

**Crystal and Molecular Structures of
Bis(μ -chloro)bis[*o*-(dimesitylphosphino)-3,5-dimethylbenzyl]-
dipalladium(II) Acetone Solvate,
[Pd(P(mes)₂C₆H₂(CH₃)₂CH₂)Cl]₂·2(CH₃COCH₃), and Its
Platinum Analogue
[Pt(P(mes)₂C₆H₂(CH₃)₂CH₂)Cl]₂·2(CH₃COCH₃). Cyclometalated
Complexes of the Bulkiest Known Phosphine
Trimesitylphosphine**

Elmer C. Alyea,* George Ferguson,* John Malito, and Barbara L. Ruhl

*Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and
Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1*

Received August 9, 1988

The single-crystal X-ray structures have been determined for both cyclopalladation and cycloplatination complexes of the very bulky trimesitylphosphine ligand. The two complexes are isomorphous and crystallize in the triclinic system $P\bar{1}$. Crystal data for [Pd(P(mes)₂C₆H₂(CH₃)₂CH₂)Cl]₂·2(CH₃COCH₃): $a = 10.717$ (3) Å, $b = 16.329$ (4) Å, $c = 8.614$ (3) Å, $\alpha = 102.75$ (2)°, $\beta = 108.13$ (2)°, $\gamma = 86.47$ (2)°, $V = 1397.2$ Å³, $Z = 1$. For [Pt(P(mes)₂C₆H₂(CH₃)₂CH₂)Cl]₂·2(CH₃COCH₃): $a = 10.666$ (2) Å, $b = 16.370$ (4) Å, $c = 8.623$ (2) Å, $\alpha = 103.11$ (2)°, $\beta = 108.14$ (2)°, $\gamma = 86.40$ (2)°, $V = 1393.4$ Å³, $Z = 1$. The square-planar dimeric complexes have inversion symmetry about the M₂Cl₂ rhombus. Principal dimensions are as follows: for the Pd(II) complex, Pd-P = 2.240 (1) Å, Pd-Cl = 2.400 (1) and 2.488 (1) Å, Pd-C = 2.028 (5) Å, P-Pd-C = 78.9 (2)°, C-Pd-Cl = 92.9 (2)°; for the Pt(II) complex, Pt-P = 2.210 (1) Å, Pt-Cl = 2.386 (1) and 2.474 (1) Å, Pt-C = 2.035 (1) Å, P-Pt-C = 80.8 (1)°, C-Pt-Cl = 93.0 (1)°. The data are discussed in relation to other known cyclometalated systems of palladium(II) and platinum(II), and comparisons are made which suggest that the trend observed for M-C bond distances correlates with other trends, especially ease of synthesis.

Introduction

The study of tertiary phosphine complexes of divalent palladium and platinum is important due to the proven effectiveness of these complexes in organic synthesis¹ and as homogeneous catalysts.² Any modification of the phosphine, whether present as a cocatalyst or as an ancillary ligand, usually leads to changes in the catalyst activity and/or selectivity. Ideally, the choice of a given phosphine for its particular steric or electronic properties could greatly facilitate catalyst design. Unfortunately however, it is usually very difficult in tertiary phosphine chemistry to distinguish electronic from steric effects.³

We have long been concerned with this problem in our own studies of the steric effects in metal phosphine complexes,⁴ particularly those of trimesitylphosphine (P(mes)₃).⁵ We believe that the study of this very bulky

ligand^{6,7} is a step toward the desired differentiation of steric and electronic effects since in this case, the former clearly outweigh the latter.⁵ Our preliminary results for the reactions of P(mes)₃ with various metals, especially Pd(II) and Pt(II),⁸ tend to suggest that P(mes)₃ may approach the upper limit to tertiary phosphine steric bulk.

Generally, tertiary phosphine ligands stabilize the 2:1 monomeric species [MX₂(PR₃)₂] (M = Pd, Pt; X = halide, pseudohalide) which may or may not dimerize upon heating.⁹ Bulky phosphine ligands tend to favor the direct formation of the 1:1 dimers¹⁰ and will often undergo internal metalation reactions¹¹ to further minimize steric crowding. Trimesitylphosphine reacts with divalent pal-

(5) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Parvez, M. *Inorg. Chim. Acta* 1977, 37, 45. (b) Alyea, E. C.; Dias, S. A.; Stevens, S. *Inorg. Chim. Acta Lett.* 1980, 44, 207. (c) Alyea, E. C.; Ferguson, G.; Somogyvari, A. *Inorg. Chem.* 1982, 21, 1369. (d) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Siew, P. Y. *Croat. Chem. Acta* 1984, 57, 457. (e) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. *Inorg. Chem.* 1985, 24, 3719.

(6) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.

(7) Blount, J. F.; Maryanoff, C. A.; Mislou, K. *Tetrahedron Lett.* 1975, 913.

(8) (a) Dias, S. A.; Alyea, E. C. *Trans. Met. Chem. (Weinheim, Ger.)* 1979, 4, 205. (b) Alyea, E. C.; Malito, J. *J. Organomet. Chem.* 1988, 340, 119. (c) Malito, J. M.Sc. thesis, University of Guelph, 1987.

(9) (a) McAuliffe, C. A., Ed. *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*; MacMillan: London, 1973. (b) Levason, W.; McAuliffe, C. A. *Phosphine, Arsine and Stibine Complexes of Transition Elements*; Elsevier: Amsterdam, 1978. (c) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973. (d) Hartley, F. R. *Coord. Chem. Rev.* 1981, 35, 143. (e) Hartley, F. R. *Coord. Chem. Rev.* 1982, 41, 319.

(10) (a) Chatt, J.; Venanzi, L. *J. Chem. Soc.* 1955, 2787. (b) Chatt, J. *Ibid.* 1951, 652.

(11) (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 73. (b) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* 1976, 18, 327. (c) Omae, I. *Ibid.* 1980, 32, 235.

(1) (a) Henry, P. M. *Adv. Organomet. Chem.* 1975, 13, 363. (b) Trost, B. M. *Tetrahedron* 1977, 33, 2615. (c) Heck, R. F. *Platinum Met. Rev.* 1980, 24, 58. (d) Sakurai, H.; Kamiyama, Y.; Nakadaira, U. *J. Am. Chem. Soc.* 1977, 99, 3879.

(2) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Alyea, E. C.; Meek, D. W. *Adv. Chem. Ser.* 1982, No. 196. (c) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York, 1983. (d) Garrou, P. E. *Chem. Rev.* 1985, 85, 171. (e) Lyons, J. E. *Adv. Chem. Ser.* 1974, No. 132, 64. (f) Heck, R. F. *Acc. Chem. Res.* 1965, 2, 10. (g) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (h) Hartley, F. R. *Adv. Organomet. Chem.* 1977, 15.

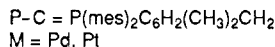
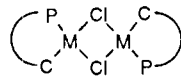
(3) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 183.

(4) (a) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Roberts, P. J. *J. Chem. Soc., Dalton Trans.* 1979, 948. (b) Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Khan, M. *Inorg. Chem.* 1978, 17, 2965.

Table I. Crystal and Data Collection Parameters for $[M(P(mes)_2C_6H_2(CH_3)_2CH_2)Cl]_2$ (M = Pd, Pt)

	M = Pd	M = Pt
formula	$C_{54}H_{64}Cl_2P_2Pd_2 \cdot 2(C_3H_6O)$	$C_{54}H_{64}Cl_2P_2Pt_2 \cdot 2(C_3H_6O)$
fw	1116.85	1294.23
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a , Å	10.717 (3)	10.666 (2)
b , Å	16.329 (4)	16.370 (4)
c , Å	8.614 (3)	8.623 (2)
α , deg	102.75 (2)	103.11 (2)
β , deg	108.13 (2)	108.14 (2)
γ , deg	86.47 (2)	86.40 (2)
V , Å ³	1397.2	1393.4
$F(000)$	576	640
Z	1	1
D_{calcd} , g cm ⁻³	1.33	1.54
cryst size, mm	0.08 × 0.10 × 0.40	0.10 × 0.14 × 0.50
color	yellow	pale yellow
$\mu(MoK\alpha)$, cm ⁻¹ (λ , Å)	8.2 (0.71073)	52.5 (0.71073)
setting angle range	$7 < \theta < 14^\circ$	$10 < \theta < 12^\circ$
unique reflectns	6478 (6677 collected)	5263 (5396 collected)
unique reflectns ($I > 3\sigma(I)$)	3771	4682
R	0.043	0.030
R_w	0.051	0.041
highest peak final difference map, e Å ⁻³	0.72	3.30

ladium and platinum chloro starting materials over a wide range of reaction conditions to afford only the cyclometalated dimers for which we have earlier assigned the abbreviated structure shown below.⁸



The X-ray crystal data presented in this paper establish this structure and augment the limited data for related metalated species available in the literature. In comparing our data to those for similar systems involving bulky phosphine ligands, we find that many of the trends observed in the literature¹¹ for the promotion of cyclometalation can be correlated with the resulting M-C bond lengths; i.e., $d(M-C)$ values correlate directly with the ease of synthesis of cyclometalated complexes of bulky tertiary phosphine ligands.

Experimental Section

Synthetic, analytical, and spectroscopic details for $[M(P(mes)_2C_6H_2(CH_3)_2CH_2)Cl]_2$ (M = Pd, Pt) are given elsewhere.⁸ The crystals used here were grown by very slow precipitation from a 1:1 acetone/dimethyl sulfoxide solvent mixture at ambient temperatures in the dark. Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the ranges shown in Table I. There were no systematic absences. The crystals proved to be isomorphous; full data sets were acquired for each at a temperature of 21 °C by using the ω - 2θ scan technique. Data were collected to a maximum 2θ of 54.0 and 50.0° for M = Pd and Pt, respectively. Lorentz and polarization corrections were applied; and the structures were solved by using the Patterson heavy-atom method and difference Fourier syntheses. Refinement was by full-matrix least-squares calculations with anisotropic thermal parameters. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded (C-H

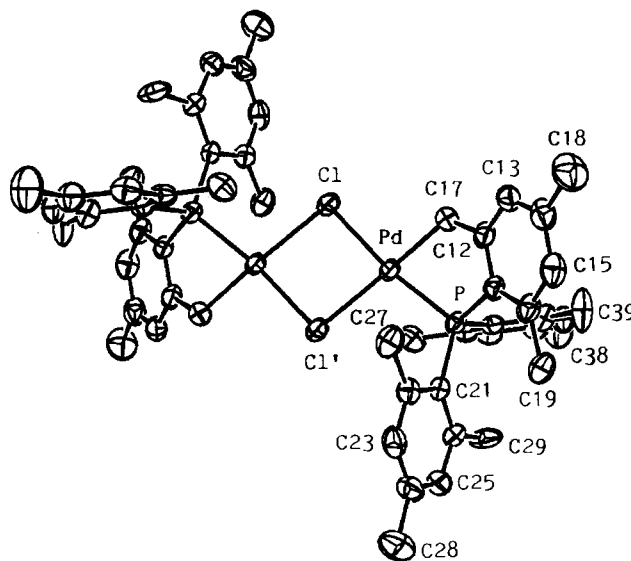


Figure 1. An ORTEP diagram for $[Pd(P-C)Cl]_2$ with 50% probability ellipsoids and an indication of the numbering scheme. Ring and methyl carbons are numbered C1-C6 and C7-C9 ($i = 1-3$), respectively.

= 0.95 Å). Scattering factors were taken from Cromer and Waber.¹² Anomalous dispersion effects were included in F_c .¹³ For the observed data, the final cycle of refinement included 307 variable parameters and converged (largest parameter shifts were 0.02 and 0.01 times esd for M = Pd and Pt, respectively) with the unweighted and weighted agreement factors shown in Table I. There were no chemically significant features in the final difference Fourier map. All calculations were performed on a PDP-11 computer using the SDP-PLUS programs.¹⁴ Final atomic coordinates are presented in Table II.

Results and Discussion

The two complexes, $[M(P-C)Cl]_2$ (M = Pd, Pt), are very stable as solids,⁸ but crystals suitable for single-crystal X-ray diffraction were extremely difficult to grow. Most attempts led to the formation of unsuitable needlelike particles, but very slow evaporation of a 1:1 acetone-DMSO solution finally yielded suitable crystals. In each case, the ¹H NMR spectra of the redissolved crystals ($CDCl_3$) showed the presence of stoichiometric amounts of acetone and some DMSO (trace only). The former does in fact appear within the unit cell of each molecule but is omitted from the discussion which follows.

The two molecules are isostructural and lie about crystallographic inversion centers; an ORTEP diagram for the palladium complex (Figure 1) shows the three adjacent metalocycles. This is as expected on the basis of IR and NMR data.⁸ Also as expected, on the basis of stereochemical arguments, the two phosphorus atoms are in a mutually trans arrangement about the M-M vector. The immediate environment about each metal center (see Table III) is approximately square-planar. The environment about phosphorus has been distorted from the pseudotetrahedral angles observed in free $P(mes)_3$.⁷ The original C_3 symmetry of the $P(mes)_3$ moiety has been destroyed upon cyclometalation as the non-metalated rings have moved further apart. The geometry about C17, the metalated carbon, is tetrahedral.

(12) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(13) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* 1964, 17, 781.

(14) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthoff-Hazelkamp, R., van Koningsveld, H., Bassi, G., Eds., Delft University Press: Delft, Holland, 1978; pp 64-71.

Table II. Final Fractional Coordinates for [M(P(mes)₂C₆H₂(CH₃)₂CH₂)Cl]₂ (M = Pd, Pt) with Estimated Standard Deviations in Parentheses^a

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
Pd	0.00008 (4)	0.10698 (3)	0.10945 (5)	2.441 (7)	Pt	0.00048 (2)	0.10858 (1)	0.10904 (2)	2.297 (4)
Cl	-0.0952 (1)	-0.0303 (1)	0.0970 (2)	3.31 (3)	Cl	-0.0901 (1)	-0.0287 (1)	0.0991 (2)	3.19 (3)
P	-0.0773 (1)	0.1950 (1)	0.2967 (2)	2.35 (3)	P	-0.0777 (1)	0.1950 (1)	0.2934 (2)	2.13 (2)
O	-0.4616 (7)	0.5478 (4)	0.2825 (11)	11.1 (3)	O	-0.4589 (7)	0.5474 (4)	0.2923 (11)	10.5 (3)
Cl ^b	-0.4968 (10)	0.6839 (6)	0.3966 (16)	14.7 (3)	Cl ^b	-0.5030 (10)	0.6826 (6)	0.3873 (15)	11.0 (3)
C2 ^b	-0.4386 (8)	0.6033 (5)	0.4009 (12)	7.6 (2)	C2 ^b	-0.4329 (8)	0.6037 (5)	0.4107 (11)	6.8 (2)
C3 ^b	-0.3385 (12)	0.5930 (8)	0.5604 (15)	12.3 (4)	C3 ^b	-0.3368 (12)	0.5908 (8)	0.5650 (14)	10.4 (4)
C11	-0.1216 (5)	0.2842 (3)	0.1935 (6)	2.5 (1)	C11	-0.1215 (5)	0.2830 (3)	0.1932 (6)	2.5 (1)
C12	-0.0392 (5)	0.2860 (3)	0.0987 (6)	2.9 (1)	C12	-0.0395 (5)	0.2858 (3)	0.0948 (6)	2.8 (1)
C13	-0.0574 (6)	0.3460 (3)	0.0031 (7)	3.6 (1)	C13	-0.0591 (6)	0.3470 (3)	0.0018 (7)	3.3 (1)
C14	-0.1591 (6)	0.4034 (3)	-0.0007 (7)	4.0 (1)	C14	-0.1601 (6)	0.4034 (3)	-0.0003 (7)	3.7 (1)
C15	-0.2390 (6)	0.4004 (3)	0.0951 (7)	3.8 (1)	C15	-0.2417 (6)	0.4001 (3)	0.0955 (7)	3.5 (1)
C16	-0.2238 (5)	0.3417 (3)	0.1949 (7)	3.1 (1)	C16	-0.2235 (5)	0.3414 (3)	0.1946 (7)	3.1 (1)
C17	0.0649 (5)	0.2190 (3)	0.0983 (7)	3.5 (1)	C17	0.0644 (5)	0.2193 (3)	0.0899 (7)	3.0 (1)
C18	-0.1838 (8)	0.4657 (4)	-0.1123 (9)	5.8 (2)	C18	-0.1850 (8)	0.4673 (4)	-0.1098 (9)	5.4 (2)
C19	-0.3165 (5)	0.3436 (3)	0.2955 (8)	3.8 (1)	C19	-0.3170 (5)	0.3429 (4)	0.2956 (7)	3.8 (1)
C21	-0.2274 (5)	0.1579 (3)	0.3222 (6)	2.5 (1)	C21	0.0532 (4)	0.2299 (3)	0.4951 (6)	2.3 (1)
C22	-0.3302 (5)	0.1303 (3)	0.1730 (6)	2.8 (1)	C22	0.0840 (5)	0.3142 (3)	0.5793 (6)	3.0 (1)
C23	-0.4476 (5)	0.1030 (3)	0.1813 (8)	3.6 (1)	C23	0.1887 (5)	0.3308 (3)	0.7264 (7)	3.4 (1)
C24	-0.4662 (5)	0.1007 (3)	0.3317 (8)	3.9 (1)	C24	0.2634 (5)	0.2699 (4)	0.7975 (7)	3.7 (1)
C25	-0.3653 (5)	0.1254 (3)	0.4734 (7)	3.3 (1)	C25	0.2334 (5)	0.1874 (3)	0.7116 (7)	3.4 (1)
C26	-0.2458 (5)	0.1544 (3)	0.4755 (6)	2.6 (1)	C26	0.1321 (5)	0.1666 (3)	0.5642 (6)	2.6 (1)
C27	-0.3254 (6)	0.1330 (4)	-0.0000 (7)	3.8 (1)	C27	0.0123 (7)	0.3902 (4)	0.5293 (9)	5.4 (2)
C28	-0.5984 (6)	0.0750 (5)	0.3370 (10)	5.8 (2)	C28	0.3723 (7)	0.2911 (5)	0.9607 (9)	5.7 (2)
C29	-0.1472 (5)	0.1826 (4)	0.6471 (7)	4.2 (1)	C29	0.1071 (6)	0.0748 (3)	0.4893 (7)	3.5 (1)
C31	0.0540 (4)	0.2296 (3)	0.4983 (6)	2.5 (1)	C31	-0.2274 (4)	0.1575 (3)	0.3189 (6)	2.5 (1)
C32	0.0838 (5)	0.3138 (3)	0.5839 (7)	3.1 (1)	C32	-0.3331 (5)	0.1304 (3)	0.1693 (6)	2.8 (1)
C33	0.1861 (5)	0.3297 (3)	0.7319 (7)	3.5 (1)	C33	-0.4494 (5)	0.1023 (4)	0.1796 (8)	3.7 (1)
C34	0.2624 (5)	0.2671 (4)	0.7983 (7)	3.7 (1)	C34	-0.4701 (5)	0.1001 (4)	0.3287 (8)	3.8 (1)
C35	0.2327 (5)	0.1862 (4)	0.7137 (7)	3.6 (1)	C35	-0.3664 (5)	0.1265 (3)	0.4730 (7)	3.3 (1)
C36	0.1314 (5)	0.1651 (3)	0.5653 (6)	2.7 (1)	C36	-0.2467 (5)	0.1550 (3)	0.4731 (6)	2.8 (1)
C37	0.0100 (7)	0.3897 (4)	0.5319 (9)	5.5 (2)	C37	-0.3298 (6)	0.1316 (4)	-0.0028 (7)	3.7 (1)
C38	0.3700 (7)	0.2888 (5)	0.9642 (9)	6.1 (2)	C38	-0.6009 (7)	0.0763 (5)	0.3394 (10)	5.7 (2)
C39	0.1106 (5)	0.0738 (3)	0.4854 (7)	3.6 (1)	C39	-0.1474 (6)	0.1846 (5)	0.6440 (7)	4.4 (1)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(\text{Å}^2/3) [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^b Atoms C1, C2, and C3 are solvent atoms.

Earlier far-IR data⁸ are corroborated by the M-Cl bond distance values found here. All four M-Cl bond distances fall within the literature range for $d(\text{M-Cl})$ (M = Pd, Pt) (2.32–2.51 Å)¹⁵ and $d(\text{M-Cl})$ trans to C17 is longer than $d(\text{M-Cl})$ trans to P. More specifically, for the M = Pt case, the latter bond distance falls just within the range observed for a Pt-Cl bond trans to PR₃ (2.36–2.39 Å)¹⁶ while that trans to C17 is relatively long with respect to other σ -bonded complexes (2.40–2.42 Å).¹⁶ These long M-Cl bonds are offset by the relatively short M-C17 and M-P bond distances (see below).

As is usually observed for approximately linear P-M-Cl arrangements,¹⁷ $d(\text{M-P}) < d(\text{M-Cl})$ with $d(\text{Pt-P}) < d(\text{Pd-P})$. The M-P bond distances in either case are slightly shorter or at least among the shortest values observed for similar bonds in a wide range of M-PR₃ (M = Pd, Pt) complexes (2.24–2.35 Å).^{4,9a,c,17a} Shaw¹⁸ has already suggested that if cyclometalation is a thermodynamic effect, then it should result in decreased steric interaction and formation of a strong M-P bond by what is essentially an enhanced σ -interaction.

Our earlier ¹³C NMR analysis⁸ suggests that M-P $d\pi-d\pi$ back-bonding in [M(P[~]Cl)]₂ (M = Pd, Pt) is negligible.

(15) (a) Cowman, C. D.; Thibeault, J. C.; Ziolo, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 3209. (b) de Renzi, A.; di Blasio, B.; Paiaro, G.; Panunzi, A.; Pedone, C. *Gazz. Chim. Ital.* **1976**, *106*, 765. (c) Bordner, J.; Wertz, D. W. *Inorg. Chem.* **1974**, *13*, 1639. (d) Hewitt, T. G.; deBoer, J. J. *J. Chem. Soc. A* **1971**, 817. (e) Black, M.; Mais, R. H. B.; Owston, P. G. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1760. (f) Watkins, S. F. *J. Chem. Soc.* **1970**, 168.

(16) Manojlovic-Muir, L.; Muir, K. W. *Inorg. Chim. Acta* **1974**, *10*, 47.

(17) (a) Mather, C. G.; Pidcock, A.; Rapsay, G. J. *N. J. Chem. Soc. Dalton Trans.* **1973**, 2095. (b) Mather, C. G.; McLaughlin, G. M.; Pidcock, A. *Ibid.* **1973**, 1823.

(18) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for [M(P(mes)₂C₆H₂CH₃)₂CH₂)Cl]₂ (M = Pd, Pt) with Standard Deviations in Parentheses^a

M = Pd		M = Pt	
Pd-Cl'	2.488 (1)	Pt-Cl'	2.474 (1)
Pd-Cl	2.400 (1)	Pt-Cl	2.386 (1)
Pd-P	2.240 (1)	Pt-P	2.210 (1)
Pd-C17	2.028 (5)	Pt-C17	2.035 (4)
P-C11	1.833 (5)	P-C11	1.809 (4)
P-C21	1.845 (5)	P-C21	1.854 (4)
P-C31	1.860 (5)	P-C31	1.837 (4)
Cl-Pd-Cl	85.65 (4)	Cl-Pt-Cl	83.57 (4)
Cl'-Pd-P	102.52 (5)	Cl'-Pt-P	102.50 (3)
Cl'-Pd-C17	174.6 (2)	Cl'-Pt-C17	173.7 (1)
Cl-Pd-P	171.78 (5)	Cl-Pt-P	173.70 (3)
Cl-Pd-C17	92.9 (2)	Cl-Pt-C17	93.0 (1)
P-Pd-C17	78.9 (2)	P-Pt-C17	80.8 (1)
Pd-Cl-Pd	94.35 (4)	Pt-Cl-Pt	96.43 (4)
Pd-P-C11	100.0 (2)	Pt-P-C11	100.1 (1)
Pd-P-C21	114.5 (1)	Pt-P-C21	111.5 (1)
Pd-P-C31	111.5 (2)	Pt-P-C31	114.8 (1)
C11-P-C21	108.0 (2)	C11-P-C21	108.2 (2)
C11-P-C31	108.5 (2)	C11-P-C31	108.3 (3)
C-21-P-C31	113.2 (2)	C21-P-C31	112.9 (2)
Pd-C17-C12	111.6 (3)	Pt-C17-C12	110.8 (3)

^a Cl' denotes the atom bonded to M trans to metalating carbon.

We feel that the X-ray data presented here do not contract this suggestion. The P-C11 bond is the shortest of the P-C bonds in accord with the greater than 6 ppm shielding observed for C11 relative to C21 and C31 in the ¹³C NMR.⁸ Furthermore, the ¹J(³¹P-¹³C) values increase in magnitude as C_{ipso} (uncoordinated P(mes)₃) < C21, C31 < C11, implying an increased interaction between P and the ipso

Table IV. Bond Distance Data (Å) for $[M(P-C)X]_2$

M	P-C	X	M-C	M-P	M-X	M-X ^b
Pt	P ^t Bu ₂ CH ₂ C(CH ₃) ₂ CH ₂	Cl	2.06	2.200	2.402	2.406
Pt	P ^t Bu ₂ C(CH ₃) ₂ CH ₂	Pz ^a	2.059 (22)	2.216 (7)	2.080 (19)	2.119 (18)
Pt	P ^t Bu ₂ C(CH ₃) ₂ CH ₂	Cl	2.062 (6)	2.187 (12)	2.409 (2)	2.455 (2)
Pt	P(mes) ₂ C ₆ H ₂ (CH ₃) ₂ CH ₂	Cl	2.035 (4)	2.210 (1)	2.386 (1)	2.474 (1)
Pd	P ^t Bu ₂ C(CH ₃) ₂ CH ₂	Cl	2.058 (4)	2.207 (1)	2.427 (1)	2.469 (1)
Pd	P(<i>o</i> -tol) ₂ C ₆ H ₄ CH ₂	I	2.079 (7)	2.266 (2)	2.665 (1)	2.723 (1)
Pd	P(mes) ₂ C ₆ H ₂ (CH ₃) ₂ CH ₂	Cl	2.028 (5)	2.240 (1)	2.400 (1)	2.488 (1)

^a X is the donor atom in bridging pyrazolato. ^b X' denotes the atom bonded to M trans to metalating carbon.

carbon of the metalated ring relative to free P(mes)₃. The C17–C12 bond lengths (M = Pd, 1.514 (7) Å; M = Pt, 1.507 (6) Å) as might be expected are not different from the other ring carbon–ortho methyl carbon distances (average: M = Pd, 1.508 (7) Å; M = Pt, 1.504 (6) Å), but unlike ortho methyl carbons C19, C27, C29, C37, and C39, the metalated carbon C17 shows no coupling to phosphorus.⁸ We tentatively suggest, therefore, that electron density on the metalated mesityl ring moves from one side of the ring (i.e., away from C17) toward the P–C11 bond so that the short M–P bonds observed are due to a specific σ -effect, i.e. the enhanced σ interaction predicted by Shaw.¹⁸

There have been very few X-ray determinations for chloro-bridged, dimeric cyclometalated Pd and Pt phosphine compounds. Shaw et al.¹⁹ reported the structure of $[Pt(P^tBu_2CH_2C(CH_3)_2CH_2)Cl]_2$ and Goel et al.,²⁰ the similar structures of cyclopalladated and cycloplatinated complexes of P^tBu₃. The latter authors²¹ also reported the crystal structure for the analogous pyrazolato-bridged platinum species. Rheingold and Fultz²² recently reported the first crystal structure for an orthometalated triarylphosphine complex, $[Pd(P(o-tol)_2C_6H_4CH_2)I]_2$, which was found as a side product during polyene arylation reactions.²³ Interestingly, we had failed to effect cycloplatination of P(*o*-tol)₃ in $Pt(P(o-tol)_3)_2X_2$ (X = Cl, I)⁴ and currently have observed no cyclometalation in direct reactions of P(*o*-tol)₃ with divalent palladium chloro salts.²⁴

Table IV summarizes the important bond distances for these cyclometalated complexes all of which show the trans configuration with approximate square-planar geometry about M. In each case, except that for orthometalated P(*o*-tol)₃, $d(M-P)$ values are very low. Our earlier arguments against π -back-bonding (see above) are corroborated by ³¹P NMR data since for the P^tBu₃ case, ³¹P NMR spectra show that $^1J(^{195}Pt-^{31}P)$ values for cycloplatinated P(^tBu)₃ are usually higher than those for noncycloplatinated P(^tBu)₃.²⁵ Thus, the short M–P bonds observed for cyclometalated systems might be due simply to the

enhanced s character in the M–P bonds. The longer bond lengths observed for the P(*o*-tol)₃ case must be a reflection of this ligand's reluctance to orthometalate.^{4,24}

The Pt–P bond distance (Table IV) is shortest for cycloplatinated P(mes)₃, the phosphine which has the greatest tendency to cyclometalate. Similarly, the Pd–C distances decrease in the phosphine order P(*o*-tol)₃ > P(^tBu)₃ > P(mes)₃. This is also the inverse of the order based on ease of cyclometalation. Obviously, P(*o*-tol)₃ corresponds to a special case. Its reluctance to undergo orthometalation notwithstanding its large steric bulk ($\theta = 194^\circ$)^{4,6} must be due to this ligand's inherent "intermeshing ability".²⁶ Ligand profile calculations for P(*o*-tol)₃ in $Pt(P(o-tol)_3)_2I_2$ ⁴ have shown that although this complex is very crowded, one of the *o*-tolyl rings is rotated until the Pt–P–C–C(H) torsion angle is close to 0°. The large P(*o*-tol)₃ ligand is effectively locked into a certain conformation which maximizes the Pt to CH₃ distances, preventing orthometalation. The remaining three ligands, however, follow an order for ease of cyclometalation that might be predicted on the basis of trends observed in the literature;^{11,27} i.e., five-membered ring formation (P(^tBu₂CH₂C(CH₃)₃) and P(mes)₃) is favored over four-membered ring formation (P(^tBu)₃) and aryl substituents on phosphorus (P(mes)₃) favor reaction over alkyl substituents P(^tBu₂CH₂C(CH₃)₃).

The cyclometalation reactions of P(mes)₃ are receiving further attention.

Acknowledgment. This work was supported by operating grants to E.C.A. and G.F. from NSERC of Canada and a University Research Grant from Imperial Oil Ltd. (Canada) to J.M.

Registry No. $[Pd(P(mes)_2C_6H_2(CH_3)_2CH_2)Cl]_2 \cdot 2(C_3H_6O)$, 119787-39-2; $[Pt(P(mes)_2C_6H_2(CH_3)_2CH_2)Cl]_2 \cdot 2(C_3H_6O)$, 119787-40-5.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and bond distances, bond angles, and torsional angles (15 pages); listings of observed and calculated structure factors (118 pages). Ordering information is given on any current masthead page.

(19) Mason, R.; Textor, M.; Al-Salem, N.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* 1976, 292.

(20) Goel, A. B.; Goel, S.; Vanderveer, D. *Inorg. Chim. Acta*, 1981, 54, L267.

(21) Goel, A. B.; Goel, S.; Vanderveer, D. *Inorg. Chim. Acta* 1984, 92, L9.

(22) Rheingold, A. L.; Fultz, W. C. *Organometallics* 1984, 3, 1414.

(23) Mitsudo, T.; Fischetti, W.; Heck, R. F. *J. Org. Chem.* 1984, 49, 1640.

(24) Alyea, E. C.; Malito, J., unpublished observations.

(25) (a) Clark, H. C.; Goel, A. B.; Goel, R. G.; Goel, S.; Ogini, W. O. *Inorg. Chim. Acta* 1978, 31, L441. (b) Ogini, W. O. Ph.D. Thesis, University of Guelph, August, 1981.

(26) (a) Immirzi, A.; Musco, A.; Mann, B. E. *Inorg. Chim. Acta* 1977, 21, L37. (b) Clark, H. C. *Isr. J. Chem.* 1977, 15, 210. (c) Alyea, E. C.; Costin, A.; Fey, G. T.; Ferguson, G.; Goel, R. G.; Restivo, R. J. *J. Soc., Dalton Trans.* 1974, 1294. (d) Clark, H. C.; Dymanski, M. J.; Oliver, J. D. *J. Organomet. Chem.* 1970, 154, C40. (e) Porzio, W.; Musco, A.; Immirzi, A. *Inorg. Chem.* 1980, 19, 2537.

(27) (a) Shaw, B. L. *J. Organomet. Chem.* 1980, 200, 307. (b) Shaw, B. L. *Adv. Chem. Ser.* 1982, No. 196, 101.