Contribution from the Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and
East Tennessee State University, Kingsport University Center, Kingsport, Tennessee 37660

Cyclometalation of 2-*p*-Tolylbenzthiazole and 2-*p*-Tolylbenzoxazole with Palladium(II) Acetate. Synthesis and Crystal Structures of the Acetate-Bridged Dimers $[(MeC_6H_3C_7H_4NS)Pd]_2(\mu\text{-}O_2CMe)_2$ and $[(MeC_6H_3C_7H_4NO)Pd]_2(\mu\text{-}O_2CMe)_2$

MELVYN ROWEN CHURCHILL,*[1] HARVEY J. WASSERMAN,[1] and GLENDA J. YOUNG[2]

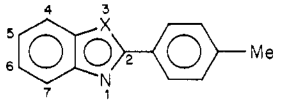
Received June 5, 1979

The reaction of palladium(II) acetate with 2-arylbenzthiazoles or 2-arylbenzoxazoles leads to dimeric cyclometalated products. The 2-*p*-tolyl derivatives $[(MeC_6H_3C_7H_4NS)Pd]_2(\mu\text{-}O_2CMe)_2$ (**1**) and $[(MeC_6H_3C_7H_4NO)Pd]_2(\mu\text{-}O_2CMe)_2$ (**2**) have each been characterized via an X-ray diffraction study. These complexes are isomorphous and crystallize in the centrosymmetric monoclinic space group $P2_1/n$ with $Z = 4$. Unit cell parameters are as follows: **1**, $a = 9.980$ (2) Å, $b = 22.802$ (6) Å, $c = 13.438$ (3) Å, $\beta = 104.46$ (2)°, $V = 2961.3$ (11) Å^3, ρ(calcd) = 1.75 g cm^{-3} for mol wt 778.8; **2**, $a = 9.908$ (1) Å, $b = 22.387$ (4) Å, $c = 13.350$ (2) Å, $\beta = 104.53$ (1)°, $V = 2866.5$ (7) Å^3, ρ(calcd) = 1.73 g cm^{-3} for mol wt 747.7. Diffraction data (Mo Kα) were collected with a Syntex P2$_1$ automated diffractometer, and the structures were solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The resulting discrepancy indices are as follows: **1**, $R_F = 4.0\%$ and $R_{wF} = 4.1\%$ for all 3876 reflections [2θ(max) = 45°]; **2**, $R_F = 4.6\%$ and $R_{wF} = 4.1\%$ for all 2687 independent reflections [2θ(max) = 40°; two forms averaged]. In each molecule the palladium(II) ion is bonded to a *nitrogen* atom of the thiazole or oxazole ring (rather than sulfur in **1** or oxygen in **2**) and to an ortho carbon atom of the *p*-tolyl group. In addition, the resulting $[(MeC_6H_3C_7H_4NX)Pd]$ systems (X = S (**1**) or O (**2**)) are linked together by two mutually cis acetate bridges to form dimeric $[(MeC_6H_3C_7H_4NX)Pd]_2(\mu\text{-}O_2CMe)_2$ molecules.

Introduction

"Orthometalation" or "the cyclometalation reaction" (and the associated activation of aromatic C–H bonds) has been the subject of a number of review articles[3–5] and has been described in recent articles by a number of research groups, including that of Kaesz.[6,7]

In investigating new metal-directed reactions of polyheterosubstituted aromatic compounds, we have found that both 2-*p*-tolylbenzthiazole (**3**) and 2-*p*-tolylbenzoxazole (**4**) react with Pd(II) salts.



3 (X = S; 2-*p*-tolylbenzthiazole, $MeC_6H_4C_7H_4NS$)
4 (X = O; 2-*p*-tolylbenzoxazole, $MeC_6H_4C_7H_4NO$)

In particular, we found that both **3** and **4** reacted with palladium(II) acetate, yielding *dimeric* orthometalated products (**1** and **2**, respectively). Single-crystal X-ray diffraction studies of these complexes have been undertaken for two principal reasons: (1) to determine unequivocally the nature of the Pd–ligand bonding (i.e.: Is there C,N or C,S bonding to palladium in **1**? Is there C,N or C,O bonding to palladium in **2**?); (2) to ascertain the full three-dimensional structural configurations of these complex dimeric molecules.

Our results appear in this paper.

Experimental Section

(A) Preparation of Complexes. Synthesis of $[(MeC_6H_3C_7H_4NS)Pd]_2(\mu\text{-}O_2CMe)_2$ (1). A mixture of 2.25 g of 2-*p*-tolylbenzthiazole[8] and 2.24 g of palladium(II) acetate in 25 mL of acetic acid was heated and stirred under nitrogen for 4 h. The resulting brick red precipitate was filtered off and recrystallized from di-

Table I. Experimental Data for the X-ray Diffraction Studies

	benzthiazole deriv (1)	benzoxazole deriv (2)
	(A) Crystal Parameters[a]	
cryst system	monoclinic	monoclinic
space group	$P2_1/n$[b]	$P2_1/n$[b]
a, Å	9.9802 (17)	9.9081 (11)
b, Å	22.8022 (59)	22.3865 (38)
c, Å	13.4382 (30)	13.3502 (20)
β, deg	104.455 (15)	104.529 (10)
V, Å^3	2961.3 (11)	2866.5 (7)
Z	4	4
mol wt	778.8	747.4
ρ(calcd), g cm^{-3}	1.75	1.73
T, °C	24.0 (3)	24.9 (3)
	(B) Measurements of Data	
radiation	Mo Kα ($\bar{\lambda}$ 0.710 730 Å)	
monochromator	highly oriented graphite, equatorial	
reflcns measd	$\pm h,+k,+l$ (one form)	$\pm h,+k,\pm l$ (two forms)
2θ range, deg	4.0–45.0	4.0–40.0
scan type:	ω	θ–2θ
scan speed, deg/min	1.50 (in ω)	4.0 (in 2θ)
scan range, deg	0.7 (0.5° offset from center of bkgd)	$[2\theta(K\alpha_1) - 0.9] \rightarrow [2\theta(K\alpha_2) + 0.9]$
reflcns collected	4066 total, yielding 3876 independent	5375 total, yielding 2687 independent
data averaging		$R(I) = 2.0\%$ for 2677 pairs of reflection
stds	3 every 97 reflections; no significant changes in intensity observed	
abs coeff, cm^{-1}	13.7	12.8
reflcns used for empirical absn cor: hkl, 2θ (deg), T_{max}/T_{min}	222, 12.24, 1.17 312, 15.59, 1.12 314, 20.07, 1.13 453, 23.20, 1.14 505, 29.54, 1.14 703, 33.59, 1.15	$\bar{2}13$, 11.15, 1.18 $\bar{3}14$, 15.63, 1.15 $4\bar{1}\bar{5}$, 20.21, 1.18 $4\bar{3}6$, 22.79, 1.15 $50\bar{7}$, 26.68, 1.15 $60\bar{8}$, 31.34, 1.19

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ component of the 24 reflections of the forms {582}, {613}, {$\bar{2}$66}, {$\bar{1}$27}, {1,12,2}, and {$\bar{7}$14}, all with 2θ = 21–30°. [b] Nonstandard setting of space group $P2_1/c$ (C_{2h}^5; No. 14) having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$.

---

(1) SUNY at Buffalo.
(2) East Tennessee State University.
(3) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.
(4) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327.
(5) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.
(6) Crawford, S. S.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 3193.
(7) Crawford, S. S.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 3201. (See also previous papers in this series on metalation reactions, by Kaesz and co-workers.)
(8) Bogert, M. T.; Meyer, M. *J. Am. Chem. Soc.* **1922**, *44*, 1568.

0020-1669/80/1319-0762$01.00/0

Table II. Final Positional Parameters with Esd's for the Benzthiazole Derivative (1)[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pd(1)	0.167 94 (4)	0.068 84 (2)	0.239 01 (3)	C(11′)	0.450 01 (56)	−0.041 87 (23)	0.328 85 (39)
S(3)	0.308 50 (19)	−0.011 41 (7)	−0.019 41 (13)	C(12′)	0.391 35 (66)	−0.097 51 (27)	0.309 97 (46)
N(1)	0.186 64 (46)	0.015 29 (19)	0.122 02 (32)	C(13′)	0.447 04 (78)	−0.139 52 (29)	0.257 91 (51)
C(2)	0.277 73 (58)	0.035 52 (23)	0.074 23 (40)	C(14′)	0.562 77 (81)	−0.126 06 (30)	0.224 31 (49)
C(4)	0.153 89 (79)	−0.114 38 (29)	−0.038 79 (52)	C(15′)	0.627 75 (69)	−0.070 66 (26)	0.238 44 (42)
C(5)	0.054 22 (85)	−0.146 16 (30)	−0.007 22 (55)	C(16′)	0.380 3 (10)	−0.202 21 (29)	0.239 82 (66)
C(6)	−0.004 89 (71)	−0.124 87 (31)	0.068 14 (55)	O(1)	0.318 27 (39)	0.097 15 (17)	0.474 57 (27)
C(7)	0.034 58 (67)	−0.071 30 (28)	0.116 25 (45)	O(2)	0.149 09 (40)	0.131 36 (16)	0.343 99 (29)
C(8)	0.134 26 (60)	−0.039 57 (25)	0.085 52 (41)	O(1′)	0.053 37 (37)	0.008 76 (18)	0.308 25 (28)
C(9)	0.193 16 (66)	−0.061 59 (25)	0.006 89 (45)	O(2′)	0.229 60 (37)	−0.024 71 (16)	0.432 61 (28)
C(10)	0.336 18 (57)	0.091 17 (23)	0.100 46 (39)	C(21)	0.225 12 (59)	0.132 26 (24)	0.435 07 (45)
C(11)	0.287 52 (53)	0.119 15 (24)	0.178 01 (37)	C(22)	0.198 93 (67)	0.183 77 (26)	0.501 96 (45)
C(12)	0.338 33 (60)	0.176 52 (24)	0.209 86 (40)	C(21′)	0.105 02 (58)	−0.023 08 (23)	0.383 65 (41)
C(13)	0.432 20 (62)	0.203 73 (24)	0.166 58 (43)	C(22′)	0.007 69 (63)	−0.065 37 (26)	0.418 67 (47)
C(14)	0.482 17 (62)	0.175 23 (28)	0.091 43 (46)	H(4)	0.194 0	−0.128 9	−0.090 9
C(15)	0.434 67 (59)	0.118 11 (26)	0.056 06 (42)	H(5)	0.025 9	−0.183 1	−0.037 7
C(16)	0.486 57 (80)	0.265 27 (26)	0.201 07 (50)	H(6)	−0.074 2	−0.147 3	0.087 6
Pd(2)	0.387 54 (4)	0.023 80 (2)	0.401 68 (3)	H(7)	−0.005 9	−0.057 1	0.168 5
S(3′)	0.757 12 (16)	0.060 19 (7)	0.282 32 (13)	H(12)	0.306 4	0.196 0	0.261 9
N(1′)	0.555 65 (42)	0.062 81 (18)	0.369 63 (31)	H(14)	0.549 0	0.194 1	0.063 2
C(2′)	0.617 22 (54)	0.029 81 (24)	0.315 24 (39)	H(15)	0.468 1	0.098 8	0.004 3
C(4′)	0.811 48 (68)	0.174 13 (32)	0.356 76 (51)	H(4′)	0.885 0	0.178 8	0.324 2
C(5′)	0.777 65 (76)	0.218 16 (29)	0.417 16 (54)	H(5′)	0.829 9	0.253 4	0.426 9
C(6′)	0.671 02 (79)	0.212 01 (29)	0.462 94 (53)	H(6′)	0.651 8	0.242 9	0.504 7
C(7′)	0.589 58 (63)	0.161 90 (27)	0.450 36 (47)	H(7′)	0.514 7	0.158 4	0.481 9
C(8′)	0.620 66 (55)	0.117 33 (25)	0.390 74 (40)	H(12′)	0.311 5	−0.106 7	0.333 3
C(9′)	0.735 20 (56)	0.123 61 (25)	0.345 64 (41)	H(14′)	0.600 9	−0.155 6	0.189 7
C(10′)	0.565 64 (57)	−0.028 87 (24)	0.291 77 (39)	H(15′)	0.707 1	−0.061 8	0.214 1

[a] Hydrogen atoms were assigned isotropic thermal parameters of 7.0 Å^2.

Table III. Anisotropic Thermal Parameters[a] for Nonhydrogen Atoms for the Benzthiazole Derivative (1)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd(1)	3.725 (21)	3.737 (21)	3.053 (19)	0.781 (16)	1.251 (15)	0.545 (16)
S(3)	6.93 (10)	4.268 (79)	5.623 (85)	−0.136 (70)	3.206 (76)	−0.905 (66)
N(1)	4.19 (23)	3.59 (23)	3.52 (21)	0.40 (18)	1.04 (18)	0.09 (18)
C(2)	4.57 (29)	3.45 (27)	3.52 (25)	0.80 (23)	1.56 (22)	0.37 (21)
C(4)	7.99 (44)	4.12 (32)	6.09 (37)	−0.22 (32)	2.50 (33)	−0.55 (29)
C(5)	8.45 (48)	4.53 (35)	5.74 (37)	−0.62 (35)	0.47 (34)	−0.28 (30)
C(6)	5.90 (38)	5.53 (39)	6.25 (39)	−1.20 (31)	0.57 (31)	1.23 (32)
C(7)	5.46 (34)	4.77 (33)	4.38 (29)	−0.65 (28)	0.88 (25)	0.54 (26)
C(8)	4.70 (30)	3.69 (28)	3.71 (27)	0.29 (24)	0.48 (23)	0.72 (23)
C(9)	5.92 (34)	3.59 (29)	4.73 (30)	0.39 (26)	1.48 (26)	−0.13 (24)
C(10)	4.48 (28)	3.40 (27)	3.45 (25)	1.09 (23)	1.38 (22)	0.45 (21)
C(11)	3.68 (25)	3.87 (27)	3.05 (24)	1.25 (22)	0.71 (20)	1.05 (21)
C(12)	4.83 (30)	3.53 (28)	3.74 (26)	0.48 (24)	0.98 (22)	0.74 (22)
C(13)	5.16 (31)	3.57 (28)	4.19 (29)	0.41 (24)	0.53 (25)	1.02 (23)
C(14)	5.12 (33)	4.67 (33)	5.09 (31)	0.43 (26)	1.88 (25)	1.37 (26)
C(15)	4.70 (29)	4.77 (31)	4.07 (27)	0.43 (26)	2.21 (23)	1.27 (25)
C(16)	8.69 (45)	3.49 (31)	5.68 (34)	−1.70 (30)	0.93 (31)	−0.47 (26)
Pd(2)	2.930 (20)	3.296 (20)	3.613 (20)	0.462 (15)	1.016 (15)	0.406 (16)
S(3′)	4.354 (76)	5.733 (88)	5.672 (83)	0.203 (67)	2.371 (65)	0.347 (70)
N(1′)	3.16 (20)	3.24 (21)	3.73 (20)	0.58 (17)	0.79 (16)	0.58 (17)
C(2′)	3.38 (25)	3.87 (28)	3.63 (25)	0.99 (22)	1.21 (20)	0.65 (22)
C(4′)	4.99 (35)	6.69 (41)	5.77 (35)	−1.29 (32)	1.19 (28)	0.77 (32)
C(5′)	6.28 (39)	4.55 (34)	6.21 (38)	−1.69 (30)	0.56 (31)	0.41 (30)
C(6′)	6.87 (42)	4.29 (33)	6.41 (39)	−0.18 (31)	1.01 (33)	−0.54 (29)
C(7′)	4.57 (32)	4.41 (31)	5.29 (31)	0.36 (26)	1.05 (25)	−0.05 (27)
C(8′)	3.61 (27)	3.74 (28)	3.72 (26)	0.31 (23)	0.37 (21)	0.79 (22)
C(9′)	3.66 (27)	4.60 (30)	4.33 (28)	−0.57 (24)	0.59 (22)	1.02 (23)
C(10′)	4.11 (27)	4.00 (29)	3.51 (25)	1.02 (23)	1.11 (21)	0.79 (22)
C(11′)	4.15 (28)	3.08 (26)	3.27 (24)	0.81 (22)	0.34 (21)	0.26 (20)
C(12′)	5.54 (34)	4.09 (31)	4.98 (32)	0.53 (27)	0.77 (26)	−0.03 (26)
C(13′)	7.20 (44)	4.51 (34)	5.40 (34)	0.42 (31)	0.81 (31)	−0.18 (28)
C(14′)	8.27 (47)	4.77 (37)	5.11 (35)	1.25 (32)	2.45 (33)	−0.55 (27)
C(15′)	6.94 (36)	3.80 (29)	3.83 (27)	1.62 (28)	2.06 (26)	−0.06 (23)
C(16′)	12.09 (64)	3.31 (33)	10.48 (56)	−1.86 (38)	2.71 (47)	−1.64 (35)
O(1)	3.97 (19)	4.92 (20)	4.06 (18)	1.13 (17)	1.17 (15)	−0.15 (16)
O(2)	4.92 (20)	4.29 (20)	3.85 (19)	1.41 (16)	1.67 (16)	0.13 (15)
O(1′)	3.51 (18)	5.70 (22)	4.16 (19)	0.45 (16)	1.53 (15)	1.21 (17)
O(2′)	3.23 (19)	4.89 (20)	4.74 (19)	0.01 (15)	0.97 (15)	1.64 (16)
C(21)	3.62 (27)	3.92 (28)	4.10 (30)	−0.14 (23)	2.21 (24)	−0.08 (23)
C(22)	6.56 (36)	4.54 (31)	5.15 (31)	0.98 (20)	2.57 (27)	−1.43 (25)
C(21′)	3.75 (29)	3.46 (26)	3.66 (26)	0.39 (22)	1.63 (22)	0.23 (22)
C(22′)	4.96 (32)	4.89 (31)	6.04 (34)	−0.97 (26)	2.15 (27)	1.37 (27)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Final Positional Parameters with Esd's for the Benzoxazole Derivative (**2**)

atom	x	y	z	atom	x	y	z
Pd(1)	0.16757 (6)	0.07342 (3)	0.24351 (4)	C(11′)	0.4468 (8)	−0.0404 (4)	0.3274 (5)
O(3)	0.2886 (6)	−0.0026 (3)	0.0038 (4)	C(12′)	0.3919 (9)	−0.0975 (4)	0.3064 (6)
N	0.1805 (7)	0.0168 (3)	0.1279 (5)	C(13′)	0.4505 (11)	−0.1392 (5)	0.2499 (7)
C(2)	0.2708 (9)	0.0348 (4)	0.0781 (6)	C(14′)	0.5660 (11)	−0.1206 (5)	0.2157 (7)
C(4)	0.1735 (12)	−0.0991 (5)	−0.0532 (8)	C(15′)	0.6219 (9)	−0.0636 (4)	0.2355 (7)
C(5)	0.0773 (14)	−0.1382 (5)	−0.0322 (10)	C(16′)	0.3857 (13)	−0.2025 (4)	0.2295 (9)
C(6)	0.0120 (11)	−0.1285 (5)	0.0487 (9)	O(1)	0.3147 (6)	0.0962 (3)	0.4814 (4)
C(7)	0.0381 (10)	−0.0773 (5)	0.1086 (7)	O(2)	0.1621 (6)	0.1385 (2)	0.3516 (4)
C(8)	0.1335 (9)	−0.0379 (4)	0.0861 (7)	O(1′)	0.0431 (5)	0.0148 (3)	0.3094 (4)
C(9)	0.2005 (10)	−0.0495 (5)	0.0082 (7)	O(2′)	0.2180 (5)	−0.0274 (2)	0.4271 (4)
C(10)	0.3387 (9)	0.0905 (4)	0.1012 (6)	C(21)	0.2314 (9)	0.1373 (4)	0.4418 (7)
C(11)	0.2925 (8)	0.1200 (4)	0.1792 (6)	C(22)	0.2142 (9)	0.1896 (4)	0.5092 (6)
C(12)	0.3506 (9)	0.1769 (4)	0.2121 (6)	C(21′)	0.0945 (10)	−0.0214 (4)	0.3826 (7)
C(13)	0.4503 (9)	0.2031 (4)	0.1686 (7)	C(22′)	−0.0108 (8)	−0.0633 (4)	0.4148 (7)
C(14)	0.4937 (9)	0.1706 (5)	0.0901 (7)	H(4)	0.2184	−0.1061	−0.1071
C(15)	0.4397 (9)	0.1147 (4)	0.0580 (6)	H(5)	0.0541	−0.1730	−0.0736
C(16)	0.5099 (10)	0.2653 (4)	0.2053 (7)	H(6)	−0.0509	−0.1575	0.0622
Pd(2)	0.38004 (6)	0.02285 (3)	0.40478 (4)	H(7)	−0.0071	−0.0698	0.1622
O(3′)	0.7211 (6)	0.0603 (3)	0.2980 (4)	H(12)	0.3208	0.1975	0.2650
N′	0.5480 (6)	0.0641 (3)	0.3776 (5)	H(14)	0.5612	0.1876	0.0592
C(2′)	0.6101 (8)	0.0332 (4)	0.3199 (6)	H(15)	0.4715	0.0932	0.0069
C(4′)	0.8258 (10)	0.1586 (5)	0.3516 (8)	H(4′)	0.8978	0.1556	0.3163
C(5′)	0.8119 (11)	0.2081 (5)	0.4126 (10)	H(5′)	0.8766	0.2399	0.4178
C(6′)	0.7074 (11)	0.2130 (4)	0.4662 (7)	H(6′)	0.7037	0.2470	0.5079
C(7′)	0.6084 (9)	0.1672 (4)	0.4576 (7)	H(7′)	0.5347	0.1701	0.4911
C(8′)	0.6211 (8)	0.1175 (4)	0.3985 (6)	H(12′)	0.3131	−0.1087	0.3305
C(9′)	0.7285 (8)	0.1150 (5)	0.3466 (7)	H(14′)	0.6076	−0.1477	0.1776
C(10′)	0.5624 (8)	−0.0251 (4)	0.2910 (6)	H(15′)	0.6998	−0.0517	0.2108

Table V. Anisotropic Thermal Parameters for the Benzoxazole Derivative (**2**)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd(1)	3.06 (3)	3.62 (3)	2.81 (3)	0.39 (3)	0.83 (2)	0.66 (3)
O(3)	5.4 (3)	5.2 (4)	4.0 (3)	0.4 (3)	1.4 (3)	−0.8 (3)
N	3.5 (3)	4.1 (4)	2.3 (3)	0.2 (3)	0.2 (3)	0.3 (3)
C(2)	4.3 (5)	4.3 (6)	2.0 (4)	1.0 (4)	0.2 (4)	−0.2 (4)
C(4)	7.7 (7)	4.9 (6)	6.0 (6)	0.8 (5)	2.2 (5)	−1.2 (5)
C(5)	8.8 (8)	3.8 (6)	8.1 (8)	1.2 (6)	−0.8 (7)	−0.8 (6)
C(6)	5.8 (6)	5.9 (7)	6.5 (6)	−0.6 (5)	−0.2 (5)	0.6 (6)
C(7)	5.5 (5)	4.9 (6)	3.5 (5)	−0.8 (5)	−1.0 (4)	0.3 (5)
C(8)	4.1 (5)	3.4 (5)	3.3 (4)	0.3 (4)	−0.6 (4)	0.3 (4)
C(9)	4.5 (5)	4.9 (6)	4.3 (5)	0.6 (5)	0.9 (4)	−0.5 (5)
C(10)	3.7 (4)	4.2 (5)	2.6 (4)	0.9 (4)	0.7 (4)	0.3 (4)
C(11)	3.8 (4)	3.7 (5)	2.6 (4)	0.4 (4)	0.1 (3)	1.4 (4)
C(12)	4.2 (4)	4.2 (5)	3.3 (4)	0.5 (4)	1.2 (4)	1.3 (4)
C(13)	3.9 (4)	5.0 (5)	4.4 (5)	0.5 (4)	0.7 (4)	2.6 (4)
C(14)	4.2 (5)	5.9 (6)	4.7 (5)	0.4 (5)	2.1 (4)	1.7 (5)
C(15)	4.7 (5)	4.9 (5)	3.8 (4)	0.2 (4)	1.2 (4)	1.1 (4)
C(16)	7.1 (6)	3.5 (5)	5.8 (5)	−2.0 (4)	1.5 (4)	0.8 (4)
Pd(2)	2.28 (3)	3.17 (3)	3.29 (3)	0.25 (2)	0.68 (2)	0.42 (3)
O(3′)	3.3 (3)	4.9 (3)	4.7 (3)	0.1 (3)	1.4 (2)	0.3 (3)
N′	2.4 (3)	3.4 (4)	3.0 (3)	−0.0 (3)	0.5 (3)	0.3 (3)
C(2′)	1.8 (4)	3.9 (5)	3.3 (4)	0.3 (4)	0.5 (3)	1.0 (4)
C(4′)	4.1 (5)	5.7 (6)	7.2 (6)	−0.3 (5)	1.8 (4)	1.3 (5)
C(5′)	4.2 (5)	5.0 (6)	10.2 (8)	−1.8 (5)	0.5 (5)	2.9 (6)
C(6′)	5.2 (5)	4.2 (5)	6.4 (6)	−0.6 (5)	0.5 (5)	0.0 (4)
C(7′)	3.7 (5)	4.3 (5)	5.7 (5)	0.4 (4)	0.8 (4)	0.8 (5)
C(8′)	3.0 (4)	3.9 (5)	3.9 (4)	0.5 (4)	0.3 (4)	1.0 (4)
C(9′)	2.6 (4)	5.2 (6)	4.4 (5)	−0.4 (4)	0.7 (4)	1.8 (4)
C(10′)	3.0 (4)	3.5 (5)	2.8 (4)	0.9 (4)	0.4 (3)	0.2 (4)
C(11′)	2.7 (4)	3.2 (5)	2.6 (4)	0.8 (3)	0.1 (3)	0.3 (3)
C(12′)	4.0 (4)	4.2 (5)	4.0 (4)	0.5 (4)	0.5 (4)	0.0 (4)
C(13′)	5.7 (6)	6.0 (6)	4.4 (5)	1.2 (5)	0.0 (5)	0.3 (5)
C(14′)	5.8 (6)	6.8 (7)	4.4 (5)	1.3 (5)	2.2 (4)	−0.5 (5)
C(15′)	4.6 (5)	4.3 (5)	4.4 (5)	−0.2 (4)	1.0 (4)	0.3 (4)
C(16′)	10.8 (8)	2.6 (5)	11.9 (9)	−1.6 (5)	3.3 (7)	−3.3 (5)
O(1)	3.4 (3)	4.6 (3)	3.5 (3)	0.4 (3)	1.0 (2)	0.0 (2)
O(2)	3.9 (3)	4.5 (3)	3.6 (3)	0.9 (2)	1.5 (3)	0.4 (2)
O(1′)	3.0 (3)	5.0 (3)	5.1 (3)	−0.3 (2)	1.7 (2)	0.8 (3)
O(2′)	2.0 (2)	4.3 (3)	4.5 (3)	0.2 (2)	0.6 (2)	1.2 (2)
C(21)	2.4 (4)	4.5 (5)	2.6 (4)	0.0 (4)	0.3 (4)	0.8 (4)
C(22)	6.8 (5)	4.0 (5)	4.6 (5)	0.9 (4)	2.1 (4)	−1.7 (4)
C(21′)	4.4 (5)	2.5 (4)	3.6 (4)	0.4 (4)	1.6 (4)	0.7 (4)
C(22′)	3.7 (4)	4.3 (5)	6.1 (5)	−1.3 (4)	2.6 (4)	0.6 (4)

Table VI. Interatomic Distances (Å)

atoms	distances 1	distances 2
(A) Palladium···Palladium Distances		
Pd(1)···Pd(2)	2.871 (1)	2.842 (1)
(B) Palladium–Ligand Bond Lengths		
Pd(1)–N(1)	2.036 (4)	2.026 (7)
Pd(2)–N(1′)	2.038 (4)	2.014 (6)
Pd(1)–C(11)	1.975 (5)	1.972 (8)
Pd(2)–C(11′)	1.973 (5)	1.963 (8)
Pd(2)–O(1)	2.138 (4)	2.121 (6)
Pd(1)–O(1′)	2.140 (4)	2.136 (6)
Pd(1)–O(2)	2.047 (4)	2.060 (6)
Pd(2)–O(2′)	2.051 (4)	2.043 (5)
(C) Heteroatom–Carbon Distances		
N(1)–C(2)	1.320 (7)	1.305 (11)
N(1′)–C(2′)	1.305 (7)	1.299 (10)
N(1)–C(8)	1.397 (7)	1.377 (12)
N(1′)–C(8′)	1.398 (7)	1.390 (11)
X(3)–C(2)	1.737 (6)[a]	1.342 (11)[b]
X(3′)–C(2′)	1.713 (6)[a]	1.351 (10)[b]
X(3)–C(9)	1.721 (7)[a]	1.377 (12)[b]
X(3′)–C(9)	1.719 (6)[a]	1.379 (12)[b]
(D) Distance in "Benzo" Rings		
C(4)–C(5)	1.380 (11)	1.375 (18)
C(5)–C(6)	1.381 (11)	1.408 (18)
C(6)–C(7)	1.392 (10)	1.384 (15)
C(7)–C(8)	1.374 (9)	1.381 (14)
C(8)–C(9)	1.423 (8)	1.392 (13)
C(9)–C(4)	1.363 (9)	1.367 (15)
C(4′)–C(5′)	1.385 (10)	1.402 (16)
C(5′)–C(6′)	1.363 (11)	1.403 (16)
C(6′)–C(7′)	1.388 (9)	1.404 (14)
C(7′)–C(8′)	1.377 (8)	1.388 (13)
C(8′)–C(9′)	1.428 (8)	1.409 (12)
C(9′)–C(4′)	1.368 (9)	1.361 (15)
(E) Internal Distances in "Tolyl" Systems		
C(10)–C(11)	1.408 (7)	1.403 (11)
C(11)–C(12)	1.429 (8)	1.421 (12)
C(12)–C(13)	1.369 (8)	1.395 (12)
C(13)–C(14)	1.394 (8)	1.428 (13)
C(14)–C(15)	1.426 (9)	1.386 (14)
C(15)–C(10)	1.411 (8)	1.384 (13)
C(10′)–C(11′)	1.398 (8)	1.394 (11)
C(11′)–C(12′)	1.394 (8)	1.391 (12)
C(12′)–C(13′)	1.382 (9)	1.413 (14)
C(13′)–C(14′)	1.376 (11)	1.399 (15)
C(14′)–C(15′)	1.411 (9)	1.389 (15)
C(15′)–C(11′)	1.424 (8)	1.364 (12)
(F) External Distances from "Tolyl" Systems		
C(2)–C(10)	1.404 (8)	1.415 (13)
C(2′)–C(10′)	1.440 (8)	1.408 (12)
C(13)–C(16)	1.534 (8)	1.543 (13)
C(13′)–C(16′)	1.570 (10)	1.551 (14)
(G) Distances within Acetate Groups		
C(21)–O(1)	1.241 (7)	1.259 (11)
C(21)–O(2)	1.269 (7)	1.228 (10)
C(21′)–O(1′)	1.248 (7)	1.272 (10)
C(21′)–O(2′)	1.254 (7)	1.226 (11)
C(21)–C(22)	1.541 (8)	1.512 (12)
C(21′)–C(22′)	1.524 (8)	1.543 (12)

[a] X(3) represents S(3) for benzthiazole derivative. [b] X(3) represents O(3) for benzoxazole derivative.

chloromethane/hexane; yield 3.69 g (94%). Anal. Calcd for $C_{32}H_{26}O_4N_2S_2Pd_2$: C, 49.30; H, 3.36; N, 3.59; Pd, 27.30; S, 8.23. Found: C, 49.27; H, 3.55; N, 3.81; Pd, 26.0; S, 8.23 (mp 256–258 °C dec).

Synthesis of $[(MeC_6H_3C_7H_4NO)Pd]_2(\mu\text{-}O_2CMe)_2$ (2). A mixture of 2.09 g of 2-*p*-tolylbenzoxazole[9] and 2.24 g of palladium(II) acetate in 25 mL of acetic acid was heated and stirred under nitrogen for 6 h. The dark red precipitate was filtered off and recrystallized from acetone; yield 3.38 g (90%). Anal. Calcd for $C_{32}H_{26}O_6N_2Pd_2$: C, 51.42; H, 3.51; N, 3.75; Pd, 28.6. Found: C, 51.40; H, 3.61; N, 3.75; Pd, 30.3 (mol wt (ebullioscopic, in toluene) 807; mp 262–264 °C dec).

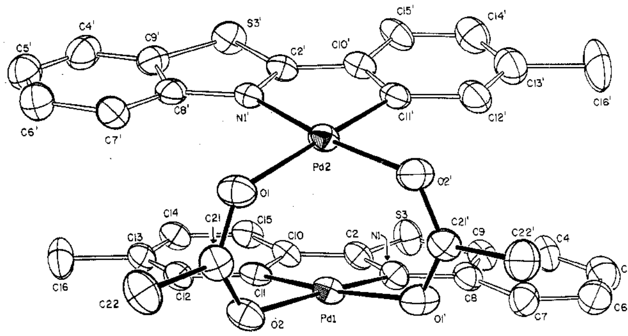


Figure 1. Labeling of atoms in the benzthiazole derivative (**1**), $[(MeC_6H_3C_7H_4NS)Pd]_2(\mu\text{-}O_2CMe)_2$ (ORTEP-II diagram; 50% probability ellipsoids).

Synthesis of $[(MeC_6H_3C_7H_3MeNO)Pd]_2(\mu\text{-}O_2CMe)_2$ (5). A mixture of 0.558 g of 6-methyl-2-*p*-tolylbenzoxazole and 0.61 g of palladium(II) acetate in 15 mL of acetic acid was heated with stirring under nitrogen for 3 h. After the mixture was cooled, a golden red precipitate was filtered off and recrystallized from dichloromethane/hexane: yield 0.81 g (84%); mp 258–261 °C dec.

(B) Collection and Processing of X-ray Data. Complex 1. A deep red crystalline parallelepiped (0.2 × 0.2 × 0.4 mm) was jam-fit into a 0.2-mm diameter thin glass capillary, which was flame sealed and fixed (with beeswax) into an aluminum pin inserted into a eucentric goniometer head, which was secured to the goniostat of a fully automated Syntex P2$_1$ four-circle diffractometer. Crystal alignment, determination of the orientation matrix and accurate cell dimensions, and intensity data collection (Mo Kα radiation) were carried out as described previously.[10] Details appear in Table I. A survey of the complete data set revealed the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$, consistent with the space group $P2_1/n$ (which is an alternative setting of $P2_1/c$ (C_{2h}^5)).

Data were collected for absorption by an empirical method based on a series of ψ scans of close-to-axial reflections. Equivalent data were then averaged ($R(I)$ = 2.80%) and corrected for Lorentz and polarization effects.

Complex 2. A crystalline parallelepiped of dimensions 0.12 × 0.20 × 0.20 mm was mounted as described above and found to be isomorphous with the previous species (see Table I). Two complete (4° < 2θ < 40°) asymmetric sets of data were collected for this crystal. Following correction for absorption, equivalent data were averaged ($R(I)$ = 2.0%) and were corrected for Lorentz and polarization effects.

(C) Solution and Refinement of the Structures. All calculations were performed by using the Syntex XTL system, consisting of the following: (a) a Data General Nova 1200 computer with 24K of 16-bit word memory and with a parallel floating-point processor for 32- and 64-bit arithmetic, (b) a Diablo moving-head disk unit with 1.2 million 16-bit words, (c) a Versatec electrostatic printer/plotter, and (d) a locally modified version of the XTL conversational crystallographic program package.

Analytical scattering factors for neutral palladium, sulfur, oxygen, carbon, nitrogen, and hydrogen atoms were used throughout the analysis;[11a] both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[11b] were applied to all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where the weights are defined in eq 1; p, the so-called "ignorance factor", was set at a value of 0.01.

$$w = [\{\sigma_c(|F_o|)\}^2 + \{p|F_o|\}^2]^{-1} \qquad (1)$$

---

(9) Skraup, S. *Justus Liebigs Ann. Chem.* **1919**, *419*, 1.

(10) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(11) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1973; Vol. IV: (a) pp 99–101; (b) pp 149–150.

Table VII. Interatomic Angles (Deg) with Esd's

	angle			angle	
atoms	1	2	atoms	1	2
(A) Angles about Palladium Atoms					
N(1)-Pd(1)-C(11)	81.17 (20)	80.39 (30)	O(1)-Pd(2)-N(1')	97.63 (16)	95.60 (24)
N(1')-Pd(2)-C(11')	81.24 (20)	80.39 (29)	O(1')-Pd(1)-N(1)	96.52 (16)	94.73 (24)
C(11)-Pd(1)-O(2)	92.90 (19)	93.45 (28)	N(1)-Pd(1)-O(2)	172.71 (17)	173.49 (25)
C(11')-Pd(2)-O(2')	92.59 (19)	93.48 (27)	N(1')-Pd(2)-O(2')	173.24 (16)	173.72 (24)
O(2)-Pd(1)-O(1')	89.72 (15)	91.54 (22)	C(11)-Pd(1)-O(1')	174.83 (18)	173.99 (28)
O(2')-Pd(2)-O(1)	88.64 (15)	90.58 (21)	C(11')-Pd(2)-O(1)	177.51 (19)	175.35 (27)
(B) External Angles of the *p*-Tolylbenzthiazole Ligand					
Pd(1)-N(1)-C(8)	135.2 (4)	141.7 (6)	C(10)-C(2)-X(3)	127.0 (4)	124.5 (8)
Pd(2)-N(1')-C(8')	135.2 (4)	140.5 (6)	C(10')-C(2')-X(3')	126.1 (4)	126.3 (7)
Pd(1)-N(1)-C(2)	111.9 (4)	112.2 (6)	C(2)-C(10)-C(15)	125.2 (5)	127.5 (8)
Pd(2)-N(1')-C(2')	113.2 (4)	113.5 (5)	C(2')-C(10')-C(15')	123.7 (5)	125.0 (8)
N(1)-C(2)-C(10)	119.1 (5)	120.7 (8)	N(1)-C(8)-C(7)	127.0 (5)	131.4 (8)
N(1')-C(2')-C(10')	117.8 (5)	118.7 (7)	N(1')-C(8')-C(7')	127.9 (5)	133.4 (8)
C(2)-C(10)-C(11)	113.4 (5)	110.5 (8)	X(3)-C(9)-C(4)	128.8 (5)	128.8 (9)
C(2')-C(10')-C(11')	113.6 (5)	112.4 (7)	X(3')-C(9')-C(4')	128.8 (5)	127.8 (9)
C(10)-C(11)-Pd(1)	113.6 (4)	115.6 (6)	C(12)-C(13)-C(16)	121.0 (5)	120.2 (8)
C(10')-C(11')-Pd(2)	114.0 (4)	114.9 (6)	C(12')-C(13')-C(16')	120.0 (6)	119.3 (9)
C(10)-C(11)-C(12)	118.3 (5)	117.9 (7)	C(14)-C(13)-C(16)	118.8 (5)	117.9 (8)
C(10')-C(11')-C(12')	118.3 (5)	118.0 (7)	C(14')-C(13')-C(16')	120.7 (7)	117.2 (9)
(C) Angles within Heterocyclic Rings					
C(8)-N(1)-C(2)	112.6 (5)	105.9 (7)	C(2')-X(3')-C(9')	90.0 (3)	108.4 (8)
C(8')-N(1')-C(2')	111.5 (4)	106.1 (7)	X(3)-C(9)-C(8)	109.8 (4)	108.4 (8)
N(1)-C(2)-X(3)	113.9 (4)	114.7 (8)	X(3')-C(9')-C(8')	109.9 (4)	108.0 (8)
N(1')-C(2')-X(3')	116.1 (4)	114.9 (7)	C(9)-C(8)-N(1)	112.9 (5)	107.0 (8)
C(2)-X(3)-C(9)	90.7 (3)	104.0 (7)	C(9')-C(8')-N(1')	112.5 (5)	106.7 (8)
(D) Angles within "Benzo" Rings					
C(9)-C(4)-C(5)	118.2 (7)	115.9 (11)	C(9')-C(4')-C(5')	117.7 (6)	115.0 (10)
C(4)-C(5)-C(6)	120.9 (7)	122.3 (12)	C(4')-C(5')-C(6')	121.5 (7)	123.5 (10)
C(5)-C(6)-C(7)	121.9 (7)	121.1 (11)	C(5')-C(6')-C(7')	122.0 (7)	119.4 (9)
C(6)-C(7)-C(8)	117.7 (6)	116.3 (9)	C(6')-C(7')-C(8')	117.9 (6)	118.1 (9)
C(7)-C(8)-C(9)	120.1 (5)	121.6 (9)	C(7')-C(8')-C(9')	119.6 (5)	119.9 (8)
C(8)-C(9)-C(4)	121.4 (6)	122.8 (9)	C(8')-C(9')-C(4')	121.3 (6)	124.1 (9)
(E) Internal Angles of Tolyl Rings					
C(15)-C(10)-C(11)	121.4 (5)	122.0 (8)	C(15')-C(10')-C(11')	122.6 (5)	122.6 (8)
C(10)-C(11)-C(12)	118.3 (5)	117.9 (7)	C(10')-C(11')-C(12')	118.3 (5)	118.0 (7)
C(11)-C(12)-C(13)	121.1 (5)	121.5 (8)	C(11')-C(12')-C(13')	121.3 (6)	121.6 (8)
C(12)-C(13)-C(14)	120.2 (6)	117.8 (8)	C(12')-C(13')-C(14')	119.2 (7)	117.2 (9)
C(13)-C(14)-C(15)	121.2 (6)	121.5 (9)	C(13')-C(14')-C(15')	123.4 (7)	122.1 (9)
C(14)-C(15)-C(10)	117.7 (5)	119.2 (8)	C(14')-C(15')-C(10')	115.1 (6)	118.6 (9)
(F) Angles in Acetate Bridges					
Pd(1)-O(2)-C(21)	122.7 (4)	124.4 (5)	Pd(2)-O(2')-C(21')	126.1 (4)	126.4 (6)
O(2)-C(21)-C(22)	115.3 (5)	116.6 (8)	O(2')-C(21')-C(22')	116.4 (5)	117.4 (8)
O(2)-C(21)-O(1)	127.3 (5)	125.0 (8)	O(2')-C(21')-O(1')	126.7 (5)	127.0 (8)
C(22)-C(21)-O(1)	117.4 (5)	118.4 (8)	C(22')-C(21')-O(1')	116.9 (5)	115.6 (7)
C(21)-O(1)-Pd(2)	127.0 (4)	127.6 (5)	C(21')-O(1')-Pd(1)	124.6 (4)	123.1 (5)

Complex 1. After the data had been placed on an (approximate) absolute scale via a Wilson plot, a three-dimensional Patterson synthesis yielded the positions of the two independent palladium atoms. These were refined, after which a difference-Fourier synthesis revealed the positions of all nonhydrogen atoms. Full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all nonhydrogen atoms converged with $R_F = 4.4\%$, $R_{wF} = 4.6\%$, and GOF = 2.44. A difference-Fourier map failed to show the positions of most hydrogen atoms, so those for the 14 aromatic hydrogen atoms were included in the model in idealized positions with $d(\text{C–H}) = 0.95$ Å[12] and with isotropic thermal parameters of 7.0 Å^2. Two cycles of least-squares refinement led to convergence with $R_F = 4.0\%$, $R_{wF} = 4.1\%$, and GOF = 2.18 for all 3876 reflections. The final residuals for those 3470 reflections with $|F_o| > 3.0\sigma\{|F_o|\}$ were $R_F = 3.4\%$, $R_{wF} = 4.1\%$, and GOF = 2.29.

There was no evidence of secondary extinction. A final difference-Fourier synthesis showed a peak of height 0.55 e Å^{-3} (at 0.107, 0.195, 0.488) as its most intense feature. The function $\sum w(|F_o| - |F_c|)_2$ showed no significant dependence on $|F_o|$, $(\sin\theta)/\lambda$, sequence number, or identity or parity of the Miller indices. The weighting scheme is thus satisfactory.

Final positional and thermal parameters for **1** are collected in Tables II and III.

Complex 2. The structure was solved, as for **1**, by a combination of Wilson plot, Patterson synthesis, difference-Fourier synthesis, and full-matrix least-squares refinement techniques. The refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms led to convergence with $R_F = 5.0\%$ and $R_{wF} = 4.3\%$. A difference-Fourier map failed to yield the positions of the hydrogen atoms, so the aromatic hydrogen atoms were included in idealized positions ($d(\text{C–H}) = 0.95$ Å[12] and $B(\text{H}) = 7.0$ Å^2). Two further cycles of least-squares refinement yielded $R_F = 4.8\%$, $R_{wF} = 4.2\%$, and GOF = 1.79. At this point a careful survey of $|F_o|$ and $|F_c|$ values suggested that the data were affected by secondary extinction. The $|F_o|$ values of all data were therefore corrected by using the approximation shown in eq 2. The value of k, obtained by a least-squares analysis of $|F_o|$

$$|F_o^{\text{cor}}| = |F_o^{\text{uncor}}|(1.0 + kI_o) \qquad (2)$$

and $|F_c|$ value for intense low-order reflections, was 1.98×10^{-8}. A further two cycles of least-squares refinement led to final convergence

---

(12) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

Table VIII. Pertinent Least-Squares Planes[a] and Esd's

(A) Benzthiazole Complex (1)

Planes

atom	dev, Å	atom	dev, Å
Ia: $-0.7061X + 0.3631Y - 0.6079Z = -1.9421$			
Pd(1)	0.0040 (4)	O(2)	0.0727 (39)
C(11)	−0.0841 (52)	O(1′)	−0.0697 (38)
N(1)	0.0771 (45)		
IIa: $-0.3184X + 0.3029Y - 0.8734Z = -5.3650$			
Pd(2)	0.0029 (4)	O(1)	0.0380 (36)
C(11′)	0.0462 (52)	O(2′)	−0.0428 (37)
N(1′)	−0.0443 (41)		
Ib: $-0.5561X + 0.4568Y - 0.6943Z = -1.7671$			
C(4)	0.000 (7)	C(7)	−0.001 (6)
C(5)	−0.004 (8)	C(8)	−0.004 (6)
C(6)	−0.005 (7)	C(9)	0.004 (6)
Ic: $-0.5862X + 0.4041Y - 0.7022Z = -1.8551$			
C(10)	0.008 (5)	C(13)	0.009 (6)
C(11)	−0.006 (5)	C(14)	−0.007 (6)
C(12)	−0.003 (6)	C(15)	−0.002 (6)
IIb: $-0.4314X + 0.3958Y - 0.8107Z = -5.1796$			
C(4′)	0.010 (7)	C(7′)	0.003 (6)
C(5′)	0.003 (7)	C(8′)	0.010 (5)
C(6′)	−0.010 (7)	C(9′)	−0.016 (6)
IIc: $-0.3859X + 0.3161Y - 0.8667Z = -5.3080$			
C(10′)	0.008 (5)	C(13′)	0.006 (7)
C(11′)	−0.010 (5)	C(14′)	−0.008 (7)
C(12′)	0.003 (6)	C(15′)	0.000 (6)
IIIa: $0.7704X + 0.5563Y - 0.3115Z = 0.5267$			
O(1)	0.002 (4)	O(2)	0.002 (4)
C(21)	−0.006 (6)	C(22)	0.002 (6)
IIIb: $0.3517X - 0.6999Y - 0.6217Z = -2.8124$			
O(1′)	0.003 (4)	O(2′)	0.003 (4)
C(21)	−0.007 (5)	C(22′)	0.002 (6)

Dihedral Angles (Deg)

Ia–IIa	24.46	IIb–IIc	6.16	Ic–IIc	15.73
Ib–Ic	3.51	Ib–IIb	10.39	IIIa–IIIb	85.68

[a] Weighted planes ($w = \sigma^{-2}$); Cartesian (Å) coordinates.

(B) Benzoxazole Complex (2)

Planes

atom	dev, Å	atom	dev, Å
Ia: $-0.6837X + 0.4069Y - 0.6058Z = -1.8259$			
Pd(1)	0.0109 (6)	O(2)	0.0419 (57)
C(11)	−0.0547 (78)	O(1′)	−0.0455 (55)
N	0.0473 (66)		
IIa: $-0.3662X + 0.3424Y - 0.8652Z = -5.2259$			
Pd(2)	−0.0075 (6)	O(1′)	0.0300 (53)
C(11′)	0.0358 (72)	O(2′)	−0.0276 (52)
N′	−0.0306 (61)		
Ib: $-0.5928X + 0.4814Y - 0.6456Z = -1.7512$			
C(4)	0.002 (11)	C(7)	0.003 (9)
C(5)	0.012 (13)	C(8)	0.010 (9)
C(6)	−0.014 (12)	C(9)	−0.013 (10)
Ic: $-0.5652X + 0.4369Y - 0.6998Z = -1.7444$			
C(10)	0.009 (8)	C(13)	0.004 (9)
C(11)	−0.001 (8)	C(14)	0.004 (9)
C(12)	−0.006 (8)	C(15)	−0.010 (9)
IIb: $-0.4053X + 0.4452Y - 0.7984Z = -4.8867$			
C(4′)	0.000 (11)	C(7′)	0.010 (9)
C(5′)	0.003 (12)	C(8′)	−0.007 (8)
C(6′)	−0.008 (10)	C(9′)	0.002 (9)
IIc: $-0.4087X + 0.3311Y - 0.8505Z = -5.2595$			
C(10′)	−0.004 (8)	C(13′)	−0.001 (9)
C(11′)	0.000 (7)	C(14′)	−0.002 (9)
C(12′)	0.002 (8)	C(15′)	0.004 (9)
IIIa: $0.8356X + 0.4810Y - 0.2653Z = 0.6440$			
O(1)	0.000 (6)	O(2)	0.000 (6)
C(21)	−0.001 (9)	C(22)	0.000 (9)
IIIb: $0.2930X - 0.6753Y - 0.6768Z = -3.1126$			
O(1′)	0.004 (6)	O(2)	0.004 (5)
C(21′)	−0.012 (9)	C(22′)	0.003 (9)

Dihedral Angles (Deg)

Ia–IIa	23.96	IIb–IIc	7.20	Ic–IIc	13.88
Ib–Ic	4.32	Ib–IIb	14.05	IIIa–IIIb	84.28

with R_F = 4.6%, R_{wF} = 4.1%, and GOF = 1.77 for all 2687 data; for those 2285 reflections with $|F_o| > 3.0\sigma(|F_o|)$, the final residuals were R_F = 3.5% and R_{wF} = 4.0%, with GOF = 1.89.

The largest peak on a final difference-Fourier synthesis was of height 0.54 e Å^{-3} (at 0.471, 0.431, 0.112). The model was complete. The usual tests of $\sum w(|F_o| - |F_c|)^2$ (vide supra) indicated that the weighting scheme was satisfactory.

Final positional and thermal parameters for **2** are collected in Tables IV and V.

Discussion of the Molecular Structures

The two species examined crystallographically, $[(MeC_6H_3C_7H_4NS)Pd]_2(\mu\text{-}O_2CMe)_2$ (**1**) and $[(MeC_6H_3C_7H_4NO)Pd]_2(\mu\text{-}O_2CMe)_2$ (**2**), are isomorphous and isostructural.

Interatomic distances and their estimated standard deviations (esd's) are compared in Table VI; interatomic angles (with eds's) are compared in Table VII. Selected least-squares planes, and deviations of atoms therefrom, are collected in Table VIII. The crystals consist of discrete dimeric molecules, separated by normal van der Waals distances. The dimeric species each possess approximate (noncrystallographic) C_2 symmetry. The scheme used for labeling atoms in the benzthiazole complex is shown in Figure 1. Stereoscopic views of this molecule are presented in Figure 2. The numbering scheme for the benzoxazole derivative is given in Figure 3; a stereoscopic view of this molecule is shown in Figure 4.

The gross molecular configuration of these species is related closely to such other *cis*-bis(μ-carboxylato)-dipalladium complexes as dimeric (η^3-allyl)palladium acetate (**6**) (Pd···Pd = 2.94 Å),[13] bis(μ-acetato)-bis{2-(methylallyl)-3-norbornyl}dipalladium(II) (**7**) (Pd···Pd = 2.960 (1) Å),[14] bis(μ-acetato)-dichlorobis(dimethylphenylphosphine)dipalladium(II) (**8**) (Pd···Pd = 2.944 (2) Å).[15]

The palladium···palladium distances are 2.871 (1) Å in the benzthiazole derivative (**1**) and 2.842 (1) Å in the benzoxazole derivative (**2**). All of these palladium···palladium distances are regarded as nonbonding; the covalent radius of square-planar Pd(II) has been estimated as approximately 1.31 Å.[16]

---

(13) Churchill, M. R.; Mason, R. *Nature (London)* **1964**, *204*, 777.

(14) Zocchi, M.; Tieghi, G.; Albinati, A. *J. Chem. Soc., Dalton Trans.* **1973**, 883.

(15) Wong-Ng, W.; Cheng, P.-T.; Kocman, V.; Luth, H.; Nyburg, S. C. *Inorg. Chem.* **1979**, *18*, 2620.

(16) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91–164 (see, particularly, Section X-A on pp 153–5).

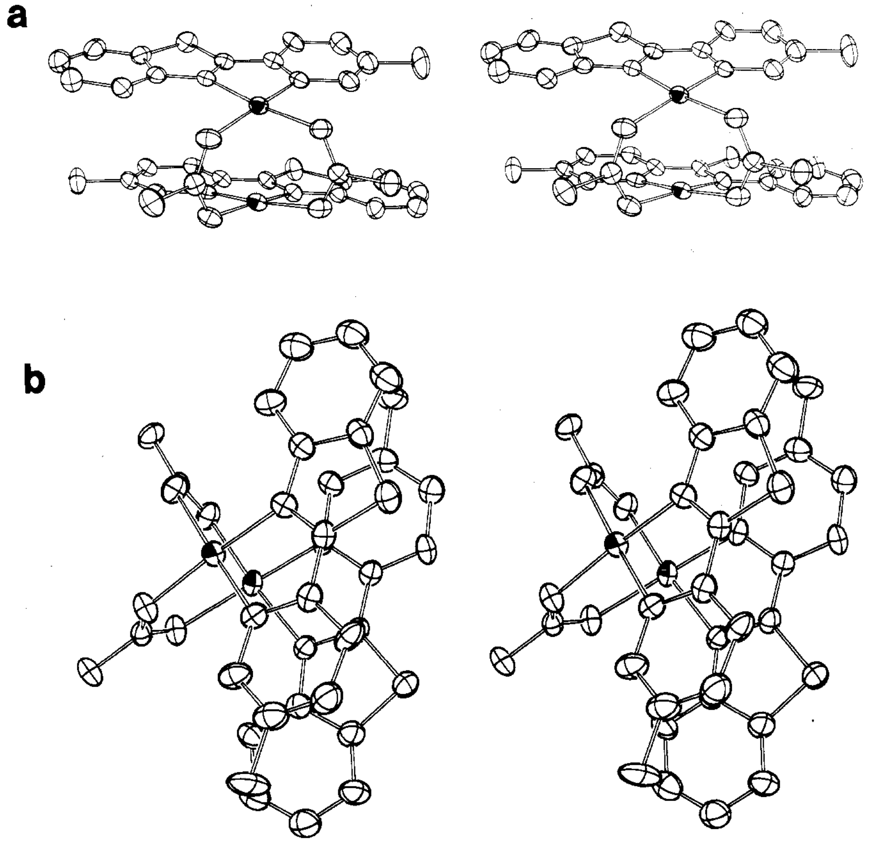
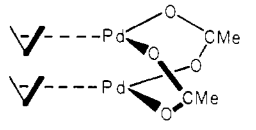
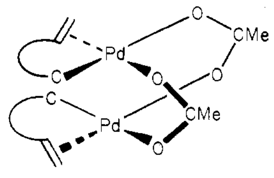


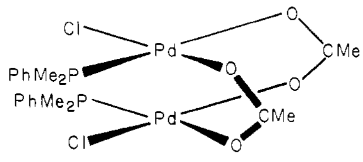
Figure 2. Stereoscopic views of the benzthiazole deriative (**1**): (a) with the molecular C_2 axis lying almost along the viewing direction; (b) with the C_2 axis approximately horizontal.



6



7
(schematic)



8

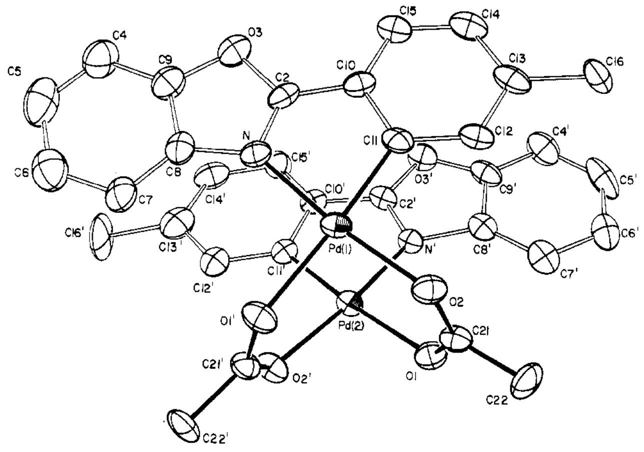


Figure 3. Labeling of atoms in the benzoxazole derivative (**2**), $[(MeC_6H_3C_7H_4NO)Pd]_2(\mu\text{-}O_2CMe)_2$ (ORTEP-II diagram, 50% probability ellipsoids).

Each palladium atom is in a slightly distorted square-planar coordination environment. As might be expected, the benzoxazole ligands in **2** are N,C bonded to palladium(II) atoms, rather than O,C bonded. A rather surprising result is that the benzthiazole ligands in **1** are also N,C bonded to palladium(II); one would have expected that S,C bonding to palladium might produce a more strongly bonded complex.

The square-planar coordination sphere about the palladium(II) atoms in both **1** and **2** therefore consists of a *nitrogen atom* of the benzthiazole or benzoxazole system, an *ortho carbon atom* of the *p*-tolyl group, and *two oxygen atoms* (one from each of the μ-acetate ligands). The Pd–N and Pd–C bonds form the basis for five-membered chelate rings; the "bite" angles are N(1)–Pd(1)–C(11) = 81.17 (20)° and N(1′)–Pd(2)–C(11′) = 81.24 (20)° in the benzthiazole complex (**1**) and N(1)–Pd(1)–C(11) = 80.39 (30)° and N(1′)–Pd(1)–C(11′) = 80.39 (29)° in the benzoxazole complex (**2**). The palladium–nitrogen (sp^2) bond lengths are Pd(1)–N(1) = 2.036 (4) Å and Pd(2)–N(1′) = 2.038 (4) Å [average 2.037 ± 0.001 Å][17] for **1** and 2.026 (7) and 2.014 (6) Å [average 2.020 ± 0.008 Å][17] for **2**. These values are in reasonable agreement with the predicted value of 2.01 Å (based upon r(Pd(II)) = 1.31 Å and r(N) = 0.70 Å).[18]

In contrast to this, the palladium–carbon (sp^2) bond lengths are all substantially *shorter* than the predicted value of 2.05 Å (based upon $d(C(sp^3)-C(sp^3))$ = 1.537 ± 0.005 Å,[19] d(C-

---

(17) The esd on average values is indicated by an initial "±" sign and is calculated as the scatter: $\sigma = [\sum_{i=1}^{i=N}(d_i - \bar{d})^2/(N-1)]^{1/2}$.

(18) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; Table 7-2, p 224.

(19) *Chem. Soc., Spec. Publ.* **1965**, *No. 18*, pp S14s–S15s.

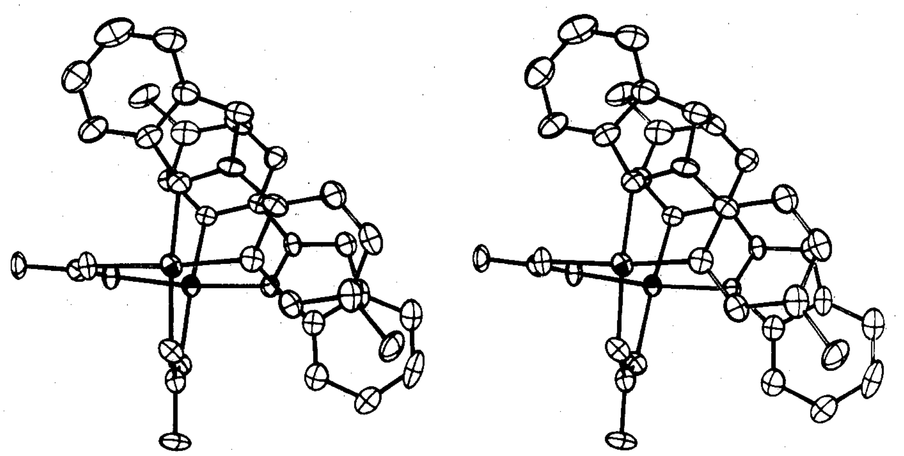


Figure 4. Stereoscopic view of the benzoxazole derivative (**2**).

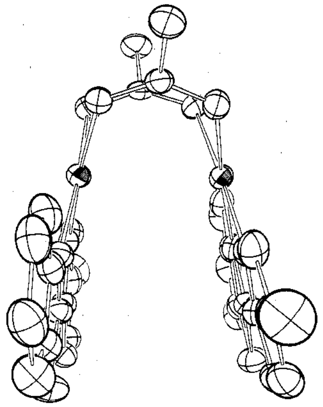
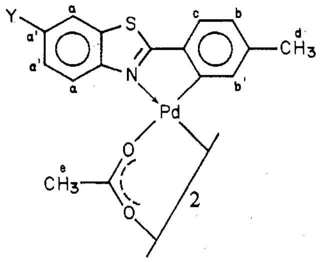


Figure 5. The benzthiazole derivative, showing the nonparallel nature of the square-planar coordination environments of the palladium(II) atoms. The benzoxazole derivative is closely similar.

Table IX. ^{1}H NMR Spectrum



complex	H atom(s)	τ value	rel intens
1	a + a'	complex multiplet centered at 7.5	4
	b	6.24 doublet, *J* = 3.9 Hz	1
	b'	6.34, singlet	1
	c	6.75, doublet, *J* = 3.9 Hz	1
	d	2.25, sharp singlet	3
	e	1.71, sharp singlet	3
2	a + a'	7.38, singlet (accidental overlap)	4
	b	6.42, doublet, *J* = 4.0 Hz	2
	b'	6.42, singlet	
	c	6.95, doublet, *J* = 4.0 Hz	1
	d	2.28, sharp singlet	3
	e	1.71, sharp singlet	3
5	a + a'	7.09, singlet (accidental overlap)	3
	b	6.39, doublet, *J* = 4.0 Hz	1
	b'	6.34, singlet	1
	c	6.85, doublet, *J* = 4.0 Hz	1
	d	2.26, sharp singlet	3
	e	1.70, sharp singlet	3
	Y	2.42, sharp singlet	3

(sp^3)–$C(sp^2)$) = 1.510 ± 0.005 Å,[19] and r(Pd(II)) = 1.31 Å). This suggests some multiple-bond character in the Pd–C(aryl) linkages.

Individual Pd(II)–$C(sp^2)$ distances in the present structures are Pd(1)–C(11) = 1.975 (5) Å and Pd(2)–C(11′) = 1.973 (5) Å [average 1.974 ± 0.001 Å] in the benzthiazole complex and 1.972 (8) and 1.963 (8) Å [average 1.968 ± 0.006 Å] in the benzoxazole complex.

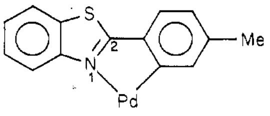
The trans-lengthening influence of σ-bonded carbon is illustrated clearly and unambigously by the lengthening of the palladium–oxygen distances trans to carbon, relative to those trans to nitrogen. Thus, in the benzthiazole derivative, we have Pd(1)–O(1′) = 2.140 (4) Å and Pd(2)–O(1) = 2.138 (4) Å [average 2.139 ± 0.001 Å] vs. Pd(1)–O(2) = 2.047 (4) Å and Pd(2)–O(2′) = 2.051 (4) Å [average 2.049 ± 0.003 Å]. Similarly, in the benzoxazole derivative, we find values of 2.121 (6) and 2.136 (6) Å [average 2.129 ± 0.011 Å] vs. 2.060 (6) and 2.043 (5) Å [average 2.052 ± 0.012 Å].

As a result of Pd(1) and Pd(2) being bridged by two mutually cis μ-acetate ligands, the planar, aromatic chelating N,C bonded benzthiazole or benzoxazole ligands are forced to lie above one another in the dimeric molecules. This leads to interligand repulsions on the "open" side of the molecule and results in the coordination planes of the palladium atoms being tilted at an angle of 24.46° to one another in the benzthiazole derivative and at an angle of 23.96° to one another in the benzoxazole derivative (see Table VIII). These deformations are clearly illustrated by Figure 5. The two acetate bridges are separated by a dihedral angle of 85.68° in the benzthiazole complex and 84.28° in the benzoxazole complex.

Within the benzthiazole ligands of **1** the "benzo" rings are each planar within experimental error. [Root-mean-square deviations are 0.004 Å for plane Ib (atoms C(4)→C(9)) and 0.011 Å for plane IIb (atoms C(4′)→C(9′)).] The bonds at the fused positions, C(8)–C(9) and C(8′)–C(9′), are 1.423 (8) and 1.428 (8) Å (respectively) and appear to be lengthened from the remainder of bonds within this hexaatomic ring (1.363 (9)→1.392 (10) Å for the system C(4)–C(5)–C(6)–C(7)–C(8)–C(9) and 1.363 (11)→1.388 (9) Å for the system C(4′)–C(5′)–C(6′)–C(7′)–C(8′)– C(9′)).

Similar distances are found within the benzoxazole ligands of **2**. However, the smaller crystal used and lesser amount of available data (2θ(max) = 40°, vs. 45° for the benzthiazole derivative) lead to larger esd's on interatomic distances, and the bonds at the fused positions can no longer be demonstrated to be lengthened.

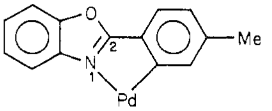
Within the pentaatomic heterocyclic thiazole ring of **1** the sulfur-carbon distances appear to be close to equivalent: S(3)-C(2) = 1.737 (6) Å, S(3)-C(9) = 1.721 (7) Å; S(3′)-C(2′) = 1.713 (6) Å, S(3′)-C(9′) = 1.719 (6) Å. In contrast to this, the nitrogen-carbon distances are decidedly nonequivalent, with N(1)-C(2) = 1.320 (7) Å vs. N(1)-C(8) = 1.397 (7) Å and N(1′)-C(2′) = 1.305 (7) Å vs. N(1′)-C(8′) = 1.398 (7) Å. Resonance forms such as **9** (with a formal double bond for N(1)-C(2)) are clearly favored.



9

It should be noted that the large size of the sulfur atom results in marked reduction of the C-S-C angles (to 90.7 (3)° for C(2)-S(3)-C(9) and 90.0 (3)° for C(2′)-S(3′)-C(9′)) relative to other internal angles within the planar thiazole rings.

In the oxazole rings of complex **2**, the oxygen-carbon distances are almost equivalent with O(3)-C(2) = 1.342 (11) Å, O(3′)-C(2′) = 1.351 (10) Å, O(3)-C(9) = 1.377 (12) Å, and O(3′)-C(9′) = 1.379 (12) Å. As with the thiazole ring (vide supra), the nitrogen-carbon distances are again inequivalent, with N(1)-C(2) = 1.305 (11) Å vs. N(1)-C(8) = 1.377 (12) Å and N(1′)-C(2′) = 1.299 (10) Å vs. N(1′)-C(8′) = 1.390 (11) Å. The resonance form **10** is thus favored.



10

The tolyl rings are regular, with carbon-carbon distances in **1** ranging from 1.369 (8) to 1.429 (8) Å in the C(10)→C(15) ring and from 1.376 (11) to 1.424 (8) Å in the C(10′)-C(15′) system. The C-Me linkages are C(13)-C(16) = 1.534 (8) Å and C(13′)-C(16′) = 1.570 (10) Å. The analogous distances in **2** are 1.384 (13)-1.428 (13) Å in the C(10)→C(15) ring, 1.364 (12)-1.413 (14) Å for the C(10′)-C(15′) system, and 1.543 (13) and 1.551 (14) Å for the C-Me distances.

Distances and angles within the acetate groups in **1** and **2** are all normal.

Finally we note that details of the ^{1}H NMR spectrum of the complex appear in Table IX.

Conclusions

We have shown that $Pd(O_2CMe)_2$ reacts with 2-*p*-tolylbenzthiazole, 2-*p*-tolylbenzoxazole, and their derivatives to provide dimeric cyclometalated products in which palladium is N,C bonded to a deprotonated 2-*p*-tolylbenzthiazole or 2-*p*-tolylbenzoxazole ligand. Dimerization is accomplished via two mutually cis acetate bridges. Interligand repulsions lead to the molecule "opening up" on the side opposite to the *cis*-bis(μ-acetato) systems. Unlike the situation in symmetrical binuclear $M_2(O_2CR)_4$ and $M(O_2CR)_4L_2$ complexes, the PdO_2NC coordination planes in the halves of the molecule are canted at ~24° to one another.

Acknowledgment. This work was supported by the National Science Foundation, through Grant CHE77-04981 (to M.R.C.).

Registry No. **1**, 72509-65-0; **2**, 72509-64-9; **5**, 72509-63-8.

Supplementary Material Available: Listings of data-processing formulas and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

Notes

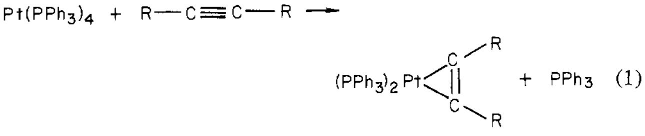
Contribution from the Institute of Industrial Science,
University of Tokyo, Minatoku, Tokyo, Japan,
and the Department of Chemistry, University of Colorado,
Boulder, Colorado 80309

Synthesis and Structure of the Binuclear Platinum(I)-Dimethyl Acetylenedicarboxylate Complex $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$

Yasuyuki Koie, Sumio Shinoda, Yasukazu Saito,*
Brian J. Fitzgerald, and Cortlandt G. Pierpont*

Received April 18, 1979

Among the earliest examples of organometallic transition-metal complexes containing alkyne ligands were those prepared by the addition of an alkyne to $Pt(PPh_3)_4$ (eq 1).[1,2] We have recently found that the addition of dimethyl acetylenedicarboxylate to $Pt(CO)_2(PPh_3)_2$ under an atmosphere of carbon monoxide yields the binuclear complex $Pt_2(CO)_2(PPh_3)_2(MeO_2CC_2CO_2Me)$ (eq 2). Additionally, if the triphenyl-



$$Pt(PPh_3)_4 + R-C\equiv C-R \longrightarrow (PPh_3)_2Pt(RC\equiv CR) + PPh_3 \quad (1)$$

$$Pt(PPh_3)_2(CO)_2 + R_2C_2 \xrightarrow{CO} Pt_2(CO)_2(PPh_3)_2(R_2C_2) \leftarrow Pt(PPh_3)_2(R_2C_2) + CO \quad (2)$$

$$R = CO_2CH_3$$

---

*To whom correspondence should be addressed: Y.S., University of Tokyo; C.G.P., University of Colorado.

(1) S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, **14**, 245 (1976).
(2) E. O. Greaves and P. M. Maitlis, *J. Organomet. Chem.*, **6**, 104 (1966).
(3) M. A. Bennett and T. Yoshida, *J. Am. Chem. Soc.*, **100**, 1750 (1978).