frequently accompanied by a small amount of **1**.

Since the structure of **2** could not be determined from the spectroscopic data,[10] a single-crystal X-ray analysis was undertaken.[11] The crystal structure consists of well-separated $[Rh_2(CO)(PNP)_2]^{2+}$ dications, BPh_4^- anions, and CH_2Cl_2 solvate molecules. The molecular structure of the dication is shown in Figure 1 along with selected distances and angles. The two rhodium atoms are bonded together with a short separation of 2.674 (1) Å and have different coordination geometries. The one is ca. square planar with trans phosphorus atoms (P1–Rh1–P2 = 172.5 (2)°) and with the CO group positioned ca. trans to the other Rh atom (C–Rh1–Rh2 = 166.5 (5)°). The other Rh atom has an approximate square-pyramidal geometry with cis phosphorus and cis pyridyl nitrogen atoms in the basal plane (P3–Rh2–P4 = 102.1 (2)° and N14–Rh2–N23 = 98.6 (4)°) and with Rh1 occupying the apical position. The phosphorus atoms are trans to the nitrogen atoms in the basal plane (P3–Rh2–N14 = 174.6 (3)° and P4–Rh2–N23 = 173.4 (3)°). The two PNP ligands bridge the Rh atoms, but the four P atoms are not coplanar as is commonly found in this type of complex (e.g., complex **1**). The torsion angles P2–Rh1–Rh2–P3 and P1–Rh1–Rh2–P4 are –36 and 35°, respectively. The square planes around Rh1 and Rh2 are approximately orthogonal with a dihedral angle of 89°. Both pyridyl groups form five-membered PN chelates with the same Rh atom with P–Rh–N bite angles of 77.1 (3) and 82.5 (3)°. The trans Rh–P distances (average 2.308 (4) Å) are similar to values found in dppm- and PNP-bridged binuclear complexes of Rh(I)[5] and the Rh–P distances (Average 2.233 (4) Å) which are trans to nitrogen atoms are shorter due to the decreased trans influence of nitrogen compared with phosphorus. The Rh–N bond distances in **2** (average 2.15 (1) Å) are similar to values found in **1** (2.19 Å)[5] and in $[Rh(nbd)(PNP)]PF_6$ (2.15 Å).[6]

The formation of the Rh–Rh bond in **2** gives a 16-electron count for Rh1 and an 18-electron count for Rh2 assuming that both rhodium atoms are in the +1 oxidation state. The bond distances which involve the rhodium atoms support this assignment. Complex **2** can be converted into **1** by the addition of CO to an acetone solution of **2** at room temperature. Work in progress involves the addition of other small molecules to complex **2** and an investigation of its catalytic properties.

Acknowledgment. We thank the National Science Foundation (Grant CHE 81-08490) for support of this work and the Johnson-Matthey Co for a generous loan of rhodium salts. M.P.A. is a participant in the U.S. Air Force Institute of Technology Graduate School Program.

Registry No. 1, 86307-73-5; 2, 86307-76-8; $[Rh(CO)_2Cl_2]Li$, 86307-77-9; Rh, 7440-16-6.

Supplementary Material Available: Tables of atomic fractional coordinates and thermal parameters for $[Rh_2(CO)(\mu\text{-}PNP)_2]^{2+}$ (55 pages). Ordering information is given on any current masthead page.

---

[10] Anal. Calcd for $C_{109}H_{90}N_2OP_4B_2Rh_2$ (**2**): C, 72.93; H, 5.05; N, 1.56; P., 6.90. Found: C, 72.25; H, 5.13; N, 1.57; P. 6.79. **2**: IR (KBr disk) ν(CO) 1982, ν(pyridyl C–N) 1599 cm^{-1}; $^{31}P\{^1H\}$ NMR (acetone solution, 121.5 MHz, ambient temperature) consists of two well-separated doublets of triplets of equal intensity, δ_1 61.5 and δ_2 37.7 vs. external H_3PO_4 with J_d = 136 and 130 Hz, respectively, and J_t = 30.5 and 30.5 Hz.

[11] A red-orange crystal of $\mathbf{2}\cdot 2CH_2Cl_2$ was mounted inside of a sealed capillary tube in its mother liquor (CH_2Cl_2–C_2H_5OH). This procedure was necessary since crystals removed from solution readily lost solvent rendering them unsuitable for X-ray analysis: space group $P\bar{1}$ (No. 2), 23 °C, a =17.011 (8) Å, b = 17.426 (5) Å, c = 18.497 (6) Å, α = 103.34 (3)°, β = 103.23 (4)°, γ = 91.89 (4)°, Z = 2, Mo $K\bar{\alpha}$ graphite monochromatized (λ = 0.71069 Å), CAD 4 diffractometer, ω–2θ scans, $2\theta_{max}$ = 44°, full-matrix least squares, R = 0.085; 6342 reflections with $F_o^2 \gtrsim 1.0\, \sigma(F_o^2)$, 749 parameters. See ref 5 for details of structure solving package.

Synthesis and Structural Analysis of *trans*-Bis[2-{1,1-bis(methoxycarbonyl)propyl}pyridine]palladium(II): A Novel, Stable Six-Membered Organopalladium(II) Complex Possessing sp^3-Carbon–Metal Bonds

George R. Newkome,* Wallace E. Puckett,
Vinod K. Gupta,[1] and Frank R. Fronczek

Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Received May 2, 1983

Summary: The first example of a stable palladium(II) complex having trans, bis[carbon(sp^3)–metal] bonds in a six-membered chelate ring is reported. Synthesis, ^1H and ^{13}C NMR spectroscopy, and a single-crystal X-ray structure establish the assignment. It crystallizes in the monoclinic space group $P2_1/n$ with cell constants of a = 10.022 (2) Å, b = 23.820 (4) Å, c = 10.808 (2)Å, β = 107.20 (2)°, and Z = 4. Bond lengths average 2.038 (7) Å for Pd–N and 2.181 (9) Å for Pd–C bonds.

Throughout the past decade, much interest and synthetic effort has been devoted to understand and utilize stable cyclometalated complexes containing transition-metal ions.[2] The five-membered cyclic core **1** has been a common denominator in the majority of such cyclometalated complexes, thus instilling support to the "five-membered ring theory" advanced by Matsuda et al.[3] The rationale for enhanced stability imparted by a five-membered ring is based on the necessity for such complexes to possess a ligand–metal–carbon bond angle (θ) of ca. 90°. While this simple premise appears to have general validity, it by no means precludes other stable multimembered cyclometalated rings. We, as well as others, have demonstrated that at least with one transition metal, palladium, considerable distortions from idealized coordination geometry can occur without undue losses in complex stability or metal–ligand bond character.[4]

To date, few cyclometalated complexes containing a six-membered ring with an N donor have been reported,[5] of these only three possess both pyridine and sp^2 (aromatic) C donor atoms[6] and five possess a N donor and an sp^3-C donor atom.[7] The latter were unstable in solution, and until now no crystal structures or other compelling spectroscopic evidence of formulation have been presented. We herein report the synthesis, spectral correlations, and

---

[1] On leave from University of Delhi, Delhi, India, 1980–1983.

[2] (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (b) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (c) Hartley, F. R. *Coord. Chem. Rev.* **1981**, *35*, 143.

[3] Matsuda, S.; Kikkawa, S.; Omae, I. *Kogyo Kagaku Zasshi* **1966**, *69*, 646; *Chem. Abstr.* **1966**, *65*, 18612e.

[4] (a) Newkome, G. R.; Fronczek, F. R.; Gupta, V. K.; Puckett, W. E.; Pantaleo, D. C.; Kiefer, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 1782. (b) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; BackerHirks, J. D. J. *J. Chem. Soc., Chem. Commun.* **1979**, 670.

[5] Cameron, N. D.; Kilner, M. *J. Chem. Soc., Chem. Commun.* **1975**, 687. Holton, R. A.; Nelson, R. V. *J. Organomet. Chem.* **1980**, *201*, C35. Ros, R.; Renaud, J.; Roulet, R. *Ibid.* **1975**, *87*, 379. Hugentobler, M.; Klaus, A. J.; Mettler, H.; Rys, P.; Wehrle, G. *Helv. Chim. Acta* **1982**, *65*, 1202.

[6] Hiraki, K.; Fuchita, Y.; Takecki, K. *Inorg. Chem.* **1981**, *20*, 4316. Fuchita, Y.; Hiraki, K.; Kage, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 955. Nonoyama, M. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 281.

[7] (a) Ros, R.; Renaud, J.; Roulet, R. *J. Organomet. Chem.* **1974**, *77*, C4. (b) Holton, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 8083. (c) Schwarzenbach, D.; Pinkerton, A.; Chapius, G.; Wenger, J.; Ros, R.; Roulet, R. *Inorg. Chim. Acta* **1977**, *25*, 255. (d) Ros, R.; Michelin, T. A.; Boschi, T.; Roulet, R. *Inorg. Chim. Acta* **1979**, *35*, 43. (e) Sano, K.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1982**, 695.

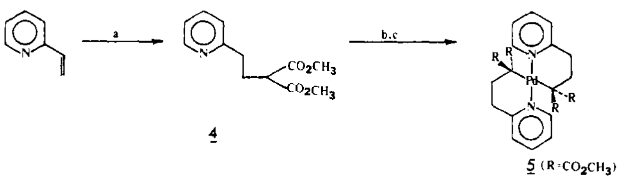
0276-7333/83/2302-1247$01.50/0

Table I. Coordinates for Non-Hydrogen Atoms for $Pd(C_{12}H_{14}NO_4)_2$[a]

atom	x	y	z	atom	x	y	z
Pd	0.18986 (5)	0.12248 (2)	0.18449 (4)	C8	−0.0117 (7)	0.1593 (3)	0.0780 (6)
O(1)	−0.0472 (5)	0.2394 (2)	0.1973 (5)	C9	0.0104 (7)	0.2178 (3)	0.1253 (5)
O(2)	0.1076 (6)	0.2471 (1)	0.0854 (6)	C10	−0.0197 (8)	0.1504 (2)	−0.0586 (7)
O(3)	−0.0049 (5)	0.1836 (2)	−0.1375 (5)	C11	0.1437 (11)	0.3018 (3)	0.1431 (8)
O(4)	−0.0489 (5)	0.0960 (2)	−0.0922 (4)	C12	−0.0481 (9)	0.0803 (2)	−0.2210 (8)
O(5)	0.5738 (5)	0.0869 (1)	0.2201 (5)	C13	0.3066 (7)	0.1614 (3)	−0.0227 (6)
O(6)	0.4913 (6)	0.1554 (2)	0.3203 (5)	C14	0.3728 (9)	0.1580 (3)	−0.1191 (7)
O(7)	0.4358 (6)	0.0824 (2)	0.5135 (4)	C15	0.3960 (7)	0.1054 (4)	−0.1601 (6)
O(8)	0.2548 (5)	0.0257 (2)	0.4201 (4)	C16	0.3579 (9)	0.0587 (3)	−0.1050 (8)
N(1)	0.1298 (5)	0.1406 (2)	0.3445 (5)	C17	0.2947 (8)	0.0635 (3)	−0.0081 (6)
N(2)	0.2677 (5)	0.1150 (2)	0.0312 (4)	C18	0.2635 (8)	0.0164 (3)	0.0629 (7)
C(1)	0.2096 (7)	0.1742 (3)	0.4354 (6)	C19	0.3513 (7)	0.0140 (2)	0.2058 (6)
C(2)	0.1694 (7)	0.1915 (3)	0.5418 (7)	C20	0.3664 (7)	0.0698 (3)	0.2824 (6)
C(3)	0.0429 (9)	0.1729 (3)	0.5517 (6)	C21	0.4884 (7)	0.1033 (3)	0.2737 (6)
C(4)	−0.0387 (7)	0.1384 (2)	0.4571 (7)	C22	0.3613 (7)	0.0609 (3)	0.4169 (7)
C(5)	0.0054 (7)	0.1234 (3)	0.3524 (6)	C23	0.5943 (9)	0.1928 (3)	0.2959 (8)
C(6)	−0.0823 (7)	0.0920 (3)	0.2392 (6)	C24	0.2394 (9)	0.0143 (4)	0.5453 (6)
C(7)	−0.1296 (7)	0.1304 (3)	0.1180 (6)				

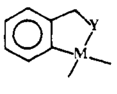
[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Scheme I[a]

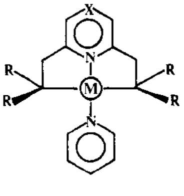


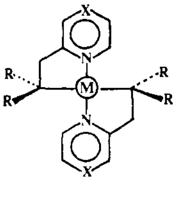
[a] a, $CH_2(CO_2CH_3)_2$, NaOMe, MeOH, reflux, 12 h; b, $PdCl_2$, LiCl, CH_3CN, room temp., 6 h; c, K_2CO_3, 55 °C, 24 h.

first structure proof of a cyclopalladated complex containing pyridine and sp^3-C–metal bonds in a six-membered chelate ring.



1
(Y= donor atom)





2 (X=CH or N) 3

Several stable cyclopalladated complexes, e.g., 2 and 3, have been prepared in our laboratories.[8-10] Since each of these complexes conforms to the five-membered ring theory, the related six-membered ring homologues will afford timely insight into the geometrical and chemical aspects as well as stability relationships. To this end we prepared the homologous complex 5 by the procedure shown in Scheme I.

Ligand 4[11] was prepared (70%) by Michael addition of dimethyl sodiomalonate to 2-vinylpyridine and characterized (^1H NMR) by the triplet at δ 3.38 for the methine proton and multiplets at δ 2.76 and 2.28 for the α- and β-hydrogens, respectively. The ^{13}C NMR data further endorse structure 4. Complex 5 was prepared (80%) by initial N-complexation; then upon abstraction of the acidic hydrogens with anhydrous K_2CO_3 cyclometalation occurred. Recrystallization of 5[11] from CH_2Cl_2–C_6H_{12} afforded yellow crystals (mp 155 °C dec), which were characterized by ^1H NMR via loss of the triplet at δ 3.38, and typical heteroaromatic proton shifts caused by coordination.[10] Interestingly in 5, both ^1H (singlets at δ 2.75 and 3.26) and ^{13}C [spikes are at δ 173.7 and 175.9 (C=O) as well as δ 49.6 and 50.5 (OMe)] NMR spectra show the presence of two different methoxycarbonyl groups, which are indicative of conformational stability in the six-membered ring, placing one ester group in an axial and the other in an equatorial position. Ring flipping does not occur upon warming (>-110 °C) as evidenced by ^1H NMR temperature independence. The ^{13}C NMR spectral data, which are indicative of subtle structural and electronic changes, for both 3 (X = CH, R = CO_2CH_3) and 5 are strikingly similar except for C(2) δ 171.8 and 162.8, respectively) and C–Pd (δ 53.6 and 45.6, respectively).[12] The relatively small downfield shift for C(2) in 5 compared to 3 is because of diminished, but similar, angular strain ($\angle CH_2$—C=N = θ = 116° and 114°, respectively). Also the upfield shift for C—Pd in 5 is the result of reduced C-C-Pd angle strain (108°) as compared to 3 (100°). These results correlate well with the X-ray data, which show that the bond angles within 5 are much closer to ideal, with respect to both the six-membered ring and favorable palladium(II) geometry than are those found in 3.

For determination of the salient bond angles, bond distances, and interatomic distances, a single-crystal X-ray analysis of 5 was undertaken.

A small crystal of dimensions 0.06 × 0.08 × 0.32 mm was used for data collection on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. Cell dimensions and crystal orientation were determined by a least-squares fit of the setting angles of 25 reflections having 21° < 2θ < 24°. Crystal data are as follows: $Pd(C_{12}H_{14}NO_4)_2$, mol wt 578.9, monoclinic space group $P2_1/n$, $Z = 4$, $a = 10.022$ (2) Å, $b = 23.820$ (4) Å, $c = 10.808$ (2) Å, $\beta = 107.20$ (2)°, $d_{calcd} = 1.560$ g cm^{-3}, μ(Mo Kα) = 7.900 cm^{-1}.

One quadrant of data having 1° < θ < 23° was collected by the ω–2θ scan method, employing scan rates varying from 0.21 to 4.0° min^{-1} in order to measure all significant data with $I \sim 50\sigma(I)$. A maximum of 300 s was spent on any single scan. Data reduction included corrections for background, Lorentz, and polarization effects, as well as

---

[8] Newkome, G. R.; Kawato, T. *Inorg. Chim. Acta Lett.* **1979**, *37*, L481. Newkome, G. R.; Kawato, T.; Kohli, D. K.; Puckett, W. E.; Oliver, B. D.; Chiari, G.; Fronczek, F. R.; Deutsch, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 3423.

[9] Gupta, V. K., unpublished results.

[10] Newkome, G. R.; Gupta, V. K.; Fronczek, F. R. *Organometallics* **1982**, *1*, 907; **1983**, *2*, 785.

[11] Satisfactory spectral and analytical data (C, H, N; ±0.3%) were obtained for all new compounds.

[12] Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E., unpublished results.

Table II. Bond Distances (Å) and Angles (deg) in the Coordination Sphere

Bond Distances			
Pd-N(1)	2.038 (7)	Pd-N(2)	2.037 (7)
Pd-C(8)	2.190 (9)	Pd-C(20)	2.172 (9)
Bond Angles			
N(1)-Pd-N(2)	171.4 (3)	N(2)-Pd-C(8)	97.1 (3)
N(1)-Pd-C(8)	84.5 (3)	N(2)-Pd-C(20)	83.9 (3)
N(1)-Pd-C(20)	96.4 (3)	C(8)-Pd-C(20)	168.2 (3)
Pd-N(1)-C(1)	119.3 (6)	Pd-N(2)-C(13)	120.3 (7)
Pd-N(1)-C(5)	120.3 (6)	Pd-N(2)-C(17)	119.7 (6)
Pd-C(8)-C(7)	109.9 (6)	Pd-C(20)-C(19)	107.4 (6)
Pd-C(8)-C(9)	100.1 (6)	Pd-C(20)-C(21)	103.1 (7)
Pd-C(8)-C(10)	103.8 (6)	Pd-C(20)-C(22)	107.5 (6)

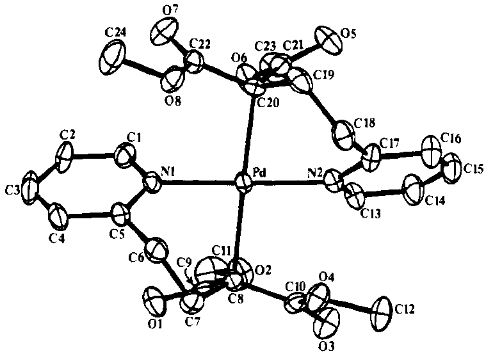


Figure 1.

an empirical absorption correction, based upon ψ scans of reflections near $\chi = 90°$; the minimum relative transmission coefficient was 0.963. Of 3410 unique data measured 1909 had $I > 3\sigma(I)$ and were used in the refinement.

The structure was solved by heavy-atom methods. Refinement was accomplished by full-matrix least squares based on F with weights $w = \sigma^{-2}(F_o)$. All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package programs.[13] All non-hydrogen atoms were located from difference maps and included as fixed contributions with isotropic $B = 5.0$ Å^2 (7.0 Å^2 for methyl groups). At convergence, $R = 0.035$, $R_w = 0.041$ for 316 variables. A final difference map exhibited no peaks larger than 0.36 e Å^{-3}. Final coordinates are listed in Table I; important distances and angles are given in Table II.

The central Pd atom in **5** is σ bonded with two carbon atoms and coordinated by two pyridine nitrogens corroborating the net overall square-planar trans configuration and nearly C_2 symmetry (Figure 1). The pyridine rings are tipped by 62.9° (av) out of the coordination plane, as compared to 31.5° in **3**.[10] In both **3** and **5**, the alkyl bridges swing upward on the *same* side of the mean coordination plane. Palladium and the coordinating atoms [N(1,2); C(8,10)] form an approximate plane with displacements less than ±0.2 Å, with the metal atom nearly in the best plane. Neither the Pd–N (average 2.038 Å) nor Pd–C (average 2.181 Å) bond lengths are unusual; all are similar to those found in analogous five-membered ring complexes.[10] Intraannular N–Pd–C angles average 84.2°, over 4° larger than those found in **3**. The pyridine rings are planar and exhibit normal angles and bond distances. The six-membered cyclic ring, however, adopts a twist boat conformation.

The six-membered palladacycle **5** is different from previous examples in that it has *two* (rather than one) trans six-membered cyclometalated rings and most were acetate or halo-bridged dimers.[5-7] It thus appears that the original assumption, that metal ions preferring square-planar geometry favor five-membered rings, is unnecessarily limiting. Six-membered rings can readily accommodate the square-planar central metal; in fact, when compared with analogous five-membered ring complexes, no unusual or unfavorable geometries or interactions can be found. Further, **5** is prepared by identical reaction conditions and in similar yields to the five-membered ring counterparts. Studies in competitive complexation as well as in higher order cyclometalated complexes are in progress.

Acknowledgment. We wish to thank the National Science Foundation for partial support of this work and Reilly Tar for generous samples of 2-vinylpyridine as well as Johnson Matthey Inc. for inclusion in their metals loan program.

Registry No. 4, 86480-63-9; 5, 86480-64-0; $PdCl_2$, 7647-10-1; dimethyl sodiomalonate, 108-59-8; 2-vinylpyridine, 100-69-6.

Supplementary Material Available: Tables of coordinates for hydrogen atoms, bond distances and bond angles, anisotropic thermal parameters, and structure factors and experimental details (22 pages). Ordering information is given on any current masthead page.

---

[13] Frenz, B. A.; Okaya, Y. "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1980.

Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 1. Application to the Hexacarbonyldiiron Moiety

Jeffrey S. McKennis* and Evan P. Kyba*

Department of Chemistry, University of Texas
Austin, Texas 78712

Received April 29, 1983

Summary: Three bis-bridged diiron species, μ,μ^1-(1-X-2-Y-benzene)hexacarbonyldiiron [X = Y = PPh (**3a**); X = S, Y = PPh (**3b**); X = Y = S (**3c**)], have been prepared by the thermal reaction of the corresponding dihydro forms of the ligand and excess nonacarbonyldiiron. Reduction of **3a–c** with 2 equiv of electrons gives rise to a dianion in which cleavage of an Fe–X bond has occurred in contrast to the reductive behavior of $(\mu\text{-PPh}_2)_2\text{Fe(CO)}_6$ which cleaves an Fe–Fe bond. The dianion derived from **3a** reacts with excess trifluoracetic acid to give the phosphorus and iron-protonated species. Methylation (MeI) of $(\mathbf{3a})^{2-}$ gave a complex with the structure assigned as $[\text{1-P(Me)Ph-}\mu\text{-2-PPhC}_6\text{H}_4][\mu\text{-C(O)Me}](\text{CO})_5\text{Fe}_2$. An analogous complex was obtained on methylation of $(\mathbf{3b})^{2-}$.

Phosphido-bridged transition-metal complexes have attracted considerable attention recently owing to the enhanced stability of the phosphido bridge relative to the traditional tertiary phosphine ligand.[1] In particular, it has been hoped that special stability could be accorded to various phosphido-bridged bimetallic and cluster complexes and ultimately lead to the development of new transition-metal catalysts.

Although bis(phosphido)-bridged bimetallic complexes with the general structure A (X = Y = PR_2) have been

---

[1] Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* 1981, *103*, 1394 and references therein.