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Preliminary communication

FACILITATION OF THE SUBSTITUTION REACTIONS OF SULPHUR DIOXIDE CLUSTER COMPOUNDS OF PLATINUM BY AMINE *N*-OXIDES

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Summary

Me_3NO has been used to facilitate the substitution reactions of the *triangulo*-platinum clusters $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$ ($PR_3 = PCy_3$ or PPh_3) with CO and halide anions. In the absence of Me_3NO a benzene solution of $[Pt_3(SO_2)_3(PCy_3)_3]$ gives only partially substituted products with CO, but the addition of Me_3NO leads to a high yield conversion to $[Pt_3(CO)_3(PCy_3)_3]$. Me_3NO has also been used in the synthesis of the novel 44-electron anionic clusters $[Pt_3(\mu\text{-}X)(\mu\text{-}SO_2)_2(PCy_3)_3]^-$ (X = Cl or Br).

The facilitation of substitution reactions of metal carbonyls by trimethylamine *N*-oxide (Me_3NO) is well documented, and has been found to be particularly efficient for compounds where the CO stretching frequency exceeds 2000 cm^{-1} [1,2]. Since Me_3NO is known to react with SO_2 to form the adduct Me_3NSO_3 [3], we have investigated the effect of Me_3NO on the substitution reactions of the *triangulo*-platinum cluster compounds $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$ ($PR_3 = PPh_3$ or PCy_3) [4,5].

A benzene solution of $[Pt_3(SO_2)_3(PCy_3)_3]$ (**1a**) reacts with CO (1 atm, rt) to give $[Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2(PCy_3)_3]$ (**2**) as the predominant product, and smaller quantities of $[Pt_2(\mu\text{-}SO_2)(CO)_2(PCy_3)_2]$ are also formed. The *triangulo*-cluster **2** was characterised by ^{31}P and ^{195}Pt NMR and the data are summarised in Table 1. The relevant ^{31}P NMR spectrum is shown in Fig. 1. Even with prolonged exposure to CO and with the reaction temperature raised to 60°C no conversion to the fully substituted derivative was observed. Addition of Me_3NO to (**2**) led to the isolation of the fully substituted derivative $[Pt_3(CO)_3(PCy_3)_3]$ [5] in high yield (90%) even under ambient conditions. The extent of the acceleration of the rate induced by Me_3NO depended on the mole ratio, 3 mol equivalents 6–8 h and 20 mol equivalents 2–3 h for complete conversion.

The accelerating effect of Me_3NO has also been utilized in the synthesis of a new class of anionic 44-electron *triangulo*-cluster compounds of platinum with bridging halide ligands. The addition of quaternary ammonium halide salts, R_4NX (X = Cl

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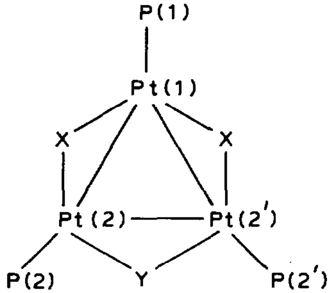
TABLE 1

SUMMARY OF $^{31}P\{^1H\}$ AND $^{195}Pt\{^1H\}$ NMR DATA



$[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PCy_3)_3]$

	P(1)	P(2)	P(2')	Pt(1)	Pt(2)	Pt(2')
δ (ppm)	82.2	61.9	61.9	−4011	−4515	−4515
J (Hz) P(1)		51	51	5134	449	449
P(2)			62	372	4055	301
P(2')				372	301	4055
Pt(1)					1830	1830
Pt(2)						

$[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$

	P(1)	P(2)	P(2')	Pt(1)	Pt(2)	Pt(2')
δ (ppm)	4.0	17.3	17.3			
J (Hz) P(1)		62	62	4599	431	431
P(2)			46	300	5469	345
P(2')				300	345	5469

$[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_3]^-$

	P(1)	P(2)	P(2')	Pt(1)	Pt(2)	Pt(2')
δ (ppm)	12.9	28.9	28.9	−5977	−4653	−4653
J (Hz) P(1)		59	59	4341	352	352
P(2)			45	314	4963	245
P(2')				314	245	4963
Pt(1)					968	968
Pt(2)						

or Br), in ethanol, to solutions of $[Pt_3(SO_2)_3(PPh_3)_3]$ (**1b**) in benzene gives high yields of the corresponding salts $[Pt_3(\mu\text{-}X)(\mu\text{-}SO_2)_2(PPh_3)_3]^-$ (X = Cl, **3a**; X = Br, **3b**). The corresponding reaction with $[Pt_3(SO_2)_3(PCy_3)_3]$ (**1a**) is very slow and incomplete even after 2 d. The addition of Me_3NO leads to complete conversion to $[Pt_3(\mu\text{-}X)(SO_2)_2(PCy_3)_3]^-$ (X = Cl, **3c**; X = Br, **3d**) after 15 min at room temperature. The anionic 44-electron cluster compounds **3** have been characterised using ^{31}P and ^{195}Pt NMR techniques and some representative results are summarised in Table 1. The ^{195}Pt NMR spectrum of $[Pt_3(\mu\text{-}Cl)(\mu\text{-}SO_2)_2(PCy_3)_3]^-$ is illustrated in Fig. 2 together with the computer simulated spectrum.

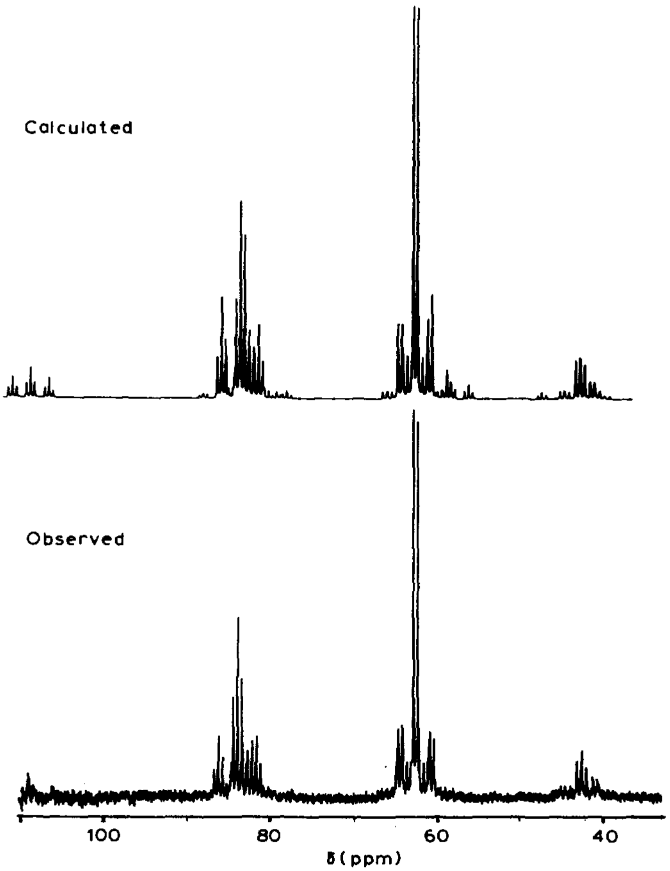


Fig. 1. The $^{31}P\{^1H\}$ NMR spectrum of $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PCy_3)_3]$.

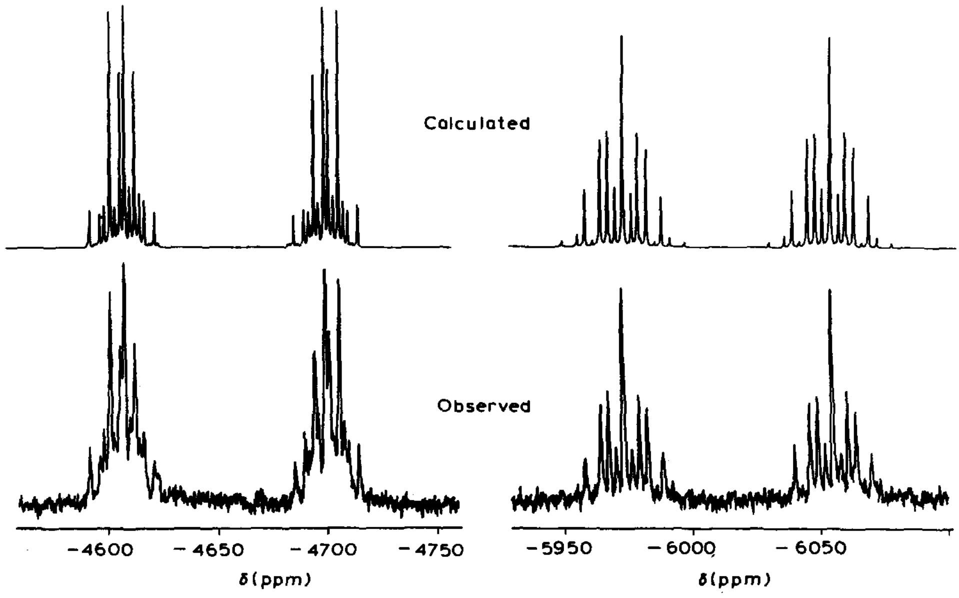


Fig. 2. The $^{195}Pt\{^1H\}$ NMR spectrum of $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_3]^-$.

The anionic *triangulo*-clusters **3** are more nucleophilic than the corresponding neutral 42-electron clusters **1a** and **1b** and, for example, will react with $[AuPR_3]^+$ to give successively tetrahedral Pt_3Au and Pt_3Au_2 cluster compounds. These compounds have been characterised by single crystal X-ray diffraction studies [6–8] and shown to retain a platinum–platinum bonded triangle of metal atoms. The metal–metal bond lengths in these clusters have been interpreted by means of molecular orbital calculations [9].

The usefulness of the labilization process described here for substitution reactions of other mono- and poly-nuclear SO_2 compounds is currently being investigated.

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