Thermal and Methyllithium-assisted Cyclometallation Reactions of η^3-Allyl(methyl)(tertiary phosphine or phosphite)platinum(II) Complexes

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The complexes $[Pt(\eta^3\text{-}C_3H_5)Me(L)]$ [L = $P(C_6H_4Me\text{-}o)_3$, $PPh_2(C_6H_4Me\text{-}o)$, $PPh_2(CH_2Ph)$, PPr_3 and $P(OPh)_3$] have been prepared and characterized by ^1H and ^{13}C NMR spectroscopy. Four of these complexes decompose in boiling toluene to give the cyclometallated complexes $[Pt(\eta^3\text{-}C_3H_5)(P\text{–}C)]$ (P–C = cyclometallated phosphine or phosphite), which have also been characterized spectroscopically. The complex $[Pt(\eta^3\text{-}C_3H_5)\{o\text{-}CH_2C_6H_4P(C_6H_4Me\text{-}o)_2\}]$ exists as a novel pair of conformers in solution. Addition of an equivalent of methyllithium to a solution of $[Pt(\eta^3\text{-}C_3H_5)Me\{P(C_6H_4Me\text{-}o)_3\}]$ in toluene promotes cyclometallation of the phosphine ligand, giving the cyclometallated product without heating, while using tetrahydrofuran does not give a cyclometallated product. A tentative mechanism of the methyllithium-assisted cyclometallation reaction is proposed based on the product analysis.

The cyclometallation of tertiary phosphine or phosphite ligands complexed to transition metals is still a growing area of interest and examples of such a reaction are well documented in several reviews.[1] A variety of palladium(II) and platinum(II) complexes containing cyclometallated phenyl,[2] *o*-tolyl,[3] mesityl,[4] benzyl,[5] propyl,[3a] neopentyl[6] or *tert*-butyl[7] phosphine ligands or a phenyl phosphite ligand[8] have hitherto been isolated. However, these were usually complexes of the type $[M_2(\mu\text{-}X)_2(P\text{–}C)_2]$, $[MX(P\text{–}C)L]$ or $[M(P\text{–}C)_2]$ (M = Pd or Pt; P–C = cyclometallated phosphine or phosphite; X = halide, methyl or other monodentate anionic ligand; L = neutral ligand); no examples of cyclometallated complexes containing an allyl group (C_3H_5) as a coexisting organic ligand, *i.e.*, $[M(\eta^3\text{-}C_3H_5)(P\text{–}C)]$ (M = Pd or Pt), have been found so far.

During our studies[9,10] on the thermolysis of $[M(\eta^3\text{-}C_3H_5)Me(L)]$ (M = Pd or Pt, L = tertiary phosphine), we found that the platinum(II) complexes with L = $P(C_6H_{11})_3$, PPh_3 or $PMePh_2$ decompose, in diphenylmethane (100 °C, 2 h), with the evolution of propene and methane in a mole ratio of *ca.* 7:3, while for the same complex with L = $P(C_6H_4Me\text{-}o)_3$, the ratio is reversed. The increase in the amount of methane relative to propene suggested the ready cyclometallation of the coordinated $P(C_6H_4Me\text{-}o)_3$ and prompted us to prepare the first complexes of the type $[Pt(\eta^3\text{-}C_3H_5)(P\text{–}C)]$ from $[Pt(\eta^3\text{-}C_3H_5)Me(L)]$ by means of thermolysis. This paper describes the details of these reactions together with their promoting effect by methyllithium.

Experimental

All synthetic reactions were carried out in an atmosphere of nitrogen unless otherwise stated. Solvents and reagents were redistilled under and purged with argon, respectively. The diethyl ether solutions of LiMe (0.87 or 1.13 mol dm^{-3}) were gifts from Tosoh Akzo Corporation. The allyl complexes $[\{Pt(C_3H_5)Cl\}_4]$[11] and $[Pt(\eta^3\text{-}C_3H_5)Cl(L)]$[12] were synthesized by published methods. Tertiary phosphines, phosphites and other reagents were obtained commercially and used without further purification. Standard gases were also obtained commercially.

Synthesis of $[Pt(\eta^3\text{-}C_3H_5)Me(L)]$ [L = $P(C_6H_4Me\text{-}o)_3$ **1**, $PPh_2(C_6H_4Me\text{-}o)$ **2**, $PPh_2(CH_2Ph)$ **3**, $P(OPh)_3$ **4** *or* PPr_3 **5**].—Complexes **1**–**4** were synthesized from $[Pt(\eta^3\text{-}C_3H_5)Cl(L)]$ and LiMe in toluene at −10 °C according to the reported method.[10] Complex **5** was obtained by the reaction of $[\{Pt(C_3H_5)Cl\}_4]$ with PPr_3 in dichloromethane, followed by reaction with LiMe in toluene at −10 °C without isolating the oily intermediate $[Pt(\eta^3\text{-}C_3H_5)Cl(PPr_3)]$. Complex **1** was purified by column chromatography on silica gel with benzene as the eluent.

Thermolysis.—Isolation of the cyclometallated complexes $[Pt(\eta^3\text{-}C_3H_5)(P\text{–}C)]$ [P–C = $o\text{-}CH_2C_6H_4P(C_6H_4Me\text{-}o)_2$ **6**, $o\text{-}CH_2C_6H_4PPh_2$ **7**, $o\text{-}C_6H_4CH_2PPh_2$ **8** *or* $o\text{-}C_6H_4OP(OPh)_2$ **9**]. The general procedure was as follows. A toluene solution containing **1**, **2**, **3** or **4** was refluxed for 2 h and the darkened solution allowed to stand until it reached room temperature. Silica gel was added to the solution to remove some decomposed by-products and the mixture was stirred for 30 min. After filtration and evaporation, the residue was washed successively with small portions of diethyl ether and of hexane, each several times and dried *in vacuo*.

The product obtained from **2** by this procedure, however, was a mixture of **7** and *cis*-$[Pt(o\text{-}CH_2C_6H_4PPh_2)_2]$ **10**. Upon recrystallization from dichloromethane–hexane at −20 °C complex **10** precipitated as a colourless crystalline solid containing dichloromethane as solvent of crystallization. Another product isolated from the filtrate was confirmed, on the basis of its ^1H NMR data, as complex **7** still contaminated with a small amount of **10**.

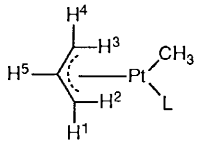
To examine the route to **10**, the σ-allyl complex $[Pt(\sigma\text{-}C_3H_5)Me\{PPh_2(C_6H_4Me\text{-}o)\}_2]$ was prepared from the reaction between **2** and $PPh_2(C_6H_4Me\text{-}o)$ in dichloromethane[10] and the complex was thermolysed under the same conditions as those for cyclometallation. However, the ^1H NMR spectrum of the complex isolated showed that the σ-allyl complex had been recovered unchanged. In contrast, when the σ-allyl complex was thermolysed without solvent at 180 °C for 2 h a darkened oily substance was obtained. After cooling to room temperature, the addition of benzene precipitated a white solid, which was filtered off and dried *in vacuo*. This was confirmed by its ^1H NMR spectrum to be complex **10**. The filtrate was worked-up in the same manner as described above to give another crop of **10**.

Table 1 Yields and analytical data for complexes **1**–**10**

	Complex[a]	Yield (%)	Analysis (%)[b] C	H
1	[Pt(η^3-C_3H_5)Me{P(C_6H_4Me-*o*)$_3$}]	66	53.7 (54.1)	5.1 (5.3)
2	[Pt(η^3-C_3H_5)Me{PPh_2(C_6H_4Me-*o*)}]	83	53.0 (52.4)	4.8 (4.8)
3	[Pt(η^3-C_3H_5)Me{PPh_2(CH_2Ph)}]	90	52.5 (52.4)	4.8 (4.8)
4	[Pt(η^3-C_3H_5)Me{P(OPh)$_3$}]	95	45.9 (47.1)	3.9 (4.1)
5	[Pt(η^3-C_3H_5)Me(PPr_3)]	86	35.4 (38.0)	6.9 (7.1)
6	[Pt(η^3-C_3H_5){*o*-$CH_2C_6H_4$P(C_6H_4Me-*o*)$_2$}]	64	53.9 (53.4)	4.8 (4.7)
7	[Pt(η^3-C_3H_5)(*o*-$CH_2C_6H_4PPh_2$)]	4[c]	56.5[d] (51.7)	4.3[d] (4.1)
8	[Pt(η^3-C_3H_5)(*o*-$C_6H_4CH_2PPh_2$)]	25	51.8 (51.7)	4.1 (4.2)
9	[Pt(η^3-C_3H_5){*o*-C_6H_4OP(OPh)$_2$}]	75	46.7 (46.2)	3.5 (3.5)
10	*cis*-[Pt(*o*-$CH_2C_6H_4PPh_2$)$_2$]·0.5CH_2Cl_2	4[c]	58.4 (58.7)	4.2 (4.2)

[a] **1**–**3** and **6**–**9** are white solids, **4** a pale yellow solid, **5** a yellow oil and **10** colourless crystals. [b] Calculated values in parentheses. [c] Calculated from the elemental analysis values (C, 56.54; H, 4.25%) of the product by assuming that it contained only **7** and **10**. [d] Data for the product obtained from the filtrate after recrystallization; the sample still included a small amount of **10** as an impurity.

Table 2 Proton NMR data for the [Pt(η^3-C_3H_5)Me(L)] complexes[a]



Complex	H^1	H^2	H^3	H^4	H^5	Pt-CH_3	Others
1	3.00(br)	*b*	1.96(t) 10.7 * 10.7§ 66.9 **	3.41(m)	4.52(m)	0.52(d) 6.6§ 87.4**	$C_6H_4CH_3$ 2.11(s)
2	3.43(dd) 7.3 * 1.5†	2.22(d) 13.2 * 41.0**	2.12(ddd) 13.0 * 2.6† 10.4§ 64.7**	3.52(m)	4.56(m)	0.66(d) 6.4§ 86.9**	$C_6H_4CH_3$ 2.29(s)
3	3.09(d) 6.1 *	1.98(d) 12.8 * 41.5**	2.05(t) 12.2 * 12.2§ 64.7**	3.49(m)	4.36(m)	0.74(d) 6.7§ 86.7**	CH_2Ph 3.83(d) 10.4§ 36.6**
4	3.01(d) 6.1 *	1.53(d) 12.8 * 65.9**	1.91(t) 13.4 * 13.4§ 59.8	3.42(m)	4.07(m)	1.00(d) 6.1§ 89.1**	
5[c]	3.37(dd) 7.3 * 1.8†	2.05(d) 12.8 * 42.7**	2.17(t) 11.6 * 11.6§ 59.8**	3.56(m)	4.30(m)	1.22(d) 5.5§ 86.7**	

[a] 400 MHz. Chemical shifts (δ) from $SiMe_4$ as internal standard in $CDCl_3$, $J(H^5\text{-}H)$, $J(H^4\text{-}H)$, J(PH) and J(Pt–H) values (Hz) indicated by *, †, § and ** respectively. [b] Overlapped with the tolyl signal. [c] In C_6D_6.

Complex **5** was not cyclometallated even in refluxing toluene, and was therefore heated without solvent at 140 °C for 30 min. To the resulting darkened oily substance, benzene and silica gel were added and the mixture then treated as above. However, the brown oily substance obtained was a mixture of the starting complex and by-products not containing an allyl moiety.

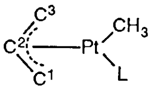
Yields and analytical data are summarized in Table 1, while ^{1}H and ^{13}C NMR data are collected in Tables 2–5.

Gas analysis. To determine the gases evolved from the thermal cyclometallation reactions, diphenylmethane was used as the solvent in order to compare the data with that obtained previously.[10] A solution sample was placed in a Schlenk tube and degassed several times by the freeze–pump–thaw method. A standard gas (propane) of constant volume was introduced to the tube through a manometer, and the sample was then thermolysed and the gases evolved analysed by gas chromatography. The area of a gas chromatographic peak in comparison with that of a standard was used for quantitative purposes. The area was corrected for the solubility of a particular gas relative to propane in the solvent employed. A YANACO G-180 gas chromatograph was used with Porapak Q (80–100 mesh, 2 m) or TCP C-22 (60–80 mesh, 8 m) as the packing material.

Data obtained from the thermolysis experiments are given in Table 6.

Reaction of **1** *with Methyllithium in Toluene.—Gas analysis and confirmation of products.* Complex **1** (0.133 g, 0.239 mmol) and toluene (20 cm^3) were placed in a Schlenk tube, degassed several times by the freeze–pump–thaw method, and then charged with argon. A diethyl ether solution of LiMe (0.239 mmol) was added at −10 °C, and then the solution was brought to room temperature. As the reaction proceeded a white precipitate of benzyllithium separated out. The reaction was

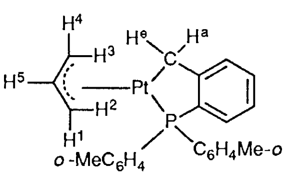
Table 3 Carbon-13 NMR data for the [Pt(η^3-C_3H_5)Me(L)] complexes[a]



Complex	C^1	C^2	C^3	Pt–CH_3	Others
1	63.5(s)	108.2(s)	47.4(d) (47.0)	−17.3(s) [844.5]	$C_6H_4CH_3$ 22.7(s)
2	61.4(s) (22.0)	109.1(d)	49.5(d) (41.1) [157.0]	−18.0(d) (4.0) [807.0]	$C_6H_4CH_3$ 22.2(d) (10.3)
3	59.7(s) [20.0]	109.2(s)	50.1(d) (42.6) [155.4]	−18.0(s) [805.5]	CH_2Ph 35.9(d) (30.9) [35.2]
4	59.3(s)	112.0(d) (5.9) [14.6]	53.1(d) (67.5) [140.8]	−21.7(d) (11.7) [771.6]	
5[b]	53.0(s) [29.3]	109.0(d) (3.0) [19.1]	50.8(d) (41.1) [135.0]	−21.3(d) (5.9) [796.7]	

[a] 100.5 MHz. Chemical shifts (δ) from $SiMe_4$ as internal standard in $CDCl_3$; J(PC) and J(Pt–C) values (Hz) in parentheses and square brackets, respectively. [b] In C_6D_6.

Table 4 Proton NMR data for the cyclometallated complex **6** in $CDCl_3$ at −20 °C[a]



Complex	H^1	H^2	H^3	H^4	H^5	CH_3	H^e	H^a
6 (major)	3.74(dd) 7.3 * 1.5 †	2.35(d) 13.7 * 48.8 **	2.20(ddd) 12.5 * 2.7 † 9.8 § 67.1 **	3.61(m)	4.45(m)	2.49(s) 2.34(s)	4.08(dd) 16.5 ‡ 4.3 § 95.2 **	3.33(d) 86.1 **
6 (minor)	3.82(dd) 7.3 * 1.8 †	2.33(d) 12.8 * 44.6 **	2.27(ddd) *b*	3.68(m)	4.56(m)	2.54(s) 2.25(s)	3.60(dd) 16.2 ‡ 6.9 § 73.9 **	3.50(d) 112.9 **

[a] Same as footnote *a* in Table 2, J_{gem} value (Hz) is indicated by ‡. [b] Unresolved.

allowed to continue for 24 h at room temperature. The gases evolved 2 and 24 h after the initiation of the reaction were analysed by gas chromatography as above. In this case the peak area of argon was used as the standard for quantitative purposes. After 24 h, the reaction mixture was filtered and the filtrate evaporated to dryness to leave a white solid (0.108 g). The product was identified as a mixture of **1** and the cyclometallated complex **6** in the mole ratio of 1:2.6 on the basis of ^1H NMR spectroscopy.*

A control experiment without the reactant complex, *i.e.*, reaction between toluene and LiMe, was also carried out for gas chromatography. Toluene itself reacted with LiMe to give a white precipitate. In a blank test for the toluene solution containing only **1**, the formation of any gases was not recognized both after 2 and 24 h.

Data for the methyllithium-assisted cyclometallation reactions are listed in Table 7.

Isolation of **6**. To isolate complex **6** as a pure solid, the reaction of **1** with LiMe was carried out in a mole ratio of 1:1.5. Thus a diethyl ether solution of LiMe (0.296 mmol) was added to a solution of **1** (0.109 g, 0.196 mmol) in toluene (20 cm^3) at −10 °C. The resulting solution was warmed slowly to room temperature and stirred for 24 h. The solution gradually turned to a white suspension. After filtration, the filtrate was evaporated to dryness to leave a yellowish white solid. This was identified as **6** on the basis of the ^1H NMR data. The yield was 0.069 g (65%), approximately the same as that by the thermolysis method. Recrystallization from dichloromethane–hexane at −20 °C gave a white solid (0.040 g).

When an excess of methanol was added to the white suspension before filtration, a transparent solution was obtained. The solvent was evaporated to dryness, extracted with benzene and dried again to leave a white solid (0.039 g). The product was confirmed as a mixture of **1** and a small amount of **6** by ^1H NMR spectroscopy.

Quantitative analysis of benzyllithium. To a solution of **1** (0.165 g, 0.297 mmol) in toluene (20 cm^3) was added a diethyl ether solution of LiMe (0.297 mmol) at −10 °C. The resulting solution was brought to room temperature and stirred for 24 h. The precipitated benzyllithium was filtered off and dried *in vacuo*. After washing with two 5 cm^3 portions of hexane, the sample was again dried *in vacuo* for 10 h. Methanol (0.5 cm^3) was added to the white solid thus obtained and after 5 min the liquid components were vacuum distilled into and trapped in a clean, evacuated vessel under liquid nitrogen. Dichloromethane (0.02 cm^3, 0.314 mmol) was added as an internal standard and the sample was analysed by gas chromatography for the formation of toluene. In this case a SHIMADZU-GC8A gas chromatograph was employed with Chemipack C18 (80–100 mesh, 2 m) as the packing material. The amount of toluene formed was 0.143 mmol (48.1% based on LiMe).

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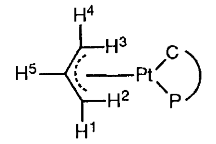
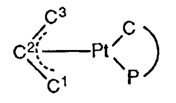
* Integration values of the overlapped signals of H^5 for complexes **1** and **6** and of the methyl proton signal for **1** were used for calculation of the ratio [**1**]/[**1** + **6**].

Table 5 Proton and carbon-13 NMR data for the cyclometallated complexes **7**–**10** in $CDCl_3$ [a]





Complex	H^1	H^2	H^3	H^4	H^5	Others	
7	3.91(dd) 6.3* 2.8†	2.29(d) 13.4* 44.4**	2.26(ddd) 12.6* 2.5† 10.1§ 65.0**	3.77(m)	4.52(m)	Pt–CH_2	3.93(d) 17.1‡ 105.2**
						Pt–CH_2	3.57(d) 110.8**
8	3.96(d) 7.3*	2.48(d) 13.4* 41.5**	2.86(t) 10.4* 10.4§ 65.9**	3.83(m)	4.85(m)	$CH_2C_6H_4$	3.80–3.95
						Pt–*o*-aryl H	8.20(d) 7.3†† 58.6**
9	3.64(d) 7.3*	1.97(d) 13.4* 41.5**	2.61(t) 14.6* 14.6§ 59.8**	3.79(m)	4.55(m)	Pt–*o*-aryl H	7.96(d) 7.3†† 64.7**
10						Pt–CH_2	3.48(d) 7.3§ 75.2**

Complex	C^1	C^2	C^3	Others	
7	56.0(s) 36.7**	110.1(s)	49.6(d) 39.7§ 160.0**	Pt–CH_2	17.2(s) 783.5**
8	52.5(s) 39.6**	112.9(s)	56.1(d) 39.7§ 173.0**	$CH_2C_6H_4$	44.1(d) 41.1§ 94.1**
9	54.7(s) 39.6**	115.7(d) 5.9§ 23.7**	56.5(d) 58.7§ 158.4**		
10				Pt–CH_2	34.3(d) 89.5§ 804.3**

[a] Same as footnote *a* in Tables 2 and 4. J_{vic} value (Hz) is indicated by ††. *J*(PC) and *J*(Pt–C) values are also indicated by § and ** respectively.

Table 6 Gases evolved in the thermolysis of $[Pt(\eta^3-C_3H_5)Me(L)]$ in solution [a]

Complex	Total mol per Pt	Evolved gas ratio			
		Methane	Ethene	Propene	But-1-ene
1	0.89	64.8		35.2	
2	1.37	58.3	0.1	41.1	0.5
3	0.93	70.7	0.2	28.8	0.4
4	1.03	76.7		23.3	
5 [b]	0.48	22.7	0.8	74.3	2.1
c	0.17	37.4	1.1	61.5	

[a] Thermolysis of the sample (50 mg) in degassed Ph_2CH_2 (1 cm^3) under the conditions of 100 °C, 1 h for **1**–**4** and of 130 °C, 1 h for **5**. [b] Ethane (0.1%) was also detected. [c] Data for $[Pt(\eta^3-C_3H_5)Me(PPh_3)]$ (100 °C, 2 h); see ref. 10.

Reaction of **1** *with Methyllithium in Tetrahydrofuran* (*thf*).—The reaction of **1** (0.123 g, 0.221 mmol) with LiMe (0.221 mmol) in thf (20 cm^3) was carried out in a similar manner as that in toluene. In this case no precipitate appeared. After 2 and 24 h, gas chromatography was also performed. The solvent was finally evaporated to dryness, the residue extracted with benzene, and again the solvent evaporated to leave a white solid. However, the ^1H NMR spectrum of the product revealed that it was not complex **6** but **1**. The recovery of **1** was 0.101 g (82%). A control experiment, *i.e.*, determination of gases evolved from the reaction between thf and LiMe, was also examined.

Data for these reactions are listed in Table 7.

Measurements.—Proton (400 MHz) and carbon-13 (100.5 MHz) NMR spectra were recorded on a JEOL JNM GX-400 instrument, with $SiMe_4$ as internal standard.

Results and Discussion

The complexes $[Pt(\eta^3-C_3H_5)Me(L)]$ [L = $P(C_6H_4Me-o)_3$ **1**, $PPh_2(C_6H_4Me-o)$ **2**, $PPh_2(CH_2Ph)$ **3**, $P(OPh)_3$ **4** or PPr_3 **5**] can be prepared readily either by methylation of $[Pt(\eta^3-C_3H_5)Cl(L)]$ using LiMe or directly from $[\{Pt(C_3H_5)Cl\}_4]$, L and LiMe in good yields as air- and thermally-stable solids or an oily substance (Table 1). The complexes have been characterized fully by ^1H and ^{13}C NMR spectroscopy (Tables 2 and 3). The broadening of the *syn* proton (H^1) signal for **1** can be attributed to the presence of rotamers as a result of the bulky phosphorus substituents. Complexes **4** and **5** are very difficult to obtain in an analytically pure state and probably contain some impurities; however they are essentially pure on the NMR spectral basis and can be used for the cyclometallation reactions without further purification.

Thermolysis.—Isolation of the cyclometallated complexes. When complexes **1**–**4** in toluene are heated under reflux for 2 h, the co-ordinated phosphine and phosphite ligands are cyclometallated with the evolution of methane, giving the complexes $[Pt(\eta^3-C_3H_5)(P–C)]$ **6**–**9** in 4–75% yields as air- and thermally-stable white solids [equation (1), Table 1]. The tripropyl-phosphine complex **5** is the most stable of the $[Pt(\eta^3-C_3H_5)Me(L)]$ complexes and is not cyclometallated even in boiling toluene. When heated at 140 °C for 30 min without solvent the complex melted with decomposition, but no evidence of cyclometallation was obtained from the ^1H NMR

$$[Pt(\eta^3-C_3H_5)Me(L)] \xrightarrow{heat} [Pt(\eta^3-C_3H_5)(P–C)] + CH_4 \quad (1)$$

Table 7 Gases evolved in the reaction of complex **1** with LiMe in thf or toluene at room temperature[a]

Entry	Reaction system[b]	Total mol per Pt	Evolved gas ratio				
			Methane	Ethene	Ethane	Propene	But-1-ene
After 2 h							
1	A	0.22	92.8	7.2			
2	B	0.61[c]	94.1	5.9			
3	C	0.84	77.0	4.5	18.2	0.3	
4	D	0.41[c]	89.4	8.1	2.5		
After 24 h							
5	A	1.38	73.9	14.0	7.1	5.0	
6	B	1.02[c]	90.7	8.0	1.3		
7	C	1.53	78.6	0.5	9.3	7.0	4.6
8	D	0.40[c]	98.4	0.5	1.1		

[a] Complex **1** (0.123 g, 0.221 mmol) in thf (20 cm^3) or **1** (0.133 g, 0.239 mmol) in toluene (20 cm^3) was allowed to react with an equivalent of LiMe. [b] A = **1** + LiMe + thf, B = LiMe + thf, C = **1** + LiMe + toluene and D = LiMe + toluene. [c] Total mol/LiMe.

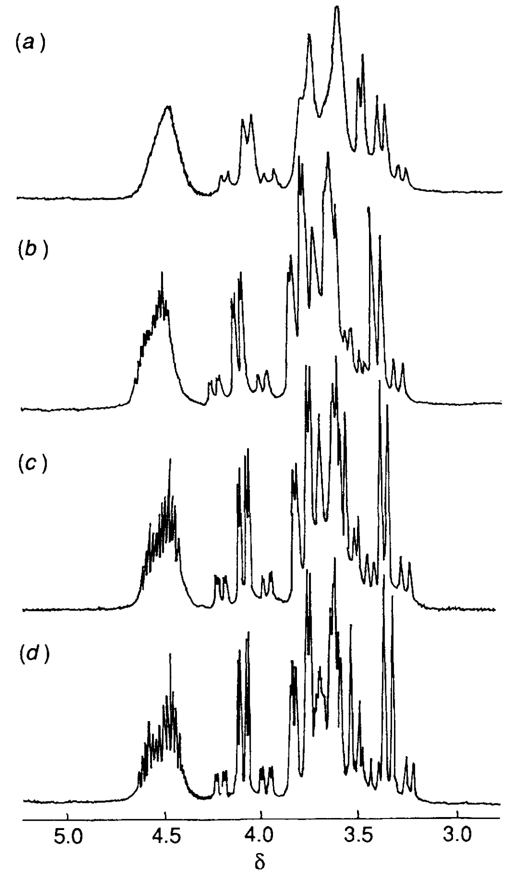
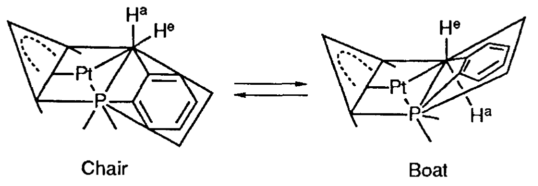


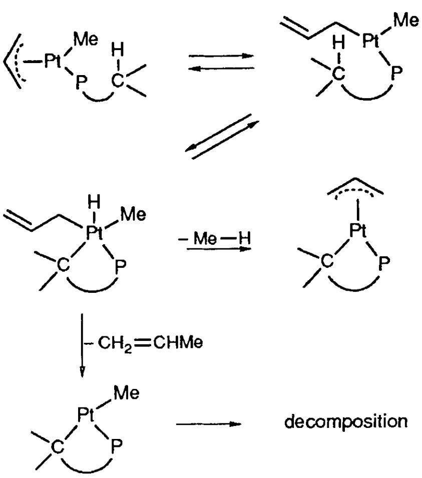
Fig. 1 Variable-temperature ^{1}H NMR spectra of complex **6** in CDCl$_3$: (*a*) at 27, (*b*) 10, (*c*) 0 and (*d*) −20 °C

spectrum of the product. Cyclometallated complexes with five-membered rings are generally the most stable[1] and a variety of these are known.[3–6,8] Complexes **6**–**9** also have five-membered rings. The presence of bulky substituents on phosphorus are known to promote internal metallation.[3a,3b,4,7] In this connection, Shaw[13] suggested that the change in entropy on metallation of a bulky phosphine would be considerably less than for a freely rotating tertiary phosphine ligand of low bulk. In contrast with our case, cyclometallated propyl phosphine complexes [PtX(P–C)L] (X = halide) have been isolated with L = PBu^t_2Pr or PBu^tPr_2.[3a] At least one reason for the low yield of **7** comes from the formation of the more stable *cis*-bis-(cyclometallated) complex **10**. The same complex has been prepared by Longoni *et al.*[3b] by the reaction of [PtCl$_2$(SEt$_2$)$_2$] or [PtCl$_2$(PBu$_3$)$_2$] with [K(*o*-CH$_2$C$_6$H$_4$PPh$_2$)] and shown to have a high decomposition point of 306 °C. In order to examine the route to **10**, we thermolysed [Pt(σ-C$_3$H$_5$)Me{PPh$_2$(C$_6$H$_4$-Me-*o*)}$_2$] under the same conditions as for **2**. However, no cyclometallation reaction occurred, indicating that the σ-allyl complex is not an intermediate in the formation of **10** from **2**.

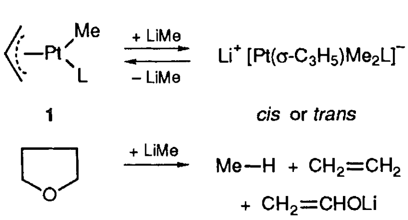
*Proton and Carbon-*13 *NMR Spectra.*—The ^{1}H NMR spectrum of **6** in CDCl$_3$ at 27 °C shows a broad signal pattern over the whole region of the field measured, suggesting dynamic behaviour of the complex in solution. However, all the signals gradually sharpen with a decrease in temperature, thus giving a stereochemically rigid spectrum at −20 °C. Fig. 1 shows these spectral changes in the limited region of δ 3.0–5.0. As can be seen from Fig. 1(*d*), the signals at δ *ca.* 4.5, which can be assigned to the central allyl proton, clearly consist of two multiplets of low and high intensities. These incompletely separated but well resolved signals coalesce to a broad singlet at 27 °C, indicating that the signals do not arise from a mixture of two different species but from two conformers interconverting in solution. These conformers are probably the chair and boat forms shown below.



In the chair form, H^e, one of the methylene protons of the cyclometallated tolyl group, occupies an equatorial position with respect to the co-ordination plane and couples with the ^{31}P nucleus, while the axial proton H^a does not. These protons are converted to H^a and H^e, respectively, in the boat form. In fact, two methylene signals accompanied by ^{195}Pt satellites appear at δ *ca.* 4.1 and 3.3, the former as a doublet of doublets due to couplings with ^{31}P and geminal proton nuclei and the latter as a doublet with geminal coupling. Like the central proton, each of the *syn* protons (H^1 and H^4) of the allyl group also appear as a couple of signals corresponding to the major and minor conformers. However, signals of the methylene protons for the minor conformer are concealed under the intense signals of the *syn* protons, although the signal for one of the methylene protons can be seen partially at δ *ca.* 3.5. On the other hand, the *anti* proton signals of the allyl group, which appear in the range δ 2.2–2.4, overlap with the intense tolyl signals, and hence cannot be identified clearly. Measurement of the two-dimensional ^{1}H NMR (COSY) spectrum of **6** in CDCl$_3$ at −20 °C led to the complete assignment of all of the signals observed and to further confirmation of the presence of the conformers in solution. These assignments are indicated in Table 4, together with the data obtained from the low-



Scheme 1 Mechanism of thermal cyclometallation



Scheme 2 Reaction of **1** with LiMe in thf; L = $P(C_6H_4Me\text{-}o)_3$

temperature spectrum. Although a distinction cannot be made as to which form is the major conformer, we suppose that the complex prefers the boat form from the observation of rather smaller coupling of the H^c proton to ^{31}P (4.3 *versus* 6.9 Hz for the minor conformer) and of smaller allyl ⋯ $P(C_6H_4Me\text{-}o)$ interactions in this form. The complex cation, $[Pd(\eta^3\text{-}C_3H_5)\{\text{-}CMe_2(N_2C_3H_3)_2\}]^+$ ($N_2C_3H_3$ = pyrazol-1-yl) has been found to undergo similar behaviour in solution.[14] In this case, however, the major isomer was tentatively assigned to the chair form. Equilibrium constants for equation (2), estimated roughly on the basis of the signal intensity,* are 0.45 (−30 °C) and 0.66 (27 °C).

$$\text{Major conformer} \overset{K}{\rightleftharpoons} \text{Minor Conformer} \qquad (2)$$

When two *o*-tolyl groups in $P(C_6H_4Me\text{-}o)_3$ are substituted by phenyl groups, the steric bulk around the metal centre in the cyclometallated complex will be reduced appreciably. Therefore, even if two conformers similar to those found for **6** are present in solution, interconversion between them will be rapid on the NMR time-scale. In fact, the ^1H and ^{13}C NMR spectra of complex **7** in $CDCl_3$ are well resolved at room temperature. These spectral data are listed in Table 5, together with those for **8**–**10**.

Correlation with gaseous products. As can be seen from Table 6, complexes **1**–**4** decompose thermally in diphenylmethane with the evolution of methane and propene in mole ratios of 1.84–3.29:1. These high ratios differ from **5** (0.30:1) and $[Pt(\eta^3\text{-}C_3H_5)Me(PPh_3)]$ (0.60:1), listed in Table 6 for comparison. The total number of moles of gases evolved per Pt on thermolysis are 1.37–0.89 for **1**–**4** and greater values of 0.48 for **5** and 0.17 for $[Pt(\eta^3\text{-}C_3H_5)Me(PPh_3)]$. These results are consistent with the ready cyclometallations of **1**–**4** and with the lack of evidence for the cyclometallation of **5**. The especially high total amount of the gas (1.37 mol per Pt) and the relatively high percentage of propene (41%) for complex **2**, may be correlated to the low yield, *i.e.*, the instability of the product complex **7** and its ready conversion to **10**.

The evolution of propene subsidiary to methane in this thermolysis suggests that the cyclometallation is occurring *via* the five-co-ordinate Pt^{IV} intermediate shown in Scheme 1.

Methyllithium-assisted Cyclometallation.—Complexes **1**–**4** are not cyclometallated at room temperature in solution. However, the addition of methyllithium to a toluene solution of **1** induced cyclometallation and complex **6** was isolated in 65% yield (room temperature, 24 h). On the contrary, in rather polar solvents such as thf, cyclometallation of **1** did not occur even in the presence of LiMe and 82% of **1** was recovered unchanged. Toluene and ethereal solvents like thf are known to react with alkyllithium reagents.[15] For example, toluene is metallated by LiBu in diethyl ether–thf at room temperature to give benzyllithium,[16] and almost quantitatively in the presence of *N,N,N′,N′*-tetramethylethylenediamine.[17] On the other hand, thf is decomposed by alkyllithium (C–O bond fission) to give ethene and the lithium enolate of acetaldehyde.[18] Therefore, we determined the gaseous components liberated chromatographically in the following reactions: (*a*) **1** with LiMe in thf, (*b*) thf with LiMe, (*c*) **1** with LiMe in toluene and (*d*) toluene with LiMe. The results of the analyses at 2 and 24 h after the initiation of these reactions are listed in Table 7.

In these reactions methane is the main gaseous product, but the amount of propene is extremely diminished compared to thermolysis in diphenylmethane, implying the removal of thermal side reactions. First, we consider the results obtained with the system in which cyclometallation does not occur, *i.e.*, the reactions in thf. As can be seen from entries 1 and 2 in Table 7, the amounts of methane evolved during the 2 h reactions are greater in the absence of complex **1** (0.61 × 0.941 compared with 0.22 × 0.928 mol per Pt). This suggests that in the first stage of the reaction in the presence of **1** the methyl anion functions as a nucleophile to attack the central metal atom rather than as a base to abstract a proton. If this is so, the anion *cis*-or *trans*-$[Pt(\sigma\text{-}C_3H_5)Me_2(L)]^-$ will probably be produced in solution and comes to equilibrium with complex **1**. Methyllithium in thf also reacts slowly with the solvent itself with the evolution of methane and ethene. As the reaction proceeds, therefore, the above-mentioned equilibrium is shifted to the left and the reaction finally goes back into the starting complex **1**, liberating the totally stoichiometric amount of methane. These assumptions are supported by the data for the 24 h reactions (entries 5 and 6). Thus, approximately one equivalent of methane per Pt is detected in both reactions (1.38 × 0.739 and 1.02 × 0.907) and 82% of the starting complex is recovered in the reaction of entry 5. Therefore, the reaction of **1** with LiMe in thf can be described as shown in Scheme 2.

Contrary to the reactions in thf, the amounts of methane evolved for the 2 and 24 h reactions in toluene, are both greater in the presence of complex **1** (compare 0.84 × 0.770 with 0.41 × 0.894 mol per Pt). This means that the complex itself participates in the reaction that results in the evolution of methane. As can be seen from entry 7, the total amount of methane finally evolved, *i.e.*, 1.20 mol per Pt, is in excess of the equivalent moles of the LiMe initially added. This is consistent with the formation of the cyclometallated complex. On the basis of these results, a mechanism for the cyclometallation of **1** is proposed in Scheme 3. First the methyl group of a *o*-tolyl group is lithiated by LiMe to give complex **11** in solution with concomitant elimination of methane. A second pathway, where a methyl anion attacks the central platinum atom, is ruled out by considering the result of the reaction in thf. Nucleophilic attack of the lithiated methyl group on the platinum atom gives the cyclometallated complex **6**, regenerating LiMe in the reaction system. The presence of equilibrium A may return **6** to

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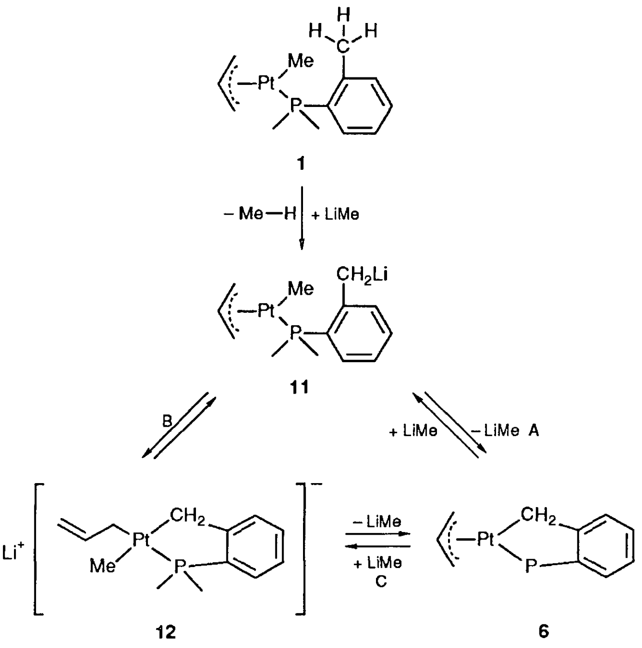
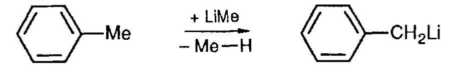
* Integration values of the overlapped signals of H^5 for the major and minor conformers and of one (a doublet of doublets) of the methylene proton signals for the major conformer were used for calculation of the ratio [major]/([major] + [minor]).





(3)

Scheme 3 Mechanism of methyllithium-assisted cyclometallation in toluene

the original lithiated complex. The LiMe regenerated or originally present as a reactant reacts slowly with the solvent itself according to equation (3); therefore, equilibrium A is shifted forward until the LiMe initially added is completely consumed by both reactions. Recently, such a reaction of toluene with LiMe has been assumed in the first stage of the reaction of $[\mathrm{RhCl(PMe_3)_4}]$ with LiMe in toluene.[19] Another pathway, which proceeds through two equilibria (B and C) with intervention of the σ-allyl complex **12** cannot be ruled out, however.

As described in the Experimental, the reaction of **1** with LiMe in toluene produced a white precipitate thought to be benzyllithium. The benzyllithium isolated as a white powder was transformed to toluene by the addition of methanol and the amount was determined by gas chromatography. The yield of toluene was 48.1% based on the LiMe used. As noted earlier, the amount of methane evolved during this reaction was 1.20 mol per Pt; this corresponds to a 120% yield based on the reactions of **1** to **6** in Scheme 3. The solid isolated from the reaction mixture after reaction for 24 h consisted of a mixture of the cyclometallated product **6** and unreacted **1** in a mole ratio of 2.6:1. This indicates that the LiMe involved in lithiation of the *o*-tolyl phosphine, in order to liberate methane, corresponds to 72.2% of that used in this reaction. Thus the amount of LiMe reacted with toluene is equal to 120 − 72.2, *i.e.*, 47.8%. The value should be just the amount of the benzyllithium that is expected to be produced. The excellent agreement between the calculated and found values seems to justify the validity of the mechanism proposed.

Thus the reaction of **1** with one equivalent of LiMe in toluene affords the cyclometallated complex **6**, but a significant amount of the starting complex still remains unchanged. Therefore, it was necessary to use a *ca.* 50% excess of LiMe in order to isolate **6** in a good yield. Contrary to our expectations, the addition of methanol to decompose the LiMe remaining resulted in a marked lowering of the yield of **6** with the regeneration of **1**. This can be understood by consideration of the mechanism shown in Scheme 3. The presence of an excess of LiMe allows equilibria A and C to shift towards **11** and **12**, and hence the added methanol reacts exclusively with them, whereupon **1** is regenerated.

It was reported recently by Bennett and Latten[20] that the complex $[\mathrm{RuHCl}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{PPh_3})]$ reacts readily with a 2.5-fold equivalent of LiMe at −78 °C to form the *ortho*-metallated complex $[\mathrm{RuH}(o\text{-}\mathrm{C_6H_4PPh_2})(\eta^6\text{-}\mathrm{C_6Me_6})]$. The complex was thought to arise by internal oxidative addition of a C–H bond to the metal in a 16-electron Ru^0 species, $[\mathrm{Ru}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{PPh_3})]$. This in turn could be formed either by reductive elimination of methane from an undetected hydrido(methyl) complex $[\mathrm{RuH(Me)}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{PPh_3})]$ or by base-promoted elimination of HCl from $[\mathrm{RuHCl}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{PPh_3})]$. However, the detailed mechanism has not been clarified.

Acknowledgements

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