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Carbonyl Trichlorostannate Complexes of Platinum: Chemistry and ^{119}Sn, ^{195}Pt, and ^{13}C NMR Spectroscopy

IAN R. HERBERT, PAUL S. PREGOSIN and H. RUEGGER

Laboratorium für Anorganische Chemie, ETH Zürich, Universitätstrasse 6, CH-8092 Zurich, Switzerland

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Abstract

The reactions of the carbonyl anion $[PtCl_3(CO)]^-$ with $SnCl_2$ in the presence of CO in both methylene chloride and acetone are reported. In the former solvent, only $Pt^{II}–SnCl_3$ species are formed. These have been identified by ^{13}C, ^{119}Sn and ^{195}Pt NMR measurements as *cis*-$[PtCl_2(SnCl_3)(CO)]^-$, (I), *trans*-$[PtCl(SnCl_3)_2(CO)]^-$, (II), and $[Pt(SnCl_3)_4(CO)]^{2-}$, (III). Salts of these complexes have been isolated. In contrast, when acetone is the solvent, reduction of the platinum occurs to give two new complexes. On the basis of NMR measurements, we assign one of these as the Pt^I dimer $[Pt_2(SnCl_3)_4(CO)_2]^{2-}$, (IV), and the other as a platinum triangle (VI) containing terminal CO ligands and two types of Sn ligand. The Pt^{II} compound (IV) can also be generated by treating a CH_2Cl_2 solution of *trans*-$[PtCl(SnCl_3)_2(CO)]^-$, (II), with dihydrogen. NMR spectroscopic data, including those from measurements on samples of the complexes containing ^{13}C-enriched CO, are reported and discussed.

Introduction

Carbonyl complexes of platinum(II) are important intermediates in the hydroformylation reaction catalysed by platinum salts in conjunction with tin(II) chloride [1]. Previous studies have shown that: (a) a wide variety of polytrichlorostannate platinum complexes are stable [2] and (b) the $SnCl_3$ ligand plays various roles in the catalysis [3]. Specifically, model studies suggest that the $SnCl_3$ is displaced by CO when phosphine ligands are present [4] and that cationic platinum(II) species are important intermediates [5].

We considered it useful to study the chemistry of platinum(II) with CO and $SnCl_3$ ligands since this mixture forms a hydroformylation catalyst which has not yet been investigated. We report here the preparation and multinuclear NMR spectroscopy of a series of platinum complexes containing both CO and $SnCl_3$, as well as reduction of the metal to yield novel dimeric and cluster compounds.

Experimental

NMR spectra were measured on solutions contained in 10 mm tubes using a Bruker WM-250 spectrometer. The ^{13}C, ^{119}Sn, and ^{195}Pt measurements were performed without proton decoupling using pulse angles of *ca.* 30, 60, and 75°, respectively. Values of $\delta(^{195}Pt)$ and $\delta(^{119}Sn)$ are quoted in ppm relative to external $Na_2[PtCl_6]$ and $SnMe_4$, respectively, and are accurate to 0.5 ppm. Carbon-13 chemical shifts were measured relative to internal CH_2Cl_2 or $(CH_3)_2CO$ and then corrected to TMS using 54.02 and 30.43 ppm, respectively, and are accurate to within ±0.1 ppm. Coupling constants involving ^{13}C are accurate to ±2 Hz; all other coupling constants have an accuracy of ±12 Hz. Computer simulations of NMR spectra were performed using the program PANIC supplied by the Bruker organization. The sub-spectra due to individual isotopomers were simulated and then stored as experimental files. These were then added together in appropriate ratios within the NMR program to give the full simulation.

The complex $[NBu^n_4][PtCl_3(CO)]$ was prepared as in reference [6]. The salt $[PPh_4]_2[PtCl_4]$ was prepared by treating an aqueous solution of $K_2[PtCl_4]$ with 2 equivalents of $[PPh_4]Cl$ in water to give a pale-pink solid which was collected, washed with water, and dried.

$[NBu^n_4][PtCl_2(SnCl_3)(CO)]$

A CH_2Cl_2 solution (2 ml) of $[NBu^n_4][PtCl_3(CO)]$ (114 mg, 0.2 mmol) was stirred over $SnCl_2$ (38 mg, 0.2 mmol) until all the solid had dissolved (*ca.* 5 min). Addition of diethyl ether to the pale-orange solution, followed by cooling to −15 °C, led to the formation of yellow–orange crystals, which were collected and dried *in vacuo*. Yield 107 mg (70%). *Anal.* Found: C, 26.99; H, 4.50; N, 1.95; Cl, 23.52. Calc.: C, 26.81; H, 4.77; N, 1.84; Cl, 23.27%.

$[NBu^n_4][PtCl(SnCl_3)_2(CO)]$

A CH_2Cl_2 solution (5 ml) of $[NBu^n_4][PtCl_3(CO)]$ (400 mg, 0.7 mmol) was stirred over $SnCl_2$ (265 mg, 1.4 mmol under an atmosphere of CO for *ca.* 15

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min until the solid had dissolved. Evaporation of the solvent using a gentle stream of CO led to a yellow–orange solid which was dried *in vacuo*. Yield quantitative. *Anal.* Found: C, 21.54; H, 3.81; N, 1.47; Cl, 26.14. Calc.: C, 21.47; H, 3.82; N, 1.47; Cl, 26.09%.

$[PPh_4]_2[Pt(SnCl_3)_4(CO)]$

This complex was prepared by stirring a mixture of $[PPh_4]_2[PtCl_4]$ (508 mg, 0.5 mmol) and $SnCl_2$ (379 mg, 2 mmol) in CH_2Cl_2 (10 ml) under an atmosphere of CO for 1 h. The solvent was then evaporated under a stream of CO gas to leave an orange solid, which was dried *in vacuo*. Yield quantitative. *Anal.* Found: C, 31.94; H, 2.25; Cl, 25.05. Calc.: C, 32.66; H, 2.24; Cl, 23.61%.

Reaction of $[NBu^n_4][PtCl(SnCl_3)_2(CO)]$ with Dihydrogen

A CH_2Cl_2 solution of $[NBu^n_4][PtCl(SnCl_3)_2(CO)]$ was treated with H_2 for 15 min during which time the solution became orange–red in colour. The exit gases were passed through a methanol solution of neutral red made basic with sodium methoxide. As the reaction proceeded, this indicator solution turned from yellow to red due to the production of H^+. The NMR spectra of the reaction solution show the presence of complex (**IV**).

Reaction of $PtCl_2$ with $SnCl_2/Cl^-$ and CO

$PtCl_2$ (133 mg, 0.5 mmol), $SnCl_2$ (237 mg, 1.25 mmol) and NEt_4Cl (206 mg, 1.25 mmol) were mixed together as solids in a reaction vessel filled with CO. Acetone (3 ml) was introduced and the mixture stirred for *ca.* 0.5 h, to give a bright red liquor and an off-white precipitate. Recrystallisation of the precipitate from nitromethane gave colourless crystals with analysis appropriate for $[NEt_4]_2[SnCl_6]$. *Anal.* Found: C, 32.08; H, 6.72; N, 4.85; Cl, 35.59. Calc.: C, 32.46; H, 6.82; N, 4.73; Cl, 35.93%. NMR measurements on the red liquor showed it to contain a mixture of approximately 85% $[Pt_3(SnCl_x)_y(CO)_3]^{z-}$, (**VI**), and 15% $[Pt(SnCl_3)_5]^{3-}$. Addition of CH_2Cl_2 and cooling the solution to -15 °C afforded bright-red crystals of (**V**) as its $[NEt_4]^+$ salt. Yield 255 mg.

Samples Enriched with ^{13}CO

$[NBu^n_4][PtCl_2(SnCl_3)(CO)]$, (**I**), containing ^{13}C-enriched CO was generated *in situ* by stirring a CH_2Cl_2/CD_2Cl_2 solution of $[NBu^n_4]_2[Pt_2(\mu\text{-}Cl)_2Cl_2(SnCl_3)_2]$ [7] (147 mg, 0.1 mmol) under an atmosphere of ^{13}CO (*ca.* 90% ^{13}C) for *ca.* 15 min until the solution was yellow in colour. Following NMR measurements on (**I**), the solution was stirred over 1 equivalent of $SnCl_2$ for *ca.* 10 min to give $[PtCl(SnCl_3)_2(^{13}CO)]^-$, (**II**). This in turn was reacted with dihydrogen as described above to give (**IV**). A sample of $[Pt(SnCl_3)_4(^{13}CO)]^{2-}$, (**III**), was formed *in situ* using a procedure similar to that for the unenriched compound. Likewise, the reaction of $PtCl_2$ and $SnCl_2/Cl^-$ was repeated with ^{13}C to afford (**VI**).

Results and Discussion

Reactions in Dichloromethane

The reactions of $[PtCl_3(CO)]^-$ with tin(II) chloride in dichloromethane are described qualitatively by eqns. (1)–(3).

$$[PtCl_3(CO)]^- + SnCl_2 \longrightarrow \underset{\textbf{I}}{cis\text{-}[PtCl_2(SnCl_3)(CO)]^-} \qquad (1)$$

$$(\textbf{I}) + SnCl_2 \longrightarrow \underset{\textbf{II}}{trans\text{-}[PtCl(SnCl_3)_2(CO)]^-} \qquad (2)$$

$$\textbf{II} + 2SnCl_2 + Cl^- \longrightarrow \underset{\textbf{III}}{[Pt(SnCl_3)_4(CO)]^{2-}} \qquad (3)$$

NMR parameters for (**I**), (**II**), and (**III**) are presented in Table I. The ^{195}Pt NMR spectrum of (**I**) shows a resonance at -4125 ppm flanked by two sets of satellites appropriate for coupling of ^{195}Pt to ^{119}Sn ($I = 1/2$, 8.6% natural abundance) and ^{117}Sn ($I = 1/2$, 7.6% natural abundance). The value of $^1J(^{195}Pt, ^{119}Sn)$ of 24817 Hz is consistent with the presence of a Pt–$SnCl_3$ bond [2]; moreover, measurement of the intensities of the tin satellites relative to the central resonance indicates that only one Sn atom is bound to platinum [8]. The ^{119}Sn NMR spectrum shows the expected 1:4:1 pattern. Since the $SnCl_3^-$ ligand is thought to be a reasonable π-acceptor [9], we assign (**I**) as the *cis*-isomer. NMR measurements on a sample of (**I**) containing 90% ^{13}C-enriched CO reveal a ^{13}C carbonyl resonance which shows both ^{195}Pt and $^{119}Sn/^{117}Sn$

TABLE I. NMR Parameters for the Monomeric Complexes [a]

	I[b]	II	III
$\delta(^{13}C)$	156.7	160.4	170.0
$\delta(^{119}Sn)$	-244[c]	17	-147
$\delta(^{195}Pt)$	-4125[c]	-4449[c]	-5681
$^1J(^{195}Otm^{13}C)$	1761	1685	1402
$^1J(^{195}Pt, ^{119}Sn)$	24817[c]	18628[c]	14658
$^2J(^{119}Sn, ^{13}C)$	72	86	198
$^2J(^{119}Sn, ^{117}Sn)$		46118[c]	5740

[a] Chemical shifts in ppm, coupling constants in Hz; at 243 K in CH_2Cl_2/CD_2Cl_2 unless otherwise stated. [b] Ambient temperature. [c] In CH_2Cl_2/C_6D_6.

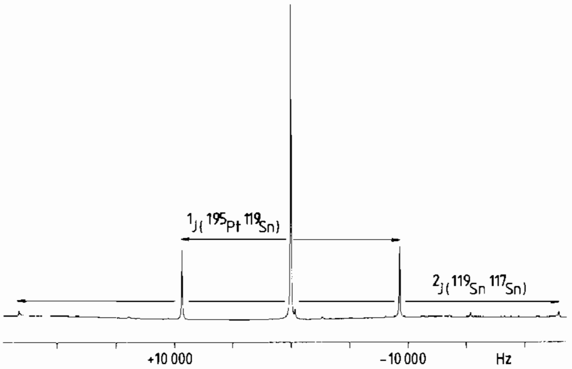

Fig. 1. ^{119}Sn NMR spectrum (243 K) of *trans*-$[PtCl(SnCl_3)_2(CO)]^-$, (**II**).

satellites. The magnitude of $^2J(^{119}Sn, ^{13}C)$ is in keeping with a *cis*-arrangement for CO and Sn*.

The ^{195}Pt NMR spectrum of (**II**) shows a resonance at −4449 ppm, which again has ^{119}Sn and ^{117}Sn satellites. The intensities of these satellites relative to the central signal are now in keeping with the coordination of two $SnCl_3$ ligands to platinum.

The ^{119}Sn spectrum of (**II**) (see Fig. 1) shows a resonance at 17 ppm flanked by ^{195}Pt satellites at $\pm{}^1J(^{195}Pt, ^{119}Sn)/2$. In addition, the spectrum also shows two weak satellites [separation $^2J(^{119}Sn, ^{117}Sn)$] arising from the isotopomer $[PtCl(^{119}SnCl_3)(^{117}SnCl_3)(CO)]^-$. The centre of these lines does not correspond to $\nu(^{119}Sn)$: instead, a small 'AB' distortion results because $^2J(^{119}Sn, ^{117}Sn)$ is relatively large (46 118 Hz) compared to the $^{119}Sn/^{117}Sn$ chemical shift difference (*ca.* 4.12 MHz measured at 5.87 T). This large two-bond coupling is consistent with a *trans*-arrangement for the two Sn atoms [2].

We note that treatment of $[PtCl_3(CO)]^-$ with two equivalents of $SnCl_2$ in CH_2Cl_2 gives not only (**II**), but also small amounts of $[PtCl_2(SnCl_3)_2]^{2-}$ [10] and other non-carbonyl compounds. However, (**II**) is essentially the only species present when the reaction is carried out under an atmosphere of CO. Complexes (**I**) and (**II**) were isolated as their $[NBu^n_4]^+$ salts; their vibrational spectroscopic characteristics have been reported previously [11, 12].

When a CH_2Cl_2 solution of $[NBu^n_4][PtCl_3(CO)]$ is treated with four equivalents of $SnCl_2$ in the presence of chloride ion, a further complex is formed, which we assign as the five-coordinate compound $[Pt(SnCl_3)_4(CO)]^{2-}$ (**III**). However, we find that this is most conveniently prepared by the method shown in eqn. (4), and in this way we have isolated (**III**) as its $[PPh_4]^+$ salt.

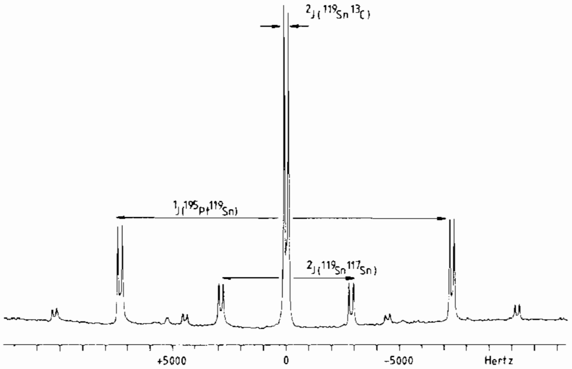

Fig. 2. ^{119}Sn NMR spectrum (183 K) of $[Pt(SnCl_3)_4(^{13}CO)]^{2-}$, (**III**).

$$[PtCl_4]^{2-} + 4SnCl_2 + CO \xrightarrow[1\ h]{CH_2Cl_2} \underset{\textbf{III}}{[Pt(SnCl_3)_4(CO)]^{2-}} \qquad (4)$$

The ^{195}Pt NMR spectrum of (**III**) is similar in form to those observed for (**I**) or (**II**) except that the Sn satellites are more intense. The ^{119}Sn spectrum comprises a resonance at −147 ppm flanked by ^{195}Pt and ^{117}Sn satellites. The relative intensities of the tin satellites are in keeping with a formulation having 4 equivalent $SnCl_3^-$ ligands. The presence of CO as the fifth ligand was confirmed by NMR measurements on a sample of (**III**), prepared as in eqn. (4), but using 90% ^{13}C-enriched CO. At −90 °C the ^{119}Sn NMR spectrum shows sharp signals, and each resonance (see Fig. 2) now exhibits a doublet splitting corresponding to $^2J(^{119}Sn, ^{13}C)$.

There have been two earlier reports of Pt–Sn carbonyl complexes with very similar NMR parameters to those we observe for (**III**). The first [13], from this laboratory, proposed that the product of reaction of $[Pt(SnCl_3)_3(1,5\text{-COD})]^-$ with CO was the dicarbonyl $[Pt(SnCl_3)_3(CO)_2]^-$; we now believe this to be the monocarbonyl (**III**). The second report [5a], by Clark and co-workers, concerns a complex they assigned as *trans*-$[PrCl(SnCl_3)_2(CO)]^-$; their NMR data closely resemble the parameters we give for (**III**), and not (**II**).

Complexes (**II**) and (**III**) show rather broad ^{119}Sn resonances at ambient temperature, in keeping with intermolecular exchange of $SnCl_3$ as observed in other Pt–Sn complexes [14]. In addition, as we see broad ^{13}C resonances for (**II**) and (**III**) at ambient temperature, intermolecular exchange of CO also seems likely. Indeed, solutions of (**II**) and (**III**) slowly lose CO upon standing. The NMR spectra of (**III**) show sharp signals from −30 to −90 °C and do not alter significantly within this range (*i.e.* the four $SnCl_3$ ligands remain equivalent), suggesting that the intramolecular exchange processes associated with five-coordinate complexes are still rapid (*cf.* the behaviour of $[Pt(SnCl_3)_5]^{3-}$ [15].

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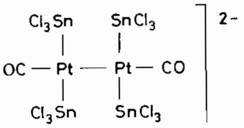
*The data base is insufficient to generalize; however, for the complexes (**I**)–(**III**), for which we have analyses and NMR data, a value of *ca.* 70 Hz seems reasonable for a $^2J(^{119}Sn, ^{13}CO)$ *cis*-coupling.

Reaction of (II) with Dihydrogen

Our measurements show that treatment of a CH_2Cl_2 solution of **(II)** with dihydrogen leads to a mixture consisting mainly of the starting material and a new Pt–Sn compound **(IV)**. Interestingly, this new species is not a hydride, since the only protons we observe belong to the solvent and the $[NBu^n{}_4]^+$ cation. The ^{195}Pt and ^{119}Sn NMR spectra of **(IV)** (recorded without proton decoupling*) show a central resonance flanked by rather complex sets of satellites. From an analysis of these NMR spectra, and those measured on a sample of **(IV)** containing ^{13}C-enriched CO, we assign this complex as the anionic Pt(I) dimer, **(IV)**.



IV

We base our conclusion on the following evidence:

(i) The ^{119}Sn spectrum shows two pairs of ^{195}Pt satellites of equal intensity, with separations of 21 874 and 135 Hz, which we attribute to $^1J(^{195}Pt, ^{119}Sn)$ and $^2J(^{195}Pt, ^{119}Sn)$ respectively. Corresponding ^{119}Sn (and ^{117}Sn) satellites are observed in the ^{195}Pt spectrum. This confirms the formulation of **(IV)** as a dimer.

(ii) Lines due to the isotopomer containing two ^{195}Pt nuclei and one ^{119}Sn (or ^{117}Sn) nucleus have been located in the ^{195}Pt spectrum. From these we measure a value of 1233 Hz for $J(^{195}Pt, ^{195}Pt)$, which is consistent with a one-bond interaction [17].

(iii) The ^{119}Sn spectrum also shows two pairs of ^{117}Sn satellites for $^2J(^{119}Sn, ^{117}Sn)$ and $^3J(^{119}Sn, ^{117}Sn)$, with separations of 31 015 and 630 Hz respectively. The larger coupling is only consistent with a *trans* Sn–Pt–Sn unit [2].

(iv) Analysis of the NMR spectra of a sample of **(IV)** containing ^{13}C-enriched CO leads to values of $^1J(^{195}Pt, ^{13}C)$, $^2J(^{195}Pt, ^{13}C)$ and $^3J(^{13}C, ^{13}C)$, in keeping with a) terminal CO ligands, and b) a *trans* OC–Pt–Pt–CO unit [18].

The NMR parameters for **(IV)**, which are presented in Table II, have been used as input for simulations of its ^{13}C, ^{119}Sn and ^{195}Pt NMR spectra, and good fits between calculated and observed spectra were obtained in all cases.

When **(II)** is reacted with dihydrogen, a methoxide solution of neutral red becomes acidic after contact with the exit gases from the reaction. Assuming that the H^+ arises from an unstable hydride, we propose that **(IV)** is produced by a route similar to that shown in eqns. (5), (6) and (7).

TABLE II. NMR Parameters for $[Pt_2(SnCl_3)_4(CO)_2]^{2-}$ [a]

$\delta(^{13}C)^b$	191.0
$\delta(^{119}Sn)$	14
$\delta(^{195}Pt)$	-4471
$^1J(^{195}Pt, ^{119}Sn)$	21874
$^1J(^{195}Pt, ^{195}Pt)$	1233
$^2J(^{195}Pt, ^{119}Sn)$	-135
$^2J(^{119}Sn, ^{117}Sn)$	31015
$^3J(^{119}Sn, ^{117}Sn)$	640
$^1J(^{195}Pt, ^{13}C)^b$	1503
$^2J(^{195}Pt, ^{13}C)^b$	39[c]
$^2J(^{119}Sn, ^{13}C)^b$	68[d]
$^3J(^{119}Sn, ^{13}C)^b$	25[d]
$^3J(^{13}C, ^{13}C)^b$	13

[a] –30 °C, CH_2Cl_2/C_6D_6. [b] Ambient temperature, CH_2Cl_2/CD_2Cl_2. [c] Same sign as $^1J(^{195}Pt, ^{13}C)$. [d] The two couplings have opposite signs.

$$\underset{\textbf{II}}{[PtCl(SnCl_3)_2(CO)]^-} \xrightarrow{H_2} [PtClH_2(SnCl_3)_2(CO)]^- \quad (5)$$

$$[PtClH_2(SnCl_3)_2(CO)]^- \xrightarrow{-HCl} [PtH(SnCl_3)_2(CO)]^- \quad (6)$$

$$[PtH(SnCl_3)_2(CO)]^- + \textbf{II} \xrightarrow{-HCl} \underset{\textbf{IV}}{[Pt_2(SnCl_3)_4(CO)]^{2-}} \quad (7)$$

if the H_2 activation is heterolytic*. Alternatively, eqns. (5) and (6) may by combined.

$$[PtCl(SnCl_3)_2(CO)]^- \xrightarrow{-H_2} [PtH(SnCl_3)_2(CO)]^- + HCl \quad (8)$$

The formation of a Pt^I dimer from a Pt^{II} hydride complex (eqn. (9)) has previously been demonstrated [19]. Note that eqns. (7) and (9) are identical if Cl

$$[PtCl_2H(CO)]^- + [PtCl_3(CO)]^- \underset{+HCl}{\overset{-HCl}{\rightleftharpoons}} \underset{\textbf{V}}{[Pt_2Cl_4(CO)_2]^{2-}} \quad (9)$$

replaces $SnCl_3$ in the former.

Finally, we note that when we treat a CH_2Cl_2 solution of **(V)** [20] with 4 equivalents of $SnCl_2$, complex **(IV)** is one of the major products. Reaction of **(V)** with just one equivalent of $SnCl_2$ affords an $SnCl_2$ bridged dimer [21].

Reactions in Acetone

When $[PtCl_3(CO)]^-$ is reacted in acetone with $SnCl_2$ instead of CH_2Cl_2, the product, either **(I)**, **(II)**

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*Hydride complexes give relatively large $^1J(Pt, H)$ and $^2J(Sn, H)$ coupling constants [16].

*Suggested by a referee.

or (III), is a function of the ratio [Pt complex]/$SnCl_2$]. Moreover, non-carbonyl anionic complexes such as *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$ are also formed. If the reaction is carried out under an atmosphere of CO, we find a different chemistry prevails. Treatment of an acetone solution of $[PtCl_3(CO)]^-$ with 2 to 3 equivalents of $SnCl_2$ under CO leads to the formation of **(IV)** and an additional Pt–Sn complex (the latter species predominates for higher Sn:Pt ratios). This new complex, **(VI)**, can also be prepared by reacting $PtCl_2$ with 2.5 equivalents of $SnCl_2$ in acetone in the presence of NEt_4Cl and carbon monoxide. We have isolated a sample of **(VI)** as a red crystalline solid; however, solution NMR measurements show it to contain *ca.* 15% $(NEt_4)_3[Pt(SnCl_3)_5]$. Unfortunately we have not been able to obtain a sample free from this impurity.

Physical measurements allow us to conclude:

(i) The structure contains a triangle of equivalent Pt atoms.

(ii) Each Pt carries a terminal CO ligand.

(iii) There are two types of $SnCl_n$ ligand.

Point (i) is unequivocally shown by ^{195}Pt and ^{13}C measurements on the ^{13}CO-enriched complex (see Fig. 3). Moreover, the IR stretch at $\nu(CO) = 2055$ cm^{-1} and the $^1J(^{195}Pt, ^{13}C)$ value of 1750 Hz [22] support our assignment of terminal CO ligands.

Room temperature NMR measurements reveal (a) sharp ^{13}CO signals, (b) a single sharp ^{195}Pt resonance with broad $^{117,119}Sn$ satellites and (c) a single broad ^{119}Sn resonance, indicating exchange of tin ligands. At −50 °C, the ^{119}Sn spectrum shows two $SnCl_n$ types, $\delta = -24(A), -47(B)$, which appear* to be in the ratio 1:1. Lowering the temperature to −100 °C changes the relative signal intensities such that the ratio is now about 1(A):3(B).

The various $^nJ(^{195}Pt, ^{119}Sn)$ and $^nJ(^{119,117}Sn)$ values (see Table III) suggest an unusual arrangement of the tin ligands based on the following:

(a) At −50 °C one type of $^{119}SnCl_3$, A, is associated with three Pt atoms (based on the 1:12:51:88:51:12:1 pattern in the ^{119}Sn spectrum) and couples to a second type A $^{117}SnCl_n$, $^nJ = 26\,173$ Hz, in such a way as to suggest a *trans* orientation of these two tin ligands. The $^1J(^{195}Pt, ^{119}Sn)$ value of 8806 Hz is modest.

(b) At −50 °C, type B tin resonance shows an unusually small $^nJ(^{195}Pt, ^{119}Sn)$ value, 813 Hz, suggestive of either a two- or three-bond Pt–Sn coupling constant or an average of one $^1J(^{195}Pt, ^{119}Sn)$ with several other two- and/or three-bond coupling contants. The $^2J(^{119}Sn_B, ^{117}Sn_B)$ value (2728 Hz) and the $^2J(^{119}Sn_A, ^{119}Sn_B)$ are reasonable for a pseudo *cis*-orientation of these two spins.

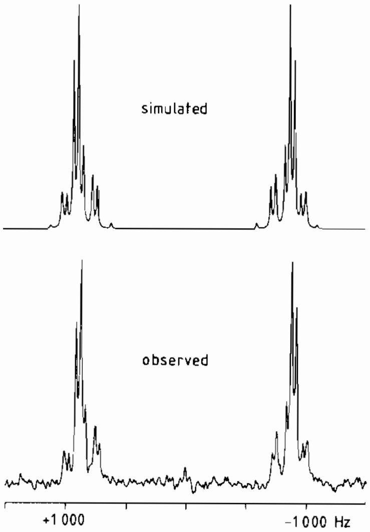

Fig. 3. Observed and simulated ^{13}C NMR spectra (293 K) of $[Pt_3(SnCl_3)_4(^{13}CO)_3]^{2-}$, (V). (The weak resonances at the centre of the observed spectra are due to isotopomers containing one or more ^{12}C ligands).

TABLE III. Selected NMR Parameters for $[Pt_3(CO)_3(SnCl_x)_y]^{z-}$, (VI)[a]

Ambient temperature			
$\delta(^{13}C)$	175.5	$^1J(^{195}Pt, ^{13}C)$	1750[b]
$\delta(^{195}Pt)$	−4580	$^2J(^{195}Pt, ^{13}C)$	40[b]
		$^1J(^{195}Pt, ^{195}Pt)$	250
223 K			
$\delta(^{119}Sn_A)$	−24	$J(^{195}Pt, ^{119}Sn_A)$	8806
$\delta(^{119}Sn_B)$	−47	$J(^{195}Pt, ^{119}Sn_B)$	813
$J(^{119}Sn_A, ^{117}Sn_A)$	26173	$J(^{119}Sn_A, ^{119}Sn_B)$	806
$J(^{119}Sn_B, ^{117}Sn_B)$	2728		
173 K			
$\delta(^{119}Sn_A)$	−22	$J(^{195}Pt, ^{119}Sn_A)$	8784
$\delta(^{119}Sn_B)$	−41	$J(^{195}Pt, ^{119}Sn_B)$	20603
		$J(^{119}Sn_A, ^{119}Sn_B)$	775

[a] In $(CH_3)_2CO/(CD_3)_2CO$. [b] These couplings have the same sign.

(c) At −100 °C, tin resonance B shows new broad ^{195}Pt satellites with $^1J(^{195}Pt, ^{119}Sn) = 20\,603$ Hz, suggestive of a terminal Pt–Sn bond.

At this point, a composition such as $[Pt_3(CO)_3(SnCl_x)_y]^{z-}$ seems reasonable. X-ray fluorescence measurements on the impure solid suggest that we have four tin atoms per triangle of platinum atoms. Since our microanalytical data are ambiguous, we cannot be sure of the exact composition; however, all the available evidence suggests a composition of the form $[Pt_3(CO)_3(SnCl_x)_y]^{z-}$. We suggest that

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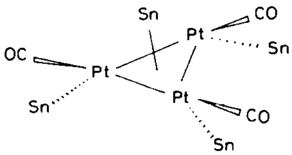
*We observe more than 30 signals in the spectrum of (VI) covering a range of *ca.* 35 KHz; thus an exact integral is difficult to obtain.



at −100 °C the spins for **(VI)** may be situated as shown. Platinum clusters containing bridging $SnCl_x$ and terminal $SnCl_3$ ligands are known [23, 24] although there are no ^{119}Sn or ^{195}Pt NMR data for these compounds.

We do not know the structure of **(VI)**, but we feel that the ease with which both **(IV)** and **(VI)** are generated indicates that lower oxidation states and/or higher molecular weight complexes should be considered when discussing the catalytic mixture which stems from platinum salts, tin(II) chloride and CO.

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