Rigid-Rod Polymers, Oligomers, and Model Complexes with Pt−Pt Bonds in the Backbone

Michael J. Irwin, Guochen Jia, Jagadese J. Vittal, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

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Reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$, dppm = $Ph_2PCH_2PPh_2$, with PhC≡CH in methanol gives $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-PhCCH})]$, **1**, or, in the presence of base, $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2]$, **2**, or $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2(\mu\text{-PhCCH})]$, **4**. Complex **2** reacts with chlorinated solvents to re-form $[Pt_2Cl_2(\mu\text{-dppm})_2]$, but in the presence of base, $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2(\mu\text{-OH}\cdots Cl)]$, **3**, may be formed. Complexes **1** and **3** have been characterized by X-ray structure determinations, and the conditions for formation of **2** have been optimized as a model reaction for polymer formation by using diacetylenes. Reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with HC≡CArC≡CH in methanol in the presence of base gives insoluble oligomers characterized as Cl-$[Pt_2(\mu\text{-}C{\equiv}CArC{\equiv}C)_2(\mu\text{-dppm})_2]_x[Pt_2Cl(\mu\text{-dppm})_2]$, **5**, that is as a diacetylide bridged oligomer with chloride end groups; depending on the diacetylide used *x* varies from *ca.* 3−12. Cationic polymers $[Pt_2(\mu\text{-dppm})_2(\mu\text{-L-L})]_x(BF_4)_{2x}$, **6** or **7**, are formed by reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with diisocyanide ligands C≡NArN≡C or with the diphosphine ligand $Ph_2PC_6H_4PPh_2$, respectively. In contrast, the diphosphine ligand *i*-$Pr_2PC_6H_4C_6H_4P$-*i*-Pr_2, having a longer spacer group, gives the cyclic complex $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}i\text{-}Pr_2PC_6H_4C_6H_4P\text{-}i\text{-}Pr_2)]_2(BF_4)_4$. The polymeric complexes **5**−**7** are insoluble or sparingly soluble in common organic solvents. They represent rare examples of conjugated, rigid-rod oligomers or polymers with metal−metal bonds in the backbone.

Introduction

There are several known types of linear-chain polynuclear complexes containing platinum, many of which have unusual properties. These include the stacked, one-dimensional conductors, such as $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$,[1] and the rigid rod polymers, such as $[Pt(PR_3)_2\text{-}(\mu\text{-}C{\equiv}CRC{\equiv}C\text{-})]_n$, which may exhibit liquid-crystalline, optical nonlinear or electrical conducting properties.[2] Recently, it was shown that halogen bridged, linear-chain complexes such as the mixed-valence Pt(II)/Pt(IV) complex $[Pt(NH_2Et)_4][PtCl_2(NH_2Et)_4]Cl_4\cdot 4H_2O$ and the barrel-shaped complex ion $K_4[Pt_2(P_2O_5H_2)_4X]\cdot nH_2O$ (X = Cl, Br, I), which contain no metal−metal bonds, are semiconductors.[3] There are relatively few reports of polymeric arrays containing metal−metal bonds in the backbone,[4] and with this in mind, it was of interest to synthesize polynuclear complexes containing Pt−Pt bonds linked by conjugated organic ligands. The properties could then be compared to those of the related compounds without metal−metal bonds.[2]

This paper describes the synthesis and characterization of some linear-chain polymers containing Pt−Pt bonds bridged by the conjugated ligands, including diacetylides $^-C{\equiv}CArC{\equiv}C^-$, diisocyanides C≡NArN≡C, and diphosphines PR_2ArPR_2, where Ar is an aromatic spacer group, and of some model complexes. The ligands used in this research have previously been employed in the synthesis of rigid rod polymers of platinum(II) or gold(I).[2,5]

Experimental Section

The complexes $[Pt_2Cl_2(\mu\text{-dppm})_2]$,[6] $[Pt_2(PPh_3)_2(\mu\text{-dppm})_2](BF_4)_2$,[7] and $[Pt_2(C{\equiv}NXy)_2(\mu\text{-dppm})_2](BF_4)_2$,[8] where Xy = 2,6-$Me_2C_6H_3$, 1,4-bis(diphenylphosphino)benzene,[9] 4,4′-(i-Pr)$_2$-$PC_6H_4C_6H_4P$(i-Pr)$_2$,[10] diisocyanoarenes,[11] and dialkynylarenes,[10] were prepared by literature methods.

NMR spectra were recorded by using a Gemini 300 spectrometer. ^1H NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative

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to tetramethylsilane. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. IR spectra were recorded as Nujol mulls on a Perkin-Elmer FTIR spectrometer. Thermal analyses (DSC and TGA) were carried out by using a Perkin-Elmer DSC 7 and TAC7/DX differential scanning calorimeter and thermogravimetric analyzer, respectively. Molecular weight measurements were determined using a Waters 600 GPC equipped with a Waters 410 differential refractor as a detector. Molecular modeling was carried out using the Cache 3.8 molecular modeling program.

[Pt_2Cl_2(*μ*-dppm)$_2$(*μ*-HC=CPh)], 1. A mixture of [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol) and PhC$\equiv$CH (0.10 g, 0.98 mmol) in MeOH (30 mL) was stirred at room temperature overnight. The reaction mixture initially became clear, and then a yellow precipitate formed. The precipitate was collected by filtration, washed with MeOH, and dried. Yield: 78 mg, 72%. NMR in C_6D_6: $\delta(^{31}P) = 3.18$ [m, $^1J(PtP) = 3280$ Hz, $^2J(PtP) = 170$ Hz, $^2J(PP) = 14$ Hz], 5.44 [m, $^1J(PtP) = 3360$ Hz, $^2J(PtP) = 125$ Hz, $^2J(PP) = 14$ Hz]. NMR in CD_2Cl_2: $\delta(^1H) = 2.8-3.2$ [br m, 2H, CH_2]; 3.6−3.8 [m, 2H, CH_2], 6.5−8.0 [m, 45H, Ph]. Anal. Calcd for $C_{58}H_{50}Cl_2P_4Pt_2$: C, 52.3; H, 3.8. Found: C, 52.1; H, 3.8.

[Pt_2(C$\equiv$CPh)$_2$(*μ*-dppm)$_2$], 2. A mixture of [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol), PhC$\equiv$CH (0.10 g, 0.98 mmol), and NaOMe (50 mg, 0.92 mmol) in MeOH (40 mL) was stirred at room temperature for 3 h to give a yellow precipitate. The solvent was then evaporated under vacuum, and the residue was extracted with benzene. The benzene was evaporated and the residue was washed with MeOH, to give a yellow precipitate, which was collected by filtration, washed with MeOH and dried. Yield: 88 mg, 80%. NMR in C_6D_6: $\delta(^{31}P) = 2.07$ [s, $^1J(PtP) = 2930$ Hz, $^2J(PtP) = -70$ Hz]; $\delta(^1H) = 4.86-5.15$ [br m, 4H, CH_2]; 6.16−7.90 [m, 50H, Ph]. IR: $\nu(C\equiv C) = 2095$ cm^{-1}. FAB-MS: $m/z = 1362$ {26%, [HPt_2(CCPh)$_2$(*μ*-dppm)$_2$]$^+$}; 1260 {100%, [Pt_2(CCPh)(*μ*-dppm)$_2$]$^+$}; 1159 {75%, [Pt_2(*μ*-dppm)$_2$]$^+$}. Anal. Calcd for $C_{66}H_{54}P_4Pt_2$: C, 58.2; H, 4.0. Found: C, 58.4; H, 3.9.

[Pt_2(C$\equiv$CPh)$_2$(*μ*-dppm)$_2$(*μ*-OH···Cl)], 3. Over a 12 h period, pentane was allowed to diffuse into a saturated solution of crude **2** in 1,2-dichloroethane. Two large crystals were removed, and an X-ray diffraction study confirmed the structure of **3** (see below). After a further day, several smaller crystals had formed which were found to be [Pt_2Cl_2(*μ*-dppm)$_2$] by the ^{31}P NMR spectrum.

[Pt_2(C$\equiv$CPh)$_2$(*μ*-dppm)$_2$(*μ*-HC=CPh)], 4. To a suspension of [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol) and NaOMe (50 mg, 0.90 mmol) in MeOH (40 mL) was added PhC$\equiv$CH (0.10 g, 0.98 mmol). The resulting mixture was stirred at room temperature for 2 days to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, and dried. Yield: 70 mg, 59%. NMR in C_6D_6: $\delta(^{31}P) = 1.69$ [m, $^1J(PtP) = 3180$ Hz, $^2J(PP) = 16$ Hz]; 2.78 [m, $^1J(PtP) = 3230$ Hz, $^2J(PP) = 16$ Hz]; $\delta(^1H) = 2.7-3.2$ (br m, 2H, CH_2], 3.7−3.9 [m, 2H, CH_2], 6.3−8.1 [m, 55H, Ph]. IR: $\nu(C\equiv C) = 2089$ cm^{-1}. FAB-MS: $m/z = 1463$ {100%, [Pt_2(CCPh)$_2$(*μ*-dppm)$_2$](HCCPh)]$^+$}; 1260 {6%, [Pt_2(CCPh)(*μ*-dppm)$_2$]$^+$}; 1159 {33%, [Pt_2(*μ*-dppm)$_2$]$^+$}. Anal. Calcd for $C_{74}H_{60}P_4Pt_2$: C, 60.7; H, 4.1. Found: C, 60.4; H, 4.4.

Cl[Pt_2(*μ*-C$\equiv$CC$_6$H$_4$C$\equiv$C)(*μ*-dppm)$_2$]$_x$[Pt_2Cl(*μ*-dppm)$_2$], 5a. A mixture of [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol), HC$\equiv$CC$_6$H$_4$C$\equiv$CH (17 mg, 0.081 mmol) and NaOMe (50 mg, 0.92 mmol), in a mixed solvent of MeOH (20 mL)/THF (10 mL) was stirred at room temperature overnight to give a yellow precipitate, which was collected by filtration, washed with MeOH, H_2O, and MeOH, and dried. Yield: 90 mg, 81%. The compound has low solubility in common organic solvents. IR: $\nu(C\equiv C) = 2089$ cm^{-1}. FAB-MS: $m/z = 1318$ [Pt_2(CCC$_6$H$_4$CC)(dppm)$_2$Cl$^+$]; 1283 [Pt_2(CCC$_6$H$_4$CC)(dppm)$_2$$^+$]; 1194 [$Pt_2$(dppm)$_2Cl^+$]; 1159 [$Pt_2$(dppm)$_2$$^+$]. Anal. Calcd for $(C_{66}H_{52}P_4Pt_2)_5(C_{50}H_{44}Cl_2P_4Pt_2)$: C, 55.0; H, 3.7. Found: C, 54.9; H, 3.8.

Cl[Pt_2(*μ*-C$\equiv$CC$_6$H$_2$Me$_2$C$\equiv$C)(*μ*-dppm)$_2$]$_x$[Pt_2Cl(*μ*-dppm)$_2$], 5b. A mixture of [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol), HC$\equiv$CC$_6$H$_2$Me$_2$C$\equiv$CH (17 mg, 0.080 mmol), and NaOMe (50 mg, 0.92 mmol) in a mixed solvent of MeOH (20 mL)/THF (10 mL) was stirred at room temperature overnight to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, H_2O, and MeOH, and dried. Yield: 93 mg, 82%. The compound is insoluble in common organic solvents. IR: $\nu(C\equiv C) = 2084$ cm^{-1}. FAB-MS: 1311 [Pt_2(CCC$_6$H$_2$Me$_2$CC)(dppm)$_2$$^+$]; 1194 [trace, Pt_2(dppm)$_2$Cl$^+$]; 1159 [Pt_2(dppm)$_2$Cl$^+$]. Anal. Calcd for $(C_{62}H_{52}P_4Pt_2)_{12}(C_{50}H_{44}Cl_2P_4Pt_2)$: C, 56.2; H, 4.0. Found: C, 56.2; H, 3.9. Note that the analytical data are also reasonably close to the expected value for the polymer $(C_{62}H_{52}P_4Pt_2)_x$. Anal. Calcd C, 56.8; H, 4.0.

Cl[Pt_2(*μ*-C$\equiv$CC$_6$H$_4$C$_6$H$_4$C$\equiv$C)(*μ*-dppm)$_2$]$_x$[Pt_2Cl(*μ*-dppm)$_2$], 5c. A mixture of [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol), HCCC$_6$H$_4$C$_6$H$_4$CCH (16 mg, 0.079 mmol), and NaOMe (50 mg, 0.92 mmol) in a mixed solvent of MeOH (20 mL)/THF (10 mL) was stirred at room temperature overnight to give a yellow precipitate, which was collected by filtration, washed with MeOH, H_2O, and MeOH and dried. Yield: 89 mg, 80%. The compound is insoluble in common organic solvents. IR: $\nu(C\equiv C) = 2087$ cm^{-1}. FAB-MS: $m/z = 1394$ [Pt_2(CCC$_6$H$_4$C$_6$H$_4$CC)(dppm)$_2$Cl$^+$]; 1359 [Pt_2(CCC$_6$H$_4$C$_6$H$_4$CC)(dppm)$_2$+]; 1194 [Pt_2(dppm)$_2$Cl$^+$]; 1159 [Pt_2(dppm)$_2$$^+$]. Anal. Calcd for $(C_{66}H_{52}P_4Pt_2)_3(C_{50}H_{44}Cl_2P_4Pt_2)$: C, 56.1; H, 3.9. Found: C, 55.8; H, 3.8.

[Pt_2(*μ*-dppm)$_2$(CNC$_6$H$_4$NC)]$_x$(BF$_4$)$_{2x}$, 6a. To a mixture of [Pt_2Cl_2(*μ*-dppm)$_2$] (50 mg, 0.041 mmol) and NaBF$_4$ (0.10 g, 0.90 mmol) in MeOH (30 mL) was added CNC$_6$H$_4$NC (5.3 mg, 0.041 mmol). The resulting mixture was stirred overnight to give an orange solid. The solid was collected by filtration, washed with MeOH, H_2O, MeOH, and ether, and dried. Yield: 40 mg, 67%. The compound is insoluble in common organic solvents. IR: $\nu(N\equiv C) = 2159$ cm^{-1}. Anal. Calcd for $C_{58}H_{48}B_2F_8N_2P_4Pt_2 \cdot 2H_2O$: C, 46.6; H, 3.5. Found: C, 46.6; H, 3.7.

[Pt_2(*μ*-dppm)$_2$(CNC$_6$H$_3$MeNC)]$_x$(BF$_4$)$_{2x}$, 6b. This was prepared in a similar way from [Pt_2Cl_2(*μ*-dppm)$_2$] (50 mg, 0.041 mmol) and NaBF$_4$ (0.10 g, 0.90 mmol) in MeOH (30 mL) with CNC$_6$H$_3$MeNC (5.8 mg, 0.041 mmol). Yield: 42 mg, 70%. The compound is insoluble in common organic solvents. IR: $\nu(N\equiv C) = 2160$ cm^{-1}. Anal. Calcd for $C_{59}H_{50}B_2F_8N_2P_4Pt_2$: C, 48.0; H, 3.4. Found: C, 47.8; H, 3.7.

[Pt_2(*μ*-dppm)$_2$(CNC$_6$Me$_4$NC)]$_x$(BF$_4$)$_{2x}$, 6c. This was prepared in a similar way from [Pt_2Cl_2(*μ*-dppm)$_2$] (50 mg, 0.041 mmol) and NaBF$_4$ (0.10 g, 0.90 mmol) in MeOH (30 mL) with CNC$_6$Me$_4$NC (7.5 mg, 0.041 mmol). Yield: 48 mg, 77%. The compound is insoluble in common organic solvents. IR: $\nu(N\equiv C) = 2157$ cm^{-1}. Anal. Calcd for $C_{62}H_{56}B_2F_8N_2P_4Pt_2 \cdot 2H_20$ C, 47.9; H, 3.9. Found: C, 46.7; H, 3.6.

[Pt_2(*μ*-dppm)$_2$(CNC$_6$H$_2$*t*Bu$_2$NC)]$_x$(BF$_4$)$_{2x}$, 6d. This was prepared in a similar way from [Pt_2Cl_2(*μ*-dppm)$_2$] (50 mg, 0.041 mmol) and NaBF$_4$ (0.10 g, 0.90 mmol) in MeOH (30 mL) with CNC$_6$H$_2$*t*Bu$_2$NC (8.8 mg, 0.042 mmol). Yield: 46 mg, 73%. The compound is insoluble in common organic solvents. IR: $\nu(N\equiv C) = 2160$ cm^{-1}. Anal. Calcd for $C_{66}H_{64}B_2F_8N_2P_4Pt_2 \cdot 2H_2O$ C, 48.7; H, 4.0. Found: C, 49.0; H, 4.0.

[Pt_2(*μ*-dppm)$_2$(PPh$_2$C$_6$H$_4$PPh$_2$)]$_x$(BF$_4$)$_{2x}$, 7a. A mixture of [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol) and PPh$_2$C$_6$H$_4$PPh$_2$ (3.6 mg, 0.081 mmol) in MeOH (30 mL) was stirred at room temperature for 4 h to give a clear yellow solution. To the reaction mixture was then added NaBF$_4$ (0.20 g, 1.8 mmol), and the resulting mixture was stirred overnight to give a yellow precipitate. The MeOH was then removed completely, and the residue was washed with H_2O to give a yellow powder, which was collected by filtration, washed with H_2O, MeOH, benzene, and ether, and dried. Yield: 115 mg, 80%. NMR in acetone-*d*$_6$: $\delta(^{31}P) = -13$ to $+18$ [br, m, Ph$_2$P]; $\delta(^1H) = 4.3-8.7$ [br m, CH_2 and Ph], 2.7 [s, H_2O]. Anal. Calcd for $C_{80}H_{86}B_2F_8N_2P_6Pt_2 \cdot 2H_2O$: C, 52.9; H, 4.0. Found: C, 52.8; H, 4.2.

[Pt_2(*μ*-dppm)$_2$((i-Pr)$_2$PC$_6$H$_4$C$_6$H$_4$P(i-Pr)$_2$)]$_2$(BF$_4$)$_4$, 8. This was prepared in a similar way from [Pt_2Cl_2(*μ*-dppm)$_2$] (0.10 g, 0.081 mmol) and P(i-Pr)$_2$C$_6$H$_4$C$_6$H$_4$P(i-Pr)$_2$ (3.2 mg, 0.081 mmol) in MeOH (30 mL) with NaBF$_4$ (0.20 g, 1.8 mmol). Yield: 120 mg, 86%. NMR in acetone-*d*$_6$: $\delta(^{31}P) = -2.50$ [s,

J(PtP) = 2900 Hz, dppm]; 21.12 [s, ^1J(PPt) = 2540 Hz, ^2J(PtP) = 1660 Hz, Pr_2P]; $\delta(^1H)$ = 4.4–5.5 [br m, CH_2]; 6.7–8.6 [br m, Ph]; 2.8 [s, H_2O]. Anal. Calcd for $C_{74}H_{80}B_2F_8N_2P_6Pt_2 \cdot 2H_2O$: C, 50.6; H, 4.6. Found: C, 50.1; H, 4.6.

X-ray Structure Determinations. Yellow, cubic crystals of [Pt_2Cl_2(μ-dppm)$_2$(μ-HC=CPh)], **1**, were grown from a mixture of CH_2Cl_2 and n-pentane at room temperature; a crystal with dimensions of 0.26 × 0.26 × 0.20 mm was used. A large yellow, cubic crystal of [$Pt_2(CCPh)_2$(μ-dppm)$_2$(μ-OH)]Cl, **3**, was grown from a mixture of $C_2H_4Cl_2$ and n-pentane at room temperature and was cut to give a fragment of dimensions 0.37 × 0.35 × 0.25 mm. In each case, the crystal was wedged inside a Lindemann capillary tube, flame sealed, and used for the X-ray analysis. The diffraction experiments were carried out using a Siemens P4 diffractometer with XSCANS software package[12] using graphite-monochromated Mo Kα radiation at 25 °C.

For **1**, the cell constants were obtained by centering 38 high-angle reflections ($16.7 \le 2\theta \le 25.0°$). The Laue symmetry $4/m$ was determined by merging symmetry-equivalent reflections. A total of 6179 reflections were collected in the θ range 1.9–23.0° ($-1 \le h \le 23$, $-1 \le k \le 23$, $-1 \le l \le 15$) in θ–2θ scan mode at variable scan speeds (1–10 deg/min). Background measurements were made at the ends of the scan range. Four standard reflections were monitored at the end of every 297 reflections collected. At the end of the data collection, the faces of the data crystal were indexed and the distances between them were measured. A Guassian absorption correction was applied to the data (μ = 4.498 mm^{-1}). The maximum and minimum transmission factors are 0.508 and 0.429, respectively. In the primitive system with Laue symmetry $4/m$, the systematic absences ($00l$, $l = 4n + 1$) indicated that the space group is either $P4_1$ (No. 76) or $P4_3$ (No. 78). The choice of the space group $P4_1$ was confirmed by refining the Flack parameter.[13]

For **3**, the cell constants were obtained by centering 25 high-angle reflections ($24.8 \le 2\theta \le 25.0°$). The Laue symmetry $2/m$ was determined by merging symmetry-equivalent reflections. A total of 9414 reflections were collected in the θ range 1.9–22.5° ($-1 \le h \le 19$, $1 \le k \le 19$, $1 \le l \le 19$) in θ–2θ scan mode at variable scan speeds (1–10 deg/min). Background measurements were made at the ends of the scan range. An empirical absorption correction was applied to the data on the basis of ψ scan reflections. The systematic absences indicated the space group $P2_1/c$.

The data processing, solution, and the initial refinements were done using SHELXTL-PC[14] programs. The final refinements were performed using SHELXL-93[15] software programs. For **1**, anisotropic thermal parameters were refined for all the Pt, Cl, P, and carbon atoms C(1), C(2), C(9), and C(10). Half a molecule of ethanol solvate was located in the difference Fourier. The C–O and C–C distances were fixed and not refined. A common isotropic thermal parameter was refined for the solvent atoms. The hydrogen atoms were included in the calculated positions for the purpose of structure factor calculations only. All the phenyl rings in the dppm ligands were treated as regular hexagons with C–C = 1.395 Å. The isotropic thermal parameters of the phenyl carbon atoms (C(3)–C(8)) attached to the C(2) atom were somewhat large. A satisfactory disorder model could not be formulated from the difference Fourier map. Refinement of the anisotropic thermal parameters for these carbon atoms did not yield a satisfactory result. A 2-fold symmetry was applied to this ring using soft constraints. In the final least-squares refinement cycles of F^2, the model converged at $R1$ = 0.0532, w$R2$ = 0.1263, and Goof = 1.039 for 4201 observations with $F_o \ge 4\sigma(F_o)$ and 239 parameters, and $R1$ = 0.0759 and w$R2$ = 0.1439 for all 5169 data. In the final difference Fourier synthesis the electron density fluctuates in the range 0.776 to −0.624 e Å^{-3}, of which the top peak was associated with the atom C(25) at a distance of 1.27 Å. The mean and maximum shift/esd values in the final cycles are 0.002 and 0.042, respectively. The absolute structure parameter was refined to −0.01(2). For **3**, anisotropic thermal parameters were refined for all the Pt, Cl, P, O(1), and the carbon atoms C(1)–C(4). One molecule of water in two positions (occupancies 0.5/0.5), two molecules of methanol solvate (disordered in three positions), and half a molecule of pentane were located in the difference Fourier map. Anisotropic thermal parameters were refined for the oxygen atoms O(2) and O(3) of the water molecules. The C–C distance and the C–C–C angles were fixed for the pentane molecule and not refined. Similarly the C–O distances were fixed at 1.385 Å for all the methanol molecules. A common isotropic thermal parameter was refined for each group of solvate molecules. The hydrogen atoms of the cation were included in the calculated positions for the purpose of structure factor calculations only. All the phenyl rings were restrained to have the symmetry C_{2v}. In the final least-squares refinement cycles on F^2, the model converged at $R1$ = 0.0507, w$R2$ = 0.1092, and Goof = 1.018 for 5902 observations with $F_o \ge 4\sigma(F_o)$ and 414 parameters, and $R1$ = 0.0809 and w$R2$ = 0.1286 for all 7956 data. In the final difference Fourier synthesis the electron density fluctuates in the range 0.832 to −0.948 e Å^{-3}, of which the top peak was associated with Pt(1) at a distance of 1.04 Å. The mean and maximum shift/esd values in the final cycles are 0.001 and 0.008, respectively. The experimental details and crystal data are in Table 1, while complete positional and thermal parameters, bond distances and angles, and anisotropic thermal parameters have been included in the Supporting Information.

Table 1. Crystal Data and Experimental Details for 1·0.5EtOH and 3·H_2O·2MeOH·0.5C_5H_{12}

	complex	
	1·0.5C_2H_5OH	**3**·H_2O·2CH_3OH·0.5C_5H_{12}
formula	$C_{59}H_{53}Cl_2O_{0.5}P_2Pt_2$	$C_{70.5}H_{71}Cl_1O_4P_4Pt_2$
fw	1354.97	1531.78
T, K	298	298
λ, Å	0.710 73	0.710 73
space group	$P4_1$	$P2_1/c$
a, Å	21.273(2)	18.206(2)
b, Å	21.273(2)	13.455(1)
c, Å	14.408(3)	26.303(2)
β, deg		108.03(1)
V, Å^3	6520(2)	6126.8(9)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.38	1.661
μ, mm^{-1}	4.498	4.76
F(000)	2644	3036
NO[a]	4201	5902
$R1$[b]	0.0532	0.0507
w$R2$[c]	0.1263	0.1092
S[d]	1.039	1.018

[a] NO = number of observed reflections with $F_o > 4\sigma(F_o)$. [b] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. [d] S = goodness of fit = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

Results and Discussion

Model Compounds and the Reactions of [Pt_2Cl_2(μ-dppm)2] with PhC≡CH. When this work began, several cationic, diplatinum(I) complexes of the type [Pt_2(μ-dppm)$_2L_2$][X]$_2$ had been prepared by the reaction of [Pt_2Cl_2(μ-dppm)$_2$] with the ligands L (L = monodentate phosphine or isocyanide) in the presence of anions X^- = [BF_4]$^-$, [PF_6]$^-$, and [ClO_4]$^-$ (eq 1).[7,8] Thus it could

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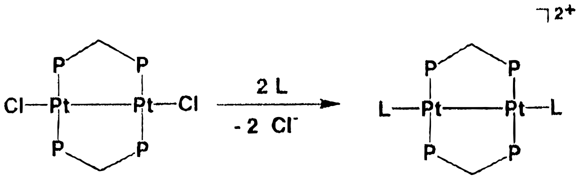
(12) *XSCANS*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

(13) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

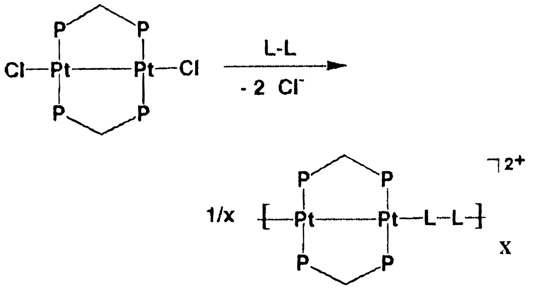
(14) Sheldrick, G. M. *SHELXTL-PC*; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1990.

(15) Sheldrick, G. M. *SHELXL-93*; Department fuer Anorg. Chemie, University of Goettingen: Goettingen, Germany, 1993.

reasonably be expected that polymeric compounds could be synthesized by the similar reactions of [$Pt_2Cl_2(\mu$-dppm$)_2$] with diphosphine or diisocyanide ligands (eq 2).



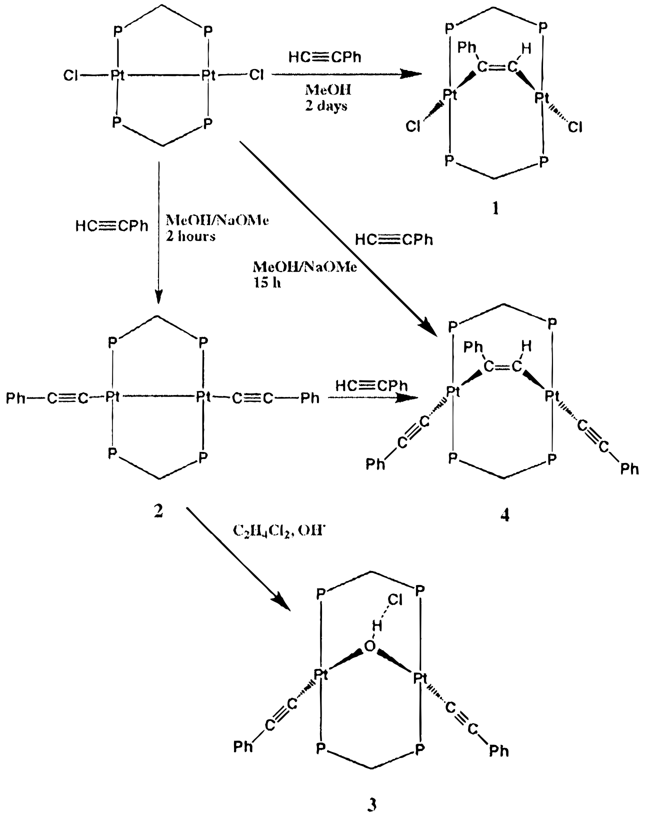
(1)



(2)

However, the model compounds for neutral diacetylide-bridged polymers are [$Pt_2(\mu$-dppm$)_2(C{\equiv}CR)_2$] and the reported synthetic route is not suitable for the synthesis of polymers.[16a] Therefore the reactions of [$Pt_2Cl_2(\mu$-dppm$)_2$] with the alkyne PhCCH have been studied under various conditions in order to determine if it is possible to prepare [$Pt_2(\mu$-dppm$)_2(C{\equiv}CPh)_2$] in good yield and hence to test the feasibility of the synthesis of the related polymers.

Scheme 1



Phenylacetylene reacted at room temperature with [$Pt_2Cl_2(\mu$-dppm$)_2$] in methanol to give the pale yellow compound [$Pt_2Cl_2(\mu$-PhCCH$)(\mu$-dppm$)_2$], **1** (Scheme 1). Normally, electronegative substituents on the alkyne are required for such reactions to be successful[16] but it has been shown that simple alkynes will add to [$Pd_2Cl_2(\mu$-dppm$)_2$] in the presence of acid.[16a] In the present case, the solvent methanol may serve as a weak acid to reversibly protonate the metal–metal bond of [$Pt_2Cl_2(\mu$-dppm$)_2$] and hence catalyze the addition of phenylacetylene. The ^{31}P NMR spectrum of **1** in benzene displays two signals at $\delta = 3.18$ [$^1J(PtP) = 3280$ Hz, $^2J(PtP) = 170$ Hz, $^2J(PP) = 14$ Hz] and at $\delta = 5.44$ [$^1J(PtP) = 3360$ Hz, $^2J(PtP) = 125$ Hz, $^2J(PP) = 14$ Hz], consistent with an unsymmetrical A-frame structure. The ^1H NMR spectrum gave two resonances for the protons CH^aH^b of the dppm ligands as expected for an A-frame structure. Unfortunately, the PhCC*H* proton resonance was not resolved, presumably because it is obscured by the phenyl group resonances. On the basis of the analytical and NMR data, it was not possible to distinguish between the proposed structure **1**, with a μ-PhC=CH group, and the isomeric vinylidene structure, with a μ-C=CHPh group. There are precedents for both types of complex.[16–19] Thus, reactions of alkynes having electron-withdrawing substituents (e.g. RC≡CR with R = CO_2Me or CF_3) with the complexes [$Pt_2X_2(\mu$-dppm$)_2$], X = Cl or CCPh,[16,17] [$Pt_2H(\mu$-H)Me$(\mu$-dppm$)_2$]SbF_6,[18] and [$Pt_2Me_2(\mu$-H$)(\mu$-dppm$)_2$]PF_6[18] are known to give complexes with structures analogous to **1**, but phenylacetylene could well behave differently since it does not contain electronegative substituents. Vinylidene-bridged diplatinum complexes such as [$Pt_2(\mu$-C=CHPh$)(C{\equiv}CPh)(PEt_3)_4$]BF_4, [$Pt_2(\mu$-C=CHPh$)(C{\equiv}CPh)(PEt_3)_3X$] (X = Cl, Br, I, NCS, SPh), and [$Pt_2(\mu$-C=CHPh$)(PEt_3)_3X_2$] (X = Cl, Br, I, NCS, SPh) are known to contain the $Pt_2(\mu$-C=CHPh) group.[19] Since the NMR and IR data do not distinguish between the two likely bonding modes, the structure of **1** was determined crystallographically.

The molecular structure of **1** is shown in Figure 1, and selected bond lengths and angles are presented in Table 2. The expected presence of a *trans,trans*-$Pt_2(\mu$-dppm$)_2$ unit in **1** is confirmed. More importantly, it is shown that the phenylacetylene is present in the di-σ-bonded, parallel bonding mode, $Pt_2(\mu$-PhC=CH), and has not isomerized to the phenylvinylidene isomeric form. Overall then, each platinum has the square-planar *trans*-PtP_2ClC donor set expected for a d^8 platinum(II) center. Clearly, the complex can be described as having a type of A-frame structure. This is analogous to the structure of [$Pd_2Cl_2(\mu$-$CF_3C{=}CCF_3)(\mu$-dppm$)_2$],[16c] but although similar platinum complexes have been prepared, none has been characterized by an X-ray

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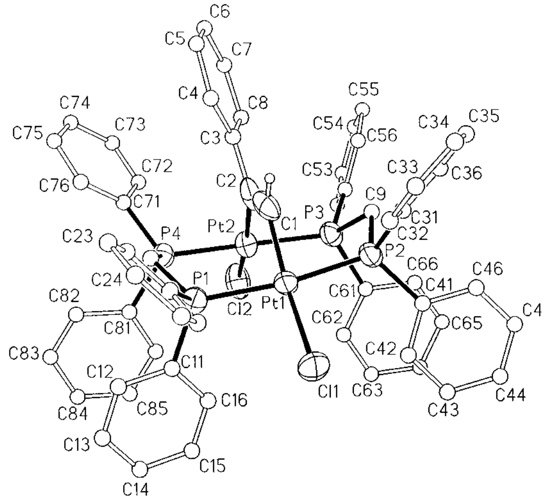

Figure 1. View of the structure of $[Pt_2Cl_2(\mu\text{-}PhCCH)(\mu\text{-}dppm)_2]$.

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

Pt(1)−C(1)	2.00(2)	Pt(1)−P(2)	2.286(4)
Pt(1)−P(1)	2.290(4)	Pt(1)−Cl(1)	2.395(5)
Pt(2)−C(2)	2.02(1)	Pt(2)P(3)	2.284(5)
Pt(2)−P(4)	2.288(4)	Pt(2)−Cl(2)	2.409(5)
P(1)−C(10)	1.83(2)	P(1)−C(11)	1.83(1)
P(1)−C(21)	1.83(1)	P(2)−C(41)	1.81(1)
P(2)−C(31)	1.85(1)	P(2)−C(9)	1.85(2)
P(3)C(51)	1.80(1)	P(3)−C(61)	1.83(1)
P(3)−C(9)	1.84(2)	P(4)−C(10)	1.79(1)
P(4)−C(81)	1.81(1)	P(4)−C(71)	1.82(1)
C(1)−C(2)	1.31(2)	C(2)C(3)	1.543(5)
C(1)−Pt(1)−P(2)	83.0(5)	C(1)−Pt(1)−P(1)	88.4(5)
P(2)−Pt(1)−P(1)	170.0(2)	C(1)−Pt(1)−Cl(1)	162.8(5)
P(2)−Pt(1)−Cl(1)	97.0(2)	P(1)Pt(1)Cl(1)	92.7(2)
C(2)−Pt(2)−P(3)	87.8(4)	C(2)−Pt(2)−P(4)	84.7(4)
P(3)−Pt(2)−P(4)	169.7(2)	C(2)−Pt(2)−Cl(2)	165.6(3)
P(3)−Pt(2)−Cl(2)	92.1(2)	P(4)−Pt(2)−Cl(2)	96.9(2)
C(10)−P(1)−C(11)	103.0(6)	C(10)−P(1)−C(21)	105.3(7)
C(11)−P(1)−C(21)	104.2(6)	C(10)−P(1)−Pt(1)	115.6(5)
C(11)−P(1)−Pt(1)	116.8(4)	C(21)−P(1)−Pt(1)	110.7(5)
C(41)−P(2)−C(31)	103.5(5)	C(41)−P(2)−C(9)	103.2(7)
C(31)−P(2)−C(9)	102.2(7)	C(41)−P(2)−Pt(1)	120.1(4)
C(31)−P(2)−Pt(1)	110.3(4)	C(9)−P(2)−Pt(1)	115.5(5)
C(51)−P(3)−C(61)	102.4(6)	C(51)−P(3)−C(9)	102.3(7)
C(61)−P(3)−C(9)	101.9(7)	C(51)−P(3)−Pt(2)	113.9(4)
C(61)−P(3)−Pt(2)	116.8(4)	C(9)−(3)−Pt(2)	117.4(6)
C(10)−P(4)−C(81)	101.0(7)	C(10)−P(4)−C(71)	103.5(6)
C(81)−P(4)−C(71)	105.1(5)	C(10)−P(4)−Pt(2)	114.1(5)
C(81)−P(4)−Pt(2)	119.9(4)	C(71)−P(4)−Pt(2)	111.6(4)
C(2)−C(1)−Pt(1)	121(1)	C(1)−C(2)−C(3)	115(1)
C(1)−C(2)−Pt(2)	124(1)	C(3)−C(2)−Pt(2)	120(1)
P(3)−C(9)−P(2)	114.9(9)	P(4)−C(10)−P(1)	119.4(8)

structure determination.[16,17] This also appears to be the first structure of a complex of this type in which the alkyne does not have electronegative substituents.

The Pt···Pt separation of 3.480(4) Å in **1** falls well outside the range considered typical of Pt−Pt single bonds [ca. 2.53−2.89 Å].[20] In addition, the angles C(2)-C(1)Pt(1) and C(1)C(2)Pt(2) of 121(1) and 124(1)°, respectively, are close to those expected for sp^2 hybridization at C(1) and C(2). Thus the bonding in the $Pt_2(\mu\text{-}PhCCH)$ group is best considered in terms of a diplatinated alkene with no metal−metal bonding.[16,17] Most other features of the coordination sphere about the Pt centers are as expected. The Pt−Cl distances of 2.395(5) and 2.409(5) Å are near the upper end of the range of Pt−Cl distances in square-planar Pt(II) complexes, due to the high trans influence of the σ-carbon donor.[21] The Pt−P bond lengths in **1** [2.286(4) and 2.290(4) Å] are comparable with those in the A-frame complex $[Pt_2Cl_2(\mu\text{-}dppm)_2(\mu\text{-}CH_2)]$, and in addition, the PPtP angles are similarly distorted from linearity at 169.7(2) and 170.0(2)°.[22] In $[Pt_2Cl_2(\mu\text{-}dppm)_2(\mu\text{-}CH_2)]$, the C−Pt−Cl angles are close to linear, but in **1** they are much more distorted at 162.8(5) and 165.6(3)°, although the Pt−C bond lengths in **1** are not unusual at 2.00(2) and 2.02(1) Å. Finally, each Pt_2P_2C unit adopts an envelope conformation with the CH_2 flap toward the HC≡CPh ligand, presumably to reduce steric interactions by directing the axial phenyl groups of the dppm ligands away from the apex ligand, in this case the μ-PhCCH group.[22]

It is clear from the above that alkynylplatinum complexes cannot be prepared simply by reaction of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ with an alkyne but that a base must be present to deprotonate the alkyne. Reaction products of phenylacetylene with $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ in the presence of base varied depending on reaction conditions. The reaction with PhCCH and NaOMe in methanol at room temperature for 2 h gave a yellow compound identified as $[Pt_2(C{\equiv}CPh)_2(\mu\text{-}dppm)_2]$, **2**, in good yield (Scheme 1).[16a] The spectroscopic data are in good agreement with the literature[16a] and prove that a linear, symmetric structure containing a Pt−Pt bond is present.[23] In particular, the ^{31}P NMR spectrum contains a singlet at $\delta = 2.07$, with $^1J(PtP) = 2930$ Hz and $^2J(PtP) = -70$ Hz, and the large negative value observed for $^2J(PtP)$ is indicative of a metal−metal-bonded diplatinum(I) complex.[16,23]

Several related binuclear alkynylplatinum complexes have been reported. The Pt(II) complexes $[Pt_2(C{\equiv}CR)_4(\mu\text{-}L\text{-}L)_2]$ (R = Ph, Me, CF_3, p-tolyl; L-L = dppm, depm, dmpm, dippm) have been prepared by the reactions of $PtCl_2(L\text{-}L)$ with RC≡CLi[24,25] or with RC≡CH in the presence of alkoxides.[26,27] The Pt_2Au cluster complexes $[Pt_2(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-}AuX)(\mu\text{-}dppm)_2$ (X = Cl, I) were obtained from $[Pt_2(C{\equiv}C\text{-}t\text{-}Bu)_2(\mu\text{-}AuC{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}dppm)_2]$, which was synthesized by reaction of $[Pt_2(\mu\text{-}dppm)_3]$ with AuC≡C-t-Bu.[28]

The complex $[Pt_2(C{\equiv}CPh)_2(\mu\text{-}dppm)_2]$, **2**, models the related polymers linked by diacetylides, and so several attempts were made to grow crystals suitable for X-ray diffraction. Unfortunately, crystals grown from benzene or THF solutions were not of suitable size, while, in chloroform or methylene chloride, **2** reacts to give $[Pt_2Cl_2(\mu\text{-}dppm)_2]$. Crystals of **2** can be obtained from 1,2-dichloroethane but are usually unsuitable for Xray structure determination. In one case, two crystals

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[23] ^{31}P NMR of these types of compounds has been extensively treated earlier.[6]

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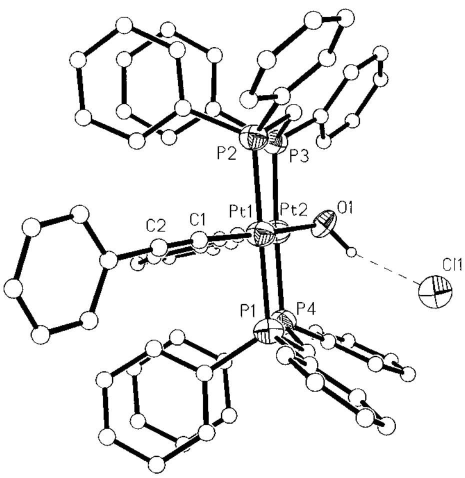

Figure 2. View of the structure of $[Pt_2(CCPh)_2(\mu\text{-OH}\cdots Cl)(\mu\text{-dppm})_2]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) in 3

Pt(1)−Pt(2)	3.1431(7)	Pt(1)−C(1)	1.93(1)
Pt(1)−O(1)	2.098(7)	Pt(1)−P(1)	2.307(3)
Pt(1)−P(2)	2.309(3)	Pt(2)−C(3)	1.95(1)
Pt(2)−O(1)	2.074(7)	Pt(2)−P(4)	2.302(3)
Pt(2)−P(3)	2.303(3)	P(1)−C(1a)	1.81(1)
P(1)−C(10)	1.83(1)	P(1)−C(1b)	1.85(1)
P(2)−C(1d)	1.82(1)	P(2)−C(1c)	1.83(1)
P(2)−C(20)	1.84(1)	P(3)−C(1f)	1.82(2)
P(3)−C(20)	1.83(1)	P(3)−C(1e)	1.83(1)
P(4)−C(1h)	1.81(1)	P(4)−C(1g)	1.82(1)
P(4)−C(10)	1.83(1)	C(1)−C(2)	1.19(2)
C(2)−C(11)	1.45(2)	C(3)−C(4)	1.22(2)
C(4)−C(21)	1.43(2)		
C(1)−Pt(1)−O(1)	177.3(4)	C(1)−Pt(1)−P(1)	89.9(4)
O(1)−Pt(1)−P(1)	92.7(2)	C(1)−Pt(1)−P(2)	91.5(4)
O(1)−Pt(1)−P(2)	86.0(2)	P(1)−Pt(1)−P(2)	178.6(1)
C(1)−Pt(1)−Pt(2)	140.3(4)	O(1)−Pt(1)−Pt(2)	40.8(2)
P(1)−Pt(1)−Pt(2)	89.76(8)	P(2)−Pt(1)−Pt(2)	89.02(8)
C(3)−Pt(2)−O(1)	175.8(4)	C(3)−Pt(2)−P(4)	90.2(4)
O(1)−Pt(2)−P(4)	92.5(2)	C(3)−Pt(2)−P(3)	92.6(4)
O(1)−Pt(2)−P(3)	84.5(2)	P(4)−Pt(2)−P(3)	176.5(1)
C(3)−Pt(2)−Pt(1)	141.9(4)	O(1)−Pt(2)−Pt(1)	41.4(2)
P(4)−Pt(2)−Pt(1)	89.10(8)	P(3)−Pt(2)−Pt(1)	89.88(8)
Pt(2)−O(1)−Pt(1)	97.8(3)	P(4)−C(10)−P(1)	115.4(7)
P(3)−C(20)−P(2)	115.4(6)	C(2)−C(1)−Pt(1)	176(1)
C(1)−C(2)−C(11)	177(1)	C(4)−C(3)−Pt(2)	173(1)
C(3)−C(4)−C(21)	177(1)		

grown from a highly concentrated solution of crude **2** in $C_2H_4Cl_2$ did prove suitable, but reaction with solvent and base had occurred and the crystals proved to be $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2(\mu\text{-OH}\cdots Cl)]$, **3** (Scheme 1). Complex **3** is formed only in low yield, and the mechanism of formation is not clear. It is likely that the primary reaction is with the chlorinated solvent to give $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2(\mu\text{-Cl})]Cl$ and ethylene, and this intermediate then reacts further to give $[Pt_2Cl_2(\mu\text{-dppm})_2]$ or reacts with base to give **3**. The molecular structure of **3** is shown in Figure 2 and is characterized by the bond lengths and angles listed in Table 3.

The structure of **3** is that of a typical "A-frame" with a *trans*,*trans*-$Pt_2(\mu\text{-dppm})_2$ bridged by a μ-OH···Cl group and with a terminal phenylacetylide ligand bound to each platinum atom. The Pt···Pt separation of 3.143(1) Å, as was the case for **1**, falls well outside the range of Pt−Pt σ-bond lengths.[20] The platinum centers have square-planar stereochemistry. Thus the angles C−Pt−O = 175.8(4) and 177.3(4)° and P−Pt−P = 176.5(1) and 178.6(1)° are all close to linear. The conformation of the $Pt_2(\mu\text{-dppm})$ groups is similar to that in complex **1**, with the methylene group in each dppm unit directed toward the μ-OH···Cl bridge, presumably to minimize steric repulsions.[22] The bond parameters associated with the PtC≡CPh and $Pt_2(\mu\text{-dppm})$ groups are unexceptional (Table 3).[28,29] The μ-OH group is positioned symmetrically relative to the two Pt centers with Pt−O = 2.074(7) and 2.098(7) Å. The hydrogen atom of the μ-OH···Cl group was not located in the structure determination, but it is presumed to be hydrogen bonded to the chloride ion. Thus, the distance O···Cl of 3.172 Å is shorter than the van der Waals distance of ca. 3.3 Å. When the hydrogen atom is placed in the idealized position in the $Pt_2(\mu\text{-OH})$ unit with d(O−H) = 0.97 Å, the distance H···Cl and angle O−H···Cl are calculated to be 2.24 Å and 159.4°, respectively, again supporting a strong hydrogen bond H···Cl. The structure is very similar to that found for $[Ir_2(CO)_2(\mu\text{-OH}\cdots Cl)(\mu\text{-dppm})_2]$, which has terminal IrCO units in place of the PtCCPh units of **3** and which has d(O···Cl) = 3.10(2) Å, d(H···Cl) = 2.13 Å, and angle O−H···Cl = 163°. For this complex, the H atom was located in the X-ray structure determination but was not refined.[30] Interestingly, most other hydroxoplatinum complexes containing the ligand dppm have chelating rather than bridging dppm ligands.[31]

The final product isolated from this reaction system is a bright yellow solid characterized as $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2(\mu\text{-HC{=}CPh})]$, **4**. This was isolated when a mixture of $[Pt_2Cl_2(\mu\text{-dppm})_2]$, NaOMe, and PhC≡CH in MeOH was stirred at room temperature for 2 days (Scheme 1). If the reaction time was less than 15 h, the isolated product was contaminated by $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2]$, **2**. Hence it appears that **4** is formed by addition of phenylacetylene to the Pt−Pt bond of **2**. A related complex is $[Pt_2(C{\equiv}CPh)_2(\mu\text{-C{\equiv}CPh})(\mu\text{-dppm})_2]^+$, which is formed by reaction of $[Pt(dppm)_2]^{2+}$ with $Hg(C{\equiv}CPh)_2$.[32] Formally this is related to **4** by addition or loss of H^-. The spectroscopic data for **4** are consistent with a structure containing two phenylacetylide units and a coordinated PhC=CH or C=CHPh ligand. The FAB-MS gave a parent ion due to $[Pt_2(CCPh)_2(\mu\text{-dppm})_2](HCCPh)]^+$. The ^{31}P NMR spectrum of **4** in benzene contained two resonances at $\delta = -1.69$ with $^1J(PtP) =$ 3180 Hz and at 2.78 ppm with $^1J(PtP) = 3230$ Hz. The ^{31}P NMR parameters are similar to those reported for **1** and for $[Pt_2Cl_2(\mu\text{-HC{=}CCF_3})(\mu\text{-dppm})_2]$.[17] Thus, although the vinylidene structure is not eliminated as a possibility, all the evidence is consistent with the presence of a μ-PhCCH group in **4**.

From the above studies, the optimum conditions for formation of $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2]$, **2**, were determined, and these same conditions were then used in the synthesis of diacetylide-bridged polymers, as outlined below.

Formation of Oligomers with Diacetylide Bridges. Reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with 1 equiv of the appropriate diacetylene HC≡CArC≡CH in the presence of NaOMe gave insoluble, yellow, oligomeric diacetylide bridged complexes, characterized as $Cl[-Pt_2(C{\equiv}CArC{\equiv}C)(\mu\text{-dppm})_2]_x[Pt_2(\mu\text{-dppm})_2]Cl$, **5** (eq 3). Ana-

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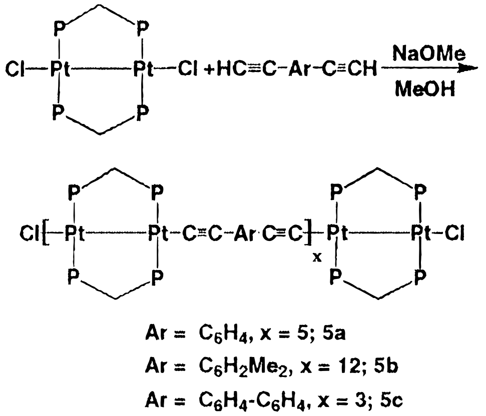
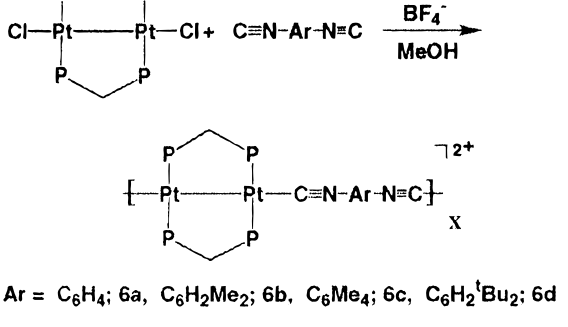
(29) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637.
(30) Li, J. J.; Sharp, P. R. *Inorg. Chem.* **1994**, *33*, 183.
(31) Yam, V. W. W.; Chan, L. P.; Lai, T. F. *Organometallics* **1993**, *12*, 2197.
(32) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247.



(3)

lytical data indicate that the average value of *x* is *ca.* 3 when Ar = 4,4′-C_6H_4-C_6H_4, 5 when Ar = 1,4-C_6H_4, and 12 when Ar = 1,4-C_6H_2-2,5-Me_2. Since the complexes are insoluble, it is not possible to determine molecular weights in solution. The IR spectra of **5** are similar to that of $[Pt_2(C{\equiv}CPh)_2(\mu\text{-dppm})_2]$, having a medium-intensity band near 2087 cm^{-1} due to $\nu(C{\equiv}C)$ but no band near 3300 cm^{-1} assignable to $\nu(CC{-}H)$, thus supporting the presence of chloride rather than acetylene end groups. The presence of chloride end groups is strongly supported by FAB mass spectral data. The major peak in each oligomer **5** is due to the ion $[Pt_2(dppm)_2(CCArCC)]^+$, but **5a**,**c** also give minor peaks due to the ions $[Pt_2(dppm)_2(CCArCC)Cl]^+$ and $[Pt_2(dppm)_2Cl]^+$. Oligomer **5b**, for which the analytical data indicate the longest chain length, gives no peak corresponding to $[Pt_2(dppm)_2(CCArCC)Cl]^+$ and only a barely detectable peak due to $[Pt_2(dppm)_2Cl]^+$. It is clear that the chain growth steps in the formation of **5** are not efficient, thus leading to oligomers only. A likely cause is the very low solubility of the oligomers **5**, which results in precipitation from solution before extensive chain growth can occur. This is consistent with the observation that the derivative with Ar = $C_6H_2Me_2$, in which the methyl substituents give increased solubility, gives the highest value of the degree of polymerization *x*. The XPS spectra of the oligomers **5** give very similar Pt 4f7/2 binding energies as in the model compound **2** (Table 4).

Formation of Polymers with Diisocyanide Bridges. Reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with 1 equiv of a diisocyanide $C{\equiv}NArN{\equiv}C$ (Ar = C_6H_4, C_6H_3Me, C_6Me_4, $C_6H_2t\text{-}Bu_2$) in methanol in the presence of excess $NaBF_4$ gave the pale-yellow (Ar = C_6Me_4) or pale orange (Ar = C_6H_4, C_6H_3Me, $C_6H_2tBu_2$) polymeric complexes $[Pt_2(\mu\text{-dppm})_2(C{\equiv}NArN{\equiv}C)]_x(BF_4)_{2x}$, **6** (eq 4). The solids are insoluble in common organic solvents and so were characterized by their analytical data and by comparison of their IR spectra with that of the known model complex $[Pt_2(\mu\text{-dppm})_2(C{\equiv}N\text{-}4\text{-tolyl})_2]^{2+}$, which is formed from the similar reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with 2 equiv of $4\text{-}MeC_6H_4N{\equiv}C$.[8] Thus, the IR spectra of **6** display strong bands due to $\nu(N{\equiv}C)$ in the range 2157–2160 cm^{-1}, similar in intensity and frequency to the corresponding band in the spectrum of $[Pt_2(\mu\text{-dppm})_2(C{\equiv}N\text{-}4{-}tolyl)_2]_2(ClO_4)_2$ [$\nu(N{\equiv}C)$ = 2168 cm^{-1}).[8] For comparison, the CN stretching frequencies for the free diisocyanides range from 2100 to 2115 cm^{-1}. The increase (ca. 45 cm^{-1}) in the CN stretching frequency of the isocyanide on coordination is well documented.[33] If the end group was a monodentate diisocyanide, a band due to free isocyanide might be expected but was not resolved. We suggest that the chain length is great enough that the end-group band is too weak to observe but cannot rule out the possibility that there is a different end group. The XPS spectra of the oligomers **6** give very similar Pt 4f7/2 binding energies as in the model compound $[Pt_2(C{\equiv}NXy)_2(\mu\text{-dppm})_2]^{2+}$ (Table 4).

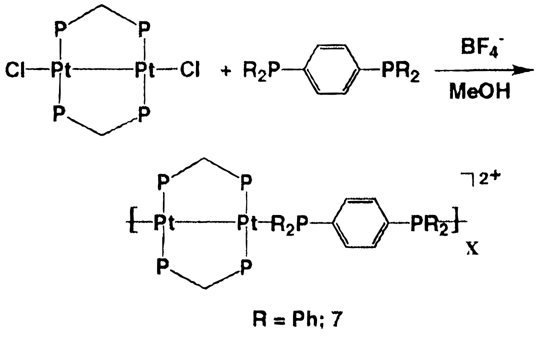


(4)

Table 4. Platinum 4f7/2 Binding Energies (BE's) from XPS of Selected Diplatinum(I) Model Complexes, Oligomers and Polymers

complex	Pt 4f7/2 BE (eV)
$[Pt_2Cl_2(\mu\text{-dppm})_2]$	72.3
2	72.8
5b	72.2
5c	72.4
$[Pt_2(CNXy)_2(\mu\text{-dppm})_2][BF_4]_2$	73.3
6a	73.2
6c	73.2
6d	73.2
$[Pt_2(PPh_3)_2(\mu\text{-dppm})_2][BF_4]_2$	72.8
8	73.2

A Chain and a Ring with Diphosphine Bridges. The reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with 1 equiv of $Ph_2PC_6H_4PPh_2$ in methanol in the presence of excess $NaBF_4$ yielded a yellow solid, characterized as $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}PPh_2C_6H_4PPh_2)]_x(BF_4)_{2x}$, **7** (eq 5). The compound is soluble in acetone and slightly soluble in halogenated solvents such as dichloromethane and chloroform but insoluble in benzene, hexane, and ether. The ^{31}P NMR spectrum of **7** contains a series of complicated broad multiplets in the region $\delta = -13$ to $+18$, and the resonances in the ^1H NMR spectrum are also broad, suggesting that **7** is polymeric. The molecular weight determination by GPC was not possible, since the solubility of **7** in tetrahydrofuran was poor.



(5)

The analogous reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with 1 equiv of $i\text{-}Pr_2PC_6H_4C_6H_4Pi\text{-}Pr_2$ also gave a yellow solid

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(33) Achar, S.; Scott, J. D.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 2325.

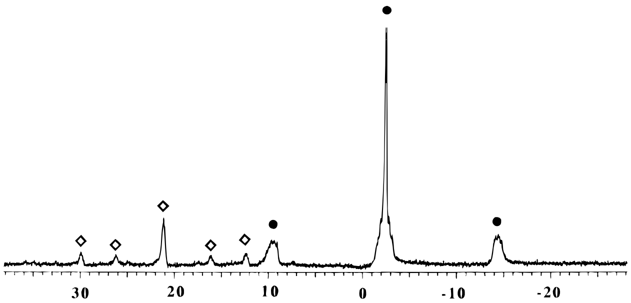
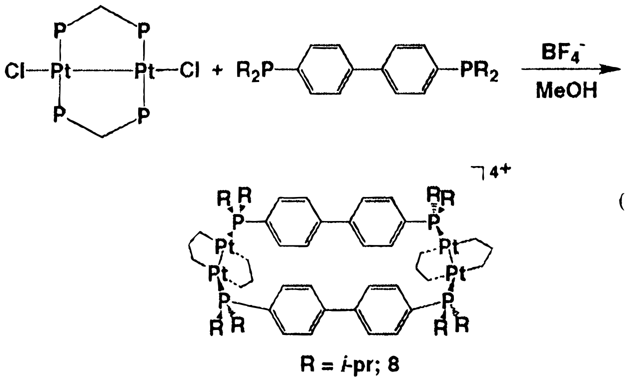


Figure 3. ^{31}P NMR spectrum (121.5 MHz) of complex **8**. The peaks marked with a closed circle are due to dppm, and those marked with a diamond are due to the *i*-Pr_2P phosphorus atoms. Note the two sets of ^{195}Pt satellite peaks due to $^1J(PtP)$ and $^2J(PtPtP)$ for the *i*-Pr_2P resonance. The *cis* coupling $^2J(PPtP)$ between *i*-Pr_2P and Ph_2P phosphorus atoms of 14 Hz is barely resolved in this spectrum.

but with very different NMR properties, and the product is characterized as the ring compound $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}i\text{-}Pr_2PC_6H_4C_6H_4P i\text{-}Pr_2)]_2(BF_4)_4$, **8** (eq 6). The ^{31}P NMR spectrum of **8** (Figure 3) is sharp and well resolved and contains single resonances for the phosphorus atoms of dppm at $\delta = -2.50$, with $^1J(PtP) = 2900$ Hz, and of *i*-Pr_2-$PC_6H_4C_6H_4P$*i*-Pr_2 at $\delta = 21.12$, with $^1J(PPt) = 2540$ Hz and $^2J(PtP) = 1660$ Hz. The large value of $^2J(PtP)$ is characteristic of a linear Pt−Pt−P linkage.[7] This spectrum and the much higher solubility compared to **7** appeared to be inconsistent with a polymeric structure for **8**. The molecular size was investigated by GPC analysis of **8** in comparison to the known complex $[Pt_2(dppm)_2(PPh_3)_2]^{2+}$ in tetrahydrofuran solution, employing linear polystyrene standards. Of course, absolute molecular weights cannot be determined in this way, but relative molecular weights may be expected. The apparent molecular weight was 693 for the complex $[Pt_2(dppm)_2(PPh_3)_2]^{2+}$ and 1638 for **8**, which is fully consistent with a 2-fold increase in molecular size. Both the model compound and **8** gave single sharp peaks in the GPC, indicating that a molecular compound was present rather than a polymer with a distribution of molecular weights. Hence the cyclic structure **8** is supported by this measurement.



(6)

Why do the two diphosphines give different product types? Molecular modeling studies show that the 4,4′-biphenyl spacer group in *i*-$Pr_2PC_6H_4C_6H_4P$-*i*-Pr_2 is long enough to bridge two diplatinum(I) units without undue steric effects (Figure 4) but that the single benzene spacer in $PPh_2C_6H_4PPh_2$ is not. The major problems in the latter case arise from strong steric effects between the phenyl substituents of the dppm ligands across the ring. Very large angle distortions at platinum are necessary in order to decrease these interactions, and the ring structure has very high energy (it is calculated to be *ca.* 130 kJ mol^{-1} higher in energy than **8**); hence the chain structure is preferred.

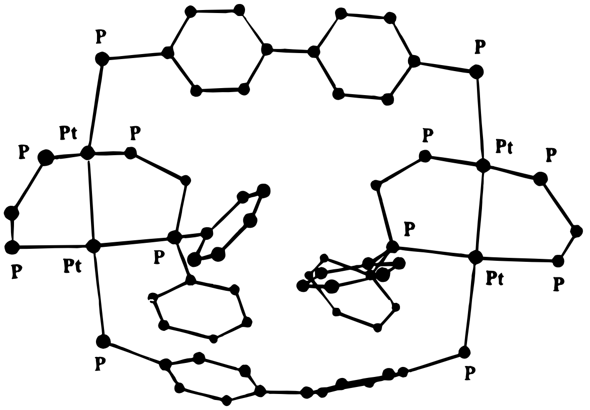


Figure 4. Structure of complex **8** as predicted by molecular mechanics calculations. Only four phenyl substituents of the dppm ligands are shown for clarity, but it can be seen that the biphenyl spacer is long enough so that steric effects between phenyl groups are not severe.

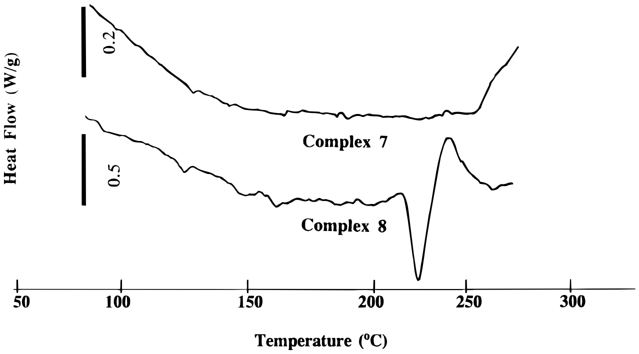


Figure 5. Differential scanning calorimetry (DSC) traces for the polymeric complex **7** and the cyclic complex **8** (the scales are shown by the solid bars). Note the sharp melting transition for **8** but not for **7**. These are traces obtained after heating the samples to 150 °C, followed by cooling to room temperature, and then reheating.

Thermal Properties of the Polymers. The thermal properties of the oligomers or polymers **5**−**7** were carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Each complex underwent major weight loss in the temperature range 330−480 °C, but further slow weight loss occurred at higher temperatures so that the weight loss associated with a residue of pure platinum was not obtained at the maximum temperatures studied.

DSC studies show that the compounds **5**−**7** exhibit broad endothermic transitions over the temperature range *ca.* 30−200 °C. In contrast, complex **8** gave a melting endotherm beginning at 228 °C, again indicating that it is not a polymer (Figure 5). When samples of **5**−**7** were heated to 150 °C for 30 min and then cooled and reheated, the broad endotherm in the region 25−125 °C was not observed. Similar observations were made during the study of polymers prepared by the oxidative addition of 2-bromoethyl methacrylate to $[PtMe_2(bu_2bipy)]$, followed by free radical polymerization. In this case, it was argued that the polymers precipitated in a strained conformation and on heating relaxed to a less strained form.[32] A similar effect may be occurring here.

Conclusions

It is clear from this work that rigid-rod oligomers and polymers with Pt—Pt bonds in the backbone, analogous to those already known without the metal—metal bonds,[2] can be prepared. The oligomers can be neutral if the bridging ligands are diacetylides or cationic if the bridging ligands are diisocyanides. The case in which the bridging ligands are diphosphines is more complex, due to the angular coordination at phosphorus, and rings can be formed if the spacer group between the phosphorus donors is long enough to allow this.

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Supporting Information Available: Tables of complete atomic coordinates and thermal parameters, bond distances and angles, and anisotropic parameters for complexes **1** and **3** (16 pages). Ordering information is given on any current masthead page.

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