280 (27 000), 316 (27 000), 324 (29 600), 384 (5900), 526 (6500), 576 (6300), 658 (2670). ^{1}H NMR ($(CD_3)_2CO$): δ 2.64, 6H, s, CH_3; 5.56, 4H, s, CH_2; 6.01, 2H, t, H4′; 6.18, 2H, d, H3′; 6.93, 1H, s, H5; 7.48, 2H, t, H5″; 8.00, 2H, d, H5′; 8.08, 2H, t, H4″; 8.35, 1H, t, H4‴; 8.39, 2H, d, H6″; 8.73, 2H, d, H3″; 8.93, 2H, d, H3‴,5‴. Vapor diffusion of pentane into an acetone solution of **6** gave crystals suitable for single-crystal X-ray structure analysis.

Synthesis of 1,3,5-Tris(bromomethyl)-2,4-dimethylbenzene. A mixture of 1,3-dimethylbenzene (2.65 g, 25 mmol), paraformaldehyde (2.50 g, 82.5 mmol), and hydrobromic acid (40% solution in acetic acid, 17.5 mL) was refluxed in acetic acid (12.5 mL) for 72 h. The resulting solution was poured into water, and the solid was filtered and washed with hot petroleum ether (2 × 50 mL). Recrystallization from petroleum ether/ethyl acetate (2:1) gave 1,3,5-tris(bromomethyl)-2,4-dimethylbenzene (5.55 g, 58%), mp 151−152 °C. Anal. Calcd for $C_{11}H_{13}Br_3$: C, 34.32; H, 3.40; Br, 62.28.

(32) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.
(33) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.
(34) von Braun, J.; Nelles, J. *Chem. Ber.* **1934**, *67*, 1094.

Table 1. X-ray Crystal Structure Summary

	3	6	16
formula	$C_{18}H_{23}ClN_4OPdS$	$C_{31}H_{28}F_6N_7PRu$	$C_{32}H_{44}Cl_2N_8O_2Pd_2$
fw	485.31	744.64	856.45
cryst syst	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$Pbca$	$P\bar{1}$
a (Å)	11.686(4)	18.581(4)	14.546(5)
b (Å)	7.925(2)	14.233(3)	15.461(7)
c (Å)	21.587(6)	23.088(5)	16.435(4)
α (deg)	90	90	90.69(3)
β (deg)	91.93(2)	90	99.17(2)
γ (deg)	90	90	106.55(3)
V (Å^3)	1998(1)	6106(2)	3491(2)
Z	4	8	4
F(000)	984	3008	1736
μ (mm^{-1})	1.182	0.638	1.225
temp (K)	168(2)	151(2)	153(2)
color and habit	colorless block	dark purple plate	colorless block
cryst size (mm)	0.54 × 0.38 × 0.22	0.64 × 0.51 × 0.10	0.32 × 0.24 × 0.21
D_{calc} (g cm^{-3})	1.613	1.620	1.629
2θ range	4−55	4−50	4−50
no. of reflns collected	4812	5369	13848
no. of unique reflns	4592	5369	12210
R_{int}	0.0301		0.0520
no. of reflns with $I > 2\sigma(I)$	3035	3075	6820
GooF	0.839	0.772	0.865
a	0.0391	0.0301	0.0591
no. of parameters	274	417	871
R [$I > 2\sigma(I)$]	0.0376	0.0399	0.0563
$wR2$ (all data)	0.0822	0.0807	0.1359

Found: C, 34.60; H, 3.25; Br, 62.19. ^{1}H NMR ($CDCl_3$): δ 2.43, 6H, s, CH_3; 4.48, 4H, s, 1,5- CH_2; 4.57, 2H, s, 3-CH_2; 7.25, 1H, s, H6. ^{13}C NMR ($CDCl_3$): δ 14.87, CH_3; 29.00, 3-CH_2; 32.25, 1,5-CH_2; 132.10, C6; 134.38, C2,4; 136.40, C3; 137.85, C1,5.

Synthesis of 1,3,5-Tris(pyrazol-1-ylmethyl)-2,4-dimethylbenzene (7). A mixture of 1,3,5-tris(bromomethyl)-2,4-dimethylbenzene (1.00 g, 2.6 mmol), pyrazole (0.58 g, 8.6 mmol), benzene (25 mL), 40% aqueous sodium hydroxide (5 mL), and 40% aqueous tetrabutylammonium hydroxide (3 drops) was refluxed for 20 h. Separation, drying, and concentration of the organic layer gave a crude product, which was recrystallized from petroleum ether to give **7** (0.57 g, 63%), mp 79−80 °C. Anal. Calcd for $C_{20}H_{22}N_6$: C, 69.34; H, 6.40; N, 24.26. Found: C, 69.09; H, 6.18; N, 24.03. ^{1}H NMR ($CDCl_3$): δ 2.23, 6H, s, CH_3; 5.31, 4H, s, 1,5-CH_2; 5.40, 2H, s, 3-CH_2; 6.19, 1H, t, 3-H4′; 6.25, 2H, t, 1,5-H4′; 6.64, 1H, s, H6; 7.00, 1H, d, 3-H5′; 7.24, 2H, d, 1,5-H5′; 7.53, 3H, d, H3′. ^{13}C NMR ($CDCl_3$): δ 15.03, CH_3; 49.99, 3-CH_2; 54.36, 1,5-CH_2; 105.43, 3-C4′; 105.89, 1,5-C4′; 127.93, 3-C5′; 129.01, 1,5-C5′; 130.16, C6; 133.38, C2,4; 133.45, C3; 137.02, C1,5; 139.37, 3-C3′; 139.51, 1,5-C3′.

Synthesis of 1,3,5-Tris(3,5-dimethylpyrazol-1-ylmethyl)-2,4-dimethylbenzene (8). Reaction of 1,3,5-tris(bromomethyl)-2,4-dimethylbenzene (0.80 g, 2.1 mmol) with 3,5-dimethylpyrazole (0.66 g, 6.9 mmol), as above, gave a crude product which precipitated from the reaction mixture on cooling. Further product was isolated by treating the filtrate as above. These were recrystallized from benzene to give **8** (0.61 g, 68%), mp 181−182 °C. Anal. Calcd for $C_{26}H_{34}N_6$: C, 72.52; H, 7.96; N, 19.52. Found: C, 72.75; H, 8.03; N, 19.14. ^{1}H NMR ($CDCl_3$): δ 1.98, 6H, s, 1,5−5′-CH_3; 2.01, 3H, s, 3−5′-CH_3; 2.17, 3H, s, 3−3′-CH_3; 2.20, 6H, s, 1,5−3′-CH_3; 2.22, 6H, s, 2,4-CH_3; 5.08, 4H, s, 1,5-CH_2; 5.24, 2H, s, 3-CH_2; 5.28, 1H, s, 3-H6; 5.76, 3H, s, H4′. ^{13}C NMR ($CDCl_3$): δ 10.80, 1,5−5′-CH_3; 11.26, 3−5′-CH_3; 13.47, 1,5−3′-CH_3; 13.55, 3−3′-CH_3; 14.92, 2,4-CH_3; 47.97, 3-CH_2; 50.86, 1,5-CH_2; 105.32, 1,5-C4′; 105.42, 3-C4′; 123.42, C6; 133.19, C3; 133.62, C2,4; 133.92, C1,5; 138.96, 3-C5′; 139.45, 1,5-C5′; 147.03, 3-C3′; 147.45, 1,5-C3′.

Cyclopalladation of 7. Preparation of PdCl[C_6Me_2-($CH_2Me_2pz)_3$-*N,C,N*] (9). A mixture of **7** (61 mg, 0.18 mmol) and palladium acetate (40 mg, 0.18 mmol) was refluxed in glacial acetic acid (5 mL) for 21 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>5 equiv) and this was stirred in acetone/water (3:2, 5 mL) for 2 days and filtered to give **9** (72 mg, 74%), mp > 280 °C dec. Anal. Calcd for $C_{20}H_{21}N_6ClPd\cdot 3H_2O$: C, 44.38; H, 5.02; N, 15.52; Cl, 6.55. Found: C, 44.43; H, 4.84; N, 15.32; Cl, 6.80. ^{1}H NMR (DMSO): δ 2.49, 6H, s, CH_3; 5.44, 2H, s, 3-CH_2; 5.44, 2H, br s, and 5.84, 2H, br s, 1,5-CH_2; 6.27, 1H, t, 3-H4′; 6.52, 2H, t, 1,5-H4′; 7.47, 1H, d, 3-H5′; 7.60, 1H, d, 3-H3′; 7.90, 2H, d, 1,5-H5′; 8.38, 2H, d, 1,5-H3′. ^{13}C NMR (CD_2Cl_2): δ 16.09, 2,4-CH_3; 49.85, 3-CH_2; 53.64, 1,5-CH_2; 104.97, 3-C4′; 106.33, 1,5-C4′; 129.25, 3-C5′; 129.93, C3; 132.62, C2,4; 133.14, 1,5-C5′; 133.22, C1,5; 138.53, 3-C3′; 142.36, 1,5-C3′; 144.85, C6.

Cyclopalladation of 8. Preparation of PdCl[C_6Me_2-($CH_2Me_2pz)_3$-*N,C,N*] (10). A mixture of **8** (60 mg, 0.14 mmol) and palladium acetate (31 mg, 0.14 mmol) was refluxed in glacial acetic acid (5 mL) for 22 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>5 equiv), and this was stirred in acetone/water (3:2, 5 mL) for 5 days and filtered to give crude **10**. This was subsequently recrystallized by vapor diffusion of pentane into a dichloromethane solution of the crude product to give **10** (62 mg, 77%), mp > 300 °C. Anal. Calcd for $C_{26}H_{33}N_6ClPd$: C, 54.65; H, 5.82; N, 14.71; Cl, 6.20. Found: C, 54.94; H, 6.07; N, 14.70; Cl, 6.10. ^{1}H NMR (DMSO): δ 2.03, 3H, s, 3−5′-CH_3; 2.34, 6H, s, 2,4-CH_3; 2.37, 3H, s, 3−3′-CH_3; 2.47, 6H, s, 1,5−5′-CH_3; 2.54, 6H, s, 1,5−3′-CH_3; 5.07, 2H, s, 3-CH_2; 5.48, 2H, d, and 5.60, 2H, d, 1,5-CH_2; 5.87, 1H, s, 3-H4′; 6.06, 2H, s, 1,5-H4′. ^{13}C NMR (CD_2Cl_2): δ 11.16, 3−5′-CH_3; 11.79, 1,5−5′-CH_3; 13.43, 3−3′-CH_3; 14.97, 2,4-CH_3; 15.79, 1,5−3′ CH_3; 46.96, 3-CH_2; 50.97, 1,5-CH_2; 104.74, 3-C4′; 106.93, 1,5-C4′; 130.08, C3; 132.68, C2,4; 134.28, C1,5; 138.72, 3-C5′; 140.49, 1,5-C5′; 147.15, 3-C3′; 147.83, C6; 151.93, 1,5-C3′.

Preparation of the Complex 11. A mixture of **7** (60 mg, 0.12 mmol) and dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) (43 mg, 0.12 mmol) was refluxed in ethanol/water (3:1, 10 mL) under an argon atmosphere for 9 h. The solvent was then removed under reduced pressure to give the chloride salt of **11** (found $M^{\bullet+}$ 483.0642; calcd for $C_{20}H_{22}N_6ClRu$ $M^{\bullet+}$ 483.0638). This was dissolved in water and filtered. Ammonium hexafluorophosphate (102 mg, 0.60 mmol) was added

to the filtrate to give a pale yellow/green precipitate of the PF_6 salt of **11** (10 mg, 11%), mp > 240 °C dec. ^{1}H NMR (CD_3CN): δ 2.51, 6H, s, CH_3; 5.58, 2H, d, 1,5-CH_2; 6.03, 2H, s, 3-CH_2; 6.12, 2H, d, 1,5-CH_2; 6.88, 3H, t, 1,3,5-H4′; 6.89, 1H, s, H6; 8.21, 2H, d, 1,5-H5′; 8.24, 1H, d, 3-H5′; 8.49, 3H, d, 1,3,5-H3′.

Monocyclopalladation of 12. Preparation of PdCl-[C_6H(CH_2pz)$_4$-*N,C,N*] (14). A mixture of **12** (309 mg, 0.78 mmol) and palladium acetate (87 mg, 0.39 mmol) was refluxed in glacial acetic acid (20 mL) for 2 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>5 equiv), and this was stirred in acetone/water (3:2, 5 mL) for 44 h and filtered to give crude **14** as a white precipitate (172 mg, 80%). This was used in this form for subsequent reactions, although a sample was purified by vapor diffusion of acetone into a DMSO solution of the crude product, mp > 300 °C. Anal. Calcd for $C_{22}H_{21}ClN_8Pd$: C, 48.99; H, 3.92; N, 20.78; Cl, 6.57. Found: C, 48.61; H, 3.72; N, 20.50; Cl, 6.93. ^{1}H NMR (DMSO): δ 5.55, 4H, s, 3,5- CH_2; 5.39, 2H, br s, and 6.03, 2H, br s, 2,6-CH_2; 6.34, 2H, t, 3,5-H4′; 6.51, 2H, t, 2,6-H4′; 6.94, 1H, s, H4; 7.54, 2H, d, 3,5-H5′; 7.82, 2H, d, 3,5-H3′; 7.90, 2H, d, 2,6-H5′; 8.17, 2H, d, 2,6-H3′. ^{13}C NMR (DMSO): δ 52.50, 2,4-CH_2; 52.86, 1,5-CH_2; 105.62, 2,4-C4′; 106.37, 1,5-C4′; 128.08, C3; 129.88, 2,4-C5′; 132.57, C2,4; 132.78, 1,5-C5′; 135.02, C1,5; 139.00, 2,4-C3′; 142.54, 1,5-C3′; 146.29, C6. Unreacted **12** was recovered by removing the acetone from the filtrate under reduced pressure and filtering the resulting precipitate (94 mg).

Double Cyclopalladation of 12. Preparation of [C_6-(CH_2pz)$_4$($PdCl)_2$-*N,C,N*] (15). (a) A mixture of **12** (54 mg, 0.14 mmol) and palladium acetate (61 mg, 0.27 mmol) was refluxed in glacial acetic acid (5 mL) for 21 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>10 equiv), and this was stirred in acetone/water (3:2, 5 mL) for 4 days and filtered to give impure **15** as a yellow/brown precipitate. Isolation of **15** from this product mixture was not achieved.

(b) A mixture of **14** (66 mg, 0.12 mmol) and palladium acetate (27 mg, 0.12 mmol) was refluxed in glacial acetic acid (5 mL) for 24 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>5 equiv), and this was stirred in acetone/water (3:2, 5 mL) for 4 days and filtered to give **15** as a white precipitate (69 mg, 85%), mp > 300 °C. Anal. Calcd for $C_{22}H_{20}Cl_2N_8Pd_2$: C, 38.85; H, 2.96; N, 16.47; Cl, 10.42. Found: C, 39.16; H, 3.12; N, 16.50; Cl, 10.18. ^{1}H NMR (DMSO): δ 5.47, 4H, br s, and 6.15, 4H, br s, CH_2; 6.51, 4H, t, H4′; 7.93, 4H, d, H5′; 8.33, 4H, d, H3′. ^{13}C NMR (DMSO): δ 53.22, CH_2; 106.60, C4′; 132.13, C1,2,4,5; 132.39, C5′; 142.43, C3′; C3,6, not observed.

Double Cyclopalladation of 13. Preparation of [C_6-(CH_2Me_2pz)$_4$($PdCl)_2$-*N,C,N*] (16). A mixture of **13** (78 mg, 0.15 mmol) and palladium acetate (67 mg, 0.30 mmol) was refluxed in glacial acetic acid (5 mL) for 28 h. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (>10 equiv), and this was stirred in acetone/water (3:2, 5 mL) for 4 days and filtered to give crude **16** as a yellow/brown precipitate. Vapor diffusion of methanol into a DMSO solution of the crude product yielded crystals of **16** suitable for single-crystal X-ray structure determination (37 mg, 27%), mp > 300 °C. Anal. Calcd for $C_{30}H_{36}N_8Cl_2Pd_2$·$2CH_3OH$: C, 44.88; H, 5.18; N, 13.08; Cl, 8.28. Found: C, 44.76; H, 5.01; N, 13.23; Cl, 8.45. ^{1}H NMR (DMSO): δ 2.51, 12H, s, 5′-CH_3; 2.55, 12H, s, 3′-CH_3; 5.50, 4H, d, and 5.58, 4H, d, CH_2; 6.03, 4H, s, H4′. ^{13}C NMR (DMSO): δ 11.58, 5′-CH_3; 14.79, 3′-CH_3; 50.07, CH_2; 106.66, C4′; 131.81, C1,2,4,5; 141.24, C5′; 143.10, C3,6; 150.55, C3′.

Attempted Cycloruthenation of 12. A mixture of trichloro(terpyridine)ruthenium(III) (101 mg, 0.23 mmol) and silver tetrafluoroborate (143 mg, 0.73 mmol) was refluxed in acetone (20 mL) for 3 h and then filtered, and the solvent was removed under reduced pressure. The ligand **12** (35 mg, 0.089 mmol) was added, and this mixture was refluxed in 1-butanol (10 mL) for 20 h and then filtered. The residue was washed repeatedly with water. To the aqueous washings was added excess ammonium hexafluorophosphate, which gave a complex mixture of compounds as a brown precipitate. Separation of the components of this mixture was not achieved.

X-ray Crystallography. The crystal data, data collection, and refinement parameters for the three structures are listed in Table 1. All measurements were made with a Nicolet P4s diffractometer using graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation. Cell parameters were determined by least-squares refinement on diffractometer angles for at least 15 accurately centered reflections. Throughout data collections (ω scan mode), the intensities of three standard reflections were monitored at regular intervals and in no case showed variations of >5%. Intensities were corrected for Lorentz and polarization effects and for minor absorption using a technique based on azimuthal ψ scans.

The structures were solved by direct methods using SHELXS[35] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-93.[36] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. The functions minimized were $\sum w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$.

Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles for **3**, **6**, and **16** (24 pages). Ordering information is given on any current masthead page.

OM9800851

(35) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(36) Sheldrick, G. M. *SHELXL-93*; University of Gottingen, Germany, 1993.