

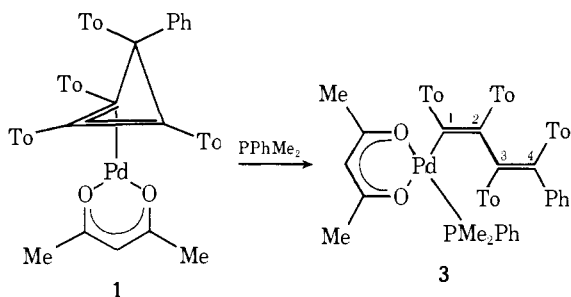
Crystal Structures of [Pd{1- η -C₄(tolyl)₄Ph}(Me₂PhP)(acac)] and of [Pd{1:3,4- η -C₄(tolyl)₄Ph}(S₂CN-*i*-Pr₂)], Obtained by Ring Opening of Cyclobutenylpalladium Complexes

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Abstract: Reaction of the cyclobutenyl complex [Pd(η^3 -C₄To₄Ph)(acac)] with PhMe₂P gave the η^1 -butadienyl complex [Pd{1- η -C₄To₄Ph}(Me₂PhP)(acac)] (**3**) having the geometry expected for a conrotatory opening of the cyclobutenyl ring. The cyclobutenyl complex [Pd(η^3 -C₄To₄Ph)(S₂CN-*i*-Pr₂)] underwent spontaneous ring opening to give a mixture of two complexes [Pd(1:3,4- η -C₄To₄Ph)(S₂CN-*i*-Pr₂)], **4a** and **4b**, which were both present in individual crystals. The difference between the isomers was manifested only as a disorder in the *p*-methyl groups on the phenyls (D and E) attached to the terminal carbon C(4) of the butadienyl ligand. The two isomers represent the products of a conrotatory and a formally disrotatory ring opening. The complex **3** crystallized in the monoclinic space group *P*2₁/*c* (*C*_{2h}⁵, no. 14) with unit cell of dimensions *a* = 11.890 (6), *b* = 16.548 (8), *c* = 22.52 (1) Å, and β = 96.34 (1)°. The structure was determined by single-crystal x-ray diffraction. Block diagonal matrix least-squares refinement gave a final value for *R* of 0.054 for 4891 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The structure consists of a square planar palladium bonded to PMe₂Ph, C(1) of a phenyltetra(*p*-tolyl)butadienyl ligand, and chelated to acac. The complex **4** crystallized in the monoclinic space group *P*2₁/*c* (*C*_{2h}⁵, no. 14) with unit cell of dimensions *a* = 15.95 (2), *b* = 11.28 (2), *c* = 22.83 (3) Å, and β = 108.0 (1)°. The structure was determined by single-crystal x-ray diffraction; block diagonal matrix least-squares refinement gave a final value for *R* of 0.057 for 3409 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The structure consists of a *i*-Pr₂NCS₂Pd unit with the palladium also σ bonded to C(1) and π bonded to C(3)-C(4) of a phenyl(tetra-*p*-tolyl)butadienyl ligand. Population analysis showed that one methyl was disordered to the extent of 60% on the C(4) phenyl cis (*Z*) to the *p*-tolyl on C(3) and 40% on the C(4) phenyl trans (*E*) to the C(3) *p*-tolyl.

In the preceding paper¹ we have described the ring-opening reactions of the η^3 -cyclobutenyl complexes **1** and **2** to give butadienyl complexes. In the case of **1** only a single ring-opened product, **3**, was isolated and in order to ascertain which of the



four possible isomers had been formed an x-ray crystal structure determination was carried out. When complex **2** was allowed to ring open, a mixture of two virtually inseparable ring-opened isomers (**4**) was obtained as shown by NMR spectroscopy and analytical HPLC. This material could be crystallized and in order to determine the nature of the ring-opening reaction an x-ray crystal structure was again undertaken.

Experimental Section

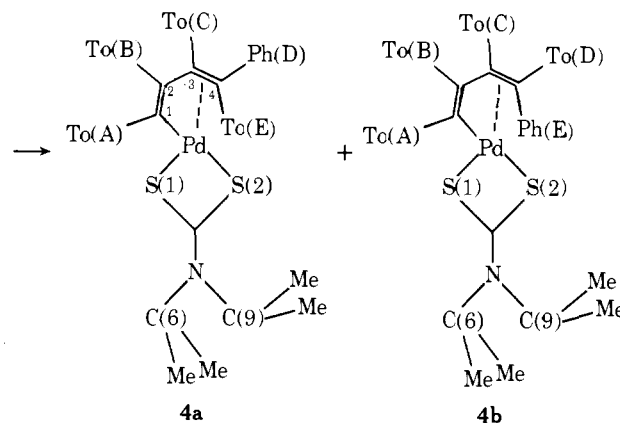
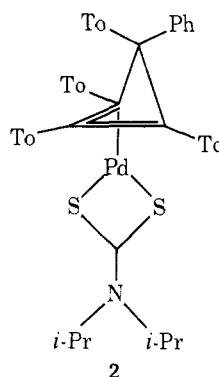
Structure Determination of [Pd{1- η -C₄To₄Ph}(Me₂PhP)(acac)] (**3**).

A crystal of **3** of approximate dimensions 0.40 × 0.38 × 0.10 mm was selected from a batch grown from dichloromethane/methanol at 0 °C.

Crystal data: C₅₁H₅₁O₂PPd, complex **3**, mol wt 833.3; monoclinic, *a* = 11.890 (6), *b* = 16.548 (8), *c* = 22.52 (1) Å, β = 96.34 (1)°, *Z* = 4; space group *P*2₁/*c* (*C*_{2h}⁵, no. 14) from systematic absences; ρ (calcd) = 1.256, ρ (obsd) = 1.25 g cm⁻³; Mo K α radiation, λ = 0.710 69 Å. The cell constants were determined from least-squares fit to the setting angles of 48 reflections centered manually.

Three-dimensional x-ray data with 6.5° < 2 θ < 50° were collected from a crystal mounted along a C face diagonal, using a Stoe STADI-2 automatic diffractometer in the stationary counter-moving crystal mode, with graphite monochromated Mo K α radiation.

Angular step scan ranges were varied for each reflection to allow



for peak width variation; a counting time of 1 s was used for each 0.01° of the scan. Background counts were measured for 25 s at each end of the scan range. Reflections with intensity $I < 3\sigma(I)$ were not used, nor those with background differences $\Delta > 4\sigma(B)$. Lorentz and polarization corrections were applied; no allowance was made for extinction or absorption since $\mu = 4.9$ cm⁻¹; a total of 4891 independent reflections were obtained.

The atomic coordinates were found by conventional Patterson and Fourier methods, and refined using block diagonal least squares. The two phenyl and four *p*-tolyl moieties were treated as groups of fixed

Table I. Atomic Position and Thermal Parameters for Complex 3 [Pd(η^1 -C₄To₄Ph)(PMe₂Ph)(acac)]^a

Atom	X	Y	Z	B ₁₁	B ₂₂	B ₃₃	B ₂₃	B ₁₃	B ₁₂
Pd	13 108 (5)	9129 (3)	36 574 (2)	546 (4)	245 (2)	136 (1)	37 (3)	-64(3)	8(6)
P	2036 (2)	-318 (1)	3544 (1)	61 (2)	22 (1)	13 (0)	-3 (1)	0 (1)	-2 (2)
O(1)	146 (5)	698 (3)	2893 (2)	73 (5)	40 (3)	19 (1)	5 (3)	-26 (4)	-8 (6)
O(2)	509 (5)	2015 (3)	3764 (2)	66 (5)	29 (2)	21 (1)	3 (3)	-6 (4)	25 (5)
C(F1)	-383 (7)	1266 (6)	2596 (4)	64 (7)	52 (4)	17 (2)	16 (5)	-13 (6)	-15 (9)
C(F2)	-519 (7)	2042 (5)	2790 (4)	67 (7)	45 (4)	21 (2)	18 (5)	6 (6)	0 (9)
C(F3)	-149 (7)	2361 (5)	3361 (4)	61 (7)	39 (4)	22 (2)	18 (5)	11 (6)	21 (8)
ME(F1)	-920 (10)	1019 (8)	1966 (4)	152 (12)	73 (7)	21 (2)	3 (7)	-57 (9)	-15 (15)
ME(F2)	-560 (10)	3203 (6)	3533 (5)	140 (12)	41 (5)	32 (3)	10 (6)	-4 (9)	80 (12)
ME(P1)	2473 (6)	1192 (4)	4348 (3)	50 (5)	20 (3)	10 (1)	2 (3)	3 (4)	12 (6)
ME(P2)	3146 (6)	1840 (4)	4306 (3)	46 (5)	23 (3)	12 (1)	2 (3)	6 (4)	1 (6)
C(P1)	3170 (6)	2297 (4)	3728 (3)	47 (5)	26 (3)	14 (2)	4 (3)	9 (5)	0 (7)
C(P2)	3158 (7)	3103 (4)	3690 (3)	69 (6)	21 (3)	15 (2)	4 (3)	18 (5)	0 (7)
C(P3)	2003 (8)	-566 (5)	2749 (3)	120 (10)	43 (4)	11 (2)	-14 (4)	11 (6)	-21 (10)
C(P4)	3493 (7)	-577 (5)	3820 (4)	57 (6)	34 (3)	22 (2)	-9 (4)	0 (6)	18 (7)
C(P5)	1163 (5)	-1098 (3)	3834 (3)	67 (7)	20 (3)	20 (2)	-4 (3)	15 (5)	0 (7)
C(P6)	1485 (4)	-1458 (4)	4388 (3)	113 (9)	37 (4)	21 (2)	15 (5)	22 (7)	9 (10)
C(1)	789 (6)	-2037 (4)	4612 (2)	137 (12)	43 (5)	34 (3)	25 (6)	42 (10)	11 (12)
C(2)	-229 (5)	-2256 (3)	4282 (3)	148 (13)	33 (4)	49 (4)	3 (7)	74 (12)	-13 (12)
C(3)	-551 (4)	-1897 (4)	3728 (3)	115 (11)	45 (5)	46 (4)	-12 (7)	37 (10)	-45 (12)
C(4)	145 (6)	-1318 (4)	3504 (2)	86 (8)	40 (4)	30 (3)	-10 (5)	7 (7)	-37 (10)
C(A1)	2490 (4)	664 (2)	4905 (2)	55 (6)	21 (3)	11 (1)	-5 (3)	5 (5)	-9 (6)
C(A2)	3504 (3)	300 (3)	5136 (2)	49 (5)	26 (3)	10 (1)	2 (3)	-1 (4)	5 (6)
C(A3)	3508 (3)	-278 (3)	5588 (2)	61 (6)	30 (3)	12 (2)	4 (4)	9 (5)	-4 (7)
C(A4)	2497 (4)	-492 (2)	5808 (2)	77 (7)	29 (3)	13 (2)	2 (4)	5 (5)	-26 (8)
C(A5)	1482 (3)	-129 (3)	5577 (2)	64 (7)	37 (4)	15 (2)	2 (4)	13 (5)	-18 (8)
C(A6)	1479 (3)	449 (3)	5125 (2)	50 (6)	32 (3)	12 (2)	1 (4)	2 (5)	-4 (7)
MEA	2501 (7)	-1096 (3)	6281 (2)	111 (9)	55 (5)	18 (2)	30 (5)	8 (7)	-33 (11)
C(B1)	3930 (4)	2157 (3)	4838 (2)	61 (6)	21 (3)	13 (2)	2 (3)	-1 (5)	-4 (7)
C(B2)	5045 (4)	2360 (3)	4744 (2)	65 (7)	26 (3)	20 (2)	2 (4)	-1 (6)	-11 (7)
C(B3)	5803 (3)	2631 (3)	5220 (2)	73 (7)	31 (4)	27 (2)	-1 (5)	-14 (7)	-16 (8)
C(B4)	5453 (4)	2698 (3)	5790 (2)	105 (9)	29 (3)	22 (2)	-8 (4)	-34 (7)	-7 (9)
C(B5)	4347 (4)	2494 (3)	5884 (2)	98 (8)	31 (4)	19 (2)	-8 (4)	-1 (7)	-15 (9)
C(B6)	3590 (3)	2224 (3)	5408 (2)	84 (7)	30 (3)	12 (2)	-3 (4)	7 (5)	-6 (8)
MEB	6245 (5)	2981 (5)	6289 (3)	146 (13)	50 (5)	32 (3)	-18 (6)	-53 (10)	-30 (13)
C(C1)	3317 (4)	1795 (3)	3174 (2)	61 (6)	22 (3)	13 (2)	7 (3)	14 (5)	-3 (7)
C(C2)	2548 (4)	1858 (3)	2660 (2)	76 (7)	27 (3)	14 (2)	5 (4)	2 (5)	-9 (7)
C(C3)	2749 (4)	1445 (3)	2141 (2)	102 (9)	33 (4)	16 (2)	2 (4)	8 (6)	-14 (9)
C(C4)	3719 (4)	971 (3)	2136 (2)	128 (10)	34 (4)	16 (2)	-3 (5)	28 (7)	-9 (11)
C(C5)	4488 (4)	909 (3)	2649 (2)	99 (8)	33 (3)	22 (2)	-1 (5)	32 (6)	6 (10)
C(C6)	4287 (4)	1321 (3)	3168 (2)	77 (7)	29 (3)	16 (2)	4 (4)	13 (6)	13 (8)
MEC	3929 (7)	540 (4)	1593 (2)	215 (17)	53 (5)	24 (3)	-28 (6)	60 (11)	7 (15)
C(D1)	3389 (5)	3514 (4)	3117 (2)	92 (7)	22 (3)	14 (2)	2 (4)	13 (6)	-10 (8)
C(D2)	2540 (4)	3965 (4)	2791 (3)	102 (9)	37 (4)	22 (2)	21 (5)	2 (7)	1 (10)
C(D3)	2718 (5)	4278 (4)	2233 (3)	134 (11)	47 (5)	23 (2)	30 (5)	-16 (8)	-32 (11)
C(D4)	3743 (5)	4141 (4)	2002 (2)	160 (12)	53 (5)	19 (2)	10 (6)	10 (8)	-64 (14)
C(D5)	4591 (4)	3690 (4)	2328 (3)	138 (12)	47 (5)	24 (3)	9 (5)	48 (9)	-37 (12)
C(D6)	4414 (5)	3376 (4)	2886 (3)	94 (8)	33 (4)	22 (2)	3 (4)	29 (7)	-23 (9)
C(E1)	2914 (5)	3686 (3)	4184 (2)	96 (8)	21 (3)	15 (2)	7 (4)	15 (6)	10 (8)
C(E2)	1987 (5)	3551 (3)	4503 (3)	95 (8)	34 (4)	21 (2)	3 (5)	20 (7)	17 (9)
C(E3)	1679 (5)	4139 (4)	4899 (3)	124 (10)	43 (4)	26 (2)	-7 (6)	28 (8)	41 (12)
C(E4)	2298 (5)	4856 (3)	4976 (2)	191 (15)	40 (5)	23 (2)	-14 (5)	3 (9)	58 (13)
C(E5)	3226 (5)	4884 (3)	4658 (3)	180 (14)	35 (4)	32 (3)	-14 (6)	28 (11)	-1 (13)
C(E6)	3534 (5)	4396 (4)	4262 (3)	135 (11)	29 (4)	30 (3)	-5 (5)	27 (9)	-18 (10)
MEE	1976 (9)	5471 (4)	5391 (3)	275 (22)	55 (6)	30 (3)	-34 (7)	34 (13)	80 (19)

^a Fractional coordinates and anisotropic thermal parameters $\times 10^4$ (except $\times 10^5$ for Pd). Estimated standard deviations in the least significant figure(s) are given in parentheses in this and subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + kIB_{23} + hIB_{13} + khB_{12})]$.

overall geometry, allowing refinement of rotation and translation; anisotropic temperature factors were used for the nonhydrogen atoms. Hydrogen atoms were not included in the refinement which converged at $R = 0.054$.

Atomic scattering factors were taken from ref 2. Programs used are part of the Sheffield x-ray system, and calculations were performed on the Sheffield University ICL 1907 computer. A listing of the observed and calculated structure amplitudes is available.³

Structure Determination of [Pd{1,3,4- η -C₄To₄Ph}(S₂CN-*i*-Pr₂)] (4). A crystal of 4 of approximate dimensions 0.43 \times 0.21 \times 0.18 mm was selected from a batch grown from dichloromethane/methanol solution: the complex 4 was obtained as described in the preceding paper.¹

Crystal data: C₄₅H₄₇NPdS₂ complex (4); mol wt 772.4; monoclinic, $a = 15.95$ (2), $b = 11.28$ (2), $c = 22.83$ (3) Å, $\beta = 108.0$ (1)°, $Z = 4$; space group $P2_1/c$ (C_{2h}^2 , no. 14) from systematic absences; ρ (calcd) = 1.313, ρ (obsd) = 1.31 g cm⁻³; Mo K α radiation; $\lambda = 0.71069$ Å. The cell constants were determined from least-squares fit to the setting angles of 48 reflections centered manually.

Three-dimensional x-ray data with $6.5^\circ < 2\theta < 50^\circ$ were collected from a crystal mounted along the b axis, using a Stoe STAD1-2 automatic diffractometer in the stationary counter-moving crystal mode, with graphite monochromated Mo K α radiation.

Angular step scan ranges were varied for each reflection to allow for peak width variation, a counting time of 1 s was used for each 0.01° of the scan, and background counts were measured for 45 s at each

Table II. Atomic Positional and Thermal Parameters for Complex 4 $[Pd(1:3,4-\eta-C_4To_4Ph)(S_2CN-i-Pr)]^a$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pd	34 913 (5)	3346 (8)	5914 (3)	382 (3)	1041 (7)	189 (1)	-71 (8)	122(3)	-5 (11)
S(1)	4934 (2)	-48 (2)	1128 (1)	36 (1)	108 (3)	19 (1)	-12 (2)	9 (1)	-1 (3)
S(2)	3984 (2)	1994 (3)	1293 (1)	51 (1)	113 (3)	25 (1)	-20 (2)	7 (2)	15 (4)
N	5625 (5)	1474 (8)	2059 (3)	50 (4)	134 (10)	18 (2)	-24 (7)	6 (5)	-34 (11)
C(5)	4942 (6)	1212 (9)	1569 (4)	46 (5)	103 (11)	19 (2)	-14 (8)	25 (5)	-39 (12)
C(6)	5620 (8)	2501 (11)	2495 (5)	83 (8)	126 (14)	28 (3)	-46 (11)	7 (3)	-28 (17)
C(7)	5651 (10)	3690 (13)	2216 (7)	106 (10)	118 (15)	58 (5)	16 (15)	34 (12)	4 (21)
C(8)	4863 (9)	2355 (13)	2782 (5)	99 (9)	182 (18)	26 (3)	-36 (12)	51 (9)	13 (21)
C(9)	6441 (6)	737 (11)	2205 (5)	42 (5)	156 (15)	28 (3)	-23 (10)	10 (6)	-1 (14)
C(10)	7190 (9)	1428 (16)	2072 (8)	74 (9)	259 (25)	69 (6)	-31 (21)	94 (12)	-62 (24)
C(11)	6720 (9)	246 (15)	2873 (5)	86 (8)	231 (21)	28 (3)	20 (15)	13 (8)	68 (24)
C(1)	3235 (6)	-1202 (8)	115 (4)	43 (5)	84 (10)	16 (2)	-8 (7)	15 (5)	-7 (11)
C(2)	2445 (6)	-1014 (9)	-296 (4)	41 (5)	97 (10)	19 (2)	18 (8)	25 (5)	17 (11)
C(3)	2219 (5)	273 (9)	-232 (4)	30 (4)	101 (10)	19 (2)	-2 (9)	11 (4)	12 (12)
C(4)	2012 (5)	678 (9)	290 (4)	35 (4)	99 (11)	20 (2)	-7 (7)	16 (3)	4 (11)
C(E1)	1716 (4)	-179 (6)	686 (3)	40 (4)	112 (11)	21 (2)	-3 (9)	25 (8)	7 (12)
C(E2)	1043 (4)	-983 (7)	413 (2)	42 (5)	148 (14)	29 (3)	-3 (11)	25 (7)	-34 (14)
C(E3)	747 (4)	-1767 (6)	779 (3)	45 (5)	192 (17)	25 (3)	0 (12)	23 (6)	-34 (16)
C(E4)	1123 (4)	-1747 (6)	1418 (3)	56 (6)	141 (15)	39 (4)	31 (12)	43 (8)	20 (16)
C(E5)	1796 (4)	-942 (7)	1691 (2)	59 (6)	158 (15)	29 (3)	11 (12)	29 (7)	4 (16)
C(E6)	2092 (4)	-158 (6)	1325 (3)	63 (6)	131 (13)	21 (2)	8 (9)	28 (6)	23 (15)
MEE	817 (8)	-2558 (9)	1797 (5)	7.73 (46)					
C(D1)	1813 (5)	1971 (5)	376 (3)	40 (5)	107 (11)	20 (2)	-15 (8)	12 (5)	33 (12)
C(D2)	1115 (4)	2226 (6)	604 (3)	47 (5)	140 (14)	22 (3)	-23 (10)	10 (6)	24 (14)
C(D3)	888 (4)	3402 (7)	671 (3)	78 (8)	133 (15)	36 (4)	-22 (13)	28 (9)	38 (18)
C(D4)	1359 (5)	4323 (5)	511 (3)	91 (9)	114 (15)	40 (4)	-45 (12)	1 (10)	66 (18)
C(D5)	2057 (4)	4068 (6)	283 (3)	73 (7)	111 (13)	31 (3)	-21 (11)	8 (8)	21 (16)
C(D6)	2283 (4)	2892 (7)	216 (3)	55 (6)	113 (13)	27 (3)	-3 (10)	9 (7)	4 (14)
MED	1125 (7)	5539 (5)	580 (5)	7.73 (46)					
C(C1)	2216 (4)	1088 (5)	-767 (2)	35 (4)	87 (10)	19 (2)	1 (8)	14 (5)	9 (11)
C(C2)	1465 (3)	1730 (6)	-1086 (3)	39 (5)	119 (12)	23 (3)	-3 (9)	10 (6)	18 (13)
C(C3)	1469 (3)	2425 (5)	-1591 (3)	55 (6)	122 (13)	27 (3)	11 (10)	23 (7)	-8 (14)
C(C4)	2224 (4)	2478 (5)	-1777 (2)	59 (6)	104 (12)	21 (3)	-7 (9)	15 (6)	-32 (14)
C(C5)	2974 (3)	1836 (6)	-1459 (3)	56 (6)	113 (12)	24 (3)	5 (9)	26 (7)	5 (14)
C(C6)	2970 (3)	1141 (5)	-954 (3)	49 (5)	98 (11)	23 (3)	-10 (9)	30 (6)	-5 (12)
MEC	2228 (7)	3198 (8)	-2300 (3)	77 (8)	187 (18)	32 (3)	68 (13)	30 (8)	4 (19)
C(B1)	1869 (4)	-1818 (5)	-784 (3)	42 (5)	119 (12)	15 (2)	-4 (6)	18 (5)	-17 (12)
C(B2)	1051 (4)	-1420 (5)	-1160 (3)	31 (4)	130 (13)	26 (3)	7 (10)	4 (6)	-22 (12)
C(B3)	497 (3)	-2186 (6)	-1588 (3)	58 (6)	126 (14)	26 (3)	-7 (11)	7 (7)	-11 (15)
C(B4)	761 (4)	-3350 (5)	-1640 (3)	62 (6)	130 (14)	22 (3)	-17 (10)	8 (7)	-29 (15)
C(B5)	1579 (4)	-3749 (5)	-1264 (3)	65 (7)	119 (13)	27 (3)	-29 (10)	-12 (7)	-9 (16)
C(B6)	2133 (3)	-2983 (6)	-836 (3)	63 (6)	103 (12)	30 (3)	-1 (10)	13 (7)	26 (15)
MEB	188 (6)	-4143 (8)	-2083 (4)	81 (8)	147 (16)	37 (4)	-22 (13)	-23 (9)	-40 (18)
C(A1)	3873 (4)	-2208 (5)	247 (3)	36 (4)	93 (10)	17 (2)	-10 (8)	10 (5)	16 (11)
C(A2)	3796 (4)	-3165 (6)	614 (3)	76 (7)	118 (13)	19 (2)	12 (10)	13 (7)	19 (15)
C(A3)	4463 (4)	-4016 (5)	786 (3)	83 (8)	134 (14)	23 (3)	-2 (10)	4 (8)	75 (18)
C(A4)	5207 (4)	-3909 (5)	591 (3)	61 (7)	150 (16)	26 (3)	-49 (11)	-7 (7)	69 (17)
C(A5)	5234 (4)	-2952 (6)	224 (3)	53 (6)	123 (14)	34 (4)	-14 (11)	13 (7)	36 (15)
C(A6)	4617 (4)	-2102 (5)	51 (3)	52 (6)	123 (13)	27 (3)	-15 (10)	19 (7)	-3 (14)
MEA	5897 (5)	-4789 (8)	769 (5)	89 (9)	184 (19)	41 (4)	-32 (15)	-14 (9)	133 (22)

^a Fractional coordinates and anisotropic thermal parameters $\times 10^4$ (except $\times 10^5$ for Pd). Estimated standard deviations in the least significant figure(s) are given in parentheses in this and subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + kB_{23} + hkB_{13} + khB_{12})]$.

end of the scan range. Reflections with intensity $I < 3\sigma(I)$ were not used, nor those with background differences $\Delta > 3\sigma(B)$. Lorentz and polarization corrections were applied; no allowance was made for extinction or absorption since $\mu = 6.0 \text{ cm}^{-1}$; a total of 3409 independent reflections were obtained.

The atomic positions were found by conventional Patterson and Fourier methods, and refined using block diagonal least squares. At a fairly advanced stage of the refinement the methyl carbon [Me(E)] of the *p*-tolyl group attached to C(4) showed a high thermal vibration parameter and a difference Fourier synthesis showed a significant amount of electron density in the para position of the other phenyl group (D) attached to C(4). These two observations suggested that the *p*-methyl substituent was disordered between the two sites. Refinement was therefore continued with the substituents on the carbon chain treated as groups of fixed geometry. Initially the populations of the methyl carbon atoms of the two possible *p*-tolyl groups attached to C(8) were allowed to refine, keeping a net population of one for the

two sites. The thermal parameters of these two atoms (kept as isotropic) converged and the thermal parameters of the other nonhydrogen atoms were allowed to go anisotropic; however, in the case of the disordered group some of the apparently anisotropic motion probably reflects the slight change in position of these ring carbon atoms associated with the presence of either a phenyl or a tolyl group. The isotropic thermal parameters of the two methyl groups were correlated together and allowed to refine in a matrix which included their population parameter. Refinement converged at $R = 0.057$ at which stage the population at the two sites refined to a ratio of 0.60/0.40, the site with the higher population being *cis* to the *p*-tolyl substituent on C(9). The positions of the hydrogen atoms have been calculated (assuming C-H distances of 1.0 Å) and found to be in positions of positive electron density on a difference Fourier synthesis. Their positions are not included in the structure factor calculation but the hydrogen atom in the ortho position of the "phenyl/tolyl" ring (E) attached to C(4) is calculated to be at a distance of 2.9 Å from the

Table III. Bond Lengths (Å) and Angles (deg) in Complex [Pd(η^1 -C₄T₀₄Ph)(PMe₂Ph)(acac)] (3)

A. Geometry about Pd			
Pd-C(1)	2.016 (7)	C(1)-Pd-O(2)	89.7 (2)
Pd-O(1)	2.117 (5)	C(1)-Pd-P	93.2 (2)
Pd-O(2)	2.084 (5)	O(1)-Pd-O(2)	88.5 (2)
Pd-P	2.239 (2)	O(1)-Pd-P	88.9 (2)
The least-squares plane through Pd-C(1)-O(2)-P is given by $0.6832X + 0.4064Y - 0.6067Z = -3.9063^{14}$			
Distances (Å) from this plane:			
Pd	-0.003	O(1)	0.074
P	-0.069	O(2)	-0.076
		C(1)	0.074
B. Butadienyl Ligand			
C(1)-C(2)	1.347 (9)	Pd-C(1)-C(2)	119.4 (5)
C(2)-C(3)	1.509 (10)	C(1)-C(2)-C(3)	121.8 (6)
C(3)-C(4)	1.336 (10)	C(2)-C(3)-C(4)	123.7 (6)
		C(3)-C(4)-C(D1)	120.3 (6)
		C(3)-C(4)-C(E1)	125.5 (6)
		C(D1)-C(4)-C(E1)	114.2 (6)
C(1)-C(A1)	1.528 (8)	Pd-C(1)-C(A1)	116.6 (4)
C(2)-C(B1)	1.532 (8)	C(A1)-C(1)-C(2)	123.9 (6)
C(3)-C(C1)	1.526 (8)	C(1)-C(2)-C(B1)	122.5 (6)
C(4)-C(D1)	1.510 (9)	C(B1)-C(2)-C(3)	115.7 (5)
C(4)-C(E1)	1.519 (9)	C(2)-C(3)-C(C1)	116.7 (5)
		C(C1)-C(3)-C(4)	119.4 (6)
The plane through C(1)-C(2)-C(3) is given by $0.7627X - 0.5977Y - 0.2471Z = -2.1166^{14}$			
The plane through C(2)-C(3)-C(4) is given by $0.9901X + 0.0123Y + 0.1397Z = 4.0267^{14}$			
The angle between these planes = 135.5°			
The plane through C(2)-C(3)-C(C1) is given by $-0.9785X - 0.0921Y - 0.1847Z = -4.6725^{14}$			
The plane through C(4)-C(D1)-C(E1) is given by $-0.9454X - 0.0330Y - 0.3244Z = -5.5312^{14}$			
The angle between the normals to these planes = 8.9°			
C. acac Ligand			
O(1)-C(F1)	1.278 (10)	Pd-O(1)-C(F1)	122.8 (5)
C(F1)-C(F2)	1.372 (12)	O(1)-C(F1)-C(F2)	126.2 (8)
C(F1)-Me(F1)	1.545 (17)	O(1)-C(F1)-Me(F1)	114.6 (8)
C(F2)-C(F3)	1.416 (12)	Me(F1)-C(F1)-C(F2)	119.2 (8)
C(F3)-O(2)	1.267 (10)	C(F1)-C(F2)-C(F3)	127.1 (8)
C(F3)-Me(F2)	1.540 (14)	C(F2)-C(F3)-O(2)	126.0 (8)
		C(F2)-C(F3)-Me(F2)	119.3 (8)
		Me(F2)-C(F3)-O(2)	114.7 (7)
		Pd-O(2)-C(F3)	124.6 (5)
The best least-squares plane through O(1)-O(2)-C(F1)-C(F2)-C(F3) is given by $0.8783X + 0.2830Y - 0.3853Z = -2.6281^{14}$			
Distances (Å) from this plane:			
O(1)	-0.0225	C(F1)	0.0157
O(2)	0.0344	C(F2)	0.0236
		C(F3)	-0.0513
The angle between the normal to this plane and that to the plane Pd-C(1)-O(1)-O(2)-P = 18.4°			
D. Me ₂ PhP Ligand			
P-C(P1)	1.822 (6)	Pd-P-Me(P1)	110.4 (3)
P-Me(P1)	1.833 (9)	Pd-P-Me(P2)	122.5 (8)
P-Me(P2)	1.825 (8)	Pd-P-C(P1)	111.2 (2)
		Me(P1)-P-Me(P2)	101.4 (4)
		Me(P1)-P-C(P1)	103.9 (3)
		Me(P2)-P-C(P1)	105.6 (3)

metal, slightly less than the sum of the van der Waals radii.

Atomic scattering factors were taken from ref 2. Programs used are part of the Sheffield x-ray system, and calculations were performed on the Sheffield University ICL 1907 computer. A listing of the observed and calculated structure amplitudes is available.³

Atomic, positional, and thermal parameters with estimated standard deviations are given in Tables I (for 3) and II (for 4). Interatomic distances and angles are given in Tables III and IV.

Table IV. Bond Lengths (Å) and Angles (deg) in Complex 4 [Pd(1:3,4- η -C₄T₀₄Ph)(S₂CN-*i*-Pr₂)]

A. Geometry about Pd			
Pd-C(1)	2.020 (9)	C(1)-Pd-S(1)	97.4 (3)
Pd-S(1)	2.288 (3)	S(1)-Pd-S(2)	74.1 (1)
Pd-S(2)	2.431 (3)	S(2)-Pd-C(1)	170.4 (3)
Pd-X	2.180 (9)	S(2)-Pd-X	110.7 (3)
		C(1)-Pd-X	77.6 (3)
The plane through Pd-S(1)-S(2) is given by $0.5307X + 0.4839Y - 0.6958Z = 2.0029^{14}$			
Distances (Å) from this plane:			
		C(1)	-0.158
		C(2)	+0.051
		C(3)	+0.442
		C(4)	-0.498
The best least-squares plane through Pd-S(1)-S(2)-C(1) is given by $0.5143X + 0.4620Y - 0.7225Z = 1.8379^{14}$			
Distances from this plane:			
Pd	0.058	C(1)	-0.034
S(1)	0.005	C(3)	-0.396
S(2)	-0.029	C(4)	+0.572
B. Butadienyl Ligand			
C(1)-C(2)	1.335 (13)	Pd-C(1)-C(2)	103.4 (7)
C(2)-C(3)	1.515 (13)	C(1)-C(2)-C(3)	106.6 (8)
C(3)-C(4)	1.408 (13)	C(2)-C(3)-C(4)	121.2 (8)
C(1)-C(A1)	1.491 (11)	C(3)-C(4)-C(D1)	122.3 (8)
C(2)-C(B1)	1.509 (11)	C(3)-C(4)-C(E1)	120.2 (8)
		C(D1)-C(4)-C(E1)	115.1 (7)
C(3)-C(C1)	1.529 (11)	Pd-C(1)-C(A1)	122.2 (5)
C(4)-C(D1)	1.519 (11)	C(A1)-C(1)-C(2)	134.3 (8)
C(4)-C(E1)	1.495 (11)	C(1)-C(2)-C(B1)	130.6 (8)
		C(B1)-C(2)-C(3)	122.6 (8)
		C(2)-C(3)-C(C1)	116.2 (7)
		C(C1)-C(3)-C(4)	122.6 (8)
		C(3)-C(4)-C(D1)	122.3 (8)
The plane through C(1)-C(2)-C(3) is given by $0.6843X + 0.2568Y - 0.6824Z = 2.9564^{14}$			
and that through C(2)-C(3)-C(4) by $0.8681X + 0.1995Y + 0.4545Z = 3.047^{14}$			
Angle between the normals to these planes = 70.4°			
The plane through C(4)-C(D1)-C(E1) is given by $0.6971X + 0.0900Y + 0.7113Z = 2.6115^{14}$			
and that through C(3)-C(2)-C(C1) by $0.8746X + 0.2026Y + 0.4405Z = 3.0788^{14}$			
Angle between the normals to these planes = 19.7°			
C. Dithiocarbamate Ligand			
S(1)-C(5)	1.739 (10)	Pd-S(1)-C(5)	89.0 (3)
S(2)-C(5)	1.708 (10)	Pd-S(2)-C(5)	85.2 (4)
C(5)-N	1.331 (13)	S(1)-C(5)-S(2)	111.2 (6)
N-C(6)	1.530 (15)	S(1)-C(5)-N	121.8 (8)
N-C(9)	1.494 (14)	S(2)-C(5)-N	127.0 (8)
C(6)-C(7)	1.49 (2)	C(5)-N-C(6)	123.3 (4)
C(6)-C(8)	1.55 (2)	C(5)-N-C(9)	119.6 (9)
C(9)-C(10)	1.53 (2)	C(6)-N-C(9)	117.1 (8)
C(9)-C(11)	1.55 (2)	N-C(6)-C(7)	113 (1)
		N-C(6)-C(8)	111 (1)
		C(7)-C(6)-C(8)	114 (1)
		N-C(9)-C(10)	111 (1)
		N-C(9)-C(11)	113 (1)
		C(10)-C(9)-C(11)	112 (1)
The least-squares plane through S(1)-S(2)-S(5)-N is given by $0.6165X + 0.5274Y - 0.5846Z = 2.902^{14}$			
[out of plane distances to C(6), -0.14 Å and C(9), 0.11 Å]			
and that through N-C(6)-C(9) by $0.5687X + 0.6079Y - 0.5541Z = 2.8102^{14}$			
The angle between the normals to these planes is 5.6°			

Results and Discussion

Molecular Structure of Complex 3. The unit cell of complex 3 contains pairs of centrosymmetrically related enantiomers, and a view of one of them is given in Figure 1.

Table V. Comparison of the Molecular Geometries of the Butadienyl Ligands in Complexes 3–6

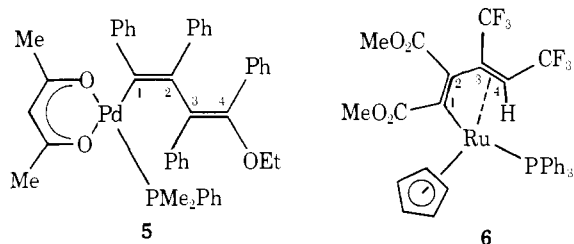
	3	5 ^a	4	6
A. Bond Lengths, Å				
M–C(1)	2.016 (7)	2.007 (5)	2.020 (9)	2.082 (5)
–C(2)	2.923 (7)	2.930 (6)	2.667 (9)	2.659 (4)
–C(3)	3.175 (7)	3.165 (6)	2.302 (9)	2.185 (5)
–C(4)	4.234 (7)	4.137	2.278 (9)	2.171 (6)
C(1)–C(2)	1.347 (9)	1.357 (9)	1.335 (13)	1.348 (7)
C(2)–C(3)	1.510 (10)	1.513 (9)	1.515 (13)	1.509 (8)
C(3)–C(4)	1.336 (10)	1.349 (9)	1.408 (13)	1.428 (7)
B. Bond Angles, deg				
MC(1)C(2)	119.4 (5)	119.8 (5)	103.4 (7)	99.4 (4)
C(1)C(2)C(3)	121.8 (6)	120.2 (6)	106.6 (8)	105.5 (4)
C(2)C(3)C(4)	123.7 (6)	122.7 (6)	121.2 (8)	117.2 (4)
MC(1)C(A1)	116.6 (4)	117.2 (4)	122.2 (6)	135.7 (3)
C(A1)C(1)C(2)	123.9 (5)	122.7 (6)	134.3 (8)	124.6 (4)
C(1)C(2)C(B1)	122.5 (6)	123.8 (6)	130.6 (8)	128.0 (5)
C(B1)C(2)C(3)	115.7 (5)	116.0 (6)	122.6 (8)	126.2 (5)
C(2)C(3)C(C1)	116.7 (5)	117.2 (6)	116.2 (7)	115.7 (4)
C(C1)C(3)C(4)	119.4 (6)	119.7 (6)	122.6 (8)	124.4 (5)
C(3)C(4)C(D1)	120.3 (6)	117.2 (6) ^b	122.3 (8)	124.2 (5)
C(3)C(4)C(E1)	125.5 (6)	127.4 (6)	120.2 (8)	
C(D1)C(4)– C(E1)	114.2 (6)	115.2 (6) ^c	115.1 (7)	
Dihedral angle θ^d	135.5	129.0	70.4	61.6

^a Average values based on two independent molecules. ^b $\angle C(3)C(4)O$. ^c $\angle OC(4)C(E1)$. ^d Angle between the planes defined by C(1)C(2)C(3) and C(2)C(3)C(4).

The coordination about the metal is close to the expected square planar, but the angle PPdC(1) is opened to 93.1°, presumably to allow for nonbonded interactions between substituents on the phosphine and the *p*-tolyl group (A) at C(1). The Pd–P bond [2.239 (2) Å] is somewhat shorter than usual (2.30–2.35 Å,⁴) but the Pd–O (acac) bonds (2.084, 2.117 Å) are well within normal values (2.00–2.12 Å) and the Pd–C bond length (2.016 Å) is also close to that found for other Pd–C(sp²) σ bonds (1.99–2.06 Å).^{4–8}

The σ -butadienyl ligand occupies the fourth coordination site and is only bonded to the metal via C(1). The ligand is not planar and hence not conjugated, and there is a dihedral angle of 135.5° between the planes defined by C(1)–C(2)–C(3) and C(2)–C(3)–C(4). The x-ray structure shows *E* (trans) arrangement of the *p*-tolyl substituents on C(3) and C(4) and this confirms that the ring opening of **1** has occurred in the expected conrotatory manner.

The structure may most usefully be compared to that of the very closely related molecule **5** and a comparison of the mo-



lecular parameters shows them to be almost indistinguishable.⁷ Table V lists bond lengths and angles associated with the butadienyl ligands in the two molecules.

Molecular Structure of Complexes 4a and 4b. The unit cell contains pairs of centrosymmetrically related enantiomers, the

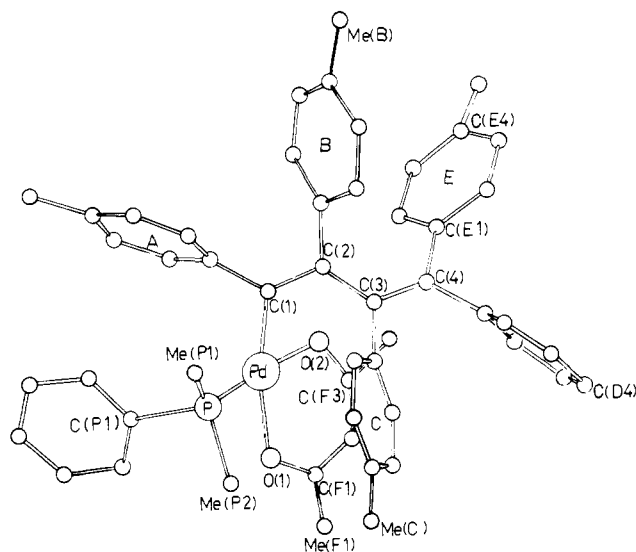


Figure 1. The structure of complex **3**, $[Pd(1-\eta-C_4(tolyl)_4Ph)(Me_2PhP)(acac)]$, shown as a projection onto the best plane defined by the atoms C(1)–C(4) of the σ -butadienyl ligand.

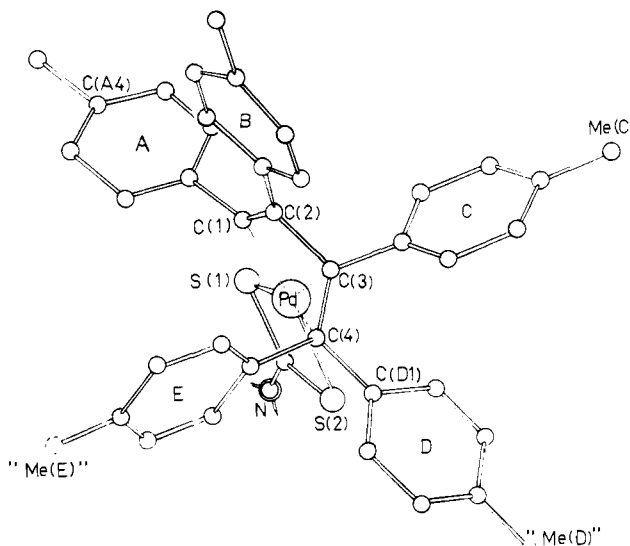


Figure 2. The structure of complex **4**, $[Pd(1:3,4-\eta-C_4To_4Ph)(S_2C-N-i-Pr_2)]$, shown as a projection on the plane through the atoms C(2)–C(3)–C(4) of the 1:3,4- η -butadienyl ligand. The disordered methyls Me(D) and Me(E) are shown as dotted circles.

isomers **4a** and **4b** only being distinguished by a disorder involving the methyl groups Me(D) and Me(E) (Figure 2). A population refinement indicates a ratio of 0.40:0.60 (esd 0.02) of **4a**:**4b**. This value is in good agreement with that derived from NMR and HPLC studies in solution and it presumably reflects the equilibrium isomer ratios.

The molecular structure, shown in Figure 2, indicates that the metal is coordinated to a bidentate dithiocarbamate, σ bonded to one end of a butadienyl chain at C(1) and π bonded at the other end to C(3)–C(4). The best least-squares plane through Pd–C(1)–S(1)–S(2) intersects the C(3)–C(4) bond asymmetrically 0.58 Å from C(4) and the four coordination sites defined by this point, X, C(1), S(1), and S(2), form a distorted square planar arrangement about the metal with the angles X–Pd–C(1) = 77.6°, X–Pd–S(2) = 110.7°, C(1)–Pd–S(1) = 97.4°, and S(1)–Pd–S(2) = 74.1°.

The bond lengths and bond angles observed are quite typical for a bidentate dithiocarbamate bonded to palladium⁹ and for related compounds.^{10,11} However, Pd–S(1) [2.288 (3) Å], which is trans to X, is somewhat shorter than normal (2.32–

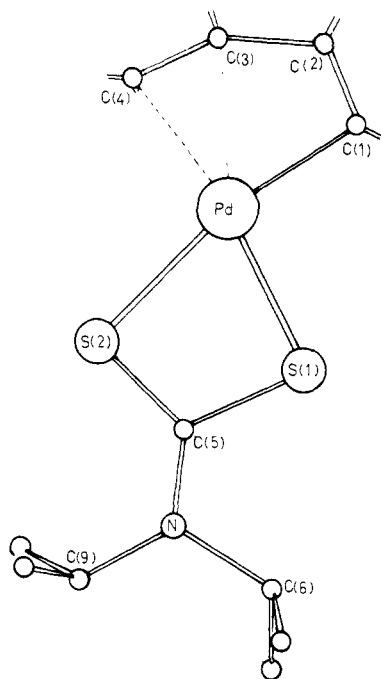
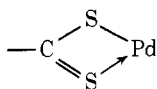


Figure 3. The arrangement of the isopropyl groups in the *i*-Pr₂NCS₂ ligand of complex **4** shown as a projection onto the best plane through the atoms C(5)–N–S(1)–S(2).

2.35 Å)^{9,10} and is significantly shorter than Pd–S(2) [2.431 (3) Å]. This asymmetry and the lengthening of Pd–S(2) may be ascribed to the high trans influence of the Pd–C σ bond, and is also reflected, though at a lower level of significance (3σ), in the shortening of C(5)–S(2) [1.708 (10) Å] by comparison with C(5)–S(1) [1.739 (10) Å] and suggests some localization toward



However, the C–N bond is short [1.331 (13) Å] as is usual in such compounds¹¹ and indicates some double bond character to be present. This is also shown by the fact that C(9) and C(6) are very nearly in the plane defined by S(1)–S(2)–C(5)–N; indeed the angle between this plane and the plane N–C(6)–C(9) is only 5.6°. Solution NMR studies show no evidence for rotation about the C–N bond even at 60 °C¹ and confirm that the planarity of the *i*-Pr₂NCS₂ ligand is retained in solution. The isopropyl methyl groups are arranged as shown in Figure 3. Although rotation about the N–*i*-Pr bonds occurs readily at ambient temperature in solution,¹ no disorder of the methyl groups in the crystal could be observed in the final difference Fourier synthesis.

A detailed account of the structure of one other 1:3,4- η -butadienyl complex, **6**, has been given¹² and Table V compares the molecular parameters for the butadienyl ligand in complex **4** with those for **6** and for the η^1 -butadienyl complex **3**. The similarity between the ligands in **4** and **6** is striking despite the fact that they have totally different substituents and are part of quite different molecules. The major differences between the ligands arise from the slightly larger size of Ru compared to Pd [Pd–C(1) 2.020 (9) vs. Ru–C(1) 2.082 (5) Å] and from the tighter binding of the C(3)–C(4) bond to Ru which leads to very significantly 0.11 Å (12σ) shorter M–C(3) and M–C(4) bonds for the ruthenium complex **6**. This latter effect also manifests itself in changes in the bond angles at C(1) and in the angle C(2)–C(3)–C(4) in the two complexes. Since the other angles are all very similar the butadienyl ligand may be thought of as hinged at C(1) and C(3).

The tighter binding to C(3)–C(4) in the ruthenium complex **6** is probably a consequence of the presence of the strongly

electron-withdrawing CF₃ groups at C(3) and C(4); consistent with this is the fact that the C(3)–C(4) bond is somewhat longer (0.020 Å, 2σ) in **6** than in **4**.

Although the difference [0.024 (9) Å for **4** and 0.014 (6) Å for **6**] between the M–C(3) and the M–C(4) distances is small in the two complexes, the fact that in each case it is in the same direction by a similar margin indicates that the effect is real and that the metal is closer to the terminal carbon. This point is of particular significance since it has been suggested that the isomers **4a** and **4b** arise by a stereomutation of the C(3)–C(4) bond and that this takes place via a metallocyclopentenyl intermediate, the formation of which from **4a** would only require a small shift (ca. 0.2 Å) of C(4) toward the Pd to form a σ bond.

Such processes are presumably also possible in other 1:3,4- η -butadienyl complexes but present indications are that this path for isomerization requires a moderately high activation energy and that such reactions are therefore likely to be slow. If this proposal is correct it also suggests that, since the M–C(4) distance will be shorter in a more strongly π -bonded butadienyl (for example, in **6**), stereomutation should occur more easily there.

The butadienyl ligand is not planar and not conjugated in any of the four complexes; a convenient measure of this nonplanarity is the angle (θ) between the planes C(1)–C(2)–C(3) and C(2)–C(3)–C(4). As reference points we have taken $\theta = 0^\circ$ for the planar *s*-cis and 180° for the planar *s*-trans conformer. On this basis the angles in the complexes **3** and **5** which contain the monohapto butadienyl ligands are 135.5 and 129° (average of 125.6 and 132.4° for the two independent molecules), respectively, while the angles in the complexes which contain the trihapto butadienyl ligand are 70.4° (for **4**) and 61.6° (for **6**). This shows that, as may be anticipated, on coordination of C(3)–C(4) the conformation changes from one that is skew *s*-trans to one that is skew *s*-cis.

As is to be expected, the coordination of C(3)–C(4) in **4** results in a significantly longer (0.067 Å, 5σ) bond than in **3**. The coordination is also shown by the bending back of the substituents on C(3)–C(4) which may be conveniently defined in terms of the angle (α)¹³ between the normal to the planes defined by C(2)–C(3)–C(C1) and C(4)–C(D1)–C(E1) and which is 8.9° for the uncoordinated bond in **3** and 19.7° for C(3)–C(4) in **4**.

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Supplementary Material Available: Tables of observed and calculated structure amplitudes for complexes **3** and **4** (49 pages). Ordering information is given on any current masthead page.

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