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Synthesis and Structure of $[Pt_3(\mu\text{-dppm})_2(\mu\text{-PPh}_2)L_2](O_3SCF_3)$ (dppm = Bis(diphenylphosphino)methane; L = CO, *t*-BuNC)

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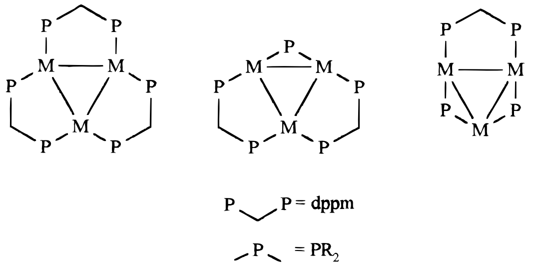
Treatment of $[Pt_2(\mu\text{-dppm})_2Cl_2]$ with 2 mequiv of AgO_3SCF_3 and bicyclo[2.2.1]hept-2-ene, respectively, in $MeOH/CH_2Cl_2$ results in a P−C cleavage of one dppm ligand to give $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)$ (**1a**) and the methoxyphosphonium salt $[PMePh_2(OMe)](O_3SCF_3)$. Treatment of **1a** with CO (1 atm) or 2 mequiv of *t*-BuNC gives $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)L_2](O_3SCF_3)$ where L = CO (**1b**) or *t*-BuNC (**1c**). The reaction of **1b** or **1c** with 1 mequiv of dppm and $[Pt(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_3]$, respectively, gives $[Pt_3(\mu\text{-dppm})_2(\mu\text{-PPh}_2)L_2](O_3SCF_3)$ where L = CO (**2a**) or *t*-BuNC (**2b**). The new compounds were characterized by multinuclear NMR, FAB-MS, IR, and chemical analysis, **1a**, **2a**, and **2b** additionally by single-crystal X-ray diffraction. In **1a**, the orientation of the C=C double bonds is nearly in plane with the other ligands coordinated to the Pt atoms. The molecular structures of **2a** and **2b** show Pt_3 triangles whose edges are spanned by two dppm ligands and one PPh_2 ligand. There are bonds between the platinum atoms bridged by the dppm ligands (2.6456(8) and 2.6733(6) Å for **2a** and 2.6463(11) and 2.6534(12) Å for **2b**) while the separations of the Pt atoms bridged by the PPh_2 ligand are very long (**2a**, 3.5949(6) Å; **2b**, 3.470(1) Å) and are clearly considered as nonbonding. The CO or *t*-BuNC ligands are coordinated terminally to the Pt atoms bridged by the PPh_2 ligand. The P atom of the phosphido group exhibits a short intramolecular contact to the third Pt atom of 2.954(3) Å (**2a**) or 2.933(5) Å (**2b**), which is significantly below the sum of the van der Waals radii of phosphorus and platinum.

Introduction

An impressive chemistry derives from the Puddephatt cluster $[Pt_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ containing the *triangulo*-$[Pt_3]^{2+}$ system with a formal oxidation number of $^2/_3$.[1,2] The coordinatively unsaturated cluster can mimic some of the properties of a metal surface as chemisorption and related phenomena as well as catalytic activity. The ability to coordinate small molecules under mild conditions mimics the adsorption at a Pt(111) surface at low temperatures. The cluster has been found a useful catalyst for the water gas shift reaction. Clusters of the $M_3(\mu\text{-dppm})_3$ type are bifunctional recognition hosts: The Lewis acidic M_3 triangle and the hydrophobic phenyl groups encycling the M_3 skeleton form a cavity being the basis of an interesting host−guest chemistry.[2,3] Various heteronuclear clusters in which one or two metals (e.g. Re,[4] Ru,[5] Ir,[6] Sn, Hg, or Au[2]) are bound to the $Pt_3(\mu\text{-dppm})_3$ core derive from $[Pt_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ and are, in part, models for heterometallic catalysis. Related subvalent group 10 metal clusters based on the $[Ni_3(\mu\text{-dppm})_3]^{2+}$ or $[Pd_3(\mu\text{-dppm})_3]^{2+}$ core have been reported.[7,8]

The three metal atoms are locked together in a triangle by μ-dppm ligands, preventing any cluster fragmentation. We are interested in potential new features upon substituting one or two of the neutral dppm ligands of the $M_3(\mu\text{-dppm})_3$ core by anionic μ-PR_2 groups, indicated as follows:



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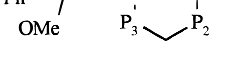
In this paper we report the synthesis and characterization of $Pt_3(\mu\text{-dppm})_2(\mu\text{-}PPh_2)$ type clusters.

Experimental Section

General Information. NMR spectra were recorded using a Bruker AC 200 spectrometer. ^1H and ^{13}C chemical shifts are relative to Me_4Si and were determined by reference to the residual ^1H and ^{13}C solvent peaks. $^{31}P/^{195}Pt$ chemical shifts are reported relative to 85% H_3PO_4/1 M Na_2PtCl_6, used as an external reference. Coupling constants are reported in hertz. In the NMR data, the P and Pt atoms are labeled as in the crystal structures. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer; mass spectra, on a Finnigan MAT 95 instrument. Elemental analyses were provided by the Institut für Physikalische Chemie der Universität Wien. Unless otherwise noted, reagents were from commercial suppliers. The compounds $[Pt(\eta^2\text{-bicyclo}[2.2.1]\text{hept-2-ene})_3]$ and $[Pt_2(\mu\text{-dppm})_2Cl_2]$ were prepared according to literature procedures.[9,10] The solvents were dried using standard procedures. All operations were carried out under standard Schlenk conditions.

$[Pt_2(\mu\text{-dppm})(\mu\text{-}PPh_2)(\eta^2\text{-bicyclo}[2.2.1]\text{hept-2-ene})_2](O_3SCF_3)$ (1a). To a solution of $[Pt_2(\mu\text{-dppm})_2Cl_2]$ (1.00 mmol, 1.27 g) and bicyclo[2.2.1]hept-2-ene (0.94 g, 10 mmol) in CH_2Cl_2 (70 mL) was added a solution of AgO_3SCF_3 (0.51 g, 2.00 mmol) in MeOH (10 mL). The solution was stirred for 2 days at 40 °C and then filtered, and the solvent was removed by evaporation under reduced pressure. The solid residue was washed with cold MeOH and dried under vacuum. Recrystallization from MeOH gave pale yellow crystals of **1a**. Yield: 70%. Anal. Calcd for $C_{52}H_{52}F_3O_3P_3Pt_2S$: C, 48.15; H, 4.04. Found: C, 48.58; H, 4.01. ^1H NMR (CD_2Cl_2): bicyclo[2.2.1]hept-2-ene δ 3.43 (m, 4H, $^2J(PtH) = 56.8$, HC═CH), 1.86 (m, 4H, CH), 1.00 (m, 8H, CH_2), −0.04 (m, 4H, CH_2 bridge). ^{13}C NMR (CD_2Cl_2): bicyclo[2.2.1]hept-2-ene δ 79.5 ($^1J(PtC) = 145$, $^2J(PtC) = 24$, C═C), 43.1 ($^3J(PtC) = 13$, CH_2 bridge), 41.4 ($^2J(PtC) = 37$, CH), 27.4 ($^3J(PtC) = 38.8$, CH_2); dppm δ 61.2 (t, $^2J(PtC) = 106.3$, $^1J(PC) = 27.4$, PCH_2P). ^{31}P NMR (CD_2Cl_2): δ 229.0 (t, $^2J(PP) = 184.9$, $^1J(PtP) = 2617$, PPh_2), 0.8 (d, $^2J(PCP) = 55.7$, $^1J(PtP) = 3001$, $^2J(PtP) = 54.9$, dppm). ^{195}Pt NMR (CD_2Cl_2): δ −5786 (ddd, $^1J(PtPt) = 2133$). MS (FAB, positive ions; *m*/*z*) 1147.3 (M^+), 1053.2 ($M^+ - C_7H_{10}$), 959.1 ($M^+ - 2C_7H_{10}$).

The methoxyphosphonium salt **$[PMePh_2(OMe)](O_3SCF_3)$** was present in the MeOH fraction. ^1H NMR (CD_2Cl_2): δ 7.8 (m, 10H, Ph), 4.0 (d, $^3J(PH) = 12.2$, 3H, OCH_3), 2.8 (d, $^2J(PH) = 13.4$, 3H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 57.8 (dq, $^1J(CH) = 151.7$, $^2J(PC) = 7.4$, OCH_3), 10.4 (dq, $^1J(CH) = 133.2$, $^1J(PC) = 66.6$, CH_3). ^{31}P NMR (CD_2Cl_2): δ 74.5. The ^1H and ^{31}P NMR data are in good agreement with those reported in the literature.[11]



1d

$[Pt_2(\mu\text{-dppm})(\mu\text{-}PPh_2)(\sigma\text{-}CH_2PPh_2(OMe))(\eta^2\text{-bicyclo}[2.2.1]\text{hept-2-ene})](O_3SCF_3)$ (1d). ^{31}P NMR (CH_2Cl_2/MeOH, 1/1): δ 186.5 (ddd, $^2J(P1P2) = 171.3$, $^2J(P1P3) = 313.6$, $^3J(P1P4) = 4.6$, $^1J(Pt1P1) = 2393$, $^1J(Pt2P1) = 3352$, P1), −2.6 (dd, $^2J(P2P3) = 53.5$, $^1J(Pt1P2) = 3053$, $^2J(Pt2P2) = 90$, P2), 9.33 (ddd, $^3J(P3P4) = 15.3$, $^2J(Pt1P3) = 70$, $^1J(Pt2P3) = 3004$, P3), 76.2 (dd, $^2J(Pt2P4) = 34$, P4).

$[Pt_2(\mu\text{-dppm})(\mu\text{-}PPh_2)(CO)_2](O_3SCF_3)$ (1b). This species was obtained by bubbling CO for 2 min at room temperature through a solution of **1a** (0.03 mmol, 38.9 mg) in CH_2Cl_2 (0.5 mL). Petroleum ether (bp 50−70 °C) (2 mL) was added under an atmosphere of CO, and the white precipitate formed was collected by filtration and washed with the petroleum ether and dried in vacuo. Yield: 77%. Anal. Calcd for $C_{40}H_{32}F_3O_5P_3Pt_2S$: C, 41.25; H, 2.77. Found: C, 41.35; H, 2.69. ^{31}P NMR (CD_2Cl_2): δ 210.9 (t, $^2J(PP) = 221.7$, $^1J(PtP) = 2642$, PPh_2), 4.1 (d, $^2J(PCP) = 62.8$, $^1J(PtP) = 2838$, $^2J(PtP) = 43$, dppm). ^{195}Pt NMR (CD_2Cl_2): δ −4885 (ddd, $^1J(PtPt) = 1803$). IR (Nujol; cm^{-1}): ν(CO) 2072 w, 2057 s.

$[Pt_2(\mu\text{-dppm})(\mu\text{-}PPh_2)(t\text{-BuNC})_2](O_3SCF_3)$ (1c). To a solution of **1a** (0.1 mmol, 130 mg) in CH_2Cl_2 (0.8 mL) was added *t*-BuNC (23 μL, 0.2 mmol). The reaction mixture was stirred for 15 min, and the solvent and bicyclo[2.2.1]hept-2-ene were removed in vacuo, affording a red air-stable powder. Yield: 98%. Anal. Calcd for $C_{48}H_{50}F_3N_2O_3P_3Pt_2S$: C, 45.21; H, 3.95; N, 2.19. Found: C, 45.43; H, 3.86; N, 2.11. ^{31}P NMR (CD_2Cl_2): δ 193.4 (t, $^2J(PP) = 259.4$, $^1J(PtP) = 2824$, PPh_2), 4.1 (d, $^2J(PCP) = 61.0$, $^1J(PtP) = 2960$, $^2J(PtP) = 55.7$, dppm). ^{195}Pt NMR (CD_2Cl_2): δ −5038 (ddd, $^1J(PtPt) = 1552$). IR (Nujol; cm^{-1}): ν(NC) 2149 s.

$[Pt_3(\mu\text{-dppm})_2(\mu\text{-}PPh_2)(CO)_2](O_3SCF_3)$ (2a). A solution of **1b** (0.05 mmol, 58 mg) in CH_2Cl_2 (0.8 mL) was stirred with dppm (0.05 mmol, 19.2 mg) and $[Pt(\eta^2\text{-bicyclo}[2.2.1]\text{hept-2-ene})_3]$ (0.05 mmol, 23.9 mg) under 1 atm of CO for 15 min. The solvent and bicyclo[2.2.1]hept-2-ene were removed, affording a yellow air-stable powder. Recrystallization from CH_2Cl_2/ethyl acetate gave yellow crystals of **2a**. Yield: 63%. Anal. Calcd for $C_{65}H_{54}F_3O_5P_5Pt_3S$: C, 44.76; H, 3.12. Found: C, 44.39; H, 2.93. ^{31}P NMR (CD_2Cl_2): δ 61.1 ($^2J(P1P2) = 282.5$, $^3J(P1P4) = 2.4$, $^2J(Pt1P1) = 297$, $^1J(Pt2P1) = 2211$, P1), 13.1 ($^2J(P2P3) = -6.82$, $^3J(P2P4) = 106.1$, $^3J(P2P5) = -0.3$, $^2J(Pt1P2) =$ ca. 0, $^1J(Pt2P2) = 2674$, $^3J(Pt3P2) = 144$, P2), 17.9 ($^2J(P4P5) = -8.35$,$^1J(Pt1P4) = 2716$, $^2J(Pt2P4) =$ ca. 0, $^2J(Pt3P4) = 562$, P4). ^{195}Pt NMR (CD_2Cl_2): δ −4995 ($^1J(Pt1Pt2) = 789$, Pt1), −4658 (Pt2). MS (FAB; *m*/*z*): 1687.8 ($M^+trif^- -$ 2CO), 1538.2 ($M^+ -$ 2CO). IR (Nujol; cm^{-1}): ν(CO) 2041 s, 2020 vs.

$[Pt_3(\mu\text{-dppm})_2(\mu\text{-}PPh_2)(t\text{-BuNC})_2](O_3SCF_3)$ (2b). A solution of **1c** (0.05 mmol, 64 mg) in CH_2Cl_2 (0.8 mL), dppm (0.05 mmol, 19.2 mg), and $[Pt(\eta^2\text{-bicyclo}[2.2.1]\text{hept-2-ene})_3]$ (0.05 mmol, 23.9 mg) was stirred for 5 min. The solvent and bicyclo[2.2.1]hept-2-ene were removed in vacuo, affording a yellow air-stable powder. Recrystallization from CH_2Cl_2 gave **2b** as yellow crystals. Yield: 76%. Anal. Calcd for $C_{73}H_{72}F_3N_2O_3P_5Pt_3S$: C, 47.28; H, 3.91; N, 1.51. Found: C, 46.88; H, 3.88; N, 1.46. ^{31}P NMR (CD_2Cl_2): δ 62.5 ($^2J(P1P2) = 319.0$, $^3J(P1P4) = -1.73$, $^2J(Pt1P1) = 372$, $^1J(Pt2P1) = 2226$, P1), 13.6 ($^2J(P2P3) = -7.90$, $^3J(P2P4) = 117.1$, $^3J(P2P5) = -3.59$, $^2J(Pt1P2) =$ ca. 0, $^1J(Pt2P2) = 2698$, $^3J(Pt3P2) = 128$, P2), 16.0 ($^2J(P4P5) = -5.86$, $^1J(Pt1P4) = 2601$, $^2J(Pt2P4) =$ ca. 0, $^2J(Pt3P4) = 588$, P4). ^{195}Pt NMR (CD_2Cl_2): δ −5050 ($^1J(Pt1Pt2) = 891$, Pt1), −4832 (Pt2). MS (FAB, positive ions; *m*/*z*): 1704.3 (M^+). IR (Nujol; cm^{-1}): ν(NC) 2167 s, 2136 vs.

X-ray Structure Determinations. Crystals of compounds **1a**, **2a**, and **2b** were examined by similar procedures. Crystals were mounted on a glass fiber, and X-ray data were collected on a Siemens P4 diffractometer using Mo Kα radiation (monochromator: highly oriented graphite crystal, ω-scan). Unit cell parameters were determined and refined from 30−41 randomly selected reflections in the θ range 5.3−12.5°, obtained by the P4 automatic routine. Every 97 reflections, 3 standard reflections were measured. Data were corrected for Lorentz−polarization and absorption effects (ψ-scans). The structures were solved by direct methods and subsequent

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Table 1. Crystal Data and Structure Refinement

	1a·2MeOH	**2a**·3CH_2Cl_2	**2b**
empirical formula	$C_{52}H_{52}F_3O_3P_3Pt_2S·2MeOH$	$C_{65}H_{53}F_3O_5P_5Pt_3S·3CH_2Cl_2$	$C_{73}H_{72}F_3N_2O_3P_5Pt_3S$
fw	1361.17	1998.03	1854.51
crystal system	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
unit cell dimens	$a = 13.514(3)$ Å, $b = 18.532(2)$ Å, $c = 20.942(4)$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$	$a = 11.592(4)$ Å, $b = 26.965(2)$ Å, $c = 22.816(2)$ Å, $\alpha = 90°$, $\beta = 91.26(2)°$, $\gamma = 90°$	$a = 15.601(6)$ Å, $b = 26.597(5)$ Å, $c = 17.071(4)$ Å, $\alpha = 90°$, $\beta = 90.31(3)°$, $\gamma = 90°$
vol, nm^3	5.245(2)	7.130 (3)	7.083 (4)
Z	4	4	4
density (calcd), Mg/m^3	1.724	1.861	1.739
temp, K	213(2)	213(2)	218(2)
abs coeff, mm^{-1}	5.517	6.294	6.108
color, habit	light yellow prism	yellow prism	yellow prism
crystal size, mm	0.45 × 0.45 × 0.4 mm	0.8 × 0.18 × 0.18 mm	0.4 × 0.25 × 0.15 mm
θ range for data collcn, deg	2.67−23.50	2.59−21.75	2.51−20.35
index ranges	$-5 \le h \le 15$, $-1 \le k \le 21$, $-1 \le l \le 23$	$0 \le h \le 11$, $0 \le k \le 28$, $-23 \le l \le 23$	$0 \le h \le 15$, $-1 \le k \le 26$, $-17 \le l \le 17$
no. of reflcns collected	6495	8890	7639
no. of indep reflcns	5727 ($R_{int} = 0.0168$)	8387 ($R_{int} = 0.0290$)	6913 ($R_{int} = 0.0529$)
no. of reflcns with $I > 2\sigma(I)$	5166	6578	4946
max and min transm	0.838 and 0.677	0.953 and 0.846	0.904 and 0.565
data/restraints/parameters	5609/4/648	7862/0/820	6324/7/812
goodness-of-fit on F^2	1.050	1.037	1.033
final R indices [$I > 2\sigma(I)$]	R1 = 0.0285, wR2 = 0.0565	R1 = 0.0360, wR2 = 0.0757	R1 = 0.0501, wR2 = 0.1055
R indices (all data)	R1 = 0.0368, wR2 = 0.0593	R1 = 0.0576, wR2 = 0.0850	R1 = 0.0869, wR2 = 0.1246
absolute structure parameter	−0.014(8)		
largest diff peak and hole, $e\ nm^{-3}$	694 and −568	1421 and −816	1188 and −1253
scan speed, deg/min in ω	4.0	5.0	5.0
scan range (ω), deg	0.75	0.7	0.65
weighting scheme	calc $w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 4.3664P]$ where $P = (F_o^2 + 2F_c^2)/3$	calc $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 29.6800P]$ where $P = (F_o^2 + 2F_c^2)/3$	calc $w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 37.5663P]$ where $P = (F_o^2 + 2F_c^2)/3$

difference Fourier techniques (SHELXS-86).[12] Refinement on F^2 with all measured reflections was carried out by full-matrix least-squares techniques (SHELXL-93).[13]

Pale yellow crystals of $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)·2MeOH$ were obtained by slowly cooling a boiling methanolic solution of **1a** to room temperature. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at C1, C2, C8, and C9 were refined isotropically with a fixed distance of 0.95 Å to the C atoms. All other hydrogen atoms were placed at calculated ideal positions (riding model). Hydrogen atoms at the MeOH molecules were omitted. One of the solvent molecules was found to be disordered and was refined in two positions with 0.5 occupancy.

Yellow crystals of $[Pt_3(\mu\text{-dppm})_2(\mu\text{-PPh}_2)(CO)_2](O_3SCF_3)·3CH_2Cl_2$ were grown by slow diffusion of ethyl acetate into a solution of **2a** in CH_2Cl_2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated ideal positions (riding model).

Yellow crystals of $[Pt_3(\mu\text{-dppm})_2(\mu\text{-PPh}_2)(t\text{-BuNC})_2](O_3SCF_3)$ were grown by slow evaporation of a solution of **2b** in CH_2Cl_2. All non-hydrogen atoms of the $[Pt_3(\mu\text{-dppm})_2(\mu\text{-PPh}_2)(t\text{-BuNC})_2]^+$ cation were refined anisotropically. Hydrogen atoms were placed at calculated ideal positions (riding model). The $O_3SCF_3^-$ anion was found to be disordered in two positions: one lies nearby an inversion center with S1 = C11, F1 = O1, F2 = O2, and F3 = O3; the other has an occupancy of 0.5 at a common position. Only S2 could be refined anisotropically.

Crystal data and details of the structure determinations and refinements are collected in Table 1.

Listings of positional and thermal parameters, complete bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1a**·2MeOH, **2a**·3CH_2Cl_2, and **2b** (32 pages). Ordering information is given on any current masthead page.

Results and Discussion

$[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)L_2](O_3SCF_3)$ (L = Bicyclo[2.2.1]hept-2-ene (1a), CO (1b), *t*-BuNC (1c)). The reaction of $[Pt_2(\mu\text{-dppm})_2Cl_2]$ with 2 mequiv of AgO_3SCF_3 and bicyclo[2.2.1]hept-2-ene, respectively, in CH_2Cl_2/MeOH gives $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_2](O_3SCF_3)$ (**1a**) and the methoxyphosphonium salt $[PMePh_2(OMe)](O_3SCF_3)$[11] according to Scheme 1.

This reaction involves the fission of the bond between the aliphatic carbon and one phosphorus atom of one dppm ligand. The cleavage of P−C bonds of dppm in the coordination sphere of various metals has been previously observed: in one type, a metal-mediated oxidative P−C bond cleavage gives PPh_2 and CH_2PPh_2 fragments. Either both P groups or only the PPh_2 group is retained in the coordination sphere of the metal.[14−18]

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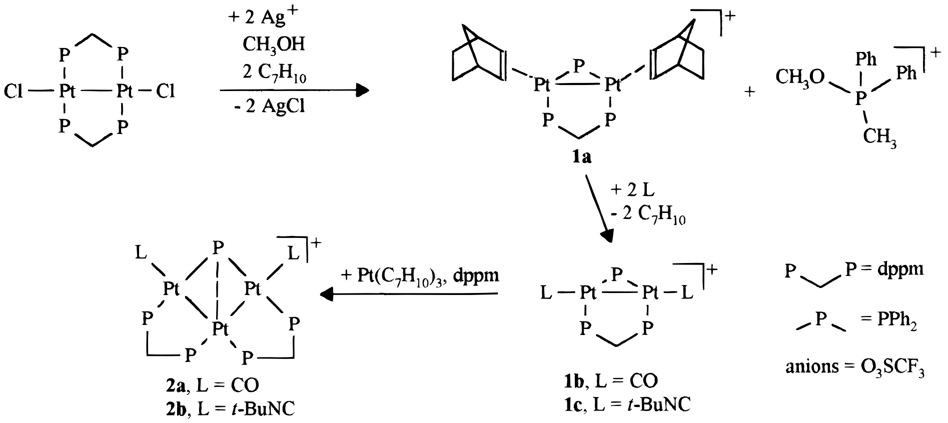
Scheme 1



A second type, formally a hydrolysis of dppm, involves a nucleophilic attack by hydroxide ions at one phosphorus atom to produce $Ph_2P(O)H$ and $MePh_2P$.[19]

The reaction sketched in Scheme 1 does not occur in the absence of bicyclo[2.2.1]hept-2-ene. This may be in keeping with recent evidence indicating that the P−C cleavage in a Ru complex is more sensitive to an electronic supersaturation than to a transient unsaturation.[14]

No platinum intermediate carrying a CH_2PPh_2 ligand was detected when the present reaction was monitored by ^{31}P NMR. In the presence of the base $CaCO_3$ however, [Pt_2(μ-dppm)(μ-PPh_2)(σ-CH_2PPh_2(OMe))(η^2-bicyclo[2.2.1]hept-2-ene)](O_3SCF_3) (**1d**) was identified as an intermediate by ^{31}P NMR spectroscopy (see Experimental Section), indicating a possible mechanism: The fission of the P−C bond results in [Pt_2(μ-dppm)(μ-PPh_2)(CH_2PPh_2)(η^2-bicyclo[2.2.1]hept-2-ene)](O_3SCF_3)$_2$. A nucleophilic attack by methanol at the phosphorus atom of the CH_2PPh_2 group gives **1d** and 1 mequiv of trifluoromethanesulfonic acid. In the absence of $CaCO_3$, the products **1a** and [$PMePh_2$(OMe)](O_3SCF_3) are finally formed via acidolysis of the Pt−C σ-bond by HO_3SCF_3 and subsequent coordination of bicyclo[2.2.1]-hept-2-ene.

In this context, it is interesting to note, that the side-on-coordinated CH_2PPh_2 ligand in [$Ru_2(CO)_2(PR_3)$(η^2-CH_2PPh_2)(μ-O_2CMe)(μ-dppm)(μ-PPh_2)]$^+$, which was also generated via a CH_2−P cleavage of dppm, was extruded by the nucleophilic attack of PR_3 at the carbon site to give [$PPh_2CH_2PR_3$]$^+$ whereas the nucleophile MeOH attacks at the P atom in the present reaction.[14]

The [Pt_2(μ-dppm)(μ-PPh_2)] framework was previously described in the complex [Pt_2(μ-dppm)(μ-PPh_2)(PPh_3)$_2$]$^+$, which was obtained by fragmentation of the trinuclear clusters [Pt_3(μ-PPh_2)$_2$(PPh_3)$_3$X]$^+$ (X = Cl, H, PR_2, SR) with dppm.[20]

As indicated in Scheme 1, the bicyclo[2.2.1]hept-2-ene ligands of **1a** are readily substituted by CO or *t*-BuNC to give **1b** and **1c**.

A X-ray crystallographic study of **1a** was undertaken. A drawing of the cation of **1a** is shown in Figure 1.

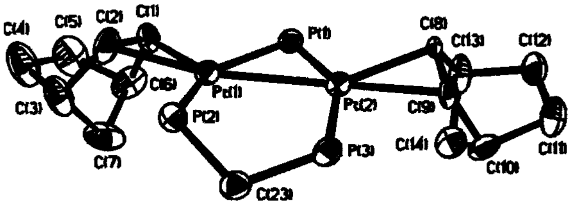


Figure 1. Molecular structure of **1a**. The trifluoromethanesulfonate anion and phenyl groups are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 1a

Pt(1)−Pt(2)	2.7047(6)	Pt(1)−C(1)	2.181(9)
Pt(1)−P(1)	2.236(2)	Pt(1)−C(2)	2.203(10)
Pt(1)−P2)	2.299(2)	Pt(2)−C(8)	2.204(9)
Pt(2)−P(1)	2.232(2)	Pt(2)−C(9)	2.193(8)
Pt(2)−P(3)	2.291(2)	C(1)−C(2)	1.409(14)
		C(8)−C(9)	1.386(12)
P(2)−Pt(1)−Pt(2)	91.57(6)	Pt(1)−P(1)−Pt(2)	74.52(7)
P(2)−Pt(1)−P(1)	143.96(9)	C(23)−P(2)−Pt(1)	112.4(3)
Pt(2)−Pt(1)−P(1)	52.68(6)	C(23)−P(3)−Pt(2)	113.8(3)
P(3)−Pt(2)−Pt(1)	94.74(7)	P(2)−C(23)−P(3)	110.0(5)
P(3)−Pt(2)−P(1)	147.06(9)	C(1)−Pt(1)−P(1)	87.4(3)
Pt(1)−Pt(2)−P(1)	52.80(6)	C(2)−Pt(1)−P(2)	91.2(3)
C(8)−Pt(2)−P(1)	91.3(2)	C(1)−Pt(1)−C(2)	37.5(4)
C(9)−Pt(2)−P(3)	85.4(2)	C(8)−Pt(2)−C(9)	36.8(3)

Selected bond distances and angles are listed in Table 2.

Crystals of **1a** contain one trifluoromethanesulfonate anion and two methanol molecules for each [Pt_2(μ-dppm)(μ-PPh_2)(bicyclo[2.2.1]hept-2-ene)$_2$]$^+$ cation. The anion and the methanol molecules show no unusual structural features and will not be considered further here.

The orientation of the C═C double bonds is nearly coplanar with the other ligands coordinated to the Pt atoms: the deviations of the π-bonded carbon atoms from the least-squares planes spanned by the platinum atoms and the corresponding two cis phosphorus atoms amount to 0.04(1) and −0.27(1) Å for C1 and C2 and −0.41(1) and −0.14(1) Å for C8 and C9. An approximately "in-plane" geometry for olefin ligands is characteristic for three-coordinated Pt(0) complexes.[21] In Pt(II) complexes, alkenes are usually coordinated "up-

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right" to the metal atom, with the C=C double bond perpendicular to the platinum coordination plane,[21] but there also exist a few examples of "in-plane" and intermediate orientation, which were attributed to the geometry and steric demands of the olefins.[22] The "in-plane" coordination geometry of the alkenes in **1a** may be favored by the ample P1−Pt1−P2/P1−Pt2−P3 angles of ca. 214.5° (average) within the $Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)$ framework. A search in the Cambridge Structural Database for Pt(I)−olefin complexes gave $[Pt_2(\mu\text{-(CF}_3)_2\text{-CO}))(\eta^4\text{-cycloocta-1,5-diene})_2]$ as the sole structurally characterized example. All C=C double bonds are oriented "upright" in this complex.[23]

The C=C double bonds of the bicyclo[2.2.1]hept-2-ene ligands show a lengthening to 1.40 Å (average); the Pt−C(π) bond lengths with a mean distance of 2.20 Å correspond to those found for other platinum π-olefin complexes.[24] Both of the bridging methylene groups of the bicyclo[2.2.1]hept-2-ene ligands are on the same side of the platinum coordination plane. The bicyclo[2.2.1]-hept-2-ene molecules are positioned directly in the middle between the cis-phosphorus atoms with an angle X−Pt−P of 107° (average; X = midpoint of the C=C double bond).

In the $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\text{bicyclo[2.2.1]hept-2-ene})_2]^+$ cation, the Pt1−Pt2 distance (2.7047(6) Å) lies in the range of Pt−Pt bond lengths found for diplatinum(I) complexes[25] and is very similar to the Pd−Pd separation (2.688(2) Å) in the related Pd(I) complex $[Pd_2(\mu\text{-}i\text{-Pr}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{PPh}_3)_2]^+$.[20] The five-membered ring formed by the two Pt atoms and the dppm ligand adopts an envelope conformation with the methylene carbon at the flap.

The $^{31}P\{^1H\}$ NMR spectra of **1a**−**c** recorded at ambient temperature in CD_2Cl_2 show the pattern of an A_2X spin system and are flanked by satellites due to coupling with ^{195}Pt nuclei. The chemical shifts and coupling constants of **1a**−**c** are similar to the values reported for $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)(\text{PPh}_3)_2]^+$.[20] The chemical shift of P1 increases and the value of ^1J(PtP1) decreases in the order $PPh_3 \approx t$-BuNC/CO/bicyclo[2.2.1]hept-2-ene. The $^{195}Pt\{^1H\}$ NMR spectra of **1a**−**c** exhibit resonances at −5786 ppm (**1a**), −4885 ppm (**1b**), and −5038 ppm (**1c**). There is a remarkably large difference between the shifts of **1a** and **1b**, which is however difficult to evaluate in view of a lack of comparable data. The $^{195}Pt\{^1H\}$ NMR spectra of **1a**−**c** also reveal the pattern of the isotopomers containing two ^{195}Pt nuclei, from which the ^1J(PtPt) couplings are extracted, which decrease in the order PPh_3 > *t*-BuNC > CO > bicyclo-[2.2.1]hept-2-ene.

$[Pt_3(\mu\text{-dppm})_2(\mu\text{-PPh}_2)L_2](O_3SCF_3)$ (L= CO (2a), *t*-BuNC (2b)). Upon treatment of **1b** with the zerovalent platinum complex $[Pt(\eta^2\text{-bicyclo[2.2.1]hept-2-ene})_3]$ and dppm, the cationic trinuclear cluster **2a** is formed according to Scheme 1. Similarly, the related cluster **2b** is obtained from **1c**. The solid-state structures of **2a** and **2b** are shown in Figures 2 and 3, and selected interatomic distances and angles are collected in Table 3.

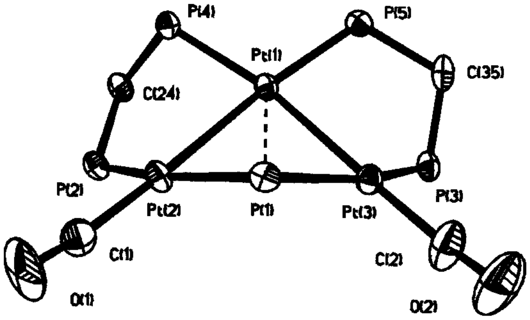

Figure 2. Molecular structure of **2a**. The trifluoromethanesulfonate anion and phenyl groups are omitted for clarity.

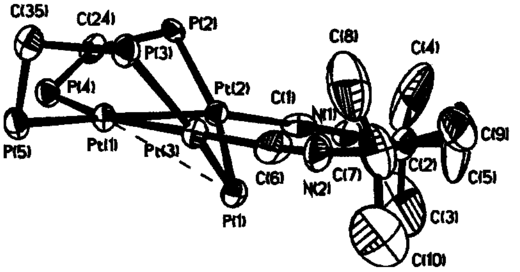

Figure 3. Molecular structure of **2b**. The trifluoromethanesulfonate anion and phenyl groups are omitted for clarity.

The cluster skeleton of **2a** and **2b** consists of a Pt_3 triangle with the edges spanned by two bridging dppm ligands and one bridging phosphido group. The dppm-bridged platinum atoms involve short Pt−Pt distances (2.6456(8) and 2.6733(6) Å for **2a** and 2.6463(11) and 2.6534(12) Å for **2b**) whereas a long Pt−Pt separation is observed between the phosphido-bridged Pt atoms (**2a**, 3.5949(6) Å; **2b**, 3.470(1) Å). The carbonyl ligands are η^1-coordinated to the terminal Pt atoms of the bent Pt_3 chain with a Pt−C−O angle of 173.7° (average), a mean Pt−C distance of 1.90 Å, and a C−O bond length of 1.13 Å (average). The terminal isonitrile ligands in **2b** exhibit approximately linear geometries (mean Pt−C−N angle 174.5°; mean C−N−C angle 176°), the Pt−C distance is 1.96 Å (average), and the C−N bond length is 1.15 Å (average). Each of the three Pt atoms in **2a** and **2b** shows an approximately square planar coordination geometry as indicated in Figures 2 and 3. The least-squares planes through Pt2 and Pt3 are twisted by 37.7° (average) with respect to the least-squares plane through Pt1 in **2a** (**2b**: 39.7°, average). Due to the folding of the Pt coordination planes, the P atom of the phosphido bridge adopts a position with a short contact to Pt1 (**2a**, 2.954(3) Å; **2b**, 2.933(5) Å) which is distinctly less than the van der Waals estimate of 3.6 Å. There are examples for μ_2-phosphido groups with a short contact to a third metal atom known in the literature. The M−P distances range from 3.002 Å, attributable to weak electronic interaction, to 2.466 Å, representing a triply bridging phosphido group.[26,27] The

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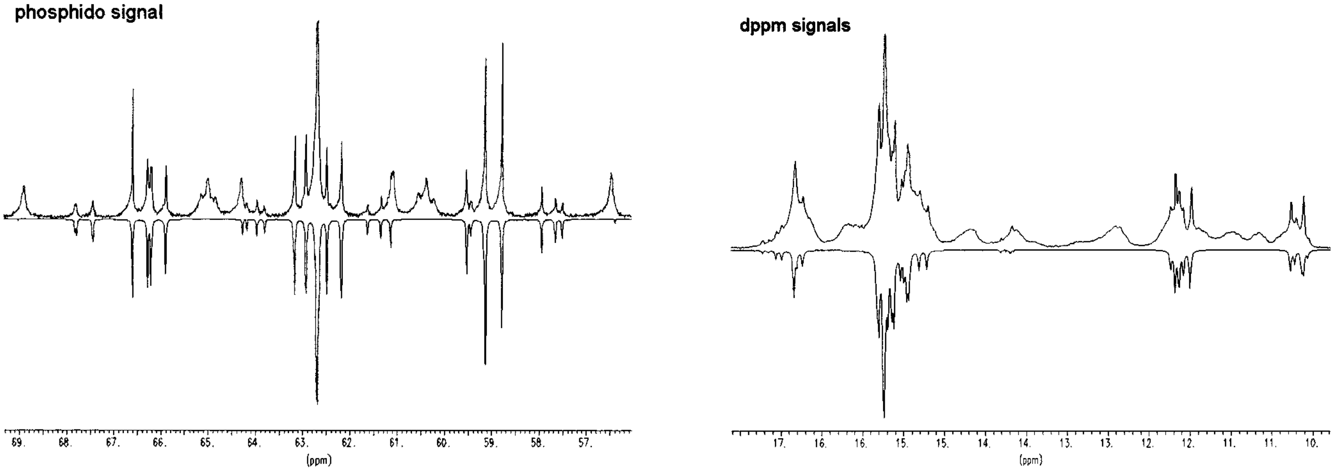

Figure 4. Experimental $^{31}P\{^1H\}$ NMR spectrum of **2b** (upper trace) and simulated spectrum (lower trace, isotopomer without ^{195}Pt nuclei). Additional peaks in the experimental spectrum with respect to the simulated spectrum result from the isotopomers containing ^{195}Pt nuclei; especially in the dppm region, the signals are overlapping with the platinum satellites, which are broadend by chemical shift anisotropy and probably by scalar relaxation of the second kind (coupling of ^{195}Pt with ^{14}N of the isonitriles).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 2a and 2b

2a		**2b**	
Pt(1)−Pt(2)	2.6733 (6)	Pt(1)−Pt(2)	2.6463 (11)
Pt(1)−Pt(3)	2.6456 (8)	Pt(1)−Pt(3)	2.6534 (12)
Pt(1)−P(4)	2.289 (3)	Pt(1)−P(4)	2.263 (5)
Pt(1)−P(5)	2.275 (3)	Pt(1)−P(5)	2.261 (5)
Pt(2)−P(1)	2.285 (3)	Pt(2)−P(1)	2.275 (4)
Pt(2)−P(2)	2.321 (3)	Pt(2)−P(2)	2.279 (4)
Pt(3)−P(1)	2.276 (2)	Pt(3)−P(1)	2.294 (5)
Pt(3)−P(3)	2.284 (2)	Pt(3)−P(3)	2.310 (5)
Pt(2)−C(1)	1.913 (12)	Pt(2)−C(1)	1.97 (2)
Pt(3)−C(2)	1.893 (12)	Pt(3)−C(6)	1.94 (2)
O(1)−C(1)	1.124 (12)	N(1)−C(1)	1.15 (2)
O(2)−C(2)	1.132 (13)	N(2)−C(6)	1.14 (2)
Pt(3)−Pt(1)−Pt(2)	85.04 (2)	Pt(3)−Pt(1)−Pt(2)	81.80 (4)
Pt(2)−Pt(1)−P(4)	83.87 (7)	Pt(2)−Pt(1)−P(4)	90.47 (12)
P(4)−Pt(1)−P(5)	102.06 (9)	P(4)−Pt(1)−P(5)	103.4 (2)
P(5)−Pt(1)−Pt(3)	89.01 (7)	P(5)−Pt(1)−Pt(3)	84.13 (12)
P(4)−Pt(1)−Pt(3)	168.87 (6)	P(4)−Pt(1)−Pt(3)	169.91 (12)
P(5)−Pt(1)−Pt(2)	174.02 (7)	P(5)−Pt(1)−Pt(2)	165.92 (12)
P(1)−Pt(2)−C(1)	98.4 (3)	P(1)−Pt(2)−C(1)	96.7 (5)
C(1)−Pt(2)−P(2)	98.9 (3)	C(1)−Pt(2)−P(2)	102.2 (5)
P(2)−Pt(2)−Pt(1)	90.79 (6)	P(2)−Pt(2)−Pt(1)	88.59 (11)
Pt(1)−Pt(2)−P(1)	72.65 (6)	Pt(1)−Pt(2)−P(1)	72.71 (12)
P(2)−Pt(2)−P(1)	161.98 (9)	P(2)−Pt(2)−P(1)	160.7 (2)
C(1)−Pt(2)−Pt(1)	168.3 (4)	C(1)−Pt(2)−Pt(1)	169.2 (5)
P(3)−Pt(3)−C(2)	99.4 (3)	P(3)−Pt(3)−C(6)	93.1 (6)
C(2)−Pt(3)−P(1)	99.6 (3)	C(6)−Pt(3)−P(1)	104.3 (6)
P(1)−Pt(3)−Pt(1)	73.33 (6)	P(1)−Pt(3)−Pt(1)	72.31 (11)
Pt(1)−Pt(3)−P(3)	88.16 (7)	Pt(1)−Pt(3)−P(3)	90.17 (12)
P(3)−Pt(3)−P(1)	160.45 (9)	P(3)−Pt(3)−P(1)	162.0 (2)
C(2)−Pt(3)−Pt(1)	171.0 (4)	C(6)−Pt(3)−Pt(1)	176.4 (6)
Pt(3)−P(1)−Pt(2)	104.04 (9)	Pt(3)−P(1)−Pt(2)	98.8 (2)
Pt(2)−P(2)−C(24)	113.0 (3)	Pt(2)−P(2)−C(24)	110.7 (6)
C(35)−P(3)−Pt(3)	106.8 (3)	C(35)−P(3)−Pt(3)	112.8 (6)
C(24)−P(4)−Pt(1)	107.9 (3)	C(24)−P(4)−Pt(1)	115.8 (6)
Pt(1)−P(5)−C(35)	115.2 (3)	Pt(1)−P(5)−C(35)	105.5 (5)
O(1)−C(1)−Pt(2)	172.5 (11)	N(1)−C(1)−Pt(2)	176 (2)
O(2)−C(2)−Pt(3)	174.9 (12)	N(2)−C(6)−Pt(3)	173 (2)
P(2)−C(24)−P(4)	106.5 (5)	P(2)−C(24)−P(4)	110.2 (9)
P(5)−C(35)−P(3)	108.9 (5)	P(5)−C(35)−P(3)	106.0 (8)
		C(1)−N(1)−C(2)	178 (2)
		C(6)−N(2)−C(7)	174 (2)

Pt···P distances in **2a** and **2b** may be classified as van der Waals contacts.[28]

In contrast to those of other dppm-bridged triplatinum complexes,[2] the Pt_2PCP rings in **2a** and **2b** do not show envelope conformations but are twisted.

Clusters **2a** and **2b** are based on the $[Pt_3]^{2+}$ or $Pt^I_2Pt^0$ system involving the formal oxidation number of $^2/_3$ like the Puddephatt cluster $[Pt_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ and various derivatives.[2] The formal substitution of one dppm ligand in the $Pt_3(\mu\text{-dppm})_3$ framework of $[Pt_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ by a PPh_2 group has interesting implications: First, there are only two Pt−Pt bonds in the Pt_3 system of **2a**, whereas the platinum atoms in $[Pt_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ are arranged in the form of an almost equilateral triangle (Pt−Pt distances 2.613−2.650 Å).[1] Second, two η^1-CO ligands are coordinated to the Pt atoms in **2a**, making an electron count of 44, whereas the Puddephatt cluster contains one μ_3-CO and thus has 42 electrons.

Other examples involving the $[Pt_3]^{2+}$ core comprise $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_8](PF_6)_2$ (44 e),[29] $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6(PPh_3)_2](PF_6)_2$,[29,30] and $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_4(\eta^2\text{-dppen})_2](PF_6)_2$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethene) (44 e),[31] which all adopt a linear Pt_3 chain. The A-frame type cluster $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_4(\mu\text{-dppm})_2](PF_6)_2$ (44 e) involves a bent triplatinum chain with an average Pt−Pt bond length of 2.593 Å and a nonbonded Pt−Pt distance of 3.304(2) Å.[29,32] The two dppm ligands doubly bridge the nonbonded platinum atoms, and this represents an arrangement of the $Pt_3(\mu\text{-dppm})_2$ fragment which is isomeric with that of **2a** and **2b**. The 42 e cluster $Pt_3(\mu\text{-Ph})(\mu\text{-}SO_2)(\mu\text{-}PPh_2)(PPh_3)_3$ exhibits a triangular Pt skeleton (Pt−Pt 2.8155(10), 2.6958(12), 2.7810(14) Å).[33]

There also exist clusters involving a $[Pt_3]^{4+}$ or

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$Pt^{I}_2Pt^{II}$ system: the 44 e cluster $Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2$ exhibits an interesting skeletal isomerism and exists alternately in a cyclic (Pt−Pt 2.956(3), 2.956(3), 3.074(4) Å) or open triangle form (Pt−Pt 2.758(3), 2.758(3), 3.586(2) Å) depending on the crystallization conditions.[34] Extended Hückel calculations showed that the former isomer is slightly more stable. Other examples are the recently reported $Pt_3(\mu\text{-}t\text{-}Bu_2P)_3(H)(CO)_2$ (44 e, with two short (2.7247(6), 2.7165(6) Å) and one long (3.6135(6) Å) Pt−Pt distances)[35] and the abovementioned 42-electron clusters $[Pt_3(\mu\text{-}PPh_2)_2(PPh_3)_3X]^+$ (X = Cl, H, PR_2, SR).[20]

A $[Pt_3]^{6+}$ system exhibiting a bent Pt_3 chain arrangement is present in $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$ with an electron count of 44, which is consistent with two Pt−Pt bonds (2.772(1) and 2.899(1) Å) between the Pt^{II} centers.[27]

The NMR parameters of **2a** and **2b** are closely related; therefore, only those of **2b** are discussed here. The $^{31}P\{^1H\}$ NMR spectrum of **2b** recorded at ambient temperature in CD_2Cl_2 consists of an AA′BB′X spin system with satellites due to the isotopomers containing ^{195}Pt nuclei. The resonance at 62.5 ppm is assigned to the phosphido ligand. The ^{31}P chemical shift of bridging phosphido groups is sensitive to the M−P−M angle, and the value for **2b** indicates the absence of a bond between Pt2 and Pt3.[36] This is confirmed by the crystal structure showing a large Pt−P−Pt angle (98.8°) and no metal−metal bonding between Pt2 and Pt3. The signal is flanked by two sets of Pt satellites (^1J(Pt2P1) = 2226 Hz, ^2J(Pt1P1) = 372 Hz). The relatively large value of ^2J(Pt1P1) can be explained by some through-space coupling, if the short Pt1−P1 distance found in the crystal structure (2.93 Å) is maintained in solution.[35] The ^{31}P chemical shifts and P−P coupling constants of **2a** and **2b** were obtained by computer simulation of the experimental spectrum.[37] Figure 4 shows the experimental and the simulated $^{31}P\{^1H\}$ NMR spectra of **2b**.

The $^{195}Pt\{^1H\}$ NMR spectrum of **2b** exhibits two resonances at −5050 (Pt1; td) and −4832 ppm (Pt2, Pt3; dddd). Both sets of signals are flanked by satellites due to the presence of the isotopomers $^{195}Pt1^{195}Pt2Pt3$ and $^{195}Pt1Pt2^{195}Pt3$ (^1J(Pt1Pt2) = 891 Hz); the subspectrum resulting from the isotopomer $Pt1^{195}Pt2^{195}Pt3$ was not observed.

Supporting Information Available: Listings of positional and thermal parameters, all bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1a**·2MeOH, **2a**·$3CH_2Cl_2$, and **2b** (32 pages). Ordering information is given on any current masthead page.

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