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# Synthesis and $^{13}C$ NMR study of the *triangulo*-clusters $[Pt_3(\mu\text{-}CO)_{3-n}(\mu\text{-}SO_2)_n(PR_3)_3]$ ($n = 0–3$)

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## Abstract

$[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ was prepared in high yield by the reaction of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ with $H_2O_2$. The carbonyl ligands in $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ ($PR_3 = PPh_3$, $PPh_2Bz$, $PCy_3$, $P^iPr_3$) may be completely replaced by sulfur dioxide to give $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$ or partially by one $SO_2$ to give $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PR_3)_3]$ ($PR_3 = PCy_3$ and $P^iPr_3$). On the other hand, the addition of one molar equivalent of carbon monoxide to $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$ ($PR_3 = PCy_3$; $P^iPr_3$) gave the complexes $[Pt_3(\mu\text{-}CO)(\mu\text{-}SO_2)_2(PR_3)_3]$. Complete simulation of the $^{13}C$ NMR spectra could be achieved with the help of $^{195}Pt$ NMR data. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Platinum complexes; Cluster complexes; Carbonyl complexes; Sulfur dioxide complexes

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## 1. Introduction

A recurrent structural feature in cluster chemistry of transition metals of Group 10 and 11 with $d^{10}$-electron configuration is the trimetallic unit $M_3$ [1]. Since the pioneering work by Chatt and Chini [2], a large number of platinum *triangulo*-clusters of general formula $[Pt_3(\mu\text{–}X)_3L_3]$ have been reported. All have 42 valence electrons, tertiary phosphine as terminally bonded ligand L, and CO [2–11], $SO_2$ [11–17] or RCN [18,19] as bridging ligands X.

Till now these homonuclear platinum clusters have been studied by $^{31}P$ and $^{195}Pt$ NMR, besides IR spectroscopy and X-ray analysis. To further investigate the effect of σ-donor and π-acceptor properties of CO and $SO_2$ bridging ligands in this type of compounds, we now report their experimental and calculated $^{13}C$ NMR spectra.

We report also a simple and high yield synthesis of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$, a compound only scantily described previously [20,21].

## 2. Synthesis

The reaction of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ [2] with $H_2O_2$ at 45°C in acetone/dichloromethane solution results in the quantitative oxidation of one free $PPh_3$ [22] coming from the dissociative equilibrium

$$[Pt_3(\mu\text{-}CO)_3(PPh_3)_4] \rightleftarrows \underset{\mathbf{(1a)}}{[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]} + PPh_3$$

Such an equilibrium has been confirmed by $^{31}P$ NMR studies on analogous *triangulo* clusters of platinum [23]. Similarly, $[Pt_3(\mu\text{-}CO)_3(PPh_2Bz)_3]$ (**2a**) [2] may be easily obtained from the corresponding tetraphosphine derivative.

Initial attempts of $^{13}C$-enrichment of $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ ($PR_3 = PPh_3$ (**1a**), ($PPh_2Bz$ (**2a**), $P^iPr_3$ (**4a**)) by exchange reaction under 1 atm of $^{13}CO$ failed as the trimeric nuclearity was not preserved, giving instead tetranuclear and/or pentanuclear species $[Pt_4(\mu\text{-}CO)_5(PR_3)_4]$ and $[Pt_5(CO)(\mu\text{-}CO)_5(PR_3)_4]$. Chatt and Chini had encountered similar reactivity of CO on $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ [2]. The enriched clusters $[Pt_3(\mu\text{-}^{13}CO)_3(PR_3)_3]$ (**1a***, **2a*** and **4a***) may be obtained more expensively by the appropriate reported methods [2,10] using 99% $^{13}C$-enriched CO. Only the triplatinum clusters containing bulky phosphines, such as $PCy_3$, retain

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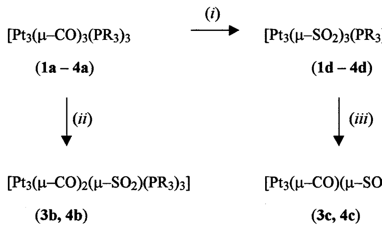


Scheme 1. (*i*) Excess of $SO_2$; (*ii*) 1 equiv. of $SO_2$; (*iii*) 1 equiv. of CO. Bold numbers **1**, **2**, **3**, **4** refer to $PR_3 = PPh_3$, $PPh_2Bz$, $PCy_3$, $P^iPr_3$, letters **a**, **b**, **c**, **d** refer to substitution degree of $SO_2$ ($n = 0$, 1, 2, 3), respectively.

their nuclearity in solution under CO. This allows $^{12}CO/^{13}CO$ exchange already after some minutes, and complete substitution giving $[Pt_3(\mu\text{-}^{13}CO)_3(PCy_3)_3]$ (**3a***) may be attained using a large excess of $^{13}CO$.

The reaction conditions to isolate the whole range of $CO/SO_2$ mixed derivatives $[Pt_3(\mu\text{-}CO)_{3-n}(\mu\text{-}SO_2)_n(PR_3)_3]$ ($n = 0$–3) are summarised in Scheme 1. Compounds **3a**–**3d** have already been reported in the literature [5,16].

## 3. Experimental

### 3.1. General remarks

All reactions were performed under pure dry dinitrogen. Benzene, toluene and diethyl ether were refluxed over sodium, treated with $LiAlH_4$ and distilled and stored over molecular sieves. All other solvents were of reagent grade purity and were used without further purification.

IR spectra were taken on a Perkin–Elmer 983 and a Perkin–Elmer FT–IR 2000 spectrometers, as Nujol mulls between CsI discs or solutions in $CaF_2$ cells.

$^{13}C$, $^{31}P\{H\}$ and $^{195}Pt\{H\}$ NMR spectra were recorded on Bruker 200, 360 and 400 MHz spectrometers. The reported values result from simulations (GNMR 4.0 program) of the experimental spectra taking into account the relative populations of all isotopomers. $\delta_C$ in ppm relative to TMS, $\delta_P$ relative to 85% $H_3PO_4$ (external), $\delta_{Pt}$ relative to $Na_2PtCl_6$ in $D_2O$. The $^{31}P$ and $^{195}Pt$ data reported below for **2a**–**4a** and **3d** in $CD_2Cl_2$ at 293 K are in fair to good agreement with those reported in the literature [5,16]. **2a**: $\delta_P$ 56.0; $\delta_{Pt}$ $-4447$ ppm; $^1J$(Pt–Pt) 1644; $^1J$(P–Pt) 4765; $^2J$(P–Pt) 484; $^3J$(P–P) 62 Hz. **3a**: $\delta_P$ 71.0; $\delta_{Pt}$ $-4421$ ppm; $^1J$(Pt–Pt) 1571; $^1J$(P–Pt) 4395; $^2J$(P–Pt) 415; $^3J$(P–P) 57 Hz. **4a**: $\delta_P$ 79.4; $\delta_{Pt}$ $-4435$ ppm; $^1J$(Pt–Pt) 1622; $^1J$(P–Pt) 4433; $^2J$(P–Pt) 418; $^3J$(P–P) 57 Hz. **3d**: $\delta_P$ 77.4; $\delta_{Pt}$ $-4024$ ppm; $^1J$(Pt–Pt) 722; $^1J$(P–Pt) 3754; $^2J$(P–Pt) 307; $^3J$(P–P) 48 Hz.

The starting compounds $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ and $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ were prepared according to the methods of Chatt and Chini [2] and Venanzi and co-workers [10], respectively.

### 3.2. Preparation of $[Pt_3(CO)_3(PPh_3)_3]$ (1a)

$[Pt_3(CO)_3(PPh_3)_4]$ (10.18 g, 5.92 mmol) was stirred in 200 ml of acetone and 100 ml of dichloromethane. 15 ml of $H_2O_2$ (37%) were added at 45°C. The red solution was stirred for 15 min at 45°C, then kept at 10°C and quickly evaporated under reduced pressure to a volume of ca. 130 ml, giving red microcrystals of **1a** which were filtered and recrystallized from dichloromethane/ethanol. Yield 7.32 g (85%). M.p. 185–190°C dec. *Anal.* Calc. for $C_{57}H_{45}O_3P_3Pt_3$: C, 47.02; H, 3.11. Found: C, 46.83; H, 3.08%. IR, $\nu$(CO): Nujol, 1842m, 1784vs $cm^{-1}$. $^{31}P$ and $^{195}Pt$ NMR ($CD_2Cl_2$, 243 K): $\delta_P$ 55.0; $\delta_{Pt}$ $-4525$ ppm; $^1J$(Pt–Pt) 1728; $^1J$(P–Pt) 4891; $^2J$(P–Pt) 468; $^3J$(P–P) 54 Hz.

### 3.3. Preparation of $[Pt_3(CO)_3(PPh_2Bz)_3]$ (2a)

$PtCl_2$(1,5-cyclooctadiene) (748 mg, 2 mmol) was suspended in an ethanol (95%, 60 ml) THF (40 ml) mixture and then treated with diphenylbenzylphosphine (1.1 g, 4.0 mmol). The resulting mixture was stirred for 3 h until the white $PtCl_2(PPh_2Bz)_2$ complex was formed.

Table 1
Infrared data[a] for $[Pt_3(\mu\text{-}^{12}CO)_n(\mu\text{-}SO_2)_{3-n}(PR_3)_3]$ and $[Pt_3(\mu\text{-}^{13}CO)_{3-n}(\mu\text{-}SO_2)_n(PR_3)_3]$[b]

| | | $\nu$(CO) ($cm^{-1}$) | $\nu$($SO_2$) ($cm^{-1}$) |
|---|---|---|---|
| **(1a)** | $[Pt_3(\mu\text{-}^{12}CO)_3(PPh_3)_3]$ | 1854w, 1793vs | – |
| **(1a*)** | $[Pt_3(\mu\text{-}^{13}CO)_3(PPh_3)_3]$ | 1812w, 1753vs | – |
| **(2a)** | $[Pt_3(\mu\text{-}^{12}CO)_3(PPh_2Bz)_3]$ | 1853vw, 1788vs | – |
| **(2a*)** | $[Pt_3(\mu\text{-}^{13}CO)_3(PPh_2Bz)_3]$ | 1810vw, 1747vs | – |
| **(3a)** | $[Pt_3(\mu\text{-}^{12}CO)_3(PCy_3)_3]$ | 1831w, 1763vs | – |
| **(3a*)** | $[Pt_3(\mu\text{-}^{13}CO)_3(PCy_3)_3]$ | 1789w, 1723vs | – |
| **(4a)** | $[Pt_3(\mu\text{-}^{12}CO)_3(P^iPr_3)_3]$ | 1834w, 1769vs | – |
| **(4a*)** | $[Pt_3(\mu\text{-}^{13}CO)_3(P^iPr_3)_3]$ | 1789w, 1729vs | – |
| **(3b)** | $[Pt_3(\mu\text{-}^{12}CO)_2(\mu\text{-}SO_2)(PCy_3)_3]$ | 1851s, 1791vs | 1213m, 1069s |
| **(3b*)** | $[Pt_3(\mu\text{-}^{13}CO)_2(\mu\text{-}SO_2)(PCy_3)_3]$ | 1805s, 1745vs | 1209m, 1070s |
| **(4b)** | $[Pt_3(\mu\text{-}^{12}CO)_2(\mu\text{-}SO_2)(P^iPr_3)_3]$ | 1854s, 1791vs | 1206m, 1061s |
| **(4b*)** | $[Pt_3(\mu\text{-}^{13}CO)_2(\mu\text{-}SO_2)(P^iPr_3)_3]$ | 1803m, 1752vs | 1207m, 1067s |
| **(3c)** | $[Pt_3(\mu\text{-}^{12}CO)(\mu\text{-}SO_2)_2(PCy_3)_3]$ | 1857vs | 1235m, 1089m, 1071s |
| **(3c*)** | $[Pt_3(\mu\text{-}^{13}CO)(\mu\text{-}SO_2)_2(PCy_3)_3]$ | 1816vs | 1235m, 1088m, 1070s |
| **(4c)** | $[Pt_3(\mu\text{-}^{12}CO)(\mu\text{-}SO_2)_2(P^iPr_3)_3]$ | 1861vs | 1224m, 1082m, 1069s |
| **(4c*)** | $[Pt_3(\mu\text{-}^{13}CO)(\mu\text{-}SO_2)_2(P^iPr_3)_3]$ | 1818vs | 1225m, 1079m, 1068s |
| **(1d)** | $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ | – | 1271s, 1258m, 1084vs |
| **(2d)** | $[Pt_3(\mu\text{-}SO_2)_3(PPh_2Bz)_3]$ | – | 1264s, 1088vs |
| **(3d)** | $[Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3]$ | – | 1242s, 1075vs |
| **(4d)** | $[Pt_3(\mu\text{-}SO_2)_3(P^iPr_3)_3]$ | – | 1245s, 1077vs |

[a] $\nu$(CO) in $CH_2Cl_2$; $\nu$($SO_2$) in Nujol.

[b] Asterisks indicate compounds with $^{13}CO$ content >98%.

Carbon monoxide was bubbled through the suspension. On addition of an excess of KOH (ca. 10 mmol) in $H_2O$ (20 ml), the mixture slowly turned red and absorbed carbon monoxide. After 2 h of stirring, the solvent was partially removed under reduced pressure and the red–brown solid was removed, washed with water and ethanol and then dried in vacuo. This solid, which appeared to be a mixture of **2a** and $[Pt_3(CO)_3(PPh_2Bz)_4]$ (IR spectrum), was dissolved in dichloromethane and filtered through a silica gel pad (30 cm) and eluted with diethyl ether. The red filtrate was evaporated to dryness in vacuo and the residue washed with methanol. Dichloromethane (20 ml) and acetone (40 ml) were added and the red solution was warmed at 40°C and treated with 1.5 ml of $H_2O_2$ (37%). The solution darkened and immediately was cooled at 0°C and quickly evaporated under reduced pressure to a volume of ca. 25 ml, giving red microcrystals of **2a** which were recrystallized from dichloromethane/methanol. Yield 0.95 g (63%). M.p. 193–198°C, dec. *Anal.* Calc. for $C_{60}H_{51}O_3P_3Pt_3$: C, 48.10; H, 3.43. Found: C, 48.32; H, 3.50%. IR, $\nu$(CO): Nujol, 1783s cm$^{-1}$.

### *3.4. Preparation of $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ (**1d**)*

$[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ (0.50 g, 0.343 mmol) was dissolved in benzene (120 ml, $N_2$ atm) and $SO_2$ was periodically bubbled through the solution as long as its IR spectrum showed the disappearance of any $\nu$(CO) absorption (ca. 24 h). The volume of the suspension was reduced in vacuo to 25 ml, hexane was added and the mixture was cooled at 0°C. The pale orange microcrystals were filtered off, washed with cold benzene, hexane and dried in vacuo. Yield 0.49 g (91%). *Anal.* Calc. for $C_{54}H_{45}O_6P_3Pt_3S_3$: C, 41.46; H, 2.90. Found: C, 41.04; H, 2.93%. $^{31}P$ and $^{195}Pt$ NMR ($CDCl_3$, 293 K): $\delta_P$ 62.4; $\delta_{Pt}$ $-4209$ ppm; $^1J$(Pt–Pt) 594; $^1J$(P–Pt) 4090; $^2J$(P–Pt) 429; $^3J$(P–P) 53 Hz.

### *3.5. Preparation of $[Pt_3(\mu\text{-}SO_2)_3(PPh_2Bz)_3]$ (**2d**)*

As for **1d** starting with $[Pt_3(\mu\text{-}CO)_3(PPh_2Bz)_3]$ (0.225 g, 0.15 mmol) in 60 ml of benzene and gaseous $SO_2$ until disappearance of any $\nu$(CO) absorption (ca. 20 h). Yield 0.208 g (86%) as pale orange microcrystals. *Anal.* Calc. for $C_{57}H_{51}O_6P_3Pt_3S_3$: C, 42.62; H, 3.20. Found: C, 42.78; H, 3.25%. $^{31}P$ and $^{195}Pt$ NMR ($CDCl_3$, 293 K): $\delta_P$ 64.3; $\delta_{Pt}$ $-4090$ ppm; $^1J$(Pt–Pt) 644; $^1J$(P–Pt) 3891; $^2J$(P–Pt) 402; $^3J$(P–P) 53 Hz.

### *3.6. Preparation of $[Pt_3(\mu\text{-}SO_2)_3(P^iPr_3)_3]$ (**4d**)*

$SO_2$ was bubbled periodically through a stirred dichloromethane solution (50 ml) of $[Pt_3(\mu\text{-}CO)_3$-

Table 2
Molar fractions of $^{195}Pt$ and $^{13}CO$ isotopomers of $[Pt_3(CO)_3L_3]$ for three selected (1, 50 and 98%) enrichment in $^{13}CO$, and spin systems used in calculations (italics)

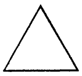
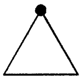
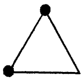
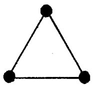
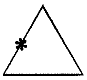
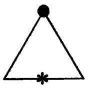
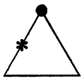
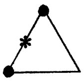
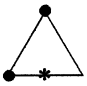
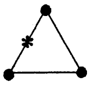
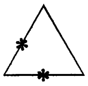
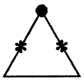
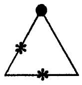
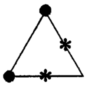
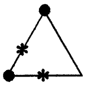
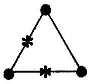
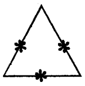
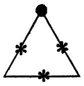
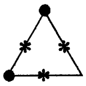
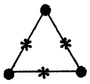
| | | | | |
|---|---|---|---|---|
| **1%**<br>**50%**<br>**98%** | 0.2815<br>0.0363<br>–  | 0.4312<br>0.0556<br>–  | 0.2202<br>0.0284<br>–  | 0.0375<br>0.0048<br>–<br>*$X_3$*  |
| **1%**<br>**50%**<br>**98%** | 0.0085<br>0.1088<br>0.0003  | 0.0044<br>0.0556<br>0.0002<br>*AX* <br>0.0087<br>0.1112<br>0.0003<br>*AY*  | 0.0022<br>0.0284<br>0.0001<br>*$AX_2$* <br>0.0044<br>0.0568<br>0.0002<br>*AXY*  | 0.0011<br>0.0145<br>–<br>*$AXY_2$*  |
| **1%**<br>**50%**<br>**98%** | –<br>0.1088<br>0.0167  | –<br>0.0556<br>0.0085<br>*AA'X* <br>–<br>0.1112<br>0.0171<br>*ABX*  | –<br>0.0284<br>0.0044<br>*AA'XX'* <br>–<br>0.0568<br>0.0087<br>*ABXY*  | –<br>0.0145<br>0.0022<br>*AA'XX'Y*  |
| **1%**<br>**50%**<br>**98%** | –<br>0.0363<br>0.2730<br>*$A_3$*  | –<br>0.0556<br>0.4183<br>*$AA'_2X$*  | –<br>0.0284<br>0.2136<br>*AA'A"XX'*  | –<br>0.0048<br>0.0363<br>*AA'A"XX'X"*  |

Table 3
$^{31}P$ and $^{195}Pt$ NMR data of clusters $[Pt_3(\mu\text{-}CO)_{3-n}(\mu\text{-}SO_2)_n(P^iPr_3)_3]$ ($n = 0$–$3$) in $CD_2Cl_2$ at 293 K; $\delta$ in ppm; $J$ in Hz

| | | $P_2$ | $P_3$ | $Pt_1$ | $Pt_2$ | $Pt_3$ |
|---|---|---|---|---|---|---|
| $Pt_3(CO)_3(P^iPr_3)_3$ **(4a)** | | | | | | |
| $\delta_P = 79.4$ | $P_1$ | 57 | 57 | 4433 | 418 | 418 |
| | $P_2$ | | 57 | 418 | 4433 | 418 |
| | $P_3$ | | | 418 | 418 | 4433 |
| $\delta_{Pt} = -4435$ | $Pt_1$ | | | | 1622 | 1622 |
| | $Pt_2$ | | | | | 1622 |
| $Pt_3(CO)_2(SO_2)(P^iPr_3)_3$ **(4b)** | | | | | | |
| $\delta_{P1} = 96.8$ | $P_1$ | 51 | 51 | 4383 | 433 | 433 |
| $\delta_{P2} = \delta_{P3} = 75.6$ | $P_2$ | | 61 | 366 | 4081 | 299 |
| | $P_3$ | | | 366 | 299 | 4081 |
| $\delta_{Pt1} = -3978$ | $Pt_1$ | | | | 1827 | 1827 |
| $\delta_{Pt2} = \delta_{Pt3} = -4584$ | $Pt_2$ | | | | | 196 |
| $Pt_3(CO)(SO_2)_2(P^iPr_3)_3$ **(4c)** | | | | | | |
| $\delta_{P1} = \delta_{P2} = 92.2$ | $P_1$ | 48 | 53 | 3992 | 371 | 338 |
| | $P_2$ | | 53 | 371 | 3992 | 338 |
| $\delta_{P3} = 72.3$ | $P_3$ | | | 320 | 320 | 3901 |
| $\delta_{Pt1} = \delta_{Pt2} = -4061$ | $Pt_1$ | | | | 1770 | 650 |
| $\delta_{Pt3} = -4714$ | $Pt_2$ | | | | | 650 |
| $Pt_3(SO_2)_3(P^iPr_3)_3$ **(4d)** | | | | | | |
| $\delta_P = 91.3$ | $P_1$ | 49 | 49 | 3748 | 326 | 326 |
| | $P_2$ | | 49 | 326 | 3748 | 326 |
| | $P_3$ | | | 326 | 326 | 3748 |
| $\delta_{Pt} = -4054$ | $Pt_1$ | | | | 705 | 705 |
| | $Pt_2$ | | | | | 705 |

$(P^iPr_3)_3]$ (0.30 g, 0.261 mmol). After 2.5 days a pale orange solution was obtained where the IR spectrum showed the disappearance of any $\nu$(CO) absorption. The volume of the solution was reduced in vacuo to 15 ml, hexane was added and the mixture was cooled to 0°C. The precipitate was filtered, washed with hexane and dried in vacuo. Yield 0.239 g (73%) as orange microcrystals. *Anal.* Calc. for $C_{27}H_{63}O_6P_3Pt_3S_3$: C, 25.78; H 5.05. Found: C, 25.61; H, 5.00%. $^{31}P$ and $^{195}Pt$ NMR ($CDCl_3$, 293 K): $\delta_P$ 91.3; $\delta_{Pt}$ −4054 ppm; $^1J$(Pt–Pt) 705; $^1J$(P–Pt) 3748; $^2J$(P–Pt) 326; $^3J$(P–P) 49 Hz.

### 3.7. Preparation of $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(P^iPr_3)_3]$ (4b)

$[Pt_3(\mu\text{-}CO)_3(P^iPr_3)_3$ (0.135 g, 0.117 mmol) was dissolved in dichloromethane (50 ml) at −20°C and 1 equiv. of $SO_2$ (2.87 ml at 25°C and 1 atm) was added with a gas syringe. After stirring for 1 h, the orange mixture was concentrated in vacuo and n-heptane added. The precipitate obtained was recrystallized from dichloromethane/n-heptane. Yield 0.098 g (70%) as orange microcrystals. *Anal.* Calc. for $C_{29}H_{63}O_4P_3Pt_3S$: C, 29.37; H, 5.35. Found: C, 29.60; H, 5.44%. $^{31}P$ and $^{195}Pt$ NMR data: see Table 3.

### 3.8. Preparation of $[Pt_3(\mu\text{-}CO)(\mu\text{-}SO_2)_2(P^iPr_3)_3]$ (4c)

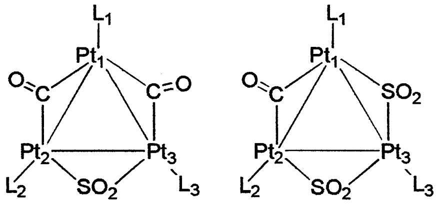
Complex **4d** (0.133 g, 0.106 mmol) was dissolved in dichloromethane (70 ml) at room temperature and 1 equiv. of CO (2.59 ml measured at 25°C and 1 atm) was added with a gas syringe. After stirring for 1.5 h, the pale orange solution was concentrated in vacuo and n-heptane added. The yellow–orange precipitate was recrystallized from dichloromethane/n-heptane. Yield 0.11 g (85%). *Anal.* Calc. for $C_{28}H_{63}O_5P_3Pt_3S_2$: C, 27.52; H, 5.20. Found: C, 27.71; H, 5.28%. $^{31}P$ and $^{195}Pt$ NMR data: see Table 3.

### 3.9. Preparation of $^{13}CO$ enriched clusters

The $^{13}C$ isotopically labelled derivatives were prepared similarly as above, using $^{13}CO$ enriched to 99%, or a suitable $^{12}CO/^{13}CO$ mixture for selected enrichments. The IR data are collected in Table 1.

## 4. Spectroscopic characterisation of the compounds

The calculation of the $^{13}C$ NMR data of the clusters $[Pt_3(^*CO)_3L_3]$ was based on the spectra corresponding to selected enrichments in $^{13}CO$. Up to 20 isotopomers may contribute to a given spectrum. These arise from the number of $^{195}Pt$ nuclei (0 to 3), the number of $^{13}C$ nuclei (0 to 3), and their relative positions. Table 2 shows the relative populations of the various isotopomers used in the calculations for three selected enrichments: 1, 50, and 98% $^{13}CO$. The values of



Scheme 2.

$^1J$(Pt–Pt) were also needed for the calculations and are reported in Section 3, or in the literature for **2a**–**4a** [5], and **3b**–**3d** [16]. The results of the calculations of the $^{31}$P and the $^{195}$Pt NMR data of the clusters **4a**–**4c** are given in Table 3, with the numbering scheme shown in Scheme 2.

The values of the molar fractions of the various isotopomers and of the $^1J$(Pt–Pt) coupling constants were introduced as input data in the GNMR 4.0 program to simulate the $^{13}$C NMR spectra of the *triangulo*-clusters. An example of such a simulation is shown in Fig. 1, concerning [$Pt_3(*CO)_3(P^iPr_3)_3$] with their selected enrichments, and a summary of all $^{13}$C NMR data is given in Table 4, (the $J$(C–P) coupling constants are all smaller than 2–3 Hz).

Table 1 shows as expected a decrease of $\nu$(CO) values of 39–46 cm$^{-1}$ upon substituting $^{12}$CO by $^{13}$CO.

The IR frequencies for the series **4a**, **4b** and **4c** move to higher $\nu$(CO) and those of **4b**, **4c** and **4d** move to higher $\nu(SO_2)$ as the proportion of $SO_2$ in the cluster increases, since $SO_2$ is a better π-acceptor than CO. The $^1J$(Pt–C) values of **4a***, **4b*** and **4c*** (Table 4) also increase as the proportion of $SO_2$ in the cluster increases. Consistently, the weighted average of the three $^1J$(Pt–Pt) values, and the three $^1J$(Pt–P) values (Table 3) decrease on going from **4a** (1622 and 4433 Hz, respectively), **4b** (1512, 4196), **4c** (1025, 3960) to **4d** (705, 3748).

The effect of the identity of the phosphine ligands on the NMR parameters is less clear cut, since both their basicity and cone angle vary on modifying the substituents at phosphorous. Clusters with $PCy_3$ must be

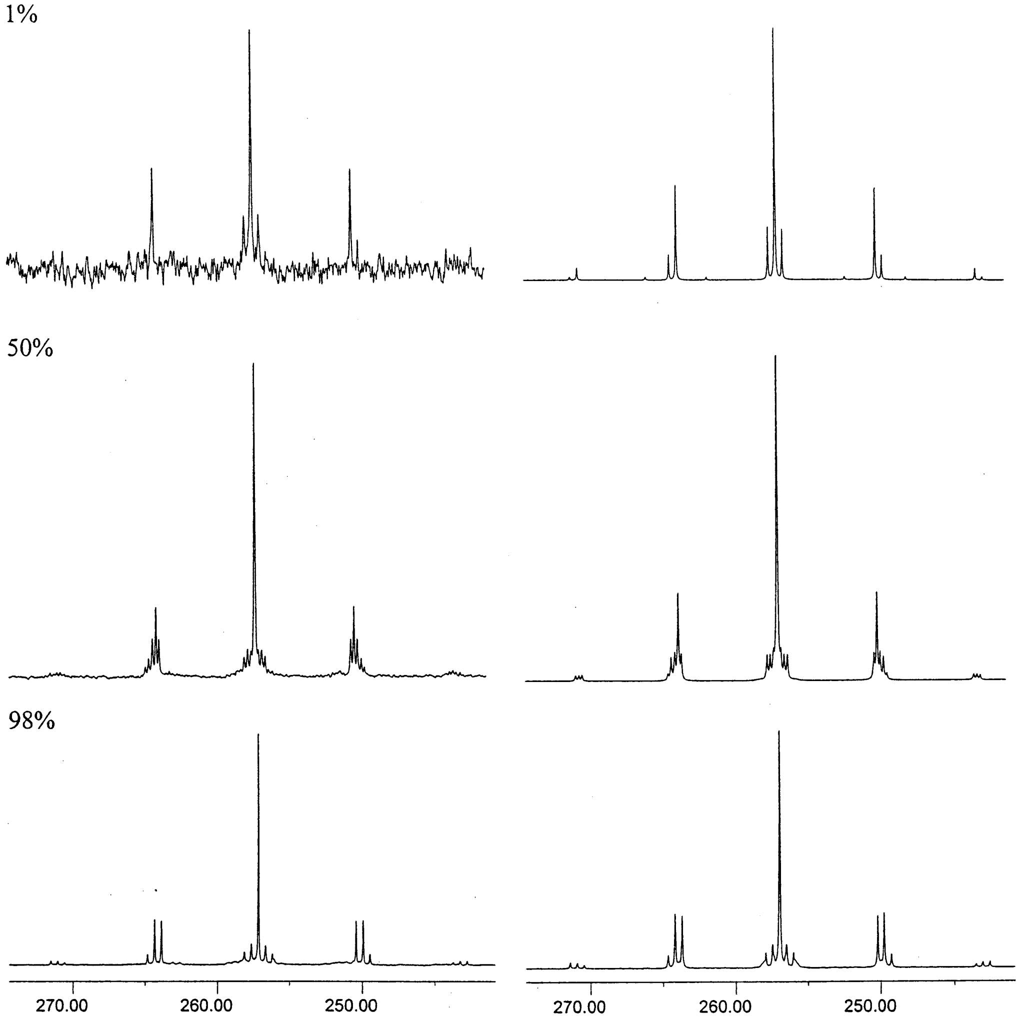


Fig. 1. Observed (left) and simulated (right) $^{13}$C NMR spectra of [$Pt_3(*CO)_3(P^iPr_3)_3$] with the selected enrichments: 1, 50 and 98% $^{13}$CO.

Table 4
$^{13}$C NMR data for $[Pt_3(\mu\text{-}^{13}CO)_{3-n}(\mu\text{-}SO_2)_n(PR_3)_3]$ [a] ($n = 0$–$2$) in $CD_2Cl_2$

| | $PR_3$ | $\delta_C$ | $^1J$(Pt–C) | $^2J$(Pt–C) | $^2J$(C–C) | $^1J$(Pt–Pt) |
|---|---|---|---|---|---|---|
| **(1a*)** [b] | $PPh_3$ | 245.5 | 723 | 44.1 | 22.6 | 1728 |
| **(2a*)** [c] | $PPh_2Bz$ | 251.6 | 718 | 45.3 | 22.7 | 1644 |
| **(3a*)** [d] | $PCy_3$ | 259.2 | 692 | 55.4 | 22.9 | 1571 |
| **(4a*)** [e] | $P^iPr_3$ | 256.7 | 701 | 50.1 | 23.9 | 1622 |
| **(3b*)** [e] | $PCy_3$ | 238.8 | 752 | 59.7 | 22.8 | |
| **(4b*)** [e] | $P^iPr_3$ | 237.8 | 758 | 59.4 | 23.3 | |
| **(3c*)** [e] | $PCy_3$ | 220.2 | 796 | 75.0 | – | |
| **(4c*)** [e] | $P^iPr_3$ | 219.3 | 783 | 76.7 | – | |

[a] $\delta_C$ in ppm; $J$ in Hz.
[b] At 233 K.
[c] At 223 K.
[d] At 243 K.
[e] At 293 K.

left out of the comparisons. Indeed, $[Pt_3(\mu\text{-}SO_2)_3(PCy_3)]$ for example has unusually large Pt–Pt bond distances owing to the preponderance of steric repulsions between the cyclohexyl groups and the bridging ligands [1b]. For the clusters bearing three μ-COs, the $\nu$(CO) values (Table 1) and $^1J$(Pt–C) values (Table 4) do indeed decrease along the sequence **1a***, **2a*** and **4a***, which corresponds to increasing basicity of the phosphine ligand. However, the corresponding values of $^1J$(Pt–Pt) and $^1J$(Pt–P) (Section 3) do also decrease along the same sequence, when they should increase instead if increasing basicity were the sole factor.

In conclusion, the only correlation found to hold in these *triangulo*-clusters is between the variations of the $\nu$(CO), $^1J$(Pt–C), $^1J$(Pt–Pt) and $^1J$(Pt–P) values and the variation of the π-acceptor capability of the bridging ligands.

The reactions of these clusters with alkenes and alkynes are currently being examined.

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## References

[1] (a) D. Imhof, L.M. Venanzi, Chem. Soc. Rev. 23 (1994) 185. (b) A.D. Burrows, D.M.P. Mingos, Coord. Chem. Soc. Rev. 154 (1996) 19. (c) L. Bengtsson-Kloo, C.M. Iapalucci, G. Longoni, S. Ulvenlud, Inorg. Chem. 37 (1998) 4335.

[2] J. Chatt, P. Chini, J. Chem. Soc. (A) (1970) 1538.

[3] A. Albinati, Inorg. Chim. Acta 22 (1977) L31.

[4] T. Yoshida, S. Otsuka, J. Am. Chem. Soc. 99 (1977) 2134.

[5] A. Moor, P.S. Pregosin, L.M. Venanzi, Inorg. Chim. Acta 48 (1981) 153.

[6] R.G. Goel, W.O. Ogini, R.C. Srivastava, J. Organomet. Chem. 214 (1981) 405.

[7] G.K. Anderson, H.C. Clark, J.A. Davies, Organometallics 1 (1982) 550.

[8] C.S. Browning, D.H. Farrar, R.R. Gukathasan, S.A. Morris, Organometallics 4 (1985) 1750.

[9] D.G. Evans, M.F. Hallam, D.M.P. Mingos, R.W.M. Wardle, J. Chem. Soc., Dalton Trans. (1987) 1889.

[10] K-H. Dahmen, A. Moor, R. Naegeli, L.M. Venanzi, Inorg. Chem. 30 (1991) 4285.

[11] J.M. Richey, D.C. Moody, Inorg. Chim. Acta 74 (1983) 271.

[12] D.C. Moody, R.R. Ryan, Inorg. Chem. 16 (1977) 1052.

[13] C.E. Briant, D.G. Evans, D.M.P. Mingos, J. Chem. Soc., Dalton Trans. (1986) 1535.

[14] M.F. Hallam, D.M.P. Mingos, J. Organomet. Chem. 315 (1986) C35.

[15] S.G. Bott, M.F. Hallam, O.J. Ezomo, D.M.P. Mingos, I.D. Williams, J. Chem. Soc., Dalton Trans. (1988) 1461.

[16] S.G. Bott, A.D. Burrows, O.J. Ezomo, M.F. Hallam, J.G. Jeffrey, D.M.P. Mingos, J. Chem. Soc., Dalton Trans. (1990) 3335.

[17] R.A. Burrow, D.H. Farrar, J.J. Irwin, Inorg. Chim. Acta 181 (1991) 65.

[18] C.E. Briant, D.I. Gilmour, D.M.P. Mingos, R.W.M. Wardle, J. Chem. Soc., Dalton Trans. (1985) 1693.

[19] J.L. Haggitt, D.M.P. Mingos, J. Organomet. Chem. 462 (1993) 365.

[20] W. Zhai, Z. Zhao, Youji Huaxve, (1986) 134 (Chem. Abstr. 107 (1986) 115724j); A. Jiang, Q. Cong, Jiegon Huaxve, 4 (1985) 96 (Chem. Abstr. 105 (1985) 124739d).

[21] M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. (1982) 1309.

[22] D.B. Copley, F. Fairbrother, J.R. Miller, A. Thompson, Proc. Chem. Soc. (1964) 300.

[23] A. Moor, P.S. Pregosin, L.M. Venanzi, Inorg. Chim. Acta 61 (1982) 135.