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Synthesis and Thermolysis of Dimethylbis(trialkylphosphine)platinum(II) Complexes in Which the Phosphine Ligands Contain Adamantyl, Adamantylmethyl, and Methyl Groups[1]

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This paper describes syntheses of (1-adamantylmethyl)dimethylphosphine (**1**), bis(1-adamantylmethyl)methylphosphine (**2**), tris(1-adamantylmethyl)phosphine (**3**), 1-adamantyldimethylphosphine (**4**), di-1-adamantylmethylphosphine (**5**), and the platinum complexes L_2PtMe_2 (**7**, L = **1**; **8**, L = **2**; **9**, L = **4**). Thermal decomposition of **7** and **8** yields cyclometalated products; **9** decomposes by a complex, poorly defined route. The paper discusses factors that render phosphines susceptible to intramolecular reactions.

Introduction

Although platinum complexes react intramolecularly with the C–H bonds of coordinated ligands, no example of *intermolecular* C–H bond activation by soluble platinum complexes has been reported. In contrast, other transition metal,[2-7] lanthanide,[8] and actinide[9] complexes react with both saturated and unsaturated hydrocarbons. This lack of *intermolecular* reactivity on the part of platinum is due primarily to the facility of the competing *intramolecular* reactions. Metallacycle formation,[10] β-

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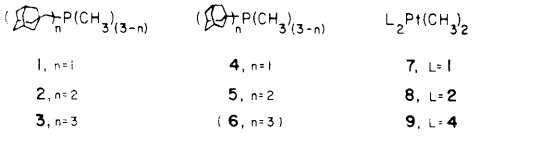
hydride elimination,[11] and ligand alkylation[12,13] are well-documented.

We reasoned that dimethylbis(trialkylphosphine)platinum(II) complexes containing the mixed phosphine ligands $R_nP(CH_3)_{3-n}$ (R = 1-adamantylmethyl, 1-adamantyl; n = 1–3) might be more resistant to intramolecular reactions than organoplatinum complexes containing other alkyl groups on platinum and more commonly used trialkyl- and triarylphosphines. The methyl group directly bonded to platinum appears to be inert; α-hydrogen activation has not been reported for platinum(II) complexes.[14] As for the phosphine ligand, oxidative addition of the C–H bond of a methyl group on phosphorus is rare for platinum complexes,[15,16] and metalation of either the 1-adamantylmethyl or 1-adamantyl moiety would produce complexes that appear strained. In addition, we expected these bulky phosphines to dissociate readily from platinum and to generate the coordinatively unsaturated intermediates normally required for C–H bond activation.[17]

This paper details the synthesis of the phosphines **1–5** and the dimethylbis(trialkylphosphine)platinum(II) complexes **7–9**. Thermal decomposition of these platinum



complexes occurs smoothly at temperatures between 165 and 215 °C in cyclohexane-d_{12} and benzene-d_6. Analysis of the decomposition products establishes that the ligands are *not* resistant to intramolecular reactions. In cyclohexane-d_{12}, thermolysis of **7**, **8**, and **9** generates methane containing no deuterium. The ^{31}P NMR spectra of the reaction mixtures reveal that cyclometalated species are produced in the thermolysis of **7** and **8**; we were not able to identify the platinum-containing products in the decomposition of **9**. Thermolysis of complexes **7–9** in benzene-d_6 produces significant amounts of CH_3D and toluene in each case, probably (in the case of **7** and **8**) as the result of a heterogeneous reaction.

In this paper we describe the synthesis of these phosphines and discuss the structural features characteristic of phosphines that are resistant to intramolecular reactions.

Experimental Section

General Data. Diethyl ether and THF were distilled from sodium-benzophenone under argon. Cyclohexane-d_{12} was stirred over nitric acid/sulfuric acid (1/4, v/v), washed with distilled water, dilute aqueous sodium hydroxide, distilled water, and brine, dried over magnesium sulfate, and passed through silica; and distilled from Na/K under argon. Benzene-d_6 was stirred over sulfuric acid and then treated similarly. Deuteriated solvents were stored over $LiAlH_4$ in Schlenk flasks. Acetone was dried over magnesium sulfate and distilled; 95% ethanol was distilled. Methylene chloride was dried over K_2CO_3. Chlorodimethylphosphine was prepared by the literature procedure[18] or purchased from Strem Chemicals. Dichloromethylphosphine was purchased from Alfa. (1,5-Cyclooctadiene)dimethylplatinum was prepared according to the literature procedure.[19] Triply sublimed magnesium turnings (Alfa) were used in Grignard reactions. Alkyllithium and Grignard reagents were titrated with 2-butanol/toluene under argon with 1-naphthylphenylamine[20] as an indicator. The latter was recrystallized twice from distilled water/95% ethanol (3/1, v/v); any purple oil that fell out of the hot solution was removed via pipet. Melting and boiling points are uncorrected. ^1H NMR spectra were recorded at 300 MHz; ^{31}P NMR spectra were recorded at 121.5 MHz. ^1H NMR shifts are relative to tetramethylsilane: the residual solvent peak (C_6HD_5, δ 7.15; $CHCl_3$, δ 7.25; C_6HD_{11}, δ 1.38; $CHDCl_2$, δ 5.35) was used as an internal reference. ^{31}P NMR shifts are relative to 85% H_3PO_4 at δ 0.00, with shifts downfield of the reference considered positive. Elemental analyses were performed by Spang or Galbraith.

1-Adamantylmethyl bromide was prepared following the procedure of Wilkinson et al.[21]

(1-Adamantylmethyl)magnesium bromide was prepared from 1-adamantylmethyl bromide and magnesium turnings in diethyl ether in 70% yield.[21]

(1-Adamantylmethyl)dimethylphosphine (1). A three-necked, 500-mL, round-bottomed flask was equipped with a stir bar, pressure-adjusted dropping funnel, and a condenser topped by an argon inlet. The apparatus was flame-dried under argon. The reaction flask was charged with (1-adamantylmethyl)magnesium bromide (127 mL, 0.11 M, 14 mmol), and a solution of chlorodimethylphosphine (*Caution*! pyrophoric) (1.0 mL, 1.0 g, 10 mmol) in 20 mL of diethyl ether was placed in the addition funnel. The phosphine solution was added at −78 °C over a 45-min period. The reaction mixture (white precipitate, colorless solution) was allowed to warm slowly to room temperature and then heated under reflux overnight. The reaction mixture was cooled to 0 °C, and the reaction was quenched with 100 mL of degassed aqueous NH_4Cl [aqueous NH_4Cl in distilled water (1/1, v/v)]. The ethereal layer was transferred by cannula to an argon-purged flask containing magnesium sulfate. The aqueous layer was extracted once with ether; the extract was combined with the ethereal supernatant. The solution was filtered through a medium porosity frit into an argon-purged flask. The magnesium sulfate was rinsed once with ether; the rinse was similarly filtered into the distillation flask. Solvent was removed under argon. Vacuum distillation afforded the phosphine as a colorless oil, bp 85 °C (0.15 torr), in 93% yield: ^1H NMR (C_6D_6) δ 2.0–1.6 (m, 15 H), 1.16 (d, J_{P-H} = 4.0 Hz, 2 H), 0.91 (d, J_{P-H} = 3.3 Hz, 6 H); ^{31}P NMR (C_6D_6) δ −65.0 (s).

This phosphine was not characterized by elemental analysis due to difficulties in purification and handling. The bis(phos-

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(14) Activation of a C–H bond of a methyl group bonded to platinum would produce a platinum carbene, e.g., $L_2Pt(CH_2)(CH_3)(H)$ or $L_2Pt(CH_2)$ (after reductive elimination of methane). This reaction appears to be kinetically slow or reversible. Puddephatt and co-workers have proposed that platinum carbenes are involved in the rearrangements of platinacyclobutanes, but other authors have disputed this claim. See: Ling, S. S. M.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 412–413. Johnson, T. H.; Cheng, S.-S. *J. Am. Chem. Soc.* **1979**, *101*, 5277–5280. The only platinum carbene complexes isolated thus far are those containing a heteroatom-stabilized carbene moiety. See: Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press: London, 1974; pp 282–292. Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; pp 101–102, 348–350.

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(16) The apparent inertness of methyl groups bonded to phosphorus may mask a rapid equilibrium between the non-metalated and metalated species.[5]

(17) Dissociation of phosphine has been demonstrated to be the rate-determining step in the oxidative addition of the C–H bonds of alkyl ligands in dialkylbis(trialkylphosphine)platinum complexes in the absence of added phosphine.[10,11]

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phine)dimethylplatinum complex **7** was analyzed instead (see below).

Bis(1-adamantylmethyl)methylphosphine (2). The phosphine was synthesized using a procedure analogous to that employed for **1** from (1-adamantylmethyl)magnesium bromide and dichloromethylphosphine. After the solvent had been removed, the residual white solid was dried under vacuum (0.2 torr) overnight. Recrystallization from hot, degassed 95% ethanol, followed by cooling to 0 °C, resulted in white granules. These were dried in vacuo (0.007 torr) overnight. The yield of white granules, mp 99–101 °C (sealed capillary under N_2), was 66%: ^{1}H NMR (C_6D_6) δ 1.94 (s, br, 6 H), 1.66 (s, br, 24 H), 1.27 (d of d, J_{P-H} = 2.8, $^2J_{H-H}$ = 14.0 Hz, 2 H), 1.12 (d of d, J_{P-H} = 4.7, $^2J_{H-H}$ = 14.0, 2 H), 0.96 (d, J_{P-H} = 3.8 Hz, 3 H); ^{31}P NMR (C_6D_6) δ −68.7 (s).

The phosphine was not analyzed directly, but the bis(phosphine)dimethylplatinum complex **8** was fully characterized by elemental analysis (see below).

Tris(1-adamantylmethyl)phosphine (3). The phosphine was prepared by a procedure analogous to that described for **1** from (1-adamantylmethyl)magnesium bromide and phosphorus trichloride. After the ether was removed, the residue was suspended in hot, degassed 2-propanol. The mixture was cooled to 0 °C before the supernatant was removed via cannula. The residue was dried in vacuo (0.005 torr) for 24 h. The yield of white powder, mp >300 °C (sealed evacuated capillary), was 66%. The phosphine appears to be completely air-stable. Two recrystallizations from acetone–ether, followed by cooling to −15 °C, produced analytically pure white crystals: ^{1}H NMR ($CDCl_3$) δ 1.94 (s, br, 9 H), 1.7–1.5 (m, br, 36 H), 1.17 (d, J_{P-H} = 3.3 Hz, 6 H); ^{31}P NMR ($CDCl_3$) δ −72.7 (s). Anal. Calcd for $C_{33}H_{51}P$: C, 82.79; H, 10.74; P, 6.47. Found: C, 82.56; H, 10.72; P, 6.70.

1-Adamantylmagnesium Bromide. The Grignard reagent was prepared from 1-bromoadamantane and magnesium turnings in diethyl ether according to the literature procedure.[22] After the reaction was complete, the total volume of the ethereal solution was measured, and the concentration of the Grignard reagent was determined by titration. Yields calculated from these data averaged 40–45%.

Lithiation of 1-bromoadamantane in diethyl ether at −30 °C,[23] followed by treatment with magnesium bromide etherate,[24] resulted in comparable yields of Grignard reagent. Attempts to prepare 1-adamantylmagnesium chloride from Rieke magnesium[25] or magnesium turnings and 1-chloroadamantane were unsuccessful.

1-Adamantyldimethylphosphine (4). The phosphine was prepared from 1-adamantylmagnesium bromide (158 mL, 0.13 M, 21 mmol) and chlorodimethylphosphine (1.7 mL, 1.7 g, 18 mmol), following the procedure described for **1**, except that addition of chlorodimethylphosphine to the Grignard reagent was carried out at 0 °C.[26] The reaction mixture was heated under reflux for 28 h. Workup of the reaction mixture and removal of ether left an oily yellow paste consisting mostly of adamantane; smaller amounts of biadamantyl, 1-(1-adamantyl)ethyl ethyl ether,[29] phosphorus-containing byproducts, and the desired phosphine were also present.

Distillation of the phosphine at this point yielded impure product. Instead 1-adamantyldimethylphosphine was isolated and purified via the phosphine dibromide.[30] The oily paste was dissolved in 150 mL of hexane. The pale yellow, slightly cloudy solution was treated at room temperature with a solution of bromine (1.1 mL, 3.2 g, 20 mmol) in 30 mL of hexane. The red color of the bromine disappeared immediately with concomitant formation of a fine yellow precipitate. After the precipitate had settled, the yellow supernatant was removed via cannula. The solid was resuspended in fresh hexane; the supernatant was again removed via cannula. This washing process was repeated twice. The precipitate was suspended in 100 mL of hexane and treated at 0 °C with *n*-butyllithium in hexane[31] (10 mL, 2.6 M, 26 mmol). The ice bath was removed, and the mixture was stirred at room temperature for 3 h. The reaction was quenched at 0 °C with 100 mL of NH_4Cl (1/1, v/v). The yellow supernatant was dried over degassed $MgSO_4$ and filtered through a medium porosity frit into an argon-purged flask. The solvent was removed under argon; final traces were removed in vacuo (1 torr). Vacuum distillation afforded the product as a colorless oil, bp 81–82 °C (1 torr), in 36% yield: ^{1}H NMR (C_6D_6) δ 1.84 (s, br, 3 H), 1.9–1.5 (m, 12 H), 0.78 (d, J_{P-H} = 3.2 Hz, 6H); ^{31}P NMR (C_6D_6) δ −30.8 (s). The phosphine was further characterized as its bis(phosphine)dimethylplatinum complex, **9**.

Di-1-adamantylmethylphosphine (5). The phosphine was prepared according to the procedure described for the preparation of **4** from 1-adamantylmagnesium bromide and dichloromethylphosphine. Purification was again effected via the phosphine dibromide, which was subsequently treated with *n*-butyllithium in hexane as described above. The hexane was removed by distillation, leaving a yellow oil which solidified upon cooling. The yellowish white solid was recrystallized from degassed 95% ethanol and then dried overnight in vacuo (0.5 torr). The yield of white solid, mp 137–140 °C (sealed capillary under N_2), was 0.64 g (22%): ^{1}H NMR (C_6D_6) δ 1.88 (s, br, 18 H), 1.66 (s, br, 12 H), 0.87 (d, J_{P-H} = 4.7 Hz, 3 H); ^{31}P NMR (C_6D_6) δ 8.4 (s); mass spectrum (70 eV), m/z (relative intensity) 316 (3, M^+), 135 (100). Despite several recrystallizations from degassed 95% ethanol, an analytically pure sample could not be obtained.

Tri-1-adamantylphosphine (6). All attempts to prepare this complex from 1-adamantylmagnesium bromide and phosphorus trichloride were unsuccessful.

***cis*-Bis[(1-adamantylmethyl)dimethylphosphine]dimethylplatinum(II) (7).** A 100-mL, round-bottomed flask with a side arm was equipped with a stir bar and a pressure-adjusted dropping funnel. The flask was charged with (1,5-cyclooctadiene)dimethylplatinum(II)[19] (1.53 g, 4.59 mmol) and flushed with argon. The complex was dissolved in 25 mL of diethyl ether. The addition funnel was charged with a solution of (1-adamantylmethyl)dimethylphosphine (1.0 mL, 2.0 g, 9.3 mmol) in 25 mL of ether. The phosphine solution was added at room temperature over a 15 min period. After 12 h at room temperature, a fine white solid had precipitated. Solvent was removed by rotary evaporation. The residue was washed with 95% ethanol and recrystallized from pentane. Cooling to −15 °C produced colorless cubes: mp 226–227 °C (evacuated sealed capillary); 1.62 g, 55%; ^{1}H NMR (C_6D_6) δ 1.93 (s, br, 6 H), 1.79 (s, br, 12 H), 1.64 (s, br, 12 H), 1.50 (d with Pt satellites, J_{P-H} = 9.4, J_{Pt-H} = 19.8 Hz, 4 H), 1.22 (d with Pt satellites, J_{P-H} = 7.0, J_{Pt-H} = 19.6 Hz, 12 H), 1.00 (d of d with Pt satellites, J_{P-H} = 6.4, $J_{P'-H}$ = 8.2, J_{Pt-H} = 67.3 Hz, 6 H); ^{31}P NMR (C_6D_6) δ −23.0 (s with Pt satellites, J_{Pt-P} = 1781 Hz). Anal. Calcd for $C_{28}H_{52}P_2Pt$: C, 52.08; H, 8.12; P, 9.59.

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(26) Attempts to prepare **4** from 1-adamantyllithium[23] (prepared in hexane from 1-chloroadamantane and lithium powder containing 2% Na)[27] and chlorodimethylphosphine were unsuccessful, presumably due to the complete insolubility of 1-adamantyllithium in inert (i.e., saturated hydrocarbon) solvents. Neither sonication nor prolonged reflux produced the desired phosphine. Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed only starting material and minor, unidentified products. Tetramethylbisphosphine and dimethylphosphine were not observed.[28]

(27) The commercially available lithium dispersion, which contains 1% sodium, fails to react with 1-chloroadamantane. The 2% Na/Li dispersion used in this work was kindly supplied by E. J. Corey and Neil Boaz.

(28) The ^{31}P NMR shifts of tetramethylbisphosphine and dimethylphosphine are δ 59.5 and −99, respectively: Maier, L. *J. Inorg. Nucl. Chem.* **1962**, *24*, 275–283. Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Wiley: New York, 1973; p 80. No peaks were observed at these chemical shifts.

(29) Adamantane, biadamantyl, and 1-(1-adamantyl)ethyl ethyl ether were identified by ^{1}H NMR spectroscopy. These compounds, which are byproducts of Grignard formation, were also observed by Molle et al.[22]

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Table I. Products of the Thermolysis of 7, 8, and 9

complex	solv	Δ, °C/h	appearance[a] of soln	% conversn	products: phosphorus-containing[b]	gaseous[c]: methane (d_1/d_0)	gaseous[c]: ethane	gaseous[c]: ethylene	other[d,e]: PhMe	other[d,e]: AdH
7	C_6D_{12}	215/1	yellow	100	**10** (93%)	100 (0)	<1	<1		*f*
7	C_6D_6	215/1	yellow brown	93	**10** (64%)	100 (0.35)	<1	<1	0.10[g]	0.05
7	C_6D_6(Hg)[h]	215/1	colorless[i]	72	**10**[j]	100 (0.16)	*f*	*f*	0.02[g]	*f*
3	C_6D_{12}	165/0.5	pale yellow	100	**11**, **14**[k]	100 (0)	*f*	*f*		*f*
8	C_6D_6	165/0.5	pale yellow	100	**11** (69%), **14** (3%)	100 (0.09)	*f*	*f*		*f*
8	C_6D_6	165/0.5; 180/6[l]	pale yellow	100	**14** (49%)	100 (0.54)	<1	*f*	0.17[g]	0.15
8	C_6D_6(Hg)[h]	180/6.5	colorless[m]	100	**11**[n]	100 (0.20)	*f*	*f*	0.04[g]	*f*
9	C_6D_{12}	215/2.5	brown	53	**4** (6%)	89 (0)	6	5		*f*
9	C_6D_6	215/2.5	dark brown	93	**4** (22%)[o]	98 (1.17)	1	1	0.49[g]	*f*
9	C_6D_6(Hg)[h]	215/2.5	colorless[i]	*p*	**4**, **15**[l]	98 (1.78)	1	1	0.12[g]	0.04

[a] No precipitates were observed in the absence of Hg(0). [b] Absolute yields based on the Pt complex; determined by quantitative ^{31}P NMR. [c] Relative yields; determined by GC. [d] Absolute yields expressed as equivalents per unit of Pt complex; determined by GC. [e] Cyclohexane reaction solutions were checked for cyclohexene and bicyclohexyl; in no case was either product observed. Similarly, biphenyl was never observed in benzene reaction solutions. [f] Not observed. [g] Isotopic composition corresponding to 4–6 deuterium atoms/molecule of PhMe. [h] Mercury(0) was added to the reaction solution. [i] Mercury bead looked dirty and a gray-black precipitate was observed. [j] Absolute yield not determined. [k] The relative yields of **11** and **14** are 94 and 6%, respectively. Because the starting material **8** is almost completely insoluble in C_6D_{12}, the absolute yields could not be determined by ^{31}P NMR. Once heated, however, the mixture becomes (and remains) completely homogeneous. [l] After 0.5 h at 165 °C, only **11** (69%) and **14** (6%) were observed by ^{31}P NMR. The thermolyzed sample was then heated for an additional 6 h at 180 °C. [m] The mercury bead was clean and shiny. [n] **14** was not observed. [o] Small amounts of *trans*-**15** are observed at intermediate stages but not at the conclusion of the decomposition. [p] Not determined; see Experimental Section. Both *cis*- and *trans*-**9** remained.

Table II. ^{31}P and ^{1}H NMR Data for 1, 2, 7, 8, 10, and 11

compd[a]	^{31}P NMR[b]: δ	^{31}P NMR[b]: J_{P-P}	^{31}P NMR[b]: J_{P-P}	^{1}H NMR of Pt-bonded Me group[c]: δ	^{1}H NMR of Pt-bonded Me group[c]: J_{P-H}	^{1}H NMR of Pt-bonded Me group[c]: $J_{P'-H}$	^{1}H NMR of Pt-bonded Me group[c]: J_{Pt-H}
1	−65.0						
cis-7	−23.0	1791		1.00	6.4	8.2	67.3
trans-7	−19.2	2854		0.33	6.3		51.0
10[d]	12.0	2017	9	0.75	7.0	8.5	67.3
	−21.9	1528	9				
2[e]	−68.7						
cis-8	−13.3	1771		1.00	6.6	8.0	66.9
trans-8[e]	−14.2	2842		0.35	11		54
11[f]	23.4	2038	9	0.60	6.9	8.3	66.9
	−21.5	1485	9				
	22.5	2041	*g*				
	−20.4	1483	*g*				

[a] Dissolved in C_6D_6 unless otherwise specified. [b] Chemical shifts in ppm (δ) relative to 85% H_3PO_4; downfield shifts positive. Coupling constants in Hz. [c] Relative to tetramethylsilane. [d] The methyl group integrates to three protons relative to the rest of the spectrum [δ 2.4–0.8 (m, 45 H)]. [e] In $CDCl_3$. [f] The methyl group integrates to three protons relative to the rest of the spectrum [(δ 2.6–1.1 (m, 73 H)]. [g] Broad singlets.

Found: C, 51.81; H, 8.00; P, 9.79.

***cis*-Bis[bis(1-adamantylmethyl)methylphosphine]dimethylplatinum(II) (8).** The complex was prepared by a procedure similar to that used to prepare **7** from (1,5-cyclooctadiene)dimethylplatinum[19] (0.501 g, 1.50 mmol) and bis(1-adamantylmethyl)methylphosphine (1.06 g, 3.11 mmol) in diethyl ether. The complex was recrystallized from hot THF. Cooling to −15 °C produced colorless crystals, mp 202–203 °C, in 60% yield (0.82 g): ^{1}H NMR (C_6D_6) δ 2.1 (d of m, $^2J_{H-H}$ = 14.2 Hz, 4 H), 1.97 (br s, 12 H), 1.95–1.85 (br "d", 12 H), 1.8–1.6 (m, 36 H), 1.6–1.45 (m, 10 H), 1.00 (d of d with Pt satellites, J_{P-H} = 6.6, $J_{P'-H}$ = 8.0, J_{Pt-H} = 66.9 Hz, 6 H); ^{31}P NMR (C_6D_6) δ −13.3 (s with Pt satellites, J_{Pt-P} = 1771 Hz). Anal. Calcd for $C_{48}H_{80}P_2Pt$: C, 63.06; H, 8.82; P, 6.78. Found: C, 62.81; H, 8.75; P, 6.60.

Bis(1-adamantyldimethylphosphine)dimethylplatinum(II) (9). The complex was prepared by a procedure similar to that described for **7** from 1-adamantyldimethylphosphine (0.50 mL, 0.50 g, 2.5 mmol) and (1,5-cyclooctadiene)dimethylplatinum(II).[19] The white powder obtained after solvent removal was recrystallized from diethyl ether. The complex was obtained as fine white crystals, mp 204–205 °C dec, in 22% yield. ^{1}H NMR (C_6D_{12}) revealed the complex to be a 2:1 mixture of the cis and trans isomers: δ 1.94 (s, br, 10 H), 1.85 (s, br, 8 H), 1.72 (s, br, 12 H), 1.4–1.2 (overlapping peaks; d with Pt satellites, J_{P-H} = 6.6, J_{Pt-H} = 18.5 Hz; "t" with Pt satellites, $|^2J_{P-H} + {}^4J_{P-H}|$ = 2.8, J_{Pt-H} = 14.1 Hz; 12 H), 0.42 (d of d with Pt satellites, J_{P-H} = 6.3, $J_{P'-H}$ = 7.1, J_{Pt-H} = 67.4 Hz, 4 H), −0.21 ("t" with Pt satellites, $|^2J_{P-H} + {}^4J_{P-H}|$ = 5.7, J_{Pt-H} = 50.1 Hz, 2 H). The proton NMR is extremely solvent-dependent; the chemical shifts of the platinum-bonded methyl groups, in particular, may vary as much as 1 ppm depending on the solvent. ^{31}P NMR (C_6D_6): δ 0.2 (s with Pt satellites, J_{Pt-P} = 1799 Hz), 3.8 (s with Pt satellites, J_{Pt-P} = 2926 Hz). Anal. Calcd for $C_{26}H_{48}P_2Pt$: C, 50.56; H, 7.83; P, 10.03. Found: C, 50.27; H, 7.67; P, 9.80.

Metallacycle 10. A 10-mm o.d. Pyrex thermolysis tube was charged with **7** (0.152 g, 0.235 mmol) and evacuated. Cyclohexane (2.0 mL) was added via syringe under an atmosphere of argon. The sample was freeze–pump–thaw degassed three times; on the fourth cycle, the tube was sealed under vacuum (0.010 torr). The sample was heated at 215 °C for 1 h. The tube was cracked open, and the yellow solution was concentrated to dryness on the rotary evaporater. The yellow oil was dissolved in warm pentane; crystals formed upon cooling to −10 °C. After a second recrystallization, the crystals were dried over KOH in vacuo. A second crop was isolated from the mother liquor and recrystallized similarly. The yield of colorless crystals was 49 mg (33%); mp 161 °C (capillary sealed under argon). ^{1}H and ^{31}P NMR data are reported in Table II. MS (chemical ionization, isobutane): *m/z* (relative intensity) 631 (4), 630 (4), 629 (7, $^{195}M^+$), 628 (5), 627 (4), 618 (5), 617 (19), 616 (20), 615 (82), 614 (100, $^{195}M^+ - CH_3$), 613 (78), 612 (6), 611 (9), 405 (3), 404 (3, $^{195}M^+ - CH_3 - 1$), 403 (4), 402 (2), 227 (6), 211 (8), 210 (6), 209 (3), 149 (2). Anal. Calcd for $C_{27}H_{48}P_2Pt$: C, 51.50; H, 7.68; P, 9.84. Found: C, 51.60, 51.57; H, 7.93, 7.73; P, 9.68, 9.95.

Metallacycle 11. Each of three 10-mm o.d. Pyrex thermolysis tubes was charged with ca. 50 mg of **8** and evacuated; then cyclohexane (2.0 mL) was added to each tube under argon. After three freeze–pump–thaw cycles, the tubes were sealed under vacuum (0.010 torr). The samples were heated at 165 °C for 35 min. The tubes were cracked open; the combined solutions were concentrated to a yellow oil on the rotary evaporater. The oil solidified upon addition of methanol. The methanol was removed under reduced pressure, and the white solid was dissolved in warm methylene chloride. Colorless crystals formed upon cooling to −10 °C. The complex was recrystallized a second time by layering methanol over a saturated solution of **11** in THF and cooling the mixture to −10 °C. A second crop was isolated from the mother liquor. The white crystals were dried in vacuo over KOH. The total yield was 37% (55 mg): mp >275 °C (capillary sealed under argon). ^{1}H and ^{31}P NMR data are reported in Table II. Anal. Calcd for $C_{47}H_{76}P_2Pt$: C, 62.85; H, 8.53; P, 6.90. Found: C, 62.67; H, 8.76; P, 7.16. Attempts to obtain a mass spectrum (either CI or EI) of **11** were unsuccessful.

***trans*-Bis[bis(1-adamantylmethyl)methylphosphine]dichloroplatinum(II)** was prepared according to the procedure of Cheney and Shaw.[12] A 250-mL, three-necked, round-bottomed flask equipped with a Liebig condenser topped by an argon inlet and a stirring bar was charged with bis(benzonitrile)dichloroplatinumII) 0.375 g, 0.794 mmol) and purged with argon. A solution of bis(1-adamantylmethyl)methylphosphine (0.56 g, 1.63 mmol, 2.05 equiv) in 80 naphthalene of degassed 1-propanol was added via cannula. The mixture was heated under reflux for 1 h. The mixture never became homogeneous, but the suspended solid gradually turned from yellow to off-white. The solid was isolated by Buchner filtration and washed with diethyl ether. Recrystallization from benzene/methanol gave yellow (almost yellow-green) crystals. Small second and third crops were isolated from the mother liquors. The crystals were dried in vacuo over KOH. The total yield was 68% (0.515 g, 0.540 mmol): mp >300 °C (capillary sealed under argon); ^{1}H NMR ($CDCl_3$) δ 2.09 (d of t, $^2J_{H-H}$ = 14.5, $|^2J_{P-H} + {}^4J_{P-H}|$ = 3.8 Hz, 4 H), 1.95 (br s, 12 H), 1.9–1.8 (br "d", 12 H), 1.8–1.7 (br "d", 12 H), 1.7–1.5 (superimposed peaks: br m; t, $|^2J_{P-H} + {}^4J_{P-H}|$ = 3.8 Hz; d of t, $^2J_{H-H}$ = 14.6, $|^2J_{P-H} + {}^4J_{P-H}|$ = 3.4 Hz; 34 H); ^{31}P NMR ($CDCl_3$) δ −12.1 (s with Pt satellites, J_{Pt-P} = 2380 Hz). Anal. Calcd for $C_{46}H_{74}Cl_2P_2Pt$: C, 57.85; H, 7.81; Cl, 7.42; P, 6.49. Found: C, 57.88, 57.80; H, 7.78, 7.82; Cl, 7.49, 7.46; P, 6.41.

Bis[bis(1-adamantylmethyl)methylphosphine]platinum(0) (14) was prepared according to the procedure described by Yoshida and Otsuka.[32] An oven-dried, 100-mL, three-necked, round-bottomed flask equipped with a stirring bar, a pressure-adjusted addition funnel, and a Liebig condenser topped by an argon inlet was charged with sodium (0.47 g, 0.020 mol) and purged with argon. The Na was suspended in 7 mL of THF; a solution of naphthalene (0.207 g, 1.62 mmol) in 13 mL of THF was added via cannula. After a few minutes, the solution turned dark olive-green. The mixture was stirred at room temperature for 2 h. The sodium naphthalene solution was added in aliquots via cannula to a Schlenk flask containing a suspension of *trans*-bis[bis(1-adamantylmethyl)methylphosphine]dichloroplatinum(II) (0.225 g, 0.236 mmol) in 20 mL of THF. The green color of the initial portions was discharged immediately; the color faded more slowly with subsequent additions. Addition of sodium naphthalene was discontinued when the green color persisted for >15 min. The solution was stirred at room temperature for 3 h; the solvent was then removed in vacuo. The yellow residue was extracted six times with degassed benzene; the pale yellow solution was filtered through a fine frit. Removal of the solvent in vacuo left a white gummy solid. A small portion of the product was analyzed by ^{1}H and ^{31}P NMR spectroscopy: ^{1}H NMR (C_6D_6) δ 2.25–2.05 (m, 36 H), 1.9–1.7 (m, 24 H), 1.45–1.30 [superimposed peaks; δ 1.42 (d of t, $^2J_{H-H}$ = 14.2, $|^2J_{P-H} + {}^4J_{P-H}|$ = 3.1 Hz); 1.37 (d of t, $^2J_{H-H}$ = 14.2, $|^2J_{P-H} + {}^4J_{P-H}|$ = 3.3 Hz), 1.34 (t, $|^2J_{P-H} + {}^4J_{P-H}|$ = 2.5 Hz, 14 H)]; ^{31}P NMR (C_6D_6) δ −4.1 (s with Pt satellites, J_{Pt-P} = 3888 Hz).

The complex was further characterized as the methyl iodide derivative. The white solid was dissolved in 20 mL of THF, and the yellow solution was treated with 0.75 mL of degassed MeI. The solution was stirred at room temperature overnight. Removal of the solvent left a yellow solid, which was transferred to a sublimater. Naphthalene was removed by sublimation (0.05 torr, 90 °C, 8 h). The residue was dissolved in warm THF; upon cooling to −10 °C, cream-colored crystals formed. After a second recrystallization, the crystals were dried in vacuo (0.03 torr) at 78 °C. The yield of *trans*-bis[bis(1-adamantylmethyl)methylphosphine]iodomethylplatinum(II), mp >250 °C (capillary sealed under argon), was 11% (27 mg, 0.026 mmol): ^{1}H NMR ($CDCl_3$) δ 1.95–1.5 (m, 75 H), 0.55 ("t" with Pt satellites, $|^2J_{P-H} + {}^4J_{P-H}|$ = 7, J_{Pt-H} = 82 Hz, 3 H); ^{31}P NMR ($CDCl_3$) δ −16.3 (br s with Pt satellites, J_{Pt-P} = 2713 Hz). Anal. Calcd for $C_{47}H_{77}IP_2Pt$: C, 55.02; H, 7.56; I, 12.37; P, 6.04. Found: C, 55.05; H, 7.65; I, 12.46; P, 6.32.

(1,5-Cyclooctadiene)methylphenylplatinum(II).[33] A 250-mL, round-bottomed flask was equipped with a stir bar, a pressure-adjusted dropping funnel, and a Liebig condenser topped by an argon inlet. The flask was charged with chloro(1,5-cyclooctadiene)phenylplatinum(II)[19] (0.3152 g, 0.758 mmol) and purged with Ar. The platinum complex was suspended in 50 mL of diethyl ether; the addition funnel was charged with a solution of methylmagnesium bromide (2.0 mL, 2.8 M in Et_2O, 5.6 mmol; diluted up to 50 mL with Et_2O). Addition took place at −8 °C (acetone–ice bath) over a 15-min period. The reaction mixture slowly become homogeneous as the mixture was allowed to warm to 0 °C. After 1 h, TLC [pentane/Et_2O (1/1, v/v) on silica] showed one spot at R_f 0.56. The reaction was quenched with 50 mL of aqueous ammonium chloride [saturated aqueous ammonium chloride/distilled water (1/1, v/v)] at 0 °C. The ethereal layer was washed twice with brine, dried over magnesium sulfate, and concentrated to dryness on the rotary evaporater. The white crystals were dissolved in ether/pentane and passed through a plug of neutral alumina. The solvent was removed on the rotary evaporater, and the white flakes were dried over KOH in vacuo (0.01 torr). The yield of white crystals, mp 107–108.5 °C, was 0.22 g (75%): ^{1}H NMR (CD_2Cl_2) δ 7.24 (m with Pt satellites, J_{Pt-H} = 67.9 Hz, 2 H), 7.05 (m, 2 H), 6.86 (m, 1 H), 5.09 ("t", br, J_{Pt-H} = 40.9 Hz, 2 H), 4.80 ("t", br, J_{Pt-H} = 39.8 Hz, 2 H), 2.42 (m, 8 H), 0.76 (s with Pt satellites, J_{Pt-H} = 82.6 Hz, 3 H). Anal. Calcd for $C_{15}H_{20}Pt$: C, 45.56; H, 5.10. Found: C, 45.65; H, 5.30.

***cis*-Bis(1-adamantyldimethylphosphine)methylphenylplatinum(II) (15).** The cis complex was synthesized via a procedure analogous to that described for **7** from (1,5-cyclooctadiene)methylphenylplatinum(II) (0.20 g, 0.51 mmol) and **4** (0.22 mL, 0.22 g, 1.1 mmol) in diethyl ether. The yellow oil obtained after the usual workup solidified upon addition of pentane. Two recrystallizations from MeOH/Et_2O, followed by cooling to −15 °C, afforded colorless cubes, mp 165–170 °C dec, in 28% yield: TLC [pentane/ethyl ether (1/1, v/v) on silica] R_f 0.54; ^{1}H NMR (C_6D_6) δ 7.79 (m with Pt satellites, J_{Pt-H} = 55 Hz, 2 H), 7.32 (m, 2 H), 1.9–1.65 (m, 18 H), 1.65–1.5 (m, 12 H), 1.16 (d with Pt satellites, J_{P-H} = 6.9, J_{Pt-H} = 18.1 Hz, 6 H), 1.05–0.85 (overlapping peaks; d of d with Pt satellites, J_{P-H} = 6.7, $J_{P'-H}$ = 8.3, J_{Pt-H} = 68.5 Hz; d with Pt satellites, J_{P-H} = 7.2, J_{Pt-H} = 19.4 Hz; 9 H total) (the signal due to the para phenyl hydrogen is obscured by the residual solvent peak); ^{31}P NMR (C_6D_6) δ −3.2 (d with Pt satellites, J_{P-P} = 12, J_{Pt-P} = 1787 Hz), −4.1 (d with Pt satellites, J_{P-P} = 12, J_{Pt-P} = 1719 Hz). Anal. Calcd for $C_{31}H_{50}P_2Pt$: C, 54.77; H, 7.41; P, 9.11. Found: C, 54.96; H, 7.36; P, 9.09.

No cis–trans isomerization of **15** is observed when a sealed tube containing a solution of *cis*-**15** in C_6D_6 is heated at 80 °C for 1.3 h. Heating the solution at higher temperatures (145 °C, 10 min) causes isomerization to *trans*-**15** [^{31}P NMR δ 1.5 (J_{Pt-P} = 2883 Hz); ^{1}H NMR δ 0.53 ("t" with platinum satellites, $|^2J_{P-H} + {}^4J_{P-H}|$ = 6.0, J_{Pt-H} = Hz)], but substantial decomposition occurs. The products of decomposition are toluene and a complex tentatively identified as bis(1-adamantyldimethylphosphine)platinum(0). The identification of this product is based on the similarity of its ^{31}P NMR spectrum [δ 32.8 (J_{Pt-P} = 4219 Hz)] to that of other L_2Pt^0 complexes[34] and on literature precedent for the formation of L_2Pt^0

(32) Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 101–107.

(33) Clark, H. C.; von Werner, K. *J. Organomet. Chem.* **1975**, *101*, 347–358.

(34) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979; p 92.

upon thermolysis of *cis*-$L_2Pt(R)Ar$.[35]

Thermolyses. Small-scale thermolyses of the bis(trialkylphosphine)dimethylplatinum(II) complexes were conducted in 5-mm o.d. NMR tubes and followed by ^{31}P and/or ^1H NMR spectroscopy. Thin-walled NMR tubes (Wilmad catalog number 528-PP) were used if the solvent was C_6D_{12} and the reaction temperature was less than 200 °C. For reactions in which the solvent was C_6D_6 and/or the reaction temperature was greater than 200 °C, medium-walled NMR tubes (Wilmad catalog number 524-PP) were used to minimize the risk of explosion during thermolysis or breakage during freeze–pump–thaw cycles.

The NMR tube was attached to a 14/20 inner joint, washed with distilled water and acetone, and flame-dried under vacuum (0.01 torr). Once the tube had cooled, it was charged with the platinum complex and reevacuated for at least an hour. Then deuteriated solvent, previously subjected to two freeze–pump–thaw cycles, was vacuum-transferred from $LiAlH_4$ into the tube. The amount of solvent in the tube was determined by comparison with a calibrated NMR tube. The tube was freeze–pump–thawed twice; on the third cycle the tube was sealed under vacuum (0.01 torr). Gentle warming was generally necessary to dissolve the platinum complex.

The tubes were heated in the vapors of refluxing solvents (cyclohexane, 80 °C; *m*-xylene, 145 °C; mesitylene, 165 °C; *o*-dichlorobenzene, 180 °C; *n*-dodecane, 215 °C). The progress of the reaction was checked periodically by ^{31}P NMR spectroscopy. The NMR tube was positioned coaxially in a 10-mm o.d. tube containing C_6D_6 and a sealed capillary of H_3PO_4. Yields were determined by the integration of the central peak(s) of the platinum complex relative to the H_3PO_4 standard. Relaxation delays of at least $5T_1$ were used to ensure accurate integration. Results are summarized in Table I.

Thermolyses in the Presence of Hg(0). Flame-dried Pyrex thermolysis tubes (6-mm o.d., ca. 8 in. long) were charged with 4–11 mg of platinum complex and a small bead of Hg(0) (100–200 mg). The tube was attached to the vacuum line and evacuated to 0.01 torr for at least 1 h. Benzene-d_6 (0.3 mL, previously subjected to three freeze–pump–thaw cycles) was vacuum-transferred from $LiAlH_4$ into the thermolysis tubes. The contents of the tubes were freeze–pump–thawed twice; on the third cycle, the tubes were sealed under vacuum (0.015 torr). The length of each thermolysis tube was 6–7 cm.

Each tube was thermolyzed in a heated oil bath using the off-axis stirring technique described elsewhere.[36] Thermolysis temperatures and the length of heating are summarized in Table I. In each case, the thermolyzed reaction solutions were completely colorless. In the thermolyses of **7** and **9**, the mercury bead looked dirty and a fine black precipitate was generated. Thermolysis of **8** in the presence of Hg(0) left the bead of mercury shiny and clean.

The gas and liquid phases were analyzed by GC and GC/MS as described above. The liquid phase was diluted with C_6D_6, and the products of each thermolysis were identified by ^1H and ^{31}P NMR spectroscopy. In all cases the same products were obtained in the presence and absence of Hg(0). The percent conversion was estimated by quantitative ^{31}P NMR spectroscopy. Since the decomposition reactions are not quantitative, the conversions reported here are best considered to be approximations. In particular, it was difficult to gauge the extent of decomposition of **9** because the ultimate decomposition product **4** was formed in low yield. Substantial amounts of *cis*- and *trans*-**9** as well as *trans*-bis(1-adamantyldimethylphosphine)methylphenylplatinum(II) (**15**) were observed, indicating that decomposition was not complete. Free 1-adamantyldimethylphosphine (**4**) was also present. These results are summarized in Table I.

Thermal decompositions appear to proceed more slowly in the presence of Hg(0) than in its absence. This difference may be a consequence of the different reaction conditions used for thermal decompositions in the presence of Hg(0), or it may reflect the poisoning of a heterogeneous reaction that would, in the absence of mercury, accelerate the decomposition.

Identification of Products. The identity of metallacycle **10** was established by ^1H and ^{31}P NMR spectroscopy, MS, and elemental analysis; **11** was characterized by ^1H and ^{31}P NMR spectroscopy and elemental analysis. (See Results and Discussion and Table II.) Bis[bis(1-adamantylmethyl)methylphosphine]platinum(0) (**14**) was identified by comparison of its ^1H and ^{31}P NMR spectra with those of an authentic sample. Attempts to synthesize *trans*-bis(1-adamantyldimethylphosphine)methylphenylplatinum(II) (*trans*-**15**) independently were unsuccessful, but *cis*-**15** was readily synthesized and completely characterized. Upon thermolysis, *cis*-**15** isomerizes to the trans complex. The ^1H and ^{31}P NMR spectra of the complex produced by isomerization is indistinguishable from the reaction product identified as *trans*-**15**. The phosphine **4** was identified by comparison of the ^{31}P NMR spectrum of the reaction product with that of an authentic sample. Hydrocarbons were identified by their GC retention times and GC/MS.

Analysis of the Hydrocarbon Reaction Products. Both gas and liquid phases were analyzed by GC/MS and GC. Absolute yields of methane, ethane, and ethylene were not determined. The electronically integrated areas used as the basis for relative yields were corrected for the difference in response factors (CH_4, 1.00; C_2H_6, 1.99; C_2H_4, 2.04). We assumed that deuteriation did not influence these response factors. Deuterium incorporation was determined by comparison with the mass spectra of authentic mixtures of CH_4 and CH_3D. The latter was prepared by quenching (D_2O) an aliquot of CH_3Li that had been freeze–pump–thawed three times. The mass spectrum obtained was in excellent agreement with literature values.[37]

Cyclohexane, methylcyclohexane, adamantane, and bicyclohexyl were separated on a 5% SE-30 on Chromosorb P column. The same column was used to separate toluene, *n*-nonane (added as an internal standard after the thermolysis tube was cracked open), adamantane, and biphenyl. The electronically determined peak areas were corrected for the difference in response factors (toluene, 1.00; *n*-nonane, 1.39; adamantane, 1.39). Cyclohexane and cyclohexane were separated on 25% $AgNO_3$–TEG on Chromosorb P.

Deuterium incorporation in toluene was determined by GC/MS analysis. The mass spectra of authentic $C_6D_5CH_3$, $C_6HD_4CH_3$, and $C_6D_5CH_2D$ are not available. We assume that each of these species has a substantial M^+ peak as well as a $(M-1)^+$ base peak. On the basis of this assumption, the toluene observed is calculated to contain 4–6 D/molecule. A typical analysis produces the following mass spectrum at 70 eV: m/z (relative intensity) 99 (3), 98 (24), 97 (90), 96 (100), 95 (79), 94 (28), 93 (18), 92 (8), 91 (2).

The results of the NMR, GC, and GC/MS analyses are summarized in Table I.

Results and Discussion

The syntheses of phosphines **1–3** and platinum complexes **7** and **8** were straightforward. Efforts to prepare bis[tris(1-adamantylmethyl)phosphine]dimethylplatinum(II) by a similar route failed. Attempts to synthesize dichlorobis[tris(1-adamantylmethyl)phosphine]platinum(II) using Zeise's salt,[38] potassium tetrachloroplatinate,[39] or bis(benzonitrile)dichloroplatinum[12] were also unsuccessful.

(35) Thermolysis of the square-planar complex *trans*-methylphenylbis(triethylphosphine)nickel(II) produces toluene and bis(triethylphosphine)nickel(0): Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262–7270. In contrast, thermal decomposition of *cis*-(4-ethylphenyl)methylbis(tricyclopentylphosphine)platinum(II) yields numerous products, including methane, ethane, 4-ethylbenzene, 4,4′-diethylbiphenyl, and 4-ethyltoluene, in addition to bis(tricyclopentylphosphine)platinum(0): Brainard, R. L. Ph.D. Dissertation, Massachusetts Institute of Technology. Cambridge, MA, 1985. Only reductive elimination of Ar_2 (and not ArR) from Pt(II) complexes has been thoroughly investigated: Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892–1897.

(36) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819–1830.

(37) Juentzel, L. E., Ed. *Index of Mass Spectral Data*; American Society for Testing and Materials: Ann Arbor, MI, 1963.

(38) Chock, P. B.; Halpern, J.; Paulik, F. E. *Inorg. Synth.* **1973**, *14*, 90–92. Hus, C.-Y.; Leshner, B. T.; Orchin, M. *Inorg. Synth.* **1978**, *19*, 114–116.

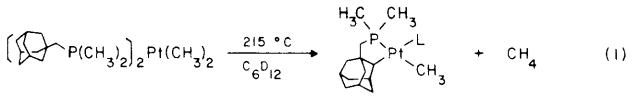
(39) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 245–249.

The syntheses of phosphines **4** and **5** were equally straightforward in principle but considerably more difficult in practice due to purification problems. Ligands of satisfactory purity could be obtained only after precipitation of the phosphines as dibromide adducts and removal of hydrocarbon contaminants by repeated rinsing with hexane. Treatment of the dibromide adduct with *n*-butyllithium regenerated the free phosphine, and subsequent distillation (in the case of **4**) or recrystallization (in the case of **5**) afforded phosphines of usable purity. All attempts to synthesize **6** were unsuccessful; the reaction presumably stops at di-1-adamantylchlorophosphine.[40] The complete insolubility of 1-adamantyllithium in inert (i.e., saturated hydrocarbon) solvents rendered the reagent useless for the synthesis of these phosphines.

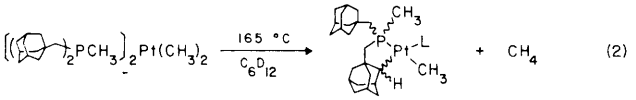
Bis(1-adamantyldimethylphosphine)dimethylplatinum(II) (**9**) was readily prepared but only complex mixtures were obtained when di-1-adamantylmethylphosphine was allowed to react with (1,5-cyclooctadiene)dimethylplatinum or bis(benzonitrile)dichloroplatinum.[12] The reactions of **5** were not further investigated.

Compounds **7**, **8**, and **9** were thermolyzed in cyclohexane-d_{12} and benzene-d_6, and the extent of reaction and product yields were determined by ^{31}P NMR spectroscopy (Table I). Isotopic composition and relative (not absolute) yields of the gaseous products were determined for each thermolysis. All reactions *appeared* to be homogeneous.

Thermal decomposition in cyclohexane-d_{12} produced reaction solutions ranging in color from light yellow (in the case of **8**) to brown (in the case of **7** and **9**). In no case was precipitation of solids or formation of platinum mirrors observed. The major gaseous product in cyclohexane-d_{12} was CH_4 (isotopic purity >97%, the limit of our detection). The lack of deuterium incorporation suggests that the methane is generated by an intramolecular reaction. No bicyclohexyl or cyclohexene was formed.[41] The platinum-containing products resulting from the thermolysis of **7** or **8** are compounds assigned the structures **10** and **11** (eq 1 and 2). In the case of **9**, no new species (except of a trace of free phosphine) are observed by ^{31}P NMR spectroscopy.

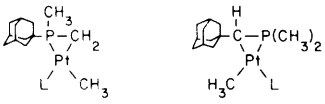


7 **10**



8 **11**

The structure of the products **10** and **11** was assigned on the basis of ^{31}P and ^1H NMR spectra (Table II). The ^{31}P NMR spectrum of **10** consists of a pair of doublets, each with platinum satellites. One doublet is shifted markedly downfield from the resonance of the unmetalated ligand. This pronounced downfield shift is diagnostic of five-membered phosphorus-containing metallacycles.[42] (Three-membered phosphaplatinacycles such as **12** and **13** would be expected to show a pronounced *upfield* shift of the metalated phosphine relative to the non-metalated



12 **13**

ligand.[42,43]) The magnitude of the phosphorus-platinum coupling constants and the small phosphorus–phosphorus coupling constants[12,44] are consistent with a cis configuration of the phosphine ligands. The ^1H NMR spectrum of **10** shows a methyl group with platinum satellites, integrating to three protons relative to the rest of the spectrum, with two different P–H coupling constants.

Compound **11** (derived from **8**) appears to be a mixture of two diastereomeric metallacycles.[45] The ^{31}P NMR spectrum of the product mixture exhibits two sets of signals: a pair of doublets with platinum satellites and a pair of broad singlets, also with satellites (Table II). One singlet and one doublet are strongly deshielded, as expected for a five-membered phosphorus-containing metallacycle, and the phosphorus–phosphorus coupling constants are small for both diastereomers. Again, the relatively small phosphorus–platinum and phosphorus–phosphorus coupling constants are consistent with a cis configuration of the phosphine ligands. A cyclometalated complex with trans phosphine ligands would be expected to have a larger (2800–3000 Hz) P–Pt coupling constant.

We note that the chemical shifts of the diastereomers differ by about 1 ppm (121 Hz) but their phosphorus–platinum coupling constants are virtually identical. The small difference in the chemical shifts and the similarity of the coupling constants is typical of diastereomeric complexes.[46] The ^1H NMR spectrum of the mixture of diastereomers shows a single type of platinum-bonded methyl group coupled to two inequivalent phosphorus atoms.

The thermal decompositions of **7**, **8** and **9** in benzene-d_6 were considerably less clean. Complexes **7** and **8** again undergo cyclometalation, but yields of **10** and **11** are lower in C_6D_6 than in C_6D_{12}. Continued thermolysis of **11** produces bis(di-1-adamantylmethylphosphine)platinum(0) (**14**). Complete thermolysis of **9** yields the free phosphine **4** as the only identifiable product; at intermediate stages in the thermolysis, however, *trans*-bis(1-adamantyldimethylphosphine)methylphenylplatinum(II) (**15**) is observed. The reaction solutions range in color from dark yellow to brown, but no solids are observed. Variable amounts of CH_3D are generated along with CH_4. Analysis of the reaction mixture by GC and GC/MS reveals traces of partially deuteriated (d_4 to d_6) toluene.

(40) Similarly, treatment of phosphorus trichloride with excess *tert*-butylmagnesium chloride produces di-*tert*-butylchlorophosphine: Hoffmann, H.; Schellenbeck, P. *Chem. Ber.* **1967**, *100*, 692–693.

(41) The trace of perdeuterated methylcyclohexane that was observed by GC and GC/MS was also detected in unreacted C_6D_{12}.

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(45) Racemic cyclopalladated dimers form separable diastereomers upon cleavage with chiral amines. See: Sokolov, V. I.; Sorokina, T. A.; Troitskaya, L. L.; Solovieva, L. I.; Reutov, O. A. *J. Organomet. Chem.* **1972**, *36*, 389–390. Dunina, V. V.; Zalevskaya, O. A.; Smolyakova, I. P.; Potapov, V. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1985**, *54*, 2049–2055. Dunina, V. V.; Zaleskaya, O. A.; Smolyakova, I. P.; Potapov, V. M. *Doklady Chemistry (Engl. Transl.)* **1985**, *278*, 323–324. Zalevskaya, O. A.; Dunina, V. V.; Potapov, V. M.; Kuzmina, L. G.; Sruchkov, Yu. T. *J. Gen. Chem. USSR (Engl. Transl.)* **1985**, *55*, 1191–1198.

(46) See, for example: Ansell, C. W. G.; Cooper, M. K.; Dancey, K. P.; Duckworth, P. A.; Henrick, K.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Chem. Commun.* **1985**, 439–441. Brown, J. M.; Chaloner, P. A. *Tetrahedron Lett.* **1978**, 1877–1880. Abicht, H.-P.; Spencer, J. T.; Verkade, J. G. *Inorg. Chem.* **1985**, *24*, 2132–2134. Morandini, F.; Consiglio, G.; Lucchini, V. *Organometallics* **1985**, *4*, 1202–1208.

Solutions of **7**, **8**, and **9** were thermolyzed in benzene-d_6 in the presence of Hg(0) in order to determine if the small quantities of toluene and CH_3D observed were produced by heterogeneous, platinum(0)-catalyzed reactions.[35] In contrast to the yellow or brown solutions obtained on thermolysis in the absence of Hg(0), thermal decomposition of benzene-d_6 solutions of **7**, **8**, and **9** in the presence of Hg(0) produced completely colorless solutions. The mercury bead is covered with a black film after thermolysis of **7** and **9** but appears to be virtually unchanged after thermolysis of **8**. The phosphorus-containing products are the same, but the hydrocarbon products are markedly affected by the presence of Hg(0) (Table I). The yield of toluene decreases in all cases. The amount of CH_3D relative to CH_4 decreases when **7** and **8** are thermolyzed in the presence of mercury but increases when **9** is allowed to decompose in the presence of Hg(0).

The uncertainties associated with using mercury to poison heterogeneous reactions prohibit a straightforward interpretation of these results. The fact that the presence of mercury reduces the amounts of CH_3D (relative to CH_4) and toluene produced in the thermal decompositions of **7** and **8** implies that these products originate, at least in part, from heterogeneous processes. That some CH_3D and toluene are still observed may indicate either that a homogeneous reaction is partially responsible for these products or that mercury has only a limited ability to poison this heterogeneous reaction.

Conclusions

These results indicate that the phosphines (1-adamantylmethyl)dimethylphosphine (**1**), bis(1-adamantylmethyl)methylphosphine) (**2**), and 1-adamantyldimethylphosphine (**4**) are *not* inert with respect to intramolecular reactions: platinum complexes of **1** and **2** decompose by cyclometalation of a 1-adamantylmethyl substituent and complexes of **4** decompose by poorly defined pathways.

The characteristics required to render a phosphine ligand "inert" are still unclear.[47] At present it is easier to summarize ligands that undergo cyclometalation[13] or P–C bond cleavage[48] under some conditions than to predict ligands that will prove resistant to intramolecular reactions. Nonetheless it is apparent that some ligands are intrinsically more susceptible to intramolecular reactions than others. For example, cleavage of the P–C bond (with or without rearrangement of the organometallic complex) is generally important only for triarylphosphines.[48] Cyclometalation occurs most readily when the ligand is bulky and a five-membered metallacycle results.[12,13,49] Four- and six-membered metallacycles are formed somewhat less readily, and three-membered metallacycles are usually formed only when no other options for cyclometalation are available.[43,50] Incorporation of the phosphine ligands into bidentate chelates also seems to suppress cyclometalation.[51] These trends can be rationalized by assuming that relief of steric congestion at the metal center provides an important driving force for cyclometalation and that the C–H bond must be suitably oriented with respect to the metal center to undergo oxidative addition.[52] Having suggested structural features that render a ligand susceptible to intramolecular reactions, we note that it remains unclear why complexes such as $(PPh_3)_2ReH_7$,[2] $\{IrH_2(Me_2CO)_2[P(p\text{-}C_6H_4F)_3]_2\}SbF_6$,[3] $(\eta^5\text{-}C_5Me_5)(PPh_3)IrH_2$,[4] $(\eta^5\text{-}C_5Me_5)(PMe_3)IrH_2$,[4] $(\eta^5\text{-}C_5H_5)(PMe_3)_3Re$,[5] and $(\eta^5\text{-}C_5Me_5)Rh(PMe_2Pr)H_2$[6] oxidatively add solvent C–H bonds in preference to or in competition with intramolecular reactions, despite the fact that all of these compounds contain phosphines that cyclometalate or undergo P–C bond cleavage readily under different conditions.

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Registry No. **1**, 105944-78-3; **2**, 105944-79-4; **3**, 105944-80-7; **4**, 105458-59-1; **5**, 105944-81-8; *cis*-**7**, 105944-70-5; *trans*-**7**, 106032-87-5; *cis*-**8**, 105944-71-6; *trans*-**8**, 106032-88-6; *cis*-**9**, 105944-72-7; *trans*-**9**, 106032-85-3; **10**, 105991-03-5; **11**, 105969-33-3; **14**, 105944-74-9; *cis*-**15**, 105944-76-1; *trans*-**15**, 106032-86-4; $ClPMe_2$, 811-62-1; Cl_2PMe, 676-83-5; Cl_3P, 7719-12-2; (1,5-COD)$PtMe_2$, 12266-92-1; $(PhCN)_2PtCl_2$, 14873-63-3; (1,5-COD)Pt(Me)Ph, 58058-38-1; (1,5-COD)Pt(Ph)Cl, 51177-65-2; MeBr, 74-83-9; 1-adamantylmethyl bromide, 14651-42-4; 1-adamantyl bromide, 768-90-1; *trans*-bis[bis(adamantylmethyl)methylphosphine]dichloroplatinum(II), 105944-73-8; *trans*-bis[bis(adamantylmethyl)methylphosphine]iodomethylplatimum, 105944-75-0; bis(1-adamantyldimethylphosphine)platinum(0), 105944-77-2.

(47) Ligands for L_2PtMe_2 that have proved to be unsatisfactory for some reason (solubility, stability of the organometallic complex, ease of complexation) include trimethylphosphine, 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, hexamethylphosphoric triamide, tris(pentafluorophenyl)phosphine, 2,2′-bipyridine, and tetrahydrothiophene. Tris(pentafluorophenyl)phosphine fails to displace 1,5-cyclooctadiene from (1,5-cyclooctadiene)dimethylplatinum(II); the other ligands form L_2PtMe_2 complexes that are too insoluble in hydrocarbon solvents to be useful for mechanistic studies.

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