

# Studies of Trinuclear Palladium Clusters by $^{31}\text{P}$ NMR Spectroscopy: Reactivity of $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$ Complexes ( $\text{R} = \text{Et}$ or $\text{Ph}$ ) and the Synthesis of $[\text{Pd}_3(\text{PPh}_2)_3(\text{PR}_3)_3][\text{BF}_4]$

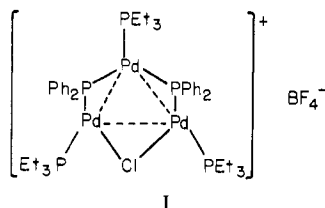
S. JAMES CARTWRIGHT, KEITH R. DIXON,\* and ALEXANDER D. RATTRAY

Received July 19, 1979

A study of the reactivity of the new palladium clusters  $[\text{Pd}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  ( $\text{R} = \text{Et}$  or  $\text{Ph}$ ) is described. The products are characterized mainly by  $^{31}\text{P}$  NMR studies, and these spectra are discussed in detail. The bridging chloride and terminal tertiary phosphine ligands are all labile, and, in particular, reaction with diphenylphosphine and *p*-toluidine leads to elimination of HCl and formation of  $[\text{Pd}_3(\mu\text{-PPh}_2)_3(\text{PR}_3)_3][\text{BF}_4]$  clusters.  $[\text{Pd}_3(\mu\text{-PPh}_2)_3(\text{PPh}_3)_3]^+$  is also formed by reaction of  $[\text{Pd}(\text{PPh}_3)_4]$  with  $[\text{Pd}_2\text{Cl}_2(\mu\text{-PPh}_2)_2(\text{PPh}_2)_2]$ . Reaction of  $[\text{Pd}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  with  $\text{H}_2\text{O}_2$  and HCl leads to a remarkable, stereospecific ring opening with oxidation of all the palladium atoms to  $\text{Pd}^{\text{II}}$ . The product, *cis,cis,cis*- $[\text{Cl}(\text{PR}_3)\text{Pd}(\mu\text{-PPh}_2)(\mu\text{-Cl})\text{Pd}(\mu\text{-PPh}_2)(\mu\text{-Cl})\text{PdCl}(\text{PR}_3)]$ , reacts with 2 mol of  $\text{PR}_3$  to yield *trans*- $[\text{PdCl}_2(\text{PR}_3)_2]$  and  $[\text{Pd}_2\text{Cl}_2(\mu\text{-PPh}_2)_2(\text{PR}_3)_2]$ . This entire oxidative degradation sequence is almost quantitative.

## Introduction

We have recently reported the synthesis and  $^{31}\text{P}$  NMR spectra of a new class of palladium cluster complexes,  $[\text{Pd}_3\text{X}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{SCF}_3$ ;  $\text{R} = \text{Et}, \text{Ph}$ ).<sup>1</sup> A preliminary X-ray diffraction study<sup>2</sup> has shown the  $\text{X} = \text{Cl}$  and  $\text{R} = \text{Et}$  derivative to have the planar structure I in which



the palladium triangle is almost equilateral with the Cl-bridged distance 289 pm and the other two Pd-Pd distances are equal at 293 pm. The average formal oxidative state of the palladium atoms is  $4/3$ , and the cluster is the first well-characterized example in a palladium oxidation state other than zero. It may be compared with the  $\text{Pd}^0$  cluster  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CN-}t\text{-Bu})_5]$ , which has an almost equilateral  $\text{Pd}_3$  triangle with shorter bond lengths (273–276 pm)<sup>3</sup> than the present cluster, and with  $[\text{Pt}_3\text{Ph}(\mu\text{-PPh}_2)_3(\text{PPh}_3)_2]$ , which has an average formal oxidation state of  $4/3$ , two short Pt-Pt distances (279 pm), and one nonbonding distance (363 pm).<sup>4</sup> The only other palladium clusters which are well characterized are examples of the  $[\text{Pd}_3(\text{CO})_3\text{L}_3]$  type, where  $\text{L} =$  tertiary phosphine.<sup>5,6</sup> Presumably these have CO-bridged, triangular structures, but no X-ray diffraction studies are available.

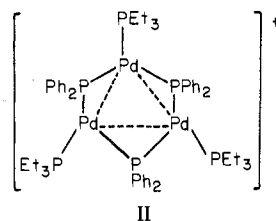
This paper describes studies of reactivity of the  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  complexes. The parent complex ( $\text{X} = \text{Cl}$ ;  $\text{R} = \text{Ph}$ ) is readily synthesized on a several gram scale,<sup>1</sup> and the results show that an extensive chemistry is accessible. Designed synthesis of these systems from monomer and dimer fragments is also a possibility. Both opportunities are unusual in cluster chemistry where products are often obtained in small quantities from essentially "chance" reactions.

## Results

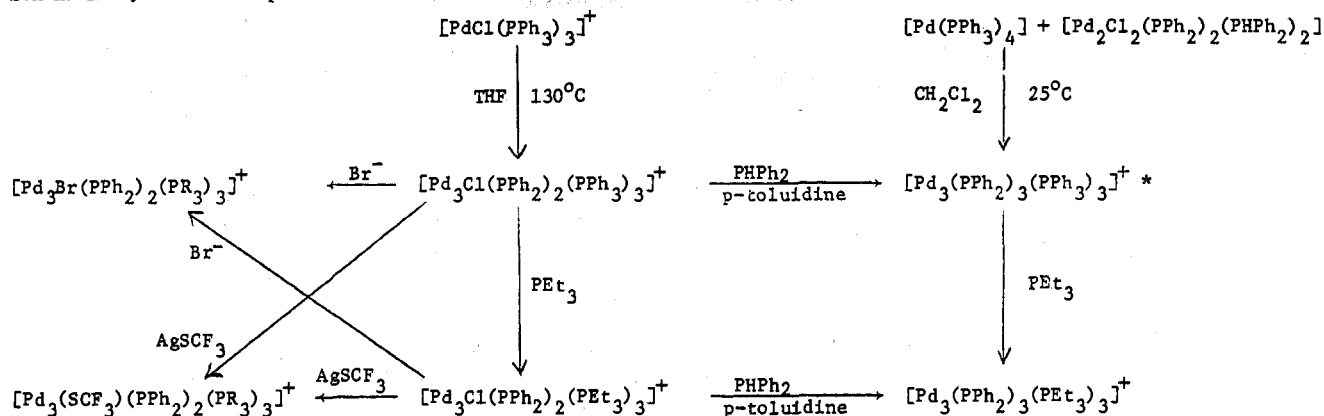
(A) **Synthesis of Tripalladium Cluster Cations.** The reactions employed to date for these syntheses are summarized in

Scheme I. As described previously,<sup>1</sup>  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$  is formed in high yield by prolonged heating of  $[\text{PdCl}(\text{PPh}_3)_3][\text{BF}_4]$  in tetrahydrofuran, and this reaction provides an entry to the chemistry of these systems. The ability of the cluster to survive phosphine-exchange reactions without cleavage, coupled with the relative lability of the bridging halide (as evidenced by the reactions with  $\text{Br}^-$  and  $\text{AgSCF}_3$ ),<sup>1</sup> suggested that a fully symmetrical, tris( $\mu$ -diphenylphosphido) derivative might be accessible by elimination of HCl between  $\text{PPh}_2$  and the  $\mu$ -chloro cluster. The reaction of  $\text{PPh}_2$  with  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$  was studied first because triethylphosphine is generally a stronger base toward palladium than is diphenylphosphine, and complications due to phosphine-exchange reactions are thus avoided. In the presence of *p*-toluidine (as HCl scavenger) reaction between  $\text{PPh}_2$  and  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$  is almost instantaneous at 25 °C, and a very dark, red-purple solid being analyzed as  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  can be isolated in high yield. As previously observed<sup>1</sup> for the  $\mu$ -chloro clusters, the color of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  is associated with a very intense electronic absorption ca. 400 nm ( $\lambda_{\text{max}} = 258, 336, 400,$  and 513 nm for  $\epsilon = 67800, 21300, 28400,$  and 14200, respectively, in ethanol solution). This suggests that the cluster unit is intact, and this is confirmed by the infrared spectrum which is very similar to that of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$  except for a complete absence of absorption in the  $\nu(\text{Pd-Cl})$  region ca. 300  $\text{cm}^{-1}$ .

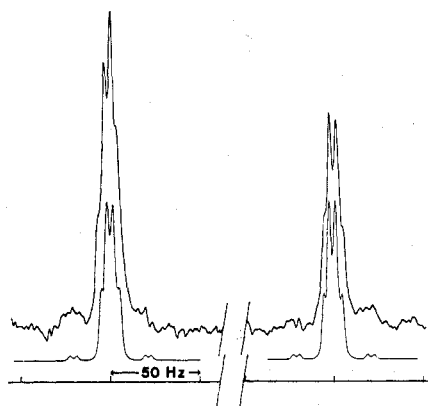
Proton-decoupled  $^{31}\text{P}$  NMR spectra of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  show only two resonances ( $\delta +13.8, -132.0$  ppm), each of which is a poorly resolved quartet ( $J \approx 3.5$  Hz) under high resolution (see Figure 1). Our previous work<sup>1</sup> showed that  $^{31}\text{P}$  NMR spectra of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$  (see structure I) can be analyzed in the  $\text{ABB}'\text{XX}'$  spin system ( $\text{A} = \text{B} = \text{B}' =$  phosphorus in terminal ligands;  $\text{X} = \text{X}' =$  phosphorus in bridging ligands).  $J_{\text{AB}} = 93$  Hz,  $J_{\text{AX}} = -14$  Hz, and  $J_{\text{XX}'} \sim 80$  Hz. Moreover, the analysis of the spectrum of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PPh}_2)] [\text{BF}_4]$  (see structure III and discussion below) yields values of  $^3J_{\text{PP}} = 78$  Hz for coupling between phosphorus atoms in terminal ligands and  $^2J_{\text{PP}} = 197$  Hz for coupling between phosphorus atoms in bridging ligands. Hence a structure such as II would belong to the



- (1) K. R. Dixon and A. D. Rattray, *Inorg. Chem.*, **17**, 1099 (1978).
- (2) G. W. Bushnell, K. R. Dixon, P. M. Moroney, A. D. Rattray, and Ch'eng Wan, *J. Chem. Soc., Chem. Commun.*, 709 (1977).
- (3) S. Otsuka, Y. Tatsumo, M. Miki, T. Aoki, M. Matsumoto, H. Yoshida, and K. Nakatsu, *J. Chem. Soc., Chem. Commun.*, 445 (1973).
- (4) N. J. Taylor, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 448 (1975).
- (5) T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, **99**, 2134 (1977).
- (6) M. Hidai, M. Kokura, and Y. Uckida, *J. Organomet. Chem.*, **52**, 431 (1973).

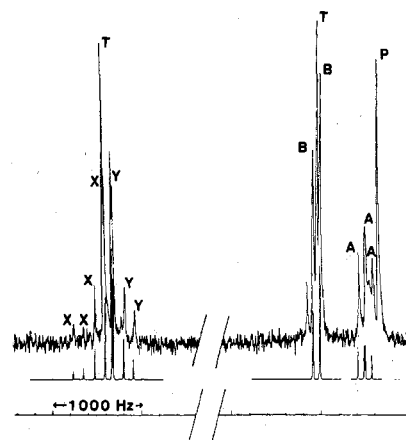
Scheme I. Syntheses of Tripalladium Cluster Cations (All Complexes Studied as  $\text{BF}_4^-$  Salts)

\* This product also contains  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PPh}_2)]^+$ , see results section.



**Figure 1.** Phosphorus-31 NMR spectrum of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  recorded at 24.3 MHz with protons decoupled. The upper trace is the experimental spectrum, and the lower trace is the computer-simulated spectrum in the AA'A'XXX'X' spin system with  $J_{AA'}$  ( $=J_{AA''}$ )  $= J_{A'A''}$   $= 80$  Hz,  $J_{XX'}$  ( $=J_{XX''}$ )  $= J_{X'X''}$   $= 200$  Hz, and all interset couplings  $< 20$  Hz.<sup>7</sup>

AA'A'XXX'X' spin system (A = terminal; X = bridging) with  $J_{AA'}$  ( $=J_{AA''}$ ) and  $J_{XX'}$  ( $=J_{XX''}$ ) both relatively large and the couplings between A and X sets all relatively small. Under these conditions the AA'A'XXX'X' system appears as a deceptively simple  $A_3X_3$  spectrum (i.e., two quartets) with apparent  $J = 1/3(J_{AX} + J_{AX'} + J_{AX''})$ . The computer simulation shown in Figure 1 was achieved by using  $J_{AA'} = 80$  Hz,  $J_{XX'} = 200$  Hz,  $1/3(J_{AX} + J_{AX'} + J_{AX''}) = 3.5$  Hz, and all individual interset values ( $J_{AX}$  etc.) less than 20 Hz.<sup>7</sup> Since the only observable is the 3.5-Hz separation, all of the individual couplings are estimates and are not well determined by the spectrum. However, it is clear from Figure 1 that the observed spectrum supports the assignment of structure II to the cation in  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$ . The low field reso-



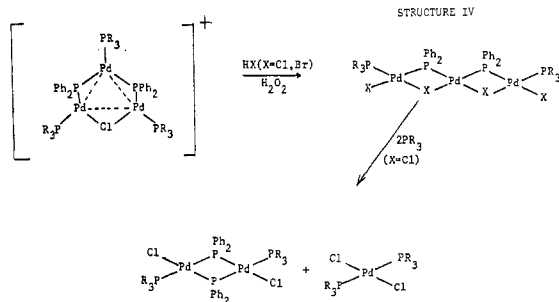
**Figure 2.** Phosphorus-31 NMR spectrum of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PHPh}_2)][\text{BF}_4]$  recorded at 24.3 MHz with protons decoupled. The upper trace is the experimental spectrum (P =  $\text{PPh}_3$ ; T =  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3]^+$ ), and the lower trace is the computer-simulated spectrum of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PHPh}_2)]^+$  in the ABB'XXY' spin system with  $J_{AB} = 78$  Hz,  $J_{XY} = 197$  Hz,  $J_{BB'} = 80$  Hz,  $J_{Y'Y''} = 200$  Hz, and all interset couplings  $< 10$  Hz.<sup>7</sup>

nance ( $\delta +13.8$ ) is assigned to the  $\text{PPh}_2$  groups and the high field resonance ( $\delta -132.0$ ) to the  $\text{PEt}_3$  groups.

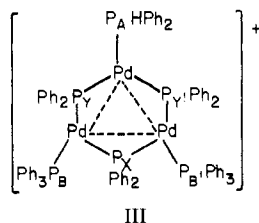
The reaction of  $\text{PPh}_2$  and *p*-toluidine with  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$  is more complex since diphenylphosphine is a stronger base for palladium than is triphenylphosphine, and displacement can occur. The infrared spectrum of the product is similar to that of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$  except for the complete absence of absorption in the  $\nu(\text{Pd}-\text{Cl})$  region and the presence of a new medium intensity band at  $850\text{ cm}^{-1}$ . Absorption in this latter region is typical of secondary phosphine complexes and may be assigned as a P-H deformation mode.<sup>8</sup> Very weak absorption in the  $\nu(\text{P}-\text{H})$  region ca.  $2300\text{ cm}^{-1}$  is also detectable. The  $^{31}\text{P}$  NMR spectrum of the product is shown in Figure 2. The peak labeled P is due to triphenylphosphine, and the peaks labeled T are assigned to the  $\text{PPh}_2$  groups ( $\delta +24.6$ ) and  $\text{PPh}_3$  groups ( $\delta -117.0$ ) of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{BF}_4]$  with a structure analogous to II above. The remaining peaks can be assigned as two  $\text{AB}_2$  systems (labeled ABB and XYY in Figure

(7) Neither the spectrum of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  nor that of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PHPh}_2)][\text{BF}_4]$  provides any definite information as to the values of the interset couplings ( $J_{AX}$ ,  $J_{AX'}$ ,  $J_{AX''}$ , etc. in the former case and  $J_{AX}$ ,  $J_{BY}$ , etc. in the latter case) although the observed line widths do set certain limits (see Figures 1 and 2). The observed  $J_{AX}$  of  $-14$  Hz in  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$  suggests a small magnitude for these couplings, and the very small magnitude of  $1/3(J_{AX} + J_{AX'} + J_{AX''})$  (3.5 Hz in  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$ ) further suggests that fortuitous cancellation of coupling constants of opposite sign may occur. At the line widths and resolution prevailing in the observed spectra the actual values of these interset couplings do not affect the computer simulations provided they are kept small.

(8) Present work; D. E. C. Corbridge, *Top. Phosphorus Chem.*, **6**, 235 (1969).

**Scheme II.** Oxidative Degradation of Triphalladium Cluster Cations (R = Ph or Et)

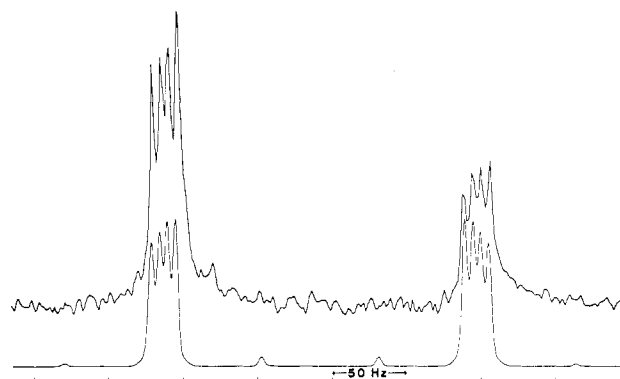
2), the low field set ( $\delta_X + 28.8$ ,  $\delta_Y + 18.0$ ;  $J_{XY} = 197$  Hz) being much more closely coupled than the high field set ( $\delta_A - 139.2$ ,  $\delta_B - 116.9$ ;  $J_{AB} = 78$  Hz). These two systems are assigned to structure III which belongs to the ABB'XYY' spin system.



The ABB' and XYY' systems appear as deceptively simple AB<sub>2</sub> and XY<sub>2</sub> systems because of large  $J_{BB'}$  and  $J_{YY'}$  couplings similar to the situation in  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$ <sup>1</sup> and  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  (above). Computer simulations and refinement of the spectrum on this basis (ABB'XYY' spin system;  $J_{AB} = 78$  Hz,  $J_{XY} = 197$  Hz,  $J_{BB'} = 80$  Hz,  $J_{YY'} = 200$  Hz; all intersite couplings,  $J_{AY}$ ,  $J_{BX}$ , etc., less than 10 Hz<sup>7</sup>) gave accurate fitting of all the principal lines and correct prediction of the positions of the two weakest X components. The small intersite (i.e.,  $J_{AY}$ ,  $J_{BX}$ , etc.) couplings are not resolved in Figure 2 (cf.  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  above).<sup>7</sup> This rather complex spectrum thus provides an excellent proof of the basic structure of these triphalladium systems. Further confirmation of the correctness of the assignments was provided by reaction of the above product mixture (i.e.,  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{BF}_4]$  and  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PPhPh}_2)][\text{BF}_4]$ ) with excess  $\text{PEt}_3$  to yield  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  as the only palladium containing product.

The preceding reactions are a satisfactory entry to the chemistry of these systems but are limited to synthesis of  $\text{PPh}_2$  (or possibly  $\text{PR}_2$  where R = aryl) bridged compounds. The bridging group is generated by cleavage of a phosphorus-phenyl bond, and phosphorus-alkyl bonds are not readily broken in this manner. A potentially more general synthesis was suggested by the oxidative degradation of the cluster described below (Scheme II). Thus a combination of a monomeric Pd<sup>0</sup> compound with a dimeric,  $\text{PR}_2$ -bridged Pd<sup>II</sup> compound (essentially the reverse of Scheme II) gives the correct average oxidation state and a possible cluster synthesis. The reaction of  $[\text{Pd}(\text{PPh}_3)_4]$  with  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPhPh}_2)_2]$  demonstrates the feasibility of this route (Scheme I). The initially yellow solutions in  $\text{CH}_2\text{Cl}_2$  immediately become dark red on mixing and  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{Cl}]$  is formed together with traces of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PPhPh}_2)][\text{Cl}]$ . Yields of the cluster complexes are relatively low because of the formation of the very insoluble  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  by phosphine exchange between the reactants.

**(B) Oxidative Degradation of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  (R = Et, Ph).** The reactions described in this section are summarized in Scheme II. Treatment of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  complexes with excess hydrochloric or hydrobromic acid results in slow degradation of the cluster to a



**Figure 3.** Phosphorus-31 NMR spectrum of  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$  recorded at 24.3 MHz with protons decoupled. The upper trace is the experimental spectrum, and the lower trace is the computer-simulated spectrum in the AA'XX' spin system with  $J_{AX} = 20.8$  Hz,  $J_{AX'} = -4.7$  Hz,  $J_{AA'} = 0.2$  Hz, and  $J_{XX'} = 64.1$  Hz. These parameters are not uniquely determined by the observed spectrum and are intended only as an illustration (see Results).

mixture of products. The reaction is faster if oxygen is present and if an  $\text{H}_2\text{O}_2/\text{HX}$  mixture is used an essentially quantitative reaction occurs in which 1 mol of tertiary phosphine is liberated from the cluster and oxidized to  $\text{POR}_3$  and all the palladium atoms are oxidized to the II oxidation state. Microanalytical data and osmometric molecular weight measurements in  $\text{CH}_2\text{Cl}_2$  solution suggest the formulation  $[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PR}_3)_2]$  for the palladium containing products. They are nonelectrolytes in nitromethane solution and are yellow in color rather than the characteristic deep red of the clusters. In our previous work<sup>1</sup> we considered a medium intensity infrared absorption ca. 388  $\text{cm}^{-1}$  to be characteristic of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  clusters, and this absorption is also present in the  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PR}_3)_3][\text{BF}_4]$  clusters discussed above. Infrared spectra of the  $[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PR}_3)_2]$  complexes show a weak absorption at about this frequency, but it is much reduced in intensity relative to the cluster spectra. Another change is that the  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PR}_3)_2]$  complexes show relatively strong absorption in the  $\nu(\text{Pd}-\text{Cl})$  region ca. 290  $\text{cm}^{-1}$  whereas the corresponding absorption in  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  complexes is very weak. These preliminary data thus suggest that the trinuclear cluster is not intact in the  $[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PR}_3)_2]$  complexes.

$[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PPh}_3)_2]$  is too insoluble for NMR study, but a 220 MHz proton spectrum of  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$  confirms the phenyl:ethyl ratio and also the chemical equivalence of the  $\text{PEt}_3$  groups. High-field spectra were used because our previous work<sup>1</sup> had shown that 220-MHz spectra were required to resolve the chemical inequivalence of the  $\text{PEt}_3$  groups in  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$ . The ethyl region of the  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$  spectrum consists of a clearly resolved doublet of triplets at  $\tau$  9.19 ( $J_{\text{P}-\text{CH}_3} = 18.0$  Hz,  $J_{\text{H}-\text{H}} = 7.6$  Hz) and a doublet of quartets at  $\tau$  8.65 ( $J_{\text{P}-\text{CH}_2} = 10.5$  Hz,  $J_{\text{H}-\text{H}} = 7.6$  Hz), indicating that no other phosphorus atoms are strongly coupled to these protons. The proton-decoupled <sup>31</sup>P NMR spectrum of  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$  is shown in Figure 3. The two 1:1:1:1 quartets at  $\delta$  -106.5 and -115.2 may be assigned to  $\text{PEt}_3$  and  $\text{PPh}_2$  groups, respectively, by selective irradiation of alkyl and aryl protons. Separation of the innermost lines is 5.2 Hz and separation of the outermost lines is 16.5 Hz in both quartets.

Clearly this <sup>31</sup>P spectrum is not first order, and, since the <sup>1</sup>H spectrum shows two chemically equivalent  $\text{PEt}_3$  groups, it seems most likely that the <sup>31</sup>P spectrum is a special case of the AA'XX' spin system. In general, spectra in the AA' region of this system consist of a strong doublet (separation  $J_{AX} + J_{AX'}$ ) and two symmetrical quartets centered on  $\delta_A$ .<sup>9</sup> An

identical spectrum appears in the  $XX'$  region centered on  $\delta_X$ . Examination of the transition energies<sup>9</sup> shows that when  $J_{AA'} = 0$  (i.e.,  $\leq$  resolution of observed spectrum), the two quartets are superimposed and the inner lines of the quartets and the strong doublet dominate the spectrum to give basically a four-line spectrum as observed for  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PET}_3)_2]$ . Since only two parameters (the separations of inner and outer pairs of lines) can be observed and there are four coupling constants, it is evident that a unique analysis is not possible.<sup>10</sup> However, the spectrum is readily computer refined and simulated by using reasonable sets of coupling constants,<sup>10</sup> and an example of such a simulation is shown in Figure 3. It is clear that  $J_{AX}$  and  $J_{AX'}$  must be relatively small ( $<$ ca. 50 Hz) because of the small values of the line separations.<sup>11</sup> Thus there can be no phosphorus atoms in mutually trans configurations, and this suggests structure IV in Scheme II as the correct assignment with the  $\text{PR}_3$  groups being the  $AA'$  groups and the  $\text{PPh}_2$  groups being  $XX'$ .

Thus the reaction of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3]^+$  with  $\text{H}_2\text{O}_2/\text{HX}$  is a remarkable, stereospecific, nearly quantitative, oxidative ring opening. The structures of the products are further confirmed by their reactions with tertiary phosphine.  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PPh}_3)_2]$  reacts with  $\text{PPh}_3$  (2 mol) to give near quantitative conversion to a 1:1 mixture of  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  and *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ . These products can be separated by toluene extraction of the monomer and identified by infrared spectroscopy, but they are too insoluble for NMR study. Reaction of  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PET}_3)_2]$  with  $\text{PET}_3$  (2 mol) gives a mixture which is difficult to separate, but <sup>31</sup>P NMR shows only  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PET}_3)_2]$  and *trans*- $[\text{PdCl}_2(\text{PET}_3)_2]$  in an approximately 1:1 ratio. The <sup>31</sup>P NMR spectrum of  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PET}_3)_2]$  has been reported previously.<sup>11,12</sup> It is another example of the  $AA'XX'$  spin system but with large couplings between the mutually trans  $\text{PET}_3$  and  $\text{PPh}_2$  groups ( $J_{AX} = 407$  Hz,  $J_{AX'} = 32.3$  Hz,  $J_{XX'} = 291$  Hz,  $J_{AA'} < 5$  Hz;  $\delta_A -125.0$ ,  $\delta_X -268.3$ ). The spectrum of *trans*- $[\text{PdCl}_2(\text{PET}_3)_2]$  is a single line identified by comparison of its chemical shift with that of authentic samples.

## Discussion

The best known examples of triangular metal atom clusters are the rhenium(III) halides (e.g.,  $[\text{Re}_3\text{Cl}_9(\text{PR}_3)_3]$ ) and the carbonyl complexes,  $[\text{M}_3(\text{CO})_{12}]$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ).<sup>13</sup> The rhenium complexes are generally considered to have double bonds between the metal atoms and the carbonyls single bonds, giving an 18-electron configuration at each metal atom in all the complexes. The platinum and palladium triangles  $[\text{M}_3(\text{CO})_3\text{L}_3]$ ,<sup>5,6,14</sup>  $[\text{Pd}_3(\text{SO}_2)_2(\text{CN}-t\text{-Bu})_3]$ ,<sup>3</sup> and  $[\text{Pt}_3(\text{CN}-t\text{-Bu})_6]$ <sup>15</sup> have 16-electron configurations at each metal if the M-M bonds are assumed to be single. The  $[\text{M}_3(\text{CO})_3\text{L}_4]$  ( $\text{M} = \text{Pd}, \text{Pt}$ )<sup>16</sup> complexes have 18-electron configurations at the metal carrying two terminal ligands and 16-electron configurations

at the other metal atoms. In molecular orbital terms most three-atom metal clusters are expected to have 48 valence electrons, corresponding to the occupation of 24 cluster valence molecular orbitals (CVMOs) with three very high molecular orbitals (an  $e'$  set and an  $a_2'$ ) left unoccupied.<sup>17</sup> However the platinum and palladium clusters noted above typically have only 42 or 44 valence electrons, and the recently characterized<sup>18</sup>  $[\text{Pt}_3(\text{CO})_6]^{2-}$  anion is also a 44-electron species. The highest lying of the CVMOs (an  $e'$  set) are unoccupied in the 44-electron compounds, and in the 42-electron species an  $a_2'$  level is also unoccupied.<sup>17</sup> The  $[\text{Pd}_3\text{X}(\text{PPh}_2)_2(\text{PR}_3)_3]^+$  cations are members of the 44-electron series, and in valence bond terms it is possible to regard the unique palladium atom (see structure I) as approximately  $\text{Pd}^0$  with an 18-electron configuration and the other palladiums as approximately  $\text{Pd}^{\text{II}}$  with 16-electron configurations. It should however be noted that we do not intend to suggest that this is the only contributing structure or that a unique assignment of oxidation states is possible in such a cluster. In the more symmetrical,  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PR}_3)_3]^+$  cluster cations (see structure II), it is clear that only average oxidation states can be assigned.

Both the rhenium complexes and the Fe, Ru, and Os carbonyls mentioned above show facile exchange of terminal ligands,<sup>12</sup> and hence the phosphine-exchange reactions in Scheme I are to be expected. The facile exchange of bridging halogen in the  $[\text{Pd}_3\text{X}(\text{PPh}_2)_2(\text{PR}_3)_3]^+$  cations is somewhat more surprising since the bridging chlorides in trirhenium clusters are not exchanged by radiochlorine<sup>19</sup> or  $\text{HBr}$ .<sup>20</sup> There seems to be no precedent for the remarkable, stereospecific ring opening shown in Scheme II. However the platinum(0) and palladium(0) complexes,  $[\text{M}(\text{PPh}_3)_4]$ , are known to catalyze the oxidation of triphenylphosphine.<sup>21</sup> Thus if the unique palladium does have significant  $\text{Pd}^0$  character in the electronic structure of the  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PR}_3)_3]^+$  cations, it is understandable that the unique tertiary phosphine (coordinated to an approximately  $\text{Pd}^0$  center) is more labile than the other two and is readily oxidized. In contrast, we have attempted reduction of the cluster cations with a wide variety of reagents including  $\text{N}_2\text{H}_4$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SnCl}_2$ ,  $\text{Na}/\text{Hg}$ , and  $\text{Zn}/\text{Hg}$ . Although generalized decomposition occurred in some reactions, in no case were we able to isolate reduced cluster species, a result which is consistent with the molecular orbital treatments described above<sup>17</sup> since the unoccupied  $e''$  orbitals of the 44-electron cluster are relatively high in energy.

Finally, we note the potentially great interest of the synthesis of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3]^+$  from  $[\text{Pd}(\text{PPh}_3)_4]$  and  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_2)_2]$ . This is a rare example of a designed cluster synthesis and suggests the possibility of a general reaction  $[\text{M}(\text{PR}_3)_4] + [\text{M}_2\text{X}_2(\text{PR}'_2)_2(\text{PR}''_3)_2]$ , leading to an extensive range of platinum and palladium clusters. This area of chemistry is currently under active investigation in our laboratories.

## Experimental Section

Our general techniques and instrumentation have been described previously.<sup>1</sup> Phosphorus-31 NMR spectra were recorded in dichloromethane solution at 24.29 MHz on a Nicolet TT14 Fourier transform spectrometer.  $[\text{P}(\text{OCH}_3)_3]$  was used as external reference and  $\text{C}_6\text{D}_6$  as external lock. Negative chemical shifts are upfield from the reference. Most usually 8192 data points were used in a 6-kHz sweep, giving resolution of 1.46 Hz, and data are thus subject to errors of this magnitude. Protons were decoupled by broad band ("noise")

- (9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959, p 141.
- (10) For example, either of the following parameter sets gives a satisfactory fit to the observed spectrum: (i)  $J_{AX} = 20.8$  Hz,  $J_{AX'} = -4.7$  Hz,  $J_{AA'} = 0.2$  Hz,  $J_{XX'} = 64.1$  Hz; (ii)  $J_{AX} = 12.0$  Hz,  $J_{AX'} = 4.6$  Hz,  $J_{AA'} = 0.04$  Hz,  $J_{XX'} = 2.7$  Hz.
- (11) Small separations could arise fortuitously if  $J_{AX}$  and  $J_{AX'}$  were individually large but coincidentally nearly equal in magnitude. However this assumption leads to absurd values for the other parameters: e.g., if  $J_{AX} = 100$  Hz and  $J_{AX'} = -84$  Hz, then a value of  $J_{XX'} \approx 3400$  Hz is required to produce the observed spectrum.
- (12) K. O'Dell, D.Phil. Thesis, University of Sussex, 1975.
- (13) R. B. King, *Prog. Inorg. Chem.*, **15**, 287 (1972), and references therein.
- (14) J. Chatt and P. Chini, *J. Chem. Soc., Dalton Trans.*, 1538, 1542 (1970).
- (15) M. Green, J. A. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 3 (1975).
- (16) A. Albinati, G. Carturan, and A. Musco, *Inorg. Chim. Acta*, **16**, L3 (1976).

- (17) J. W. Lauher, *J. Am. Chem. Soc.*, **100**, 5305 (1978).
- (18) G. Longoni and P. Chini, *J. Am. Chem. Soc.*, **98**, 7225 (1976).
- (19) B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964).
- (20) M. Elder, G. J. Gainsford, M. D. Papps, and B. R. Penfold, *J. Chem. Soc., Chem. Commun.*, 731 (1969).
- (21) G. Wilke, H. Schott, and P. Heinbach, *Angew. Chem., Int. Ed. Engl.*, **6**, 92 (1967). J. Halpern and A. L. Pickard, *Inorg. Chem.*, **9**, 2798 (1970).

irradiation at the appropriate frequencies. Simulated NMR spectra were calculated by using the UEAITR program<sup>22</sup> on an IBM 370/158 computer and plotted on a Calcomp 563 drum plotter by using a program based on the NMRPLOT program.<sup>23</sup>

The cluster complexes  $[\text{Pd}_3\text{X}(\text{PPh}_2)_2(\text{PR}_3)_3][\text{BF}_4]$  ( $\text{X} = \text{Cl, Br, SCF}_3$ ;  $\text{R} = \text{Et, Ph}$ ) were prepared as previously described,<sup>1</sup> as was  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PHPh}_2)_2]$ .<sup>24</sup> All reactions were conducted at ambient temperature (ca. 25 °C) under an atmosphere of dry nitrogen by using reagent grade solvents dried by Type 4A molecular sieves. The  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PR}_3)_3][\text{BF}_4]$  and  $[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PR}_3)_2]$  complexes were stable to the atmosphere in the solid state although the former are best stored under nitrogen. Solutions of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PR}_3)_3]^+$  salts were air sensitive, and reaction workups were carried out under a nitrogen atmosphere.

**$[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$ .** Diphenylphosphine (0.045 mL, 0.25 mmol) and *p*-toluidine (0.025 g, 0.23 mmol) were added to a stirred solution of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$  (0.264 g, 0.23 mmol) in  $\text{CH}_2\text{Cl}_2$ . After 2½ h, the dark red solution was evaporated in vacuo; the residue was extracted with tetrahydrofuran, and pentane was added to the filtered extract until precipitation just began. Cooling to 0 °C for 15 h gave the complex as deep burgundy crystals (0.207 g, 0.16 mmol), 170–175 °C. Anal. Calcd for  $\text{C}_{54}\text{H}_{75}\text{BF}_4\text{P}_6\text{Pd}_3$ : C, 49.3; H, 5.7; P, 14.1. Found: C, 49.2; H, 6.0; P, 13.9.

**Reaction of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)][\text{BF}_4]$  with  $\text{PHPh}_2$ /*p*-Toluidine.** The procedure was exactly analogous to that described above for the preparation of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$  except that the reactant was  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)][\text{BF}_4]$  (0.095 g, 0.059 mmol) and reaction was for 4½ h. The dark purple product (0.095 g, ca. 0.056 mmol) was shown by <sup>31</sup>P NMR (see Results) to be an approximately 1:3 mixture of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{BF}_4]$  and  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PHPh}_2)][\text{BF}_4]$ . Anal. Calcd for  $\text{C}_{90}\text{H}_{75}\text{BF}_4\text{P}_6\text{Pd}_3$ : C, 61.8; H, 4.3. Calcd for  $\text{C}_{84}\text{H}_{71}\text{BF}_4\text{P}_6\text{Pd}_3$ : C, 60.3; H, 4.3. Found: C, 60.9; H, 4.5. A sample of this product mixture was treated with excess  $\text{PEt}_3$  in tetrahydrofuran solution. Addition of pentane to the resulting solution gave a dark red precipitate which was shown by <sup>31</sup>P NMR to be pure  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$ .

**Reaction of  $[\text{Pd}(\text{PPh}_3)_4]$  with  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PHPh}_2)_2]$ .** Solutions of  $[\text{Pd}(\text{PPh}_3)_4]$  (0.22 g, 0.19 mmol) and  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PHPh}_2)_2]$  (0.20 g, 0.19 mmol) in dichloromethane were mixed. The mixture immediately became red-brown in color and was evaporated in vacuo. The resulting solid was extracted with tetrahydrofuran and pentane added to the filtered extract. Cooling to 0 °C gave  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{Cl}]$  as dark purple precipitate (0.05 g, 0.03 mmol). Anal. Calcd for  $\text{C}_{90}\text{H}_{75}\text{ClP}_6\text{Pd}_3$ : C, 63.7; H, 4.5. Found: C, 63.6; H, 4.5. The residue from the tetrahydrofuran extraction was a yellow solid identified by infrared spectroscopy as  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  (0.13 g, 0.11 mmol).

<sup>31</sup>P NMR spectra of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{Cl}]$  obtained as above always showed impurity peaks at  $\delta$  -59.6 and -122, and in one preparation  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PHPh}_2)]^+$  was also present. The identity of  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{Cl}]$  was therefore confirmed by reacting a sample with triethylphosphine (3 mmol). Triphenylphosphine was displaced, and the principal product, identified by <sup>31</sup>P NMR, was  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{Cl}]$ .

**$[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PR}_3)_2]$  Complexes.  $\text{X} = \text{Cl}$ ;  $\text{R} = \text{Ph}$ .** Hydrogen peroxide (30%, 0.1 mL) and concentrated hydrochloric acid (0.2 mL) were added to a stirred solution of  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$  (0.21 g, 0.13 mmol) in acetone (10 mL). After 1 h, the complex was collected as a yellow precipitate (0.16 g, 0.12 mmol). The filtrate was concentrated and filtered and water added to precipitate  $[\text{POPh}_3\text{H}_2\text{O}_2]$  (0.035 g, 0.11 mmol), identified by comparison of its infrared spectrum with that of an authentic sample.<sup>25</sup> Anal. Calcd for  $\text{C}_{60}\text{H}_{50}\text{Cl}_4\text{P}_4\text{Pd}_3$ : C, 53.1; H, 3.7; Cl, 10.5; P, 9.1. Found: C,

52.4; H, 3.8; Cl, 9.4; P, 9.3. Molecular weight: calcd, 1356; found, 1203.

$\text{X} = \text{Cl}$ ;  $\text{R} = \text{Et}$ . This preparation was similar except that  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$  (0.32 g, 0.27 mmol) was used. After 10 min, diethyl ether (5 mL) was added and the reaction mixture cooled to 0 °C for 15 h to yield the complex as yellow crystals (0.25 g, 0.23 mmol). Anal. Calcd for  $\text{C}_{36}\text{H}_{50}\text{Cl}_4\text{P}_4\text{Pd}_3$ : C, 40.5; H, 4.7; Cl, 13.3; P, 11.6. Found: C, 40.6; H, 4.9; Cl, 12.2; P, 11.6. Molecular weight: calcd, 1068; found, 1056.

$\text{X} = \text{Br}$ ;  $\text{R} = \text{Ph, Et}$ . These complexes were similarly prepared in similar yields but by using concentrated HBr instead of concentrated HCl. Anal. Calcd for  $\text{C}_{60}\text{H}_{50}\text{Br}_4\text{P}_4\text{Pd}_3$ : C, 47.0; H, 3.3; Br, 20.8; P, 8.1. Found: C, 47.5; H, 3.6; Br, 19.7; P, 8.2. Molecular weight: calcd, 1534; found, 1474. Anal. Calcd for  $\text{C}_{36}\text{H}_{50}\text{Br}_4\text{P}_4\text{Pd}_3$ : C, 34.7; H, 4.1; Br, 25.7; P, 9.9. Found: C, 34.8; H, 4.2; Br, 24.2; P, 9.1. Molecular weight: calcd, 1246; found, 1276.

The  $[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PPh}_3)_2]$  complexes were too insoluble and the  $[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$  complexes too unstable in solution for effective recrystallization. The consistently low values for halide analyses probably represent an analytical problem but could also be due to contamination, e.g., by  $[\text{Pd}_2\text{X}_2(\text{PPh}_2)_2(\text{PR}_3)_2]$  complexes. The insolubility of the  $[\text{Pd}_3\text{X}_4(\text{PPh}_2)_2(\text{PPh}_3)_2]$  complexes is also responsible for the lower accuracy of the molecular weight determinations for these complexes since very dilute solutions had to be used.

**Cleavage Reactions of  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PR}_3)_2]$  Complexes.** (a) Triphenylphosphine (0.075 g, 0.29 mmol) was dissolved in a stirred suspension of  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PPh}_3)_2]$  (0.19 g, 0.14 mmol) in dichloromethane. After 48 h, filtration gave a yellow precipitate which was washed with three 10-mL portions of boiling toluene to leave  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  (0.13 g, 0.11 mmol) as orange residue. The toluene extract was cooled and pentane added to precipitate *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$  (0.078 g, 0.11 mmol), identified by comparison of its infrared spectrum with that of an authentic sample.

$[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  has not been reported previously. It is highly soluble in common solvents, and analyses consistently gave low values for carbon probably because of contamination by  $[\text{PdCl}(\text{PPh}_2)]_n$ . Anal. Calcd for  $\text{C}_{60}\text{H}_{50}\text{Cl}_2\text{P}_4\text{Pd}_2$ : C, 61.1; H, 4.3. Found: C, 58–61; H, 4.2. Consequently the identity of  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  was confirmed in two ways: (i) by alternate syntheses using reactions of  $[\text{PdCl}_2(\text{PPh}_3)(\text{PHPh}_2)]$ <sup>26</sup> with *p*-toluidine or the known<sup>24</sup> compound  $[\text{PdCl}_2(\text{PPh}_2)_2(\text{PHPh}_2)_2]$  with triphenylphosphine (both these reactions yielded insoluble products with infrared spectra identical with those of the above samples of  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  and (ii) by reaction of  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2]$  with 2 mmol of triethylphosphine (triphenylphosphine was displaced and a soluble ( $\text{CH}_2\text{Cl}_2$ ) product obtained which was identified as  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PEt}_3)_2]$  by <sup>31</sup>P NMR).

(b) Triethylphosphine (0.068 g, 0.54 mmol) was added to a stirred suspension of  $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  under a nitrogen atmosphere at 25 °C. After 1 h, the resulting orange solution was evaporated under reduced pressure to an orange solid. <sup>31</sup>P NMR studies showed that this solid was an approximately 1:1 mixture of *trans*- $[\text{PdCl}_2(\text{PEt}_3)_2]$  ( $\delta$  -122.2) and  $[\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PEt}_3)_2]$ .

**Acknowledgment.** We thank the University of Victoria and the National Research Council of Canada for research grants.

**Registry No.**  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{BF}_4]$ , 73116-68-4;  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{BF}_4]$ , 73116-67-3;  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_2(\text{PHPh}_2)]\text{-}[\text{BF}_4]$ , 73116-64-0;  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PPh}_3)_3][\text{Cl}]$ , 73069-74-6;  $[\text{Pd}_3(\text{PPh}_2)_3(\text{PEt}_3)_3][\text{Cl}]$ , 73069-75-7; *cis,cis,cis*- $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PPh}_3)_2]$ , 72926-32-0; *cis,cis,cis*- $[\text{Pd}_3\text{Cl}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$ , 72926-33-1; *cis,cis,cis*- $[\text{Pd}_3\text{Br}_4(\text{PPh}_2)_2(\text{PPh}_3)_2]$ , 72926-34-2; *cis,cis,cis*- $[\text{Pd}_3\text{Br}_4(\text{PPh}_2)_2(\text{PEt}_3)_2]$ , 72926-35-3;  $\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_2$ , 72926-36-4;  $\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PEt}_3)_2$ , 72926-37-5;  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PEt}_3)_3][\text{BF}_4]$ , 65916-06-5;  $[\text{Pd}_3\text{Cl}(\text{PPh}_2)_2(\text{PPh}_3)_3][\text{BF}_4]$ , 65916-07-6;  $\text{Pd}(\text{PPh}_3)_4$ , 14221-01-3;  $\text{Pd}_2\text{Cl}_2(\text{PPh}_2)_2(\text{PHPh}_2)_2$ , 72983-38-1; *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ , 28966-81-6; *trans*- $[\text{PdCl}_2(\text{PEt}_3)_2]$ , 15642-19-0.

(22) R. B. Johannsen, J. A. Ferreti, and R. K. Harris, *J. Magn. Reson.*, **3**, 84 (1970).

(23) J. D. Swalen in "Computer Programs for Chemistry", Vol. I, D. F. Detos, Ed., W. A. Benjamin, New York, 1968.

(24) R. G. Hayter, *J. Am. Chem. Soc.*, **84**, 3046 (1962).

(25) J. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(26) Prepared by reaction of  $[\text{Pd}_2\text{Cl}_4(\text{PPh}_3)_2]$  with  $\text{PHPh}_2$ .<sup>27</sup>

(27) K. R. Dixon and A. D. Rattray, unpublished observations.