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Reactions of the complexes $Pt_3(\mu\text{-}CO)_3L_3$ with SO_2. Crystal structure of $Pt_3(\mu\text{-}CO)_3(P^tBu_2Ph)_3 \cdot 0.25(C_4H_8O)$

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Abstract

Reactions of the complexes $Pt_3(\mu\text{-}CO)_3L_3$, where $L = P^tBu_3$ (**1a**), $P^tBu_2{}^cPr$ (**1b**), P^tBu_2Ph (**1c**), PCy_3 (**1d**) and PCy_2Ph (**1e**), with SO_2 have been examined. The complexes **1** may be divided into two classes: those complexes (**1a**, **1b** and **1c**) which fragment to yield a dimer $Pt_2(\mu\text{-}SO_2)(CO)_2L_2$, where $L = P^tBu_3$ (**2a**), $P^tBu_2{}^cPr$ (**2b**), P^tBu_2Ph (**2c**), upon brief exposure to SO_2 and those complexes (**1d** and **1e**) which substitute CO ligands with SO_2 ligands without a change in nuclearity to yield $Pt_3(\mu\text{-}SO_2)_3L_3$, where $L = PCy_3$ (**3d**) and PCy_2Ph (**3e**). Traces of the complexes $Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2L_3$ (**4**) were observed after heating the complexes **2** under an SO_2 atmosphere for 14 h. As formation of dimeric products appeared to be favoured by larger ligands L, a method of evaluating the non-bonding interactions between the ligands L and the cluster fragment $Pt_3(\mu\text{-}CO)_3$ was used to evaluate the size to the phosphine ligands. The X-ray crystal structure of the complex $Pt_3(\mu\text{-}CO)_3(P^tBu_2Ph)_3$ (**1c**) is reported.

Introduction

The triangular platinum cluster $Pt_3(\mu\text{-}CO)_3(P^tBu_2Ph)_3$ (**1c**) shows markedly different reactivity patterns from that of the PCy_3 analogue $Pt_3(\mu\text{-}CO)_3(PCy_3)_3$ (**1d**). For example, **1c** reacts with SO_2 yielding a dimeric product $Pt_2(\mu\text{-}SO_2)(CO)_2(P^tBu_2Ph)_2$ (**2c**) [1] while **1d**, using identical conditions, undergoes CO substitution to give the trimeric product $Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3$ (**3d**) [2]. The different reactivity patterns of the clusters **1c** and **1d** do not correlate with any of the standard electronic parameters associated with the phosphine ligands [3, 4] and we propose that the observed differences predominately arise from the different steric demands of the phosphine ligands.

Steric effects are often correlated with Tolman's cone angle, an easily computed value defined as a conical angle approximating the size of the ligand [5]. This description of steric demand has received considerable attention and it usually agrees well with experimental results. The Tolman's cone angle for both PCy_3 and P^tBu_2Ph ligands is 170° and thus the method appears to lack the sensitivity to distinguish between the two phosphine ligands in the complexes **1c** and **1d**. The principle inaccuracy in Tolman's cone angle concept as a measure of ligand size is the failure to address variations due to ligand compression, unsymmetrical phosphine ligands, conformational isomerism or the meshing of ligands. The cone angle concept fails whenever either the gross symmetry of the phosphine or that of the metal site greatly differs from a cone shape. Attempts have been made to take these effects into account and some authors have exploited X-ray structural data to obtain ligand profiles [6]. An alternative approach to this problem is to undertake systematic model building, evaluate the non-bonding interactions between the ligand and the coordination site for each of the models and assume that the minimum non-bonding interaction is representative of the ligand size. This is a semi-quantitative attempt at representing the intuitive notions of steric hindrance. The classical mechanics view of chemistry has received attention in the organic chemistry literature [7]. Organometallic chemists have shown much less enthusiasm for molecular mechanics because of the diversity of bonding situations available in metal complexes [8].

The present work applies conformational analysis to the study of structure in the complexes $Pt_3(\mu\text{-}CO)_3L_3$, where $L = P^tBu_3$ (**1a**), $P^tBu_2{}^cPr$ (**1b**), P^tBu_2Ph (**1c**), PCy_3 (**1d**) and PCy_2Ph (**1e**), in which steric effects appear to dominate. As both the PCy_3 and

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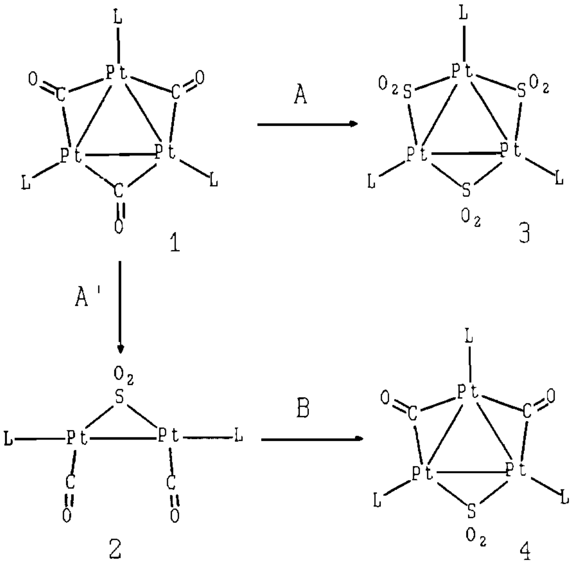
P^tBu_2Ph ligands have a Tolman's cone angle of 170°, we computed the 'steric energy' associated with docking these phosphine ligands into a cluster site. The results are used to rationalize the reactivity of the series of clusters $Pt_3(\mu\text{-}CO)_3L_3$ with SO_2.

Results and discussion

Reactions of the clusters $Pt_3(\mu\text{-}CO)_3L_3$ with SO_2

Two experimental procedures were used in the investigation of the reactivity of the trimeric complexes **1** with SO_2. As depicted in Scheme 1, the complexes **1** may substitute the three bridging CO ligands for SO_2 ligands (A) or the complexes may fragment to give to dimeric platinum species **2** upon addition of SO_2 (A'). Furthermore, if a cluster **1** fragments, the extent to which the dimer **2** aggregates to form the trimer $Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2L_3$, (**4**), containing one bridging sulfur dioxide ligand, was examined. The complex **1c** reacted to give approximately 15% of **4c** while tracers of a compound which is tentatively assigned as **4b** were observed in the baseline of the ^{31}P NMR spectrum from the extended reaction of **1b** and SO_2. The results of the reactions, together with information about the size and the basicity of the phosphine ligands, are presented in Table 1. All complexes were unambiguously characterized by ^{31}P NMR spectroscopy and these results are given in 'Experimental'.

The basicity of the phosphine ligands may be ranked using the $\nu(A_1)$ stretch of $Ni(CO)_3L$ (L = phosphine ligand) [3], presented in Table 1. The trimers **1d** and **1e** substitute their CO ligands for SO_2 while **1b** and **1c** fragment to produce **2**, however the phosphine ligands, ranked from most basic to least basic using the method proposed by Tolman [3], follow the order **a** > **d** > **b** > **e** ≈ **c**. The ordering of the ligands presented in Table 1, based upon the degree of formation trimeric products, does correlate with the strong-central ν(CO) stretching frequency associated with the bridging CO ligands of the complexes **1**.



Scheme 1. A': reaction of **1** with SO_2 at 23 °C for 10 min for L = **a**, **b** or **c**. A: reaction of **1** with SO_2 at 23 °C for 10 min for L = **d** or **e**. B: reaction of **2** with SO_2 at 53 °C for 14 h.

A rough relationship exists between the size of a phosphine ligand, as measured by the Tolman cone angle, and the reactivity of the trimeric complexes **1** with SO_2 under gentle conditions. The trimeric complexes **1** possessing smaller phosphine ligands react with SO_2 to replace the CO ligands without a change in nuclearity. The trimeric complexes **1** with larger phosphine ligands form the dimeric complexes, **2**. This observation suggests that the PCy_3 ligand is smaller than the P^tBu_2Ph ligand, although both ligands are assigned a Tolman's cone angle of 170°. In addition, the amount of $Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2L_3$ (**4**), formed during the extended reaction of the carbonyl trimer **1** with SO_2 suggests that the phosphine ligand $P^tBu_2{}^cPr$ is slightly larger than the size estimated by Tolman's method. These observations led us to attempt to define a ligand's size using computer generated models to evaluate non-bonded interactions between the phosphine ligands and the cluster fragment.

Calculation of phosphine conformations and steric energy

Model building has been used historically to understand sterically driven reactions. Models are still popular as a tool of thought as they are conceptually and technically easy to work with. While ultimately the full molecular mechanics approach is preferred, the parameters involving metal atoms are often unknown or unreliable, and this complication of the heavier elements introduces a large number of variables into the problem. A simple approach to find the most stable conformation is to systematically scan conformational space while calculating the energy of the non-bonding interactions.

Idealized structures of the complexes $Pt_3(\mu\text{-}CO)_3L_3$ were constructed using bond lengths and angles obtained by averaging typical parameters for related compounds from the Cambridge Crystallographic Database [9]. See 'Supplementary material'. We assume that the platinum trimeric complexes **1** are totally planar for simplicity. The complexes will distort from planarity when bulky phosphine ligands are used, however, we lack the force constants to predict

TABLE 1. Size and basicity parameters for the phosphine ligands L and the results of the reactions of the complexes $Pt_3(CO)_3L_3$ (**1**) with SO_2

L	θ[a] (°)	E[b] (kcal/mol)	$\nu(A_1)$[c] (cm^{-1})	$\nu(CO)$[d] (cm^{-1})	Procedure A[e]	Procedure B[f] (%)
P^tBu_3 (**a**)	184	>100	2056	1789(m), 1738(s), 1732(m)	**2**	**2**
$P^tBu_2{}^cPr$ (**b**)	167	65	2060	1752(m), 1744(s)	**2**	**2**+**4**(traces)
P^tBu_2Ph (**c**)	170	54	2062	1826(m), 1767(s), 1762(m)	**2**	**2**(85)+**4**(15)
PCy_3 (**d**)	170	29	2058	1767(s)	**3**	**3**
PCy_2Ph (**e**)	162	<1	2062	1777(s)	**3**	**3**

[a] Tolman cone angle from ref. 5. [b] Relative 'steric' energy of the minimum energy conformer as measured by the van der Waals forces option of CHEM-X. [c] From the IR spectra of the phosphine complexes $[Ni(CO)_3L]$ in toluene. [d] From the IR spectra of the complexes $[Pt_3(CO)_3L_3]$ as nujol mulls on KBr plates. [e] SO_2 bubbled through a solution of **1** at 23 °C for 10 min. [f] SO_2 bubbled through a solution of **1** at 53 °C for 14 h.

these distortions. We assert that the steric trends will be preserved in the planar case. It is also assumed that the phosphine ligands only interact with carbonyl ligands and not with other phosphine ligands. This is reasonable as the closest intramolecular H...H distance in the models is 2.7 Å, which is well into the weakly attractive tail of the Morse potential.

All of conformational space was sampled by rotating systematically about the Pt–P and P–C vectors and about each C–C vector (associated with a σ-bond) over 360° in 10° increments. The energy, E_{vdw}, of each structure was computed using the Buckingham equation and the minimum energy structure was located using the program CHEM-X [10]. As the deformations in bond length and angle are not accounted for, the compressibility of the ligand is not treated. The energy obtained in the absence of such considerations is thus an upper bound of the steric energy. If the model was refined to include such distortions, they would be in the form of steric relief, lowering the steric energy of the structure. For the problems we have selected, the range of compounds is small and we expect a similar amount of strain in each case. We would not expect a qualitative change in the ordering of the conformational energy if strain were to be included.

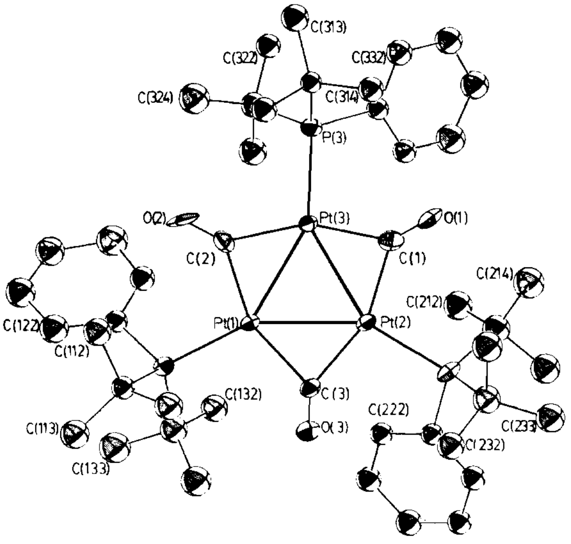
The steric energy was computed by summing E_{vdw} for cluster–ligand atom pairs using the minimum energy structure, and the values are reported in Table 1. Relative energies are reported as the absolute energies are dependent on the parameters. This sum is intended to reflect the steric interaction of the ligand with the metal site. For each site in the trimeric clusters **1**, the $P^tBu_2{}^cPr$ ligand (**b**) calculated to be 11 kcal larger than P^tBu_2Ph (**c**) and **c** is calculated to have 25 kcal more steric energy than the ligand PCy_3 (**d**). In agreement with Tolman's cone angles, P^tBu_3 (**a**) is calculated to be very much larger than **c** and PCy_2Ph (**e**) is much smaller than **d**. These results suggest the size of the phosphine ligands in **1** follow the order $P^tBu_3 \gg P^tBu_2{}^cPr > P^tBu_2Ph > PCy_3 \gg PCy_2Ph$. This ordering of phosphine ligands is consistent with that presented in Table 1 based upon the degree of formation of trimeric products.

In each of the complexes **1** there is one phosphine ligand conformation which is much more stable than all of the other possibilities. As this result suggests that only one phosphine conformer should exist, the X-ray crystal structure determination of **1c** was undertaken to allow a comparison of the observed solid state structure with that obtained by conformational analysis.

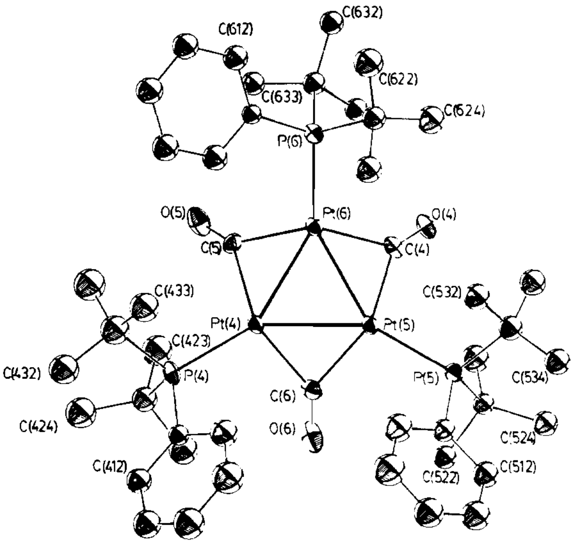
X-ray crystal structure of $Pt_3(\mu\text{-}CO)_3(P^tBu_2Ph)_3$ (1c)

The complex **1c** crystallizes in the space group [11] $P\bar{1}$ with four molecules in the unit cell. A perspective view of the two molecules together with the atom numbering scheme is given in Fig. 1 and selected intramolecular distances and angles are presented in Table 2.

The asymmetric unit contains the molecule **1c** in two distinct conformations, together with a disordered tetrahydrofuran solvent molecule. Each molecule of **1c** contains a triangular core of three Pt atoms. The angle between the Pt_3 planes, in the two different molecules, is 95.0°. The Pt–Pt distances span a range of 2.671(1) to 2.684(1) Å (9σ), which may simply reflect an underestimation of the errors or may be due to packing forces. The average Pt–Pt distance of 2.677(1) Å is typical of Pt(0) complexes [12–14]. The three carbonyl ligands lie above the plane defined by the three Pt atoms in molecule **I**, with an average dihedral angle of about 7° between the Pt_3 plane and the CO vectors. In molecule **II**, two carbonyl ligands are bent out of the plane by about 7° while one (C(3)–O(3)) is coplanar with the Pt_3 triangle. In contrast, the $Pt_3(CO)_3$ unit in $Pt_3(CO)_3(PCy_3)_3$,



I



II

Fig. 1. ORTEP diagrams of the two independent molecules of **1c** with hydrogen atoms omitted. The thermal ellipsoids are represented by 30% probability contours.

TABLE 2. Selected intramolecular bond distances (Å) and angles (°)

Molecule **I**		Molecule **II**	
Pt(2)–Pt(1)	2.673(1)	Pt(5)–Pt(4)	2.683(1)
Pt(3)–Pt(1)	2.671(1)	Pt(6)–Pt(4)	2.684(1)
P(1)–Pt(1)	2.293(5)	P(4)–Pt(4)	2.295(4)
C(2)–Pt(1)	2.027(19)	C(4)–Pt(4)	2.045(18)
C(3)–Pt(1)	2.099(16)	C(6)–Pt(4)	2.031(18)
Pt(3)–Pt(2)	2.677(1)	Pt(6)–Pt(5)	2.673(1)
P(2)–Pt(2)	2.302(5)	P(5)–Pt(5)	2.298(5)
C(1)–Pt(2)	2.032(18)	C(5)–Pt(5)	2.018(17)
C(3)–Pt(2)	2.033(18)	C(6)–Pt(5)	2.044(16)
P(3)–Pt(3)	2.292(5)	P(6)–Pt(6)	2.302(4)
C(1)–Pt(3)	1.997(20)	C(4)–Pt(6)	2.021(17)
C(2)–Pt(3)	2.019(19)	C(5)–Pt(6)	2.026(17)
C(1)–O(1)	1.160(25)	C(4)–O(4)	1.166(23)
C(2)–O(2)	1.199(23)	C(5)–O(5)	1.181(20)
C(3)–O(3)	1.134(22)	C(6)–O(6)	1.170(21)
Pt(3)–Pt(1)–Pt(2)	60.1(0)	Pt(6)–Pt(4)–Pt(5)	59.7(0)
P(1)–Pt(1)–Pt(2)	150.6(1)	P(4)–Pt(4)–Pt(5)	148.7(1)
P(1)–Pt(1)–Pt(3)	144.9(1)	P(4)–Pt(4)–Pt(6)	150.2(1)
C(2)–Pt(1)–Pt(2)	107.5(5)	C(4)–Pt(4)–Pt(5)	106.1(5)
C(2)–Pt(1)–Pt(3)	48.6(5)	C(4)–Pt(4)–Pt(6)	48.3(5)
C(2)–Pt(1)–P(1)	101.1(5)	C(4)–Pt(4)–P(4)	105.2(5)
C(3)–Pt(1)–Pt(2)	48.6(5)	C(6)–Pt(4)–Pt(5)	49.0(5)
C(3)–Pt(1)–Pt(3)	107.4(5)	C(6)–Pt(4)–Pt(6)	108.6(5)
C(3)–Pt(1)–P(1)	107.2(5)	C(6)–Pt(4)–P(4)	100.8(5)
C(3)–Pt(1)–C(2)	147.3(7)	C(6)–Pt(4)–C(4)	150.0(7)
Pt(3)–Pt(2)–Pt(1)	59.9(0)	Pt(6)–Pt(5)–Pt(4)	60.1(0)
P(2)–Pt(2)–Pt(1)	146.1(1)	P(5)–Pt(5)–Pt(4)	149.5(1)
P(2)–Pt(2)–Pt(3)	149.0(1)	P(5)–Pt(5)–Pt(6)	147.4(1)
C(1)–Pt(2)–Pt(1)	106.4(6)	C(5)–Pt(5)–Pt(4)	105.7(5)
C(1)–Pt(2)–Pt(3)	47.8(6)	C(5)–Pt(5)–Pt(6)	48.8(5)
C(1)–Pt(2)–P(2)	106.7(6)	C(5)–Pt(5)–P(5)	104.8(5)
C(3)–Pt(2)–Pt(1)	50.8(5)	C(6)–Pt(5)–Pt(4)	48.6(5)
C(3)–Pt(2)–Pt(3)	109.3(4)	C(6)–Pt(5)–Pt(6)	108.6(5)
C(3)–Pt(2)–P(2)	100.9(5)	C(6)–Pt(5)–P(5)	102.9(5)
C(3)–Pt(2)–C(1)	147.7(7)	C(6)–Pt(5)–C(5)	147.6(7)
Pt(2)–Pt(3)–Pt(1)	60.0(0)	Pt(5)–Pt(6)–Pt(4)	60.1(0)
P(3)–Pt(3)–Pt(1)	150.1(1)	P(6)–Pt(6)–Pt(4)	45.7(1)
P(3)–Pt(3)–Pt(2)	145.3(1)	P(6)–Pt(6)–Pt(5)	146.7(1)
C(1)–Pt(3)–Pt(1)	107.6(5)	C(4)–Pt(6)–Pt(4)	49.1(5)
C(1)–Pt(3)–Pt(2)	48.9(5)	C(4)–Pt(6)–Pt(5)	107.2(5)
C(1)–Pt(3)–P(3)	101.5(5)	C(4)–Pt(6)–P(6)	104.9(5)
C(2)–Pt(3)–Pt(1)	48.8(5)	C(5)–Pt(6)–Pt(4)	105.4(5)
C(2)–Pt(3)–Pt(2)	107.6(5)	C(5)–Pt(6)–Pt(5)	48.5(5)
C(2)–Pt(3)–P(3)	106.5(5)	C(5)–Pt(6)–P(6)	108.1(5)
C(2)–Pt(3)–C(1)	147.6(7)	C(5)–Pt(6)–C(4)	139.6(7)
Pt(3)–C(1)–Pt(2)	83.3(8)	Pt(6)–C(4)–Pt(4)	82.6(7)
O(1)–C(1)–Pt(2)	136.7(15)	O(4)–C(4)–Pt(4)	137.4(14)
O(1)–C(1)–Pt(3)	137.9(15)	O(4)–C(4)–Pt(6)	134.0(13)
Pt(3)–C(2)–Pt(1)	82.6(7)	Pt(6)–C(5)–Pt(5)	82.7(6)
O(2)–C(2)–Pt(1)	136.0(14)	O(5)–C(5)–Pt(5)	138.5(14)
O(2)–C(2)–Pt(3)	138.5(14)	O(5)–C(5)–Pt(6)	133.4(14)
Pt(2)–C(3)–Pt(1)	80.6(6)	Pt(5)–C(6)–Pt(4)	82.3(6)
O(3)–C(3)–Pt(1)	134.7(14)	O(6)–C(6)–Pt(4)	138.9(14)
O(3)–C(3)–Pt(2)	142.2(15)	O(6)–C(6)–Pt(5)	137.2(14)

1d is essentially planar [14], reflecting the reduced steric demand of the $\mathrm{PCy_3}$ ligands as compared with the $\mathrm{P^tBu_2Ph}$ ligand. The C–O bond lengths are normal at 1.17(2) Å and the average Pt–C distance of 2.03(2) Å ($\sigma = 1.2$) are typical of the compounds cited above.

A $\mathrm{P^tBu_2Ph}$ ligand is attached to each Pt atom and all parameters associated with the $\mathrm{P^tBu_2Ph}$ ligands are normal [1]. The Pt–P bond lengths span a range of 1.0 σ, the average being 2.297(1) Å. In molecule **I**, the conformations of the $\mathrm{P^tBu_2Ph}$ ligands are remarkably similar: each phenyl ring points in the same direction around the metal core so that the molecule has a pseudo three-fold rotation axis. In each phosphine ligand, the phenyl group is just below the $\mathrm{Pt_3}$ plane, one t-butyl group is axial, and the other group is pseudo equatorial under the CO ligand, forcing the CO ligand out of the metal plane

TABLE 3. Calculated and observed C(carbonyl)–Pt–P–C(α) torsion angles (°) for **1c**

P atom	C(phenyl)	C(axial)	C(equatorial)
Calculated	−165	75	−45
P(1)	−157.2	81.7	−46.3
P(2)	−155.2	85.1	−44.2
P(3)	−159.5	81.0	−47.2
P(4)	−155.2	84.8	−41.7
P(5)	155.5	−84.9	40.6
P(6)	−164.8	76.4	−49.5

as described above. In molecule **II**, the pseudo three-fold symmetry is broken as the phosphine ligand containing P(5) has been inverted. Thus two phenyl rings bracket one CO ligand equally and thus the CO ligand containing C(3) is not bent out of the metal plane as mentioned above.

The agreement between the computed minimum conformation of the P^{t}Bu$_2$Ph ligand in the Pt$_3$(CO)$_3$ site and the six phosphine ligands observed in the structure of **1c** is remarkable, despite the simplification of planarity of the Pt$_3$(CO)$_3$ moiety. This is consistent with our calculations which indicate that the one conformation of the phosphine ligands is much lower in energy than all others and suggests that intramolecular forces overwhelming dominate. The agreement between calculated and observed conformations is reflected in the C(carbonyl)–Pt–P–C(α-carbon) torsion angles presented in Table 3. The opposite signs for the penultimate entry in Table 3 results from the inverted configuration of the phosphine ligand containing P(5).

Conclusions

The X-ray crystal structure of the complex Pt$_3$(μ-CO)$_3$(P^{t}Bu$_2$Ph)$_3$ (**1c**) reveals phosphine ligand conformations which are in agreement with the calculated geometry using the conformational analysis algorithm of CHEM-X. The calculated minimum energy conformations of five complexes Pt$_3$(μ-CO)$_3$L$_3$ (**1**) were used in evaluating the non-bonding interactions between the ligands L and the cluster fragment Pt$_3$(μ-CO)$_3$. This data gave an ordering of the size of the phosphine ligands from largest to smallest as P^{t}Bu$_3$ $\gg$ P^{t}Bu$_2{}^c$Pr > P^{t}Bu$_2$Ph > PCy$_3$ $\gg$ PCy$_2$Ph. Estimation of ligand size by conformational energy data may be valid, although further examples of calculated and observed conformations are necessary in order to draw general conclusions. Reactions of the complexes Pt$_3$(μ-CO)$_3$L$_3$ (**1**), with SO$_2$ yields dimeric complexes Pt$_2$(μ-SO$_2$)(CO)$_2$L$_2$ when L is P^{t}Bu$_2$Ph or larger (P^{t}Bu$_3$ (**2a**), P^{t}Bu$_2{}^c$Pr (**2b**), P^{t}Bu$_2$Ph (**2c**)) and trimeric complexes Pt$_3$(μ-SO$_2$)$_3$L$_3$ for the smaller ligands (PCy$_3$ (**3d**), PCy$_2$Ph (**3e**)).

Experimental

The ^{31}P NMR spectra were collected on a Varian XL-200 nuclear magnetic resonance spectrometer operating at 80.98 MHz. The ^{31}P chemical shifts were referenced to P(OMe)$_3$ and are reported referenced to 85% H$_3$PO$_4$. IR spectra were recorded on a Nicolet 5DX FT infrared spectrophotometer using a nujol mull on NaCl plates. Calculations were performed on a Microvax II computer using the CHEM-X suite of software. Parameters for the calculation of the van der Waals energies were used as supplied by CHEM-X [10].

K$_2$PtCl$_4$ was supplied by Digital Specialities Chemicals. Deuterated solvents were purchased from Aldrich Chemical Company and Caledon Industries provided all other solvents. Reagents were bought from Aldrich Chemical Company. Reagent gases were obtained from either Canox or Matheson. P^{t}Bu$_2$Ph [15], P^{t}Bu$_2{}^c$Pr [16], and Pt$_3$(μ-CO)$_3$L$_3$ [12, 17] were prepared by literature methods.

Conformational calculations

Conformational isomers were generated by rotating around single bonds, using the CALCULATE CONFORMATIONS facility of CHEM-X [10].

Crystal data for Pt$_3$(μ$_2$-CO)$_3$(P^{t}Bu$_2$Ph)$_3$·0.25(C$_4$H$_8$O)

C$_{46}$H$_{74}$O$_{3.25}$P$_3$Pt$_3$, M = 1357.3, triclinic, a = 16.096(2), b = 22.376(3), c = 13.700(2) Å, α = 91.03(1)°, β = 92.32(1)°, γ = 89.38(1)°, U = 4777.4 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.71069 Å), space group [11] $P\bar{1}$, Z = 4, D_c = 1.89 g cm^{-3}; red plates, crystal dimensions 0.003 × 0.012 × 0.027 cm; crystal faces {100}, {1-10}, {110}, {001}; μ(Mo Kα) = 87.13 cm^{-1}.

Data collection and processing

All calculations were performed using the Enraf-Nonius structure determination package run on a DEC PDP-11/23 computer [18]. Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo Kα radiation. $\theta/2\theta$ mode with scan width 0.80 + 0.35 tan θ, scan speed 0.5–10.0° min^{-1}. A total of 18 001 reflections was measured ($1 < 2\theta < 50°$, $\pm h$, $\pm k$, $+l$). Gaussian absorption correction with a 4 × 6 × 14 grid (transmission coefficients varied from 0.89 to 1.04); no decomposition observed; the recorded intensities were corrected for Lorentz and polarization effects. A total of 8995 unique data with $I > 3\sigma(I)$ was used.

TABLE 4. Positional parameters for the non-H atoms[a]

Atom	x	y	z	U_{iso}
Pt(1)	0.16051(4)	0.32526(3)	0.64388(5)	0.0329(4)
Pt(2)	0.26364(5)	0.37573(3)	0.52209(5)	0.0350(4)
Pt(3)	0.24248(5)	0.42410(3)	0.69961(5)	0.0342(4)
P(1)	0.0473(3)	0.2674(2)	0.6706(3)	0.041(3)
P(2)	0.2971(3)	0.3876(2)	0.3619(3)	0.046(3)
P(3)	0.2525(3)	0.5096(2)	0.7940(3)	0.043(3)
O(1)	0.394(1)	0.4592(6)	0.6008(8)	0.06(1)
O(2)	0.175(1)	0.3499(6)	0.8603(9)	0.07(1)
O(3)	0.2205(9)	0.2470(6)	0.4800(9)	0.06(1)
C(1)	0.329(1)	0.4378(8)	0.602(1)	0.05(1)
C(2)	0.180(1)	0.3648(8)	0.777(1)	0.05(1)
C(3)	0.213(1)	0.2929(8)	0.515(1)	0.04(1)
C(111)	0.079(1)	0.1941(8)	0.732(1)	0.050(5)
C(112)	0.101(1)	0.210(1)	0.840(2)	0.071(6)
C(113)	0.013(2)	0.143(1)	0.723(2)	0.078(7)
C(114)	0.160(1)	0.175(1)	0.689(2)	0.073(6)
C(121)	−0.027(1)	0.3050(8)	0.747(1)	0.047(5)
C(122)	−0.088(2)	0.274(1)	0.802(2)	0.077(7)
C(123)	−0.148(2)	0.310(1)	0.855(2)	0.082(7)
C(124)	−0.143(2)	0.371(1)	0.853(2)	0.077(7)
C(125)	−0.086(2)	0.407(1)	0.799(2)	0.090(7)
C(126)	−0.026(1)	0.3671(9)	0.749(1)	0.057(5)
C(131)	−0.022(1)	0.256(1)	0.553(2)	0.069(6)
C(132)	−0.029(1)	0.316(1)	0.506(2)	0.068(6)
C(133)	−0.110(2)	0.232(1)	0.576(2)	0.088(8)
C(134)	0.024(2)	0.204(1)	0.493(2)	0.084(7)
C(211)	0.297(1)	0.471(1)	0.330(2)	0.073(6)
C(212)	0.219(2)	0.498(1)	0.368(2)	0.078(7)
C(213)	0.297(2)	0.479(1)	0.212(2)	0.082(7)
C(214)	0.379(2)	0.499(1)	0.371(2)	0.091(8)
C(221)	0.213(1)	0.3600(8)	0.277(1)	0.046(5)
C(222)	0.134(1)	0.3569(8)	0.312(1)	0.049(5)
C(223)	0.067(1)	0.3397(9)	0.247(1)	0.059(5)
C(224)	0.080(1)	0.3302(9)	0.148(2)	0.0363(6)
C(225)	0.158(1)	0.3346(9)	0.114(1)	0.055(5)
C(226)	0.227(1)	0.3506(9)	0.176(1)	0.057(5)
C(231)	0.396(1)	0.345(1)	0.332(2)	0.072(6)
C(232)	0.375(1)	0.281(1)	0.329(2)	0.070(6)
C(233)	0.437(2)	0.364(1)	0.236(2)	0.081(7)
C(234)	0.462(2)	0.358(1)	0.421(2)	0.086(7)
C(311)	0.340(1)	0.5036(7)	0.889(1)	0.042(4)
C(312)	0.335(1)	0.4386(9)	0.933(1)	0.058(5)
C(313)	0.338(1)	0.549(1)	0.978(2)	0.071(6)
C(314)	0.423(1)	0.5076(9)	0.836(1)	0.059(6)
C(321)	0.149(1)	0.5326(9)	0.847(1)	0.060(6)
C(322)	0.149(1)	0.5999(8)	0.882(1)	0.054(5)
C(323)	0.083(1)	0.525(1)	0.764(2)	0.072(6)
C(324)	0.130(2)	0.494(1)	0.936(2)	0.087(8)
C(331)	0.273(1)	0.5756(8)	0.720(1)	0.046(5)
C(332)	0.309(1)	0.6275(9)	0.763(1)	0.062(6)
C(333)	0.315(1)	0.681(1)	0.701(2)	0.070(6)
C(334)	0.293(1)	0.676(1)	0.603(2)	0.074(7)
C(335)	0.254(2)	0.625(1)	0.565(2)	0.081(7)
C(336)	0.250(1)	0.5745(8)	0.622(1)	0.053(5)
Pt(4)	0.76127(4)	0.12462(3)	0.94959(4)	0.0334(4)
Pt(5)	0.65574(4)	0.17346(3)	0.81622(5)	0.0322(4)
Pt(6)	0.74818(4)	0.07840(3)	0.76756(5)	0.0321(4)
P(4)	0.8060(3)	0.1170(2)	1.1101(3)	0.046(3)
P(5)	0.5409(3)	0.2321(2)	0.7803(3)	0.036(3)
P(6)	0.7580(3)	−0.0068(2)	0.6719(3)	0.037(3)
O(4)	0.9090(9)	0.0577(6)	0.8735(9)	0.062(9)
O(5)	0.7059(8)	0.1623(6)	0.6077(8)	0.06(1)
O(6)	0.6808(9)	0.2417(6)	1.006(1)	0.07(1)
C(4)	0.838(1)	0.0692(8)	0.874(1)	0.04(1)
C(5)	0.693(1)	0.1432(8)	0.685(1)	0.04(1)
C(6)	0.688(1)	0.1992(7)	0.956(1)	0.05(1)
C(411)	0.724(1)	0.1353(7)	1.197(1)	0.041(4)
C(412)	0.743(1)	0.1524(9)	1.297(1)	0.058(5)
C(413)	0.674(2)	0.161(1)	1.358(2)	0.073(6)
C(414)	0.596(2)	0.154(1)	1.326(2)	0.093(8)
C(415)	0.577(2)	0.136(1)	1.227(2)	0.099(8)
C(416)	0.642(1)	0.128(1)	1.160(2)	0.072(6)
C(421)	0.895(1)	0.1701(9)	1.139(1)	0.059(6)
C(422)	0.855(2)	0.234(1)	1.145(2)	0.079(7)
C(423)	0.953(2)	0.170(1)	1.045(2)	0.087(8)
C(424)	0.952(2)	0.155(1)	1.228(2)	0.091(8)
C(431)	0.833(2)	0.036(1)	1.147(2)	0.079(7)
C(432)	0.842(2)	0.030(1)	1.262(2)	0.083(7)
C(433)	0.760(2)	−0.001(1)	1.111(2)	0.082(7)
C(434)	0.916(2)	0.018(1)	1.105(2)	0.095(8)
C(511)	0.472(1)	0.2376(8)	0.885(1)	0.050(5)
C(512)	0.408(1)	0.2824(9)	0.891(2)	0.065(6)
C(513)	0.354(2)	0.281(1)	0.971(2)	0.082(7)
C(514)	0.364(2)	0.238(1)	1.038(2)	0.086(7)
C(515)	0.422(2)	0.193(1)	1.032(2)	0.099(9)
C(516)	0.477(2)	0.193(1)	0.953(2)	0.078(7)
C(521)	0.573(1)	0.3112(8)	0.750(1)	0.044(5)
C(522)	0.600(1)	0.3418(8)	0.851(1)	0.051(5)
C(523)	0.649(1)	0.304(1)	0.684(2)	0.071(6)
C(524)	0.506(1)	0.3505(9)	0.701(1)	0.060(6)
C(531)	0.468(1)	0.2007(9)	0.680(1)	0.057(5)
C(532)	0.461(1)	0.1330(9)	0.707(2)	0.067(6)
C(533)	0.510(1)	0.2035(9)	0.581(2)	0.066(6)
C(534)	0.380(1)	0.2264(9)	0.676(1)	0.064(6)
C(611)	0.780(1)	−0.0727(7)	0.742(1)	0.038(4)
C(612)	0.803(1)	−0.1303(9)	0.702(1)	0.059(5)
C(613)	0.823(1)	−0.1792(9)	0.762(2)	0.066(6)
C(614)	0.820(1)	−0.172(1)	0.864(2)	0.069(6)
C(615)	0.792(1)	−0.118(1)	0.907(2)	0.068(6)
C(616)	0.775(1)	−0.0700(9)	0.845(1)	0.061(6)
C(621)	0.655(1)	−0.0251(9)	0.607(1)	0.053(5)
C(622)	0.647(2)	−0.090(1)	0.566(2)	0.081(7)
C(623)	0.591(1)	−0.0196(9)	0.695(2)	0.068(6)
C(624)	0.635(1)	0.020(1)	0.527(2)	0.075(7)
C(631)	0.845(1)	−0.0030(8)	0.583(1)	0.050(5)
C(632)	0.840(1)	−0.0483(8)	0.497(1)	0.054(5)
C(633)	0.928(1)	−0.0124(8)	0.643(1)	0.054(5)
C(634)	0.844(1)	0.0630(8)	0.541(1)	0.050(5)
C(700)	0.430(3)	0.001(2)	0.035(4)	0.08(1)
C(701)	0.477(4)	0.967(2)	0.058(4)	0.09(2)
O(702)	0.559(5)	0.953(3)	0.021(5)	0.10(2)

[a] e.s.d.s in the least significant figure(s) are given in parentheses.

Structure analysis and refinement [18]

The positional coordinates for the Pt atoms were obtained from a three-dimensional Patterson synthesis. A series of difference Fourier syntheses and least-squares refinements revealed the positions of

TABLE 5. Chemical shifts (ppm) and couplings constants (Hz) from the ^{31}P NMR spectra of the complexes

Complex	$\delta(^{31}P)^a$	$^1J(Pt-P)$	$^2J(Pt-P)$	$^3J(Pt-P)$
1a	93.8	5226	378	39
1b	80.5	5210	389	42
1c	85.9	5059	434	50
1d	69.3	4411	429	58
1e	67.9	4650	464	59
2a	63.2	3884	303	75
2b	63.2	3999	300	72
2c	57.8	4025	343	73
3d	77.1	3802	320	48
3e	72.2	3937	354	50
4c	84.1(d)	4442	394	48
	104.2(t)	4972	475	48

^{a}Relative to 85% H_3PO_4.

the remaining 102 non-hydrogen atoms associated with the two cluster molecules and one molecule of tetrahydrofuran per unit cell disordered about a centre of inversion. After several cycles of full-matrix least-squares refinement on F the model converged at $R_1=\Sigma||F_c|-|F_o||/\Sigma|F_o||=0.0494$ and $R_2=(\Sigma w(|F_c|-|F_o|)^2/\Sigma wF_o^2)^{1/2}=0.0600$ where $w=4F_o^2/\sigma^2(F_o^2)$. (8995 observations and 568 variables, Pt, P, carbonyl C and O atoms refined with anisotropic thermal parameters and all remaining atoms refined isotropically.) In the final cycle no shift exceeded 0.01 of its standard deviation. A total difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 1.0 e^{-1} $Å^{-3}$, associated with the disordered solvent molecule at fractional coordinates (0.430, 0.002, 0.030). Final positional parameters for the non-H atoms are given in Table 4. See also 'Supplementary material'.

Reaction of $Pt_3(\mu\text{-}CO)_3L_3$ with SO_2

Procedure A

SO_2 was bubbled through a solution of $Pt_3(\mu\text{-}CO)_3L_3$ (for L = PCy_2Ph: 66 mg, 44 μmol; for L = PCy_3: 74 mg, 53 μmol; for L = P^tBu_2Ph: 74 mg, 55 μmol; for L = P^tBu_2Me: 84 mg, 73 μmol; for L = $P^tBu_2{}^cPr$: 74 mg, 60 μmol; for L = P^tBu_3: 40 mg, 31 μmol) in 2.50 ml of toluene under nitrogen for 10 min at room temperature and after a delay of 10 min, the ^{31}P NMR spectra were recorded. The ^{31}P NMR data were assigned by comparisons with spectra from authentic samples and the data are presented in Table 5.

Procedure B

SO_2 was bubbled through a solution of $Pt_3(\mu\text{-}CO)_3L_3$ in 2.5 ml of toluene at 53 ± 1 °C, for a total of 16 h. The solution was purged of SO_2 with a nitrogen stream for 15 min. The ^{31}P NMR spectra were collected.

Supplementary material

The least-squares planes, complete bond distances and angles for the P^tBu_2Ph ligands, anisotropic thermal parameters and structure amplitudes as well as the values used for ligand conformations are available from the authors on request.

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