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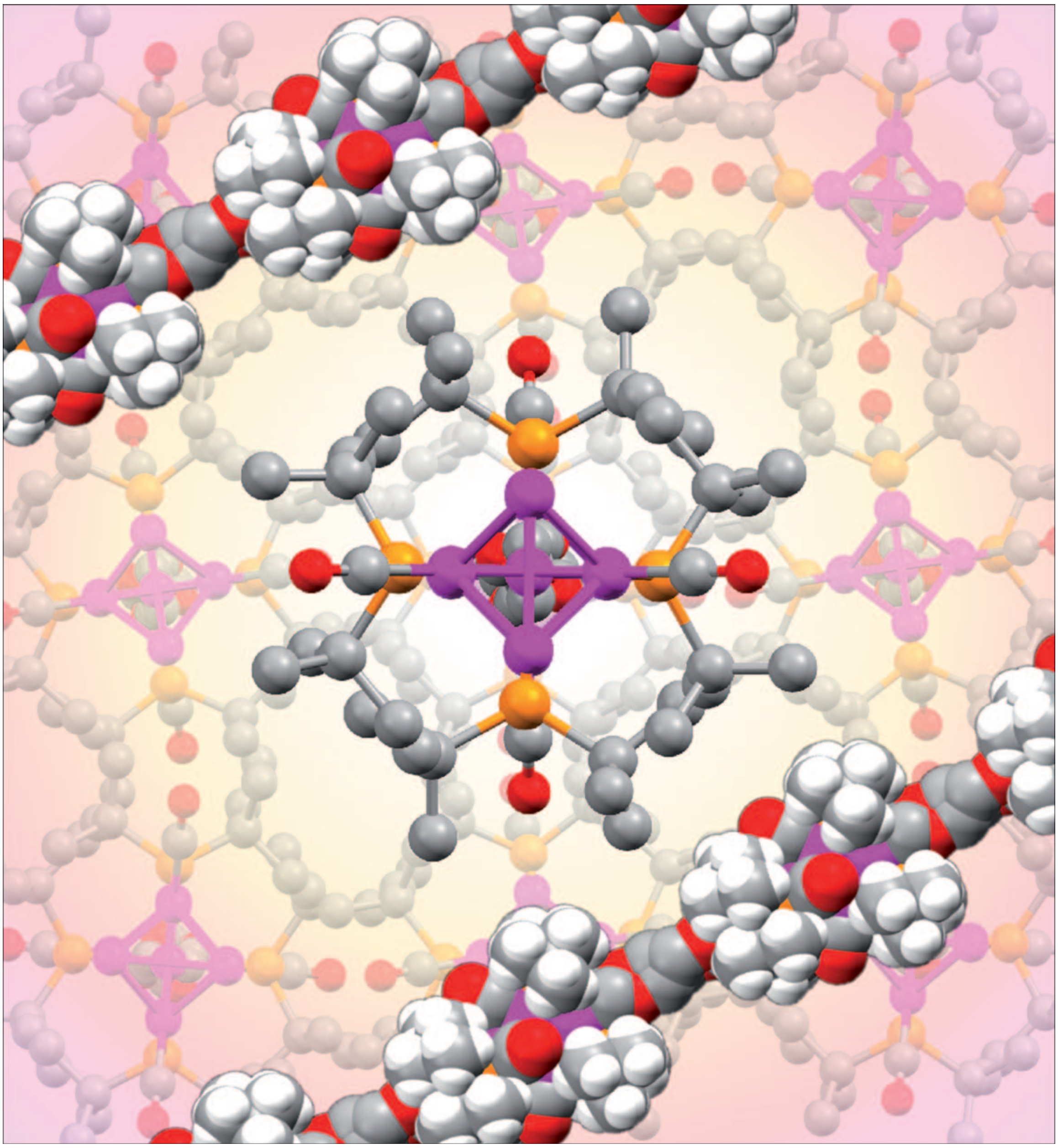
Proton-Transfer Reactions on Hexanuclear Platinum Clusters: Reversible Heterolytic Cleavage of H_2 and C−H Activation Affording a Linear, Cluster-Containing Polymer

Piero Leoni,*[a] Lorella Marchetti,[a] Veronica Bonuccelli,[a] Swagat K. Mohapatra,[a]
Alberto Albinati,[b] and Silvia Rizzato[b]



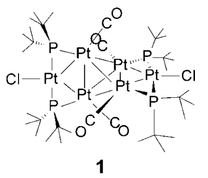
Abstract: The hexanuclear cluster $\{Pt_6\}H_2$ (**2**) contains a sterically hindered and chemically stable $\{Pt_6\} = Pt_6(\mu\text{-}PtBu_2)_4(CO)_4$ core, with the six metals forming an edge-bridged tetrahedron. The two hydrides are the reactive sites of the cluster and lie on opposite sides of the cluster, terminally bonded to the two "apical" edge-bridging platinum centres. Indeed, cluster **2** reacts with acids of different acidity ($HA = CF_3SO_3H$, HBF_4, $p\text{-}CH_3\text{–}C_6H_4\text{–}SO_3H$, CF_3COOH, PhCOOH and CH_3COOH), affording, after evolution of two equivalents of dihydrogen, the corresponding anion-substituted clusters $\{Pt_6\}A_2$ (**4**). We suggest that the reaction proceeds through a mechanism similar to the one generally accepted for the analogous protonation of mononuclear hydrides, with some of the intermediates partially characterised at low temperature. Interestingly, the reverse reaction, the heterolytic splitting of H_2 by clusters **4**, occurs readily under mild conditions. The anions in clusters **4a** and **4b** (**4a**: $A = CF_3SO_3$, **4b**: $A = BF_4$) are bonded in the solid state but very easily dissociate in solution and may be substituted under mild conditions by weak ligands, such as CH_2Cl_2 or CH_3CN. With dialkyl ethers, the reaction proceeds further with the heterolytic splitting of a C–H bond of the ethereal ligand. This process allowed us to isolate the polymer $[\{Pt_6\}(CH_2OCH_2CH_2OCH_2)]_x$ (**8**), in which the $\{Pt_6\}$ cluster units are connected by insulating spacers arising from dimethoxyethane. The results of single-crystal X-ray diffraction studies on **4a** and **8** are also reported.

Keywords: C–H activation · cluster compounds · ethers · platinum · polymers

Introduction

Soluble oligomeric or polymeric rigid-rod organometallic derivatives are attracting considerable interest as molecular components in molecular and supramolecular engineering due to their potential value in many challenging technological applications, such as nanomachine or solar-cell construction, surface functionalisation and molecular electronics.[1]

Systems containing isolated metal centres either located at the extremes or regularly intercalated into the main chain are being actively investigated,[2] and some remarkable and quite uncommon related derivatives are known in which the metal components are metal–metal-bonded bimetallic units or linear polynuclear chains.[3] Soluble polymeric or dendrimeric derivatives with alternated metal clusters and σ-bonded organic spacers are rare,[4] although they may have a great potential as materials for molecular electronics, since they possess both the remarkable properties of molecular clusters, which may function as molecular capacitors,[5] and the typical processability of polymeric materials. We have recently reported that hexanuclear platinum clusters with sizable bridging phosphides are suitable precursors for the construction of 1D or 2D ordered macromolecules. In particular, we have shown that the dichloride $\{Pt_6\}Cl_2$ (**1**) ($\{Pt_6\} = Pt_6(\mu\text{-}PtBu_2)_4(CO)_4$) is a useful synthon for the introduction of the $\{Pt_6\}$ cluster unit in cluster-containing nearly planar dendrimers,[6a] or in linear polymers and in some related pure and monodisperse shorter oligomers.[6b,c]



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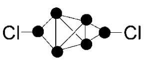

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Poly- and oligomeric derivatives, containing up to 16 $\{Pt_6\}$ units alternated by conjugated σ-bisalkynyl spacers were prepared by starting from cluster **1** and the proper terminal dialkyne under Sonogashira-type conditions and were characterised by microanalytical, spectroscopical and GPC analyses, but their linear structure could only be inferred from the X-ray crystal structures of model compounds containing only one cluster unit.[6c] Here we describe the synthesis and X-ray structural characterisation of new polymers with alternating $\{Pt_6\}$ units and insulating organometallic spacers. It is worth noting that the polymers were formed through the intermolecular activation of the C–H bonds of ethers, a reaction that has some precedent in reactions promoted by mononuclear transition-metal complexes,[7] but is unprecedented in metal-cluster chemistry.

This reaction was discovered during our studies on the reactivity of the hexanuclear dihydride $\{Pt_6\}H_2$, (**2**), easily obtained by reacting cluster **1** with $NaBH_4$. The protonation of **2** with acids HA of various strength, yielding the corresponding anion-bonded $\{Pt_6\}A_2$, and the reverse reaction, that is, the heterolytic splitting of the dihydrogen molecule by $\{Pt_6\}A_2$, will also be discussed.

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[a] Prof. P. Leoni, Dr. L. Marchetti, Dr. V. Bonuccelli,
Dr. S. K. Mohapatra
Dipartimento di Chimica e Chimica Industriale
Università di Pisa, Via Risorgimento 35.
56126 Pisa (Italy)
Fax: (+39) 05020237
E-mail: leoni@dcci.unipi.it

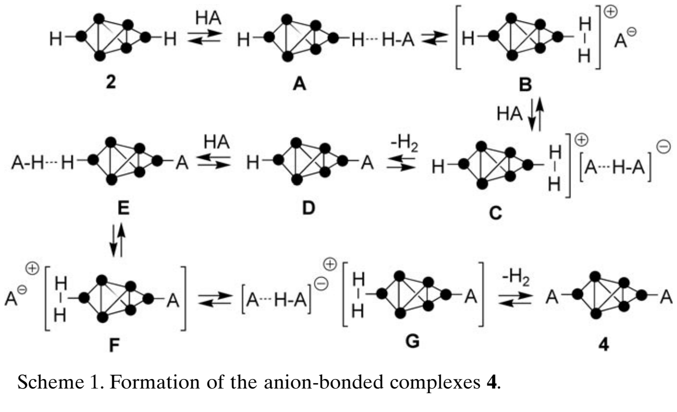
[b] Prof. A. Albinati, Dr. S. Rizzato
Dipartimento di Chimica Strutturale e
Stereochimica Inorganica (DCSSI)
Università di Milano, Via Venezian 21
I-20133 Milano (Italy)

Supporting information for this article (a view of the $\{Pt_6\}$ cluster core in the structures of compounds **4a** and **8**, with the numbering scheme and a list of selected metal–metal bond distances) is available on the WWW under http://dx.doi.org/10.1002/chem.2001000809.

Results and Discussion

Protonation of cluster 2: By adding at room temperature two equivalents of strong acids (HA = CF_3SO_3H (TfOH) or HBF_4) to a toluene solution of cluster **2**, the instantaneous and quantitative formation of the corresponding derivatives with weakly bonded anions $\{Pt_6\}A_2$ (**4a**: A = TfO, **4b**: A = BF_4) is observed.

The reaction is accompanied by the evolution of two equivalents of molecular hydrogen, as confirmed by GC analysis and by the growth, in the ^{1}H NMR spectrum of the reaction mixture, of a singlet without ^{195}Pt satellites at $\delta = 4.57$ ppm,[8a] which appears as a 1:1:1 triplet ($^1J_{(H,D)} = 43$ Hz)[8b] when **2** is reacted with TfOD. The structures of **4a**,**b**, isolated in good (> 80 %) yields, were confirmed based on the single-crystal X-ray diffraction study of **4a** (see below) and are consistent with microanalytical and spectroscopical data, the latter being as expected for $\{Pt_6\}X_2$ clusters symmetrically substituted at the two "apical" Pt centres, that is, a single ν_{CO} absorption (**4a**: 2022, **4b**: 2020 cm^{-1}), one signal in the $^{31}P\{^1H\}$ NMR spectrum for the four equivalent P nuclei (central singlet with ^{195}Pt satellites: **4a**: $\delta = 333.7$, **4b**: 331.9 ppm), one virtual triplet (vt) for the equivalent *tert*-butyl protons in the ^{1}H NMR spectrum (**4a**: $\delta = 1.51$ ppm, $^3J_{(H,P)} + {}^5J_{(H,P)} = 7.4$ Hz; **4b**: $\delta = 1.52$ ppm, $^3J_{(H,P)} + {}^5J_{(H,P)} = 7.6$ Hz), and two complex and diagnostic[9] signals in the $^{195}Pt\{^1H\}$ NMR spectrum (**4a**: $\delta = -4003$ (2 Pt), -3733 (4 Pt); **4b**: -3971 (2 Pt), -3730 ppm (4 Pt)). Weaker acids afford the corresponding derivatives **4c**–**f** (**4c**: A = *p*-CH_3-C_6H_4–SO_3, **4d**: A = CF_3COO, **4e**: A = PhCOO, **4f**: A = CH_3COO) still in high yields although with slower reaction rates (see the Experimental Section). By analogy with the generally accepted stepwise route for proton-transfer reactions between mononuclear metal hydrides and Brønsted acids,[10] the formation of the anion-bonded complexes **4** may occur through a complex series of equilibria, some of which are shown in the simplified mechanism of Scheme 1, which does not account for the possible formation of hydrogen bonded intimate ion pairs, $M(H_2)^+\cdots X^-$.[10] Moreover, especially at high concentrations of HA, related equilibria may become significant in which the reactions on the two hydride ligands are not as separated as shown in Scheme 1.[11] Even with the stronger acids, the reaction is slow enough, at low temperatures, to allow the observation of thermally unstable intermediates and their (partial) characterisation. Attempted studies of the early stages of the reaction between **2** and TfOH in toluene failed due to the quick precipitation of **4a**; to this purpose, dichloromethane was found to be more appropriate, although in this solvent **4a** (and **4b** or **2**, as well) slowly decomposes, at room temperature, to give the dichloride **1**. When a CD_2Cl_2 solution of **2** and triflic acid is prepared at −80 °C, the $^{31}P\{^1H\}$ and ^{1}H NMR spectra, acquired at the same temperature, fail to show the resonances of free H_2 and **4a**. Instead, the spectra contain only the residual signal of **2** ($\delta_P = 342.8$, $\delta_H = 1.41$ ppm (virtual triplet)), which vanishes as new broad signals, due to one symmetrically disubstituted $\{Pt_6\}X_2$ species (or more, rapidly equilibrating, species), increase at $\delta_P = 370.5$ ppm (s, with ^{195}Pt satellites) and $\delta_H = 1.36$ (vt) and 11.0 ppm (br s). By raising the temperature, all these signals disappear, leaving only the resonances due to free H_2 and **4a**. On the basis of this data, and taking into account the complexity of the system, understanding the actual nature of the intermediate is not straightforward. However, the intermediate cannot be one of the species **D**–**G**, since it appears before H_2 evolution; moreover, the broad signal at $\delta = 11.0$ ppm, observed both in the direct and the reverse (see below) reaction, may be assigned to hydrogen-bonded TfOH ($\delta_H = 8.37$ ppm at 22 °C for TfOH 0.1 M in CD_2Cl_2,[12] shifted downfield in the case of hydrogen-bonded TfOH[12,13]), matching either **A** or **C**. Structure **A** seems less likely due to the considerable downfield shift of δ_P (ca. $\delta = 28$ ppm) relative to cluster **2** and, therefore, we suggest that the intermediate is closer to structure **C**, possibly in equilibrium with the symmetrical bis(dihydrogen) complex $[\{Pt_6\}(H_2)_2]^{2+}$, not shown in Scheme 1. The lack of clearly identifiable high-field $Pt(H_2)$ (and/or Pt–H) resonances could be due to: 1) their weakness; note that the hydridic resonance in **2**, at $\delta = -0.26$ ppm in CD_2Cl_2 (m, $^1J_{(H,Pt)} = 1385$ Hz), is split into a great number of lines (spanning ca. $\delta = 7$ ppm in our spectrometer) for the couplings with the closest ^{31}P and ^{195}Pt nuclei[9b] and 2) the considerable signal broadening (all signals are quite broad in the whole range of temperatures explored). Moreover, it must be remembered that thermally unstable dihydrogen complexes, with two bulky phosphorus ligands *cis* to the $Pt(H_2)$ site, have been observed previously and characterised in detail in square-planar mononuclear platinum(II) complexes,[8a,14] but nonclassical bonding of dihydrogen in molecular clusters of transition metals has been suggested rarely and only on the basis of indirect evidence.[15] Trapping one or more kinetic intermediate (and the nature of the trapped species) in the complex pathway from **2** to **4** may depend strongly on various parameters, especially on the solvent and on the acid strength of HA. Unfortunately, as mentioned above, following the reaction with TfOH at low temperatures in apolar solvents turned out to be impossible and, therefore, we decided to investigate the (slower) reaction with weaker acids.

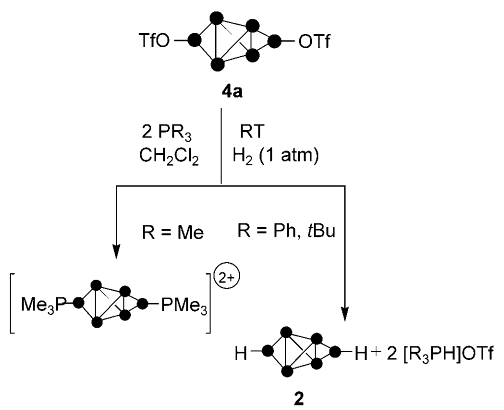


Scheme 1. Formation of the anion-bonded complexes **4**.

When two equivalents of CF_3COOH were added at room temperature to a toluene solution of **2**, the ^{1}H and

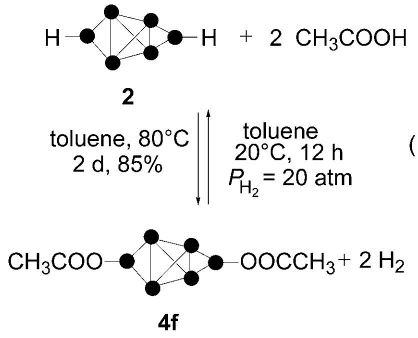
$^{31}P\{^1H\}$ NMR spectra show only the resonances of the starting materials, with the singlets of the hydrides and of the OH proton (at $\delta=-0.18$ and 5.48 ppm, respectively) severely broadened (broadening increases at low temperature without coalescence), possibly due to type **A** hydrogen-bonded species. After 2 h, together with the signal of free H_2, transient resonances that we assign to the monohydride intermediate $\{Pt_6\}(H)(O_2CCF_3)$ (structure **D** in Scheme 1) appeared in solution ($\delta_P=350.6$, 321.8 ppm (s with ^{195}Pt satellites), $\delta_H=1.45$ (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.6$ Hz), 1.37 (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.4$ Hz), −0.44 ppm (br m, Pt−H), $\delta_F=-74.14$ ppm (s with ^{195}Pt satellites, $^4J_{(F,Pt)}=12.4$ Hz)) and were then slowly replaced by the resonances of the bis(carboxylate) **4d**. The latter was formed quantitatively after two days at 60 °C and was isolated in 91 % yield as an orange solid ($\delta_P=327.0$ ppm (s with ^{195}Pt satellites); $\delta_H=1.34$ ppm (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.4$ Hz); $\delta_{Pt}=-4000$ (m, 2 Pt), −3577 ppm (m, 4 Pt); $\delta_F=-74.22$ ppm (s with ^{195}Pt satellites, $^4J_{(F,Pt)}=11.9$ Hz); $\nu_{C\equiv O}=2018$, $\nu_{C=O}=1698$ cm^{-1}). The reaction proceeded similarly when performed in CD_2Cl_2 or with CH_3COOH in place of CF_3COOH.

Heterolytic splitting of dihydrogen: It may be noted that under hydrogen pressure, the reverse reaction in Scheme 1, that is, the heterolytic cleavage of H_2, takes place. By dissolving **4a** in CD_2Cl_2 in a sapphire NMR tube at −40 °C and $P_{H2}=40$ atm., we observed only the broad resonances at $\delta_P=370.5$ ppm and $\delta_H=1.36$ and 11.0 ppm observed as transient signals in the forward reaction and assigned to intermediate **C**; by releasing the excess pressure, and returning to $P_{H2}=1$ atm., **4a** is quantitatively restored. We suggest that the heterolytic splitting of H_2 was not completed, to give a mixture of **2** and triflic acid, due to the very low basicity of the triflate anion. Indeed, the reaction can be accomplished under lower H_2 pressures, by a 1:2 mixture of **4a** and a Brønsted base stronger than the triflate ion and too bulky to form strong bonds with the two apical Pt centres. As shown in Scheme 2, in the presence of 1 atm. H_2, **4a** reacts quickly at room temperature with two equivalents of trimethylphosphine (Tolman's cone angle $\theta=118°$)[16] to afford the known cation $[\{Pt_6\}(PMe_3)_2]^{2+}$,[9c] whereas a 1:2 mixture of the dihydride **2** and the phosphonium salt $[R_3PH]OTf$ is obtained with the bulkier triphenylphosphine ($\theta=145°$)[16] or tri-*tert*-butylphosphine ($\theta=182°$).[16]



Scheme 2. Reactions of **4a**.

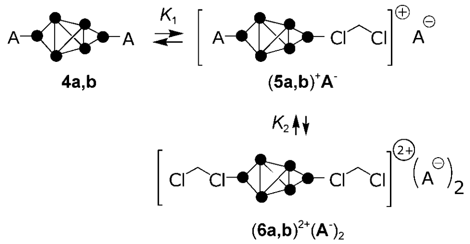
As expected from the stronger basicity of the acetate relative to the triflate ion, the diacetate **4f**, obtained by reacting a toluene solution of **2** with acetic acid (2 d, 80 °C, 85 % (isolated) yield), reacts at room temperature with H_2 ($P_{H2}=20$ atm.), and is converted quantitatively in a few hours into a 1:2 mixture of cluster **2** and acetic acid. Partial conversion is also observed when a solid sample of **4f** was left for 48 h under 50 atm. of H_2 (see the Experimental Section).



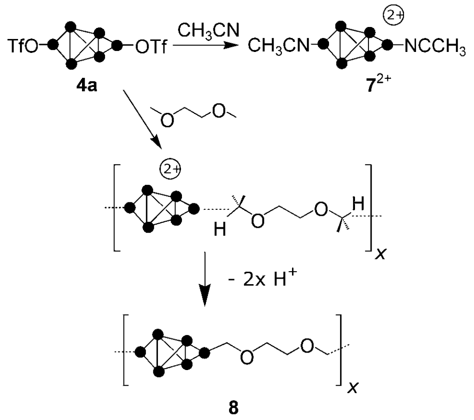
(1)

Therefore, the equilibrium in Equation (1) may be completely displaced both ways under mild conditions. These findings are akin to the remarkable results reported by Weller[17] and Adams[18] and their co-workers, and confirm that molecular clusters might play a significant role in hydrogen storage,[19] if similar reactions will be found for clusters of cheaper and lighter metals, for which a higher wt % of hydrogen may be obtainable. Moreover, the mild conditions requested for the heterolytic splitting of H_2 suggest that this system may be useful for stoichiometric or catalytic applications in related heterolytic E−H splitting reactions (see below for an example on sp^3 C−H bonds), rarely achieved on cluster substrates.

Reactions of 4a,b: The triflate or tetrafluoroborate anions in **4a**,**b** are bonded to the apical Pt atoms in the solid state, as confirmed by the X-ray molecular structure of **4a**, and by their diagnostic IR absorptions (**4a**: 1325 (SO_3), 1228 (CF_3), 1172 (CF_3), 995 (SO_3);[20] **4b**: 1152, 1127, 965 cm^{-1}).[21] However, in solution they are easily displaced, even by very weakly coordinating solvents. In fact, at 20 °C the ^{19}F NMR spectra of **4a** in CD_2Cl_2 contain two broad singlets in a 95:5 integral ratio at $\delta=-77.2$ and −79.1 ppm, respectively, assigned to metal-bonded and free triflate ions.[22] By lowering the temperature, the signals are only slightly high-field shifted, whereas the relative intensities change significantly ($\delta_F=-77.4$ and −79.4 ppm at −50 °C, ca. 50:50 integral ratio), a behaviour consistent with the anion dissociation equilibria shown in Scheme 3.[23] The presence of only two of the three expected resonances in the ^{19}F NMR spectra (for bonded triflate, in the neutral species **4a** and the monocation $\mathbf{5a}^+$,



Scheme 3. Anion dissociation equilibria for **4a**/**b**.



Scheme 4. Conversion of **4a**,**b** into dication [{Pt$_6$}(CH$_3$CN)$_2$]$^{2+}$, **7**$^{2+}$, and into polymer **8**.

and for free TfO$^-$) cannot be due to the absence (or undetectable concentration) of one of the corresponding species in solution: low concentrations of **4a** (large value of K_1) would require [TfO$^-$] ≥ [**5a**$^+$] and low concentrations of **5a**$^+$ would require $K_2 \gg K_1$, whereas the first dissociation constant for a salt is almost always larger than (or similar to) the second one.[24] More reasonably, the resonances due to **4a** and **5a**$^+$ coincide either by accidental overlapping of the signals or because of fast (relative to $\Delta\delta_F$ in Hz) exchange. This complication apart (which prevents the experimental evaluation of the values of K_1 and K_2), the data show clearly that at low temperatures solvent coordination is favoured over anion coordination. A similar behaviour has already been observed and explained by suggesting that solvent coordination is enthalpically favoured, whereas anion coordination is entropically favoured because of a lower charge separation.[25]

At 30 °C, the $^{19}F\{^1H\}$ NMR spectra of a 0.01 M CD$_2$Cl$_2$ solution of **4b** contain broad singlets at $\delta = -145.8$, -148.7 (coord.), and -150.1 ppm (uncoord.), with relative intensities 9.1:9.5:81.4, in agreement with the expected weaker binding of the tetrafluoborate than the triflate anion.[22,24–26] Again, anion dissociation increases at low temperatures (relative intensities 7.3:2.2:90.5 at −50 °C). According to the treatment given in reference [24], and by assigning the resonance at $\delta = -145.8$ to **5b**$^+$ and the one at −148.7 ppm to **4b**, we calculated the values $K_1 = 0.120$ and $K_2 = 0.103$ M ($K_1/K_2 = 1.16$) at −50 °C and $K_1 = 3.12 \times 10^{-2}$ and $K_2 = 6.47 \times 10^{-2}$ M ($K_1/K_2 = 0.482$) at 30 °C, which provide the rough estimates of $\Delta H_1^\circ = -9.49$, $\Delta S_1^\circ = -60.2$, $\Delta H_2^\circ = -3.28$ kJ mol^{-1} and $\Delta S_2^\circ = -33.6$ J mol^{-1} K^{-1}, in agreement with the suggestions given above.[27]

In CH$_3$CN or CD$_2$Cl$_2$ containing two equivalents of acetonitrile, **4a**,**b** are quantitatively converted into the known[9b] dication [{Pt$_6$}(CH$_3$CN)$_2$]$^{2+}$, **7**$^{2+}$ (Scheme 4).

In ethereal solvents, such as dimethoxyethane (DME), the protonation of **2** with TfOH proceeds, after H$_2$ evolution, with the precipitation of the new cluster-containing polymer [{Pt$_6$}(CH$_2$OCH$_2$CH$_2$–OCH$_2$)]$_n$, (**8**), which may reasonably be formed through the intermediate formation of a σ-C–H bond complex. The deprotonation of this intermediate by addition of a base is not necessary, since the solvent itself has sufficient Brønsted basicity.

Polymer **8** is quantitatively formed also by suspending **4a**,**b** in DME. Microanalytical data are in good agreement with the determined structure, but its solubility is too low for a solution NMR spectroscopic analysis. Fortunately, crystals suitable for the X-ray diffraction studies precipitated directly from the reaction mixture.

Crystal structures of 4a and of 8: ORTEP views of the structures of compounds **4a** and **8** are given in Figure 1. Both

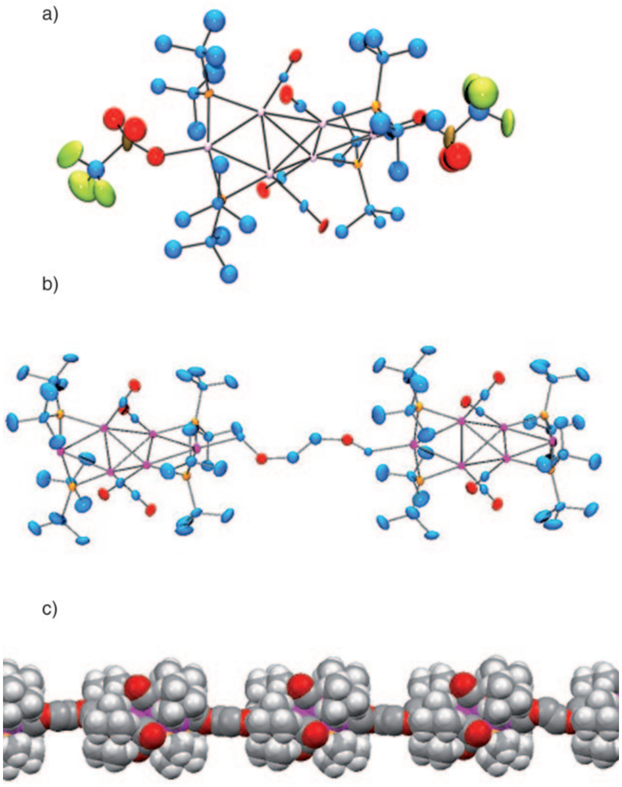


Figure 1. ORTEP views of a) **4a** and b) two monomeric units of **8**. Atoms are colour coded: C: light blue, O: red, F: yellow/green, S: brown, P: orange and Pt: pink. Ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. c) Space-filling view of a portion of the polymer's chain in **8**. Only one of the four possible orientations of the CH$_2$OCH$_2$CH$_2$OCH$_2$ generated by the crystallographic −4 axis is shown.

structures contain an hexanuclear Pt core but, whereas **4a** is monomeric, with two terminal triflate ligands, a linear polymer, with alternating $\{Pt_6\}$ and $CH_2OCH_2CH_2OCH_2$ moieties, is present in **8**. Note that in compound **8**, due to the imposed crystallographic symmetry (−4), only 1/4 of the cluster is independent. A space-filling view of the polymer is shown in Figure 1c.

The hexanuclear $\{Pt_6\}$ core stems from the condensation of two "Pt_3" units yielding a distorted tetrahedral cluster capped, on each of the two opposite edges, by a platinum atom linked, in one case, to a triflate moiety and in the other to the 2,5-dioxahexane-1,6-diyl spacer.

A view of the $\{Pt_6\}$ cluster core in both compounds is given in the Supporting Information, Figure S1, together with the numbering scheme and a list of selected metal–metal bond lengths. The shortest Pt–Pt bonds are those in the "terminal" triangles (in the range of 2.674(1)–2.701(4) Å), whereas the longest are those of the central tetrahedron (in the range of 2.848(1)–2.863(1) Å). These lengths are comparable to those found in similar neutral $\{Pt_6\}XY$ or cationic $[\{Pt_6\}(L)_2]^{2+}$ clusters.[6a,9b] All other distances are in the expected range.

The structure of **8** shows that the $\{Pt_6\}$ unit can be assembled into linear polymeric chains and confirms our previous hypothesis, based on the structure of the model cluster $\{Pt_6\}(CCPh)_2$,[6b] that the previously reported oligomeric or polymeric derivatives $[-\{Pt_6\}(CC{-}Ar{-}CC)-]_x$ (Ar = 1,4-C_6H_2-2,5-($C_{12}H_{24}$)) indeed possess linear backbones.[6c] The $\{Pt_6\}$ cluster units in **8** are eclipsed along the polymeric chains running parallel to the *c* axis, and held together by van der Waals forces to give an ordered 3D array as shown in Figure 2.

A similar packing has been observed in the structures of the non-polymeric halide derivatives $\{Pt_6\}X_2$ (**1**: X = Cl, **9**: X = I, **10**: X_2 = ICl).[9b] The intercluster Pt···Pt distance is nearly constant in the series (10.750, 10.837, 10.861 and 11.073 Å in **8**, **9**, **1** and **10**, respectively). This means that a careful selection of spacers with the proper length (and small steric footprint), keeping the cluster units separated by approximately 11 Å, may allow the synthesis of other linear polymers exhibiting a similar solid-state packing; the possibility of changing the channels dimensions will be studied in the future.

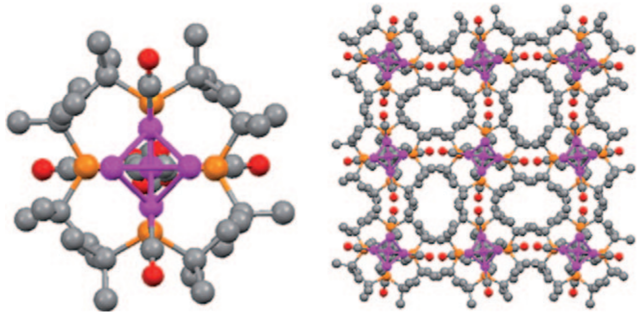


Figure 2. A single chain of **8** projected along the *c* axis (left), and the resulting crystal packing (right).

Conclusion

We have been able to show that the sterically bulky hexanuclear dihydride $\{Pt_6\}H_2$, **2**, reacts with Brønsted acids to give, after H_2 evolution, the anion-bonded derivatives $\{Pt_6\}A_2$. These give the reverse heterolytic splitting of H_2 under mild conditions and may easily activate other E−H bonds, as proven by the reaction with DME yielding polymer **8**.

It has already been shown that decorating the surface of a molecular cluster with bulky and strongly bound ligands may impart a series of attracting characteristics to the cluster itself.[6,9b,15,17,18] Sterically hindering ligands, especially when in bridging positions, may provide a remarkable stabilisation of the polynuclear metal core, which becomes more resistant to fragmentation; in addition, they may also have significant influence on the reactivity of the cluster. Steric hindrance may decrease the number of equivalent reactive sites, thus reducing the prospect of troublesome separation and purification workup on mixtures of various isomers. As we have previously shown,[6,9b] and confirmed here with the synthesis of polymer **8**, these features facilitate the utilisation of molecular clusters as organometallic synthons for macromolecular assemblies.

Furthermore, it may become difficult for a given ligand to approach more than one metal centre, which imposes a significant barrier to bridging coordination modes; as a matter of fact, in all the numerous derivatives of the hexanuclear $[Pt_6(\mu\text{-}PtBu_2)_4]$[6,9b] and trinuclear $[Pt_3(\mu\text{-}PtBu_2)_3]$[28] cores prepared so far, we have always observed only terminal modes for ligands (e.g. CO, halides, alkynyls and hydrides), which have a significant tendency to act as bridging ligands in metal clusters. This behaviour reduces the mobility of the ligands on the surface of the cluster and extends the lifetime of kinetic intermediates. Moreover, when a given ligand "sees" only one metal, the reactivity of the "single-site" M−L moiety is reminiscent (more than in other clusters) of that in mononuclear complexes; the other metal centres may be considered as "spectators", they do not participate directly in the reactions, even though they may have an electronic influence on the reactivity of the ligand-bonded metal centre. For example, the Pt−H moieties in cluster **2** react with proton donors very much like their equivalent in *trans*-$[Pt(H)_2(PR_3)_2]$ and $[PtH(PCP)]$ (PCP = η^3-$(tBu_2PCH_2)_2C_6H_3$), and indeed, they may be described as having similar geometries: the apical Pt centres in **2** may also be considered as being square planar, with two bulky PR_3 groups *cis* to the hydride ligand and the fourth position occupied by an orbital involved in the formation of the metal–metal bonds. The same oxidation state of the metal centres could not be as different as it appears at first sight; actually it is +II in the mononuclear complexes and, on the average, +I in cluster **2**, but NBO calculations[29] and XPS data[29] suggest that the two apical Pt centres are more oxidised than the inner four of the central tetrahedron.

Finally, it may be interesting to note that, whereas the above-mentioned remarkable examples of hindered molecular clusters, kinetically stabilised by bulky phosphines, described by Weller[15,17] and Adams[18] are able to oxidatively add (reversibly) a large number of H_2 molecules, our $\{Pt_6\}A_2$ clusters activate the H–H bond and the C–H bond of DME by heterolytic splitting. The extension of this procedure to other ethers and to other C–H bonds, and the possible applications to homogeneous catalysis[19e,30] are currently under investigation.

Experimental Section

General data: The reactions were carried out under a nitrogen atmosphere, by using standard Schlenk techniques. $[Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_4H_2]$ (**2**) was prepared as previously described.[9b] Solvents were dried by conventional methods and distilled under nitrogen prior to use. IR spectra were taken on pure compounds by using a Perkin–Elmer FTIR spectrometer equipped with a UATR sampling accessory. NMR spectra were recorded on a Varian Gemini 200 BB instrument; frequencies are referenced to the residual resonances of the deuterated solvent (^1H, ^{13}C), 85 % H_3PO_4 (^{31}P), and H_2PtCl_6 (^{195}Pt). The 10 mm sapphire tube was purchased from Saphikon, Milford, NH, whereas the titanium high-pressure charging head was constructed at ICCOM-CNR (Firenze, Italy).[30]

$Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_4(O_3SCF_3)_2$ (4a): CF_3SO_3H (11 μL, 0.124 mmol) was added to a red solution of complex **2** (110 mg, 0.059 mmol) in toluene (5 mL). The orange solid, which precipitated out within a few minutes was filtered off, washed several times with toluene, and then vacuum dried. Yield: 110 mg (86 %); IR: $\tilde{\nu}=2022$ (C≡O), 1325, 1228, 1172, 995 cm^{-1} (TfO^-); ^1H NMR (200 MHz, CD_2Cl_2, 25 °C): $\delta=1.51$ ppm (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.4$ Hz, 36 H; *t*Bu); $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2, 25 °C): $\delta=46.1$ (s, P*C*), 31.7 ppm (s, *C*H_3); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 25 °C): $\delta=333.7$ ppm (s); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, CD_2Cl_2, 25 °C): $\delta=-3733$ (4 Pt), −4003 ppm (2 Pt); $^{19}F\{^1H\}$ NMR (188 MHz, CD_2Cl_2, 25 °C): $\delta=-77.2$ (coord.), 79.1 ppm (uncoord.); elemental analysis calcd (%) for $C_{38}H_{72}F_6O_{10}P_4Pt_6S_2$: C 21.1; H 3.36; found: C 21.0, H 3.39; the earlier steps of the reaction were followed by dissolving complex **2** (26 mg; 0.014 mmol) in CD_2Cl_2 (0.5 mL) in a well-dried NMR tube. The solution was cooled to −80 °C and $CF_3SO_3H(D)$ (2.5 μL, 0.028 mmol) was then added. The resulting red solution was analysed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy at −80 °C and then at increasing temperatures.

$Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_4(BF_4)_2$ (4b): Compound **4b** was prepared by a procedure identical to that used for **4a** by reacting **2** with $HBF_4{\cdot}Et_2O$ (54 wt %, 17 μL, 0.123 mmol). Yield: 97 mg (81 %); IR: $\tilde{\nu}=2020$ (C≡O), 1152, 1127, 965 cm^{-1} (BF_4^-); ^1H NMR (200 MHz, CD_2Cl_2, 25 °C): $\delta=1.52$ ppm (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.6$ Hz, 36 H; *t*Bu); $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2, 25 °C): $\delta=44.8$ (s, P*C*), 31.0 ppm (s, *C*H_3); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 25 °C): $\delta=331.9$ ppm (s); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, CD_2Cl_2, 25 °C): $\delta=-3730$ (4 Pt), −3971 ppm (2 Pt); $^{19}F\{^1H\}$ NMR (188 MHz, CD_2Cl_2, 25 °C): $\delta=-145.8$, −148.7 (coord.), −150.1 ppm (uncoord.); elemental analysis calcd (%) for $C_{36}H_{72}B_2F_8O_4P_4Pt_6$: C 21.2, H 3.56; found: C 21.3, H, 3.59.

$Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_4(O_3S{-}C_6H_4{-}CH_3)_2$ (4c): Dry *p*-$CH_3{-}C_6H_4{-}SO_3H$ (12 mg, 0.070 mmol) was added to a red solution of **2** (66 mg, 0.035 mmol) in toluene (2 mL). After the mixture had been stirred for 24 h at room temperature, the solution was evaporated to dryness under reduced pressure and hexane was added. The suspension was filtered and the orange solid (64 mg, 83 % yield) was dried in vacuo. IR: $\tilde{\nu}=2016$ (C≡O), 1603, 1495, 1455, 1259, 1158, 1099, 1012 cm^{-1} (TsO^-); ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta=8.06$ (d, $^3J_{(H,H)}=8.5$ Hz, 2 H; Ar), 6.89 (d, $^3J_{(H,H)}=8.5$ Hz, 2 H; Ar), 1.96 (s, 3 H; Ar−C*H*$_3$), 1.48 ppm (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.6$ Hz, 36 H; *t*Bu); $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6 25 °C): $\delta=140.7$, 138.5, 129.1, 127.1 (s, Ar), 45.9 (P*C*), 31.8 (*C*H_3), 21.5 ppm (*C*H_3Ph); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): $\delta=330.9$ ppm (s); $^{195}Pt\{^1H\}$ NMR 42.8 MHz, (CD_2Cl_2, 25 °C): $\delta=-3668$ (4 Pt), −3980 ppm (2 Pt); elemental analysis calcd (%) for $C_{50}H_{86}O_{10}P_4Pt_6S_2$: C 27.2, H 3.93; found: C 27.3, H 3.89.

$Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_4(O_2CCF_3)_2$ (4d): CF_3CO_2H (6 μL, 0.081 mmol) was added to a solution of **2** (75 mg, 0.040 mmol) in toluene (2 mL). After the mixture had been stirred for 2 days at 60 °C, the red solution was concentrated to a small volume and hexane (5 mL) was added. An orange solid precipitated out and was filtered and vacuum dried (76 mg, 91 %). IR: $\tilde{\nu}=2018$ (C≡O), 1698 cm^{-1} (C=O); ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta=1.34$ ppm (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.4$ Hz, 36 H; *t*Bu); $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta=199.6$ (CO), 162.0 (OO*C*CF$_3$), 117.7 (OOC*C*F$_3$, $^1J_{(C,F)}=289$ Hz), 45.9 (P*C*CH$_3$), 32.1 ppm (PC*C*H$_3$); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 25 °C): $\delta=329.0$ ppm (s); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, CD_2Cl_2, 25 °C): $\delta=-3577$ (4 Pt), −4000 ppm (2 Pt); $^{19}F\{^1H\}$ NMR (188 MHz, CD_2Cl_2, 25 °C): $\delta=-74.46$ ppm ($^4J_{(F,Pt)}=7.3$ Hz); elemental analysis calcd (%) for $C_{40}H_{72}F_6O_8P_4Pt_6$: C 23.0, H 3.47; found: C 22.9, H 3.49; the earlier steps of the reaction were followed by placing complex **2** (28 mg; 0.015 mmol) in a well-dried NMR tube and adding $[D_8]$toluene to give a volume of 0.5 mL. CF_3CO_2H (2.6 μL, 0.030 mmol) was added at room temperature and the solution was analysed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

$Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_4(O_2CPh)_2$ (4e): $PhCO_2H$ (34 mg, 0.28 mmol) was added to a solution of **2** (52 mg, 0.028 mmol) in toluene (2 mL). After the mixture had been stirred for 2 days at 80 °C, the red solution was concentrated to a small volume and hexane (3 mL) was added. An orange solid precipitated and was filtered and vacuum dried (47 mg, 80 % yield). IR: $\tilde{\nu}=2012$ (C≡O), 1633 cm^{-1} (C=O); ^1H NMR (200 MHz, CD_2Cl_2, 25 °C): $\delta=8.03$ (m, 2 H; Ar), 7.37 (m, 3 H; Ar), 1.47 ppm (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.4$ Hz, 36 H; *t*Bu); $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2, 25 °C): $\delta=133.8$, 130.3, 129.9, 128.7 (s, Ar), 44.7 (P*C*), 31.1 ppm (*C*H_3); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 25 °C): $\delta=325.0$ ppm (s); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, CD_2Cl_2, 25 °C): $\delta=-3478$ (4 Pt), −4011 ppm (2 Pt); elemental analysis calcd (%) for $C_{50}H_{82}O_8P_4Pt_6$: C 28.5, H 3.92; found: C 28.6, H 3.98.

$Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_4(O_2CCH_3)_2$ (4f): CH_3CO_2H (24 μL , 0.42 mmol) was added to a solution of **2** (80 mg, 0.043 mmol) in toluene (2 mL). The orange solution was stirred for 2 days at 80 °C, then the solvent was removed under vacuum and hexane (3 mL) was added. The orange solid that was precipitated out was vacuum dried (72 mg; 85 % yield). IR: $\tilde{\nu}=2014$ (C≡O), 1633 cm^{-1} (C=O); ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta=2.34$ (s, $^4J_{(H,Pt)}=5.4$ Hz, 3 H), 1.49 ppm (vt, $^3J_{(H,P)}+{}^5J_{(H,P)}=7.5$ Hz, 36 H; *t*Bu); $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): $\delta=204.0$ (CO), 175.7 (OO*C*CH$_3$), 45.3 (P*C*), 31.6 (PC*C*H$_3$), 24.4 ppm (OOC*C*H$_3$, $^3J_{(C,Pt)}=46$ Hz); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): $\delta=323.2$ ppm (s); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, C_6D_6, 25 °C): $\delta=-3462$ (4 Pt), −3959 ppm (2 Pt); elemental analysis calcd (%) for $C_{40}H_{78}O_8P_4Pt_6$: C 24.2, H 3.97; found: C 24.3, H 3.98; the earlier steps of the reaction were followed by placing complex **2** (28 mg; 0.015 mmol) in a well-dried NMR tube and adding $[D_8]$toluene to give a volume of 0.5 mL. CH_3CO_2H (2.2 μL, 0.030 mmol) was added at room temperature and the solution was analysed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of 4a,b with CH_3CN: Complexes **4a** or **4b** (15 mg) were dissolved in CD_2Cl_2 (0.5 mL) and CH_3CN (1 μL) was added. The $^{31}P\{^1H\}$ NMR spectra showed the immediate complete conversion of **4a** or **4b** into $\mathbf{7}^{2+}$.[9b]

High-pressure NMR spectroscopic study: Compound **4a** (42 mg; 0.019 mmol) was dissolved in CD_2Cl_2 (2.0 mL) and the orange solution was transferred under nitrogen into a 10 mm sapphire tube. The tube was charged with H_2 to a pressure of 40 atm. and then introduced into the NMR probe at room temperature. ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired at different temperatures in the range from 20 to −80 °C.

Reaction of 4a with H_2 and PMe_3: PMe_3 (2.5 μL, 0.024 mmol) was added to an orange suspension, saturated with H_2 (1 atm.), of **4a** (26 mg, 0.012 mmol) in toluene (1 mL). A red solution was formed immediately and was shown to contain ($^{31}P\{^1H\}$ NMR spectroscopy) only the known complex $[\{Pt_6\}(PMe_3)_2][CF_3SO_3]_2$.[9c]

Reaction of 4a with H_2 and PR_3 (R=*t*Bu, Ph): P*t*Bu$_3$ (12 μL, 0.05 mmol) or PPh_3 (13 mg, 0.05 mmol) was added to a suspension of **4a** (28 mg, 0.013 mmol) in toluene (1 mL). The flask was filled with H_2 (1 atm.) and the mixture was stirred at room temperature. After 6 h, a red solution was formed and the salt $[PR_3H][CF_3SO_3]$ precipitated as a white solid.

The $^{31}P\{^1H\}$ NMR spectrum of the solution showed the complete conversion of **4a** into cluster **2**.

Reaction of 4f with H_2: 1) An orange solution of **4f** (30 mg; 0.015 mmol) was transferred into a stainless-steel autoclave and pressurised with 20 atm. of H_2. After the mixture had been stirred for 12 h at room temperature, the autoclave was depressurised and the red solution was transferred into a Schlenk tube. A $^{31}P\{^1H\}$ NMR spectrum showed the complete conversion in complex **2**. 2) Solid **4f** (26 mg; 0.013 mmol) was transferred into a stainless-steel autoclave and pressurised with 50 atm. of H_2. After the mixture had been stirred for 48 h at room temperature, the autoclave was depressurised, the solid was dissolved in C_6D_6, and transferred into an NMR tube. A $^{31}P\{^1H\}$ NMR spectrum showed the resonances of the complexes **4f**, **2** and $\{Pt_6\}(H)(O_2CCF_3)$ in the approximate ratio 80:10:10.

$[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(CH_2OCH_2CH_2OCH_2)]_n$ (8):
Method A: CF_3SO_3H (4 μL, 0.045 mmol) was added to a red solution of **2** (41 mg, 0.022 mmol) in DME (5 mL). After 24 h, an orange crystalline solid precipitated out. The solid was filtered, washed with Et_2O and dried in vacuo (20 mg, 47 %).

Method B: Compound **4a** (46 mg, 0.021 mmol) was dissolved in CH_2Cl_2 (1 mL) and DME (50 μL) was added. After 2 days, the orange crystalline solid that precipitated out was filtered and vacuum dried (26 mg, 63 %). IR: $\tilde{\nu} = 2007\ cm^{-1}$ (C≡O); elemental analysis calcd (%) for $C_{40}H_{80}O_6P_4Pt_6$: C 24.6, H 4.13; found: C 24.4, H 3.98.

Crystallography: Crystals of **4a** and **8** were mounted on a Bruker SMART CCD diffractometer, for the unit-cell and space-group determinations. Crystals were cooled, by using a cold nitrogen stream, to 120 (**4a**) and 150 K (**8**), respectively, for the data collection. Selected crystallographic and other relevant data are listed in Table 1. Data were corrected for Lorentz and polarisation factors with the data reduction software SAINT[32] and empirically for absorption by using the SADABS program.[33]

Table 1. Experimental data for the X-ray diffraction study of compounds: **4a** and **8**.

Compound	4a	8
formula	$C_{38}H_{72}F_6O_{10}P_4Pt_6S_2$	$C_{40}H_{72}O_6P_4Pt_6$
M_w	2161.50	1943.40
T [K]	150 (2)	120(2)
diffractometer	Bruker SMART	Bruker SMART
crystal system	monoclinic	tetragonal
space group (no.)	*C2/c* (15)	*I-42d* (122)
a [Å]	24.377(4)	17.319(2)
b [Å]	17.596(3)	17.319(2)
c [Å]	29.648(5)	17.555(1)
α [°]	90.0	90.0
β [°]	106.468(2)	90.0
γ [°]	90.0	90.0
V [Å^3]	12196(3)	5265.2(8)
Z	8	4
ρ_{calcd} [g cm^{-3}]	2.354	2.452
μ [cm^{-1}]	139.47	160.04
radiation	$Mo_{K\alpha}$ (graphite monochrom. $\lambda = 0.71073$ Å)	
θ range [°]	$2.38 < \theta < 29.36$	$2.35 < \theta < 29.43$
data collected	54570	31193
independent data	15606	3478
observed reflections (n_o)	11385	3244
$[\lvert F_o\rvert^2 > 2.0\sigma(\lvert F\rvert^2)]$ parameters (n_v)	395	142
R_{int}[a]	0.0598	0.0443
R (obsd reflns)[b]	0.0684	0.0237
R^2_w (obsd reflns)[b]	0.1460	0.0529
GOF[b]	1.048	1.076

[a] $R_{int} = \Sigma\lvert F_o^2 - \langle F_o^2\rangle\rvert / \Sigma F_o^2$. [b] $R = \Sigma(\lvert F_o - (1/k)F_c\rvert)/\Sigma\lvert F_o\rvert$. [c] $R^2_w = \{\Sigma[w(F_o^2 - (1/k)F_c^2)^2]/\Sigma w\lvert F_o^2\rvert^2]\}^{1/2}$. [d] $GOF = [\Sigma_w (F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

The structures were solved by direct and Fourier methods and refined by full matrix least-squares[34] (the function minimised being $\Sigma[w(F^2_o - 1/kF^2_c)^2]$). For both structures, no extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[35] All calculations and plotting were carried out by using the PC version of SHELX-97,[34] WINGX,[36] ORTEP[36] and Mercury programs.[37]

Structural study of compound 4a: The space group was determined from the systematic absences, whereas the low-temperature cell constants were refined by least squares, at the end of the data collection, by using 5862 reflections ($2\theta_{max} \leq 56.7°$). The data were collected by using ω scans, in steps of 0.3°. For each of the 1080 collected frames, the counting time was 30 s.

The terminal triflate ligands are disordered as can be seen from the large value of some of the displacement parameters, but it proved impossible to describe the ligand disorder with a simple model; therefore, only the ligand atoms corresponding to the strongest peaks in the difference Fourier maps were retained.

The poor quality of the crystals and the disorder of the triflate ligands prevented a full anisotropic refinement of all atoms. Thus, the final refinement was carried out by using anisotropic displacement parameters for the Pt, P, S and F atoms and for the CO groups. All other atoms were treated isotropically. However, a Hamilton's test showed no significant differences between the full anisotropic refinement and the one used.[38] H atoms were included in the refinement in their calculated positions (C−H = 0.96 Å, $B(H) = 1.5 \times B(C_{bonded})$ [Å^2]) by using a riding model.

Structural study of compound 8: The space group was determined at 120 K, whereas the cell constants were refined by least squares, at the end of the data collection, by using 9693 reflections ($2\theta_{max} \leq 56.8°$). The data were collected by using ω scans, in steps of 0.3°. For each of the 1860 collected frames, the counting time was 30 s.

The compound crystallises as an inversion twin[39] and thus data were refined by using the TWIN option in SHELX (BASF = 0.43(1)). The least-squares refinement was carried out by using anisotropic displacement parameters for all non-hydrogen atoms.

The compound crystallises as an inversion twin[39] and thus data were refined by using the TWIN option in SHELX (BASF = 0.43(1)). The least-squares refinement was carried out by using anisotropic displacement parameters for all non-hydrogen atoms.

Due to the space group symmetry, the asymmetric unit is 1/4 of the molecule and is composed by two Pt atoms (one with 0.5 occupancy), one bridging phosphido group, a CO ligand and the diethyl ether fragment leading to partial occupancy of the atoms of the bridging ligand, disordered over −4 symmetry related positions.

The contribution of the hydrogen atoms, in their calculated positions, (C−H = 0.96 Å, $B(H) = 1.5 \times B(C_{bonded})$ [Å^2]), was included in the refinement by using a riding model.

CCDC-771575 and 771576 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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