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## Palladium Clusters. 4.<sup>1-3</sup> Synthesis and <sup>31</sup>P and <sup>195</sup>Pt NMR Study of a Mixed Platinum/Palladium Cation, [PtPd<sub>2</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, and the Crystal and Molecular Structures of [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>], [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>], and [Pt<sub>0.81</sub>Pd<sub>2.19</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]

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Received May 30, 1984

Reaction of [PdCl(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] with [PtCl(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] in tetrahydrofuran at 125 °C gives [PtPd<sub>2</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>], the first example of a mixed Pt/Pd cluster. X-ray diffraction study of this product shows that it crystallizes in the triclinic space group *P*1, with *a* = 15.746 (8) Å, *b* = 20.421 (8) Å, *c* = 13.045 (7) Å,  $\alpha$  = 97.55 (5)°,  $\beta$  = 119.37 (4)°, and  $\gamma$  = 94.19 (5)°. The crystal also contained about 19% of [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] with the extra palladium atoms distributed randomly over the platinum sites. X-ray diffraction results are also reported for the following two tripalladium clusters: [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>], monoclinic *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 16.141 (11) Å, *b* = 19.512 (8) Å, *c* = 16.912 (6) Å,  $\beta$  = 97.66 (6)°; [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>], monoclinic *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 15.486 (8) Å, *b* = 16.971 (7) Å, *c* = 27.542 (16) Å,  $\beta$  = 92.80 (9)°. The M<sub>3</sub>CIP<sub>3</sub> heavy-atom core is similar in all three structures, with a triangle of metal atoms each bearing a terminal tertiary phosphine and with two edges bridged by diphenylphosphide and one bridged by chloride. The metal-metal lengths are relatively long, averaging 2.92 Å in the tripalladium clusters and 2.89 Å in the mixed species, but are clearly within bonding distance. Complete analysis and computer simulation of <sup>31</sup>P{<sup>1</sup>H} and <sup>195</sup>Pt{<sup>1</sup>H} nuclear magnetic resonance spectra show a highly shielded Pt atom (-1406.7 ppm relative to  $\Sigma$ (<sup>195</sup>Pt) = 21.4 MHz), relatively large values (80-90 Hz) for the three-bond coupling between terminal phosphorus atoms, and extreme downfield shifts (+200 to +230 ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>) for the bridging phosphorus atoms. These parameters are discussed in terms of the metal-metal bonding in the clusters, and a distinction is drawn between the deshielding effect of metal-metal bonds and the shielding effect of small angles at phosphorus in other small ring compounds.

### Introduction

The intense current interest in metal cluster complexes, both from the synthetic viewpoint and for their potential in catalytic chemistry,<sup>4-6</sup> has been responsible for a dramatic growth in the number of known systems. Nevertheless, there remain a number of important omissions and problems, two of which are addressed specifically by the present work.

First, clusters containing platinum or palladium have remained until recently relatively rare and difficult to characterize, even though these metals are of widely ranging importance in both catalysis and synthesis.<sup>7,8</sup> The situation in platinum chemistry has improved recently with the publication of a number of X-ray and spectroscopic studies but, despite the considerable and obvious potential,<sup>9</sup> there remains a dearth of information on palladium clusters. Moreover, extensive studies in the synthesis of heteronuclear clusters involving platinum<sup>10</sup> and many other metals<sup>11,12</sup> have not produced any examples containing both platinum and palladium. Dinuclear complexes containing Pt-Pd bonds have been reported,<sup>13-15</sup> but no X-ray diffraction studies are available and consequently no Pt-Pd bond lengths are known.

Second, it is somewhat surprising that rather few of the known platinum clusters (and none of the palladium ones except for the present work) utilize dialkyl- or diarylphosphide groups as bridging

ligands. The potential for cluster stabilization by these "tenaciously bridging and chemically inert"<sup>16</sup> ligands has been recognized by several groups studying other metals,<sup>17-21</sup> and it has obvious importance in catalysis since the usefulness of clusters is often limited by degradation to mononuclear species under the reaction conditions. A strongly bridging ligand with the flexibility to accommodate both metal-metal-bonded and nonbonded arrangements could facilitate opening of an M-M bond on coordination of substrate and later re-formation of the M-M bond on elimination of product. The feasibility of this process has been demonstrated recently for phosphido-bridged ruthenium clusters,<sup>22,23</sup> and clusters of the type discussed in the present work have been shown to be involved in some hydrogenation reactions catalyzed by palladium complexes.<sup>24,25</sup> The ease of preparation and stability of dinuclear phosphido-bridged platinum group complexes without metal-metal bonds has been known for a long time,<sup>26-28</sup> and the availability of the phosphorus-31 nucleus as a sensitive NMR probe is a further advantage of this ligand system.<sup>29</sup>

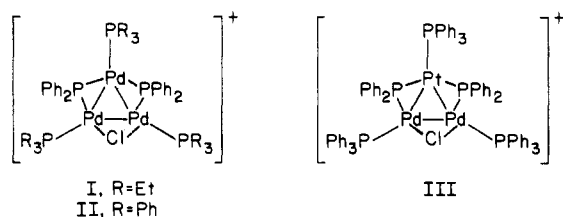
The present work involves clusters containing triangular arrays of metal atoms in fractional positive oxidation states. For platinum, recent examples of triangular clusters include [Pt<sub>3</sub>(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>3</sub>],<sup>30</sup> [Pt<sub>3</sub>(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>4</sub>],<sup>31</sup> [Pt<sub>3</sub>(SO<sub>2</sub>)<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>],<sup>32</sup> and

- (1) Bushnell, G. W.; Dixon, K. R.; Moroney, P. M.; Rattray, A. D.; Wan, C. *J. Chem. Soc., Chem. Commun.* **1977**, 709.
- (2) Dixon, K. R.; Rattray, A. D. *Inorg. Chem.* **1978**, *17*, 1099.
- (3) Cartwright, S. J.; Dixon, K. R.; Rattray, A. D. *Inorg. Chem.* **1980**, *19*, 1120.
- (4) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.
- (5) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.
- (6) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.
- (7) Henry, P. M. *Adv. Organomet. Chem.* **1975**, *13*, 363.
- (8) Tsuji, J. *Adv. Organomet. Chem.* **1979**, *17*, 141.
- (9) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 6, p 265.
- (10) Stone, F. G. A. *Inorg. Chim. Acta* **1981**, *50*, 33.
- (11) Roberts, D. A.; Geoffroy, D. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 6, p 763.
- (12) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.
- (13) Boehm, J. R.; Balch, A. L. *J. Organomet. Chem.* **1976**, *112*, C20.
- (14) Boehm, R. J.; Doonan, D. J.; Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 4845.
- (15) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 81.
- (16) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394.
- (17) Fultz, W. C.; Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 860.
- (18) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319.
- (19) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.
- (20) Atwood, J. L.; Hunter, W. E.; Jones, R. A.; Wright, T. C. *Inorg. Chem.* **1983**, *22*, 993.
- (21) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846.
- (22) MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87.
- (23) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27.
- (24) Berenblyum, A. S.; Knizhnik, A. G.; Mund, S. L. *J. Organomet. Chem.* **1982**, *234*, 219.
- (25) Berenblyum, A. S.; Aseeva, A. P.; Lakhman, L. I. *J. Organomet. Chem.* **1982**, *234*, 237.
- (26) Hayter, R. G.; Humiec, F. S. *Inorg. Chem.* **1963**, *2*, 306.
- (27) Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031.
- (28) Hayter, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 823.
- (29) Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188.
- (30) Albinati, A. *Inorg. Chim. Acta* **1977**, *22*, L31.
- (31) Albinati, A.; Carturan, G.; Musco, A. *Inorg. Chim. Acta* **1976**, *16*, L3.

[Pt<sub>3</sub>(CN-*t*-Bu)<sub>6</sub>]<sub>3</sub>,<sup>33</sup> all of which contain nearly equilateral arrangements of zero-oxidation-state metal atoms and have Pt–Pt bond lengths in the range 2.62–2.74 Å. The unusual series of complexes [Pt<sub>3</sub>(CO)<sub>6</sub>]<sub>n</sub><sup>2-</sup>, *n* = 2–5, which results from reductive carbonylation of [Pt(CO)Cl<sub>3</sub>]<sup>-</sup>, is based on stacking of triangular units, and the intratriangle Pt–Pt lengths are all close to 2.66 Å.<sup>34</sup> There are also a limited number of triangular platinum clusters in positive oxidation states, ranging from Pt(0.67) in [Pt<sub>3</sub>Ph(PPh<sub>2</sub>)(SO<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>]<sup>35</sup> through Pt(1.33) in [Pt<sub>3</sub>Ph(PPh<sub>2</sub>)<sub>3</sub>-(PPh<sub>3</sub>)<sub>3</sub>]<sup>36</sup> and [Pt<sub>3</sub>H(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>37</sup> to Pt(II) in [Pt<sub>3</sub>H<sub>6</sub>(P-*t*-Bu)<sub>3</sub>]<sub>3</sub>.<sup>38</sup> Metal–metal bond lengths in these clusters show considerably more variation, extending up to 2.82 Å for edges bridged by PPh<sub>2</sub> groups, and in the case of [Pt<sub>3</sub>Ph(PPh<sub>2</sub>)<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] one edge of the triangle is bridged by PPh<sub>2</sub> but there can be no significant metal–metal interaction at the observed 3.63 Å distance.<sup>36</sup>

The available information on palladium triangles is much more limited. Carbonyl phosphine species, [Pd<sub>3</sub>(CO)<sub>3</sub>L<sub>3</sub>], L = tertiary phosphine, have been prepared,<sup>39,40</sup> presumably having structures similar to those of the platinum analogues discussed above, but no structure determinations are available. The only tripalladium cluster to have been studied by X-ray diffraction prior to the present work was the palladium(0) complex [Pd<sub>3</sub>(SO<sub>2</sub>)<sub>3</sub>(CN-*t*-Bu)<sub>5</sub>], which contains a nearly equilateral triangle of metal atoms with Pd–Pd distances averaging 2.74 Å,<sup>41</sup> but a further example, [Pd<sub>3</sub>(CO)(dppm)<sub>3</sub>]<sup>2+</sup>, with considerably shorter bonds (average 2.598 Å) has been reported very recently.<sup>42</sup> Three other tripalladium species, [Pd<sub>3</sub>(CNMe)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>,<sup>43</sup> [Pd<sub>3</sub>(acac)<sub>2</sub>(μ-η<sup>3</sup>-C<sub>3</sub>Ph(C<sub>6</sub>H<sub>4</sub>OMe-4)<sub>2</sub>)<sub>2</sub>]<sub>2</sub>,<sup>44</sup> and [Pd<sub>3</sub>(μ-OAc)<sub>4</sub>(η<sup>3</sup>-CH(CHC(O)-*t*-Bu)<sub>2</sub>)<sub>2</sub>]<sub>2</sub><sup>45</sup> contain metal–metal bonds but the arrangement is a metal chain rather than a cluster, and a number of examples, of which palladium(II) acetate is fairly typical, contain Pd<sub>3</sub> triangles with ligand-bridged edges that are too long for appreciable metal–metal interaction (3.15 Å in the acetate<sup>46</sup>).

In our recent work we have reported the synthesis and reactivity of a new class of palladium cluster cations, typified by structures I and II but also including examples with Br, I, SCF<sub>3</sub>, or PPh<sub>2</sub>



replacing the bridging chloride.<sup>1–3</sup> Study of these species by <sup>31</sup>P NMR has shown the utility of this technique in work involving previously difficult to characterize cluster systems, and several

features of the <sup>31</sup>P spectra are diagnostic of the presence of metal to metal bonds. In the present paper we describe X-ray diffraction studies of three complexes (I–III) prepared in the course of this work, including the first example (III) of a heteronuclear cluster involving both palladium and platinum. A detailed analysis of <sup>31</sup>P NMR data for the heteronuclear cluster is also reported.

A preliminary report of the structure of I has been published previously.<sup>1</sup>

### Experimental Section

(a) **Synthesis.** Except where noted below, all operations were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. Tetrahydrofuran was dried and deoxygenated by reflux over potassium/benzophenone. Microanalysis was by the Canadian Micro-analytical Service, Vancouver, B.C., Canada. [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sup>-</sup> and [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sup>-</sup> were prepared as previously described,<sup>2</sup> and crystals suitable for X-ray diffraction study were obtained by recrystallization from absolute ethanol.

**Preparation of [PtPd<sub>2</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sup>-</sup>.** [PdCl(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sup>-</sup> (0.317 g, 0.3 mmol) and [PtCl(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sup>-</sup> (0.344 g, 0.3 mmol) were dissolved in tetrahydrofuran (60 mL) and sealed in a thick-walled Pyrex tube in vacuo. The tube was heated at 125 °C for 50 h, during which time the solution became red and a yellow precipitate formed. After cooling, the tube was opened in an atmosphere of nitrogen, the precipitate removed by filtration, and the filtrate evaporated to dryness in vacuo. The resulting solid was purified by chromatography under a nitrogen atmosphere on a Sephadex column using tetrahydrofuran as eluent. The yellow and orange fractions collected at the beginning were discarded in favor of the final deep red fraction. Crystals were obtained from this fraction by partial evaporation in vacuo followed by cooling to –20 °C: yield 40% based on palladium; mp 174 °C dec. The bulk product used for NMR study was contaminated by about 37% of the corresponding Pd<sub>3</sub> cluster (compound II). Successive recrystallizations improved the purity (e.g.: Anal. Calcd for C<sub>78</sub>H<sub>65</sub>BClF<sub>4</sub>P<sub>3</sub>Pd<sub>2</sub>Pt: C, 55.6; H, 3.9. Found: C, 55.5; H, 4.3), but the exact composition varied and complete separation of the two compounds could not be achieved. The crystal used for X-ray study contained about 19% of II.

(b) **Nuclear Magnetic Resonance.** Phosphorus-31 and platinum-195 NMR spectra were recorded in CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> solutions at 101.3 and 53.5 MHz, respectively, on a Bruker WP250 Fourier transform spectrometer locked to the solvent deuterium resonance. Protons were decoupled by broad-band (“noise”) irradiation at appropriate frequencies. <sup>31</sup>P chemical shifts were measured relative to external P(OMe)<sub>3</sub> and are reported in parts per million relative to 85% H<sub>3</sub>PO<sub>4</sub> with a conversion factor of +141 ppm. Positive values are downfield of the reference. <sup>195</sup>Pt chemical shifts are reported in parts per million relative to Zr(<sup>195</sup>Pt) = 21.4 MHz.<sup>47</sup> Simulated NMR spectra were calculated on an IBM 3031 computer and plotted on a Calcomp 1039 plotter. The programs used were a locally constructed package based on the UEAITR and NMRPLOT programs from the literature.<sup>48,49</sup>

(c) **X-ray Data Collection.** The crystals were photographed on Weissenberg and precession cameras using Cu Kα radiation. After establishment of the symmetry and an approximate unit cell, the crystals were transferred to a Picker four-circle diffractometer. The diffractometer was operated manually for compound II but was automated with a PDP11/10 computer for compounds I and III. The unit cells were refined by least squares from 2θ measurements on a sufficient number (36, 32, and 15 pairs, respectively, at ±2θ) of well-centered reflections. Table I gives the crystal data and also some of the parameters associated with the data collection and refinement. Compound I with its terminal PEt<sub>3</sub> groups is expected to be different in its cell dimensions from the other compounds, but the difference between II and III in symmetry and cell dimensions is unexpected. However, the phenomenon of polymorphism, which is not uncommon, indicates that the difference in energy between alternative packing arrangements may often be small. Crystal densities were measured by flotation. The data collection for compound I was made more difficult by severe deterioration of the material in the X-ray beam and three crystals were used. Data from these crystals were scaled relative to each other by using three scaling constants in the least-squares refinement. The data collections were completed to 2θ = 40° (Mo Kα) for all compounds, (two octants, *k*, *l* ≥ 0, for I and II; one hemisphere, *h* ≥ 0, for III). The very weak reflections were not measured

- (32) Moody, D. C.; Ryan, R. R. *Inorg. Chem.* **1977**, *16*, 1052.  
 (33) Green, M.; Howard, J. A. K.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1509.  
 (34) Calabrese, J. C.; Dahl, L. F.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2614.  
 (35) Evans, D. G.; Hughes, G. R.; Mingos, D. M. P.; Bassett, J. M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1255.  
 (36) Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448.  
 (37) Bellon, P. L.; Ceriotti, A.; Desmartin, F.; Longoni, G.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1982**, 1671.  
 (38) Frost, P. W.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G.; Gregson, D. *J. Chem. Soc., Chem. Commun.* **1981**, 1104.  
 (39) Hidai, M.; Kokura, M.; Uchida, Y. *J. Organomet. Chem.* **1973**, *52*, 431.  
 (40) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.  
 (41) Otsuka, S.; Tatsuno, Y.; Miki, M.; Aoki, T.; Matsumoto, M.; Yoshioka, H.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1973**, 445.  
 (42) Manojlovic-Muir, L.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, *83*, 1336.  
 (43) Balch, A. L.; Boehm, J. R.; Hope, H.; Olmstead, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 7431.  
 (44) Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1825.  
 (45) Ukhin, L. Y.; Dologopolova, N. A.; Kuz'mina, L. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *210*, 263.  
 (46) Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun.* **1970**, 658.

- (47) Kidd, R. G.; Goodfellow, R. J. In “NMR and the Periodic Table”; Harris, R. K.; Mann, B. E., Eds.; Academic Press: London, 1978; p 249.  
 (48) Johannsen, R. B.; Ferreti, J. A.; Harris, R. K. *J. Magn. Reson.* **1970**, *3*, 84.  
 (49) Swalen, J. D. In “Computer Programs for Chemistry”; Detar, D. F., Ed.; W. A. Benjamin: New York, 1968.

Table I. Crystal and Refinement Data for Compounds I-III

	I	II	III
system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
mol formula	$C_{42}H_{65}BClF_4P_3Pd_3$	$C_{78}H_{65}BClF_4P_3Pd_3$	$C_{78}H_{65}BClF_4P_3Pd_2Pt$
mol wt	1166.3	1598.7	1687.4
cell dimens			
<i>a</i> , Å	16.141 (11)	15.486 (8)	15.746 (8)
<i>b</i> , Å	19.512 (8)	16.971 (7)	20.421 (8)
<i>c</i> , Å	16.912 (6)	27.542 (16)	13.045 (7)
$\alpha$ , deg	90	90	97.55 (5)
$\beta$ , deg	97.66 (6)	92.80 (9)	119.37 (4)
$\gamma$ , deg	90	90	94.19 (5)
cell vol, Å <sup>3</sup>	5279 (5)	7230 (7)	3578 (3)
$\rho$ (calcd), g cm <sup>-3</sup>	1.47	1.469	1.550 <sup>a</sup>
$\rho$ (measd), g cm <sup>-3</sup>	1.49	1.486	1.568
<i>Z</i>	4	4	2
$\mu$ , cm <sup>-1</sup>	12.5	9.25	27.46
mounting direction	between <i>b</i> and <i>c</i>	<i>c</i>	<i>c</i>
cryst size, mm	0.19 × 0.56 × 0.31 0.18 × 0.63 × 0.53 0.24 × 0.94 × 0.51	0.27 × 0.09 × 0.40	0.34 × 0.11 × 0.98
transmission ( <i>I</i> / <i>I</i> <sub>0</sub> )	0.52–0.80	0.78–0.92	0.39–0.74
scan	1 min at 2.4°/min	1 min at 2.4°/min	248 steps of 0.01°, 0.25 s/step
time (bkgd), s	30 × 2	30 × 2	31 × 2
no. of indep measmts	2866 (>3 $\sigma$ <sub><i>I</i></sub> )	3610	5058 (>2.5 $\sigma$ <sub><i>I</i></sub> )
no. of params	370	263	284
cryst deterioration	severe	×0.66 over several weeks	none
weighting scheme	1/( <i>A</i> + <i>Bx</i> + <i>Cx</i> <sup>2</sup> + <i>Dx</i> <sup>3</sup> ) <sup>b</sup>	1/( $\sigma^2(F)$ + 0.001 <i>F</i> <sup>2</sup> )	1/( $\sigma^2(F)$ + 0.001 <i>F</i> <sup>2</sup> )
<i>R</i>	0.105	0.0771	0.0742
<i>R</i> <sub>w</sub>	0.135	0.1067	0.0913

<sup>a</sup> Calculated density with 19% Pd in Pt sites. <sup>b</sup> *A* = 88.8927, *B* = -0.18845, *C* = 8.997 × 10<sup>-3</sup>, *D* = -8 × 10<sup>-6</sup>, *x* = |*F*<sub>0</sub>|.

in the manual data collection. Each batch of 50 reflections was preceded by the measurement of three standard reflections. The Lorentz and polarization factors were applied and each batch was scaled to maintain the sum of the standards constant. Absorption corrections were applied by numerical integration.

(d) **Structure Solution and Refinement.** For compound I, the programs used were supplied by Penfold.<sup>50</sup> For compounds II and III, SHELX-76 supplied by Sheldrick was used.<sup>51</sup> Illustrations were drawn by using ORTEP.<sup>52</sup> The atomic scattering factors used were for neutral atoms, with corrections for anomalous dispersion.<sup>53</sup> The nine heavy atoms in each structure and the BF<sub>4</sub><sup>-</sup> group of III were given anisotropic temperature parameters. Compound I was solved by the Patterson function, and compounds II and III by direct methods. All structures were completed by the standard Fourier synthesis procedures using difference maps and were refined by the method of least squares minimizing  $\sum w\Delta^2$ , where *w* is a weight as defined in Table I and  $\Delta = ||F_o| - |F_c||$ . Hydrogen atoms were not located.

For compound I, the refinement converged with a maximum shift/esd ratio of 0.15. The final difference map had a maximum of 1.83 e Å<sup>-3</sup> and a minimum of -1.29 e Å<sup>-3</sup>, the more prominent peaks being close to the Pd and P atoms.

For compound II a rigid regular hexagon was used to model each benzene ring in the structure. The aromatic bond lengths were given the value of 1.395 Å. The external angles at the P-C bonds are close to 120° and have been deposited as Table S8 (supplementary material). The thermal motion of the BF<sub>4</sub><sup>-</sup> ion is high, and we experienced difficulty in refining this group, on which tetrahedral geometry was finally imposed by means of interrelated B-F and F-F distance constraints. The B-F length refined to 1.34 Å, and convergence was achieved with a maximum shift/esd ratio of 0.24 (associated with the BF<sub>4</sub><sup>-</sup>). The final difference map maximum was 0.90 e Å<sup>-3</sup>, and the minimum was -0.63 e Å<sup>-3</sup>.

For compound III, the benzene rings were dealt with as in compound II. The external angles at the rings are given in Table S9 (supplementary

material). The thermal vibrational parameters of the tetrafluoroborate ion were high; however, the bond lengths and angles for this ion are within the expected ranges and are deposited in Tables S6 and S9 (supplementary material). Refinement on the assumption that the crystal was a pure sample of [PtPd<sub>2</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] resulted in convergence with residuals of *R* = 0.0886 and *R*<sub>w</sub> = 0.1151. The possibility that a fraction of the Pt sites might be occupied by Pd randomly throughout the crystal was next examined by refinement of the site occupation factor for Pt. This refinement converged at the value of 0.9208 and improved the residuals to 0.0742 and 0.0913 (Table I). A check was done on the significance of this result by refining the site occupation factors for Pt in an unrelated normal platinum complex, and the deviation from unity was 0.02. Other experimental calculations, refining the site occupation factors for the Pd atoms gave no conclusive results. Thus, if the missing 8% of electron density at the Pt sites (*Z* = 78) was due to partial occupation by Pd (*Z* = 46), then approximately 19% of the sites contained Pd atoms. All the data indicated that this palladium was randomly distributed, and there was no evidence of a superlattice. There was no X-ray evidence for platinum in the Pd sites. Some contamination by the Pd<sub>3</sub> cluster is to be expected from the method of preparation, and the NMR spectroscopic results confirm that Pt occurs only at the unique apical position of the triangle. The final difference map had a maximum of 2.7 e Å<sup>-3</sup> and a minimum of -2.1 e Å<sup>-3</sup>. All maxima greater than 1.1 e Å<sup>-3</sup> were close to the metal atoms of the cluster.

## Results

(a) **Synthesis.** As we have described previously, the most convenient route to the triangular palladium clusters is via prolonged heating (120 °C) of [PdCl(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] in tetrahydrofuran.<sup>2,3</sup> The resulting phenyl-transfer reaction generates PPh<sub>4</sub><sup>+</sup> and PPh<sub>2</sub><sup>-</sup> groups and is accompanied by partial reduction of the palladium to form [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] (II). A simple phosphine-exchange reaction then leads to the triethylphosphine analogue, [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] (I). The results of X-ray diffraction studies of both the triphenyl- and triethylphosphine derivatives are described below.

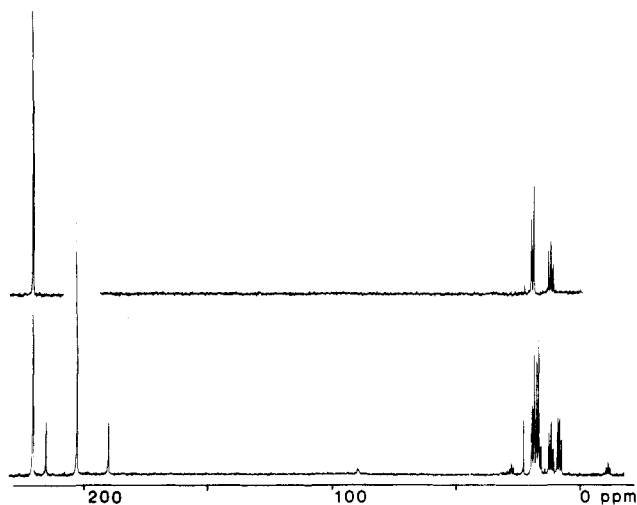
Synthesis of corresponding platinum clusters and heteronuclear derivatives containing both palladium and platinum has proved considerably more difficult. [PtCl(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] is unchanged by heating in tetrahydrofuran at 120 °C, and substitution of a higher boiling solvent (e.g. diglyme) with temperatures up to 200–225 °C results only in gradual decomposition with no in-

(50) Crystallographic programs of B. R. Penfold, University of Canterbury, Christchurch, New Zealand.

(51) Sheldrick, G. M. "SHELX-76. A System of Computer Programs for X-Ray Structure Determination"; University of Cambridge: Cambridge, England, 1976.

(52) Johnson, C. K. "ORTEP: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

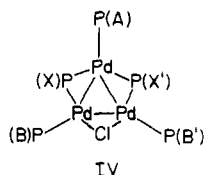
(53) Cromer, D. T.; Weber, J. T. "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 148.



**Figure 1.**  $^{31}\text{P}$  NMR spectra of the  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$  (upper trace) and  $[\text{PtPd}_2\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$  ions (lower trace) at 101.3 MHz. The lower trace also shows the presence of some tripladium cation.

dication of the intermediate formation of cluster complexes. However, repetition of the tetrahydrofuran experiments using mixtures of  $[\text{PtCl}(\text{PPh}_3)_3][\text{BF}_4]$  and  $[\text{PdCl}(\text{PPh}_3)_3][\text{BF}_4]$  did result in the heteronuclear cluster III as its  $\text{BF}_4^-$  salt. Most of our preparations used approximately equimolar mixtures of platinum and palladium substrates, but other experiments indicated that the nature of the heteronuclear product is unaffected by the relative proportions. The tripladium cluster II is naturally produced along with the heteronuclear species and we have not been successful in achieving a total separation (see Experimental Section). However, the  $^{31}\text{P}$  NMR and X-ray diffraction studies described below leave no doubt as to the identity of the heteronuclear cluster.

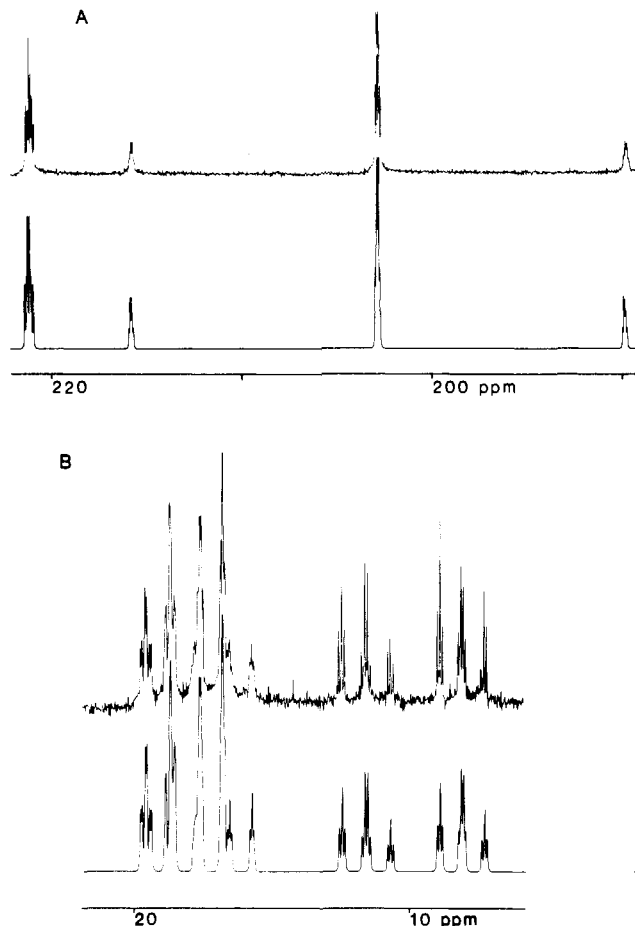
**(b) Phosphorus-31 NMR.** The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$  recorded at 101.3 MHz is shown as the upper trace in Figure 1. We have previously described this spectrum in detail at a lower frequency and, using the atom labeling shown in structure IV, found that the actual  $\text{ABB}'\text{XX}'$



spin system appeared as a deceptively simple  $\text{AB}_2\text{X}_2$  spectrum due to a relatively large value for  $^2J(\text{XX}')$ .<sup>2</sup> At 101.3 MHz the spectrum is further simplified and appears in Figure 1 as an almost first-order  $\text{AM}_2\text{X}_2$  pattern with the highest field resonance (A) due to the unique  $\text{PPh}_3$  group, the next highest (M) due to the other  $\text{PPh}_3$  groups, and the low-field resonance (X) due to the bridging  $\text{PPh}_2$  groups.

The lower trace in Figure 1 shows the spectrum obtained for the product of heating a 1:1 mixture of  $[\text{PtCl}(\text{PPh}_3)_3][\text{BF}_4]$  and  $[\text{PdCl}(\text{PPh}_3)_3][\text{BF}_4]$  in tetrahydrofuran. Comparison with the upper trace clearly shows the presence of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$  plus a second species. This second species has a very similar  $^{31}\text{P}\{^1\text{H}\}$  pattern except that the bridging  $\text{PPh}_2$  resonance and the unique  $\text{PPh}_3$  group show sidebands attributable to  $^{195}\text{Pt}$  ( $I = 1/2$ , 33.8% abundant). In each case the coupling constants (2621 and 4037 Hz, respectively) are large enough to show that these phosphorus nuclei are directly bonded to platinum. Less obvious, but apparent on careful inspection, are  $^{195}\text{Pt}$  sidebands on the  $\text{B}_2$  resonance but with a much smaller coupling constant (212.6 Hz). This coupling is consistent with a two-bond coupling, and overall the data indicate III as the correct structure for the heteronuclear complex.

Figure 2 shows the results of a detailed analysis and computer simulation of the composite spectrum of a mixture of 37%  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$  and 63%  $[\text{PtPd}_2\text{Cl}(\text{PPh}_2)_2-$



**Figure 2.** (A) Expanded-scale  $^{31}\text{P}$  NMR spectrum in the bridging phosphide region of the  $[\text{PtPd}_2\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$  ion, mixed with 37% of the corresponding tripladium cation. The upper trace shows the observed spectrum and the lower trace is a computer simulation using the parameters collected in Table VIII. (B) Expanded-scale  $^{31}\text{P}$  NMR spectrum in the terminal phosphine region of the  $[\text{PtPd}_2\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$  ion, mixed with 37% of the corresponding tripladium cation. The upper trace shows the observed spectrum and the lower trace is a computer simulation using the parameters collected in Table VIII. Note that the outermost platinum sidebands have not been included in the plots (compare Figure 1).

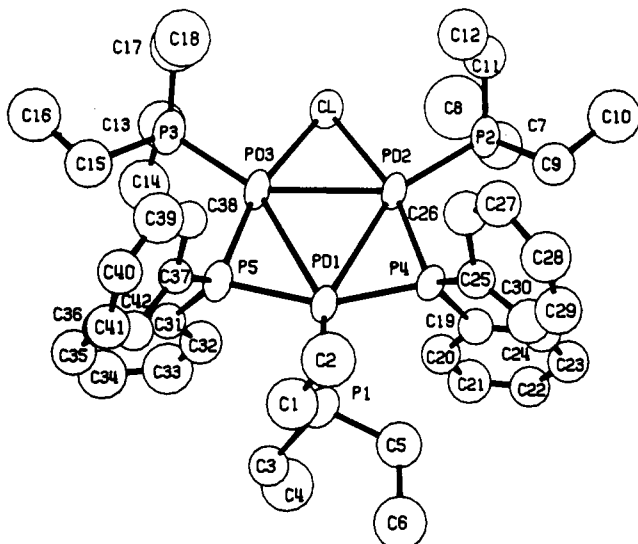
$(\text{PPh}_3)_3][\text{BF}_4]$ . The analysis follows that previously reported by us for the tripladium species,<sup>2</sup> the principal points being as follows. At 101.3 MHz the low-field  $\text{X}_2$  resonances shown in Figure 2A consist of a deceptively simple doublet [due to  $^2J(\text{AX})$ ] of triplets [due to  $1/2(^2J(\text{BX}) + ^3J(\text{BX}'))$ ], which is fully resolved for the tripladium species but overlapped for the heteronuclear cluster. The resonance of the latter also shows  $^{195}\text{Pt}$  sidebands. In the high-field A resonances shown in Figure 2B the only evidence of non-first-order character is the doubling of the central triplet. Thus estimates for  $^2J(\text{AX})$ ,  $^3J(\text{AB})$ , and  $^1J(\text{Pt-A})$  can be obtained directly from this resonance. The  $\text{B}_2$  resonances are doublets [ $^3J(\text{AB})$ ] of triplets [ $1/2(^2J(\text{BX}) + ^3J(\text{BX}'))$ ] of doublets (non-first-order character). Each set of resonances for the heteronuclear complex also exhibits  $^{195}\text{Pt}$  sidebands that provide estimates of  $^1J(\text{Pt-A})$ ,  $^1J(\text{Pt-X})$ , and  $^2J(\text{Pt-B})$ .

The preliminary parameters thus obtained were then used in conjunction with the observed line positions in a computer refinement that provided the simulated spectra shown in Figure 2 and the final refined parameters given in Table VIII. As in our previous analysis,<sup>2</sup> the only sign information concerns the relative signs of  $^3J(\text{AB})$  and  $^2J(\text{AX})$  and  $1/2(^2J(\text{BX}) + ^3J(\text{BX}'))$ . We have arbitrarily assumed that  $^3J(\text{AB})$  is positive in compiling Table VIII. The values of  $^3J(\text{BB}')$  and  $^2J(\text{XX}')$  given in Table VIII are estimates. They were held constant during the refinement and are not defined by the available data. The only limitation on their values is that they must be such as to produce the deceptively

Table II. Fractional Atomic Coordinates and Temperature Parameters for I<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> , Å <sup>2</sup>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> , Å <sup>2</sup>
Pd(1)	0.2646 (2)	-0.0035 (1)	0.3183 (1)	0.0498 (8)	C(20)	0.446 (2)	-0.073 (2)	0.438 (2)	0.075 (10)
Pd(2)	0.2398 (2)	0.0111 (1)	0.4863 (1)	0.0517 (8)	C(21)	0.531 (3)	-0.087 (2)	0.472 (2)	0.096 (12)
Pd(3)	0.2088 (2)	0.1267 (1)	0.3792 (1)	0.0553 (8)	C(22)	0.546 (2)	-0.144 (2)	0.516 (2)	0.082 (11)
Cl	0.2011 (6)	0.1257 (4)	0.5203 (5)	0.081 (4)	C(23)	0.482 (2)	-0.186 (2)	0.537 (2)	0.083 (11)
P(1)	0.2915 (6)	-0.0698 (4)	0.2116 (5)	0.070 (4)	C(24)	0.397 (2)	-0.172 (2)	0.505 (2)	0.068 (9)
P(2)	0.2356 (6)	-0.0330 (5)	0.6118 (5)	0.071 (4)	C(25)	0.205 (2)	-0.150 (2)	0.412 (2)	0.064 (9)
P(3)	0.1660 (6)	0.2386 (5)	0.3651 (6)	0.074 (4)	C(26)	0.117 (2)	-0.129 (2)	0.429 (2)	0.081 (10)
P(4)	0.2775 (5)	-0.0796 (4)	0.4209 (5)	0.052 (3)	C(27)	0.052 (2)	-0.180 (2)	0.420 (2)	0.084 (11)
P(5)	0.2306 (6)	0.0980 (4)	0.2562 (5)	0.058 (3)	C(28)	0.080 (3)	-0.248 (2)	0.405 (2)	0.102 (13)
C(1)	0.194 (3)	-0.085 (2)	0.147 (3)	0.111 (14)	C(29)	0.156 (3)	-0.266 (2)	0.398 (2)	0.091 (12)
C(2)	0.125 (3)	-0.115 (2)	0.182 (3)	0.12 (2)	C(30)	0.223 (2)	-0.221 (2)	0.407 (2)	0.082 (11)
C(3)	0.365 (2)	-0.035 (2)	0.148 (2)	0.072 (9)	C(31)	0.308 (2)	0.151 (2)	0.217 (2)	0.059 (9)
C(4)	0.456 (3)	-0.027 (3)	0.183 (3)	0.13 (2)	C(32)	0.389 (2)	0.142 (2)	0.256 (2)	0.088 (12)
C(5)	0.329 (2)	-0.153 (2)	0.240 (2)	0.090 (12)	C(33)	0.454 (3)	0.184 (3)	0.234 (3)	0.13 (2)
C(6)	0.350 (3)	-0.203 (2)	0.165 (3)	0.12 (2)	C(34)	0.435 (3)	0.234 (3)	0.172 (3)	0.12 (2)
C(7)	0.336 (3)	-0.007 (2)	0.676 (4)	0.112 (14)	C(35)	0.355 (3)	0.239 (2)	0.139 (2)	0.097 (12)
C(8)	0.336 (4)	0.068 (4)	0.697 (4)	0.21 (3)	C(36)	0.291 (2)	0.199 (2)	0.155 (2)	0.068 (9)
C(9)	0.225 (2)	-0.124 (2)	0.615 (2)	0.082 (10)	C(37)	0.139 (2)	0.094 (1)	0.185 (2)	0.051 (8)
C(10)	0.211 (3)	-0.149 (3)	0.705 (3)	0.13 (2)	C(38)	0.063 (2)	0.088 (2)	0.216 (2)	0.057 (8)
C(11)	0.154 (2)	-0.005 (2)	0.659 (2)	0.086 (11)	C(39)	-0.016 (3)	0.074 (2)	0.155 (2)	0.101 (13)
C(12)	0.068 (3)	-0.009 (2)	0.614 (3)	0.114 (14)	C(40)	-0.006 (2)	0.070 (2)	0.078 (2)	0.078 (10)
C(13)	0.244 (3)	0.297 (2)	0.416 (3)	0.112 (14)	C(41)	0.071 (2)	0.078 (2)	0.051 (2)	0.079 (11)
C(14)	0.321 (3)	0.302 (3)	0.372 (3)	0.13 (2)	C(42)	0.146 (2)	0.091 (2)	0.101 (2)	0.065 (9)
C(15)	0.140 (3)	0.273 (2)	0.259 (2)	0.103 (13)	B	0.257 (9)	0.504 (8)	0.411 (8)	0.32 (5)
C(16)	0.099 (3)	0.345 (3)	0.258 (3)	0.13 (2)	F(1)	0.278 (3)	0.460 (3)	0.474 (3)	0.26 (2)
C(17)	0.073 (3)	0.256 (2)	0.418 (3)	0.113 (14)	F(2)	0.188 (3)	0.467 (3)	0.370 (3)	0.29 (2)
C(18)	-0.005 (3)	0.210 (3)	0.384 (3)	0.14 (2)	F(3)	0.228 (3)	0.560 (3)	0.429 (3)	0.30 (2)
C(19)	0.382 (2)	-0.111 (2)	0.459 (2)	0.060 (9)	F(4)	0.320 (3)	0.490 (2)	0.381 (3)	0.35 (2)

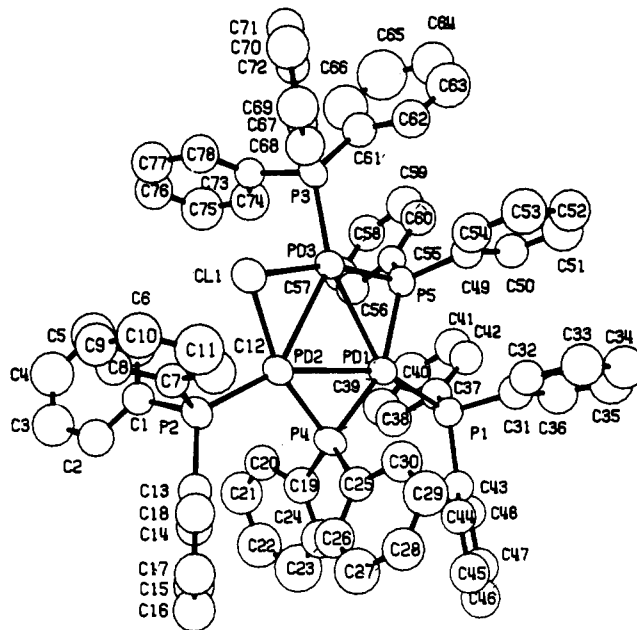
<sup>a</sup> Estimated standard deviations are given in parentheses.

Figure 3. ORTEP plot of the compound I cation, [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PET<sub>3</sub>)<sub>3</sub>]<sup>+</sup>.

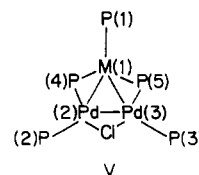
simple AB<sub>2</sub>X<sub>2</sub> pattern; i.e., <sup>2</sup>J(XX') and <sup>3</sup>J(BB') cannot have comparable magnitudes and one of them, most probably <sup>2</sup>J(XX'), must be large (>80 Hz). As in our previous analysis, the refinements tended to indicate that <sup>2</sup>J(BX) and <sup>3</sup>J(BX') are of similar magnitudes but only the mean is actually determined by the observed spectra. There are no significant differences between the parameters obtained in our previous analyses<sup>2</sup> for [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> at 24.3 and 40.5 MHz and those in Table VIII for the spectrum at 101.3 MHz.

The overall correctness of the analysis was finally confirmed by a <sup>195</sup>Pt NMR spectrum obtained at 53.4 Hz. This spectrum was centered at  $\bar{\nu} = 21\,369\,897$  Hz and consisted of a first-order doublet (<sup>1</sup>J(Pt-A)) of triplets (<sup>1</sup>J(Pt-X)) of triplets (<sup>2</sup>J(Pt-B)). The coupling constants agreed within experimental error with those derived from the <sup>31</sup>P spectrum.

(c) X-ray Diffraction Study. The structure of the M<sub>3</sub>ClP<sub>5</sub> heavy-atom core is very similar in all three cations, consisting of a triangle of metal atoms each bearing a terminal tertiary phosphine group and with two edges bridged by diphenylphosphido

Figure 4. ORTEP plot of the compound II cation, [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>.

groups and one bridged by chloride. The numbering scheme employed for this heavy-atom core is shown in structure V, and



the arrangement is illustrated in detail by the ORTEP drawings shown in Figures 3-5. Table I gives the crystal data and also some parameters concerning the experimental work and the refinement. Tables II-IV give the atomic coordinates and isotropic temperature parameters for compounds I-III. Tables V and VI give the important bond lengths and angles of the cluster cores

**Table III.** Fractional Atomic Coordinates and Temperature Parameters for II<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> , Å <sup>2</sup>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> , Å <sup>2</sup>
Pd(1)	31383 (10)	23571 (10)	38122 (6)	510 (7)'	C(38)	2599 (11)	4192 (8)	4570 (5)	87 (8)
Pd(2)	44421 (10)	23210 (11)	30752 (6)	560 (8)'	C(39)	2206 (11)	4932 (8)	4564 (5)	97 (9)
Pd(3)	26240 (10)	21594 (10)	27791 (6)	523 (7)'	C(40)	1309 (11)	4992 (8)	4577 (5)	105 (10)
Cl(1)	3832 (4)	2018 (4)	2276 (2)	78 (3)'	C(41)	805 (11)	4312 (8)	4597 (5)	94 (9)
P(1)	2692 (4)	2577 (4)	4584 (2)	59 (3)'	C(42)	1199 (11)	3572 (8)	4603 (5)	76 (7)
P(2)	5806 (4)	2526 (4)	2809 (2)	59 (3)'	C(43)	3457 (9)	2635 (10)	5117 (5)	63 (7)
P(3)	1660 (4)	2267 (4)	2133 (2)	57 (2)'	C(44)	4117 (9)	2076 (10)	5162 (5)	75 (8)
P(4)	4607 (4)	2413 (4)	3872 (2)	57 (3)'	C(45)	4671 (9)	2065 (10)	5577 (5)	98 (9)
P(5)	1817 (4)	2330 (4)	3407 (2)	53 (2)'	C(46)	4564 (9)	2613 (10)	5947 (5)	99 (9)
C(1)	5899 (11)	3458 (8)	2487 (5)	62 (7)	C(47)	3904 (9)	3171 (10)	5902 (5)	92 (9)
C(2)	6665 (11)	3892 (8)	2505 (5)	80 (8)	C(48)	3351 (9)	3182 (10)	5487 (5)	75 (7)
C(3)	6712 (11)	4598 (8)	2249 (5)	108 (10)	C(49)	1099 (9)	1534 (9)	3538 (6)	61 (7)
C(4)	5993 (11)	4870 (8)	1974 (5)	119 (10)	C(50)	445 (9)	1604 (9)	3866 (6)	71 (7)
C(5)	5226 (11)	4437 (8)	1956 (5)	122 (11)	C(51)	-61 (9)	951 (9)	3972 (6)	105 (9)
C(6)	5179 (11)	3731 (8)	2212 (5)	86 (8)	C(52)	87 (9)	229 (9)	3749 (6)	99 (9)
C(7)	6067 (9)	1796 (10)	2337 (5)	64 (7)	C(53)	741 (9)	159 (9)	3421 (6)	119 (11)
C(8)	6488 (9)	1985 (10)	1916 (5)	70 (7)	C(54)	1247 (9)	811 (9)	3315 (6)	92 (9)
C(9)	6705 (9)	1392 (10)	1593 (5)	95 (9)	C(55)	1154 (10)	3213 (7)	3377 (5)	51 (6)
C(10)	6501 (9)	609 (10)	1691 (5)	103 (9)	C(56)	1622 (10)	3916 (7)	3399 (5)	71 (7)
C(11)	6080 (9)	420 (10)	2112 (5)	129 (11)	C(57)	1190 (10)	4636 (7)	3354 (5)	77 (8)
C(12)	5863 (9)	1013 (10)	2435 (5)	100 (9)	C(58)	292 (10)	4653 (7)	3287 (5)	89 (8)
C(13)	6738 (8)	2520 (10)	3244 (5)	66 (7)	C(59)	-175 (10)	3950 (7)	3265 (5)	95 (9)
C(14)	6900 (8)	3140 (10)	3569 (5)	79 (8)	C(60)	256 (10)	3230 (7)	3310 (5)	81 (8)
C(15)	7608 (8)	3105 (10)	3901 (5)	99 (9)	C(61)	509 (8)	2315 (12)	2202 (6)	72 (7)
C(16)	8155 (8)	2451 (10)	3908 (5)	102 (9)	C(62)	123 (8)	1636 (12)	2377 (6)	87 (8)
C(17)	7993 (8)	1832 (10)	3583 (5)	93 (9)	C(63)	-770 (8)	1611 (12)	2423 (6)	123 (11)
C(18)	7284 (8)	1867 (10)	3251 (5)	87 (8)	C(64)	-1277 (8)	2264 (12)	2293 (6)	115 (10)
C(19)	5042 (10)	3314 (8)	4115 (7)	79 (8)	C(65)	-891 (8)	2942 (12)	2117 (6)	162 (14)
C(20)	4928 (10)	3989 (8)	3831 (7)	77 (8)	C(66)	1 (8)	2968 (12)	2071 (6)	130 (11)
C(21)	5217 (10)	4717 (8)	4010 (7)	116 (10)	C(67)	1666 (10)	1518 (8)	1668 (5)	53 (6)
C(22)	5621 (10)	4768 (8)	4473 (7)	129 (11)	C(68)	2257 (10)	900 (8)	1718 (5)	87 (8)
C(23)	5735 (10)	4092 (8)	4757 (7)	145 (12)	C(69)	2263 (10)	308 (8)	1367 (5)	95 (9)
C(24)	5445 (10)	3365 (8)	4578 (7)	91 (9)	C(70)	1677 (10)	334 (8)	966 (5)	99 (9)
C(25)	5203 (11)	1608 (9)	4134 (5)	67 (7)	C(71)	1086 (10)	953 (8)	916 (5)	78 (8)
C(26)	6064 (11)	1672 (9)	4303 (5)	91 (9)	C(72)	1080 (10)	1545 (8)	1267 (5)	65 (7)
C(27)	6497 (11)	1015 (9)	4497 (5)	117 (10)	C(73)	1952 (9)	3178 (8)	1848 (6)	55 (6)
C(28)	6070 (11)	294 (9)	4522 (5)	97 (9)	C(74)	1897 (9)	3870 (8)	2118 (6)	98 (9)
C(29)	5209 (11)	230 (9)	4353 (5)	113 (10)	C(75)	2231 (9)	4572 (8)	1941 (6)	118 (10)
C(30)	4775 (11)	887 (9)	4159 (5)	94 (9)	C(76)	2619 (9)	4581 (8)	1495 (6)	92 (9)
C(31)	2022 (10)	1792 (9)	4779 (6)	74 (7)	C(77)	2674 (9)	3889 (8)	1225 (6)	104 (9)
C(32)	2154 (10)	1036 (9)	4599 (6)	72 (7)	C(78)	2340 (9)	3187 (8)	1402 (6)	89 (8)
C(33)	1684 (10)	402 (9)	4772 (6)	108 (10)	F(1)	8052 (14)	2001 (16)	225 (11)	32 (2)
C(34)	1083 (10)	525 (9)	5125 (6)	110 (10)	F(2)	8767 (19)	3077 (11)	78 (11)	34 (2)
C(35)	950 (10)	1281 (9)	5305 (6)	126 (11)	F(3)	9223 (22)	2289 (20)	663 (8)	43 (2)
C(36)	1420 (10)	1915 (9)	5132 (6)	104 (9)	F(4)	9313 (19)	1931 (17)	-94 (11)	39 (2)
C(37)	2096 (11)	3512 (8)	4589 (5)	65 (7)	B(1)	8839 (11)	2325 (10)	218 (6)	61 (9)

<sup>a</sup> Estimated standard deviations are given in parentheses. Coordinates  $\times 10^n$  where  $n = 5$  for Pd and  $n = 4$  otherwise. Temperature parameters  $\times 10^4$  for Pd and  $\times 10^3$  otherwise. Primed values indicate that  $U_{eq}$  (the equivalent isotropic temperature parameter) is given.  $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i a_j (a_i a_j)$ ;  $T = \exp[-(8\pi^2 U_{iso} \sin^2 \theta) / \lambda^2]$ .

for all three compounds. Taking these data collectively, there is no doubt that the geometry is now well determined for this particular type of cluster, due largely to the inherent sensitivity of the X-ray intensities to heavy-atom positions. The bond lengths are all within the normal ranges, and the lower eight lines of Table V show agreement between the three compounds to within the accuracy of the determinations. In the top four lines of Table V, the Pd(2)–Pd(3) bond is always the shortest edge of the  $M_3$  triangle, although for compound I the difference is not significant in terms of the standard deviations, and compound III exhibits some bond shortening effects due to the presence of Pt in the M(1) site. These shortening effects seem to extend to Pd(2)–Pd(3), and since the site occupation factors and the NMR spectra give no evidence for Pt substitution at the Pd(2) and Pd(3) sites, this may be taken as evidence of electron delocalization over the metal triangle. The small difference of 0.022 (2) Å between M(1)–Pd(2) and M(1)–Pd(3) for III may be associated with asymmetry in the intramolecular interactions introduced by the PPh<sub>3</sub> on Pt(1), and this point is discussed in more detail below.

Table VII gives the bond angles at phosphorus. For the terminal phosphine groups, the angles involving metal atoms are generally larger than those subtended by two carbon atoms, but for each terminal phosphine of II and III, one of the phenyl rings has its center approximately in the  $M_3$  plane and the M–P–C angle is

strained open at  $121 \pm 1^\circ$ . On Pd(2) and Pd(3) these rings are trans to the chlorine atom, and at M(1) they are on the P(4) side. The other two phenyl groups of each terminal phosphine, and of the bridging diphenylphosphido ligands, lie above and below the  $M_3$  plane. This arrangement produces interesting asymmetric intramolecular interactions, which are clearly visible in Figures 4 and 5. On the P(1),P(5) sides the interaction is between pairs of approximately parallel phenyl ring planes whereas on the P(1),P(4) sides the phenyl ring on P(1) is approximately edge on to the nearest ring on P(4). The difference between the bond angles P(4)–M(1)–P(1) and P(5)–M(1)–P(1) is 7.3 (3)° for II and 4.0 (3)° for III in a direction reflecting the more efficient stacking on the P(5) sides. This would be a plausible intramolecular cause for the difference between the M(1)–Pd(2) and M(1)–Pd(3) bond lengths in III, but it cannot be the sole explanation since compound II has a larger angle deformation but an isosceles Pd<sub>3</sub> triangle. However, the out-of-plane distortions discussed below do suggest a satisfactory way in which the identity and stereochemical preference of M(1) can be invoked with the phenyl-ring interactions to explain the complete cluster core geometry.

Least-squares planes weighted according to the standard deviations of the atomic coordinates were calculated for the nine heavy atoms of compounds I–III, and the results are deposited

Table IV. Fractional Atomic Coordinates and Temperature Parameters for III<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> , Å <sup>2</sup>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> , Å <sup>2</sup>
Pt(1)	81223 (6)	71656 (4)	30213 (7)	409 (5)'	C(38)	3742 (10)	8993 (7)	571 (11)	103 (8)
Pd(2)	67258 (10)	80906 (7)	24558 (12)	425 (8)'	C(39)	3213 (10)	9224 (7)	-496 (11)	111 (9)
Pd(3)	84124 (10)	83651 (7)	21775 (12)	414 (8)'	C(40)	3521 (10)	9167 (7)	-1336 (11)	91 (7)
Cl	7302 (4)	9114 (3)	2126 (6)	79 (4)'	C(41)	4358 (10)	8880 (7)	-1109 (11)	132 (11)
P(1)	8798 (4)	6301 (3)	3896 (4)	51 (3)'	C(42)	4888 (10)	8650 (7)	-42 (11)	102 (8)
P(2)	5344 (4)	8488 (3)	2263 (5)	58 (3)'	C(43)	5756 (11)	9272 (7)	3349 (14)	63 (6)
P(3)	9136 (4)	9013 (3)	1424 (4)	46 (3)'	C(44)	5399 (11)	9864 (7)	3044 (14)	119 (10)
P(4)	6672 (4)	7124 (3)	3013 (4)	48 (3)'	C(45)	5795 (11)	10445 (7)	3902 (14)	132 (11)
P(5)	9212 (4)	7507 (3)	2451 (4)	49 (3)'	C(46)	6549 (11)	10452 (7)	5065 (14)	112 (9)
C(1)	8079 (9)	5679 (6)	4174 (12)	55 (5)	C(47)	6906 (11)	9859 (7)	5370 (14)	119 (10)
C(2)	7862 (9)	5865 (6)	5078 (12)	63 (6)	C(48)	6509 (11)	9269 (7)	4512 (14)	126 (10)
C(3)	7269 (9)	5412 (6)	5267 (12)	87 (7)	C(49)	8153 (7)	9189 (6)	36 (8)	43 (5)
C(4)	6892 (9)	4774 (6)	4552 (12)	94 (8)	C(50)	8248 (7)	9761 (6)	-401 (8)	54 (5)
C(5)	7109 (9)	4588 (6)	3648 (12)	90 (7)	C(51)	7506 (7)	9844 (6)	-1521 (8)	75 (6)
C(6)	7702 (9)	5041 (6)	3459 (12)	75 (6)	C(52)	6671 (7)	9355 (6)	-2203 (8)	68 (6)
C(7)	9858 (8)	6605 (7)	5411 (10)	58 (5)	C(53)	6576 (7)	8783 (6)	-1765 (8)	77 (7)
C(8)	10344 (8)	6162 (7)	6155 (10)	88 (7)	C(54)	7318 (7)	8700 (6)	-646 (8)	66 (6)
C(9)	11165 (8)	6406 (7)	7290 (10)	101 (8)	C(55)	9808 (9)	9818 (6)	2392 (12)	52 (5)
C(10)	11500 (8)	7093 (7)	7681 (10)	96 (8)	C(56)	10497 (9)	10208 (6)	2253 (12)	63 (6)
C(11)	11015 (8)	7536 (7)	6938 (10)	78 (7)	C(57)	11013 (9)	10812 (6)	3048 (12)	81 (7)
C(12)	10194 (8)	7291 (7)	5803 (10)	64 (6)	C(58)	10841 (9)	11026 (6)	3980 (12)	119 (10)
C(13)	9201 (10)	5799 (7)	3000 (12)	59 (5)	C(59)	10152 (9)	10636 (6)	4119 (12)	140 (11)
C(14)	10126 (10)	5597 (7)	3476 (12)	82 (7)	C(60)	9636 (9)	10032 (6)	3325 (12)	95 (8)
C(15)	10373 (10)	5209 (7)	2728 (12)	106 (9)	C(61)	9984 (8)	8698 (6)	963 (11)	45 (5)
C(16)	9694 (10)	5023 (7)	1503 (12)	108 (9)	C(62)	10951 (8)	8673 (6)	1837 (11)	59 (5)
C(17)	8769 (10)	5224 (7)	1027 (12)	100 (8)	C(63)	11602 (8)	8427 (6)	1503 (11)	71 (6)
C(18)	8522 (10)	5612 (7)	1775 (12)	76 (6)	C(64)	11285 (8)	8207 (6)	294 (11)	72 (6)
C(19)	6650 (9)	7171 (7)	4390 (9)	45 (5)	C(65)	10318 (8)	8232 (6)	-580 (11)	80 (7)
C(20)	7526 (9)	7440 (7)	5457 (9)	70 (6)	C(66)	9668 (8)	8478 (6)	-246 (11)	64 (6)
C(21)	7546 (9)	7506 (7)	6547 (9)	92 (8)	C(67)	9069 (10)	7051 (7)	1074 (10)	53 (5)
C(22)	6691 (9)	7304 (7)	6570 (9)	91 (7)	C(68)	9850 (10)	6955 (7)	878 (10)	74 (6)
C(23)	5816 (9)	7035 (7)	5503 (9)	94 (8)	C(69)	9660 (10)	6615 (7)	-232 (10)	98 (8)
C(24)	5795 (9)	6968 (7)	4413 (9)	63 (6)	C(70)	8690 (10)	6373 (7)	-1144 (10)	105 (8)
C(25)	5711 (9)	6461 (6)	1943 (11)	50 (5)	C(71)	7910 (10)	6469 (7)	-948 (10)	103 (8)
C(26)	5470 (9)	5887 (6)	2281 (11)	71 (6)	C(72)	8099 (10)	6809 (7)	162 (10)	82 (7)
C(27)	4730 (9)	5375 (6)	1418 (11)	105 (8)	C(73)	10505 (7)	7681 (6)	3564 (10)	49 (5)
C(28)	4230 (9)	5437 (6)	217 (11)	136 (11)	C(74)	11092 (7)	7178 (6)	3806 (10)	66 (6)
C(29)	4470 (9)	6011 (6)	-121 (11)	126 (10)	C(75)	12049 (7)	7306 (6)	4791 (10)	80 (7)
C(30)	5211 (9)	6523 (6)	742 (11)	85 (7)	C(76)	12419 (7)	7937 (6)	5533 (10)	93 (8)
C(31)	4436 (10)	7983 (7)	2458 (14)	71 (6)	C(77)	11832 (7)	8440 (6)	5291 (10)	86 (7)
C(32)	3813 (10)	7448 (7)	1533 (14)	86 (7)	C(78)	10875 (7)	8311 (6)	4306 (10)	64 (6)
C(33)	3141 (10)	7030 (7)	1656 (14)	107 (9)	B(1)	5142 (28)	2976 (24)	2267 (31)	12 (2)'
C(34)	3092 (10)	7146 (7)	2702 (14)	96 (8)	F(1)	5882 (13)	2998 (9)	1996 (15)	15 (1)'
C(35)	3715 (10)	7680 (7)	3626 (14)	122 (10)	F(2)	5332 (14)	2462 (12)	3029 (16)	17 (1)'
C(36)	4387 (10)	8099 (7)	3504 (14)	90 (7)	F(3)	4301 (14)	2663 (10)	1314 (19)	17 (1)'
C(37)	4580 (10)	8706 (7)	798 (11)	59 (5)	F(4)	5094 (21)	3509 (12)	2780 (30)	27 (3)'

<sup>a</sup> Estimated standard deviations are given in parentheses. Coordinates  $\times 10^4$  and  $n = 5$  for Pt, Pd and  $n = 4$  otherwise. Temperature parameters  $\times 10^4$  where  $n = 4$  for Pt, Pd,  $n = 3$  for Cl, P, C, and  $n = 2$  for B and F. Primed values indicate that  $U_{eq}$  (the equivalent isotropic temperature parameter) is given.  $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$ ;  $T = \exp[-(8\pi^2 U_{iso} \sin^2 \theta / \lambda^2)]$ .

Table V. Bond Lengths (Å) in the Cluster Core<sup>a</sup>

	I	II	III
M(1)-Pd(2)	2.93 (2)	2.933 (2)	2.886 (1)
M(1)-Pd(3)	2.93 (2)	2.936 (2)	2.908 (1)
Pd(2)-Pd(3)	2.89 (2)	2.906 (2)	2.878 (2)
P(1)-M(1)	2.31 (2)	2.296 (6)	2.273 (5)
P(2)-Pd(2)	2.30 (1)	2.296 (6)	2.287 (5)
P(3)-Pd(3)	2.29 (1)	2.273 (6)	2.288 (5)
P(4)-M(1)	2.27 (1)	2.274 (6)	2.274 (5)
P(4)-Pd(2)	2.22 (2)	2.204 (6)	2.201 (5)
P(5)-M(1)	2.28 (2)	2.282 (6)	2.280 (5)
P(5)-Pd(3)	2.23 (2)	2.203 (6)	2.198 (5)
Cl-Pd(2)	2.41 (1)	2.408 (6)	2.392 (5)
Cl-Pd(3)	2.41 (1)	2.394 (6)	2.389 (5)

<sup>a</sup> M(1) = Pd(1) for I and II; M(1) = 81% Pt, 19% Pd for III. Estimated standard deviations are given in parentheses.

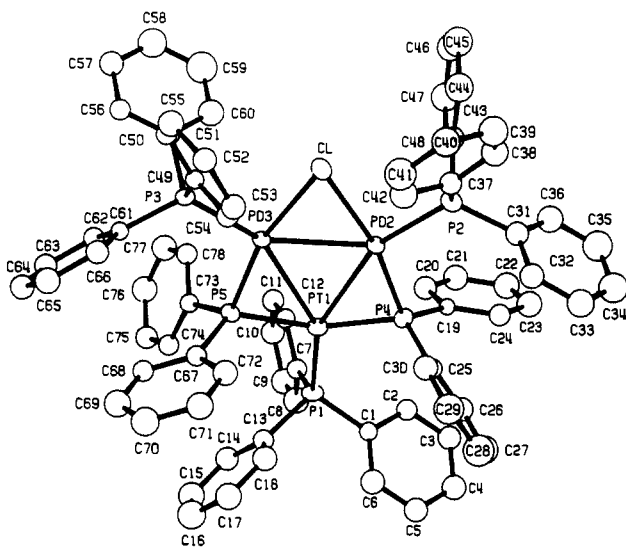
in Table S12 (supplementary material). None of these cluster cores is strictly planar ( $\chi^2 = 476, 8706, \text{ and } 13\,381$ , respectively). For compound I the maximum deviation from the plane is 0.11 Å, while for the other compounds it is 0.40 Å, a difference most probably caused by the greater steric requirements of a phenyl group compared to those of an ethyl group. Except for P(1) in compound III at -0.29 Å and Pd(4) in compound II at -0.06 Å,

all the phosphorus atoms are on the positive sides of the planes and the chlorine atoms are on the negative sides at -0.10, -0.25, and -0.40 Å for I-III, respectively. These directions may be identified in Figures 3-5 by noting that the displacement of C(40) from the plane is positive in all three structures. The marked differences between compounds II and III may be exemplified by the changes in perpendicular distances from the phosphorus atoms to the least-squares planes. For P(1)-P(5) these are -0.48, -0.27, -0.19, +0.20, and +0.08 Å, respectively. We propose that the major change involving P(1) arises because the Pt atom in III has slightly different electronic requirements from those of the Pd(1) atom in II, either with respect to coordination geometry or with respect to bond lengths. This change is transmitted asymmetrically though phenyl-ring contacts along the sides of the triangle toward Pd(2) and Pd(3), and because the groups are propeller shaped, components of the stress both parallel and perpendicular to the  $M_3$  plane are generated. In total, these effects provide an explanation both for the out-of-plane distortions and for the small observed difference of 0.022 (2) Å between the Pt-Pd(2) and Pt-Pd(3) lengths in compound III.

## Discussion

(a) **Structural Considerations.** Compounds I-III are unusual in being examples of palladium in a fractional average oxidation





**Figure 5.** ORTEP plot of the compound III cation,  $[\text{PtPd}_2\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$ .

**Table VI.** Bond Angles (deg) in the Cluster Core for Compounds I–III<sup>a</sup>

	I	II	III
Pd(2)–M(1)–Pd(3)	59.1 (8)	59.3 (1)	59.6 (1)
M(1)–Pd(2)–Pd(3)	60.3 (4)	60.4 (1)	60.6 (1)
M(1)–Pd(3)–Pd(2)	60.5 (5)	60.3 (1)	59.8 (1)
Pd(2)–Cl–Pd(3)	73.8 (8)	74.5 (2)	74.0 (1)
M(1)–P(4)–Pd(2)	81.7 (6)	81.8 (2)	80.3 (2)
M(1)–P(5)–Pd(3)	81.1 (6)	81.8 (2)	81.0 (2)
P(4)–M(1)–Pd(2)	48.3 (2)	48.0 (2)	48.7 (1)
P(5)–M(1)–Pd(3)	48.7 (3)	47.9 (2)	48.3 (1)
P(4)–Pd(2)–M(1)	50.0 (7)	50.1 (1)	51.0 (1)
P(5)–Pd(3)–M(1)	50.2 (9)	50.3 (2)	50.7 (1)
Pd(3)–Pd(2)–Cl	53.0 (4)	52.5 (1)	52.9 (1)
Pd(2)–Pd(3)–Cl	53.2 (5)	53.0 (1)	53.0 (1)
P(1)–M(1)–P(4)	102.9 (4)	105.7 (2)	104.4 (2)
P(1)–M(1)–P(5)	100.7 (4)	98.7 (2)	100.4 (2)
P(2)–Pd(2)–P(4)	101.8 (8)	104.1 (2)	104.8 (2)
P(2)–Pd(2)–Cl	95.0 (9)	93.8 (2)	91.3 (2)
P(3)–Pd(3)–P(5)	103.0 (9)	103.2 (2)	102.5 (2)
P(3)–Pd(3)–Cl	93.2 (10)	93.3 (2)	94.8 (2)

<sup>a</sup> M(1) = Pd(1) for I and II; M(1) = 81% Pt, 19% Pd for III. Estimated standard deviations are given in parentheses.

state. The only other structurally characterized species in which palladium definitely exhibits a fractional oxidation state are the triangular cation  $[\text{Pd}_3(\text{CO})(\text{dppm})_3]^{2+}$ <sup>42</sup> and the open chain anion,  $[\text{Pd}_3(\text{CNMe})_6(\text{PPh}_3)_2]^{2-}$ <sup>43</sup> with Pd–Pd distances averaging 2.598 and 2.592 Å, respectively, considerably shorter than those in compounds I–III. However, in other oxidation states, long Pd–Pd bonds are not uncommon. Examples have been observed for Pd(0) in  $[\text{Pd}_3(\text{SO}_2)_2(\text{CN}-t\text{-Bu})_5]^{41}$  and  $[\text{Pd}_4(\text{CO})_5(\text{PMePh}_2)_4]^{44}$ , 2.73–2.76 Å; Pd(I) in  $[\text{Pd}_4(\text{CO})_4(\text{OAc})_4]$ , which contains two short CO-bridged bonds, 2.663 Å, and two long acetate-bridged bonds, 2.909 Å<sup>55</sup> and Pd(II) in  $[\text{Pd}(\text{O}_2-t\text{-Bu})(\text{O}_2\text{CCl}_3)]_4$ , 2.912 and 2.933 Å.<sup>56</sup>

For triangular platinum clusters it has been suggested that short M–M distances (2.63–2.65 Å) occur in uncrowded, 42-electron species such as  $[\text{Pt}_3(\text{CN}-t\text{-Bu})_6]^{33}$  and  $[\text{Pt}_3(\text{CO})_3(\text{PCy}_3)_3]^{30}$  and that addition of 2 valence electrons (e.g.  $[\text{Pt}_3(\text{CO})_3(\text{PCy}_3)_4]$ , 2.725 Å)<sup>31</sup> or the presence of bulky bridging groups (e.g.  $[\text{Pt}_3\text{Ph}(\text{PPh}_2)_3(\text{PPh}_3)_2]$ , 2.785 Å)<sup>36</sup> produces longer bonds. Some more recent examples are difficult to rationalize within this framework

since in  $[\text{Pt}_3\text{Ph}(\text{SO}_2)(\text{PPh}_2)(\text{PPh}_3)_3]^{35}$  and  $[\text{Pt}_3(\text{SO}_2)_3(\text{PPh}_3)_3]^{32}$  the Pt–Pt distances are all relative long, 2.69–2.82 Å. Particularly puzzling are the 2.82 Å distances in  $[\text{Pt}_3\text{H}_6(\text{P}-t\text{-Bu})_3]$ , a 42-electron complex with sterically nondemanding hydride bridges.<sup>38</sup> However, long distances between metals bridged by  $\text{PPh}_2$  groups are a consistent feature of these structures and long phosphido-bridged bonds (2.86–3.02 Å) have also been noted in the rhodium cluster  $[\text{Rh}_4(\text{CO})_5(\text{PPh}_3)_5]^{-57}$ .

In general, we may conclude that although the Pd–Pd lengths in the present 44-electron complexes are relatively long at 2.89–2.936 Å, they are certainly within the normal range of Pd–Pd bonds. In particular the increase in Pd–Pd bond length from the only other structurally characterized palladium triangle,  $[\text{Pd}_3(\text{SO}_2)_2(\text{CN}-t\text{-Bu})_5]$ , which also has 44 valence electrons and  $\text{SO}_2$ -bridged M–M lengths of 2.734 Å, is consistent with the differences between  $\text{SO}_2$ - and  $\text{PPh}_2$ -bridged lengths in platinum complexes. The electronic spectrum and unusual NMR parameters that we have discussed previously<sup>2</sup> are further evidence for the occurrence of Pd–Pd bonding in the present complexes. The NMR results are discussed in more detail below.

The change induced in the phosphido-bridged M–M lengths by introducing one Pt atom is also interesting. The average values in  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$ ,  $[\text{PtPd}_2\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$ , and  $[\text{Pt}_3\text{H}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$ ,<sup>37</sup> are 2.935, 2.897, and 2.796 Å, respectively, showing a consistent shortening as Pd is replaced by Pt in the M–M interaction. This structural feature is also evident as a slight narrowing of the M–P–M bond angles from an average of 81.6° in II and III to 76.4° in the triplatinum structure. While it is commonplace that M–M bonded complexes are more abundant for the heavier elements in each transition metal triad, discrete isostructural examples showing changes in M–M lengths on descending a triad are relatively rare. Those that do exist generally show increases in bond lengths from the first-row element to the second row but essentially no change or a very slight increase from the second row to the third. Examples include the decacarbonyls of Mn, Tc, and Re, where the M–M bonds are 2.923 (3), 3.036 (6), and 3.040 (5) Å, respectively,<sup>58–60</sup> dodecacarbonyls of Ru and Os, with average M–M lengths of 2.854 and 2.877 Å, respectively,<sup>61,62</sup> and various Mo and W compounds having both single and multiple M–M bonds, the W derivatives usually having slightly longer bonds.<sup>63</sup> In cluster compounds of the present triad one may compare the isostructural  $[\text{Pd}_4(\text{PMePh}_2)_4(\text{CO})_5]$  and  $[\text{Pt}_4(\text{PMe}_2\text{Ph})_4(\text{CO})_5]$ , which have average M–M distances of 2.750 and 2.760 Å, respectively.<sup>54,64</sup>

A slight asymmetry of the metal to bridging phosphorus bonds also merits comment. Referring to structure V and Table V, we note that in clusters II and III the M(1)–P(4) and M(1)–P(5) bonds are closely similar in length, averaging 2.278 Å, but the Pd(2)–P(4) and Pd(3)–P(5) bonds are shorter, averaging 2.202 Å. The data for cluster I appear similar, but the lower accuracy of this structure makes the conclusion less certain.  $[\text{Pt}_3\text{H}(\text{PPh}_2)_2(\text{PPh}_3)_3]^+$  shows a similar asymmetry with corresponding bonds averaging 2.306 and 2.216 Å, respectively.<sup>37</sup> In clusters II and III the longer M(1)–P(4) and M(1)–P(5) bonds are comparable to the terminal M–P lengths, which average 2.286 Å. Much larger asymmetries of ca. 0.2 Å have been noted recently in two phosphido-bridged rhodium complexes  $[(\text{COD})\text{Rh}(\text{PPh}_2)_2\text{Rh}(\text{PEt}_3)_2]^{65}$  and  $[\text{Rh}(\text{PPh}_2)(\text{CO})_2]_2^{66}$ . In both of these

- (54) Dubrawski, J.; Krieger-Simonsen, J. C.; Feltham, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2089.  
 (55) Moiseev, I. I.; Stromnova, T. A.; Vargaftik, M. N.; Mazo, G. J.; Kuz'mina, L. G.; Struchkov, Y. T. *J. Chem. Soc., Chem. Commun.* **1978**, 27.  
 (56) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047.

- (57) Kreter, P. E.; Meek, D. W.; Christolph, G. G. *J. Organomet. Chem.* **1980**, *188*, C27.  
 (58) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1140.  
 (59) Gapotchenko, N. I.; Alekseev, N. V.; Kolobova, N. E.; Anisimov, K. N.; Ronova, I. A.; Johansson, A. A. *J. Organomet. Chem.* **1972**, *35*, 319.  
 (60) Gapotchenko, N. I.; Struchkov, Y. T.; Alekseev, N. V.; Ronova, I. A. *Zh. Strukt. Khim.* **1973**, *14*, 383.  
 (61) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.  
 (62) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.  
 (63) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982; p 340.  
 (64) Vranka, R. G.; Dahl, L. F.; Chini, P.; Chatt, J. *J. Am. Chem. Soc.* **1969**, *91*, 1574.  
 (65) Christolph, G. G.; Kreter, P. E.; Meek, D. W. *J. Organomet. Chem.* **1982**, *231*, C53.



Table VII. Bond Angles (deg) at the Phosphorus Atoms

I		II		III	
Angles Subtended at P(1)					
C(1),Pd(1)	109 (2)	C(31),Pd(1)	111.3 (7)	C(1),Pt(1)	120.7 (5)
C(3),Pd(1)	116 (2)	C(37),Pd(1)	108.8 (6)	C(7),Pt(1)	111.1 (5)
C(5),Pd(1)	113 (2)	C(43),Pd(1)	122.3 (6)	C(13),Pt(1)	110.5 (5)
C(1),C(3)	107 (2)	C(37),C(31)	110.0 (9)	C(13),C(7)	109.0 (7)
C(1),C(5)	104 (2)	C(43),C(31)	99.1 (7)	C(7),C(1)	101.2 (6)
C(3),C(5)	107 (2)	C(43),C(37)	104.5 (8)	C(13),C(1)	103.4 (7)
Angles Subtended at P(2)					
C(7),Pd(2)	107 (3)	C(1),Pd(2)	112.4 (6)	C(37),Pd(2)	113.0 (6)
C(9),Pd(2)	115 (2)	C(7),Pd(2)	111.0 (6)	C(43),Pd(2)	107.3 (6)
C(11),Pd(2)	112 (2)	C(13),Pd(2)	119.9 (6)	C(31),Pd(2)	120.9 (5)
C(7),C(9)	109 (2)	C(1),C(7)	102.3 (8)	C(37),C(31)	102.6 (7)
C(7),C(11)	105 (2)	C(1),C(13)	104.1 (8)	C(43),C(31)	106.4 (7)
C(9),C(11)	108 (2)	C(7),C(13)	105.3 (8)	C(43),C(37)	105.5 (8)
Angles Subtended at P(3)					
C(13),Pd(3)	111 (2)	C(61),Pd(3)	122.4 (6)	C(61),Pd(3)	121.4 (5)
C(15),Pd(3)	117 (2)	C(67),Pd(3)	118.2 (6)	C(55),Pd(3)	114.1 (5)
C(17),Pd(3)	112 (2)	C(73),Pd(3)	104.0 (5)	C(49),Pd(3)	107.3 (4)
C(13),C(15)	106 (3)	C(61),C(67)	98.4 (8)	C(49),C(61)	102.3 (6)
C(13),C(17)	102 (2)	C(61),C(73)	106.1 (9)	C(61),C(55)	103.7 (6)
C(15),C(17)	107 (3)	C(67),C(73)	106.6 (8)	C(55),C(49)	106.7 (6)
Angles Subtended at P(4)					
C(19),Pd(1)	118 (2)	C(19),Pd(1)	114.9 (6)	C(19),Pt(1)	120.8 (4)
C(19),Pd(2)	113 (2)	C(19),Pd(2)	117.2 (7)	C(19),Pd(2)	114.7 (5)
C(25),Pd(1)	116 (2)	C(25),Pd(1)	119.6 (7)	C(25),Pt(1)	115.6 (5)
C(25),Pd(2)	116 (2)	C(25),Pd(2)	112.4 (6)	C(25),Pd(2)	117.3 (5)
C(19),C(25)	110 (2)	C(19),C(25)	109.0 (9)	C(19),C(25)	106.8 (6)
Angles Subtended at P(5)					
C(31),Pd(1)	122 (1)	C(49),Pd(1)	117.8 (5)	C(67),Pt(1)	117.9 (5)
C(31),Pd(3)	114 (2)	C(49),Pd(3)	116.0 (7)	C(67),Pd(3)	112.8 (5)
C(37),Pd(1)	114 (2)	C(55),Pd(1)	119.8 (6)	C(73),Pt(1)	118.1 (5)
C(37),Pd(3)	115 (2)	C(55),Pd(3)	114.4 (5)	C(73),Pd(3)	116.3 (5)
C(31),C(37)	109 (1)	C(49),C(55)	106.0 (8)	C(67),C(73)	108.6 (6)

<sup>a</sup> Estimated standard deviations are given in parentheses.

there is one tetrahedral and one square-planar rhodium and in both cases the phosphorus bonds to the tetrahedral center are shorter than those to the planar center. It has been suggested that the bonding in the former could be described as an electron-rich d<sup>10</sup> [(PEt<sub>3</sub>)<sub>2</sub>Rh(PPh<sub>2</sub>)<sub>2</sub>]<sup>-</sup> group chelating via the lone pairs on the phosphide ligands to an electron-poor d<sup>8</sup> [Rh(COD)]<sup>+</sup> group with concurrent formation of a donor-acceptor M-M bond.<sup>65</sup> A similar interpretation could be proposed for the much smaller asymmetry found in the present clusters if some "localization" of the metal oxidation states is assumed to occur with the apical metal adopting more M(0) character and the basal palladiums adopting more Pd(II) character. The bridging phosphido groups would then be covalently bound to the basal palladiums and would act as donors to the apical metal.

However, it is probably more likely that the small effect in the present case arises because of the trans influences of the ligands most nearly trans to the affected bonds. Thus the long M(1)-P(4) and M(1)-P(5) bonds are essentially trans to each other (P-M-P averages 155.1°) whereas the short Pd(2)-P(4) and Pd(3)-P(5) bonds are essentially trans to chlorine (P-M-Cl averages 162.8°). We have previously shown by NMR studies that the bridging PPh<sub>2</sub> group has a large trans influence,<sup>29</sup> and the Pt-P coupling constants observed for III are consistent with this view.

(b) **Nuclear Magnetic Resonance Parameters.** The nuclear magnetic resonance parameters for cations I-III are collected in Table VIII together with comparison data<sup>37</sup> for [Pt<sub>3</sub>H(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, which is essentially isostructural but with a hydride bridge substituted for the chloride bridge of the present examples. In general the parameters present few surprises and require little further comment but there are three items that merit some dis-

Table VIII. Nuclear Magnetic Resonance Parameters<sup>a</sup>

	I <sup>b</sup>	II <sup>c</sup>	III <sup>d</sup>	[Pt <sub>3</sub> H(PPh <sub>2</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup> <sup>e</sup>
δ(A)	+3.3	+11.7	+8.2	+29.9
δ(BB')	+18.0	+19.2	+17.3	+61.9
δ(XX')	+204.8	+221.0	+202.7	+227.0
<sup>3</sup> J(AB)	93	89.3	82.6	86
<sup>2</sup> J(AX)	-14 <sup>f</sup>	-10.3 <sup>f</sup>	-9.6 <sup>f</sup>	17.6
<sup>1</sup> / <sub>2</sub> ( <sup>2</sup> J(BX) + <sup>3</sup> J(BX'))	15	17.0	7.3	0
<sup>3</sup> J(BB')	(25) <sup>g</sup>	(25) <sup>g</sup>	(25) <sup>g</sup>	160
<sup>2</sup> J(XX')	(400) <sup>g</sup>	(400) <sup>g</sup>	(400) <sup>g</sup>	260
<sup>1</sup> J(Pt-A)			4037	3518
<sup>2</sup> J(Pt-B)			212.6	258
<sup>1</sup> J(Pt-X)			2621	1980

<sup>a</sup> The atom-labeling scheme follows that shown in structure IV. Chemical shifts (δ) are given relative to 85% H<sub>3</sub>PO<sub>4</sub> with positive values to high field of the reference. Coupling constants (J) are in hertz. <sup>b</sup> [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>3</sub>]<sup>+</sup> at 24.3 MHz; data from ref 2. <sup>c</sup> [Pd<sub>3</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> at 101.3 MHz; present work. <sup>d</sup> [PtPd<sub>2</sub>Cl(PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> at 101.3 MHz; present work. <sup>e</sup> Data from ref 37. <sup>f</sup> Only limited sign information—see Results. <sup>g</sup> Estimated values—see Results.

ussion. First, the platinum resonance for cluster III is highly shielded. The most shielded resonance quoted by Kidd and Godfellow in their recent review<sup>47</sup> was that for the [PtI<sub>6</sub>]<sup>2-</sup> ion at -1528 ppm relative to  $\bar{\nu}(^{195}\text{Pt}) = 21.4$  MHz, and most other resonances were at much lower field. On this same scale the usual reference compound, [PtCl<sub>6</sub>]<sup>2-</sup>, is at +4521 ppm,<sup>47</sup> the triangular clusters [Pt<sub>3</sub>(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub>], studied by Moor, Pregosin, and Venanzi<sup>67,68</sup> are at about +100 ppm, and cluster III is at -1406.7

ppm. Second, we note the relatively large values (80–90 Hz) for the  $J(AB)$  coupling. In the absence of a metal–metal bond, this would be a four-bond coupling through a  $PPh_2$  bridge and thus could be compared to the  $^4J(PP)$  values (0–10 Hz) observed in the complexes  $[M_2Cl_2(PPh_2)_2(PR_3)_2]$ ,  $M = Pd$  or  $Pt$ .<sup>29</sup> The absence of a metal–metal bond in these complexes has been confirmed by an X-ray diffraction study of the  $M = Pt$ ,  $R_3 = Ph_2H$  derivative, which showed a Pt–Pt distance of 3.585 (1) Å.<sup>69</sup> The much larger coupling constants occasioned by interaction through metal–metal bonds are evident both in the present complexes and also in the about 60-Hz couplings reported for  $[Pt_3(CO)_3(PR_3)_3]$  clusters.<sup>67,68</sup>

Perhaps the most interesting NMR parameters are however the extreme downfield shifts (+200 to +230 ppm) observed for bridging phosphorus resonances, and the present clusters provided one of the first examples of this effect of a metal–metal bond on a bridging phosphorus ligand.<sup>1–3</sup> The strongly deshielding effect of the metal–metal bond is clearly seen if these values are compared with the upfield shifts (–126.7 to –138.0 ppm) found in the nonmetal–metal bonded complexes  $[M_2Cl_2(PPh_2)_2(PR_3)_2]$ ,  $M = Pd$  or  $Pt$ .<sup>29</sup> The effect seems to be general, having been noted for a variety of iron and ruthenium compounds containing phosphido bridges<sup>70,71</sup> at about the same time as our work on palladium clusters<sup>1–3</sup> and having subsequently been confirmed by several groups working with a variety of metals. Particularly striking are examples where very similar complexes are available both with and without metal–metal bonds as in the rhodium compounds  $[(COD)Rh(PPh_2)_2Rh(PEt_3)_2]$  and  $[Rh(PPh_2)(di-phos)]_2$ ,  $\delta(PPh_2) = +217$  and  $-104$ , respectively,<sup>17,65</sup> and the tungsten compounds  $[W_2(CO)_8(PPh_2)_2]$  and  $[W_2(CO)_8(PPh_2)_2]^{2-}$ ,  $\delta(PPh_2) = +180$  and  $-99$ , respectively.<sup>72</sup> The bonding in the rhodium complexes has been confirmed by X-ray diffraction studies, which show M–M distances of 2.752 and 3.471 Å, respectively.<sup>17,65</sup> A number of other studies have noted the deshielding effect of metal–metal bonds including observations of iron,<sup>21</sup> nickel,<sup>73</sup> cobalt,<sup>74,75</sup> molybdenum,<sup>76</sup> and iridium<sup>18,25</sup> dinuclear complexes and rhodium clusters.<sup>20,57</sup> A possible conflicting observation has been made by Jones and co-workers,<sup>66</sup> who have mentioned preliminary observations on  $[Rh_2((t-BuCH_2)_2P)_4(CO)_4]$ , a complex with no metal–metal bond but a deshielded

phosphorus bridge. It may be that a difference between solid-state and solution structures is involved in this example.

For various cyclic and acyclic phosphates and phosphate esters there has been a suggestion that the phosphorus chemical shift follows a bell-shaped relationship with the bond angle at phosphorus. Maximum shielding is proposed to occur at about 107° with both smaller and larger angles leading to decreased shielding.<sup>77</sup> Other authors have proposed that the effect of metal–metal bonds may also be a reflection of bond angles at phosphorus,<sup>70,71</sup> and this interpretation seems to have been generally accepted by the various groups referenced above. However, the proposed bell-shaped curve would predict deshielded phosphorus in very small rings whereas the rather few known three-membered-ring organophosphorus compounds are all highly shielded. Examples are the phosphine oxide  $(t-Bu)P(O)CH(t-Bu)CH(t-Bu)$ ,<sup>78</sup> and the phosphirans.<sup>79</sup> Moreover, for metal complexes Garrou has noted that four-member chelate rings incorporating phosphorus are normally shielded relative to larger ring chelates and analogous acyclic complexes.<sup>80</sup> Further confirmation that small rings lead to highly shielded phosphorus comes from the well-studied  $(RP)_n$  ring systems, where there is an approximately linear correlation of  $\delta(P)$  with bond angle<sup>81</sup> and there are well-defined ranges for the ring sizes:  $n = 5$ , +30 to –10 ppm;  $n = 4$ , –50 to –80 ppm;  $n = 3$ , –130 to –180 ppm.<sup>81,83</sup> It is therefore clear that the deshielding effect of metal–metal bonds is quite distinct from general bond angle and ring size effects and, bearing in mind the note of caution sounded by Jones and co-workers (see above),<sup>66</sup> the downfield shifts constitute a reliable and specific diagnostic test for the presence of metal–metal bonds.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for research grants, K. Beveridge for technical assistance in the crystal structure determinations, and C. Greenwood for recording NMR spectra.

**Registry No.** I, 65916-06-5; II, 65916-07-6; III, 96998-72-0;  $[PdCl(PPh_3)_3][BF_4]$ , 34772-26-4;  $[PtCl(PPh_3)_3][BF_4]$ , 34772-25-3.

**Supplementary Material Available:** Anisotropic temperature factors for the heavy atoms of I–III (Tables S1–S3), selected bond lengths for the light atoms of I–III (Tables S4–S6), selected bond angles for the light atoms of I–III (Tables S7–S9), intermolecular distances for II and III (Tables S10 and S11), mean planes through the nine heavy atoms for I–III (Table S12), and observed and calculated structure factor amplitudes for I–III (Tables S13–S15) (61 pages). Ordering information is given on any current masthead page.

- (68) Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* **1982**, *61*, 135.  
 (69) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349.  
 (70) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1979**, *18*, 2926.  
 (71) Carty, A. J. In "Catalytic Aspects of Metal Phosphine Complexes"; Alayea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, DC, 1982; Adv. Chem. Ser. No. 196, p 164.  
 (72) Keiter, R. L.; Madigan, M. J. *Organometallics* **1982**, *1*, 409.  
 (73) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 874.  
 (74) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1437.  
 (75) Harley, A. D.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 60.  
 (76) Petersen, J. L.; Stewart, R. P. *Inorg. Chem.* **1980**, *19*, 186.

- (77) Gorenstein, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 898.  
 (78) Quast, H.; Heuschmann, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 867.  
 (79) Chan, S.; Goldwhite, H.; Keyzer, H.; Rowsell, D. G.; Tang, R. *Tetrahedron* **1969**, *25*, 1097.  
 (80) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.  
 (81) Smith, L. R.; Mills, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3852.  
 (82) Albrand, J. P.; Cogne, A.; Robert, J. B. *J. Am. Chem. Soc.* **1978**, *100*, 2600.  
 (83) Baudler, M.; Carlsohn, B.; Kloth, B.; Koch, D. Z. *Anorg. Allg. Chem.* **1977**, *432*, 67.