added to 1 molar equiv of NaC_5Ph_5 in THF (50 mL) and the reaction stirred for 15 min. Removal of the solvent gave a brown residue that was dissolved in CH_2Cl_2 and eluted on a short Florisil column. Recrystallization from CH_2Cl_2/pentane gave **8** in 60% yields.

(η^5-Pentaphenylcyclopentadienyl)chloropalladium(II) Trimethylphosphine, 15. Trimethylphosphine (22 μL) was added to a solution of (η^5-pentaphenylcyclopentadienyl)(η^3-2-chloroallyl)palladium(II) (0.198 g) in chloroform (5 mL) under nitrogen and the solution gently refluxed at 70 °C overnight. Solvent was removed under reduced pressure and the residue columned on Florisil eluting with benzene and then chloroform. Partial evaporation of the green chloroform eluate followed by addition of hexane induced crystallization, yielding the *product* as green prisms (0.063 g, 30%), mp 187–189 °C. Anal. Calcd for $C_{38}H_{34}ClPPd$: C, 68.79; H, 5.16; Cl, 5.34. Found: C, 68.64; H, 5.36; Cl, 5.45. Similarly prepared were complexes **12–14** and **16–19**, isolated as green prisms (yields 30–65%).

(μ-Diphenylacetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 20. Dichlorobis(η^5-pentaphenylcyclopentadienyl)dipalladium(II) (0.0478 g) was stirred vigorously in dried THF (18 mL) under N_2 with 5 g of activated zinc dust and 0.121 g of diphenylacetylene until the solution turned dark green—usually about 2–4 h. The solution was then filtered and taken to dryness. The residue was taken up in benzene and chromatographed on an alumina column, eluting with benzene. The product was recrystallized from benzene/hexanes as dark green prisms (0.340 g): 65% yield; mp 241 °C dec.

(μ-Acetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 21. Dry THF (10 mL) was cooled to −50 °C and saturated at that temperature with acetylene. A 0.210-g sample of bis(μ-chloro)di(η^5-pentaphenylcyclopentadienyl)dipalladium(II) was added to the solution along with 5 g of activated Zn and the mixture stirred at 50 °C for 1 h with acetylene bubbling through the solution. The product was worked up as for **20** to give 0.149 g of bright green crystals (74% yield); mp 166–168 °C. Anal. Calcd for $C_{72}H_{52}Pd_2$: C, 76.53; H, 4.64. Found: C, 76.39; H, 4.78.

The following complexes from (a) liquid and (b) solid acetylenes were similarly prepared by (a) injection of the acetylene and (b) addition of the solid acetylene to a solution of bis(μ-chloro)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II) in dried THF (10 mL) in the presence of an excess of activated zinc. The compounds were characterized by their ^1H NMR and characteristic UV–visible spectra and by comparison with the previously reported analogue. **(μ-Hex-3-yne)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 22:** as green prisms (0.061 g, 73%), mp 255 °C dec, from hex-3-yne. **(μ-Di-*p*-tolylacetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 23:** as dark olive green prisms (0.088 g, 39%), mp 272 °C dec, from di-*p*-tolylacetylene. **(μ-Phenylacetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 24:** as green crystals (53% yield) from phenylacetylene. **(μ-Dimethylacetylenedicarboxylate)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 25:** as olive green crystals (35% yield) from dimethylacetylene dicarboxylate.

Bis(μ-carbonyl)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 26. Carbon monoxide was bubbled through a solution of bis(μ-chloro)di(η^5-pentaphenylcyclopentadienyl)dipalladium(II) (0.277 g) in dried THF (10 mL), in the presence of a large excess of activated zinc dust, for 5 min, and the resultant dark purple solution was filtered and solvent removed under reduced pressure by using a room temperature water bath. The residue was passed down a short Florisil column eluting with benzene, and evaporation of the filtrate to dryness afforded the *product* as a mauve solid (0.12 g, 45%), decomposition to a yellow solid on warming, mp 143–146 °C. Anal. Calcd for $C_{72}H_{50}O_2Pd_2$: C, 74.55; H, 4.36. Found: C, 73.92; H, 4.41.

(μ-Diphenylacetylene)bis(η^5-pentamethylcyclopentadienyl)dipalladium(I), 27. C_5Me_5Li (0.478 g) in 19 mL of dry THF was added to (0.738 g) bis(μ-chloro)bis(2-chloroallyl)dipalladium(II) in 14.6 mL of dry THF. After about 10 min the solution was a deep purple. A 0.365-g sample of diphenylacetylene and 2 g of activated zinc were added at this point, and the resulting mixture was stirred for 3 h. The green solution had a λ_{max} of 585 nm in the visible spectrum consistent with the formation of (μ-PhC≡CPh)$(Me_5C_5)_2Pd_2$, but all attempts to isolate the product from the solution were in vain.

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Registry No. **1**, 87183-80-0; **2**, 87183-81-1; **3**, 87183-82-2; **4**, 87183-83-3; **5**, 87183-84-4; **6**, 87183-85-5; **7**, 87183-86-6; **8**, 63946-67-8; **9**, 87183-87-7; **10**, 87183-88-8; **11**, 87183-89-9; **12**, 87183-90-2; **13**, 87183-91-3; **14**, 87183-92-4; **15**, 87183-93-5; **16**, 63947-95-5; **17**, 87183-94-6; **18**, 87183-95-7; **19**, 87183-96-8; **20**, 39459-32-0; **21**, 87183-97-9; **22**, 87183-98-0; **23**, 87183-99-1; **24**, 87184-00-7; **25**, 87184-01-8; **26**, 87184-02-9; **27**, 87184-03-0; 5-chloro-1,2,3,4,5-pentaphenylcyclopentadiene, 5724-11-8.

Demethylation of Methylcobalamin by Platinum(IV)/Platinum(II) Couples. Formation of Methylplatinum(IV) Products

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The demethylation of methylcobalamin (CH_3-B_{12}) by combinations of Pt(IV) ($PtCl_6^{2-}$, $Pt(CN)_4Cl_2^{2-}$, or $Pt(CN)_5Cl^{2-}$) and Pt(II) ($PtCl_4^{2-}$ or $Pt(CN)_4^{2-}$) requires platinum in both oxidation states. The reactions occur with 1:1 stoichiometry between Pt(IV) and CH_3-B_{12}. The sole B_{12} product is H_2O-B_{12}^+, whether or not oxygen is present. ^{195}Pt and ^{13}C NMR spectroscopy is used to show that the platinum products are CH_3Pt^{IV} and Pt^{II} complexes and that the methyl group is transferred to the platinum of the Pt(II) reactant. These CH_3Pt^{IV} products are susceptible to reaction with the nucleophiles OH^-, Cl^-, and CN^- to produce the corresponding organic products CH_3OH, CH_3Cl, and CH_3CN.

Introduction

Methylcobalamin (CH_3-B_{12}) has been shown to methylate a broad range of metal and metalloid ions in aqueous solution. Such reactions have attracted considerable attention for both mechanistic and environmental reasons.[2-4] In 1971 it was reported that platinum salts in both the II and the IV oxidation states were required for the deme-

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thylation of CH_3-B_{12}.[5] Taylor et al.[6] showed that a mixture of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ reacted with CH_3-B_{12} to give a stable CH_3Pt complex, for which the structure $CH_3PtCl_3^{2-}$ was suggested. Following this work we reported a kinetic study of this reaction which indicated that a complex between CH_3-B_{12} and $PtCl_4^{2-}$ occurs before demethylation can proceed.[7] At this point, many important details of the reaction were still unsolved, including the nature of the products, the identity of the platinum reactant that accepts the methyl group (Pt(II) or Pt(IV)?), the structures of intermediates, and the mechanism of the methyl-transfer step itself. The reaction is of special interest from a mechanistic standpoint because transfer of the organic group is achieved only after complex formation with the reactant. Therefore, it represents an alternative to, or possibly a special case of, direct attack on the carbon–metal bond by homolytic[8] or electrophilic[4] pathways.

This report and the one that follows represent an expansion of our earlier work to encompass combinations of the Pt(IV) complexes $PtCl_6^{2-}$, $Pt(CN)_4Cl_2^{2-}$, $Pt(CN)_5Cl^{2-}$, $Pt(CN)_5I^{2-}$, and $Pt(CN)_6^{2-}$ with the Pt(II) complexes $PtCl_4^{2-}$ and $Pt(CN)_4^{2-}$. In this paper we report the product analysis and the stoichiometry for these reactions. This was done in order to determine the inorganic platinum product and to clear up some confusion about the oxidation state of the methylplatinum product and also to determine which of the two platinum reactants accepts the methyl group. The report that follows this one deals with the kinetics and addresses the remaining mechanistic questions.

Experimental Section

Materials. $Na_2PtCl_6 \cdot 6H_2O$, K_2PtCl_4, and $Na_2Pt(CN)_4$ were purchased from D.F. Goldsmith, Inc., and were recrystallized twice from water. $Na_2Pt(CN)_4Cl_2$[9] and $Na_2Pt(CN)_5Cl$[10] were synthesized by published procedures. Methylcobalamin was obtained from Sigma Inc., or synthesized by the method of Dolphin.[11] Iodomethane (90 or 60–67% ^{13}C) was purchased from Stohler Inc.

Reaction Products and Stoichiometry. All experiments were performed under dim light and without exclusion of oxygen unless noted. Consumption ratios for Pt(IV):CH_3-B_{12} were determined with a GCA/McPherson and a Cary Model 15 spectrophotometer by titrating a solution of CH_3-B_{12} containing a tenfold excess of the Pt(II) complex with a solution of the Pt(IV) complex. The details have been described previously by Taylor et al.[6]

The ^{13}C NMR spectral studies were carried out on a Varian XL-100 (25.2 MHz) or on a Nicolet 300 (75.5 MHz) spectrometer. Spectra were recorded at 4 °C locked to the solvent D_2O, using broad-band (3000-Hz) proton decoupling. Typically, equimolar amounts of Pt(IV) and $^{13}CH_3$-B_{12} (~5 mM) were dissolved in D_2O containing an excess of the Pt(II) complex (50 mM); spectra were recorded as soon as reactions were complete. This was judged from B_{12} electronic spectra in the visible region. Decomposition of the organoplatinum complexes in certain cases was accomplished by adding solid NaCl or NaCN to the NMR tubes and allowing to stand overnight in the dark before recording the spectra again. The ^1H NMR studies were done on a Brüker 270-MHz spectrometer at 25 °C. Chemical shifts were measured with respect to internal TSP.

The ^{195}Pt NMR experiments were performed on a Nicolet 300 spectrometer. An aqueous solution (100 mL) of 3 mM $^{13}CH_3$-B_{12} (60–67% enriched), $Na_2PtCl_6 \cdot 6H_2O$, and K_2PtCl_4 was allowed to react at room temperature until the $^{13}CH_3$-B_{12} had completely disappeared (24 h). Then the H_2O-B_{12}^+ product was separated from the aqueous phase by phenol extraction. The aqueous phase was lyophilized in the dark, stored at 0 °C, and dissolved in 3 mL of D_2O just prior to recording the spectrum. A control consisting of both platinum complexes (i.e., Pt(II) and Pt(IV)) was subjected to the same extraction procedure. These spectra were recorded at 4 °C, and locked to D_2O, and $PtCl_6^{2-}$ was used as the reference.

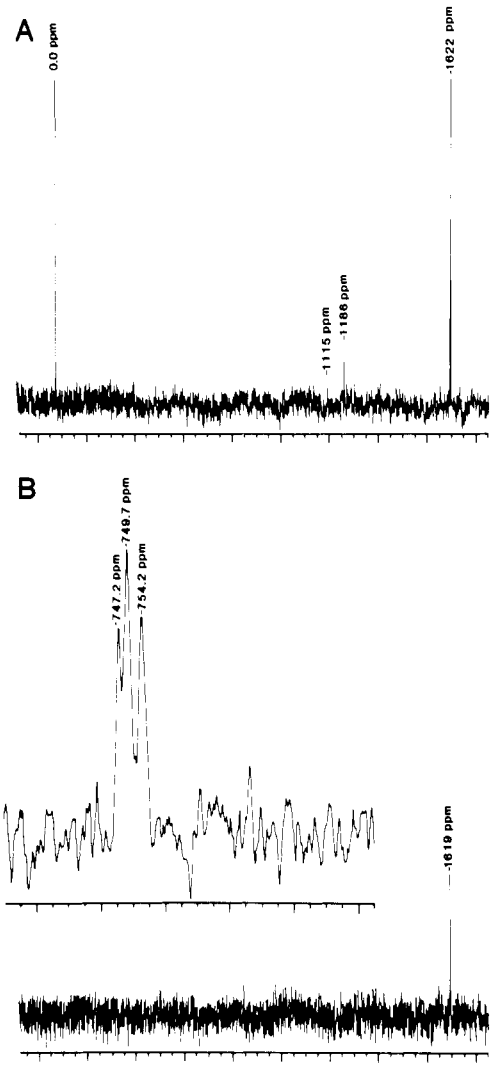

Figure 1. The ^{195}Pt NMR spectra of the reaction of CH_3-B_{12} with $PtCl_6^{2-}$ and $PtCl_4^{2-}$: (A) spectrum of Na_2PtCl_6 and K_2PtCl_4 in D_2O before addition of CH_3-B_{12} (see ref 12); (B) spectrum of the reaction mixture after complete demethylation of CH_3-B_{12}.

Results

All of the reactive Pt(IV)/Pt(II) couples examined so far, including the $PtCl_6^{2-}/PtCl_4^{2-}$ system that was studied previously,[7] demethylate CH_3-B_{12} quantitatively to H_2O-B_{12}^+, as shown by spectral changes of the corrinoid system in the visible region (isosbestic points at 340, 375, and 494 nm) and by the appearance of the resonances of H_2O-B_{12}^+ in the ^1H NMR spectrum. Spectrophotometric titration of a mixture of CH_3-B_{12} and Pt(II) complex with a solution

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Table I. ^{13}C NMR Data for the $^{13}CH_3Pt$ Products

Pt reactants	product[a] δ	product[a] J_{C-Pt}, Hz
$PtCl_4^{2-}$:$PtCl_6^{2-}$	3.3	465
$Pt(CN)_4Cl_2^{2-}$	3.4	463
$Pt(CN)_5Cl^{2-}$	3.3	462
$Pt(CN)_4^{2-}$:$PtCl_6^{2-}$	−9.6	378
$Pt(CN)_4Cl_2^{2-}$	−9.4 (major)	380
	−23.9 (minor)	280
$Pt(CN)_5Cl^{2-}$	−16.3	311

[a] TSP internal standard. Variance in δ as determined from replicate experiments, ±0.1 ppm, and in J, ±2 Hz. All experiments were carried out at least in duplicate.

of Pt(IV) complex were performed for the Pt(IV)/Pt(II) couples: $Pt(CN)_4Cl_2^{2-}/PtCl_4^{2-}$, $PtCl_6^{2-}/Pt(CN)_4^{2-}$, and $Pt(CN)_4Cl_2^{2-}/Pt(CN)_4^{2-}$. These titrations show that Pt(IV) is consumed to the extent of 0.94 ± 0.13, 1.02 ± 0.06, and 0.99 ± 0.15 mol/mol of CH_3-B_{12}, respectively. Electronic spectral changes are not affected by the absence of oxygen, which rules out B_{12r} (Co(II)) or B_{12s} (Co(I)) as products of this reaction.

The ^{195}Pt NMR spectra of a reaction of 1:1:1 $^{13}CH_3$-B_{12} (60–67% ^{13}C):$PtCl_6^{2-}$:$PtCl_4^{2-}$ are shown in Figure 1. A spectrum of the products of this reaction shows that $PtCl_6^{2-}$ is consumed in the reaction while $PtCl_4^{2-}$ at −1618.8 ppm ($PtCl_6^{2-}$ reference) remains as a product.[12] In addition a resonance appears at −750 ppm that represents the isotope triplet of a methylplatinum compound. The relative intensities of the peaks agree well with those expected for a C–Pt compound composed of 60–67% ^{13}C (i.e., in the range 1:1:1 to 1:1.25:1). The ^{13}C–^{195}Pt spin–spin coupling constant obtained from the outer peaks (453 Hz) is in the range reported for other methylplatinum compounds.[13]

Methylplatinum products were studied for each Pt(IV)/Pt(II) couple by ^{13}C NMR spectroscopy. The NMR data are listed in Table I. Reactions employing $PtCl_4^{2-}$ as the Pt(II) reactant appear to generate the same CH_3Pt product regardless of the Pt(IV) reactant (i.e., 3.4 ± 0.1 ppm). The spectrum obtained from the $PtCl_6^{2-}/PtCl_4^{2-}$ system is shown in Figure 2A. The C–Pt coupling constant of this compound is in good agreement with the organoplatinum product observed in the ^{195}Pt spectrum. The ^1H NMR spectrum of the completed reaction mixture shows a pseudotriplet in the ratio 1:4:1 at δ 3.04 (J_{H-Pt} = 78.2 Hz).

Products from reactions where $Pt(CN)_4^{2-}$ is used as the Pt(II) reactant were found to depend on the Pt(IV) reactant. For these reactions, ^{13}C spectra are shown in Figure 2B–D. Demethylation with $PtCl_6^{2-}/Pt(CN)_4^{2-}$ gives rise to a triplet attributable to a methylplatinum compound at −9.50 ± 0.1 ppm. The entire spectrum including the reference peak of TSP is broadened. The ^1H NMR spectrum of the H_2O-B_{12}^+ product in this case shows that all resonances are broadened, as well, which indicates that paramagnetic species may be present. Reproducibility was obtained in several replicates. The UV–visible spectrum did not indicate the presence of B_{12r} (i.e., Co(II)). This broadening phenomenon does not appear in any of the other systems we studied. It is not possible to quantitate the methylplatinum product by ^{13}C NMR, and furthermore, the methyl resonance is not visible in the ^1H NMR spectrum for quantitation. Therefore it is difficult to estimate the amount of paramagnetic species or any other byproduct produced. The stoichiometry between Pt(IV) and CH_3-B_{12} (1.02 (±0.06):1) suggests a low yield of paramagnetic product or else formation in a post-demethylation step.

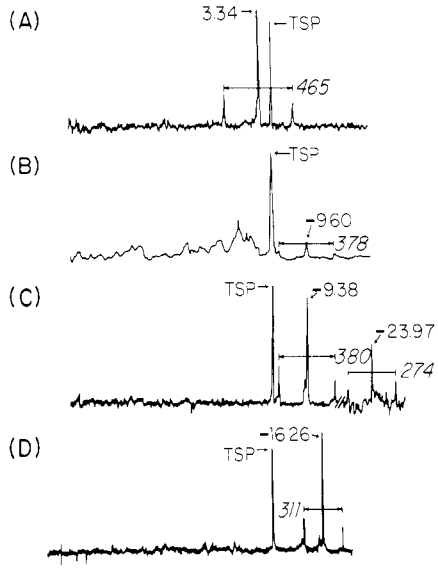

Figure 2. ^{13}C NMR spectra of reactions of $^{13}CH_3$-B_{12} (90% enriched) with Pt(IV)/Pt(II) couples: (A) $PtCl_6^{2-}/PtCl_4^{2-}$; (B) $PtCl_6^{2-}/Pt(CN)_4^{2-}$; (C) $Pt(CN)_4Cl_2^{2-}/Pt(CN)_4^{2-}$; (D) $Pt(CN)_5Cl^{2-}/Pt(CN)_4^{2-}$.

The reaction with $Pt(CN)_4Cl_2^{2-}$ also produces a resonance at −9.5 ppm; in addition, a minor peak appears at −23.9 ppm. Reaction with $Pt(CN)_5Cl^{2-}$ generates a resonance at −16.3 ppm. The product at −9.5 ppm is converted to the one at −16.3 ppm by the addition of one equivalent of NaCN to the solution.

These organoplatinum products were shown to react with nucleophiles. The product at 3.4 ppm is stable for long periods in aqueous solution (>1 week at room temperature) but is rapidly converted to a singlet at 28.8 ppm, corresponding to $^{13}CH_3Cl$, when the solution is made 1 M in NaCl or when the demethylation reaction is carried out in 1 M NaCl. The compound at −9.5 ppm is more sensitive—decomposing to $^{13}CH_3OD$ (51.8 ppm) and $^{13}CH_3Cl$ in D_2O at room temperature within a few days by reaction with the solvent or with chloride ion (~10 mM), which is generated during the demethylation reaction; when the demethylation reaction is carried out in 1 M NaCl, only CH_3Cl is produced. The compound at −16.3 ppm is stable to a 1 M Cl^- solution in D_2O at room temperature but yields $^{13}CH_3CN$ (3.0 ppm) when an excess of NaCN (50 equiv) is added. The identities of the organic products were confirmed with authentic samples by ^1H (CH_3Cl) or by both ^1H and ^{13}C (CH_3OD, CH_3CN) NMR spectroscopy. We could find no evidence for metallic platinum as a product in any of these decomposition reactions.

Discussion

The ^{195}Pt NMR data show that the demethylation of CH_3-B_{12} by the $PtCl_6^{2-}/PtCl_4^{2-}$ couple results in the consumption of the Pt(IV) reactant, but the Pt(II) reactant is either unaltered or regenerated. Together with the results of the other products studies, this leads to the reaction in eq 1, in which the methylplatinum product is

$$CH_3\text{-}B_{12} + Pt(IV) + Pt(II) \xrightarrow{H_2O} H_2O\text{-}B_{12}^+ + CH_3Pt^{IV} + Pt(II) \quad (1)$$

(12) Freeman, W.; Pregosin, P. S.; Sze, S. N.; Venanzi, L. M. *J. Magn. Reson.* **1976**, *22*, 473. The peak at −1186 ppm is $PtCl_3(H_2O)^-$ and the one at −1115 ppm may be $PtCl_2(H_2O)_2$, both from aqueous hydrolysis of $PtCl_4^{2-}$.

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formulated as a platinum(IV) complex. The ^{195}Pt chemical shift of the methylplatinum product is consistent with this assignment, since it lies between $PtCl_6^{2-}$ and $PtCl_4^{2-}$. Clearly, an upfield shift is expected for methyl substitution for chloro in $PtCl_4^{2-}$, cf. *trans*-[Pt(Me)ClL$_2$], −4509 ppm, vs. *trans*-[PtCl$_2$L$_2$], −3938 ppm, for L = PEt_3, and −4532 ppm vs. −3771 ppm, for L = $AsMe_2Ph$.[14]

We have used ^{13}C NMR to examine the nature of the methylplatinum products and to provide insight into the mechanism of the methyl group transfer from cobalt to platinum. Reactions in which $PtCl_4^{2-}$ was used as the Pt(II) reactant produce the same CH_3Pt^{IV} product regardless of the Pt(IV) complex used (Table I). This provides convincing evidence for methyl transfer to the Pt(II) reactant to generate, upon formal two-electron oxidation, $CH_3Pt^{IV}Cl_5^{2-}$, with concomitant reduction of the Pt(IV) reactant to regenerate Pt(II) as shown in eq 2.

$$*PtCl_4^{2-} + PtCl_6^{2-} \xrightarrow{CH_3\text{-}B_{12}} \underset{I}{CH_3{*}PtCl_5^{2-}} + PtCl_4^{2-} + Cl^- \quad (2)$$

$$(Pt(CN)_4Cl_2^{2-}) \rightarrow (Pt(CN)_4^{2-} + Cl^-)$$

$$(Pt(CN)_5Cl^{2-}) \rightarrow (Pt(CN)_4^{2-} + CN^-)$$

Reactions employing $Pt(CN)_4^{2-}$ as the Pt(II) reactant can be product also, in a similar manner. Thus, demethylation with $PtCl_6^{2-}$ or $Pt(CN)_4Cl_2^{2-}$ yields II at −9.5 ppm:

$$*Pt(CN)_4^{2-} + PtCl_6^{2-} \xrightarrow{CH_3\text{-}B_{12}} \underset{II}{CH_3{*}Pt(CN)_4Cl^{2-}} + PtCl_4^{2-} + Cl^- \quad (3)$$

$$(Pt(CN)_4Cl_2^{2-}) \rightarrow (Pt(CN)_4^{2-} + Cl^-)$$

Demethylation with $Pt(CN)_5Cl^{2-}$ presumably yields II as the initial product also, but in this case the CN^- liberated during the reaction displaces chloride from II to yield $CH_3Pt(CN)_5^{2-}$ (III) at −16.3 ppm. The conversion of II to III by CN^- was verified by the addition of 1 equiv of NaCN to the reaction mixture of the $Pt(CN)_4Cl_2^{2-}$/$Pt(CN)_4^{2-}$ system after completion of the demethylation reaction.

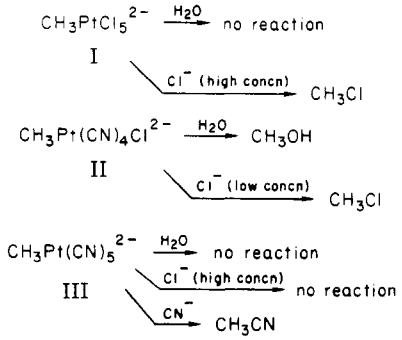
$$*Pt(CN)_4^{2-} + Pt(CN)_5Cl^{2-} \xrightarrow{CH_3\text{-}B_{12}} II + Pt(CN)_4^{2-} + CN^- \quad (4)$$

$$II + CN^- \rightarrow \underset{III}{CH_3{*}Pt(CN)_5^{2-}} + Cl^- \quad (5)$$

The NMR parameters (Table I) are supportive of the assignments for I–III. The chemical shift of the methyl carbon changes in the order $CH_3PtCl_5^{2-} > CH_3Pt(CN)_4Cl^{2-} > CH_3Pt(CN)_5^{2-}$, as expected due to the stronger electron donor ability of cyanide over chloride. The trend in $J_{C\text{-}Pt}$ follows the same order. This can be explained by hybridization arguments; that is, the σ character of the C–Pt bond in C–Pt–L should diminish as the Pt–L bond gains in Pt σ (s, d, p) character as chloride ligands are replaced with cyanide.[15] Along this same series, addition of the fifth CN^- ligand has almost as large an effect on $J_{C\text{-}Pt}$ as the first four combined. This suggests that chloride in II is trans to the methyl group, since a trans ligand has a greater effect on the hybridization of the C–Pt bond than does cis. A trans chloride may also explain the lability of the chloride to substitution with CN^- (II → III).

The methylplatinum product from demethylation of CH_3-B_{12} by $PtCl_6^{2-}$/$PtCl_4^{2-}$ has been proposed by others[16] to be $CH_3PtCl_3^{2-}$. These investigators isolated a product chromatographically that gave a ^1H NMR signal identical with the one which we observed in reaction mixtures. However, the results of our ^{195}Pt NMR experiments would appear to rule out this structure for the following reasons: (a) the ^{195}Pt chemical shift of $CH_3PtCl_3^{2-}$ is expected to appear upfied with respect to $PtCl_4^{2-}$[14] and (b) the appearance of both platinum species in the II oxidation state requires the formation of an oxidized product, and this does not occur.[17]

Scheme I. Reactions of I–III with Nucleophiles



The product $CH_3PtCl_5^{2-}$ is the first example of a CH_3-Pt^{IV} complex without stabilizing back-bonding ligands such as PR_3 or AsR_3.[18] All the methylplatinum products appear to undergo nucleophilic attack at the methyl carbon. These reactions are summarized in Scheme I. The reaction with nucleophiles helps to assign the oxidation state of the platinum as IV, since Pt^0, which is not found, would be expected to arise as the major platinum product if the oxidation state were II, i.e.

$$X^- \frown CH_3Pt^{II} \longrightarrow XCH_3 + Pt^0$$

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Registry No. CH_3-B_{12}, 13422-55-4; $^{13}CH_3$-B_{12}, 43184-67-4; H_2O-B_{12}^+, 13422-52-1; $PtCl_6^{2-}$, 16871-54-8; $Pt(CN)_4Cl_2^{2-}$, 38725-65-4; $Pt(CN)_5Cl^{2-}$, 38725-82-5; $PtCl_4^{2-}$, 13965-91-8; $Pt(CN)_4^{2-}$, 15004-88-3; $CH_3PtCl_5^{2-}$, 85625-92-9; $CH_3Pt(CN)_4Cl^{2-}$, 87136-40-1; $CH_3Pt(CN)_5^{2-}$, 87136-41-2; CH_3Cl, 74-87-3; CH_3OH, 67-56-1; CH_3CN, 75-05-8.

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(17) There are additional objections to the assignment of the methylplatinum product as $CH_3PtCl_3^{2-}$. First, the UV spectrum that was reported[16b] resembles $PtCl_6^{2-}$ more closely than $PtCl_4^{2-}$. Second, a platinum oxidation state of +2 was assigned from an ESCA study[16c] based on the fact that the two maxima are closer to those of $PtCl_4^{2-}$ than to those of $PtCl_6^{2-}$. However, the published ESCA spectrum is more readily interpreted as consisting of two pairs of peaks, one of which could represent $PtCl_4^{2-}$ (the other Pt product that we observe). The additional pair are *in between* those of $PtCl_6^{2-}$ and $PtCl_4^{2-}$; that is, at lower energies than $PtCl_6^{2-}$ but higher energies than $PtCl_4^{2-}$. This is consistent with $CH_3PtCl_5^{2-}$ but not $CH_3PtCl_3^{2-}$, since the latter would be expected to give maxima at lower energies than $PtCl_4^{2-}$, in line with the greater electron-donating ability of CH_3 compared with Cl ligands. Third, a ^{35}Cl NMR experiment[16c] to determine the number of Cl ligands in the compound by liberation with excess SCN^- may be invalid because an independent determination of the concentration of the platinum in the material that was assayed was not reported.

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