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Platinum(0) Complexes with Bulky Phosphines: Trinuclear SO_2 and CS_2 Complexes

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The synthesis and reaction chemistry of a series of trinuclear SO_2 and CS_2 complexes containing the bulky phosphines PCy_3 and $P(t\text{-}Bu)_3$ are reported.

Introduction

We recently reported the details [1] of the formation of a series of complexes of $Pt(PCy_3)_2$ and $Pt[P(t\text{-}Bu)_3]_2$ with SO_2 and CS_2. In the course of this work, we inadvertently synthesized several trinuclear complexes, which led us to undertake the present systematic study of the synthesis and reaction chemistry of trinuclear SO_2 and CS_2 complexes with bulky phosphines.

Uhlig and Walther and especially F.G.A. Stone have extolled the virtues of using 'ligand free' $[Pt(olefin)_x(PR_3)_y]$ compounds in several excellent reviews [2, 3], pointing out the advantage of using a platinum source such as $[Pt(C_2H_4)_2(PR_3)]$, which does not readily dissociate PR_3 groups. Hence a variety of synthetic procedures can be performed without undesirable deposition of metallic platinum. While there is a rapidly growing body of literature [2b] describing their use for synthesizing trimeric complexes of the form $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$, prior to this work this remarkable moiety had not been used to prepare analogous μ-SO_2 and μ-CS_2 complexes.

In this study, we describe syntheses of $[Pt_3(SO_2)_3(PR_3)_3]$ and $[Pt_3(CS_2)_3(PR_3)_3]$ trimers (where R = Cy and/or t-Bu), the latter being first reported (by an alternate procedure) in a previous paper [1]. The interconversion of carbonyl and sulfur dioxide clusters is also presented as an alternative procedure for the preparation of the SO_2 trimers.

Experimental

Procedures and reagents previously described [1] also apply for the experiments outlined below. $Pt(cod)_2$ and $Pt(C_2H_4)_2(PCy_3)$ were prepared according to the method of Spencer [4a] with minor modification. $Pt(PCy_3)_2$ was prepared from $Pt(Cod)_2$ by literature procedures [4b]. All gases were from Matheson Co. and used without further purification except where noted [1]. Infrared spectra (Nujol mulls) were recorded on Perkin Elmer Model 180 or Model 683 spectrophotometers, and mass spectra recorded on a Bendix MA-2 time of flight mass spectrometer. Elemental analyses and molecular weights were performed by Galbraith Laboratory, Knoxville, TN. All procedures were carried out under oxygen-free nitrogen except where noted.

Preparations and Reactions of Tris-μ-Sulfur Dioxide-Tris(tricyclohexylphosphine)-Triangulo-Triplatinum-(0), $Pt_3(SO_2)_3(PCy_3)_3$ (1)

From Bis(ethylene)(tricyclohexylphosphine)platinum(0), $Pt(C_2H_4)_2(PCy_3)$

Purified SO_2 gas was bubbled through a stirred n-hexane solution (30 ml, N_2 atm) containing 0.08 g (0.15 mmol) $Pt(C_2H_4)_2(PCy_3)$. The reaction mixture immediately assumed a dark red coloration, changing to an orange cast after 5 min with accompanying appearance of an orange solid. After 5 hr, the SO_2 flush was stopped, the solvent was removed *in vacuo*, the resulting orange solid (quantitative yield) was washed with n-hexane, dried for 1 hr (10^{-5} torr) and submitted for analysis. Calcd. for $Pt_3(SO_2)_3[P(C_6H_{11})_3]_3$: C, 40.04; H, 6.21; P, 5.73; S, 5.93; Pt, 36.13. Found: C, 40.95; H, 6.39; P, 5.85; S, 5.70; Pt, 33.95. Mol. Wt. Calc: 1620. Found: 1677 (toluene).

A sample of *1* was exposed to air for 12 hours in a stirred n-hexane solution. The solvent was subsequently removed, benzene introduced and the contents again stirred under air for two days. An infrared spectrum of the isolated orange solid verified that *1* had not been oxidized to the platinum–sulfato complex [1].

A second sample of *1* (0.10 g, 0.06 mmol) was added to 35 ml degassed n-hexane, followed by addition of ethylene gas (500 torr) and H_2 gas (500 torr) over the stirred solution. The reaction was followed via pressure changes for 24 hours to investigate potential catalytic effects of the trimer on ethylene hydrogenation. No appreciable pressure drop occurred

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during this time. Mass spectrometric analysis of the gases indicated ethane was not present.

0.13 g (0.08 mmol) of *1* was added to 25 ml n-hexane and CO gas passed over the stirred solution (solid quickly dissolved) for 12 hours, the reaction vessel subsequently closed off (CO pressure, 1.5 atm) and stirred for a total of 5 days. During this period, the tan contents were examined at 24-hr intervals, the infrared spectra indicating a mixture of products containing coordinated CO (terminal & bridging) and SO_2 (bridging). Variations of this procedure (time, reagents, solvents, order of addition) produced products of varying composition and infrared spectra, though terminal and bridging CO and bridging SO_2 moieties were always present.

From Tri-μ-carbonyl-Tris(tricyclohexylphosphine)-Triangulo-Triplatinum(0), $Pt_3(CO)_3(PCy_3)_3$ (2)

Carbon monoxide was passed over a stirred n-hexane solution (35 ml) containing $Pt(PCy_3)_2$ (0.20 g, 0.26 mmol) for a period of 2 hours, the reaction vessel subsequently being sealed (under CO) for 12 hr. The rust colored solution was then reduced to *ca.* 10 ml, filtered and 0.08 g (61%) of the tan solid *2* washed with cold n-hexane and dried *in vacuo* for 1 1/2 hr, m.p. 252–254 °C, dec. Calcd. for $Pt_3(CO)_3[P(C_6H_{11})_3]_3$: C, 45.32; H, 6.60; P, 6.15; Pt, 38.74. Found: C, 45.51; H, 6.75; P, 6.32, Pt, 38.42. The solid *2* was observed to be extremely soluble in petroleum ether.

0.10 g (0.07 mmol) of *2* was admitted to a flask containing 40 ml hexane, and SO_2 was passed over the stirred solution for 5 hr. During this time, the solution changed to an orange shade and contained a suspended orange solid. The solid was isolated by filtration, washed with n-hexane, examined via its infrared spectrum and found to have nearly complete loss of CO absorptions. The reaction was repeated over 1 1/2 days, yielding a tan solid identified as *1* from its infrared spectrum and elemental analysis. Calcd. for $Pt_3(SO_2)_3[P(C_6H_{11})_3]_3$: C, 40.04; H, 6.21; P, 5.73; S, 5.93; Pt, 36.13. Found: C, 40.99; H, 6.36; P, 6.04; S, 5.91; Pt, 34.91.

Preparation and Reactions of Tertiary Phosphine–Platinum Complexes with Carbon Disulfide

Tris-μ-Carbon Disulfide-Tris(tricyclohexylphosphine)-Triangulo-Triplatinum(0), $Pt_3(CS_2)_3(PCy_3)_3$ (3)

A large excess of CS_2 (*ca.* 1.5 g, 20 mmol) was condensed onto a frozen (−195 °C) solution containing 0.14 g (0.26 mmol) of $Pt(C_2H_4)_2(PCy_3)$ in 25 ml n-hexane. As the stirred contents warmed to RT, a yellow solution containing copious amounts of rust colored solid appeared. After 6 hours of stirring, the volume was reduced to *ca.* 15 ml, filtered, washed, with n-hexane, yielding a tan solid *3* (0.12 g, 84%) melting at 285 °C, dec. Calcd. for $Pt_3(CS_2)_3[P(C_6H_{11})_3]_3$: C, 41.36, H, 6.02; P, 5.61; S, 11.62; Pt, 35.36. Found: C, 41.50, H, 6.13; P, 5.46; S, 11.46; Pt, 35.12. Mol wt. Calcd: 1650. Found: 1554 (toluene).

A small portion of *3* (0.05 g) was placed in a vessel containing 25 ml n-hexane, opened to the atmosphere, and stirred for 24 hours. The solvent was then removed and the solid was shown to be starting material (*3*) via its infrared spectrum.

Tris-μ-Carbon Disulfide-Tris(tri-t-butylphosphine)-Triangulo-Triplatinum(0), $Pt_3(CS_2)_3[P(t\text{-}Bu)_3]_3$ (4)

This substance was prepared according to the literature method [1]. Similar to the procedure described for *3*, a small amount of *4* was exposed to air in a stirred hexane–petroleum ether solution (1:1) for 3 days. During this time, the solvent evaporated, leaving orange crystals which yielded the same infrared spectrum as for the title compound.

Attempts to prepare *4* via the precursor $Pt(C_2H_4)_2P(t\text{-}Bu)_3$ were unsuccessful due to the extreme instability of the latter complex. Also, attempts to obtain molecular weight data for *4* in benzene, methylene chloride, and toluene were unsuccessful due to limited solubility.

Results and Discussion

Although platinum(0) complexes with bulky phosphines are a topic of considerable current interest, the cluster chemistry of platinum is primarily based on the use of triphenylphosphine (or smaller ligands) as one of the principle ligating moieties. In the present work we have, for the most part, focused on the chemistry of trinuclear platinum(0) clusters containing bulky phosphines and CS_2 or SO_2 as ligands. The infrared data for these and other pertinent complexes are tabulated in Table I for comparison purposes.

Complexes of Sulfur Dioxide

We have found that bis(ethylene)(tricyclohexylphosphine)platinum(0) readily reacts with sulfur dioxide under mild conditions and in nearly quantitative yields to form the cyclic trimer $Pt_3(SO_2)_3(PCy_3)_3$. The structure of the complex is likely similar to the analogous $Pt_3(SO_2)_3(PPh_3)_3 \cdot C_7H_8 \cdot SO_2$ complex [5], although the spacial requirements of the bulky phosphine might alter the geometry somewhat. Molecular weight measurements suggest that the trimeric structure is maintained in solution, which undoubtedly contributes to the lack of reactivity with H_2 and ethylene.

As seen from the infrared data in Table I, it is clear that the shift to higher energies [ν(SO) 1248, 1077 cm^{-1}; δ(SO) 538 cm^{-1}] signifies the SO_2 is bridging rather than η^1-pyramidal as observed for $Pt(SO_2)$-

TABLE I. Characteristic IR Data (cm^{-1}) in Nujol.

Complex		ν(S–O)	δ(S–O)	ν(C–S)	δ(C–S)
Free SO_2	Ref. 15	1362, 1151	518		
$Pt(SO_2)(PCy_3)_2$	Ref. 1	1162, 1029	508		
$Pt(SO_2)(PPh_3)_2$	Ref. 10, 16	1182, 1149, 1035			
$Pt(SO_2)[P(t\text{-}Bu)_3]_2$	Ref. 1	1173, 1035	509		
$Pt_3(SO_2)_3(PCy_3)_3$		1248, 1077	538		
$Pt_3(SO_2)_3(PPh_3)_3$	Ref. 6	1260, 1245, 1071			
$Pd_3(SO_2)_3(PPh_3)_3$	Ref. 7	1252, 1237, 1064			
Free CS_2	Ref. 13b			1196, 1117	
$Pt(CS_2)(PPh_3)_2$	Ref. 11			1146	651
$Pt(CS_2)(PCy_3)_2$	Ref. 1			1133	658
$Pt_3(CS_2)_3(PCy_3)_3$				1113	
$Pt_3(CS_2)_3[P(t\text{-}Bu)_3]_3$	Ref. 1			1111	743

$(PCy_3)_2$ [1]. These infrared values compare favorably with those reported by Moody [6] and Werner *et al.* [7] (Table I) for $Pt_3(SO_2)_3(PPh_3)_3$ and $Pd_3(SO_2)_3(PPh_3)_3$ respectively. Also, characteristic [8] of transition metals with SO_2 in a bridging configuration, the oligomer is insensitive to O_2 and thus does not form the well known sulfato complex.

We have also observed an alternate route [9a] to the identical oligomer by first preparing the trinuclear cluster $Pt_3(CO)_3(PCy_3)_3$ [14], followed by subsequent reaction with sulfur dioxide. This process required that much greater care be exercised to insure the product is not contaminated with residual carbonyl containing materials. In addition to the enhanced speed with which the final product can be obtained, the former method is also preferred since the 'ligand free' [2c] $Pt(C_2H_4)_2(PCy_3)$ does not present opportunities for side reactions. The general utility of CO replacement in such clusters as a viable synthetic route to analogous SO_2 complexes is, however, supported by a report by Mingos and coworkers where they observed the ready conversion of $Pt_3(CO)_3(PPh_3)_4$ to $Pt_3(SO_2)_3(PPh_3)_3$ [9b].

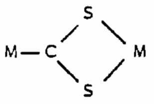
$Pt_3(SO_2)_3(PCy_3)_3$ does react with carbon monoxide, yielding a product of varying composition or a mixture of products which depend on the length of reaction and on the order of mixing. While we were not able to identify the latter product(s), the infrared spectra always suggested the presence of bridging (1210, 1065 cm^{-1}) SO_2 bands and both terminal (2005 cm^{-1}) and bridging (1775, 1833 cm^{-1}) CO bands, all of which are shifted compared to the trimeric clusters (*1*) and (*2*).

Complexes of Carbon Disulfide

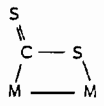
Although a number of CS_2–transition metal complexes have been reported in recent years [11], few polynuclear metal complexes containing CS_2 as a bridging unit are known [12]. In an earlier paper [1], we reported the first example of a trinuclear μ-CS_2 complex, $Pt_3(CS_2)_3[P(t\text{-}Bu)_3]_3$. The fact that $Pt[P(t\text{-}Bu)_3]_2$ but not $Pt(PCy_3)_2$ formed the trimer was rationalized on the basis of steric arguments. Since the above oligomer required CS_2 to serve a bridging function, it seemed reasonable that $Pt(C_2H_4)_2(PCy_3)$ should react with CS_2 in a manner similar to the reaction of $Pt(C_2H_4)_2(PCy_3)$ with SO_2, yielding the analogous CS_2 cluster. This approach proved to be valid and an air stable, tan solid was isolated and formulated as $Pt_3(CS_2)_3(PCy_3)_3$. The molecular weight data supports our postulation that the structure is trimeric. Further, the Pd– and Pt–SO_2 complexes described above also exhibit this structural type.

The exact nature of the CS_2 bonding is less certain than the degree of oligomerization. It has been reported [11] that a highly characteristic ν(CS) band in the region of 900 cm^{-1} exists for complexes of the type A shown below, thus excluding this bonding mode for our complexes since no such infrared band is observed (Table I).

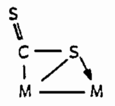
Another option [13] is that the bridging CS_2 group may be linked to one platinum via the carbon atom or through a η^2-bonded C–S linkage, while one sulfur atom is σ-bonded to the second platinum as shown in Types B and C. There have been no other polynuclear platinum(0)–CS_2 compounds reported;



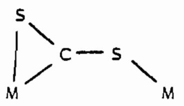
A



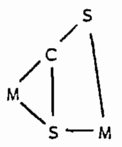
B



C



D



E

thus a direct comparison cannot be made. However, a nickel compound formulated as $[Ni(PPh_3)(CS_2)]_2$ [ν(C--S), 1122 cm^{-1}] has been described by Baird and Wilkinson [13b] and the CS_2 suggested to be bridging in a manner similar to Type C.

Two other bridging CS_2 geometries have also been reported (D and E) [12] and although they do not readily allow for M–M bonds so prevalent in platinum(0) cluster chemistry, they cannot be ruled out at this time.

It appears likely that an exact determination of the bonding in $Pt_3(CS_2)_3(PCy_3)_3$ and the analogous $Pt_3(CS_2)_3[P(t\text{-}Bu)_3]_3$ will have to await single crystal X-ray diffraction studies; however, initial attempts at growing suitable crystals of either complex have not proved successful.

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