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Fragmentation reactions of phosphido and sulphido bridged, trinuclear platinum and palladium clusters and formation of $[M_2(\mu\text{-}PPh_2)(\mu\text{-dppm})(PPh_3)_2]^+$, a new type of M(I) cation

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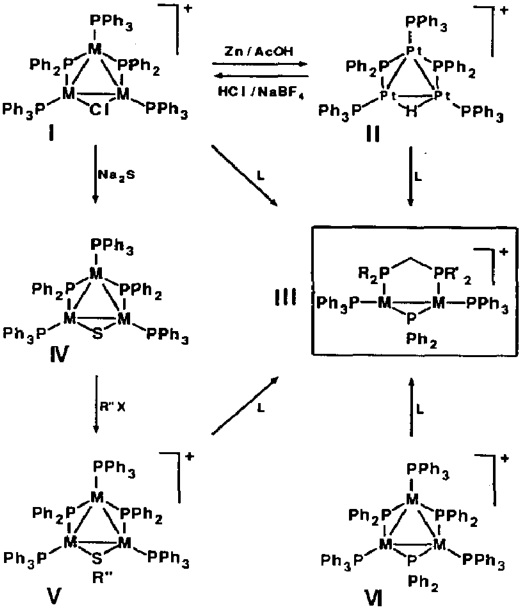
Abstract

Reactions of the trinuclear clusters, $[M_3(\mu\text{-}X)(\mu\text{-}PPh_2)_2(PPh_3)_3]^{n+}$, M = Pd or Pt, X = H, Cl, S, SR, PPh_2, $n = 0$ for S, $n = 1$ otherwise, with bis(diphenylphosphino)methane (dppm) and related ligands result in unusual cluster fragmentations to give a new type of M(I) cation, $[M_2(\mu\text{-}PPh_2)(\mu\text{-dppm})(PPh_3)_2]^+$, in which a metal–metal bond is supported by both dppm and phosphido bridges. The products indicate that the phosphido bridge is always the most robust of the set of bridging ligands.

The cluster chemistry of platinum, and to a lesser extent palladium, has been of intense interest for many years. Despite many synthetic studies, relatively little is known of the reactivity of these clusters. Recently, several groups have focussed on trinuclear clusters containing S^{2-}, SR^-, and SO_2 bridges. The robust nature of the $Pt_2(\mu\text{-}S)$ core has been noted [1] and several cluster fragmentation processes have been observed in which it becomes the basis of a dinuclear fragment. Examples are the reactions of $Pt_3(\mu\text{-}CO)_3(PBu^t_2Ph)_3$ with hydrogen sulfide or sulfur to form $Pt_2(\mu\text{-}S)(CO)_2(PBu^t_2Ph)_2$ [2], and $Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3$ with 2,6-xylyl isocyanide to form $Pt_2(\mu\text{-}SO_2)(CNR)_2(PCy_3)_2$ [3]. The $Pt_2(\mu\text{-}S)$ core has also been used as a ligand to form sulfur bridged trinuclear species [4]. Fragmentation processes involving phosphine ligands have been studied relatively little although $Pt_3(CO)_3L_3$ clusters are known to fragment to mononuclear species when small phosphine ligands are used but undergo only substitution processes with bulky phosphines [5,6]. In one case, involving cleavage of $Pd_3Cl(\mu\text{-}PBu^t_2)_3(CO)_2$ by PMe_3, the first example of a dinuclear, metal–metal bonded, phosphide bridged palladium complex, $Pd_2(\mu\text{-}PBu^t_2)_2(PMe_3)_2$, was obtained [7]. In general, cluster fragmentation processes are of interest in connection with the fate of clusters in catalytic processes where the true catalyst is often a smaller fragment.



Scheme 1. Interconversion and fragmentation reactions of trinuclear clusters. M = Pd or Pt, L = $R_2PCH_2PR'_2$, R = Ph, Pr^i or Bu^t, R' = Ph, R"X = MeI, BzBr or Me_3OBF_4.

We now report some chemistry of triplatinum and tripalladium clusters containing phosphido bridges together with Cl^-, H^-, S^{2-}, or SR^- bridges. Fragmentation reactions with $Ph_2PCH_2PPh_2$ (dppm) demonstrate the robust nature of the $M_2(\mu\text{-}PR_2)$ unit, even in preference to the sulphido bridged core mentioned above, and also provide a new type of dinuclear Pd(I) and Pt(I) complexes, in which a metal–metal bond is supported by both dppm and phosphido bridges. Complexes combining these structural features appear to be extremely rare, with only two previous examples, $Co_2(CO)_4(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)$ [8] and $Co_2(PMe_3)_2(\mu\text{-}PMe_2)(\mu\text{-}dppm)$ [9], neither of which is closely similar to the present example.

We have previously studied the synthesis and reactivity of a new class of palladium cluster cations, typified by **I** (see Scheme 1, M = Pd), which results from prolonged heating of $[PdCl(PPh_3)_3]BF_4$ in tetrahydrofuran solution [10–12]. The corresponding platinum salt does not undergo the same reaction but the hydride, **II**, originally reported as an oxalate salt by Heaton and coworkers [13], is easily converted to the BF_4^- salt of **I** (M = Pt) by bubbling HCl through a solution of **I** in methanol containing $NaBF_4$. The reaction is interesting as a further example of conversion of 42 to 44 electron complexes by substitution reactions [14]. The cations **I** or **II** undergo facile cleavage by dppm and related ligands to the dinuclear products **III**. For example addition of 1.25 molar equivalents of dppm to a solution of **I** (M = Pd) as its BF_4^- salt in dichloromethane at 25 ° under an inert atmosphere results in an almost black solution which becomes deep red after stirring for 22 h. Filtration through a 5 cm alumina column, concentration to 50% of the original volume and layering with hexane gives a crop of yellow crystals of an "A-frame" complex with phosphido and dppm bridges and terminal chlorides, $Pd_2Cl_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)_2{}^+$ as its BF_4^- salt. Filtration of the remaining red solution through alumina followed by slow evaporation gives red crystals of **III** (M = Pd, R = R' =

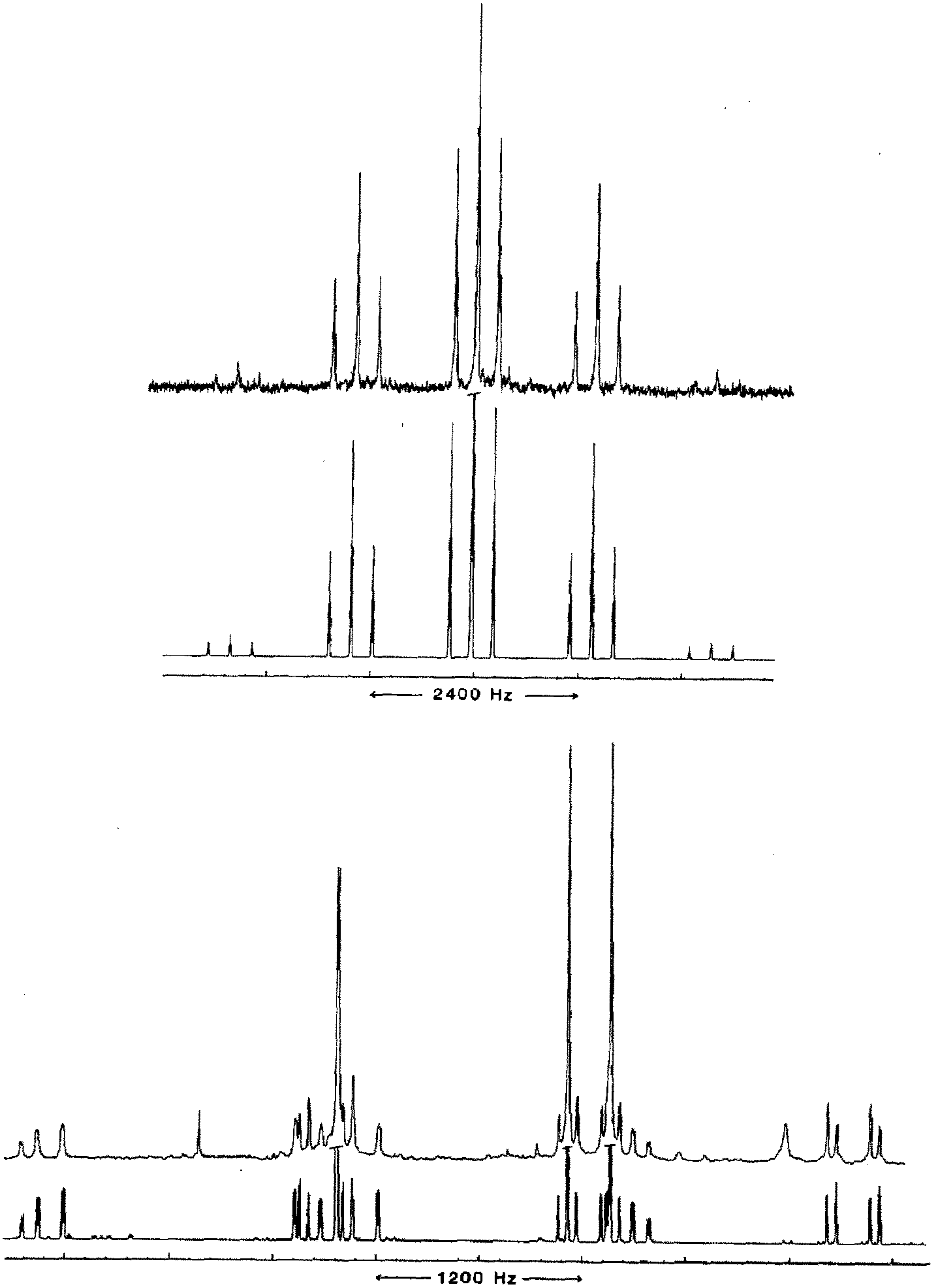


Fig. 1. Observed and calculated $^{31}P\{^1H\}$ NMR spectra of III (M = Pt, R = R′ = Ph) at 101.3 MHz in $CDCl_3$ Solution. Upper spectra show the μ-PPh_2 resonance centred at 194.7 ppm and the lower spectra show the dppm (6.3 ppm) and PPh_3 (20.8 ppm) resonances. Other parameters are given in [19].

Ph), also as a fluoroborate salt. In the corresponding reaction of **I** (M = Pt) with dppm, there is no evidence for the formation of an "A-frame" product, only complex **III**. Final yields of isolated crystals based on percent metal converted are "A-frame" 10%, **III**: M = Pd 30%, M = Pt 83%. The palladium yields are low due to separation difficulties but NMR spectra showed no other products and indicated much higher initial yields.

Subsequent reactions of **I** (M = Pd or Pt) with excess Na_2S in methanol containing a few drops of water give **IV**; and reactions of **IV** with methyl iodide (M = Pt) or Me_3OBF_4(M = Pd) in tetrahydrofuran solution give **V**. The tris(μ-phosphido) derivatives, **VI**, are obtained by reactions of **I** with exactly 1 molar equivalent of diphenylphosphine in tetrahydrofuran in the presence of *p*-toluidine as a dehydrochlorinating agent. The cleavage reactions shown in the Scheme are all similar to that described above except that the case above (**I**, M = Pd) is the only one which gives evidence of an "A-frame" complex. In all other cases complexes **III** are the only major products. It is noteworthy that in reactions of **V** (M = Pd or Pt) the phosphido bridge survives in preference to the thiolato bridge, although whether this is a kinetic or thermodynamic effect is always open to question.

The complexes were characterized mainly by ^{31}P NMR data [15*] and by the X-ray diffraction study described below [16*]. The trinuclear palladium complexes all have relatively simple ^{31}P spectra, similar to those reported previously for **I** and **VI** [10,11]. The bridge–terminal couplings are very small, resulting in broad singlets for the bridge phosphorus and AB_2 patterns for the terminal phosphorus [17*]. The trinuclear platinum cases are much more complex, due to the presence of 33.8% ^{195}Pt resulting in six different isotopomers, but they are all basically similar to the spectrum of **II** analyzed previously [13]. The main parameters are listed below [18*] and full analyses will be reported separately.

The $^{31}P\{^1H\}$ spectra of **III** (M = Pd or Pt, R = R′ = Ph) have been fully analyzed [19*] and Fig. 1 shows the results when M = Pt. The spectrum consists basically of a highly deshielded triplet of triplets for the phosphido bridge resonance, and doublets for the dppm and triphenylphosphine resonances. The presence of 33.8% ^{195}Pt produces three isotopomers (0, 1, or 2 magnetically active platinums) leading to the overall quintet appearance of the phosphido bridge resonance and the complex sidebands in the dppm and triphenyl phosphine region. Extreme downfield shifts for bridging phosphorus atoms are widely accepted as diagnostic of a supporting metal–metal bond [13] and in this respect the μ-PPh_2 groups in **III** (M = Pd, 237.4 and M = Pt, 194.7 ppm) contrast strongly with that in $Pd_2Cl_2(\mu$-$PPh_2)(dppm)_2{}^+$, where there is no metal–metal bond and the μ-PPh_2 resonance is at +74.31 ppm [17*]. The structure of a single cation of **III** (M = Pd, R = Pr^i, R′ = Ph) is shown in Fig. 2. It consists of two palladium(I) centres linked by a metal–metal bond. This bond is supported by PPh_2 and $Pr^i{}_2PCH_2PPh_2$ bridges and each palladium also carries a terminal triphenylphosphine ligand. The coordination about both palladiums is markedly non-planar and the $Pr^i{}_2PCH_2PPh_2$ ligand lies in a twisted conformation such that the P(1)–C(1)–P(5) plane is at 32° relative to the Pd(1)–Pd(2)–P(3) plane. The Pd(1)–Pd(2) bond, 2.688(2) Å, is markedly shorter

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* Reference number with asterisk indicates a note in the list of references.

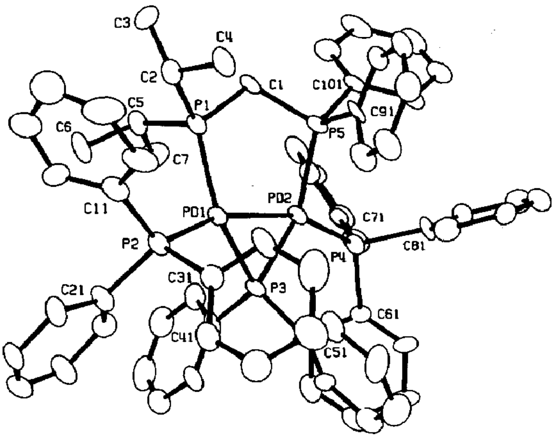

Fig. 2. ORTEP plot of a single cation of III (M = Pd, R = Pr^i, R′ = Ph). Pd(1)–Pd(2), 268.8(2) pm; Pd(1)–P(3)–Pd(2), 73.1(1)°.

than that in I (M = Pd, 2.906(2) Å) [12] but still towards the long end of the range, 2.531–2.699 Å, reported previously for dinuclear Pd(I) compounds [20].

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15 Phosphorus-31 chemical shifts were measured at 101.3 MHz relative to external $P(OMe)_3$ and are reported in parts per million relative to 85% H_3PO_4 using a conversion factor of +141 ppm. Coupling constants are in hertz.
16 Crystal data: $C_{67}H_{66}BF_4P_5Pd_2$, $M = 1325.7$, triclinic, space group $P\bar{1}$, equivalent positions x, y, z; $-x$, $-y$, $-z$; $a = 12.361(5)$, $b = 22.362(8)$, $c = 12.215(5)$ Å; $\alpha = 103.34(4)$; $\beta = 89.75(3)$; $\gamma = 99.17(3)°$; $V(\text{cell}) = 3241(2)$ Å^3; $D_m = 1.36$ g cm^{-3}, $D_c = 1.36$ g cm^{-3}; $Z = 2$; asymmetric unit is one molecule; Zr-filtered Mo-K_α radiation $\lambda = 0.71069$ Å, $\mu = 7.190$ cm^{-1}. Intensity data were collected ($\theta/2\theta$ scans) on a Picker 4-circle diffractometer. The structure was solved by direct methods using SHELX-76 and refined by full matrix least squares, $R = 0.0880$ ($R_w = 0.0744$) for 6039 absorption corrected reflections. Tables of fractional atomic coordinates, anisotropic temperature parameters, interatomic distances and angles, and observed and calculated structure factors are available from the authors.

17 $Pd_2Cl_2(\mu\text{-}PPh_2)(dppm)_2^+$: $\delta_{phosphido}$ 74.3 (quintet), δ_{dppm} 11.7 (doublet), J(PP) 11.5 Hz. Anal. Calcd. for $C_{62}H_{54}BCl_2F_4P_5Pd_2$: C, 56.2; H, 4.11. Found: C, 56.3; H 4.84%

IV (M = Pd): δ_{bridge} 168.7, δ_A 16.6, δ_B 30.3 J_{AB} 95 Hz.

V (M = Pd, R″ = Me, BF_4^- salt): δ_{bridge} 198.07, δ_A 15.4, δ_B 21.8 J_{AB} 87. Anal. Calcd. for $C_{79}H_{68}BF_4P_5Pd_3S$: C, 58.9; H, 4.26. Found: C, 57.7; H, 4.19% X-ray diffraction study of an R″ = benzyl analog is complete and will be reported elsewhere.

18 ^{31}P data for the trinuclear platinum complexes uses the following numbering scheme: terminal P(1) and P(2,3); bridge P(4,5); unique Pt(6); other Pt(7,8). Coupling constants in hertz.

I (M = Pt, BF_4^- salt): δ_1 3.1, $\delta_{2,3}$ 16.4, $\delta_{4,5}$ 127.9, J(16) 4143, J(17) 233, J(12) 75.6, J(27) 4407, J(46) 2264, J(47) 3523, J(48) 94.7, J(45) 243. Anal. Calcd. for $C_{78}H_{65}ClBF_4P_5Pt_3$: C, 50.2; H, 3.51. Found: C 49.6, H 3.50%

IV (M = Pt): δ_1 6.2, $\delta_{2,3}$ 17.3, $\delta_{4,5}$ 93.2, J(16) 4516, J(17) 230, J(12) 82.7, J(27) 4784, J(46) 2199, J(47) 2637, J(48) 74.5, J(45) 176.

V (M = Pt, R″ = Me, I^- salt): δ_1 3.8, $\delta_{2,3}$ 11.5, $\delta_{4,5}$ 169.4, J(16) 4355, J(17) 215, J(12) 74.5, J(27) 4484, J(46) 2249, J(47) 2798, J(48) 97.7, J(45) 214. Anal. Calcd. for $C_{79}H_{68}IP_5Pt_3S$: C, 49.5; H, 3.58. Found: C, 49.6; H, 3.73%

VI (M = Pt, BF_4^- salt): δ_{123} 11.4, $\delta_{4,5}$ 98.4, J(16) ca. 2200, J(4Pt) ca. 5000. Isolated as PEt_3 derivative. Anal. Calcd. for $C_{54}H_{75}BF_4P_6Pt_3$: C, 41.0; H, 4.78. Found: C, 40.3; H 4.83%

19 ^{31}P data for the complexes **III** uses the following numbering scheme: PPh_2 P(1); PPh_3 P(2,3); dppm P(4,5); Pt(6,7). Coupling constants in hertz.

III (M = Pd, R = R′ = Ph, BF_4^- salt): δ_1 237.4, $\delta_{2,3}$ 15.6, $\delta_{4,5}$ 5.7, J(12) 31.2, J(14) 208, J(23) 200, J(24) −31.8, J(25) 7.4, J(45) 60. N.B. Although these parameters give a satisfactory simulation, only J(12) and J(14) are uniquely determined by the observed spectrum. Anal. Calcd. for $C_{73}H_{62}BF_4P_5Pd_2$: C, 62.9; H, 4.48: Found: C, 62.0; H, 4.72%

III (M = Pt, R = R′ = Ph, BF_4^- salt): δ_1 194.7, $\delta_{2,3}$ 20.8, $\delta_{4,5}$ 6.3, J(12) 11.0, J(14) 251, J(16) 2781, J(23) 149, J(24) 5.8, J(25) 0, J(26) 3293, J(27) 343, J(45) 54.6, J(46) 3065, J(47) 53.4, J(67) 500. Anal. Calcd. for $C_{73}H_{62}BF_4P_5Pt_2$: C, 55.8; H, 3.98: Found: C, 56.3; H, 3.99%

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