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Registry No. $Fe^{III}P$ (monomer), 64364-99-4; $Fe^{III}P$ (dimer), 64365-02-2; ascorbic acid, 50-81-7.

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Dimethyl Compounds of Platinum(II). 2. Reactions Involving Carbon–, Silicon–, and Germanium–Halogen Bonds

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Reactions of GeR_nX_{4-n} (X = Cl, R = Me, n = 1, 2, 3; X = Cl, R = Ph, n = 2, 3; X = Br, R = Me, Ph, n = 3) with $PtMe_2$(N-N) (N-N = bipyridine, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) afforded the new compounds $[PtMe_2X(GeR_nX_{3-n})(N\text{-}N)]$. The compounds were stable to H_2O, alcohol (except for n = 3), pyridine, and PPh_3. Compounds with formula $[PtMe_2X(GeR_3)(bpy)]$ (R = Me, Ph; X = Cl) were not stable in solution and decomposed to $PtMe_2Cl(CH_2Cl)(bpy)$. Exchange reactions of $[PtMe_2Cl(MR_nCl_{3-n})(bpy)]$ with $M'R_mCl_{4-m}$ (M, M′ = Ge, Sn, Pb) were studied. Reactions with $[GeR_3Br]$ resulted in bromine exchange. In the presence of moisture SiR_nCl_{4-n} (R = Ph, Me; n = 0, 1, 2) reacted with $PtMe_2(bpy)$ in CH_2Cl_2 to give $PtMeCl(bpy)$. Reactions of CR_nCl_{4-n} gave the following results (R = Ph, Me; n = 0, 1, 2, 3): Trans oxidative addition occurred with CCl_4 and $CPhCl_3$. With CPh_2Cl_2 and CPh_3Cl the compound $PtMe_2Cl_2(bpy)$ was obtained. With $CMeCl_3$ trans addition and further reaction to the vinyl compound $[PtMe_2Cl(CH_2CCl)(bpy)]$ occurred. No reaction was observed with CMe_3Cl. Reactions of CH_nCl_{4-n} (n = 0, 2, 3) proceeded via trans oxidative addition to $[PtMe_2Cl(CH_nCl_{3-n})(bpy)]$, except in the case of CH_2Cl_2 when also cis addition was observed. The rate of the conversion cis → trans was enhanced by added $SiPh_3Cl$.

Introduction

In a previous paper oxidative-addition reactions with square-planar d^8 compounds involving tin– and lead–halogen bonds were reported.[1] It was shown that reactions of $PtMe_2$(N-N) (N-N = bipyridine, phenanthroline) with tin and lead compounds of general formula MR_nCl_{4-n} (M = Sn, R = Me, Ph, n = 0, 1, 2, 3; M = Pb, n = 2, 3) proceeded via a trans addition and the new compounds $[PtMe_2Cl(MR_nCl_{3-n})(N\text{-}N)]$ were obtained in high yield. It was shown that the stability of the products was critically dependent upon the nature of the (MR_nCl_{3-n}) group. Since several isostructural compounds of divalent platinum were known with Si, Ge, Sn, or Pb,[2-7] it was of interest to investigate the reactions of $PtMe_2$(N-N) with analogous MR_nCl_{3-n} compounds in which M = C, Si, or Ge. In addition reactions of CH_nCl_{4-n} with $PtMe_2(bpy)$ were also studied.

Experimental Section

General Information. Although the compounds prepared in this study were stable in air, several of the starting materials were susceptible to atmospheric moisture. Therefore all preparations were carried out in a dry nitrogen atmosphere. The abbreviations bpy = 2,2′-bipyridine and Ph_2Me_2phen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline are used in the text.

Chemicals. Carbon, silicon, and germanium alkyl or aryl chlorides were commercially available and were distilled prior to use. Reagent grade solvents were dried with P_2O_5 and distilled. ^1H NMR spectra in CH_2Cl_2 (ppm relative to CH_2Cl_2) or $CDCl_3$ (ppm relative to Me_4Si) were recorded on a Varian HA100 NMR spectrometer. Elemental analyses were performed by Childers Laboratories, Milford, N.J., and by Chemical Analytical Services, Berkeley, and are summarized in Table I.

Preparation of $[PtMe_2Cl(GeMe_2Cl)(Ph_2Me_2phen)]$. $GeMe_2Cl_2$ was added slowly in small drops with the aid of a syringe to a stirred solution of $PtMe_2(Ph_2Me_2phen)$[1] (0.33 mmol) in CH_2Cl_2 (~2 mL). As soon as the solution had turned yellow, further addition of $GeMe_2Cl_2$ was stopped (a slight excess was used). Subsequently hexane was added until the solution started to cloud (5–10 mL). At −20 °C bright yellow crystals were obtained in 65% yield. The compound $[PtMe_2Cl(GeMeCl_2)(Ph_2Me_2phen)]$ was obtained by a similar procedure.

Preparation of $[PtMe_2Cl(SnMe_2Cl)(Ph_2Me_2phen)]$. This compound was prepared similarly to $[PtMe_2Cl(GeMe_2Cl)(Ph_2Me_2phen)]$ in 90% yield.

Preparation of $[PtMe_2Cl(GeMeCl_2)(bpy)]$. $PtMe_2(bpy)$ (0.5 mmol) was dissolved in a minimum amount of CH_2Cl_2 (~3 mL) and subsequently $GeMeCl_3$ was added in small drops with a syringe until the solution turned yellow. Then ether (3 mL) was added to the reaction mixture in which crystallization was already observed. After 10 min at 0 °C the crystals were collected on a filter with the aid of a pipet and washed with ether/CH_2Cl_2 and ether. Light yellow crystals of $[PtMe_2Cl(GeMeCl_2)(bpy)]$ were obtained in 75% yield. Similar yields were obtained for $[PtMe_2Cl(GeMe_2Cl)(bpy)]$ and $[PtMe_2Cl(GePh_2Cl)(bpy)]$. $[PtMe_2Cl(GePh_3)(bpy)]$ was prepared similarly in 90% yield with a threefold excess of $GePh_3Cl$ added at once to the $PtMe_2(bpy)$ solution. In the case of $[PtMe_2Br(GePh_3)(bpy)]$ a twofold excess was used and the yield was also 90%. $[PtMe_2Cl(GePh_3)(bpy)]$ was unstable in CH_2Cl_2 solution and decomposed slowly to $[PtMe_2Cl(CH_2Cl)(bpy)]$.

Preparation of $[PtMe_2Cl(GeMe_3)(bpy)]$. $PtMe_2(bpy)$ (0.5 mmol) was dissolved in a minimum amount of CH_2Cl_2 (~3 mL). Immediately after the solution was cooled with an ice bath, excess

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Table I. Analytical Results

Compd[a]	% C		% H		% Cl		% N		% others	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
PtMeCl(bpy)	32.88	32.66	2.76	2.75	8.82	9.06	6.97	6.96	48.5 (Pt)	49.6 (Pt)
PtMeBr(bpy)	29.61	29.56	2.49	2.64	17.91	18.12	6.28	6.21		
$PtMe_2Cl_2(bpy)$	31.87	31.98	3.12	3.28	15.68	15.62	6.20	6.09		
$PtMe_2Cl(CHCl_2)(bpy)$	33.48	33.35	3.46	3.43	15.21	14.89	6.01	6.02	42.1 (Pt)	41.8 (Pt)
$PtMe_2Cl(CClCH_2)(bpy)$	35.15	35.06	3.37	3.41	14.82	15.06	5.86	5.81	41.0 (Pt)	40.8 (Pt)
$PtMe_2Cl$(allyl)(bpy)	39.35	39.16	4.18	4.17	7.74	7.86	6.12	6.13		
$PtMe_2Cl(CPhCl_2)(bpy)$	39.56	39.26	3.32	3.31	18.44	17.32	4.86	4.71		
$PtMe_2Cl(CCl_3)(Ph_2Me_2phen)$	47.11	46.40	3.54	3.65	19.18	19.70	3.79	3.74	25.9 (Pt)	26.4 (Pt)
$PtMe_2Cl(GeMe_3)(bpy)$	33.70	32.84	4.34	4.05	6.63	7.79	5.24	5.31		
$PtMe_2Br(GeMe_3)(bpy)$	31.12	30.10	4.00	3.88	13.80[b]	14.26	4.84	4.68		
$PtMe_2Cl(GePh_3)(bpy)$	49.99	49.30	4.06	4.10	4.92	6.20	3.89	3.85		
$PtMe_2Cl(GeMe_2Cl)(bpy)$	30.30	30.55	3.63	3.45	12.78	12.98	5.05	5.24	13.03 (Ge)	13.08 (Ge)
$PtMe_2Cl(GeMeCl_2)(bpy)$	27.14	26.95	2.98	3.01	18.49	18.68	4.87	4.81		
$PtMe_2Cl(GeMe_2Cl)(Ph_2Me_2phen)\cdot CH_2Cl_2$	44.11	44.67	4.06	4.13	16.80	16.41	3.32	3.30		
$PtMe_2Br(GePh_3)(bpy)$	47.08	46.30	3.82	3.76	10.44[b]	10.96	3.66	3.59		

[a] Decompositions (in some cases with melting) were observed at 150–240 °C. [b] % Br.

Table II. ^1H NMR Data of Pt–Ge and Pt–C Compounds (ppm Relative to CH_2Cl_2, in CH_2Cl_2 Solution)

Compound	Pt–Me resonances[a]	R′ or GeR_nCl_{3-n}[a]	bpy[b] or Ph_2Me_2phen[a,b]
PtMeCl(bpy)	−4.25 (78)		4.20, 3.83; 2.32, 2.13; 2.75–2.73
PtMeBr(bpy)	−4.21 (77)		4.41, 3.79; 2.25, 2.18; 2.85–2.70
$PtMe_3Cl(bpy)$	−4.06 (70)	−4.89 (74)	3.56; 2.31; 2.71; 2.94
$PtMe_3Br(bpy)$	−3.96 (70)	−4.79 (75)	3.64; 2.35; 2.76; 2.98
$PtMe_2Cl$(allyl)(bpy)	−4.05 (70)	−3.22 (94.5)[c]	3.51; 2.30; 2.69; 2.91
$PtMe_2Cl(CCl_3)(bpy)$	−3.54 (71)		Too insoluble
$PtMe_2Cl(CCl_3)(Ph_2Me_2phen)$	−3.18 (73)		−2.07 (2.3 Hz) (Me); 2.32 (3.8 Hz); 2.22 (Ph); 2.53
$PtMe_2Cl_2(bpy)$	−3.38 (69)		3.60; 2.41; 2.80; 3.00
$PtMe_2Cl(CPhCl_2)(bpy)$	−3.58 (71)	1.78 m, 1.50 m	3.15; 2.13; 2.67; 2.80
$PtMe_2Cl(CClCH_2)(bpy)$	−3.73 (69)	- - -	3.57; 2.35; 2.75; 2.93
trans-$PtMe_2Cl(CH_2Cl)(bpy)$[d]	−4.02 (68)	−1.77 (53)	3.52; 2.34; 2.76; 2.96
cis-$PtMe_2Cl(CH_2Cl)(bpy)$[d]	−3.93 (68), −4.66 (74)	- - -	3.96, obscured by trans isomer
$PtMe_2Cl(CClCH_2)(bpy)$ (in $CDCl_3$)[e]	1.66 (69)	5.56 (105),[f] 4.89 (40.5)[f]	8.92; 7.64; 8.03; 8.22
trans-$PtMe_2Cl(CH_2Cl)(bpy)$ (in $CDCl_3$)[e]	1.37 (68)	3.57 (53)	8.87; 7.64; 8.03; 8.24
cis-$PtMe_2Cl(CH_2Cl)(bpy)$ (in $CDCl_3$)[e]	1.46 (68), 0.71 (74)	4.79 (88),[g] 4.41 (43.5)[g]	9.36, rest obscured by trans isomer
$PtMe_2Cl(GeMe_3)(bpy)$	−4.11 (63)	−5.54 (17.5)	3.62, rest obscured by $PtMe_2(bpy)$ resonances
$PtMe_2Br(GeMe_3)(bpy)$	−4.01 (63)	−5.55 (18.3)	3.63; 2.32; 2.79; 2.95
$PtMe_2Cl(GeMe_3)(Ph_2Me_2phen)$	−3.85 (65)	−5.96 (15)	−2.03 (2.5 Hz) (Me); 2.33 (4 Hz); 2.23 (Ph); 2.51
$PtMe_2Br(GeMe_3)(Ph_2Me_2phen)$	−3.75 (66)	−5.96 (16)	−2.00 (2.7 Hz) (Me); 2.33 (4.5 Hz); 2.23 (Ph); 2.51
$PtMe_2Cl(GeMe_2Cl)(bpy)$	−4.01 (61.5)	−4.86 (11.8)	3.52; 2.35; 2.83; 2.97
$PtMe_2Cl(GeMe_2Cl)(Ph_2Me_2phen)$	−3.75 (64)	−5.29 (9.5)	−2.05 (2.9 Hz) (Me); 2.34 (4.2 Hz); 2.23; 2.52
$PtMe_2Cl(GeMeCl_2)(bpy)$	−3.88 (61)	−4.16	3.53; 2.34; 2.79; 2.95
$PtMe_2Cl(GeMeCl_2)(Ph_2Me_2phen)$	−3.62 (62)	−4.45[h]	−2.08 (3 Hz) (Me); 2.36 (4.5 Hz); 2.23 (Ph); 2.53
$PtMe_2Cl(GePh_3)(bpy)$	−3.73 (61)	1.79	3.00; 2.18; 2.62; 2.82
$PtMe_2Br(GePh_3)(bpy)$	−3.60 (62)	1.78	3.03; . . .; 2.64; 2.83
$PtMe_2Cl(GePh_2Cl)(bpy)$	−3.84 (61)	~1.90 m	3.27; ~2.14; ~2.71; ~2.80
$PtMe_2Cl(SnMe_2Cl)(Ph_2Me_2phen)$	−3.76 (59)	−5.40 (3.0)[i]	−2.03 (2.5 Hz) (Me); 2.36 (4 Hz); 2.23 (Ph); 2.51

[a] Coupling constants $J(^{195}Pt–H)$ (in Hz) are given in parentheses. [b] The chemical shifts for the H, Me, and or Ph protons are given in the sequence obtained when starting from the N atom. The first proton in the case of bpy has a coupling constant $J(^{195}Pt–H) = 12.5–14$ Hz (when observable). [c] The Pt–CH_2– protons. [d] *cis*- or *trans*- denotes the mode of the CH_2Cl_2 addition. [e] Ppm relative to Me_4Si in $CDCl_3$ solution. [f] Coupling constant $J(H–H) = 1.5$ Hz. [g] Coupling constant $J(H–H) = 8$ Hz. [h] Also at −35 °C no $J(^{195}Pt–H)$ coupling was observed. [i] $J(^{117,119}Sn–H) = 47$ Hz.

$GeMe_3Cl$ (3.0 mmole) was added in one portion. Within a few minutes light yellow crystals precipitated. As soon as the solution turned yellow ether (3 mL) was added and after another 2 min the crystals were collected on a filter and washed with ether/CH_2Cl_2 and ether. Yield 90%.

Reaction of $PtMe_2(bpy)$ with $GeMe_3Cl$. $GeMe_3Cl$ was added in small portions to a solution of $PtMe_2(bpy)$ in CH_2Cl_2 and the reaction was followed by NMR. The equilibrium of the formation reaction of [$PtMe_2Cl(GeMe_3)(bpy)$] lay far to the side of the starting materials and a large excess of $GeMe_3Cl$ was necessary in order to precipitate the product [$PtMeCl(GeMe_3)(bpy)$]. All the methyl resonances of $PtMe_2Cl(GeMe_3)(bpy)$ were slightly broadened, independent of the concentration of reactants.

Reaction of $PtMe_2Cl(GeMe_3)(bpy)$ with H_2O. Addition of trace amounts of H_2O to CH_2Cl_2 solutions of $PtMe_2Cl(GeMe_3)(bpy)$ caused a very rapid gas evolution and the compound was decomposed completely within seconds. According to ^1H NMR the products were $PtMeCl(bpy)$, hexamethylgermoxane[8] (−5.01 ppm, relative to CH_2Cl_2), and CH_4 (−5.12 ppm). This was confirmed by comparison with original samples.

Reaction of $PtMe_2(Ph_2Me_2phen)$ with $GeMe_3Cl$. A similar behavior was found as in the case of $PtMe_2(bpy)$. However the equilibrium lay more to the side of the product [$PtMe_2Cl(GeMe_3)(Ph_2Me_2phen)$]. Also sharp methyl resonances indicated that it is more stable toward dissociation than the bipyridine compound. A similar reaction, although slower, took place with traces of water.

Preparation of [$PtMe_2Br(GeMe_3)(bpy)$]. This compound was prepared similarly to its chlorine analogue with a twofold excess of $GeMe_3Br$. Yield 90%.

Dissolution of [$PtMe_2Br(GeMe_3)(bpy)$]. The compound was dissolved in CH_2Cl_2 and an NMR spectrum was recorded. The equilibrium was far to the side of $PtMe_2Br(GeMe_3)(bpy)$, which had sharp resonances. Addition of traces of H_2O gave a decomposition similar to that of the chlorine analogue, although slower.

Reaction of $PtMe_2(Ph_2Me_2phen)$ with $GeMe_3Br$. A similar reaction as with $PtMe_2(bpy)$ was observed. The reaction with H_2O was slower as was the case with the bpy analogue.

Reactions of [$PtMe_2Cl(MR_nCl_{3-n})(bpy)$] with $M'R'_mCl_{4-m}$ (M, M′ = Ge, Sn, Pb). No exchange of M and M′ was observed in CH_2Cl_2 solution in the following cases: [$PtMe_2Cl(PbPh_2Cl)(bpy)$] or [$PtMe_2Cl(PbPh_3)(bpy)$] with $GePh_3Cl$ or $GePh_2Cl_2$; [$PtMe_2Cl(GePh_2Cl)(bpy)$] with $PbPh_2Cl_2$ or $PbPh_3Cl$; [$PtMe_2Cl(GePh_2Cl)(bpy)$], [$PtMe_2Cl(GeMe_2Cl)(bpy)$], or [$PtMe_2Cl(GeMeCl_2)(bpy)$] with $GeMe_2Cl_2$, $GeMeCl_3$, $GePh_2Cl_2$, $SnMeCl_3$, $SnMe_2Cl_2$, or $SnPh_2Cl_2$; [$PtMe_2Cl(SnPh_2Cl)(bpy)$] or [$PtMe_2Cl(SnMeCl_2)(bpy)$] with $GeMeCl_3$, $GeMe_2Cl_2$, or $GePh_2Cl_2$. In many cases, however, very slow decomposition of the platinum compound occurred. Exchange of M and M′ was observed between [$PtMe_2Cl(GePh_3)(bpy)$] and $SnPh_3Cl$ of $PbPh_3Cl$ to the corresponding tin or lead platinum compounds and between [$PtMe_2Cl(SnMe_2Cl)(bpy)$] and $GeMe_2Cl_2$ to the corresponding platinum–germanium compound. All compounds [$PtMe_2Cl(MR_3)(bpy)$] (M = Ge, Sn) underwent facile substitution with more highly chlorinated $M'R'_nCl_{4-n}$ (n = 2, 3) compounds.

Preparation of $PtMeCl(bpy)$ from $PtMe_2(bpy)$ and $SiMeCl_3$. Exposure of solutions of $PtMe_2(bpy)$ in CH_2Cl_2 with a 10- to 20-fold excess of $SiMeCl_3$ for a few minutes to air resulted in the formation of $PtMeCl(bpy)$. After a few hours the orange crystals were collected on a filter and washed with ether. Yield 70–80%. Similar yields were obtained with $SiPhCl_3$, $SiPh_2Cl_2$, and $SiMe_2Cl_2$.

Preparation of [$PtMe_2Cl(CH_2Cl)(bpy)$]. A solution of $PtMe_2(bpy)$ in CH_2Cl_2 was set aside for 2 weeks (when a ten-fold excess of $SiPh_3Cl$ was added only for 2 days). Subsequently the solution was concentrated under vacuum and hexane or ether was added. (When $SiPh_3Cl$ was used, this was first removed by evaporation of all solvent and extraction with ether. The residue was then dissolved in CH_2Cl_2.) Yellow crystals of *trans*-[$PtMe_2Cl(CH_2Cl)(bpy)$] were obtained in 60% yield. The filtrate contained only cis and trans product (^1H NMR), showing that the reaction with CH_2Cl_2 was quantitative.

Reaction of [$PtMe_2(bpy)$] with CPh_2Cl_2 and CPh_3Cl. A twofold excess of trityl chloride (CPh_3Cl) (1.0 mmol) was added to a benzene suspension (15 mL) of $PtMe_2(bpy)$ (0.5 mmol). After 1–2 days stirring the reaction mixture had turned yellow and the precipitate was collected on a filter and washed with benzene. Recrystallization from CH_2Cl_2 afforded light yellow crystals of $PtMe_2Cl_2(bpy)$ in 70% yield. When 1 equiv of trityl chloride was used, only half of the $PtMe_2(bpy)$ reacted. The reaction with CPh_2Cl_2 afforded the same product.

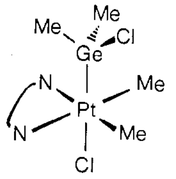

Figure 1. Proposed structure for [$PtMe_2Cl(GeMe_2Cl)(N\text{-}N)$].

Preparation of [$PtMe_2Cl(CPhCl_2)(bpy)$]. A fourfold excess of α,α,α-trichlorotoluene ($CPhCl_3$, 2.0 mmol) was added to a suspension of $PtMe_2(bpy)$ (0.5 mmol) in benzene (10 mL). After a while (1 min to several hours) the reaction started and was then complete within 15 min. As soon as the mixture was nearly colorless, hexane (10 mL) was added and the precipitate was collected on a filter. After washing with hexane/benzene and vacuum drying, the product was recrystallized from CH_2Cl_2. Yellow [$PtMe_2Cl(CPhCl_2)(bpy)$] was obtained in 80% yield.

Preparation of [$PtMe_2Cl(CCl_3)(bpy)$]. A few drops of CCl_4 were added to a CH_2Cl_2 solution of $PtMe_2(bpy)$. A rapid reaction occurred and yellow crystals of [$PtMe_2Cl(CCl_3)(bpy)$] precipitated slowly in 80% yield. The compound is only sparingly soluble in common organic solvents.

Preparation of [$PtMe_2Cl(CCl_3)(Ph_2Me_2phen)$]. $PtMe_2(Ph_2Me_2phen)$ (0.33 mmol) was dissolved in 4 mL of CH_2Cl_2/CCl_4 (90/10). In a few minutes the reaction mixture turned yellow and hexane was added until the solution started to cloud. At −20 °C yellow crystals of [$PtMe_2Cl(CCl_3)(Ph_2Me_2phen)$] were obtained in 90% yield.

Preparation of [$PtMe_2Cl(CH_2CCl)(bpy)$]. $PtMe_2(bpy)$ (0.5 mmol) was dissolved in a (30/70) mixture of 1,1,1-trichloroethane ($CMeCl_3$) and CH_2Cl_2. The reaction could be induced by brief warming. When the reaction mixture had turned yellow, stirring was continued for a few minutes and subsequently the solution evaporated to dryness under vacuum. The yellow residue was extracted with warm CH_2Cl_2 (10 mL). A remaining insoluble yellow precipitate was discarded. The CH_2Cl_2 solution was concentrated, hexane added, and the mixture set aside at −20 °C. Light yellow crystals of [$PtMe_2Cl(CH_2CCl)(bpy)$] were obtained in 60% yield. [$PtMe_2Cl(allyl)(bpy)$] and $PtMe_3Br(bpy)$ were prepared from $PtMe_2(bpy)$ and allyl chloride or MeBr in CH_2Cl_2, similar to the reported preparations[10] of [$PtMe_3Br(allyl)(bpy)$] and $PtMe_3I(bpy)$.

Results and Discussion

(I) Platinum–Germanium Compounds. Reactions of $PtMe_2(N\text{-}N)$ (N-N = bpy, Ph_2Me_2phen) with GeR_nX_{4-n} (X = Cl, R = Ph, Me, n = 1, 2, 3; X = Br, R = Ph, Me, n = 3) afforded the compounds [$PtMe_2X(GeR_nCl_{3-n})(N\text{-}N)$] according to eq 1. The ^1H NMR data of the compounds are given in Table II. Comparison of the values of the chemical shifts from the platinum–germanium compounds with those of the corresponding platinum–tin compounds (see also Table II of ref 1) showed that they are very similar. Accordingly a similar structure is proposed, which is given in Figure 1 for one example [$PtMe_2Cl(GeMe_2Cl)(N\text{-}N)$]. However comparison of the values of the $^3J(^{195}Pt\text{-}H)$ coupling constants of the methyls bonded to germanium with those bonded in tin showed a remarkable difference. In the case of the germanium compounds the values for this coupling constant increased in the order [$PtMe_2Cl(GeMeCl_2)(N\text{-}N)$] << [$PtMe_2Cl(GeMe_2Cl)(N\text{-}N)$] < $PtMe_2X(GeMe_3)(N\text{-}N)$ (X = Cl, Br). Whereas in the case of the tin compounds the order [$PtMe_2Cl(SnMeCl_2)(N\text{-}N)$] > [$PtMe_2Cl(SnMe_2Cl)(N\text{-}N)$] was found. (See Table II and in part 1[1] Table II.) Apparently the s orbitals[9] contribute to the platinum–germanium and the platinum–tin bonds with opposite trends upon increasing methyl substitution on germanium and tin.

$$PtMe_2(N\text{-}N) + GeR_nX_{4-n} \rightarrow PtMe_2X(GeR_nCl_{3-n})(N\text{-}N) \qquad (1)$$

Exchange between [$PtMe_2Cl(GeR_nCl_{3-n})(bpy)$] and GeR_nCl_{4-n} on the NMR time scale was observed only in one case: R = Me, n = 3. This exchange is clearly due to the following equilibrium

$$PtMe_2Cl(GeMe_3)(bpy) \rightleftarrows PtMe_2(bpy) + GeMe_3Cl \quad (2)$$

(although it should be mentioned that a slight dissociation also took place in the case of the corresponding bromine compound). The ^1H NMR data indicated that the dissociative step was rate determining, since the line broadening of $[PtMe_2Cl(GeMe_3)(bpy)]$ was independent of the concentration of all reactants. Solutions of $PtMe_2Cl(GeR_3)(bpy)$ in CH_2Cl_2 were unstable and decomposed into $PtMe_2Cl(CH_2Cl)(bpy)$ due to reaction of $PtMe_2(bpy)$ with the solvents (see section III). This reaction was more rapid for R = Me than for R = Ph. The bromine compounds reacted much slower than the chlorine compounds. The $PtMe_2(bpy)$ is generated according to reaction 2, and so the rate of decomposition of $PtMe_2X(GeR_3)(bpy)$ in CH_2Cl_2 is a good indication of the stability of this compound to dissociation of the plantinum–germanium bond.

Reactions with H_2O were also studied and it was found that addition of trace amounts of H_2O resulted in decomposition of $PtMe_2X(GeR_3)(N\text{-}N)$ (X = Cl, Br; N-N = bpy, Ph_2Me_2phen; R = Ph, Me) according to eq 3. More highly

$$PtMe_2X(GeMe_3)(N\text{-}N) + H_2O \rightarrow PtMeX(N\text{-}N) + {}^1/_2Me_3GeOGeMe_3 + CH_4 \quad (3)$$

chlorine substituted compounds $PtMe_2Cl(GeR_nCl_{3-n})(N\text{-}N)$ (n = 1, 2), however, were stable toward water. The rate of reaction 3 had the order Cl > Br, Me > Ph and bpy > Ph_2Me_2phen. This corresponds with the trends found for the dissociation of these compounds (eq 3). That such a dissociation is a preliminary step in reaction 3 is further substantiated by the stability to water of the more highly chlorine substituted compounds, since these compounds showed no observable dissociation. The rate of hydrolysis of $PtMe_2Cl(GeMe_3)(bpy)$ was remarkable since it was much more rapid than the hydrolysis of $GeMe_3Cl$ alone under similar conditions. This indicated that the hydrolysis might take place directly after fission of the platinum–germanium bond, when the germanium atom is probably more reactive.

Many exchange reactions were attempted between $PtMe_2Cl(MR_nCl_{3-n})(bpy)$ and $M'R'_mCl_{4-m}$ (M, M′ = Ge, Sn, Pb). Besides the results already described in part 1 the following information was obtained. More highly chlorine substituted $M'R'_mCl_{4-m}$ (M′ = Ge, Sn, Pb) replaced rapidly the MR_3 moiety (n = 3) for M = Ge or Sn but not for M = Pb, although, in this case only very short reaction times (1–5 min)[1] could be studied. Most of the other investigated exchange reactions were negative with respect to exchange of the (MR_nCl_{3-n}) by the $(M'R'_mCl_{3-m})$ moiety except for

$$PtMe_2Cl(SnMe_2Cl)(bpy) + GeMe_2Cl_2 \rightarrow PtMe_2Cl(GeMe_2Cl)(bpy) \quad (4)$$

$$PtMe_2Cl(GePh_3)(bpy) + SnPh_3Cl \rightarrow PtMe_2Cl(SnPh_3)(bpy) \quad (5)$$

Reaction 5 also took place with $PbPh_3Cl$. From these data and the results obtained in part 1 it can only be concluded that the ability to form a metal–metal bond is the greatest for the platinum–lead bond, whereas, it is not easy to differentiate between corresponding tin and germanium bonds. Reactions involving GeR_3Br (R = Me, Ph) are of interest. A very facile substitution of chlorine by bromine on platinum was observed with, e.g., $PtMe_2ClR(bpy)$ (R = Me, allyl). The products were identified by comparison of their ^1H NMR spectra with those of the original compounds.

$$PtMe_2ClR(bpy) + GeR_3Br \rightarrow PtMe_2BrR(bpy) \quad (6)$$

From the similar chemical shift changes (0.10 ± 0.02 ppm) observed for the methyls bonded to platinum in the reactions of GeR_3Br with many $[PtMe_2Cl(MR_nCl_{3-n})(bpy)$ compounds (M = C, Ge, Sn; R = Me, Ph; n = 0, 1, 2) it was clear that a similar bromine substitution on platinum took place. With M = Ge or Sn partial substitution of the chlorine bonded to germanium or tin also took place. In the case of R = Ph and n = 3 as expected only bromine substitution on platinum took place. Except for the previously described reactions of $PtMe_2X(GeR_3)(N\text{-}N)$ with H_2O (similar reactions with ROH were also observed), the platinum–germanium compounds were not affected by Lewis bases and in view of the easy hydrolysis of the germanium–chlorine bond in GeR_nCl_{4-n} this is again remarkable.

(II) Reactions of $PtMe_2(bpy)$ with SiR_nCl_{4-n}. Reactions of $PtMe_2(bpy)$ with excess SiR_nCl_{4-n} (R = Me, Ph; n = 0, 1, 2) did not afford $[PtMe_2(bpy)(SiR_nCl_{3-n})]$, as was the case with the corresponding germanium, tin, and lead compounds. Formation of intermediate products containing platinum–silicon bonds were never observed with ^1H NMR. However, with traces of water the reactions proceed as follows:

$$PtMe_2(bpy) + SiR_nCl_{4-n} \xrightarrow{H_2O} PtMeCl(bpy) \quad (7)$$

no doubt due to formed HCl by hydrolysis of SiR_nCl_{4-n}. PtMeCl(bpy) could be isolated for n = 1 or 2. From ^1H NMR it was clear that initially in the case of $SiCl_4$ the reaction also afforded [PtMeCl(bpy)]. The rate of the reaction was very dependent upon n and increased with higher chlorination of silicon, as might be anticipated. After prolonged reaction times PtMeCl(bpy) reacted further probably to $PtCl_2(bpy)$. No reaction was observed with SiR_3Cl.

For NMR studies the reactions with SiR_nCl_{4-n} with $PtMe_2(bpy)$ were carried out in CH_2Cl_2 since this was the only solvent in which $PtMe_2(bpy)$ was soluble enough. Because the reactions were rather slow (except for $SiCl_4$) some of the $PtMe_2(bpy)$ always reacted with CH_2Cl_2, the amount depending upon the rate of the reaction with SiR_nCl_{4-n}. An interesting fact is that the reaction with CH_4Cl_2 proceeded by a cis and a trans oxidative addition. Addition of $SiPh_3Cl$ increased the conversion rate of the cis into the trans product. The mechanism for this increase was, however, not clear.

(III) Platinum Carbon Compounds. No previous investigations have been reported of oxidative-addition reactions of complete series of carbon–halide compounds CR_nCl_{4-n} (n = 0, 1, 2, 3; R = Me, Ph), whereas such reactions are very common with RCH_2X or RC(O)X compounds (X = halogen).[10–13] In this investigation it was found that the reactions of $PtMe_2(N\text{-}N)$ with CR_nCl_{4-n} were very dependent upon both R and n. Only in two cases was a normal trans addition observed according to the reaction

$$PtMe_2(N\text{-}N) + CR_nCl_{4-n} \rightarrow PtMe_2Cl(CR_nCl_{3-n})(N\text{-}N) \quad (8)$$

(R = Ph, n = 0, 1). The trans mode of addition is confirmed by the ^1H NMR data of the compounds obtained (Table II). Although the reaction of $CMeCl_3$ with $PtMe_2(bpy)$ probably involved a trans addition as a first step, it is followed by a further reaction to $[PtMe_2Cl(CClCH_2)(bpy)]$, which is a novel way of preparing vinyl compounds of a transition metal:

$$PtMe_2(bpy) + CMeCl_3 \rightarrow [PtMe_2Cl(CMeCl_2)(bpy)]^* \xrightarrow{-HCl} PtMe_2Cl(CClCH_2)(bpy) \quad (9)$$

The presence of the vinyl group is clearly demonstrated by ^1H NMR (Table II). Apparently part of the HCl reacted with the platinum compounds present, since some insoluble products were also obtained in this reaction. The large difference in $^3J(^{195}Pt\text{–}H)$ values for the cis (108 Hz) and trans (40 Hz) hydrogen atoms (relative to platinum) of the vinyl group are noteworthy (Table II) and are in agreement with other α-chlorovinylic platinum compounds.[14] As anticipated no reaction was observed with CMe_3Cl. In contrast to these reactions are the reactions with CPh_nCl_{4-n} (n = 2, 3), which afforded $PtMe_2Cl_2(bpy)$ as the product. From the NMR data, which show two equivalent methyl groups with $^2J(^{195}Pt\text{–}H)$ = 69 Hz, it is clear that the chlorines are trans to each other,

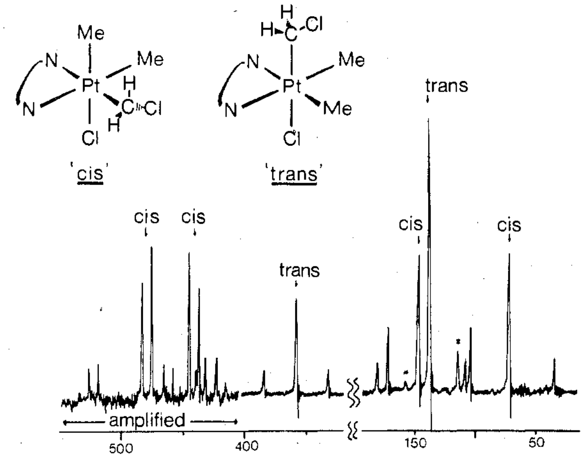

Figure 2. ^1H NMR spectrum (0–550 Hz) in $CDCl_3$ of the products obtained from the reaction of $[PtMe_2(bpy)]$ with CH_2Cl_2 after 14 h and proposed structures for *cis*- and *trans*-$[PtMe_2Cl(CH_2Cl)(bpy)]$. Resonances of $[PtMe_2(bpy)]$ are denoted with an asterisk.

one above and one below the square plane. Although an oxidative addition of CPh_nCl_{4-n} might be involved as a first step, at present it is not possible to give a mechanism for this reaction.

Reactions of CH_nCl_{4-n} were also studied in order to determine the influence of chlorine substitution on the carbon atom. Whereas CH_3Cl is known to react with dimethyl compounds of platinum in a trans oxidative-addition reaction,[1,13] such reactions with CH_2Cl_2 and $CHCl_3$ are unknown, and only in one case an oxidative addition was reported with CCl_4; the obtained product, however, could not be fully characterized.[15] If a solution of $PtMe_2(bpy)$ in CH_2Cl_2 is kept under an atmosphere of CH_3Cl, the only product formed is $[PtMe_3Cl(bpy)]$,[1] demonstrating the preference of the reaction with CH_3Cl rather than a reaction with CH_2Cl_2. However, without CH_3Cl a reaction of $PtMe_2(bpy)$ with CH_2Cl_2 took place. This reaction proceeded very slowly and was studied with ^1H NMR. Initially a mixture of a cis- and a trans-addition product formed in a ratio 2:1. After 14 h at room temperature almost all $PtMe_2(bpy)$ had reacted. The cis product converted slowly into the trans isomer and after 2 weeks the composition did not change anymore, having a cis/trans ratio of 1:4. However, when $SiPh_3Cl$ is added at the beginning of the reaction or in a later stage, the equilibrium mixture is reached after 1–2 days. Whereas the structure of the trans-addition product was clearly confirmed by its ^1H NMR spectrum (Figure 2) (equivalent methyl groups with a $^2J(^{195}Pt–H)$ value of 68 Hz), the structure of the cis product was less clear. However, comparison of the NMR data of $[PtMe_3Cl(bpy)]$ and *cis*- and *trans*-$[PtMe_2Cl(CH_2Cl)(bpy)]$ showed the following: In the case of $[PtMe_3Cl(bpy)]$ a relatively large high-field shift (−4.89 ppm relative to CH_2Cl_2) was observed for the methyl group above the square plane, compared with the value for the methyl groups in the plane (−4.06 ppm). This difference is due to the position of the methyl groups relative to the two aromatic rings of the bipyridine ligand. Since, these rings are in the square plane, this will result in more shielding for the methyl group above (or below) the plane than for the methyl group(s) in the plane. In the case of *trans*-$[PtMe_2Cl(CH_2Cl)(bpy)]$ a similar value for the methyl groups in the plane was found (−4.02 ppm). One methyl group of *cis*-$[PtMe_2Cl(CH_2Cl)(bpy)]$ had a high-field shift of −3.93 ppm corresponding with a methyl group in the plane, whereas the other methyl group had a shift of −4.66 ppm corresponding with a methyl group above the plane. Furthermore the average value of the (CH_2Cl) resonances in the cis isomer (4.60 ppm relative to Me_4Si in $CDCl_3$) was at much lower field than the corresponding value of the trans isomer (3.57 ppm relative to Me_4Si) which indicated that the (CH_2Cl) group of the cis isomer is in the plane. Based upon these data the proposed structures for *cis*- and *trans*-$[PtMe_2Cl(CH_2Cl)(bpy)]$ are given in Figure 2. With $CHCl_3$ a very slow reaction took place (several days); however, no identifiable products could be isolated. The reaction with CCl_4 was fast and proceeded via a trans addition (described earlier in this section). The rate of the oxidative addition of CH_nCl_{4-n} to $PtMe_2(bpy)$ followed the sequence $CCl_4 \gg CH_3Cl > CH_2Cl_2 \gg CHCl_3$.

In addition oxidative-addition reactions of allyl chloride, 1,1-dichloroethylene, and vinyl bromide were studied. Allyl chloride reacted quantitatively (^1H NMR) with $PtMe_2(bpy)$ in a trans manner and afforded $[PtMe_2Cl(allyl)(bpy)]$. Although, 1,1-dichloroethylene and vinyl bromide also reacted to form trans vinylic compounds of platinum according to ^1H NMR, many other products were also formed.

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Registry No. $PtMeCl(bpy)$, 50726-77-7; $PtMeBr(bpy)$, 64507-98-8; $PtMe_3Cl(bpy)$, 38194-03-5; $PtMe_3Br(bpy)$, 38194-04-6; $PtMe_2Cl(allyl)(bpy)$, 64507-97-7; $PtMe_2Cl(CCl_3)(bpy)$, 64507-96-6; $PtMe_2Cl(CCl_3)(Ph_2Me_2phen)$, 64507-95-5; $PtMe_2Cl_2(bpy)$, 64507-94-4; $PtMe_2Cl(CPhCl_2)(bpy)$, 64507-93-3; $PtMe_2Cl(CClCH_2)(bpy)$, 64507-92-2; *trans*-$PtMe_2Cl(CH_2Cl)(bpy)$, 64551-01-5; *cis*-$PtMe_2Cl(CH_2Cl)(bpy)$, 64507-91-1; $PtMe_2Cl(GeMe_3)(bpy)$, 64507-90-0; $PtMe_2Br(GeMe_3)(bpy)$, 64508-07-2; $PtMe_2Cl(GeMe_3)(Ph_2Me_2phen)$, 64508-06-1; $PtMe_2Br(GeMe_3)(Ph_2Me_2phen)$, 64508-05-0; $PtMe_2Cl(GeMe_2Cl)(bpy)$, 64508-04-9; $PtMe_2Cl(GeMe_2Cl)(Ph_2Me_2phen)$, 64508-03-8; $PtMe_2Cl(GeMeCl_2)(bpy)$, 64508-09-4; $PtMe_2Cl(GeMeCl_2)(Ph_2Me_2phen)$, 64508-08-3; $PtMe_2Cl(GePh_3)(bpy)$, 64508-10-7; $PtMe_2Br(GePh_3)(bpy)$, 64508-02-7; $PtMe_2Cl(GePh_2Cl)(bpy)$, 64508-01-6; $PtMe_2Cl(SnMe_2Cl)(Ph_2Me_2phen)$, 64508-00-5; $PtMe_2Cl(CHCl_2)(bpy)$, 64507-99-9; $PtMe_2(Ph_2Me_2phen)$, 63133-64-2; $PtMe_2(bpy)$, 52594-52-2; $GeMeCl_3$, 993-10-2; $GeMe_2Cl_2$, 1529-48-2; $GeMe_3Cl$, 1529-47-1; $GeMe_3Br$, 1066-37-1; $GePh_3Cl$, 1626-24-0; $SiMeCl_3$, 75-79-6; $SiMe_2Cl_2$, 75-78-5; $SiPhCl_3$, 98-13-5; $SiPh_2Cl_2$, 80-10-4; $SiPh_3Cl$, 76-86-8; CPh_3Cl, 76-83-5; CPh_2Cl_2, 2051-90-3; $CPhCl_3$, 98-07-7; $CMeCl_3$, 25323-89-1; H_2O, 7732-18-5; CH_2Cl_2, 75-09-2; CCl_4, 56-23-5; allyl chloride, 107-05-1; MeBr, 74-83-9.

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