Volume 17
Number 5
May 1978

Inorganic Chemistry

Contribution from the Department of Chemistry, University of Victoria, Victoria,
British Columbia, Canada V8W 2Y2

Trinuclear Palladium Clusters: Synthesis and Phosphorus-31 Nuclear Magnetic Resonance Spectra of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ and Related Complexes

KEITH R. DIXON* and ALEXANDER D. RATTRAY

Received August 26, 1977

Prolonged heating of $[PdCl(PPh_3)_3][BF_4]$ in tetrahydrofuran suspension at 125 °C in vacuo gives diamagnetic red crystals of a novel type of palladium cluster complex. $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ contains a triangular cluster of palladium atoms with edge-bridging Cl and PPh_2 groups and triphenylphosphines coordinated terminally to each palladium. It is the first well-characterized example of a palladium cluster in an oxidation state other than zero. The cluster unit is stable to bridge cleavage reagents, and simple exchange reactions using triethylphosphine or dimethyl(phenyl)phosphine, potassium halides, or $AgSCF_3$ enable synthesis of a series of related clusters $[Pd_3X(PPh_2)_2(PR_3)_3][Y]$ (R = Ph or Et, Y = BF_4, X = Cl or SCF_3; R = Ph, X = Y = Cl, Br, or I; R = Et, X = Br, Y = BF_4; R_3 = Me_2Ph, X = Cl, Y = BF_4). Phosphorus-31 NMR data for these systems are the first reported for palladium or platinum clusters. The spectra belong to the ABB′XX′ spin system (A = B = B′ = PR_3, X = X′ = PPh_2) and complete computer simulation has been achieved. For example, in $[Pd_3Cl(PPh_2)_2(PPh_3)_3]^+$: $\delta_A = 128.0$, $\delta_B = 121.2$, $\delta_X = -81.8$ ppm relative to $P(OMe)_3$; $J_{AB} = 89$, $J_{AX} = -11$ Hz. Features unique to the cluster system are the large value of J_{AB} and the large downfield shift of the PPh_2 groups (cf. $J_{AA'} < 5$ Hz, $\delta_X = +268$ ppm in $[Pd_2Cl_2(\mu\text{-}PPh_2)_2(PEt_3)_2]$ for corresponding parameters in the absence of M–M bonding).

Introduction

Despite the variety of known metal cluster complexes and the great current interest in this field, examples containing platinum or palladium are still comparatively rare and difficult to characterize.[1] The most extensively studied systems are carbonyl tertiary phosphine complexes of platinum(0),[2] and two of these complexes, $[Pt_4(CO)_5(PMe_2Ph)_4]$[3] and $[Pt_3(CO)_3\{P(C_6H_{11})_3\}_4]$,[4] have recently been characterized by x-ray diffraction studies. The latter complex contains an almost equilateral triangle of metal atoms and this arrangement is also found in $[Pt_3(SO_2)_3(PPh_3)_3]\cdot C_7H_8\cdot SO_2$[5] and $[Pt_3(CNBu^t)_6]$.[6] In other oxidation states an unusual series of complexes $[Pt_3(CO)_6]_n^{2-}$ (n = 2, 3, 4, 5) has been prepared[7] by reductive carbonylation of $[Pt(CO)Cl_3]^-$, and a rare example in a positive oxidation state, $[Pt_3Ph(PPh_2)_3(PPh_3)_2]$, is formed by a phenyl-transfer reaction during prolonged heating of $[Pt(PPh_3)_4]$ under reflux in benzene.[8]

The available information on palladium clusters is much more limited. $[Pd_3(CO)_3L_3]$ (L = tertiary phosphine) complexes have been obtained both by carbonylation of Pd^0 species[9] and also by reductive carbonylation of Pd^{II}.[10] Presumably these have triangular structures similar to the platinum analogues but no structure determinations are available. A cluster, $[Pd_4(PH_3)_4(PPh_3)_4Cl_4]$, has been reported to result from reaction of PH_3 with *trans*-$[PdCl_2(PPh_3)_2]$ but no spectroscopic or structural information was obtained.[11] The only palladium cluster for which a structure determination is available appears to be $[Pd_3(SO_2)_2(CNBu^t)_5]$ which contains a nearly symmetrical triangle of Pd atoms with bridging SO_2 groups along two edges.[12] Another possible triangular cluster was obtained by Coulson[13] from a phenyl-transfer reaction involving $[Pd(PPh_3)_4]$ and $PdCl_2$ and formulated in a preliminary communication as a molecular compound, $[Pd_3Cl_2(PPh_2)_2(PPh_3)_3]$. No further details have been published. We have now prepared a series of closely related complexes $[Pd_3X(PPh_2)_2(PR_3)_3][Y]$ (R = Ph or Et, Y = BF_4, X = Cl or SCF_3; R = Ph, X = Y = Cl, Br, or I; R = Et, X = Br, Y = BF_4; R_3 = Me_2Ph, X = Cl, Y = BF_4) and present evidence that Coulson's complex is more correctly formulated as a member of this series (X = Y = Cl, R = Ph).

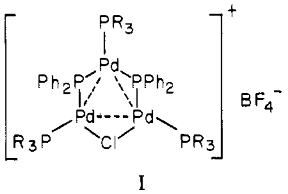
In view of the obvious potential of ^{31}P NMR spectroscopy for structure determination in this area of chemistry, it is somewhat surprising that no previous results appear to be available except for the preliminary data obtained by Coulson.[13] One problem here has been the relatively low solubility of most of the complexes.[2] The present series of palladium complexes is very soluble in polar organic solvents and the ^{31}P NMR spectra discussed below indicate that highly unusual parameters may be found when metal–metal bonding is present. An x-ray diffraction study of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ has been presented in a preliminary communication.[14]

Results

(a) Synthesis and Characterization. When $[PdCl(PPh_3)_3][BF_4]$ is suspended in tetrahydrofuran and heated at 125 °C in an evacuated sealed glass tube, the initially yellow mixture gradually becomes dark red and, after several days, diamagnetic red crystals analyzing as $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ can be isolated. This product reacts immediately with triethylphosphine at 25 °C giving essentially stoichiometric displacement of triphenylphosphine and formation of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$. Proton NMR spectra of the last product at 220 MHz show the presence of two chemically equivalent triethylphosphine groups and one chemically unique triethylphosphine group. On this basis, and by analogy with the several bridged triangular systems noted in the Introduction, the most reasonable structure for these

0020-1669/78/1317-1099$01.00/0 © 1978 American Chemical Society

new palladium clusters is I. This structure has now been confirmed by an x-ray diffraction study of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$. The metal triangle is almost equilateral with the chloro-bridged Pd–Pd distance being 289 pm and the other two Pd–Pd distances equal at 293 pm.[14]



I

The bridging chloride in the $[Pd_3Cl(PPh_2)_2(PR_3)_3]^+$ cations is quite labile and simple exchange reactions using either potassium halides or silver trifluoromethyl sulfide enable synthesis of a range of derivatives $[Pd_3X(PPh_2)_2(PR_3)_3][Y]$ (R = Ph or Et, Y = BF_4, X = Cl or SCF_3; R = Ph, X = Y = Cl, Br, or I; R = Et, X = Br, Y = BF_4). Displacement of triphenylphosphine by dimethylphosphine readily yields a derivative with R_3 = Me_2Ph, X = Cl, and Y = BF_4. The SCF_3 compounds were prepared in the hope that ^{19}F NMR spectra would yield additional structural information but in practice the results were consistent rather than diagnostic. Thus, for both $[Pd_3(SCF_3)(PPh_2)_2(PR_3)_3][BF_4]$ complexes, the appropriate resonances were triplets (J = 3.5 Hz). In a structure such as I (Cl replaced by SCF_3), this is presumably due to coupling primarily to phosphorus in the PPh_2 groups which have an approximately trans relationship to the SCF_3. Coupling to the approximately cis PR_3 groups is expected to be smaller.[15] Slight broadening of the PPh_2 resonances was detectable in the ^{31}P spectra but the line width was too large to permit resolution of coupling to fluorine.

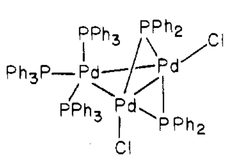
Infrared spectra of all the $[Pd_3X(PPh_2)_2(PR_3)_3][Y]$ complexes were basically similar and showed the expected ligand and anion absorptions. Phenyl–phosphine derivatives always exhibit strong absorption at ca. 500 cm^{-1} but particular patterns of absorption (R = Ph: 522 (vs), 508 (m), 489 (vs), 478 (w, sh) cm^{-1}; R = Et: 508 (m), 491 (vs), 478 (w) cm^{-1}) are characteristic of the present clusters, and a medium intensity band at 388 cm^{-1} appears to be unique to these compounds. The complexes are all red (or orange when finely powdered) due mainly to a characteristic very intense absorption at about 400 nm (e.g., for $[Pd_3Cl(PPh_2)_2(PR_3)_3][BF_4]$ in ethanol solution: R = Ph, λ_{max} 415 nm, ϵ 60 000; R = Et, λ_{max} 401 nm, ϵ 40 000). Thus, the above spectroscopic data and also the ^{31}P NMR data described below support the assignment of structures similar to I to all the $[Pd_3X(PPh_2)_2(PR_3)_3][Y]$ complexes.

Product weights from several experiments indicate that the initial process in the formation of the cluster probably involves reaction of 3 mol of $[PdCl(PPh_3)_3]^+$ to produce $[Pd_3Cl(PPh_2)_2(PPh_3)_3]^+$ and $[Ph_4P]^+$ in a 1:2 ratio. Cluster yields based on this assumption are greater than 75% but other, more complex stoichiometries cannot be excluded since variable quantities of *trans*-$[PdCl_2(PPh_3)_2]$ and metallic palladium are also products. In any case, the reaction involves transfer of two phenyl groups between phosphorus atoms and reduction of the three palladiums to an average, formal oxidation state of $^4/_3$. The nature of the reducing species is unknown[16] but it is probable that triphenylphosphine is involved since the proposed stoichiometry requires that chloride and triphenylphosphine be released in the initial reaction. We also postulate that further reaction of these two products with $[PdCl(PPh_3)_3]^+$ produces the *trans*-$[PdCl_2(PPh_3)_2]$. Yields of this last product were highly variable with the exact reaction conditions.

The only comparable reaction in the literature is that reported by Coulson,[13] viz.

$$6[Pd(PPh_3)_4] + 7[PdCl_2] \rightarrow 3[PdCl_2(PPh_3)_2] + 4[PdCl(Ph)(PPh_3)_2] + 2[Pd_3Cl_2(PPh_2)_2(PPh_3)_3]$$

which is similar to ours in requiring cleavage of a phosphorus–phenyl bond but differs in that it is an oxidative process (essentially oxidative addition of a PPh_3 to two palladium centers) whereas ours is reductive. Coulson formulated his trinuclear product, $[Pd_3Cl_2(PPh_2)_2(PPh_3)_3]$, as a molecular cluster with structure II. Comparison of this formulation with ours, $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$, suggests that the dichloro species is more correctly formulated as an ionic compound, $[Pd_3Cl(PPh_2)_2(PPh_3)_3]^+[Cl]^-$, and we have been able to synthesize this compound by ion exchange from the fluoroborate salt. The infrared spectrum of this ion-exchange product was identical with a spectrum kindly supplied by Dr. Coulson for his product. Conductance measurements for both the fluoroborate and chloride salts in nitromethane solution are in the accepted range for 1:1 electrolytes.[18] Thus, the only remaining anomaly is the molecular weight determined ebullioscopically in CH_2Cl_2 solution by Coulson which suggested an undissociated molecular structure. We have determined molecular weights osmometrically in CH_2Br_2 for both the fluoroborate and chloride salts and find that the apparent molecular weights rise rapidly with concentration, presumably due to ion pairing, and above about 3×10^{-3} m the values obtained are indistinguishable from the undissociated molecular weights within the accuracy of the experiment. This appears to be a common phenomenon for complex ionic species in these relatively nonpolar solvents[19] and probably accounts for the apparent anomaly.



II

(b) ^{31}P NMR Spectra. The proton-decoupled ^{31}P NMR spectra of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ at 24.29 and 40.49 MHz are shown in Figure 1 together with computer-simulated spectra obtained from the parameters in Table I. The actual spin system is ABB′XX′ (see structure I: A, B, and B′ are phosphorus atoms in PR_3 groups and X and X′ are in PPh_2 groups), but inspection of the observed spectrum shows that it is a "deceptively simple" case which could be completely interpreted in the AB_2X_2 spin system. Thus, analysis of the spectrum may be divided into three parts: approximate determination of parameters in the AB_2X_2 spin system; analysis of conditions under which ABB′XX′ looks like AB_2X_2; and final refinement and simulation in the ABB′XX′ system.

Assignment of the A/B region (high field) of the spectrum to the tertiary phosphines and the X region (low field) to the diphenylphosphido-bridging groups was confirmed by selective irradiation of the protons in $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ while observing the ^{31}P spectrum. Thus, irradiation in the phenyl proton region caused the X resonances to sharpen and irradiation in the ethyl region caused the A and B resonances to sharpen. Dealing first with analysis in the AB_2X_2 system we note that in Figure 1 each line of the AB_2 multiplet appears approximately as a triplet due to coupling to X_2. The triplets are numbered in accordance with previous analyses of AB_2 systems,[20] and following these analyses we obtain δ_A from triplet 3, δ_B as the mean of triplets 5 and 7, and J_{AB} as $^1/_3[(T_1 + T_6) - (T_4 + T_8)]$ (T = triplet, equation derived from ref 20, Table 6-8). The splitting in triplet 3 gives J_{AX}, and an estimate of J_{BX} is obtained from the mean splitting in triplets 5 and 7. This analysis provides preliminary parameters for the ABB′XX′ system as follows: $J_{AB} = J_{AB'}$, $J_{AX} = J_{AX'}$, and J_{BX} (apparent in AB_2X_2 system) = $^1/_2(J_{BX} + J_{BX'})$. The

Table I. ^{31}P NMR Data

	Chemical shifts[a]			Coupling constants[b]		
Compd	δ_A	$\delta_{B,B'}$	$\delta_{X,X'}$	J_{AB}	J_{AX}	$^1/_2(J_{BX} + J_{BX'})$
$[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$	128.0	121.2	−81.8	89	−11	17
$[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$	137.7	123.0	−63.8	93	−14	15
$[Pd_3Cl(PPh_2)_2(PMe_2Ph)_3][BF_4]$	163.5	150.7	−68.3	98	−12	15
$[Pd_3Br(PPh_2)_2(PEt_3)_3][BF_4]$	137.6	122.6	−68.3	93	−13	15
$[Pd_3(SCF_3)(PPh_2)_2(PPh_3)_3][BF_4]$	127.4	121.1	−78.6	89	−9	18
$[Pd_3(SCF_3)(PPh_2)_2(PEt_3)_3][BF_4]$	138.4	126.2	−57.1	89	−10	13
$[Pd_2Cl_2(PPh_2)_2(PEt_3)_2]$[c]	125.0		268.3	<5[d]	407	

[a] ppm relative to $P(OMe)_3$ external reference. Positive values are upfield from the reference. [b] Hz. The sign information is relative, not absolute. All except $[Pd_2Cl_2(PPh_2)_2(PEt_3)_2]$ derived from computer simulation in the ABB′XX′ spin system (see Results for details). $J_{AB} = J_{AB'}$. $J_{AX} = J_{AX'}$. $^1/_2(J_{BX} + J_{BX'}) = {}^1/_2(J_{B'X'} + J_{B'X})$. $J_{BB'} = 25$ Hz and $J_{XX'} = 400$ Hz (estimates only). [c] The results quoted are from present work using simulations in the AA′XX′ spin system with $J_{AX'} = 32.3$ Hz and $J_{XX'} = 291$ Hz. The results agree closely with those obtained by O'Dell.[25] [d] This value is actually $J_{AA'}$; it is included in this column because it is directly comparable with the J_{AB} values (see Discussion).

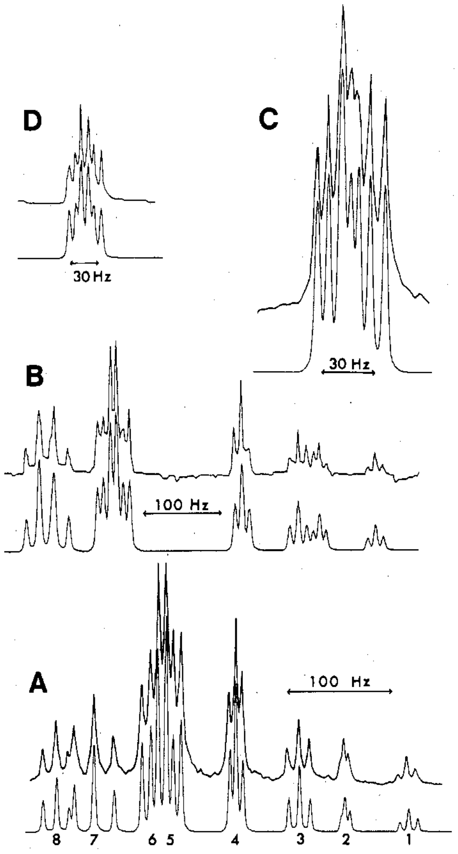


Figure 1. Phosphorus-31 NMR spectra of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$. Spectra were recorded with protons decoupled, and in each case the upper trace is the experimental spectrum and the lower trace is the computer-simulated spectrum. (A) A,B,B′ resonances at 24.3 MHz. The numbering of the resonances is explained in the Results section. (B) A,B,B′ resonances at 40.5 MHz. (C) X,X′ resonance at 24.3 MHz. (D) X,X′ resonance at 40.5 MHz.

relative signs are discussed below. For our initial calculations we assumed $J_{BX'} \approx 0$ and used the appropriate value of J_{BX} to maintain the correct mean, but in the final refinement all parameters were varied (see below). Calculations in the ABB′XX′ spin system then show that the "deceptively simple" AB_2X_2 spectrum is produced only when $J_{XX'}$ or $J_{BB'}$ is large (i.e., greater than ~80 Hz). Also, $J_{XX'}$ and $J_{BB'}$ cannot have comparable magnitudes. A very approximate estimate of $J_{BB'}$ can be obtained for $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ by computer fitting the methylene and methyl resonances for the BB′ triethylphosphine groups in the 220-MHz proton spectrum.[21] This analysis indicates a value for $J_{BB'}$ in the range 10–40 Hz. Moreover, $J_{BB'}$ is a three-bond coupling whereas $J_{XX'}$ is a two-bond coupling between phosphorus atoms in an almost trans orientation (P–Pd–P = 156°).[14] The latter coupling ($J_{XX'}$) might therefore be expected[22] to be several hundred hertz and we consider this to be the most likely explanation of the deceptively simple spectra. In support of this argument the refinement proceeded to a smaller root-mean-square error when $J_{XX'}$ was assumed large than it did for the alternate assumption of large $J_{BB'}$.

The following information regarding the relative signs of the coupling constants is available from the spectra. The asymmetry of the X resonance at 24.3 MHz (see Figure 1) would be reversed if J_{AB} and J_{AX} had the same sign. In addition to the obvious asymmetry of intensities the separation of the upfield outer pair of lines (8.7 Hz) is greater than that in the downfield outer pair (6.2 Hz). Also resonances 1, 2, 4, 5, 6, 7, 8, and X are correctly fitted only when J_{AX} and $^1/_2(J_{BX} + J_{BX'})$ have opposite signs. For example, resonance 4 in Figure 1A shows approximately double the correct splitting if this criterion is not met. No information is available on the relative signs of $J_{BB'}$ or $J_{XX'}$. The set of relative signs given in Table I was obtained by arbitrarily taking J_{AB} as positive and is not intended to imply that absolute signs have been determined.

After the above preliminary data were established, the final parameters given in Table I were obtained by computer fitting of observed line positions using the ABB′XX′ spin system and allowing all parameters to vary. No line positions were in error by >1 Hz and most were <0.3 Hz. The couplings $J_{BB'}$, $J_{XX'}$, J_{BX} ($=J_{B'X'}$), and $J_{BX'}$ ($=J_{B'X}$) are not well determined by the spectra. Estimates of $J_{BB'}$ and $J_{XX'}$ are included in Table I but for J_{BX} and $J_{BX'}$ only the mean (which is well determined) is quoted. The refinements tended to indicate that J_{BX} and $J_{BX'}$ are similar in magnitude but the exact values are not reliable.

Discussion

As noted in the Introduction, palladium cluster compounds are rare and the present compounds appear to be the first examples in a nonzero oxidation state. The extent and nature of the metal–metal interaction is therefore an important question. The Pd–Pd distances determined by x-ray diffraction are somewhat long (289 pm for the distance bridged by Cl and 293 pm for the other two distances) when compared with the 273–276-pm distance observed in $[Pd_3(\mu\text{-}SO_2)_2(CNBu^t)_5]$[12] but still well within the range where significant metal–metal interaction might be expected.

The existence of metal–metal interaction is further indicated by the electronic absorption spectra, the chemical reactivity, and the ^{31}P NMR parameters of the present complexes. Thus, the very high intensity (ϵ ~50 000) of the electronic absorption responsible for the red color of the clusters (ca. 400 nm) suggests that the transition is of the charge-transfer type, possibly between metal atoms in differing oxidation states. Palladium complexes of similar type without metal–metal interaction are normally pale yellow and, for example, $[PdCl(PPh_3)_3][BF_4]$ exhibits two absorptions in the visible: λ_{max} 521 nm, ϵ 2 200; λ_{max} 432 nm, ϵ 3 000. The dominant resonance form of the $[Pd_3X(PPh_2)_2(PR_3)_3]^+$ cations may be one in which the unique palladium is mainly Pd^0 and the two equivalent palladiums are mainly Pd^{II}. The chemical reactivity of the cluster also supports the hypothesis of metal–metal interaction since chloro bridges (for example, in $[Pd_2Cl_2(PR_3)_4]^{2+}$ cations[24]) are normally readily cleaved by halides or tertiary phosphines. The resistance of the cluster unit to this type of cleavage is demonstrated by the success of the syntheses involving halide and tertiary phosphine exchange reactions.

The ^{31}P NMR parameters (Table I) show two features unique to the cluster system: the comparatively large value of the coupling J_{AB} and the large downfield shift of the phosphorus atoms in the bridging diphenylphosphido groups. Data for $[Pd_2Cl_2(\mu\text{-}PPh_2)_2(PEt_3)_2]$ are included in Table I for comparison. The proton-decoupled ^{31}P spectrum of this complex belongs to the AA′XX′ spin system and is typical of a range of diphenylphosphido bridged platinum and palladium complexes in which there is no metal–metal interaction.[25] $J_{AA'}$ in this complex is a four-bond coupling (<5 Hz) through the diphenylphosphido bridge and should be directly comparable with J_{AB} (ca. 90 Hz) in the cluster if there was no metal–metal interaction in the latter. Comparison of the chemical shifts for the diphenylphosphido groups in the presence (ca. −70 ppm) and absence (+268 ppm) of the metal–metal interaction is even more striking. Thus, it is apparent that the observation of unusual NMR parameters may be a valuable addition to existing methods for the detection of metal–metal interactions.

Experimental Section

Data relating to the characterization of the complexes are given in the Results, in Table I, and under individual preparations below. Microanalyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., by Chemalytics Inc., Tempe, Ariz., or by Dr. D. L. McGillivray of this department. Molecular weights were determined in dibromomethane solution at 50 °C or in dichloromethane solution at 30 °C using a Hitachi Perkin-Elmer Model 115 vapor phase osmometer. Conductance measurements were made on approximately 10^{-3} M solutions in nitromethane using a pipette-type cell connected to a Radiometer Model CDM3 conductivity bridge. The cluster complexes tended to decompose on heating and melting points were not a useful method of characterization.

Infrared spectra were recorded from 4000 to 250 cm^{-1} with an accuracy of ±3 cm^{-1} on a Beckman IR 20 spectrophotometer calibrated against polystyrene film and water vapor. Solid samples were examined as Nujol mulls between cesium iodide plates. Ultraviolet and visible spectra were recorded in ca. 10^{-5} M solutions in ethanol using a Cary 17 spectrophotometer. The diamagnetism of the clusters was established by the Gouy method. ^1H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer and at 220 MHz by the Canadian 220 MHz NMR Centre, Sheridan Park, Ontario, using tetramethylsilane or dichloromethane as internal reference. Phosphorus NMR spectra were recorded in dichloromethane solution at 40.49 MHz on a JEOL PFT-100 Fourier transform spectrometer or at 24.29 MHz on a Nicolet TT14 Fourier transform spectrometer. $(P(OCH_3)_3$ was used as external reference and C_6D_6 as external lock on both instruments. Positive chemical shifts are upfield from the reference. Most usually 8192 data points were used in a 10-kHz sweep giving resolution of 2.44 Hz, and data are thus subject to errors of this magnitude. Protons were decoupled by broad-band ("noise") irradiation at the appropriate frequencies. Simulated NMR spectra were calculated using the UEAITR program[26] on an IBM 370/158 computer and plotted on a Calcomp 563 drum plotter using a program based on the NMR PLOT program.[27]

$[PdCl(PPh_3)_3][BF_4]$[24] and $[Pd_2Cl_2(PPh_2)_2(PEt_3)_2]$[28] were prepared as previously described. Unless otherwise stated below, reactions were conducted at ambient temperature under an atmosphere of dry nitrogen using reagent grade solvents dried by type 4A molecular sieves. The solid cluster products were stable to the atmosphere for extended periods but solutions tended to be air sensitive.

$[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$. $[PdCl(PPh_3)_3][BF_4]$ (12.5 g, 12.3 mmol) was sealed in vacuo in a heavy-wall Pyrex tube with tetrahydrofuran (200 mL) which had been previously dried by distillation from potassium–benzophenone. The mixture was heated at 120–130 °C for 5 days[29] during which time white crystals of $[PPh_4][BF_4]$, yellow crystals of *trans*-$[PdCl_2(PPh_3)_2]$, and some metallic palladium formed and the solution became dark red. The tube was kept at ambient temperature for 24 h to complete crystallization of $[PPh_4][BF_4]$ and *trans*-$[PdCl_2(PPh_3)_2]$ and then opened and the mixture filtered under nitrogen. Either the supersaturated, red filtrate was chilled or a small quantity of diethyl ether added to initiate crystallization of the complex (3.5 g, 2.2 mmol) as red-orange crystals. Anal. Calcd for $C_{78}H_{65}BClF_4P_5Pd_3$: C, 58.6; H, 4.1; Cl, 2.2; F, 4.8; P, 9.7. Found: C, 58.2; H, 4.5; Cl, 2.6; F, 5.3; P, 9.5. Molar conductance was 82 Ω^{-1} cm^2.

The above is the best preparative procedure and gives the purest product. In reactions designed to establish stoichiometry, solid products from the Pyrex tube were extracted with nitromethane to leave *trans*-$[PdCl_2(PPh_3)_2]$ as a yellow residue and addition of the extract to diethyl ether gave $[PPh_4][BF_4]$ as a white precipitate. The red solution from the Pyrex tube was evaporated under reduced pressure and the resulting solids were extracted with diethyl ether to give the complex as residue and $POPh_3$ in the extract. *trans*-$[PdCl_2(PPh_3)_2]$,[19] $[PPh_4][BF_4]$,[30] and $POPh_3$[31] were identified by comparison of infrared spectra with those of authentic samples. In a series of preparations, relative yields (assuming 1 mmol of $[PdCl(PPh_3)_3][BF_4]$) were as follows: the complex, 0.25–0.33 mmol; *trans*-$[PdCl_2(PPh_3)_2]$, 0.1–1.0 mmol; $[PPh_4][BF_4]$, 0.4–0.6 mmol; and $POPh_3$, 0.2–0.3 mmol.

$[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$. Triethylphosphine (0.25 g, 2.1 mmol) was added dropwise to a stirred solution of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ (1.11 g, 0.69 mmol) in acetone (30 mL). The solution was stirred for 1 h and then added slowly to a chilled mixture of diethyl ether (300 mL) and heptane (200 mL) to give the complex (0.73 g, 0.63 mmol) as an orange-red precipitate. Anal. Calcd for $C_{42}H_{65}BClF_4P_5Pd_3$: C, 43.3; H, 5.6; P, 13.3. Found: C, 42.6; H, 6.0; P, 13.0. Molar conductance was 75 Ω^{-1} cm^2. Evaporation of the ether–heptane filtrate under reduced pressure gave triphenylphosphine (0.51 g, 1.9 mmol).

$[Pd_3Cl(PPh_2)_2(PMe_2Ph)_3][BF_4]$. This complex was similarly prepared in similar yield from $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ and PMe_2Ph. The product was a red oil which was identified by ^{31}P NMR.

$[Pd_3Cl(PPh_2)_2(PPh_3)_3][Cl]$. The anion-exchange resin Rexyn R_{201} was washed with aqueous KCl solution. The treated resin was then stirred in an ethanol solution of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ (0.35 g, 0.22 mmol) for 2 h. After removal of the resin by filtration, aqueous KCl solution was added to the filtrate to yield the complex (0.33 g, 0.21 mmol) as a red precipitate which was recrystallized from methylene chloride by the slow addition of diethyl ether. Anal. Calcd for $C_{78}H_{65}Cl_2P_5Pd_3$: C, 60.5; H, 4.2. Found: C, 60.1; H, 4.4. Molar conductance was 68 Ω^{-1} cm^2.

$[Pd_3Br(PPh_2)_2(PPh_3)_3][Br]$. Aqueous KBr (0.5 g in 1 mL of H_2O) was added to a solution of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ (0.20 g, 0.13 mmol) in acetone (10 mL). The solution was stirred for 1 h and then added to aqueous KBr (50 mL) to yield the complex (0.19 g, 0.12 mmol) as a dark red precipitate which was recrystallized from methylene chloride by the slow addition of diethyl ether. Anal. Calcd for $C_{78}H_{65}Br_2P_5Pd_3$: C, 57.3; H, 4.0. Found: C, 56.8; H, 4.5. Molar conductance was 68 Ω^{-1} cm^2.

$[Pd_3I(PPh_2)_2(PPh_3)_3][I]$. This complex was similarly prepared in similar yield from $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ and KI. Anal. Calcd for $C_{78}H_{65}I_2P_5Pd_3$: C, 54.1; H, 3.8. Found: C, 54.3; H, 3.6. Molar conductance was 75 Ω^{-1} cm^2.

$[Pd_3Br(PPh_2)_2(PEt_3)_3][BF_4]$. Concentrated aqueous HBr (0.1 mL) was added to a stirred solution of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ (0.20 g, 0.17 mmol) in acetone (5 mL). After the solution was chilled, the complex was obtained as a red precipitate (0.19 g, 0.16 mmol). Anal. Calcd for $C_{42}H_{65}BBrF_4P_5Pd_3$: C, 41.7; H, 5.4. Found: C, 41.5; H, 5.6. Molar conductance was 70 Ω^{-1} cm^2.

$[Pd_3(SCF_3)(PPh_2)_2(PPh_3)_3][BF_4]$. A solution of $AgSCF_3$ (0.048 g, 0.23 mmol) in acetone was added to a stirred acetone solution of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ (0.37 g, 0.23 mmol) under subdued lighting. AgCl (0.028 g, 0.20 mmol) precipitated immediately and was removed by filtration after stirring for 1 h. The filtrate was added to a large excess of chilled diethyl ether to yield the complex as a red precipitate (0.35 g, 0.21 mmol). Anal. Calcd for $C_{79}H_{65}BF_7P_5Pd_3S$: C, 57.0; H, 3.9. Found: C, 57.2; H, 4.2. Molar conductance was 75 Ω^{-1} cm^2.

[$Pd_3(SCF_3)(PPh_2)_2(PEt_3)_3$][$BF_4$]. This complex was similarly prepared in similar yield from [$Pd_3Cl(PPh_2)_2(PEt_3)_3$][BF_4]. Anal. Calcd for $C_{43}H_{65}BF_7P_5Pd_3S$: C, 41.9; H, 5.3. Found: C, 41.3; H, 5.4. Molar conductance was 80 Ω^{-1} cm^2.

Acknowledgment. We thank the National Research Council of Canada and the University of Victoria for research grants, Dr. A. Pidcock for access to ^{31}P NMR facilities at the University of Sussex, and Dr. D. R. Coulson for providing an infrared spectrum of his cluster complex.

Registry No. [$Pd_3Cl(PPh_2)_2(PPh_3)_3$][BF_4], 65916-07-6; [$Pd_3Cl(PPh_2)_2(PEt_3)_3$][BF_4], 65916-06-5; [$Pd_3Cl(PPh_2)_2(PMe_2Ph)_3$][$BF_4$], 65916-05-4; [$Pd_3Cl(PPh_2)_2(PPh_3)_3$][Cl], 65859-21-4; [$Pd_3Br(PPh_2)_2(PPh_3)_3$][Br], 65859-20-3; [$Pd_3I(PPh_2)_2(PPh_3)_3$][I], 65859-19-0; [$Pd_3Br(PPh_2)_2(PEt_3)_3$][$BF_4$], 65916-04-3; [$Pd_3(SCF_3)(PPh_2)_2(PPh_3)_3$][$BF_4$], 65916-03-2; [$Pd_3(SCF_3)(PPh_2)_2(PEt_3)_3$][$BF_4$], 65916-02-1; [$PdCl(PPh_3)_3$][$BF_4$], 34772-26-4.

References and Notes

(1) R. B. King, *Prog. Inorg. Chem.*, **15**, 287 (1972).
(2) R. Ugo, S. Cenini, M. F. Pilbrow, B. Deibl, and G. Schneider, *Inorg. Chim. Acta*, **18**, 113 (1976), and references therein.
(3) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Am. Chem. Soc.*, **91**, 1574 (1969).
(4) A. Albinati, G. Carturan, and A. Musco, *Inorg. Chim. Acta*, **16**, L3 (1976).
(5) D. C. Moody and R. R. Ryan, *Inorg. Chem.*, **16**, 1052 (1977).
(6) M. Green, J. A. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 3 (1975).
(7) J. C. Calabrese, L. F. Dahl, P. Chini, G. Longini, and S. Martinengo, *J. Am. Chem. Soc.*, **96**, 2614 (1974).
(8) N. J. Taylor, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.* 448 (1975).
(9) T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, **99**, 2134 (1977).
(10) M. Hidai, M. Kokura, and Y. Uchida, *J. Organomet. Chem.*, **52**, 431 (1973).
(11) F. Klanberg and E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 3296 (1968).
(12) S. Otsuka, Y. Tatsumo, M. Miki, T. Aoki, M. Matsumoto, H. Yoshida, and K. Nakatsu, *J. Chem. Soc., Chem. Commun.*, 445 (1973).
(13) D. R. Coulson, *Chem. Commun.*, 1530 (1968).
(14) G. W. Bushnell, K. R. Dixon, P. M. Moroney, A. D. Rattray, and Ch'eng Wan, *J. Chem. Soc., Chem. Commun.*, 709 (1977).
(15) K. R. Dixon, K. C. Moss, and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.* 1528 (1973).
(16) The products always contained ~1 mmol of $POPh_3$ for each mmol of cluster but the significance of this is not clear. Preliminary purification of the tetrahydrofuran (potassium–benzophenone) should exclude water and organic carbonyl species as sources of the oxygen and oxidation of PPh_3 does not occur during product workup since $POPh_3$ can be sublimed directly from the reaction products in vacuo. In view of the ease of Lewis acid catalyzed cleavage of ethers and the known ability of PPh_3 to deoxygenate many organic compounds,[17] it is possible that tetrahydrofuran itself is the source of oxygen. However, some cluster formation was still observed in reactions conducted in benzene. An anonymous reviewer suggested that the reaction may be $3[PdCl(PPh_3)_3]^+ \rightarrow [Pd_3Cl(PPh_2)_2(PPh_3)_3]^+ + 2[PPh_4]^+ + PPh_3 + PCl_2Ph_3$. The $POPh_3$ could then arise by hydrolysis of PCl_2Ph_3, possibly by moisture brought in with the reagent palladium salt.
(17) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley-Interscience, New York, N.Y., 1967, pp 1242–1249; R. C. Fuson, "Reactions of Organic Compounds", Wiley, New York, N.Y., 1962, pp 161–164.
(18) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(19) K. R. Dixon, unpublished observations.
(20) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, pp 123–128.
(21) For example, if we approximate the two triethylphosphine groups (CH_3–CH_2–P- - -P–CH_2–CH_3) as an $A_3X_2MM'X_2'A_3'$ spin system, then the methyl resonance changes from a doublet (J_{AM}) of triplets (J_{AX}) to an overlapping triplet ($J_{apparent} = {}^1/_2(J_{AM} + J_{AM'})$) of triplets ($J_{AX}$) as $J_{MM'}$ increases in magnitude.[23] Clearly, the analysis is not rigorous in our molecules since other phosphorus atoms are present but it does provide an order of magnitude for the P–P coupling ($J_{BB'}$).
(22) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 380 (1969).
(23) K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Can. J. Chem.*, **52**, 692 (1974), and references therein.
(24) K. R. Dixon and D. J. Hawke, *Can. J. Chem.*, **49**, 3252 (1971).
(25) Present work and K. O'Dell, D. Phil. Thesis, University of Sussex, 1976.
(26) R. B. Johannesen, J. A. Ferreti, and R. K. Harris, *J. Magn. Reson.*, **3**, 84 (1970).
(27) J. D. Swalen in "Computer Programs for Chemistry", Vol. I, D. F. Detar, Ed., W. A. Benjamin, New York, N.Y., 1968.
(28) R. G. Hayter, *J. Am. Chem. Soc.*, **84**, 3046 (1962).
(29) Some reactions were stopped after a shorter time if decomposition to metallic Pd was excessive.
(30) G. Wittig and E. Benz, *Chem. Ber.*, **92**, 1999 (1959).
(31) J. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

Contribution from the Department of Chemical Engineering,
Stanford University, Stanford, California 94305

Ligand and Cluster Effects in the Decomposition of Formic Acid on Cu/Ni (110) Single-Crystal Surfaces

D. H. S. YING and ROBERT J. MADIX*

Received August 29, 1977

The decomposition of formic acid on single-crystal copper–nickel alloy surfaces of (110) orientation was studied to elucidate the relative importance of surface composition on the decomposition selectivity and activity. The CO:CO_2 product ratio decreased steeply with increasing copper surface content. This pronounced effect was due to the requirement of a small cluster of four nickel atoms on the surface to form the CO-producing intermediate, adsorbed formic anhydride. The activation energy for decomposition of the anhydride increased by 2 kcal/mol over the Cu/Ni surface composition range studied, reflecting a weak ligand effect on the surface reactivity.

Introduction

Recent studies of the flash decomposition of formic acid on single-crystal surfaces of nickel and copper[1–4] have shown that the selectivity ratio CO:CO_2 varies from unity on Ni(110) to zero on Cu(110). The selectivity is governed by the degree of admixture of two different reaction pathways involving adsorbed formic anhydride or formate, respectively. Whereas on Ni(110) the flash decomposition of formic acid proceeded solely via the anhydride intermediate, on Cu(110) the formate intermediate was formed alone. This sharp difference in the chemical behavior of these two surfaces provided an interesting opportunity for studying the relative importance of ligand and cluster effects in the surface reactivity of alloys, as discussed below.

Metal alloys have long been a subject of interest in catalysis.[5–11] Major effects on selectivity and activity have been noted, and these effects have been ascribed traditionally to "electronic" and "geometric" effects. Recent photoemission work on the Ni/Cu alloy system by Spicer et al.[12,13] utilizing short electron escape depths, illustrated that the surface electronic properties of the alloy were simply the superpositions of the surface electronic properties of every *separate* metal.

0020-1669/78/1317-1103$01.00/0 © 1978 American Chemical Society