is not a feasible method of heterogenizing catalysts. However, some metals from four-membered *cyclo*-metallodisiloxanes which are active catalysts for the disproportionation of tetraalkyldisiloxanes to dialkylsilane and poly(dialkylsiloxanes).[22]

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Registry No. I, 66515-89-7; II, 66515-90-0; V, 66515-91-1; VI, 66515-92-2; VII, 66515-93-3; VIII, 66515-94-4; IX, 66515-95-5; $Co_2(CO)_8$, 10210-68-1; $Fe(CO)_5$, 13463-40-6; $Ru_3(CO)_{12}$, 15243-33-1; TMDS, 3277-26-7; TMDG, 33129-30-5; BDSM, 18163-84-3.

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Contribution from Mobil Research and Development
Corporation, Central Research Division,
Princeton, New Jersey 08540

Thermal Decomposition of Hexachloroplatinic Acid

A. E. Schweizer* and G. T. Kerr

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The thermal decomposition of hexachloroplatinic acid has been the subject of two recent publications.[1,2] However, neither article identified the intermediate phase chemically and crystallographically and, therefore, failed to recognize some important implications of the chemistry of the intermediate.

Hexachloroplatinic acid, or chloroplatinic acid, is the most readily available compound of platinum. It is a hygroscopic material sold by the platinum assay. Anhydrous chloroplatinic acid has never been reported.[3] The commerical product is probably an oxonium salt of the hexachloroplatinate(IV) anion. Therefore, the correct formula is $[H_3O]_2[PtCl_6]\cdot xH_2O$ where x is variable; for a Pt assay of 40.0%, x is 2.32.[4]

Figure 1 shows a tracing of a thermogram of a sample of chloroplatinic acid obtained in He using a du Pont Model 950 thermogravimetric analyzer. The heating rate was 10°/min.

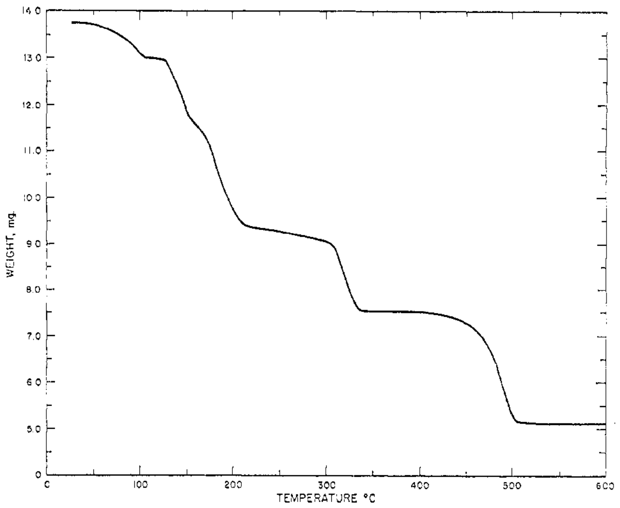

Figure 1.

Table I. Thermogravimetric Data of Chloroplatinic Acid

T, °C	sample wt, mg	% Pt obsd by anal. (H_2 reducn of separate samples)	compd present
25	13.61	40.42	$[H_3O]_2[PtCl_6]\cdot 2.04H_2O$
110–125	13.00		$[H_3O]_2[PtCl_6]\cdot 0.84H_2O$
at 220	9.35		approx $PtCl_4$
at 300	9.04		approx $PtCl_{3.5}$
350–415	7.50	73.5	$PtCl_2$[a]
above 510	5.11	100	Pt metal[b]

[a] For $PtCl_2$, theoretical % Pt = 73.32%. [b] For a 13.61-mg initial weight and 40.42% Pt, we calculate 5.50 mg of Pt at the end of the thermogram if no Pt is lost by volatilization of β-$PtCl_2$.

Identical thermograms were obtained in air or He at flow rates of 150 mL/min using either quartz or platinum sample pans. Thermograms in hydrogen gas all give elemental Pt below 100 °C. The starting material is very hygroscopic and hydrogen reduction to metal in the thermogravimetric balance was used for analysis. Also, intermediate compounds were all analyzed by hydrogen reduction to platinum. Table I shows actual weights of a typical thermogram under the stated conditions.

In air or He the final weight of metallic platinum is less than would be calculated from the initial weight of the sample and the platinum assay. When the thermogravimetric experiment at the composition shown between 350 and about 400 °C is interrupted and H_2 replaces the He purge at constant temperature, the reduction to metallic platinum occurs rapidly. The weight of platinum obtained then agrees with the platinum assay on the original sample. The formula weight of the solid in the temperature range of 350–400 °C (calculated using its weight relative to the weight of Pt metal obtained) corresponds to that of $PtCl_2$.

$PtCl_2$ is known in two different crystalline forms, α and β.[5,6] The structure of the α form has not been published. The β form contains discrete Pt_6Cl_{12} units and is volatile.[6,7] X-ray powder diffraction patterns of the $PtCl_2$ prepared by the thermogravimetric experiment were obtained using Cu Kα radiation both by photography and by use of a powder goniometer. We compared the diffractometer tracing to a powder pattern calculated from the structure of Broderson et al.[5,8] This shows that highly crystalline β-$PtCl_2$ is obtained thermogravimetrically; there was no evidence of the α form.

The weight loss above 375 °C must be due to the decomposition of $PtCl_2$ to Pt via

$$PtCl_2(s) \rightarrow Pt(s) + Cl_2(g)$$

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* To whom correspondence should be addressed at Air Products and Chemicals, Inc., Allentown, Pa. 18105

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and the volatilization of the molecular Pt_6Cl_{12}. The amount of Pt "missing" in the TG experiment has been observed to vary with sample size, heating rate, and gas flow rate. The thermodynamics and kinetics of these reactions have been studied via the reaction of Pt with Cl_2.[7]

Thermograms obtained at any heating rate from 1 to 30°/min in air or He show no plateaus corresponding to the composition $PtCl_4$. The constitutive water and HCl in the $(H_3O)_2(PtCl_6)$ cannot be removed below about 300 °C, and $PtCl_4$ begins to decompose to $PtCl_2$ and chlorine at this temperature.[9] Hence, it is not possible to prepare $PtCl_4$ in good yield in an inert atmosphere by a thermal decomposition of chloroplatinic acid. $PtCl_2$ does exhibit a narrow range of stability, from about 350 to 410 °C, and it should be possible to prepare the β-$PtCl_2$ in good yield by a thermal decomposition. Current preparation procedures for making $PtCl_2$ all suggest that thermal decomposition leads to impure products.[10,11] However, we have successfully prepared 10-g batches of pure, highly crystalline β-$PtCl_2$ by simple thermal decomposition of chloroplatinic acid in air using a tube furnace. The acid is spread into a thin layer (<5 mm thick) on the tube furnace boat, and a steady air purge through the tube is maintained, 200 mL/min, through a tube of approximately 1-L volume. The temperature is raised from room temperature to 350 °C in 50 °C steps over 3 h. The product in the furnace boat represents a 100% yield.

The volatility of Pt_6Cl_{12} in the thermal decomposition to metallic Pt offers an explanation for the ease of dispersing Pt as small crystallites on high surface area catalysts and catalyst supports.

Registry No. $[H_3O]_2[PtCl_6]\cdot xH_2O$, 26023-84-7.

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Contribution from the Paul M. Gross Chemical Laboratory,
Duke University, Durham, North Carolina 27706

A General Synthesis of Amine–Cyanoboranes

Patty Wisian-Neilson, Mrinal K. Das,
and Bernard F. Spielvogel*

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The amine–cyanoborane $Me_3N\cdot BH_2CN$ is a precursor in the synthesis of $Me_3N\cdot BH_2COOH$, the protonated boron analogue of the dipolar amino acid betaine, $Me_3N^+CH_2COO^-$.[1] Both $Me_3N\cdot BH_2COOH$ and its *N*-ethylamide derivative have demonstrated significant antitumor and hypolipidemic activity in mice.[1,2] Furthermore, several amine–cyanoboranes have also shown similar biological activity.[2] Although a number of amine–cyanoboranes have been prepared,[3–6] the methods used either resulted in low yields[3–5] or were limited as to reaction scale.[6] Therefore, in view of the potential uses of amine–cyanoboranes and their derivatives, it was desirable to find a convenient large-scale preparation of these compounds.

A number of amine–boranes, amine$\cdot BH_3$, have been prepared by the reaction of ammonium salts with lithium or sodium borohydride.[7] Using a similar procedure we have prepared a series of amine–cyanoboranes by the reaction of sodium cyanohydroborate and amine hydrochlorides in refluxing tetrahydrofuran (THF).[8]

$$\mathrm{NaBH_3CN + amine\cdot HCl \xrightarrow[65\ ^\circ C]{THF} \underset{\mathbf{1\text{-}6}}{amine\cdot BH_2CN} + H_2 + NaCl}$$

amine = Me_3N (**1**), Me_2NH (**2**), $MeNH_2$ (**3**), C_5H_5N (**4**), $PhNH_2$ (**5**), *p*-$MeC_6H_4NH_2$ (**6**)

In the cases of the reactions involving $Me_3N\cdot HCl$, $PhNH_2\cdot HCl$, and *p*-$MeC_6H_4NH_2\cdot HCl$, the crude products were solids which were readily purified by recrystallization or sublimation. Removal of the solvent from the reactions involving $Me_2NH\cdot HCl$ and $C_5H_5N\cdot HCl$, however, resulted in viscous oils which were difficult to crystallize or sublime. In these cases purification involved the dissolution of the oils in H_2O, followed by extraction of the amine–cyanoboranes into Et_2O, thereby removing the H_2O-soluble starting materials. The amine–cyanoboranes were then easily purified by sublimation. The purified products were obtained in good yields[9] and were identified by elemental analysis, IR and ^1H NMR spectroscopy, and melting point (Table I).

Although the amine–cyanoboranes were generally white crystalline solids, all attempts to crystallize or sublime **3**, the product of the reaction of $MeNH_2\cdot HCl$ and $NaBH_3CN$, were unsuccessful. Nevertheless, the viscous liquid obtained from the Et_2O extraction of the aqueous solution of the reaction products was found to have a satisfactory elemental analysis. Moreover, its ^1H NMR spectrum exhibited the expected triplet for the *N*-methyl protons due to coupling to the NH protons. Similar coupling was observed in the spectrum of $Me_2NH\cdot BH_2CN$.[6]

In a recent study of the isomers of $Me_3N\cdot BH_2(CN)$ Vidal and Ryschkewitsch[10] compared the $C{\equiv}N$ infrared frequencies of the two isomers and found that the isocyano absorption at 2135 cm^{-1} was at least 50 cm^{-1} lower then the $C{\equiv}N$ absorptions in the cyano isomer which range from 2185 to 2280 cm^{-1}. The lowest $C{\equiv}N$ absorptions in the infrared spectra of the compounds that we have prepared range from 2180 to 2200 cm^{-1} which indicates that the cyano and not the isocyano isomers were formed. Further evidence for the cyano structure in these compounds is the thermodynamic preference of the boron–carbon bond over the boron–nitrogen bond as demonstrated by the easy isomerization of $Me_3N\cdot BH_2NC$ to $Me_3N\cdot BH_2CN$[10] and $NaBH_3NC$ to $NaBH_3CN$.[11] In view of the conditions of the above reactions (i.e., refluxing THF), it is unlikely that the isocyano isomers would be isolated.

In addition, it may be noted that qualitatively the relative rates of these reactions seemed to correlate with the pK_a of the corresponding ammonium cations. For example, the reactions involving the methylamine hydrochlorides (pK_a's range from 9.8 to 11)[12] required several days to go to completion, i.e., for evolution of hydrogen to cease. On the other hand, the reactions of the hydrochlorides of the weaker bases (aniline, $pK_a = 4.6$, and pyridine, $pK_a = 5.3$)[12] were much faster and in some cases evolution of hydrogen was so vigorous that it was necessary to combine the reagents quite slowly in order to control the reaction.

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