Synthesis of Hexamethyl- and Pentamethylplatinate(IV) and Tetramethyl- and Trimethylplatinate(II) Complexes. Spectroscopic Studies of Organoplatinum Complexes[1,2]

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Abstract: Reaction of $[LiCH_3]_4$ with $[Pt(CH_3)_3I]_4$, $[Pt(CH_3)_3Cl]_4$, or $(Ph_2CH_3P)_2Pt(CH_3)_4$ in diethyl ether or tetrahydrofuran gives $Li_2[Pt(CH_3)_6]$, I. Reaction of $[LiCH_3]_4$ with $(Ph_3P)_2Pt(CH_3)_2$ or (cycloocta-1,5-diene)$Pt(CH_3)_2$ in ether gives $Li_2[Pt(CH_3)_4]$, II, while K_2PtCl_4 or $[Pt(CH_3)_3acac]_2$ reacts with $[LiCH_3]_4$ to yield a mixture of I, II, and platinum. The syntheses from bis(phosphine = L)platinum reagents $[L_2Pt^{II}(CH_3)_2]$ and $[L_2Pt^{IV}(CH_3)_4]$ produce $Li[LPt(CH_3)_3]$ or $Li[LPt(CH_3)_5]$ as intermediates. Both Raman and ^1H NMR spectra are consistent with octahedral $[Pt(CH_3)_6]^{2-}$ and square planar $[Pt(CH_3)_4]^{2-}$ species. II reacts vigorously with CH_3I and C_2H_5I and less rapidly with n-C_4H_9Cl, yielding I, $Li_2[Pt(CH_3)_5C_2H_5]$, and $Li_2[Pt(CH_3)_5(n\text{-}C_4H_9)]$, respectively. I reacts with CH_3I or C_2H_5I to give $Li_2[Pt(CH_3)_3I_3]$ and hydrocarbon products. Vibrational and ^1H NMR spectra of I and II are discussed and correlated with spectra of starting materials and with previously reported data for related compounds. The strengths of the platinum-carbon bonds appear to be insensitive to the oxidation state of the metal. These permethylplatinum(II) and -(IV) compounds are very reactive, and only the hexamethylplatinate(IV) was isolated from solution as $[LiPMDT]_2[Pt(CH_3)_6]$, PMDT = N,N,N',N'',N''-pentamethyldiethylenetriamine.

Since the syntheses of trimethylplatinum(IV) complexes were reported by Pope and Peachy in 1909,[3] there have been numerous attempts to prepare binary methylplatinum complexes, $[Pt(CH_3)_n]_m$. Several early reports of success in the preparation[4,5] and characterization[6,7] of $[Pt(CH_3)_4]_4$ and $[Pt(CH_3)_3]_2$ were subsequently shown[8,9] to be incorrect and both species are now presumed nonexistent.[10]

Although recent reviews[11-13] demonstrate the considerable success that has been achieved in the synthesis of neutral binary alkyls, $[MR_n]_m$, of the early transition metals, where R is a σ-bonded monodentate alkyl, formation of such neutral compounds of the later transition elements is largely prevented by the lack of correspondence between the common coordination numbers and oxidation states of the metals. Additionally, the early transition elements form polynuclear compounds such as $\{M[CH_2Si(CH_3)_3]_3\}_2$, M = Mo, W,[14] while metal-metal bonded complexes are unusual for later transition elements in their higher oxidation states. Formation of neutral $[MR_n]_m$ compounds in the platinum and gold triads has been found only when the ligand R meets some special condition, e.g., bridging carbon atoms in $[CuCH_2Si(CH_3)_3]_4$[15] and bidentate mononegative ylides in $[AuR]_2$, $[CuR]_2$, and $[NiR_2]_2$, R = $(CH_2)_2P(CH_3)_2^-$.[16] Synthesis of neutral methides such as $Pt(CH_3)_4$ and $Au(CH_3)_3$ therefore seems unlikely. Indeed, no binary methido compound of the group 8 metals is currently known,[17] and the only example for the group IB metals is the polymeric and moderately unstable $[CuCH_3]_n$.[18] However, the recent identification of $Li[Au(CH_3)_2]$[19,20] and $Li[Au(CH_3)_4]$[20] in solution by spectroscopic techniques and the isolation of thermally stable solids containing $[Au(CH_3)_2]^-$,[21] $[Au(CH_3)_4]^-$[21] and $[Ni(CH_3)_4]^{2-}$[22] suggest that coordinatively saturated permethylmetalate anions should exist for many common oxidation states of the later transition elements.

We report here the synthesis of the first peralkylplatinum complexes, lithium hexamethylplatinate(IV) and lithium tetramethylplatinate(II), as well as identification of the monophosphine complexes $Li[LPt(CH_3)_5]$, L = Ph_2CH_3P, Ph_3P, and $Li[Ph_3PPt(CH_3)_3]$. Extensive laser Raman and ^1H NMR spectroscopic studies of both permethylplatinates in solution have been complemented by infrared and ^{13}C NMR data and chemical characterizations of the species in solution. Conclusions on the nature of the complexes have been drawn. Additionally, we report new Raman spectroscopic data for a number of neutral organoplatinum complexes synthesized in the course of this work.

Experimental Section

Preparations. Diethyl ether was distilled from CaH_2 under dry nitrogen immediately before use. Syntheses employing methyllithium or free phosphines were carried out under dry nitrogen or argon using Schlenk-type glassware and syringe techniques.[23] Solutions of halide-free methyllithium in diethyl ether or tetrahydrofuran were prepared from $Hg(CH_3)_2$ and lithium sand; excess lithium and lithium amalgam were removed by filtration. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Microanalyses were carried out by the Departmental Microanalytical Laboratory.

Purchased materials were used as obtained: Lithium sand, 30% in mineral oil (Lithcoa); $Hg(CH_3)_2$ and Ph_3P (Eastman); N,N,N',N'',N''-pentamethyldiethylenetriamine, PMDT, and Ph_2CH_3P (K & K Laboratories); $(CH_3)_3P$ and diiodo(cycloocta-1,5-diene)platinum(II) (ROC/RIC). K_2PtCl_4 and *cis*-$(H_3N)_2PtCl_2$ were generously loaned by Matthey Bishop, Inc., Malvern, Pa., and Engelhard Industries, Murray Hill, N.J.

Well-known complexes were prepared by literature methods. The method of Baldwin and Kaska[24] was used to prepare $[Pt(CH_3)_3I]_4$ in 80% yield. This procedure is much superior to the previous standard method.[25] Both $[Pt(CH_3)_3Cl]_4$ and $[Pt(CH_3)_3OH]$ were prepared via $\{[Pt(CH_3)_3]_2SO_4\}_2$ from $[Pt(CH_3)_3I]_4$ by the methods of Pope and Peachy[3] and Morgan et al.,[26] respectively. These starting materials all gave satisfactory analyses.

$[Pt(CH_3)_3acac]_2$. This was prepared from $[Pt(CH_3)_3I]_4$ by the method of Menzies.[27] Anal. Calcd for $PtC_8H_{16}O_2$: C, 28.3; H, 4.75. Found: C, 28.3; H, 4.69.

$(Ph_3P)_2Pt(CH_3)_2$. This was prepared from K_2PtCl_4 by the method of Chatt and Shaw.[28] Anal. Calcd for $PtC_{38}H_{36}P_2$: C, 60.9; H, 4.84; P, 8.26. Found: C, 61.0; H, 5.06; P, 8.50.

(Cycloocta-1,5-diene)$Pt(CH_3)_2$, (1,5-COD)$Pt(CH_3)_2$. This was prepared by the method of Clark and Manzer.[29] Crystallization from ether yielded the product as large pale yellow crystals which probably contain traces of the starting material, (1,5-COD)PtI_2. Crystallization from n-pentane yielded a white product. Anal. Calcd for $PtC_{10}H_{18}$: Pt, 58.5; C, 36.0; H, 5.44. Found: Pt, 58.2; C, 35.8; H, 5.63.

$[(CH_3)_3P]_2Pt(CH_3)_4$ and $(Ph_2CH_3P)_2Pt(CH_3)_4$. These were synthesized in procedures derived from those reported by Ruddick and Shaw[30] for the corresponding $(CH_3)_2PhP$ and $(C_2H_5)_3P$ complexes of tetramethylplatinum(IV). Under argon, $[Pt(CH_3)_3Cl]_4$ was treated with a benzene solution of slightly more than 2 equiv of the appropriate phosphine and the mixture was stirred until homogeneous. The resulting solution of $L_2Pt(CH_3)_3Cl$, L = phosphine, was treated with a twofold excess of halide-free $[LiCH_3]_4$ in diethyl ether, and stirring was continued for several hours. Hydrolysis at 0 °C was followed by separation of the organic layer and benzene extraction of the aqueous phase. The combined extracts were dried over $CaSO_4$ and filtered, and the solvents removed in a stream of nitrogen. The crude yellow $[(CH_3)_3P]_2Pt(CH_3)_4$ was crystallized three times from light petroleum (30-60 °C) to give off-white crystals, mp 156-157 °C. Anal. Calcd for $PtC_{10}H_{30}P_2$: Pt, 47.9; C, 29.5; H, 7.42. Found: Pt, 48.1; C, 29.6; H, 7.23. The crude $(Ph_2CH_3P)_2Pt(CH_3)_4$ was crystallized twice from boiling *n*-hexane and finally from $CHCl_3$ by addition of *n*-pentane to give white crystals, mp 120 °C (effervescence). Anal. Calcd for $PtC_{30}H_{38}P_2$: Pt, 29.8; C, 54.8; H, 5.84; P, 9.45. Found: Pt, 29.8; C, 54.8; H, 6.03; P, 9.35. *Note:* The presence of iodide in the methylation step largely prevents formation of these complexes (see following procedure). Additionally, the presence of excess Ph_2CH_3P may be required in the purification of $(Ph_2CH_3P)_2Pt(CH_3)_4$ (see Data and Results section).

$[(CH_3)_3P]_2Pt(CH_3)_3I$. This was obtained in an attempted synthesis of $[(CH_3)_3P]_2Pt(CH_3)_3CD_3$. The reaction conditions and workup were identical with the procedure given for $[(CH_3)_3P]_2Pt(CH_3)_4$, with the exception that $LiCD_3$ prepared from CD_3I and lithium sand in ether was employed. The product was an off-white solid, mp 166-167 °C, whose spectroscopic properties (Raman, ^1H NMR) indicated the formation of $[(CH_3)_3P]_2Pt(CH_3)_3I$. Anal. Calcd for $PtC_9H_{27}P_2I$: Pt, 37.6; C, 20.8; H, 5.24. Found: Pt, 37.7; C, 21.1; H, 5.09.

$Li_2[Pt(CH_3)_6]$. Samples were prepared as colorless, homogeneous solutions in diethyl ether or tetrahydrofuran. Preparations were usually carried out in 5-mm precision-polished NMR tubes, which permit ^1H and ^{13}C NMR and laser Raman spectra to be collected from a single sealed sample. In a typical experiment, 0.126 g (0.343 mmol as monomer) of $[Pt(CH_3)_3I]_4$ in a 5-mm NMR tube under argon was treated with 0.8 mL of a 1.3 M solution of halide-free $[LiCH_3]_4$ in ether. The tube was chilled in liquid nitrogen and sealed under vacuum. *Caution: Argon solidifies at −189 °C; care must be taken to prevent the presence of solid argon when the seal is made.* Dissolution of the $[Pt(CH_3)_3I]_4$ required 4 h at room temperature with occasional turning of the tube. The reaction was much faster (15-30 min) when tubes were shaken or when mixtures were stirred in a small flask. The $Li_2[Pt(CH_3)_6]$ also was prepared quantitatively from $[Pt(CH_3)_3Cl]_4$ and $[LiCH_3]_4$ in THF as well as from the reaction of a ca. 1:1 mixture of $[Pt(CH_3)_3I]_4$ and Ph_3P with $[LiCH_3]_4$ in diethyl ether. Reaction of $(Ph_2CH_3P)_2Pt(CH_3)_4$ with $[LiCH_3]_4$ in ether gave only ca. 95% yield and required 10 days at 50 °C to effect replacement of the second phosphine (see also the following paragraph), while $[(CH_3)_3P]_2Pt(CH_3)_4$ was entirely unaffected by $[LiCH_3]_4$ in ether after 15 days despite addition of PMDT as an activating agent for methyllithium. The reactions of $[Pt(CH_3)_3OH]_4$ and $[Pt(CH_3)_3acac]_2$ with $[LiCH_3]_4$ in ether were quite vigorous, due to reaction of $[LiCH_3]_4$ with the hydroxide and acetylacetonate ligands, and gave mixtures of $Li_2[Pt(CH_3)_6]$ with other products (see Data and Results section).

$Li[Ph_3PPt(CH_3)_5]$ and $Li[Ph_2CH_3PPt(CH_3)_5]$. These were obtained in the methylations of $(Ph_2CH_3P)_2Pt(CH_3)_4$ and of $[Pt(CH_3)_3I]_4$ in the presence of Ph_3P, respectively. Treatment of a mixture of 0.139 g (0.378 mmol) of $[Pt(CH_3)_3I]_4$ and 0.108 g (0.412 mmol) of Ph_3P with 0.9 mL of 1.3 M $[LiCH_3]_4$ in ether for 4 h gave a homogeneous solution containing a ca. 3:2 mixture of $Li_2[Pt(CH_3)_6]$ and $Li[Ph_3PPt(CH_3)_5]$, with molar ratios estimated from ^1H NMR signals; after 5 days at room temperature the latter was converted to $Li_2[Pt(CH_3)_6]$.

Treatment of 0.0159 g (0.024 mmol) of $(Ph_2CH_3P)_2Pt(CH_3)_4$ with 1.0 mL of 1.0 M $[LiCH_3]_4$ in ether for 3 days gave $Li[Ph_2CH_3PPt(CH_3)_5]$. This did not react further in 4 days at room temperature, but gave ca. 95% conversion to $Li_2[Pt(CH_3)_6]$ in 10 days at 50 °C. Attack of $[LiCH_3]_4$ on diethyl ether to form $LiOC_2H_5$, C_2H_4, and CH_4[31] is a major side-reaction at this temperature.

Reaction of $Li_2[Pt(CH_3)_6]$ with PMDT. The procedure was similar to that used to isolate $[Li(PMDT)][Au(CH_3)_4]$ and $[Li(PMDT)][Au(CH_3)_2]$.[21] Solutions of $Li_2[Pt(CH_3)_6]$ in ether were prepared in a Schlenk apparatus under argon by stirring $[Pt(CH_3)_3I]_4$ with ca. 4 equiv of $[LiCH_3]_4$ in ether until the mixture was homogeneous. Addition of slightly over 3 equiv of PMDT gave a fine precipitate which was collected on a frit in the apparatus and washed three times with benzene to remove $[Li(PMDT)]I$ and excess PMDT. The resulting white powder was dried in vacuo and shaken into attached sample tubes which were then sealed off under vacuum. Although vibrational data, vide infra, were consistent with spectra of $Li_2[Pt(CH_3)_6]$ in solution, the Purdue Microanalytical Laboratory could not obtain reproducible microanalysis or values at all close to the theoretical, apparently because of the very great air sensitivity of the product. Analyses by Schwarzkopf Microanalytical Laboratory were closer to theoretical. Anal. Calcd for $C_{24}H_{64}N_6Li_2Pt$: C, 44.6; H, 10.0; N, 13.0; Pt, 30.2. Found: C, 43.6; H, 9.70; N, 12.2; Pt, 27.5. This corresponds to a N:Pt ratio of 6.2 which compares reasonably to the value expected if the formula unit contains two $Li(PMDT)^+$ ions.

$Li_2[Pt(CH_3)_4]$. This was prepared as colorless, homogeneous solutions in diethyl ether. In a typical experiment, 0.0703 g (0.211 mmol) of $(1,5\text{-COD})Pt(CH_3)_2$ in a 5-mm NMR tube under argon was treated with 0.6 mL of a 2.0 M solution of halide-free $[LiCH_3]_4$ in diethyl ether. The tube was chilled in liquid nitrogen and sealed under vacuum. The reaction was complete before spectroscopic data could be taken.

Solutions of $Li_2[Pt(CH_3)_4]$ also could be prepared from $(Ph_3P)_2Pt(CH_3)_2$ in a much slower reaction. A one-piece, all-glass reaction apparatus was constructed from a 6-in. test tube with side-arm, a 10-mm fine frit, and a 5-mm NMR tube. The test tube portion was charged with 0.0677 g (0.90 mmol) of $(Ph_3P)_2Pt(CH_3)_2$, argon atmosphere was provided, and 2.0 mL of 1.0 M $[LiCH_3]_4$ in ether was added via a syringe. The mixture was frozen in liquid nitrogen and the apparatus was sealed, under vacuum, at the side-arm. Dissolution of $(Ph_3P)_2Pt(CH_3)_2$ required 3 days of magnetic stirring at room temperature. The solution was filtered from the reaction tube by inverting the apparatus and chilling the NMR tube. The solution was concentrated to 1.0 mL by chilling the reaction tube above the frit to distill ether from the solution. Then the NMR tube containing the sample was sealed off from the apparatus. Initially, the solution contained both $Li_2[Pt(CH_3)_4]$ and $Li[Ph_3PPt(CH_3)_3]$. The latter was converted to $Li_2[Pt(CH_3)_4]$ after 15 days.

Reaction of K_2PtCl_4 with $[LiCH_3]_4$. A reaction apparatus (vide supra) was charged with 0.0685 g (0.165 mmol) of K_2PtCl_4 and 2.0 mL of 1.0 M $[LiCH_3]_4$ in ether, and sealed under vacuum. The K_2PtCl_4 appeared unchanged after stirring for 8 h at −78 °C; it then blackened slowly in 3 h at 0 °C, and produced considerable platinum black in 14 h at room temperature. The platinum was removed by filtering the solution into the NMR tube, which was then sealed off. The resulting colorless solution contained $Li_2[Pt(CH_3)_4]$ and $Li_2[Pt(CH_3)_6]$ in a ca. 3:2 molar ratio as indicated by the ^1H NMR intensities. A similar reaction employing *cis*-$(H_3N)_2PtCl_2$ as the platinum reagent yielded platinum black as the only apparent product.

Reaction of AuCl with $[LiCH_3]_4$. A reaction tube was charged with 0.1678 g (0.722 mmol) of AuCl (transferred in a glove bag under argon) plus 5 mL of dry diethyl ether, and chilled to −78 °C. Dropwise addition of 2.0 mL of 0.9 M $[LiCH_3]_4$ in ether with stirring gave immediate formation of colloidal gold. When the addition was complete, the mixture was warmed to room temperature and the supernatent liquid transferred via syringe to an NMR tube. The solution contained $Li[Au(CH_3)_2]$ and $Li[Au(CH_3)_4]$ in a ca. 1:1 molar ratio.

Reactions of $Li_2[Pt(CH_3)_4]$ and $Li_2[Pt(CH_3)_6]$ with Alkyl Halides. In a typical reaction, 0.0544 g (0.163 mmol) of $(1,5\text{-COD})Pt(CH_3)_2$ in a stopple-capped 5-mm NMR tube under argon was treated with 1.0 mL of 1.0 M halide-free $[LiCH_3]_4$ in ether. The tube was agitated by hand until the mixture was homogeneous, chilled in an ice bath, and treated with 0.10 mL (1.6 mmol) of CH_3I. The solution was frozen in liquid nitrogen and the tube was sealed under vacuum. The ^1H NMR was followed with time. Reactions of $Li_2[Pt(CH_3)_4]$ with C_2H_5I, *n*-C_4H_9Cl, and $(CH_3)_3SiCH_2Cl$ were carried out similarly, employing ca. 0.18 mmol of $(1,5\text{-COD})Pt(CH_3)_2$, 1.0 mL of 1.0 M $[LiCH_3]_4$, and 1.6-2.1 mmol of alkyl halide as reagents. Independent reactions of $Li_2[Pt(CH_3)_6]$ with CH_3I and C_2H_5I were carried out with 0.27 mmol of $[Pt(CH_3)_3I]_4$, 1.0 mL of 1.0 M $[LiCH_3]_4$, and 1.6 mmol of alkyl halide as reagents.

The reaction of $(1,5\text{-COD})Pt(CH_3)_2$ with CH_3I was carried out for comparison with the oxidative addition reactions to $Li_2[Pt(CH_3)_4]$. To 0.0484 g (0.145 mmol) of $(1,5\text{-COD})Pt(CH_3)_2$ in a 5-mm NMR tube was added 0.5 mL of benzene, 0.10 mL (1.6 mmol) of CH_3I and a drop of Me_4Si. The ^1H NMR was followed with time.

An additional oxidation of $Li_2[Pt(CH_3)_4]$ was attempted with $Li[Au(CH_3)_4]$. This sealed-tube reaction employed 0.0453 g (0.136 mmol) of $(1,5\text{-COD})Pt(CH_3)_2$, 0.0633 g (0.126 mmol) of $Ph_3PAu(CH_3)_3$, and 1.0 mL of 1.0 M $[LiC_3]_4$ as reagents.

Raman Spectra. Solution spectra were obtained using an instrument

Table I. Vibrational Frequencies of Methylplatinum Complexes

Compound	State or solvent	ν(Pt-CH_3), cm^{-1}		δ_s(CH_3), cm^{-1}	
		Raman	Infrared	Raman	Infrared
$Li_2[Pt(CH_3)_6]$	Ether	508 vs, p, 505 s, dp	478 vs	1250 s, p, 1205 s, dp	
$Li_2[Pt(CH_3)_6]\cdot 2PMDT$	Solid	506-508 m	467-477 vb	1246 w, 1197 m	
$[(CH_3)_3P]_2Pt(CH_3)_4$	Solid	529 s,^{a} 511 s	525 s 475 s	1237 w, 1203 w, 1193 w	1237 vw, 1204 m, 1195 m
	CS_2	528 s, p, 522 m, dp 506 s, p		1240 m, p, 1205 w, dp, 1193 m, wp	
$(Ph_2CH_3P)_2Pt(CH_3)_4$	Solid	538 s, 528 s, 503 s	541 w, 530 w, 468 m	1250 w, 1217 w, 1193 w	1251 vw, 1216 m, 1194 w
$[Pt(CH_3)_3acac]_2$	Solid	588 s, 564 vs	603 s, 592 m, 571 m^b	1274 vw, 1240 m, 1221 w^b	1271 m, 1236 m, 1217 s,^{b} 1204 s
$Li_2[Pt(CH_3)_4]$	Ether	511 m, p, 503 m, dp			
$Li[Ph_3PPt(CH_3)_3]$	Ether	538 m, ca. 515 m^c			
$(Ph_3P)_2Pt(CH_3)_2$	Solid	548 s, 533 w, 519 m^b 509 w	551 m, 537 w, 525 s^b 513 s, 505 m	1218 m, 1198 m	1219 vw, 1195 w
	$CDCl_3$	543 s, 525 m, 512^a		1219 m, 1192 m	
(1,5-COD)$Pt(CH_3)_2$	Solid	562 vs, 546 s	563 m, 548 m^d	1249 m, 1232 w^b 1215 m, 1200 m	
	$CDCl_3$	559 s, p, 542 m, dp			

[a] Appears to be overlap of two bands. [b] All bands in the regions are listed. See Discussion. [c] The band from $Li_2[Pt(CH_3)_4]$ interferes. [d] Reference 34.

Table II. ^1H NMR Data for Methylplatinum Complexes[a]

Compound	Solvent	($Pt-CH_3$) trans CH_3			($Pt-CH_3$) trans L			($P-CH_3$)		
		τ, ppm	(J_{PH})	J_{PtH}	τ, ppm	(J_{PH})	J_{PtH}	τ, ppm	(J_{PH})	J_{PtH}
$Li_2[Pt(CH_3)_6]$	Ether	10.55	(None)	40.0						
$Li[Ph_3PPt(CH_3)_5]$	Ether-d_{10}	10.32	(5.4)	41.4	9.53	(6.7)	55.0			
$Li[Ph_2CH_3PPt(CH_3)_5]$	Ether	10.38	(6)	42		*b*			*b*	
$(Ph_2CH_3P)_2Pt(CH_3)_4$	$CDCl_3$	10.05	(6.1)	43.1	9.56	(*c*)	59	8.26	(7.4)	10.3
$[(CH_3)_2PhP]_2Pt(CH_3)_4$^{d}	$CHCl_3$	10.23	(6.4)	44	9.61	(*c*)	57	8.60	(8.4)	11.5
$[(CH_3)_3P]_2Pt(CH_3)_4$	$CDCl_3$	10.35	(6.8)	44.4	9.68	(*c*)	57.0	8.68	(8.4)	11.6
$Li_2[Pt(CH_3)_4]$	Ether	10.39	(None)	43.5						
$Li[Ph_3PPt(CH_3)_3]$	Ether	10.41	(5.3)	48.7		*b*				
$(Ph_3P)_2Pt(CH_3)_2$^{e}	CH_2Cl_2				9.67	(*c*)	69.4			
(1,5-COD)$Pt(CH_3)_2$^{f}	$CHCl_3$				9.42	(None)	83.4			

[a] All coupling constants in Hz, accurate to ±0.2 Hz with decimal given, ±1 Hz otherwise. [b] Obscured by solvent. [c] Complex multiplet. [d] Reference 30. [e] Reference 35. [f] Reference 29.

which has been described recently.[32] Solutions were contained in 5-mm NMR tubes and irradiated normal to the tube axis with the 514.5-nm line of a Coherent Radiation Model 52 Ar^+ laser. Spectra were machine plotted from digital data using program RAMAN.[33] Spectra of solids were obtained with a Jarrell-Ash 25-300 spectrophotometer using 632.8- He-Ne or 647.1-nm Kr^+ excitation, or with a Jobin-Yvon Ramanor HG2 spectrophotometer using 514.5-nm Ar^+ excitation. The frequencies of sharp bands are believed to be accurate to ± 2 cm^{-1}.

Infrared Spectra. These were obtained with a Beckman IR-12 spectrometer calibrated with polystyrene film and indene. The frequencies for sharp bands are accurate to ± 2 cm^{-1}, while those for broad bands should be accurate within ± 5 cm^{-1}. Solids were run as Nujol mulls on CsI plates, while solutions were run in KBr cells. Standard techniques for handling air-sensitive materials were used.[23]

Nuclear Magnetic Resonance Spectra. Routine ^1H NMR spectra were obtained with Varian A-60A and Perkin-Elmer R-32 (90 MHz) spectrometers with probe temperatures of 40 and 35 °C, respectively. Variable temperature measurements were carried out on the latter instrument. The ^{13}C NMR spectra were obtained with a Varian CFT-20 (20 MHz) spectrometer with a probe temperature of 35 °C. Internal reference was to Me_4Si or to the methyl resonance of diethyl ether at τ 8.88 ppm (^1H) or 15.6 ppm (^{13}C), calibrated with Me_4Si.

Data and Results

Summary of Spectroscopic Data. Raman and infrared spectral data for ν(Pt-C) and δ_s(CH_3) vibrational modes of complexes studied in the course of this work are collected in Table I. Corresponding ^1H NMR data for methyl resonances are collected in Table II. The choice of ν(Pt-C) frequencies in Table I is straightforward for the platinate(II) and -(IV) complexes, $[(CH_3)_3P]_2Pt(CH_3)_4$ and (1,5-COD)$Pt(CH_3)_2$. The choice for $(Ph_2CH_3P)_2Pt(CH_3)_4$ required characterization of the ligand spectra; this was carried out by obtaining spectra of neat Ph_2CH_3P and Ph_2CH_3PAuBr to compare the free and bound ligand. Spectra of $(Ph_3P)_2Pt(CH_3)_2$ are so complex in the ν(Pt-C) region that all observed bands are reported. This is also the case for (1,5-COD)$Pt(CH_3)_2$ and $[Pt(CH_3)_3acac]_2$ in the δ_s(CH_3) region.

Platinum(IV) Compounds. Reactions of $[Pt(CH_3)_3X]_n$($X = Cl^-, I^-, OH^-$, acac$^-$) with $[LiCH_3]_4$. When $[Pt(CH_3)_3I]_4$ is treated with excess halide-free $[LiCH_3]_4$ in ether, the ^1H NMR of the resulting solution exhibits a singlet at τ 10.55 ppm with singlet satellites, $^2J(^{195}Pt-^1H) = 40.0$ Hz, while the ^{13}C NMR exhibits a singlet at -10.6 ppm, $^1J(^{195}Pt-^{13}C) = 434$ Hz (cf. τ 8.27 ppm, $J = 76$ Hz (^1H), and 13.2 ppm, $J = 686$

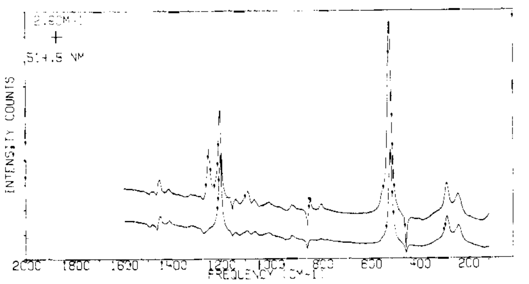

Figure 1. Raman difference spectra and depolarization measurements for $Li_2[Pt(CH_3)_6]$ in diethyl ether. The geometry is such that ρ for a depolarized band is $^6\!/_7$. Ordinate range -12 to 125×10^3 counts.

Hz (^{13}C), for $[Pt(CH_3)_3I]_4$ in $CDCl_3$ solution). The same ^{1}H spectrum results from the reaction of $[Pt(CH_3)_3Cl]_4$ with $[LiCH_3]_4$ in THF. When a similar reaction is carried out in $(C_2D_5)_2O$ in the presence of ca. 1 mol of Ph_3P per mole (monomer) of $[Pt(CH_3)_3I]_4$, the ^{1}H NMR shows, in addition to the τ 10.55 ppm singlet, two doublets at τ 10.32, ${}^3J({}^{31}P\text{-}H) = 5.4$ Hz, and τ 9.53 ppm, ${}^3J({}^{31}P\text{-}H) = 6.7$ Hz, with an intensity ratio of ca. 4:1; doublet satellites indicate ${}^2J({}^{195}Pt\text{-}{}^1H) = 41.4$ and 55.0 Hz, respectively. In 5 days at room temperature, the two doublets almost disappear in favor of the τ 10.55 ppm singlet; spectral changes are very slight after the first 2 days of the reaction. When the reaction is complete, integration of the τ 10.55 ppm signal and its satellites relative to the Ph_3P resonance and correction for the known phosphine:platinum ratio shows that this singlet is due to six methyl groups per platinum, indicating formation of $Li_2[Pt(CH_3)_6]$. Observation of ^{195}Pt satellites, as well as a separate $[LiCH_3]_4$ resonance, indicates that exchange processes are slow on the NMR time scale. The two sets of doublets indicate formation of $Li[Ph_3PPt(CH_3)_5]$ in the reaction sequence:

$$\begin{tikzcd}
{[Pt(CH_3)_3I]_4} \arrow[r, "3[LiCH_3]_4"] \arrow[d, "2[LiCH_3]_4"', "4Ph_3P"] & 4LiI + 4Li_2[Pt(CH_3)_6] \\
4LiI + 4Li[Ph_3PPt(CH_3)_5] \arrow[r, "{[LiCH_3]_4}"] & 4Ph_3P + 4Li_2[Pt(CH_3)_6]
\end{tikzcd} \qquad (1)$$

Raman difference spectra of an ether solution of $Li_2[Pt(CH_3)_6]$, prepared from $[Pt(CH_3)_3I]_4$, are illustrated in Figure 1; the data for determining the state of polarization of the Raman bands are included. The $\delta_s(CH_3)$ modes have ρ values of effectively zero for the polarized 1250-cm^{-1} band, and, within experimental error, of $^6\!/_7$ (no analyzer in the scattered beam) for the depolarized 1205-cm^{-1} band, consistent with the presence of an isotropic species. The depolarization measurements indicate that the single feature in the ν(Pt–C) region of the spectrum is due to two almost accidentally degenerate modes. Rotating the electrical vector of the incident beam 90° yields a measured ρ of 0.54 for the envelope and a highly reproducible shift in frequency from 508 to 505 cm^{-1}, indicating overlap of a polarized band at 508 cm^{-1} (or slightly above) with a depolarized band at 505 cm^{-1}. The only other features attributable to the hexamethylplatinate(IV) species are the two depolarized bands at 273 and 226 cm^{-1}; other features are due to imperfect cancellation of the solvent spectrum because of conformational changes in the ether, etc. The infrared spectrum of a solution similar to that used to collect the spectra shown in Figure 1 has a very intense band at 478 cm^{-1}, and no other absorptions which cannot be matched with features in spectra of diethyl ether and ether solutions of $[LiCH_3]_4$ and lithium halides.

Although ^{1}H NMR spectra indicate quantitative conversion of $[Pt(CH_3)X]_4$ to $Li_2[Pt(CH_3)_6]$ when X is iodide or chloride. this is not true for the hydroxide or (dimeric) acetylacetonate analogues. Both of the latter reagents react with $[LiCH_3]_4$ to produce solutions whose ^{1}H NMR spectra exhibit the τ 10.55 ppm singlet, with satellites, characteristic of $Li_2[Pt(CH_3)_6]$, but other species also are present. The solution prepared from $[Pt(CH_3)OH]_4$ has a very strong ^{1}H NMR signal at τ 9.72; the Raman spectrum has a band at 564 cm^{-1} which is much stronger than the lower frequency hexamethylplatinate(IV) mode which also is present. These data could indicate formation of a methoxy derivative of trimethylplatinum(IV). The major product from the $[Pt(CH_3)_3acac]_2$ reaction is $Li_2[Pt(CH_3)_6]$; two minor products are platinum black and a species assigned as $Li_2[Pt(CH_3)_4]$ by its ^{1}H NMR, vide infra.

Reactions of $L_2Pt(CH_3)_4$ with $[LiCH_3]_4$. When solid $(Ph_2CH_3P)_2Pt(CH_3)_4$ is treated with an ether solution of halide-free $[LiCH_3]_4$ for 5 days, the ^{1}H NMR spectrum of the supernatent liquid exhibits a doublet at τ 10.38 ppm, ${}^3J({}^{31}P\text{-}H) = 6$ Hz, with doublet satellites, ${}^2J({}^{195}Pt\text{-}H) = 42$ Hz. Since the chemical shift and the coupling to ^{195}Pt are typical of mutually trans methyl groups, and only one phosphine is present, these data indicate the formation of $Li[Ph_2CH_3PPt(CH_3)_5]$. The observed signal is due to the planar set of four methyls, while the resonance of the unique methyl trans to the phosphine, which was observed at τ 9.53 ppm in the Ph_3P analogue, vide supra, is obscured by the intense $(C_2H_5)_2O$ signal centered at τ 8.88 ppm. This species does not react further with $[LiCH_3]_4$ in 4 days at room temperature, but when maintained at 50 °C the τ 10.38 ppm doublet is gradually replaced by a τ 10.52 ppm singlet, ${}^2J({}^{195}Pt\text{-}H) = 40$ Hz; sequential spectra are very similar to those obtained in the reaction of $[Pt(CH_3)_3I]_4$ with $[LiCH_3]_4$ in the presence of Ph_3P, vide supra. The absence of coupling to phosphorus again indicates formation of $Li_2[Pt(CH_3)_6]$.

The sluggish heterogeneous reaction of solid $(Ph_2CH_3P)_2Pt(CH_3)_4$ with $[LiCH_3]_4$ in ether prompted an attempt to synthesize $Li_2[Pt(CH_3)_6]$ from ether-soluble $[(CH_3)_3P]_2Pt(CH_3)_4$. Treatment of the latter with halide-free $[LiCH_3]_4$ in ether gave a homogeneous solution whose ^{1}H NMR spectrum above τ 10 ppm showed only a τ 10.35 ppm triplet due to the starting material, ${}^3J({}^{31}P\text{-}H) = 6.8$, with triplet satellites, ${}^2J({}^{195}Pt\text{-}H) = 44.0$ Hz. The spectrum was unchanged after 15 days at room temperature, indicating that $[(CH_3)_3P]_2Pt(CH_3)_4$ is kinetically rather inert compared to the analogous $(Ph_2CH_3P)_2Pt(CH_3)_4$ complex.

Reaction of $Li_2[Pt(CH_3)_6]$ with PMDT. The solid products of this reaction gave Raman spectra with rather high backgrounds and weak peaks. In all cases, the ν(Pt–C) band was found at 505–508 cm^{-1}. The infrared spectrum of one sample as a Nujol mull had a very broad feature, 467–477 cm^{-1}. These data indicate that the platinum complex in these solids is similar to $Li_2[Pt(CH_3)_6]$ in ether solution.

Platinum(II) Compounds. Reaction of (1,5-COD)$Pt(CH_3)_2$ with $[LiCH_3]_4$. The ^{1}H NMR spectrum of (1,5-COD)$Pt(CH_3)_2$ was reported by Clark and Manzer[29] to have a methyl resonance at τ 9.42 ppm with satellites, ${}^2J({}^{195}Pt\text{-}H) = 83.4$ Hz. The 1,5-cyclooctadiene protons gave two signals at τ 7.85 and 5.35 ppm in a 2:1 intensity ratio, with ${}^2J({}^{195}Pt\text{-}H) = 40$ Hz for the latter (olefinic) protons. When (1,5-COD)$Pt(CH_3)_2$ is treated with $[LiCH_3]_4$ in ether, the resulting solution has a singlet methyl resonance at τ 10.35 ppm, while the ligand resonances occur as singlets at τ 7.66 and 4.48 ppm. Since free 1,5-COD is reported[36] to have ^{1}H NMR singlets at τ 7.67 and 4.52 ppm, a ligand displacement reaction is indicated.

The ν(Pt—C) modes of (1,5-COD)$Pt(CH_3)_2$ occur in the Raman spectrum at 559 (polarized) and 542 (depolarized) cm^{-1} in $CDCl_3$ solution, and at approximately the same positions in the crystal. The material is a good Raman scatterer, and these frequencies are consistent with infrared data reported by Kistner et al.[34] The highest frequency skeletal mode ob-

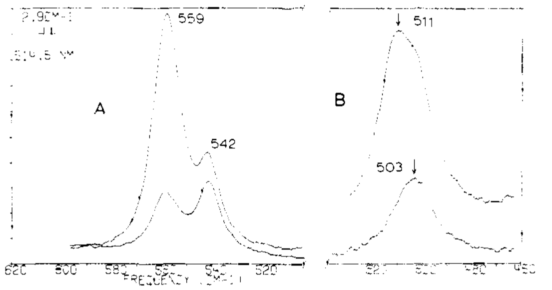

Figure 2. Raman spectra and depolarization measurements for ν(Pt-C) modes: A, (1,5-COD)Pt$(CH_3)_2$ in $CDCl_3$; B, $Li_2[Pt(CH_3)_4]$ in $(C_2H_5)_2O$. Ordinate range in counts ($\times 10^3$): A= 39-73: B, 0-11.

served in the Raman is the ν(C═C) stretch at 1527 cm^{-1}. Treatment of (1,5-COD)Pt$(CH_3)_2$ with $[LiCH_3]_4$ leads to a marked decrease in both the frequency and intensity of the Raman bands in the ν(Pt—C) region, as shown by the spectra illustrated in Figure 2. New (Pt—C) stretching bands appear at 511, 503 cm^{-1}. Additionally, the ν(C═C) mode found at 1527 cm^{-1} in (1,5-COD)Pt$(CH_3)_2$ completely disappears upon methylation and is replaced by an intense band at 1662 cm^{-1}. Since the ν(C═C) stretch also occurs at 1662 cm^{-1} in a 25% v/v solution of 1,5-cyclooctadiene in diethyl ether, the quantitative displacement of the diolefin from platinum is confirmed. These data indicate the formation of lithium tetramethylplatinate(II) according to reaction 2. The similar frequencies and lower intensities of the two (Pt—C) modes of $Li_2[Pt(CH_3)_4]$ as compared to those of $Li_2[Pt(CH_3)_6]$ are analogous to the relationships found for the corresponding ν(Au—C) modes of $Li[Au(CH_3)_2]$ and $Li[Au(CH_3)_4]$.[20]

$$2(1{,}5\text{-COD})Pt(CH_3)_2 + [LiCH_3]_4 \rightarrow 2Li_2[Pt(CH_3)_4] + 2(1{,}5\text{-COD}) \quad (2)$$

Although the ^1H NMR τ 10.35 ppm singlet of $Li_2[Pt(CH_3)_4]$ displays no coupling to ^{195}Pt at 35 °C, reasonably sharp satellites appear *either* upon cooling to -10 °C or warming to 50 °C, with $^2J(^{195}Pt\text{-}H)$ of 43.5 Hz. Additionally, chilling the solution causes the τ 11.92 ppm $[LiCH_3]_4$ resonance to gain intensity, while the τ 10.35 ppm platinate signal fades and essentially disappears at -80 °C; this behavior reverses on warming. However, there is no change in the chemical shift of either the $[LiCH_3]_4$ or $Li_2[Pt(CH_3)_4]$ resonance at any temperature used in the studies. These data indicate that reaction 2 is endothermic and reversible, but also that the mechanism which collapses the ^{195}Pt-H coupling at 35–40 °C does not involve rapid exchange of methyl groups between $Li_2[Pt(CH_3)_4]$ and $[LiCH_3]_4$. A set of three successive ^1H NMR spectra taken on the τ 10.35 ppm singlet are displayed in Figure 3.

Reaction of $(Ph_3P)_2Pt(CH_3)_2$ with $[LiCH_3]_4$. The methyl resonance of $(Ph_3P)_2Pt(CH_3)_2$ has been reported as a complex multiplet at τ 9.67, $^2J(^{195}Pt\text{-}H) = 69.4$ Hz.[35] Treatment of this material with $[LiCH_3]_4$ for 3 days yields a solution whose ^1H NMR displays a doublet at τ 10.41 ppm, $^3J(^{31}P\text{-}H) = 5.3$ Hz, with doublet satellites, $^2J(^{195}Pt\text{-}H) = 48.7$ Hz. A singlet at τ 10.39 ppm also is present. These data indicate displacement of phosphine according to the reaction sequence:

$$\begin{aligned} &4(Ph_3P)_2Pt(CH_3)_2 + [LiCH_3]_4 \rightarrow 4Ph_3P + 4Li[Ph_3PPt(CH_3)_3] \\ &4Li[Ph_3PPt(CH_3)_3] + [LiCH_3]_4 \rightarrow 4Ph_3P + 4Li_2[Pt(CH_3)_4] \end{aligned} \quad (3)$$

The τ 10.41 ppm doublet is due to the mutually trans pair of methyl groups of $Li[Ph_3PPt(CH_3)_3]$, while the resonance of the unique methyl trans to the phosphine is obscured by the intense $(C_2H_5)_2O$ triplet centered at τ 8.88 ppm, as also occurred with the $Li[Ph_2CH_3PPt(CH_3)_5]$ complex, vide supra. After 15 days, only a singlet at τ 10.35 remains.

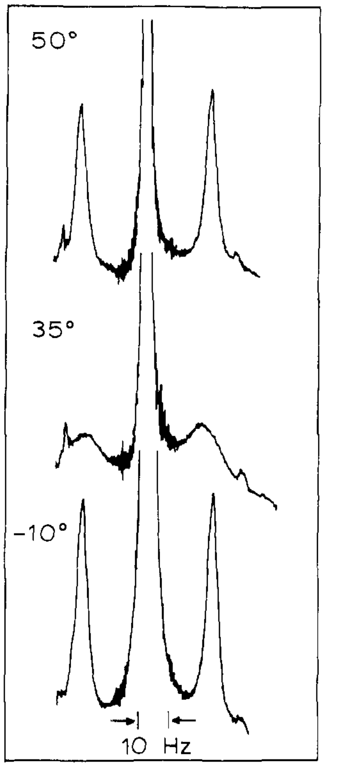

Figure 3. The 90-MHz ^1H NMR of the τ 10.35 ppm resonance of $Li_2[Pt(CH_3)_4]$ as a function of temperature.

The Raman spectrum of a solution freshly prepared from $(Ph_3P)_2Pt(CH_3)_2$ and $[LiCH_3]_4$ in ether has a sharp polarized band at 538 cm^{-1} and second polarized band at ca. 515 cm^{-1} which overlaps with the lower frequency $Li_2[Pt(CH_3)_4]$ bands. Since the isosteric $Ph_3PAu(CH_3)_3$ has polarized Raman bands at 538 and 506 cm^{-1},[20] these data confirm the presence of $[Ph_3PPt(CH_3)_3]^-$. The intensity of the 538- and ca. 515-cm^{-1} bands decreases with time, and after 15 days only the $Li_2[Pt(CH_3)_4]$ bands at 511, 503 cm^{-1} appear.

Reactions of K_2PtCl_4 and *cis*-$(H_3N)_2PtCl_2$ with $[LiCH_3]_4$. Treatment of K_2PtCl_4 with $[LiCH_3]_4$ produces platinum black as one product. The filtrate after removal of the metal exhibits two ^1H NMR singlets at τ 10.55 ppm, $^2J(^{195}Pt\text{-}H) = 40$ Hz, and τ 10.34 ppm, no satellites observed at room temperature, with the latter signal of slightly greater intensity. This indicates formation of $Li_2[Pt(CH_3)_4]$, accompanied by partial disproportionation of platinum(II) to yield $Li_2[Pt(CH_3)_6]$ and platinum metal. Raman spectra of the solution do not yield meaningful results due to the presence of four ν(Pt—C) modes from the two species, all of which occur within a 10-cm^{-1} range.

The analogous reaction of *cis*-$(H_3N)_2PtCl_2$ with $[LiCH_3]_4$ yields a great deal of platinum metal. The filtrate from the metal has only two features upfield from the τ 8.88 ppm ether triplet: the τ 11.92 ppm signal of excess $[LiCH_3]_4$ and the τ 9.84 ppm resonance of methane. As noted by a referee, the formation of methane is not surprising because of the relatively high acidity of the coordinated ammine ligands.

Reactions of $Li_2[Pt(CH_3)_4]$ and $Li_2[Pt(CH_3)_6]$ with Alkyl Halides. Clark and Manzer[29] have reported that (1,5-COD)-Pt$(CH_3)_2$ reacts with CH_3I according to reaction 4 but is unaffected by C_2H_5I; no conditions were reported.

$$(1{,}5\text{-COD})Pt(CH_3)_2 + CH_3I \rightarrow \tfrac{1}{4}[Pt(CH_3)_3I]_4 + 1{,}5\text{-COD} \quad (4)$$

We find that treatment of (1,5-COD)Pt(CH$_3$)$_2$ with a tenfold excess of CH$_3$I in benzene for 5 days yields a solution whose ^{1}H NMR displays the CH$_3$I resonance, a τ 8.94 ppm singlet, $^2J(^{195}\text{Pt–H}) = 83.0$ Hz, 1,5-COD signals at τ 8.13 and 5.37 ppm, $^2J(^{195}\text{Pt–H}) = 40$ Hz for the latter, and no other signals. These data indicate that no reaction occurs under these conditions. By contrast, solutions of Li$_2$[Pt(CH$_3$)$_4$] prepared from (1,5-COD)Pt(CH$_3$)$_2$ and [LiCH$_3$]$_4$ in ether give exothermic and essentially instantaneous reactions with either CH$_3$I or C$_2$H$_5$I, causing solvent boil-off when the solutions are initially at room temperature.

When Li$_2$[Pt(CH$_3$)$_4$] is treated with less than 1 equiv of CH$_3$I in the presence of excess [LiCH$_3$]$_4$, the ^{1}H NMR spectrum has a singlet at τ 10.56 ppm, $^2J(^{195}\text{Pt–H}) = 40.0$ Hz, plus a signal at τ 10.36 ppm due to starting material. Addition of a tenfold excess of CH$_3$I leaves only the τ 10.56 ppm signal of Li$_2$[Pt(CH$_3$)$_6$]. The analogous reaction employing C$_2$H$_5$I gives a solution with ^{1}H NMR singlets at τ 10.58 and 10.65 ppm with a 4:1 intensity ratio, $^2J(^{195}\text{Pt–H}) = 40.0$ and 37.0 Hz, respectively. These data suggest formation of Li$_2$[Pt(CH$_3$)$_5$C$_2$H$_5$]. The τ 10.58 ppm signal is due to the planar set of four methyls, the weaker τ 10.65 ppm signal is due to the unique methyl trans to the ethyl ligand, and the ethyl proton resonances are presumably hidden in baseline noise.

The very rapid reactions of CH$_3$I and C$_2$H$_5$I with Li$_2$[Pt(CH$_3$)$_4$] are followed by slower processes which first destroy any [LiCH$_3$]$_4$ present and then, when [LiCH$_3$]$_4$ is no longer present, destroy the peralkylplatinate(IV). These reactions were verified by the reactions of CH$_3$I and C$_2$H$_5$I with Li$_2$[Pt(CH$_3$)$_6$] prepared from [Pt(CH$_3$)$_3$I]$_4$, in which the molar proportion RX:Li$_2$[Pt(CH$_3$)$_6$]:LiCH$_3$ was 1.6:0.27:0.19. In all of these reactons, the τ 11.93 ppm ^{1}H NMR signal of [LiCH$_3$]$_4$ loses intensity and moves to lower field (ca. τ 11.75 ppm minimum), while the peralkylplatinate(IV) signals remain unchanged as a singlet grows in at τ 9.15–9.19 ppm, indicating formation of ethane. For C$_2$H$_5$I, this appears to require either an exchange reaction such as eq 5 or a reaction involving the platinate(IV) complex to account for the formation of ethane rather than propane.

$$\text{C}_2\text{H}_5\text{I} + \text{LiCH}_3 \rightleftharpoons \text{CH}_3\text{I} + \text{LiC}_2\text{H}_5 \qquad (5)$$

When [LiCH$_3$]$_4$ is no longer present, the peralkylplatinate(IV) signals in the ^{1}H NMR lose intensity and disappear after a maximum of 38 h. The loss of Li$_2$[Pt(CH$_3$)$_6$] in solutions containing CH$_3$I is accompanied only by formation of further C$_2$H$_6$. However, the solutions containing C$_2$H$_5$I and either Li$_2$[Pt(CH$_3$)$_6$] or Li$_2$[Pt(CH$_3$)$_5$C$_2$H$_5$] develop new ^{1}H NMR signals at τ 9.86 and 4.66 ppm due to CH$_4$ and C$_2$H$_4$, respectively, and when the reactions are complete, CH$_4$, C$_2$H$_6$, and C$_2$H$_4$ are present in approximately equal quantities ($\pm$25%).

All four of the above reactions, Li$_2$[Pt(CH$_3$)$_4$] or Li$_2$[Pt(CH$_3$)$_6$] with excess CH$_3$I or C$_2$H$_5$I, produce solutions which, after the loss of the peralkylplatinates, remain clear and colorless to slightly yellow. No signals due to organoplatinum species are then observable in the ^{1}H NMR, but Raman spectra reveal the presence of a single ν(Pt–C) band at 559 cm^{-1} in each of the solutions. Rotating the electrical vector of the incident beam 90° yields a decrease in intensity and a reproducible shift in frequency to 557 cm^{-1}, demonstrating the presence of two almost accidentally degenerate bands. A solution of Li$_2$[Pt(CH$_3$)$_3$I$_3$] prepared by dissolving [Pt(CH$_3$)$_3$I]$_4$ in a 1.0 M solution of LiI in diethyl ether gave a ν(Pt–C) band at essentially the same frequency (563 cm^{-1} on a different Raman spectrometer) but also displayed no observable ^{1}H NMR signal other than solvent bands. Stocco et al.[37] have shown that the ^{1}H NMR signal of [Pt(CH$_3$)$_3$I$_3$]$^{2-}$ occurs at ca. τ 8.2 ppm, a region obscured by ether satellites in our experiments. These data indicate that the peralkylplatinate(IV) complexes couple with CH$_3$I or C$_2$H$_5$I to give [Pt(CH$_3$)$_3$I$_3$]$^{2-}$ and hydrocarbon products.

Treatment of Li$_2$[Pt(CH$_3$)$_4$] in ether with a tenfold excess of n-C$_4$H$_9$Cl in the presence of [LiCH$_3$]$_4$ led to a gradual decrease in the τ 10.35 ppm singlet of Li$_2$[Pt(CH$_3$)$_4$], deposition of a white solid presumed to be LiCl, and simultaneous growth of signals at τ 10.55 and 10.61 ppm with a 4:1 intensity ratio, $^2J(^{195}\text{Pt–H}) = 40.1$ and 37.5 Hz, respectively. These data indicate formation of Li$_2$[Pt(CH$_3$)$_5$(n-C$_4$H$_9$)] and are interpreted in the same manner as the data for Li$_2$[Pt(CH$_3$)$_5$C$_2$H$_5$], vide supra. The reaction is fairly rapid, with completion percentages of ca. 20% in 1 h, 80% in 11 h, and 99% in 37 h under the conditions employed. Unlike the reactions involving CH$_3$I and C$_2$H$_5$I, no reaction of excess n-C$_4$H$_9$Cl with either [LiCH$_3$]$_4$ or Li$_2$[Pt(CH$_3$)$_5$(n-C$_4$H$_9$)] could be detected after 185 h at room temperature. The solution remains colorless throughout.

The reaction of (CH$_3$)$_3$SiCH$_2$Cl with a solution of Li$_2$[Pt(CH$_3$)$_4$] and [LiCH$_3$]$_4$ is rather different from the reactions of the other alkyl halides. Initially the τ 10.35 ppm singlet of Li$_2$[Pt(CH$_3$)$_4$] is gradually replaced by a τ 10.53 ppm signal, but the τ 11.95 ppm signal of [LiCH$_3$]$_4$ diminishes more rapidly and is gone after 11 h. At this point the solution darkens due to apparent formation of platinum black. No C$_2$H$_6$ resonance is apparent, and the silicon-containing products could not be identified by the ^{1}H NMR spectra.

Attempted Reaction of Li$_2$[Pt(CH$_3$)$_4$] with Li[Au(CH$_3$)$_4$]. Since Peloso[38] has found that [AuCl$_4$]$^-$ reacts with dichloroplatinum(II) complexes to form [AuCl$_2$]$^-$ and tetrachloroplatinum(IV) complexes, a reaction such as eq 6 seemed favorable.

$$[\text{Pt(CH}_3)_4]^{2-} + [\text{Au(CH}_3)_4]^- \rightarrow [\text{Pt(CH}_3)_6]^{2-} + [\text{Au(CH}_3)_2]^- \qquad (6)$$

When a mixture of (1,5-COD)Pt(CH$_3$)$_2$ and Ph$_3$PAu(CH$_3$)$_3$ is treated with excess [LiCH$_3$]$_4$ in ether, a ^{1}H NMR spectrum taken immediately has τ 10.08 and 10.35 ppm singlets characteristic of Li[Au(CH$_3$)$_4$][20] and Li$_2$[Pt(CH$_3$)$_4$], respectively, as well as signals due to unreacted Ph$_3$PAu(CH$_3$)$_3$. After 50 min, the gold is present entirely as Li[Au(CH$_3$)$_4$]. The ^{1}H NMR spectrum did not change in 184 h at room temperature. These data indicate, first, that Li[Pt(CH$_3$)$_4$], which is immediately formed from (1,5-COD)Pt(CH$_3$)$_2$, does not interact with the free Ph$_3$P which is effectively generated in situ by the slower reaction of Ph$_3$PAu(CH$_3$)$_3$. Secondly, the observation of separate resonances for Li$_2$[Pt(CH$_3$)$_4$] and Li[Au(CH$_3$)$_4$] at the same positions where each occurs alone demonstrates that there is neither substantial interaction nor rapid exchange between these species.

Reductive Elimination of C$_2$H$_6$ from (Ph$_2$CH$_3$P)$_2$Pt(CH$_3$)$_4$. When (Ph$_2$CH$_3$P)$_2$Pt(CH$_3$)$_4$ is dissolved in CDCl$_3$, the initial ^{1}H NMR spectrum shows, in addition to the phenyl resonances, three methyl resonances in the τ 8–11 ppm range in 1:1:1 intensity ratios (see data in Table II) due to two pairs of methyls bound to platinum and one pair of methyls on the phosphines. However, the τ 9.14 ppm singlet characteristic of ethane also is observed within 5 min of preparation of the solution, and the intensity of this signal grows rapidly. After 2 days the C$_2$H$_6$ signal is dominant and the remainder of the spectrum is quite complex, indicating the presence of two or more platinum species with overlapping ^{1}H NMR signals. The spectrum then simplifies with time, and after an additional 7 days only the ethane signal and two methyl resonances are observed. The methyls in the two Ph$_2$CH$_3$P ligands give a triplet at τ 7.79 ppm, $^2J(^{31}\text{P–H}) = 7.3$ Hz, with triplet satellites, $^3J(^{195}\text{Pt–H}) = 28.0$ Hz. The Pt(CH$_3$) signal, of half the intensity of the phosphine one, occurs as a triplet at τ 10.04

ppm, $^{3}J(^{31}P-H)$ = 6.5 Hz, with triplet satellites, $^{2}J(^{195}Pt-H)$ = 81.3 Hz. Comparison of these data to data reported by Ruddick and Shaw,[30] as well as the observed 2:1 intensity ratio of the resonances, indicates the formation of *trans*-$(Ph_2CH_3P)_2$- $PtCH_3Cl$. Since van Leeuwen et al.[39] have found that Ph_3PAuCH_3 reacts photochemically with $CDCl_3$ to give Ph_3PAuCl, it is likely that a similar reaction occurs in the platinum system under laboratory light. The initial product of reductive elimination of ethane should be $(Ph_2CH_3P)_2$-$Pt(CH_3)_2$, but no data were collected at times when this complex was the principal component in solution. In contrast to the behavior of $(Ph_2CH_3P)_2Pt(CH_3)_4$, the analogous $[(CH_3)_3P]_2$ $Pt(CH_3)_4$ is quite stable in $CDCl_3$, for the ^{1}H NMR spectrum does not change in 11 days at room temperature.

Discussion

Vibrational and NMR Spectra. The most useful spectroscopic data for identification of the permethylplatinate(II) and -(IV) species in solution are the ν(Pt—C) vibrational frequencies and the $^{2}J(^{195}Pt-H)$ coupling constants. These parameters vary in a systematic fashion and depend, in decreasing order of importance, on (1) the ligand trans to a methyl group, (2) the oxidation state of platinum, and (3) the ligand cis to the methyl group.

The free hexamethylplatinate(IV) ion is expected to have platinum(IV) octahedrally coordinated to the methyl ligands. With O_h symmetry, the six Pt-C coordinates transform as A_{1g} + E_g + T_{1u}, and the six modes involving symmetric deformations of the methyls will transform according to the same representations. Of these, the A_{1g} and E_g representations correspond to Raman active modes and T_{1u} to an infrared active one. As shown by the spectra illustrated in Figure 1 and the data in Table I, $[Pt(CH_3)_6]^{2-}$ gives almost ideal Raman spectra in the $\delta_s(CH_3)$ and ν(Pt-C) regions. For this isotropic species, the theoretical depolarization ratios are $\rho = 0$ for totally symmetric vibrations and $\rho = 6/7$, or 0.86, for all others with the apparatus used in obtaining the spectra. For the symmetric methyl deformations, a ρ value of effectively zero indicates that the 1250-cm^{-1} band is due to the A_{1g} mode, while ρ within experimental error (baseline definition) of 0.86 for the 1205-cm^{-1} band indicates this is due to the E_g mode. Near accidental degeneracy of the two Raman active ν(Pt-C) modes precluded ρ measurements, but the observed intensity ratio of 0.54 for the envelope is consistent with an E_g mode with somewhat greater intensity than the A_{1g} mode, as is observed for the $\delta_s(CH_3)$ scattering. The 505-cm^{-1} band in the lower spectrum, Figure 1, should contain only intensity arising from the E_g stretch.

The skeletal deformations of the PtC_6 skeleton transform according to T_{2g} + T_{1u} + T_{2u} and should be Raman active, infrared active, and inactive, respectively. The atomic motions corresponding to the six fundamentals of an MX_6 unit are given by Adams.[40] However, the Raman spectra of $Li_2[Pt(CH_3)_6]$ clearly show two fairly intense depolarized bands at 273 and 226 cm^{-1}, neither of which can be attributed to the known spectrum[20] of $[LiCH_3]_4$ in diethyl ether. The low dielectric constant of diethyl ether will certainly require ion-pairing interactions of $[Pt(CH_3)_6]^{2-}$ with etherated lithium cations, and this should perturb the anion from the full cubic symmetry expected for the free ion. Since Griffith[41] has found that interactions in crystalline $[M(NH_3)_6]Cl_3$, M = Ir, Rh, Ru, split the infrared active T_{1u} metal-nitrogen deformations into two bands without any apparent effect on the T_{1u} ν(M-N) modes, it seems reasonable that a similar splitting of the T_{2g} metal-carbon deformation of $[Pt(CH_3)_6]^{2-}$ could occur without noticeable effect on the ν(Pt-C) and $\delta_s(CH_3)$ modes.

Occurrence of the Raman active ν(Pt-C) modes of $Li_2[Pt(CH_3)_4]$ at almost the same frequencies as those of $Li_2[Pt(CH_3)_6]$ indicates rather similar electronic environments for methyl groups in the two complexes. Since the frequencies are typical of mutually trans methyl groups, one would expect normal, square planar coordination of platinum(II). With D_{4h} symmetry, the four (Pt-C) coordinates transform as A_{1g} + B_{1g} + E_u of which the first two representations correspond to the Raman active modes. The data illustrated in Figure 2 for the depolarization measurements and collected in Table I show that the 511-cm^{-1} band arises from the A_{1g} mode, while the 503-cm^{-1} band is from the B_{1g} one. The frequencies are slightly lower than the corresponding values of the isoelectronic $Au(CH_3)_4^-$, 530 and 522 cm^{-1}.[20] This is the expected consequence of a decrease in the metal ligand force constant with decreasing metal oxidation state with these isoelectronic complexes.

The values for the coupling constants, $^{2}J(^{195}Pt-H)$ also are very similar with $[Pt(CH_3)_6]^{2-}$ and $[Pt(CH_3)_4]^{2-}$ 40.0 and 43.5 Hz, respectively (cf. 65.4[35] and 57.0 Hz for methyl trans to $(CH_3)_3P$ in $[(CH_3)_3P]_2Pt(CH_3)_2$ and $[(CH_3)_3P]_2$-$Pt(CH_3)_4$, respectively). Again, the values for the permethylplatinates are closer to one another than would have been predicted from previous data. Since the coupling constant in $[Pt(CH_3)_6]^{2-}$ is quite in line with those for mutually trans methyls in $(R_3P)_2Pt(CH_3)_4$, one must conclude that $^{2}J(^{195}Pt-H)$ for $[Pt(CH_3)_4]^{2-}$ is unusually low. These data together suggest that if one performs the *gedanken* experiment of taking a $[Pt(CH_3)_6]^{2-}$ ion and effecting reduction by progressively lengthening an axial pair of Pt-C bonds until the system becomes a $[Pt(CH_3)_4]^{2-}$ ion and two methyl radicals, the equatorial methyls will experience almost no change in their electronic environment. The near identical values of the A_{1g} and $E_g\nu$(Pt-C) modes in $[Pt(CH_3)_6]^{2-}$ confirm this suggestion, for the Raman data demonstrate that the frequencies of the vibrations are insensitive to the relative phase of the motions of the equatorial and axial methyls. (This simply reflects the minor importance of the cis influence.) If the *gedanken* experiment is correct, it appears that removal of two methyl groups from $[Pt(CH_3)_6]^{2-}$ to form $[Pt(CH_3)_4]^{2-}$ leads to minimal rehybridization at platinum, so that the lone pair electron density in the platinum(II) complex resides in a ds hybrid orbital, which would presumably help delocalize the charge on the metal.

Diethyl ether and THF have quite low dielectric constants, but their donor numbers are slightly greater than that of water.[42] Consequently, one would expect solutions of $Li_2[Pt(CH_3)_6]$ or $Li_2[Pt(CH_3)_4]$ to contain solvated lithium cations ion-paired with $[Pt(CH)_3]_6^{2-}$ or $[Pt(CH_3)_4]^{2-}$. The most favorable ion-pairing arrangement in $Li_2[Pt(CH_3)_4]$ would appear to involve direct interaction of solvated lithium cations with the lone pair electron density in the axially directed platinum ds orbital proposed above. Indeed, the temperature dependence of the ^{1}H NMR spectrum of $Li_2[Pt(CH_3)_4]$, Figure 3, indicates just such an interaction. Several ^{1}H NMR experiments carried out in the course of syntheses, vide supra, show that the chemical shift of the $Li_2[Pt(CH_3)_4]$ signal is unaffected by the presence of $[LiCH_3]_4$, $Li_2[Pt(CH_3)_6]$, or $Li[Au(CH_3)_4]$. The finding that $Li_2[Pt(CH_3)_4]$ and $Li[Au(CH_3)_4]$, which contain isoelectronic anions, do not give rapid intermolecular exchange of methyl groups is particularly compelling evidence that the collapse of the ^{195}Pt satellites of $Li_2[Pt(CH_3)_4]$ is not due to rapid exchange of methyl groups bound to platinum. A similar collapse of ^{199}Hg satellites in the ^{1}H NMR of $HgCH_3I$ is reported to occur by rapid relaxation of the ^{199}Hg nucleus and not by methyl exchange. The mechanism for relaxation of ^{199}Hg was originally suggested to be coupling of ^{199}Hg to the rapidly relaxing (quadrupolar) ^{127}I nucleus,[43-45] but is now believed to

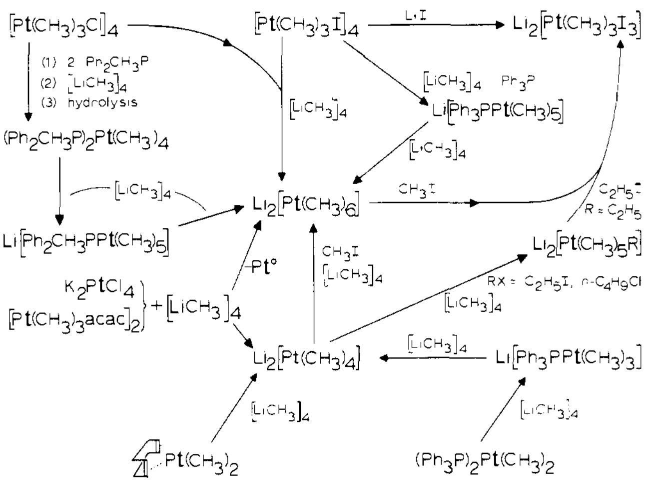

Figure 4. Syntheses and reactions of peralkylplatinates and related compounds. With the exception of $[LiPMDT]_2[Pt(CH_3)_6]$, the very reactive tri- and tetramethylplatinate(II) and penta- and hexaalkylplatinate(IV) compounds were studied only in solution.

be iodide–iodide exchange instead.[46] In support of the latter, it should be noted that the presence of iodide apparently has no effect on the ^{195}Pt satellites in substitutionally inert compounds such as *trans*-$[(CH_3)_2PhP]_2PtCH_3I$ and $[(CH_3)_2PhP]_2Pt(CH_3)_3I$.[30] On the basis of these findings and our ^1H NMR data, we suggest the following explanation for the spectra in Figure 3: At −10 °C, exchange of solvated lithium cations is slow on the NMR time scale. The ^{195}Pt nuclei therefore "see" essentially a constant environment, and a normal spectrum results. At 50 °C, the exchange process is fast on the NMR time scale. The ^{195}Pt nuclei "see" a time-averaged environment and again an apparently normal spectrum results. At 35 °C, the lithium exchange rate is at an intermediate value which induces rapid relaxation of the ^{195}Pt nuclei, and the satellites are broadened. It should be noted that exchange of lithium cations is expected to broaden the ^1H NMR bands of $Li_2[Pt(CH_3)_4]$ only in the units which contain ^{195}Pt and not in those containing the spin-zero nuclei, ^{194}Pt and ^{196}Pt. Hence the 35 °C spectrum has very broad satellites but a sharp central peak.

We conclude that the Raman data which show very similar ν(Pt–C) stretching frequencies in $Li_2[Pt(CH_3)_4]$ and $Li_2[Pt(CH_3)_6]$ are complemented by ^1H NMR data which show very similar $^2J(^{195}Pt\text{–}H)$ coupling constants in the two species as well as reasonably direct lithium–platinum interaction in $Li_2[Pt(CH_3)_4]$. All of these data are consistent with very slight differences in hybridization at platinum between $[Pt(CH_3)_4]^{2-}$ and $[Pt(CH_3)_6]^{2-}$, and hence with essentially identical platinum–carbon bonds in the two complexes. It should be noted that the proposed interaction of $[Pt(CH_3)_4]^{2-}$ with two solvated lithium cations would have no effect on the selection rules used to interpret the vibrational data under D_{4h} symmetry. By contrast, a similar interaction in $Li[Au(CH_3)_4]$ would reduce the anion symmetry from D_{4h} to C_{4v}, and the selection rules in that complex were previously noted to break down.[20]

Syntheses and Reactions. Although the literature contains a report[5] that a suspension of $[Pt(CH_3)_3I]_4$ in hexane is unaffected by $[LiCH_3]_4$, the synthesis of $Li_2[Pt(CH_3)_6]$ from the same reagents in the much better donor solvents diethyl ether and tetrahydrofuran is not surprising in view of the ready formation of dimethylaurate(I)[19] and tetramethylaurate(III)[20] complexes in the same solvents. Certainly a reaction such as eq 7, whose products are at least nominally ionic, would not occur in solvents which cannot compensate lithium for the loss of its carbanionic ligands.

$$[Pt(CH_3)_3I]_4 + 3[LiCH_3]_4 \rightarrow 4Li_2[Pt(CH_3)_6] + 4LiI \tag{7}$$

Since the presence of LiI in solutions of $Li_2[Pt(CH_3)_6]$ prepared according to reaction 7 complicates attempts to isolate the platinate(IV) by precipitation reactions, a good deal of effort was put into attempts to synthesize $Li_2[Pt(CH_3)_6]$ from $(R_3P)_2Pt(CH_3)_4$ complexes. It was observed that $(Ph_2CH_3P)_2Pt(CH_3)_4$ undergoes very slow displacement of phosphine in the heterogeneous reaction with a solution $[LiCH_3]_4$ and that the complex eliminates ethane rapidly in chloroform solution, while $[(CH_3)_3P]_2Pt(CH_3)_4$ is entirely unreactive under similar conditions. The mechanisms proposed for reductive coupling or elimination from complexes such as Ph_3PAuCH_3,[47] $Ph_3PAu(CH_3)_3$,[48] *cis*-$(Ph_3P)_2Pt(n\text{-}C_4H_9)_2$,[49] and $[(CH_3)_2PhP]_2PtCH_3(C_2H_5)_2I$[50] all involve phosphine dissociation as the first step in the reaction; a recent detailed study[51] of elimination of C_2H_6 from $[(R_3P)_2Au(CH_3)_2]^+$ complexes found a steady increase in reaction rate as the ligand was varied along the series: $(CH_3)_3P < (CH_3)_2PhP < Ph_2CH_3P < Ph_3P$. This difference was attributed primarily to increasing steric crowding of the cis phosphines, and hence to more ready phosphine dissociation. The same steric effects will be operative in $(R_3P)_2Pt(CH_3)_4$ complexes, magnified by the presence of two additional methyl groups bound at ca. 90° to both phosphines. The $(CH_3)_3P$ complex is therefore much more stable than the Ph_2CH_3P one; successful synthesis of $(Ph_2CH_3P)_2Pt(CH_3)_4$ seems to require the presence of excess phosphine through the recrystallizations to prevent decomposition. Since a six-coordinate platinum complex would appear to require ligand dissociation as the first step in a substitution reaction, the synthesis of $Li_2[Pt(CH_3)_6]$ from $(Ph_2CH_3P)_2Pt(CH_3)_4$ but not from $[(CH_3)_3P]_2Pt(CH_3)_4$ again reflects the more ready dissociation of phosphine from the former. It is worth noting that previously reported tetramethylplatinum(IV) complexes have had no more than one phenyl group per phosphine ligand,[30] and particularly that $(Ph_3P)_2Pt(CH_3)_4$ has not been reported.

By analogy with the $[(R_3P)_2Au(CH_3)_2]^+$ series, vide supra, $(Ph_3P)_2Pt(CH_3)_2$ should be among the most reactive of the dimethylbis(phosphine)platinum(II) complexes, yet its reaction with $[LiCH_3]_4$ in ether is quite sluggish, perhaps due in part to the heterogeneous nature of the reaction. By contrast, displacement of the chelating diolefin from (1,5-COD)-$Pt(CH_3)_2$ is complete within 5 min. Clark and Manzer[29] have noted that displacement of 1,5-COD from this complex is facilitated by incoming ligands of high trans influence, a condition certainly met by methide, but their substitution rates were apparently much slower even for neutral ligands with relatively high trans influence.

The reactions of $Li_2[Pt(CH_3)_4]$ with alkyl halides indicate that the tetramethylplatinate(II) complex is an extremely reactive species, and indeed may be one of the most potent nucleophiles yet discovered. Chatt and Shaw[28] found that CH_3I added readily to *trans*-$(Ph_3P)_2PtCH_3I$ only at 100 °C in a sealed tube, while Ruddick and Shaw[30] carried out the reaction of CH_3I with $[(CH_3)_2PhP]_2Pt(CH_3)_2$ at 20 °C for 2 weeks. This latter reaction may be more facile than indicated by the conditions used by Ruddick and Shaw. Clark and Manzer[52] reported *trans*-$[(CH_3)_2PhP]_2Pt(CH_3)_2$ (presumably the cis isomer was meant) reacted vigorously with neat methyl iodide. Tamaki and Kochi[19] showed that lithium dimethylaurate(I) reacts essentially instantaneously with CH_3I but at a slower, easily measurable rate with C_2H_5I. $Li_2[Pt(CH_3)_4]$ reacts completely with both CH_3I and C_2H_5I within 3 min. Similarly, $Li[Au(CH_3)_2]$ reacted only slightly with $n\text{-}C_4H_9Cl$ in 8 h,[19] but the reaction of $Li_2[Pt(CH_3)_4]$ with $n\text{-}C_4H_9Cl$ is 80% complete in 11 h under somewhat different conditions.

The partial disproportionations observed in methylations of K_2PtCl_4 and AuCl are analogous to the disproportionation reactions reported for methylations of TlX and PbX_2,[53] except that platinum and gold form stable organometallics in two oxidation states, while thallium and lead give only compounds of their highest oxidation states. Two routes are possible for disproportionation in the platinum system. One is a direct redox reaction in which two platinum(II) centers react to form platinum(0) and a platinum(IV) complex. The other is the formation of CH_3Cl from K_2PtCl_4 and $[LiCH_3]_4$, giving platinum(0) as one product, followed by rapid addition of CH_3Cl to preformed $Li_2[Pt(CH_3)_4]$. Analogous reactions are possible in the gold system.

The reactions of perkalkylplatinate(IV) complexes with alkyl halides may be contrasted with known reactions in the gold system. Thus, Ph_3PAuCH_3 with CH_3I gives, as final products, Ph_3PAuI and C_2H_6, while $Ph_3PAuC_2H_5$ with CH_3I gives Ph_3PAuI, C_4H_{10}, C_3H_8, and C_2H_6.[54] These reactions were well characterized as oxidative addition-reductive elimination sequences. In the platinum system, the reactions which begin with $Li_2[Pt(CH_3)_4]$ and an alkyl halide are clearly initiated by an oxidative addition reaction. The formation of $Li_2[Pt(CH_3)_3I_3]$ from C_2H_5I and either $Li_2[Pt(CH_3)_6]$ or $Li_2[Pt(CH_3)_5Et]$ would appear to require subsequent reductive elimination-oxidative addition processes to account for the formation of C_2H_4 and CH_4 via a β-elimination step. The operation of a β-elimination reaction in the ethylplatinum system but not in the ethylgold system is in keeping with previous findings that reductive elimination gives butane and 1-butene from $(Ph_3P)_2Pt(n\text{-}C_4H_9)_2$,[49] but *n*-octane from isoelectronic $[(Ph_3P)_2Au(n\text{-}C_4H_9)_2]^+$.[51] The reaction of Ph_3PAuCH_3 with CH_3I led to a gold(I) product because Ph_3PAuI is unreactive toward CH_3I.[54] The product of our reactions was a platinum(IV) complex, presumably because no ligands were present which will trap platinum(II) in an inert species.

The chemistry described in this paper is summarized in Figure 4. Trimethylplatinum(IV) compounds were first reported in 1907, and tetramethylplatinum(IV) complexes were described in 1967, but tetramethylplatinate(II) and hexamethylplatinate(IV) had eluded detection so far. The discovery of the permethylplatinates and the products of the ready oxidative additions of RX to $Li_2[Pt(CH_3)_4]$ represent a significant extension of the organoplatinum field. We suggest that reactions analogous to those given in Figure 4 will provide the long-sought route to higher homologues of methylplatinum(IV) complexes.

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