104155-23-9; 9, 104155-24-0; Al(SiMe$_3$)$_3$·OEt$_2$, 75441-10-0; Cp*TaCl$_4$, 71414-47-6; Cp*TaCl$_3$(PMe3), 71414-45-4; Cp*Cl$_2$Ta(PhC≡CPh), 75522-28-0; Cp*Cl$_2$Ta(PhC≡CH), 75522-33-7; Cp*Cl$_2$Ta(MeC≡CMe), 75522-31-5; Cp*TaCl$_4$(PMe$_3$), 71414-46-5; PhC≡CPh, 501-65-5; PhC≡CH, 536-74-3; MeC≡CMe, 503-17-3; Me$_3$SiC≡CSiMe$_3$, 14630-40-1.

Supplementary Material Available: Tables of general temperature factor expressions for 1 and 8, positional parameters for the hydrogen atoms of 8, and least-squares planes for 1 and 8 (5 pages); a listing of observed and calculated structure factors for 1 and 8 (26 pages). Ordering information is given on any current masthead page.

A Comparative Study of Isostructural Palladium and Platinum Methyl Complexes. The Structures of *cis*-Dimethylbis(diphenylmethylphosphine)palladium(II) and *cis*-Dimethylbis(diphenylmethylphosphine)platinum(II)

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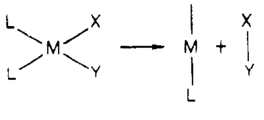
The structures of *cis*-dimethylbis(diphenylmethylphosphine)palladium(II) and *cis*-dimethylbis(diphenylmethylphosphine)platinum(II) have been determined crystallographically at −162 °C. The palladium complex crystallizes from acetone in the monoclinic space group C_{2h}^5—$P2_1/c$ with four formula units in a unit cell of dimensions a = 8.882 (3) Å, b = 26.500 (7) Å, c = 11.168 (4) Å, and β = 108.27 (4)°. The structure has been refined to an R index on F^2 of 0.038 for 4799 observations and 280 variables. The platinum congener crystallizes from a benzene/ethanol mixture with four molecules in the space group C_{2h}^5—$P2_1/c$ of the monoclinic system in a cell of dimensions a = 8.859 (4) Å, b = 26.302 (10) Å, c = 11.215 (5) Å, and β = 108.60 (2)°. The Pt structure has been refined to an R index on F^2 of 0.078 for 7678 observations and 280 variables. Both complexes possess slightly distorted square-planar geometry: P(1)–Pd–P(2) = 98.24 (4)°, P(1)–Pt–P(2) = 97.75 (6)°, C(1)–Pd–C(2) = 82.9 (1)°, and C(1)–Pt–C(2) = 81.9 (2)°. Some important bond distances are as follows: Pd–C = 2.089 (3), 2.090 (3) Å; Pt–C = 2.122 (6), 2.119 (5) Å; Pd–P = 2.326 (1), 2.321 (1) Å; Pt–P = 2.285 (2), 2.284 (2) Å. Comparison of the two structures shows a lengthening of the M–C bonds and a concomitant shortening of the M–P bonds when the central metal is changed from palladium to platinum. These structural data are correlated with differences in reactivity. In addition, sets of isostructural compounds in other metal triads are surveyed for analogous trends in bond distances.

Introduction

Alkyl complexes of the d^8 transition metals are believed to be intermediates in a variety of important catalytic processes, including the hydrogenation and carbonylation of organic species.[1] Both palladium and platinum metals in the +II oxidation state form a vast array of square-planar alkyl complexes. However, these complexes often display a significant variation in reactivity and stability. Generally, Pd(II) alkyls are less stable thermodynamically and kinetically than their Pt analogues.[2] Reductive elimination reactions, useful models for catalytic processes forming C–C bonds, are believed to occur more readily for palladium dialkyls.[3]



M = Ni, Pd, Pt; X, Y = H, CH$_3$

We were interested in examining the metal–carbon bonds in an isostructural set of palladium and platinum complexes, in an attempt to correlate structural parameters with reactivity. Here we report an X-ray crystallographic study of *cis*-Pd(CH$_3$)$_2$(P(C$_6$H$_5$)$_2$CH$_3$)$_2$ and *cis*-Pt(CH$_3$)$_2$(P(C$_6$H$_5$)$_2$CH$_3$)$_2$. The choice of these complexes for such a comparative study was dictated by their relative stability and simplicity and by the fact that preliminary crystallographic examination indicated that they are isostructural and have no imposed symmetry. Consequently the effects of crystal packing on the metrical parameters of interest can be assumed to be constant, and the presence of two independent M–Me and M–P bonds in a given structure provides a check on the estimated standard deviations. Such a check is crucial as we anticipated that we would be discussing the significance of small differences between these two structures. Prior to the present study, no structural comparisons of Pd and Pt methyl complexes had been made. In fact, there are only two reports[4,5] of structures with Pd–Me bonds in the literature.

Experimental Section

Dimethylbis(diphenylmethylphosphine)palladium(II) was synthesized by the method of Gillie and Stille[6] and was crystallized from cold acetone. Suitable crystals of the platinum complex were prepared by the published procedure of Bennett, Chee, and Robertson[7] and were crystallized from a 1:1 mixture of dry benzene and absolute ethanol. Both complexes were handled in solution

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(1) (a) See, for example, James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319–405. (b) Heck, R. F. *Acc. Chem. Res.* **1969**, *2*, 10–16.

(2) Komiya, S.; Yamamoto, A.; Yamamoto, T. *Chem. Lett.* **1978**, 1273–1276.

(3) Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. *Inorg. Chem.* **1982**, *21*, 2162–2174. Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867.

(4) Olmstead, M. M.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *52*, 47–54.

(5) Crutchley, R. J.; Powell, J.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* **1977**, *24*, L15–L16.

(6) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933–4941.

(7) Bennett, M. A.; Chee, H.-K.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061–1070.

0276-7333/86/2305-2044$01.50/0

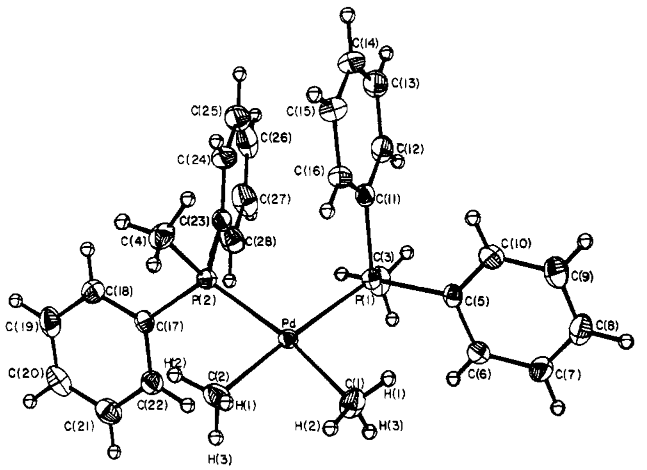

Figure 1. Thermal ellipsoid plot (50% probability) of *cis*-Pd(CH_3)$_2$(P(C_6H_5)$_2$$CH_3$)$_2$ showing the atom numbering scheme. Here and in Figure 2 the hydrogen atoms have been drawn artificially small for clarity.

with standard Schlenk techniques, but both appear to be stable in air for short periods of time in the solid state. The palladium complex appears to be somewhat light sensitive.

Photographic examination at room temperature indicated that the materials belong to the monoclinic system, space group C_{2h}^5—$P2_1/c$. Intensity data were collected at −162 °C on a Picker FACS-1 diffractometer (Pt complex) and on an Enraf-Nonius CAD-4 diffractometer (Pd complex). Lattice constants were obtained by the least-squares refinement of the setting angles of 25 independently centered reflections. Both data sets were collected with the use of Mo Kα X-radiation. Six standards were monitored periodically to check crystal and instrument stability. Crystal data are presented in Table I.

In the structure of the Pt complex the position of the Pt atom was found in a Patterson synthesis. The positions of the P and methyl C atoms were found with the use of DIRDIF.[8] The positions of the remaining non-hydrogen atoms were obtained from a series of difference electron density syntheses. Positional parameters from the previously solved structure of the Pt complex were utilized as a model for the Pd analogue. Both models were refined successfully through standard least-squares techniques.

After the first refinement of anisotropic motion the positions of the methyl hydrogen atoms were determined from a series of difference electron density maps. The positions of these hydrogen atoms and the phenyl hydrogen atoms were idealized (C–H = 0.95 Å) and were not varied in the final refinement. The final cycle of least-squares refinement was carried out on F_o^2 and was based on all the unique data, including those with $F_o^2 < 0$ for both structures. Agreement indices may be found in Table I. The final positional parameters of non-hydrogen atoms are found in Table II (Pd) and Table III (Pt). Principal bond lengths and angles are listed for both complexes in Table IV. The following data are deposited: thermal parameters for Pd and Pt (Tables SI and SII), positions of hydrogen atoms (Table SIII (Pd) and SIV (Pt)), values of $10|F_o|$ vs. $10|F_c|$ for Pd (Table SV) and Pt (Table SVI), bond lengths and angles within phenyl groups (Table SVII (Pd) and SVIII (Pt)).

Description of the Structures

The crystal structures of *cis*-Pd(CH_3)$_2$(P(C_6H_5)$_2$$CH_3$)$_2$ and *cis*-Pt(CH_3)$_2$(P(C_6H_5)$_2$$CH_3$)$_2$ consist of the packing of four molecules in the unit cell. The shortest intermolecular contact in the Pd complex is calculated to be 2.22 Å between two H(1)C(6) atoms. For the platinum complex the shortest intermolecular contact is between the H(1)C(7) and H(1)C(22) atoms, at 2.18 Å. The shortest metal···H contacts, 2.58 and 2.60 Å for the Pd and Pt complexes, respectively, are between metal and connected Me groups and are not of consequence.[9]

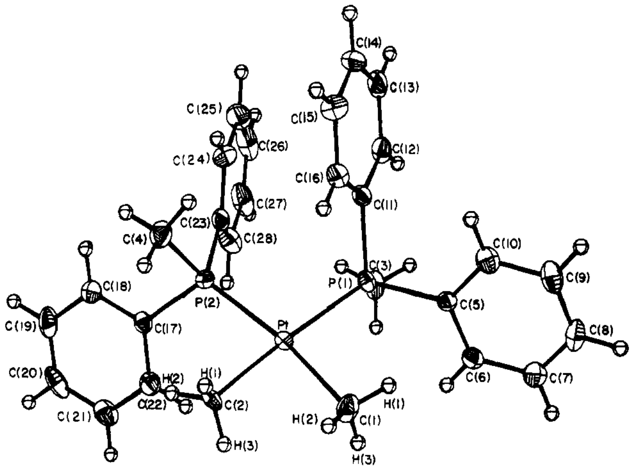

Figure 2. Thermal ellipsoid plot of *cis*-Pt(CH_3)$_2$(P(C_6H_5)$_2$$CH_3$)$_2$ with atoms drawn at the 50% probability level.

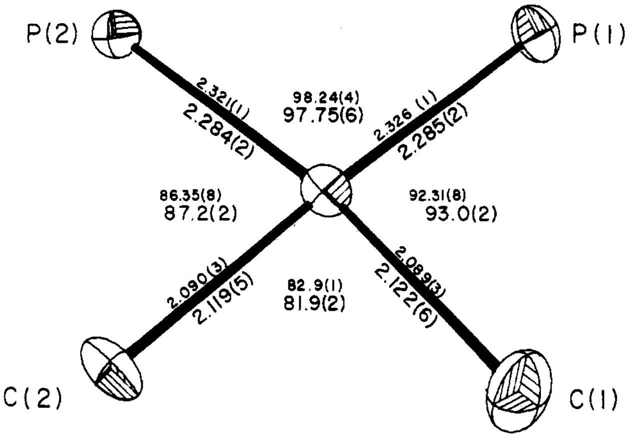

Figure 3. Coordination sphere of the two complexes. Here and in Figure 4 results for the palladium complex are in smaller type.

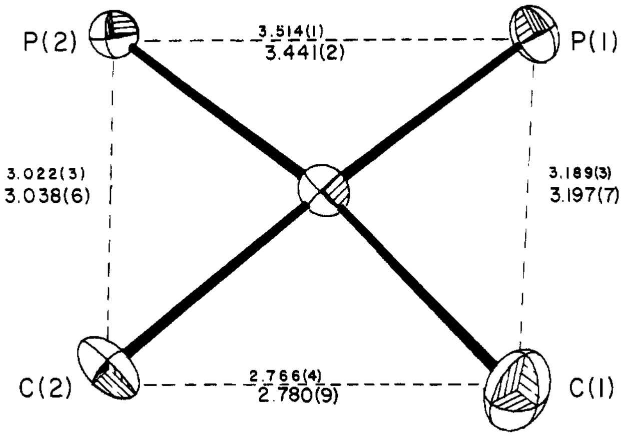

Figure 4. The inner coordination sphere of the two complexes showing nonbonded interligand distances.

The essentially isostructural nature of the two complexes is illustrated by Figures 1 (Pd) and 2 (Pt). The inner coordination sphere with the pertinent bond distances and angles for both compounds is shown in Figure 3. Nonbonded distances among the ligands in the inner coordination sphere are shown in Figure 4. Other important molecular parameters are listed in Table IV. The coor-

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(8) Beurskens, P. T.; Bosman, W. P.; Doesburg, E. M.; Gould, R. O.; van der Hark, T. E.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V. DIRDIF, an automatic procedure for phase extension and refinement of difference structure factors; Crystallography Laboratory: Toernooiveld, 6525ED, Nijmegen, The Netherlands.

(9) Davies, B. W.; Payne, N. C. *J. Organomet. Chem.* 1975, *102*, 245–257.

Table I. Crystallographic Details for *cis*-Dimethylbis(diphenylmethylphosphine)palladium(II) and *cis*-Dimethylbis(diphenylmethylphosphine)platinum(II)

formula	$C_{28}H_{32}P_2Pd$	$C_{28}H_{32}P_2Pt$
formula mass	536.9	625.6
space group	C_{2h}^5—$P2_1/c$	C_{2h}^5—$P2_1/c$
a, Å	8.882 (3)	8.859 (4)
b, Å	26.500 (7)	26.302 (10)
c, Å	11.168 (4)	11.215 (5)
β, deg	108.27 (4)	108.60 (2)
V, Å^3	2496	2476
Z	4	4
ρ_{calcd}, g cm^{-3} (−162 °C)	1.429	1.676
cryst dimens, mm	0.14 × 0.23 × 0.63	0.42 × 0.43 × 0.24
cryst volume (mm^3)	0.025	0.046
μ(Mo Kα), cm^{-1}	8.7	58.6
temp, °C	−162[a]	−162
transmissn factors	0.809–0.881	0.102–0.312
scan mode	ω	θ–2θ
scan speed,[b] min^{-1}	2° in ω	2° in 2θ
scan range, deg	1° below peak to 1° above peak	1.0 below Kα_1 to 1.0 above Kα_2
bkg counts	1/4 of scan range on either side of range	10 at end of each scan with rescan option[c]
data collected	$\pm h,-k,-l$	$\pm h,-k,l$
2θ limits, deg	4–55[d]	4–62
unique data	4799	7678
unique data with $F_0^2 > 3\sigma(F_0^2)$	2389	5773
final no. of variables	280	280
$R(F)$ ($F_0^2 > 3\sigma(F_0^2)$)	0.028	0.049
$R(F^2)$ (all F_0^2)	0.038	0.078
$R_w(F^2)$	0.074	0.117
error in observn of unit weight, e^2	1.49	2.15

[a] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. [b] Reflections were rescanned when $\sigma(I)/I > 0.33$. [c] Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570. [d] Data collection was terminated during the 2θ = 50–55° shell owing to loss of the crystal.

Table II. Positional Parameters for *cis*-Pd$(CH_3)_2(P(C_6H_5)_2CH_3)_2$

atom	x	y	z
Pd	0.455500 (22)	0.630 077 (07)	0.398 977 (16)
P(1)	0.47739 (08)	0.567 529 (24)	0.259 20 (06)
P(2)	0.24812 (08)	0.675 243 (24)	0.262 66 (06)
C(1)	0.6492 (03)	0.601 94 (11)	0.542 92 (25)
C(2)	0.4635 (04)	0.686 77 (11)	0.530 91 (24)
C(3)	0.3151 (03)	0.521 90 (11)	0.2075 (03)
C(4)	0.3221 (04)	0.735 84 (10)	0.227 10 (27)
C(5)	0.6473 (03)	0.524 54 (09)	0.307 64 (23)
C(6)	0.6526 (03)	0.488 62 (10)	0.400 14 (24)
C(7)	0.7777 (04)	0.455 18 (11)	0.440 73 (26)
C(8)	0.9008 (04)	0.457 30 (11)	0.389 25 (28)
C(9)	0.8979 (03)	0.492 40 (11)	0.298 16 (27)
C(10)	0.7723 (03)	0.526 19 (11)	0.257 50 (25)
C(11)	0.4968 (03)	0.594 55 (10)	0.114 76 (22)
C(12)	0.4340 (04)	0.572 43 (11)	−0.003 77 (25)
C(13)	0.4535 (04)	0.595 38 (13)	−0.109 24 (25)
C(14)	0.5375 (04)	0.639 73 (13)	−0.097 71 (27)
C(15)	0.6025 (04)	0.662 24 (12)	0.019 62 (26)
C(16)	0.5807 (03)	0.639 45 (10)	0.125 33 (25)
C(17)	0.0850 (03)	0.693 93 (09)	0.321 62 (23)
C(18)	−0.0304 (03)	0.727 60 (11)	0.254 03 (26)
C(19)	−0.1562 (04)	0.740 47 (11)	0.296 01 (29)
C(20)	−0.1704 (03)	0.719 42 (12)	0.404 92 (27)
C(21)	−0.0565 (04)	0.686 20 (11)	0.473 22 (28)
C(22)	0.0711 (03)	0.673 57 (10)	0.432 31 (25)
C(23)	0.1325 (03)	0.651 05 (10)	0.107 80 (22)
C(24)	0.1609 (04)	0.665 85 (12)	−0.003 09 (25)
C(25)	0.0723 (05)	0.643 80 (14)	−0.117 17 (28)
C(26)	−0.0419 (04)	0.607 96 (14)	−0.121 80 (28)
C(27)	−0.0704 (04)	0.593 52 (13)	−0.0122 (03)
C(28)	0.0168 (03)	0.615 03 (12)	0.102 07 (27)

Table III. Positional Parameters for *cis*-Pt$(CH_3)_2(P(C_6H_5)_2CH_3)_2$

atom	x	y	z
Pt	0.454 455 (24)	0.631 123 (08)	0.394576 (20)
P(1)	0.47503 (17)	0.569 43 (06)	0.25722 (14)
P(2)	0.24887 (18)	0.675 58 (06)	0.25940 (14)
C(1)	0.6519 (07)	0.602 71 (26)	0.5420 (06)
C(2)	0.4631 (08)	0.688 25 (22)	0.5298 (05)
C(3)	0.3145 (07)	0.523 25 (24)	0.2078 (07)
C(4)	0.3200 (08)	0.736 80 (24)	0.2232 (07)
C(5)	0.6455 (07)	0.526 09 (21)	0.3078 (06)
C(6)	0.6492 (08)	0.489 71 (23)	0.4000 (06)
C(7)	0.7741 (09)	0.456 21 (26)	0.4392 (07)
C(8)	0.8977 (08)	0.458 04 (26)	0.3893 (07)
C(9)	0.8957 (08)	0.493 68 (26)	0.2994 (07)
C(10)	0.7721 (07)	0.527 58 (25)	0.2596 (06)
C(11)	0.4925 (07)	0.595 57 (23)	0.1116 (05)
C(12)	0.4330 (08)	0.571 93 (24)	−0.0047 (06)
C(13)	0.4537 (09)	0.5939 (03)	−0.1099 (07)
C(14)	0.5355 (10)	0.6388 (03)	−0.1008 (07)
C(15)	0.5989 (09)	0.661 20 (29)	0.0151 (07)
C(16)	0.5790 (08)	0.640 92 (24)	0.1209 (06)
C(17)	0.0869 (07)	0.694 01 (22)	0.3182 (06)
C(18)	−0.0288 (08)	0.728 30 (25)	0.2518 (06)
C(19)	−0.1558 (08)	0.740 66 (27)	0.2939 (07)
C(20)	−0.1690 (08)	0.7186 (03)	0.4024 (07)
C(21)	−0.0562 (09)	0.685 18 (26)	0.4684 (07)
C(22)	0.0722 (08)	0.67263 (23)	0.4273 (06)
C(23)	0.1338 (07)	0.65068 (25)	0.1052 (06)
C(24)	0.1597 (09)	0.66460 (28)	−0.0061 (06)
C(25)	0.0709 (11)	0.6425 (04)	−0.1201 (07)
C(26)	−0.0430 (09)	0.6070 (04)	−0.1221 (08)
C(27)	−0.0716 (09)	0.5933 (03)	−0.0153 (08)
C(28)	0.0158 (08)	0.6147 (03)	0.1008 (07)

dination about the central metals in both complexes is essentially square-planar with a slight tetrahedral distortion. As shown in Table SIX, the average deviations from the best-weighted least-squares plane are 0.055 (Pd) and 0.051 (Pt) Å. The maximum deviation from this plane is that of atom C(2) in both complexes (0.155 Å, Pd; 0.139 Å, Pt). There is a small angle of "twist" between the P(1)–M–P(2) and C(1)–M–C(2) planes: 5.2°, Pd; 4.7°, Pt. This angle can probably be attributed to some steric congestion. But this distortion is small in comparison with other square-planar molecules. For example, *cis*-Pt$(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$ has an interplanar angle of 18.7°,[10] while *cis*-$PtCl_2(P(C(CH_3)_3)_2C_6H_5)_2$, a complex with

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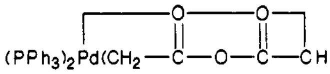
(10) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13–20.

Table IV. Selected Bond Distances (Å) and Angles (deg) in *cis*-$Pd(CH_3)_2(P(C_6H_5)_2CH_3)_2$ and *cis*-$Pt(CH_3)_2(P(C_6H_5)_2CH_3)_2$

	Pd	Pt
	Bond Distances	
M-P(1)	2.326 (1)	2.285 (2)
M-P(2)	2.321 (1)	2.284 (2)
M-C(1)	2.089 (3)	2.122 (6)
M-C(2)	2.090 (3)	2.119 (5)
P(1)-C(3)	1.831 (3)	1.817 (6)
P(1)-C(5)	1.832 (3)	1.832 (6)
P(1)-C(11)	1.822 (3)	1.824 (6)
P(2)-C(4)	1.825 (3)	1.822 (6)
P(2)-C(17)	1.837 (3)	1.826 (6)
P(2)-C(23)	1.829 (3)	1.825 (6)
	Bond Angles	
P(1)-M-P(2)	98.24 (4)	97.75 (6)
C(1)-M-C(2)	82.9 (1)	81.9 (2)
P(1)-M-C(1)	92.31 (8)	93.0 (2)
P(1)-M-C(2)	173.58 (8)	173.7 (2)
P(2)-M-C(1)	168.98 (8)	168.9 (2)
P(2)-M-C(2)	86.35 (8)	87.2 (2)
M-P(1)-C(3)	117.3 (1)	117.2 (2)
M-P(1)-C(5)	118.64 (8)	118.0 (2)
M-P(1)-C(11)	111.41 (9)	112.6 (2)
C(3)-P(1)-C(5)	100.2 (1)	99.6 (3)
C(3)-P(1)-C(11)	105.3 (1)	105.1 (3)
C(5)-P(1)-C(11)	102.0 (1)	102.4 (3)
M-P(2)-C(4)	109.3 (1)	109.9 (2)
M-P(2)-C(17)	117.18 (9)	116.6 (2)
M-P(2)-C(23)	122.33 (9)	122.0 (2)
C(4)-P(2)-C(17)	102.6 (1)	102.3 (3)
C(4)-P(2)-C(23)	103.7 (1)	103.6 (3)
C(17)-P(2)-C(23)	99.3 (1)	99.9 (3)
P(1)-C(5)-C(6)	118.5 (2)	118.4 (4)
P(1)-C(5)-C(10)	123.3 (2)	123.3 (5)
P(1)-C(11)-C(12)	123.7 (2)	123.9 (5)
P(1)-C(11)-C(16)	117.3 (2)	117.0 (5)
P(2)-C(17)-C(18)	120.6 (2)	120.6 (5)
P(2)-C(17)-C(22)	121.0 (2)	121.1 (5)
P(2)-C(23)-C(24)	122.4 (2)	123.7 (6)
P(2)-C(23)-C(28)	118.2 (2)	117.4 (5)

bulkier phosphines, has a twist angle of 31.5°.[11] In the present complexes, the interligand angles about the metals also deviate significantly from 90°. The P(1)-M-P(2) angles are 98.24 (4)° (Pd) and 97.75 (6)° (Pt). These values compare closely with the P-M-P bond angle in *cis*-$PtCl_2(P(C_6H_5)_2CH_3)_2$ of 98.11 (3)°[12] (monoclinic form). The accompanying C(1)-M-C(2) angles are 82.9 (1)° (Pd) and 81.9 (2)° (Pt). Another indication of the distortion toward a tetrahedral configuration is the inequality of the two C-M-P angles[13] in both molecules: for the Pd complex, 92.3 (8)° and 86.4 (8)°; for the Pt complex, 93.0 (2)° and 87.2 (3)°.

The Pd-P bond distances are longer than most of the known cis Pd-P distances, but this is misleading because few Pd alkyl complexes have been structurally characterized.[4,5] Phosphines trans to alkyl groups in square-planar complexes tend to have longer M-P bond distances because alkyl groups are believed to weaken the trans bond by an inductive effect.[14] It is difficult to measure the magnitude of the trans effect in this complex because there are few other examples of *cis*-dialkylbis(phosphine) complexes of Pd. The cis C-bound acetylacetone complex has Pd-P bond distances of 2.349 (2) and 2.320 (2) Å.[15] In *cis*-$[Pd(CH_2SCH_3)(PPh_3)_2]X$ ($X = PF_6$ and ClO_4) the Pd-P bond lengths are 2.350 (5) and 2.320 (3) Å.[16]


$(PPh_3)_2Pd(CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2)$

On the other hand, the Pt-P bonds of the present complex are somewhat shorter than the Pt-P distances of other *cis*-dialkylbis(tertiary phosphine)platinum(II) complexes. The Pt-P bond lengths and their corresponding J_{Pt-P} coupling constants for a number of *cis*-$Pt(X)(Y)(PR_3)_2$ compounds have been tabulated.[17] The J_{Pt-P} coupling constant of 1833 Hz in the present complex is larger than most of the values tabulated but is comparable with that of 1856 Hz[18] for *cis*-$Pt(CH_3)_2(PEt_3)_2$.

Distances within the phosphine ligands appear to be normal. One interesting feature apparent in the structures of the two complexes (Figures 1 and 2) is the nearly eclipsed configuration of phenyl rings C(11)-C(16) and C-(23)-C(28). The dihedral angles between the planes of the two phenyl rings are 15.1° (Pd) and 15.7° (Pt). The nonbonded C···C distances between the two rings are ~3.4 Å in both cases. Chee, McLaughlin, McPartlin, and Robertson[12] studied the dichloro analogue *cis*-$PtCl_2(P(C_6H_5)_2CH_3)_2$ and suggested that graphitic interactions of this sort lend additional stability to the molecules, counteracting the disruptive effect of bulky phosphine ligands in a cis configuration.

The two Pd-Me distances at 2.089 (3) and 2.090 (3) Å are equal within experimental error. These bond lengths are typical values for Pd-C(sp^3) σ bonds, which generally range from 2.01 to 2.12 Å.[19] Olmstead, Farr, and Balch[4] have reported the structure of a binuclear palladium complex with bridging phosphines and a methyl group bound to one palladium atom. Here the methyl group is disordered with an iodine atom on the adjacent metal, causing the apparent Pd-C bond to lengthen to 2.28 (4) Å. The only other structurally characterized Pd-Me moiety, prior to this study, is that of *trans*-(bicarbonato)methylbis(triethylphosphine)palladium(II) with a Pd-C bond length of 2.05 (2) Å.[5]

The two Pt-Me distances at 2.122 (6) and 2.119 (5) Å are also equal. Considerably more complexes containing the $Pt-CH_3$ group have been characterized structurally, with bond distances ranging from 2.0 to 2.2 Å. Some Pt(II)-Me complexes are tabulated in Table V.[20-41] In

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Table V. Pt–Me Distances (Å) in Some Pt(II) Complexes

complex	$Pt–CH_3$ bond dist	ref
$Pt(npz)(CH_3)(C_2F_4)$[a]	2.058 (14)	20
$Pt(CH_3)(Cl)(AsMe_3)_2(CF_3C{\equiv}CCF_3)$	2.10 (4)	21
$[Pt(CH_3)(MeC{\equiv}CMe)(PMe_2Ph)_2]$-$[PF_6]$	2.11 (3)	22
$Pt(CH_3)(I\text{-}SO_2)(PPh_3)_2$	2.120 (7)	23
$Pt(CH_3)(PMe_2Ph)_2(C(CH_3)N(CH_3)_2)$	2.147 (11)	24
$Pt(npz)(CH_3)(CF_3C{\equiv}CCF_3)$	2.069 (12)	25
$Pt(npz)(CH_3)(t\text{-}BuNC)$	2.117 (15)	26
$Pt(CH_3)(Cl)(PMePh_2)_2$	2.081 (6)	7
$Pt(CH_3)_2[P(Ph)_2{-}C_6H_4{-}CH{=}CH_2]$	2.166 (5), 2.052 (6)	27
$Pt(CH_3)(C_5H_5)(cod)$	2.068 (8)	28
$Pt(CH_3)(PPh_3)(Se_2CNEt_2)$	2.113 (25)	29
$Pt(CH_3)(Cl)(PPh_3)_2$	2.08 (1)	30
$Pt(npz)(CH_3)(CO)$	2.028 (13)	31
$Pt_2(CH_3)_3(\mu\text{-}dmpm)_2$	2.06 (4), 2.08 (3), 2.10 (3)	32
$[Pt(CH_3)(PMe_2Ph)_2(C(OCH_3)CH_3)]$-$[PF_6]$	2.13 (2)	33
$Pt(npz)(CH_3)(CH_3C{\equiv}CPh)$	2.043 (8)	9
$Pt(CH_3)(P(C_6F_5)Me_2)_3$	2.098 (1)	34
$Pt(CH_3)_2(CH_3C(CH_2PPh_2)_3)$	2.18, 2.15	35
$Pt_2(CH_3)_2(\mu\text{-}H)_2(\mu\text{-}dmpm)_2$	2.05 (2), 2.13 (2)	36
$Pt(CH_3)Cl((+)\text{-}diop)$	2.17 (1)	37
$Pt_2(CH_3)_4(\mu\text{-}dmpm)_2$	2.124 (12), 2.161 (12), 2.133 (12), 2.202 (9)	38
$Pt_2(CH_3)_4(\mu\text{-}dppm)_2$	2.09 (4), 2.08 (4), 2.14 (6), 2.05 (4)	38
$Pt(CH_3)(Cl)(PEt_3)(AsPh_3)$	2.076 (4)	39
$Pt(CH_3)(OCH_3)(dppe)$	2.106 (9)	40
$Pt(CH_3)(nbd)(cod)$	2.054 (14)	41

[a] npz = methyl[hydrotris(1-pyrazolyl)borato]; nbd = norbornene; cod = 1,5 cyclooctadiene; dmpm = bis(dimethylphosphino)methane; dppm = bis(diphenylphosphino)methane; dppe = bis(diphenylphosphino)ethane; diop = ((+)-(2*S*,3*S*)-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphine)butane.

trans-$PtCl(CH_3)(P(C_6H_5)_2CH_3)_2$, the Pt–C bond distance is 2.081 (6) Å.[7] The methyl group is trans to the chloro ligand, a weak trans effect ligand. *cis*-Dimethyl(2-vinylphenyl)diphenylphosphine)platinum[27] has a $Pt–CH_3$ bond length of 2.166 (5) Å for the methyl group trans to the phosphorus atom. Methyltris(dimethyl(pentafluorophenyl)phosphine)platinum[34] has a $Pt–CH_3$ bond length of 2.098 (1) Å. Dimethyl[tris(diphenylphosphino)methane]platinum (where the "tripod" ligand is bidentate) has Pt–Me bond lengths of 2.18 and 2.15 Å.[35] Thus, the $Pt–CH_3$ distances in the present complex are typical for *cis*-dimethylplatinum complexes.

Discussion

One of the objectives of this work has been to examine the relative differences between isostructural complexes of second- and third-row transition metals. We have found that the inner coordination spheres of these two complexes display significant differences. Thus $\Delta_{M\text{-}C} = \langle Pt\text{-}C\rangle - \langle Pd\text{-}C\rangle = +0.030$ (4) Å while $\Delta_{M\text{-}P} = \langle Pt\text{-}P\rangle - \langle Pd\text{-}P\rangle = -0.039$ (1) Å. These differences are significant and are of the opposite sign. Table VI lists examples of other structurally similar Pd and Pt complexes.[42–58] No structures of comparable accuracy have been reported in the literature that permit a reliable estimate of $\Delta_{M\text{-}C}$, the difference in metal-carbon distances for isostructural Pd and Pt complexes. There are a few structures where Δ has been determined to about the same level of significance for metal–phosphorus bond distances. For example, Δ values for the $M(CH_2{=}C{=}CH_2)(PPh_3)_2$ complexes are −0.036 (9) and −0.038 (9) Å. Similarly, $M(P(Ph)(t\text{-}Bu)_2)_2$ complexes for M = Pd and Pt have Δ values for the M–P bond lengths of −0.033 (2) Å.

From the present results and some of the data in Table VI a pattern emerges. Hard ligands, such as alkyls and halides, show longer distances to Pt than to Pd whereas soft ligands, such as phosphines, show shorter distances. This trend does not appear to be limited to the Ni triad. Table VII presents additional data on M–P distances in complexes of the platinum group metals,[59–72] and again one

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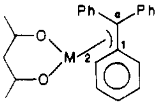
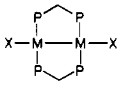
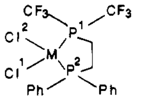
Table VI. Isostructural Complexes of Palladium and Platinum—Bond Distance Comparison

complex	bond type	bond dist Pd	Pt	Δ,[a] Å	ref
$M(CH_3)_2(P(CH_3)(C_6H_5)_2)_2$[b]	M-P	2.323 (1)	2.284 (1)	−0.039 (2)	this work
	M-C	2.090 (2)	2.120 (4)	+0.030 (4)	
K_2MCl_4	M-Cl	2.316 (4)	2.312 (6)	−0.004 (7)	42
trans-$M(Cl)(C(O)C_3H_7)(PPh_3)_2$	M-Cl	2.446 (1)	2.450 (4)	+0.004 (4)	
	M-C	1.996 (6)	2.002 (19)	+0.006 (20)	43
	M-P	2.341 (1)	2.317 (6)	−0.024 (6)	
	$M-C_\alpha$	2.103 (9)	2.081 (26)	−0.022 (28)	
	M-C(1)	2.158 (9)	2.125 (30)	−0.033 (31)	
	M-C(2)	2.202 (10)	2.153 (32)	−0.049 (34)	44
 M=Pd, X=Br M=Pt, X=Cl	M-P	2.29 (3)	2.267 (19)	−0.02 (4)	45, 46
$M(CH_2{=}C{=}CH_2)(PPh_3)_2$	M-P(1)	2.314 (2)	2.278 (9)	−0.036 (9)	
	M-P(2)	2.324 (2)	2.286 (9)	−0.038 (9)	
	M-C(1)	2.12 (1)	2.13 (3)	+0.01 (3)	47, 48
	M-C(2)	2.07 (1)	2.03 (3)	−0.04 (3)	
$M(CS_2)(PPh_3)_2$	M-P (trans to S)	2.316 (8)	2.240 (15)	−0.076 (17)	49, 50
	M-P (trans to C)	2.415 (8)	2.346 (15)	−0.069 (13)	
	M-C	2.00 (3)	2.063 (46)	+0.06 (5)	
	M-S	2.305 (1)	2.328 (16)	+0.023 (16)	
M(P(Ph)(*t*-Bu)$_2$)$_2$	M-P	2.285 (2)	2.252 (1)	−0.033 (2)	51
M(P(Ph)(*t*-Bu)$_2$)$_2$O$_2$	M-P	2.358 (7)	2.290 (6)	−0.068 (9)	52
	M-O	2.06 (1)	2.02 (1)	−0.04 (1)	
	M-P(1)	2.193 (4)	2.168 (3)	−0.025 (5)	
	M-P(2)	2.253 (4)	2.244 (2)	−0.009 (4)	53, 54
	M-Cl(1)	2.311 (4)	2.317 (3)	+0.006 (5)	
	M-Cl(2)	2.370 (4)	2.369 (3)	−0.001 (5)	
$M(NO_2)_2(PEt_3)_2$	M-P	2.338 (1)	2.31 (1)	−0.03 (1)	55, 56
	M-N	1.999 (5)	2.10 (3)	+0.10 (3)	
$MI_2[(AsMe_2)_2C_6H_4]$	M-I	3.40	3.50	+0.10 (7)	57, 58
	M-As	2.40	2.38	−0.02 (1)	

[a] Δ = ⟨Pt–X⟩ − ⟨Pd–X⟩. [b] Intensity data were collected at −162 °C. All other data collections listed were performed at ambient temperature.

Table VII. Comparative M-P Bond Distances of Isostructural Complexes of Platinum Group Metals

complex	M-P bond dist Ru	Os	Δ_{M-P},[a] Å	ref
$M(NO)_2(PPh_3)_2$[b]	2.345 (3)	2.332 (3)	−0.013 (4)	61, 62
$M(CO)_3(PR_3)_2$[b] (M = Ru, R = Me; M = Os, R = Ph)	2.340 (1)	2.35 (5)	+0.01 (5)	63, 64
$M(H)(C_{10}H_7)(dppe)_2$[c]	2.333 (3)	2.325 (6)	−0.008 (7)	65
	2.292 (4)	2.291 (7)	−0.001 (8)	
	2.301 (3)	2.301 (5)	−0.000 (6)	
$M(\mu_2\text{-}H)(\mu_2\text{-}P(H)(Ph))(CO)_{10}$[b,d]	2.339 (1)	2.345 (8)	+0.006 (8)	66, 67
$M(\mu_2\text{-}H)_2(\mu_3\text{-}P(Ph))(CO)_9$[b,d]	2.288 (5)	2.358 (10)	+0.070 (11)	66, 67
	2.278 (5)	2.320 (7)	+0.031 (12)	
	2.329 (5)	2.309 (8)	−0.020 (9)	

complex	M-P bond dist Rh	Ir	Δ_{M-P},[a] Å	ref
$[M(PMe_2Ph)_4O_2][BPh_4]$[b]				68, 69
trans P	2.389 (6)	2.394 (6)	+0.005 (8)	
trans O	2.321 (6)	2.320 (7)	−0.001 (9)	
mer-$MCl_3(PR_2Ph)_3$[b]				70, 71
trans Cl	2.325 (3)	2.280 (1)	−0.045 (3)	
(M = Rh, R = Et; M = Ir, R = Me)				
$M(NO)_2(PPh_3)_2$	2.355 (1)	2.339 (3)	−0.016 (3)	59, 60

[a] Δ_{M-P} = ⟨Os–P⟩ − ⟨Ru–P⟩ or ⟨Ir–P⟩ − ⟨Rh–P⟩. [b] Data collection performed at ambient temperature. [c] dppe = bis(diphenylphosphino)ethane. [d] Data collection performed at −40 °C.

notes generally negative values of Δ_{M-P}, although the level of significance is often rather low. Clearly, additional extensive, low-temperature data sets on isostructural complexes of second- and third-row transition metals are needed to delineate further the pattern of bond distances observed here.

According to the definition of "hard" and "soft" acids,[72] a Pt atom would be considered softer than a Pd atom because it has an additional shell of electrons. These electrons, although affected by the lanthanide contraction, are further from the Pt nucleus and are more polarizable.

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(72) Basolo, F.; Pearson, R. G. In *Mechanisms of Inorganic Reactions*, Wiley: New York, 1967.

Thus a Pt center would be expected to bond more strongly to other soft ligands, such as phosphines. One could alternatively view these differences in metal–ligand distances as an effect of the different bonding capabilities of strongly σ-bonding (i.e., alkyls, halides) and π-bonding (phosphines) ligands. Phosphines are π-acceptors; therefore Pt–P bonding should be stronger than Pd–P bonding. If bond strength can be correlated with bond distance, stronger Pt–P bonds would be expected. A more quantitative discussion of the nature of the bonding in these complexes has been presented.[73] Differences in ability to undergo reductive elimination between the Pd and Pt species may be accounted for by the M–P bond distances. A mechanism for reductive elimination for *cis*-dialkyls has been presented for Pd[6] and Pt.[74] It is believed that prior dissociation of one phosphine ligand is necessary before coupling of the alkyl groups can occur. The Pd–P bonds are longer and therefore expected to be weaker and more likely to dissociate. Thus the postulated mechanism for reductive elimination is supported by the structural data presented here.

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Registry No. *cis*-Pd(CH$_3$)$_2$(P(C$_6$H$_5$)$_2$CH$_3$)$_2$, 60885-30-5; *cis*-Pt(CH$_3$)$_2$(P(C$_6$H$_5$)$_2$CH$_3$)$_2$, 24917-50-8.

Supplementary Material Available: Tables of thermal parameters, positions of hydrogen atoms, and bond distances and angles within phenyl groups for Pd and Pt compounds (9 pages); listings of structure amplitudes for Pd and Pt compounds (52 pages). Ordering information is given on any current masthead page.

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Gas-Phase Ion Chemistry of Dimethylsilene

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A pyrolysis port fitted to the flowing afterglow instrument has been used to prepare dimethylsilene. Its ion–molecule chemistry has been explored by using fluoride and amide ions. Fluoride ion adds to dimethylsilene giving an adduct anion which has been characterized by reaction with nitrous oxide; however, complications make the use of some other characterizing anion more desirable. Thus, amide ion abstraction from dimethylsilene has been used to characterize dimethylsilene. The resulting M − 1 ion reacts sluggishly compared to its carbon analogue, the M − 1 of isobutene. The gas-phase acidity of dimethylsilene is greater than that of isobutene (390 kcal/mol); thus, the M − 1 of dimethylsilene is considerably more stable than the isobutene ion. Carbanions have been reacted with dimethylsilene to explore the possibility of carbanion addition to the carbon end of the Si=C bond. Allyl addition can be interpreted as such an addition. Cycloaddition reactions of dimethylsilene have also been studied.

Dimethylsilene, Me$_2$Si=CH$_2$ has been studied in great detail over the last 20 years.[2] From its initial discovery in 1966 as a transient intermediate in the pyrolysis of dimethylsilacyclobutane (DMSCB), its physical properties, chemical reactivity, and theoretical characterization have been detailed.[2] A variety of other silenes have also been characterized including stable ones.[2,3] Perhaps the greatest impetus for these studies has been the desire to understand the differences between the ability of carbon and silicon to participate in multiple bonding. Indeed, experimental estimates of the π-bond strength of dimethylsilene suggest that silicon forms considerably weaker π-bonds than carbon (approximately 38 vs. 65 kcal/mol for ethylene).[4] Theoretical estimates give similar results.[5]

Our interest in dimethylsilene has focused on its reactions with anionic reagents in the gas phase. In previous work, we have demonstrated that the flowing afterglow (FA) technique gives a variety of interesting results in organosilicon chemistry; in addition, silicon compounds have been useful in studying important problems fundamental to gas-phase chemistry and in preparing gas-phase species for study.[6] Thus, in early studies we reported on

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