[Bis(dicyclohexylphosphino)ethane]platinum(0). Reactions with Alkyl, (Trimethylsilyl)methyl, Aryl, Benzyl, and Alkynyl Carbon-Hydrogen Bonds[1]

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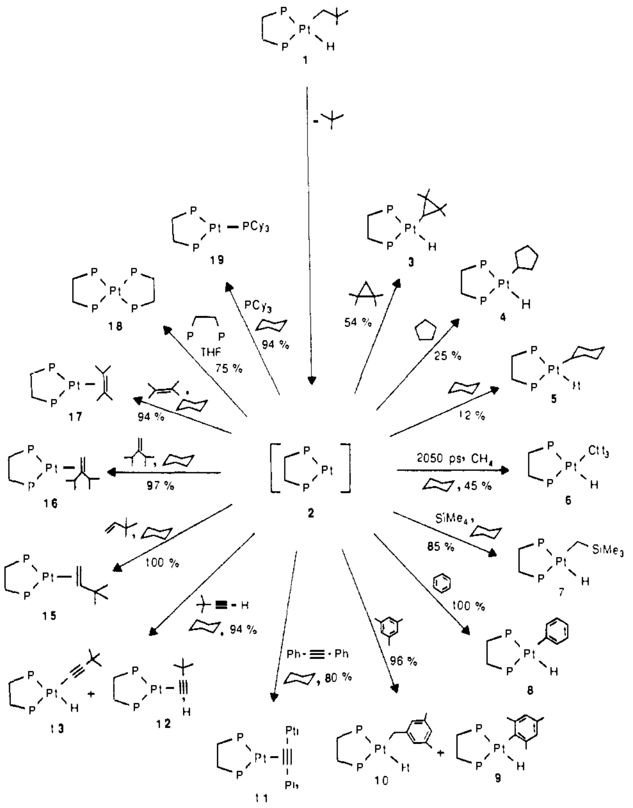
Abstract: *cis*-Hydridoneopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**1**) reductively eliminates neopentane and generates [bis(dicyclohexylphosphino)ethane]platinum(0) (**2**). This bent bis(phosphine)platinum(0) complex was not observed directly; its intermediacy was inferred from the presence of this moiety in the reaction products. The intermediate **2** reacts with alkyl, (trimethylsilyl)methyl, aryl, and benzyl carbon-hydrogen bonds. With phosphines, disubstituted alkynes, and olefins, **2** forms coordination complexes; **2** does not add olefinic or allylic C-H bonds. In the reaction of **2** with monosubstituted alkynes, C-H bond addition competes with coordination of the alkyne. The factors responsible for the reactivity of **2** relative to other coordinatively unsaturated platinum species are discussed.

The problem of activating alkanes via soluble metal complexes[2] is similar to solving Rubik's cube: there are many solutions, none of which is particularly obvious until after the fact. Saturated hydrocarbons react with lanthanide and actinide complexes via four-center mechanisms,[3-5] with cationic or neutral iridium,[6-8] rhemum,[9] and ruthenium[10,11] complexes in the presence of the dihydrogen acceptor neohexene via three-center oxidative addition mechanisms, with platinum acetates and chlorides in acidic solution via what are presumed to be oxidative addition processes with strong electrophilic character,[12,13] and with electron-rich, coordinatively unsaturated transition-metal species generated either thermally or photochemically via reactions that may involve excited-state chemistry or oxidative addition with nucleophilic character.[14-21]

We recently reported the activation of carbon-hydrogen bonds via the transient intermediate [bis(dicyclohexylphosphino)ethane]platinum(0), an electron-rich d^{10} fragment generated by the reductive elimination of neopentane from *cis*-hydridoneopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**1**).[22] This paper surveys the reactions of [bis(dicyclohexylphosphino)ethane]platinum(0) (**2**) with a variety of saturated and unsaturated hydrocarbons.

Scheme I.[a] Reactions of [Bis(dicyclohexylphosphino)ethane]platinum(0) (**2**)



[a] P P = bis(dicyclohexylphosphino)ethane.

Results

Previous work has shown that **1** eliminates neopentane on thermolysis and generates the reactive intermediate **2**.[22,23] This intermediate oxidatively adds alkyl, (trimethylsilyl)methyl, aryl, and benzyl carbon-hydrogen bonds. In contrast, reaction with olefins yields (olefin)[bis(phosphine)]platinum(0) complexes; **2** does not insert into alkene C-H bonds. Phosphines and disub-

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[2] For reviews, see: Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269; Ephritikhine, M. *Nouv. J. Chim.* **186**, *10*, 9-15.

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stituted alkynes also form coordination complexes; monosubstituted alkynes undergo competitive C–H bond addition and coordination of the alkyne.

The following section describes the reactions summarized in Scheme I. In all cases, the thermolysis of **1** produced neopentane and the reactive species **2**. (The intermediacy of **2** was inferred from the presence of this moiety in the reaction products; it was not observed directly.) The identity of the platinum-containing reaction products was established either by independent synthesis or by preparative-scale thermolysis of **1** in the presence of the appropriate reactant and purification of the product. Descriptions of these experiments follow those directly relevant to Scheme I.

Reaction of 2 with Saturated Hydrocarbons and with Tetramethylsilane. The thermolysis of **1** in 1,1,2,2-tetramethylcyclopropane, cyclopentane, and cyclohexane yielded *cis*-hydrido(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**3**), *cis*-cyclopentylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (**4**), and *cis*-cyclohexylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (**5**), respectively. When **1** was heated in cyclohexane under 2050 psi of methane, both **5** and *cis*-hydridomethyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**6**) formed. The yields of complexes **3**–**6** were low to moderate (12–54%), even under optimal conditions (dilute solution, 45 °C). When **1** was thermolyzed in alkanes at 69 °C, the yields of platinum alkyl hydrides were negligible and poorly characterized white precipitates formed.[24]

When a dilute (0.015 M) solution of **1** in 1,1,2,2-tetramethylcyclopropane[25] was heated at 45 °C, *cis*-hydrido(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**3**) was obtained in 54% yield. A minor product, identified on the basis of its ^{1}H and ^{31}P NMR spectra as *cis*-hydrido[(1,2,2-trimethylcyclopropyl)methyl][bis(dicyclohexylphosphino)ethane]platinum(II), was obtained in low yield (12%). A third product, formed in 16% yield, appears to be an (olefin)[bis(phosphine)]platinum(0) complex, but its identity could not be conclusively established. (See the Experimental Section.) The ^{31}P NMR spectrum of the third product is *not* consistent with [bis(dicyclohexylphosphino)ethane]-2,2,3,3-tetramethylplatinacyclobutane or [bis(dicyclohexylphosphino)ethane]-2,2,4,4-tetramethylplatinacyclobutane, the products of oxidative addition of a cyclopropyl carbon–carbon bond.[26] Similar yields of the three products were obtained when the thermolysis was carried out at 35 °C; at 69 °C, the yields were substantially lower and insoluble white precipitates formed.

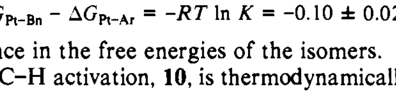
The thermolysis of **1** in cyclopentane and cyclohexane yielded *cis*-cyclopentylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (**4**) and *cis*-cyclohexylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (**5**), respectively. The maximum yields (**4**, 25; **5**, 16%) were obtained when dilute (0.015 M) solutions of **1** were thermolyzed at 45 °C. At 69 °C, the yields of **4** and **5** were negligible and insoluble white precipitates formed. The yield of **4** was comparable (23%) when **1** was thermolyzed at 35 °C.

When a 0.024 M solution of **1** in cyclohexane was heated at 45 °C under 2050 psi of methane, both **5** and *cis*-hydridomethyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**6**) formed in 10% and 45% yields, respectively. A third product, ethylene[bis(dicyclohexylphosphino)ethane]platinum(0), formed in 23% yield. (Traces of ethylene are inevitably present even in ultrahigh-purity methane.)

The intermediate **2** also reacts with acyclic alkanes such as hexane. When **1** was thermolyzed at 45 °C in hexanes, two platinum complexes formed in a combined yield of 18%. This reaction was not investigated in detail other than to ascertain by ^{1}H and ^{31}P NMR spectroscopy that the soluble products were platinum alkyl hydrides. (See the Experimental Section.) The products may result from the oxidative addition of the primary and secondary C–H bonds of *n*-hexane, the major component of hexanes, or from the addition of the C–H bonds of isomeric hexanes.

At 69 °C, cyclohexane is sufficiently unreactive toward **2** that it can be used as an inert solvent for the reaction of **1** with other compounds. (Either cyclohexane cannot compete with other reactants for **2** or *cis*-[bis(dicyclohexylphosphino)ethane]cyclohexylhydridoplatinum(II), the product of **2** and cyclohexane, decomposes readily at this temperature and regenerates **2**.) For example, when a solution of **1** in cyclohexane containing tetramethylsilane was heated at 69 °C, *cis*-hydrido[(trimethylsilyl)methyl][bis(dicyclohexylphosphino)ethane]platinum(II) (**7**) formed in 85% yield.[27]

Reaction of 2 with Aryl and Benzyl Carbon–Hydrogen Bonds. The thermolysis of **1** in benzene produced *cis*-hydridophenyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**8**) in quantitative yield.[23] When **1** was thermolyzed in mesitylene (1,3,5-trimethylbenzene), two platinum hydrides were formed, *cis*-hydrido(2,4,6-trimethylphenyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**9**) (82%) and *cis*-hydrido(3,5-dimethylbenzyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**10**) (14%). Upon continued thermolysis, the two hydrides equilibrated: K_{eq} = [**10**]/[**9**] = 1.2 at 69 °C. When independently synthesized samples of **9** and **10** were heated in mesitylene at 69 °C, the equilibrium ratios of **10** to **9** were 1.19 and 1.14, respectively. The average of these values, K_{eq} = 1.16 (eq 1), was used to calculate



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$$\Delta\Delta G = \Delta G_{\text{Pt-Bn}} - \Delta G_{\text{Pt-Ar}} = -RT \ln K = -0.10 \pm 0.02 \text{ kcal/mol}$$

the difference in the free energies of the isomers. The product of benzylic C–H activation, **10**, is thermodynamically favored by 0.1 kcal/mol over the kinetic product, **9**. Oxidative addition of an aryl C–H bond to **2** is kinetically favored; addition of a benzylic C–H bond is thermodynamically favored.

When samples of **9** and **10** were thermolyzed separately in benzene, **8** is formed. No equilibration of **9** and **10** was observed (eq 2).

Reaction of 2 with Alkynes. The thermolysis of **1** in a cyclohexane solution of diphenylacetylene produced (diphenylacetylene)[bis(dicyclohexylphosphino)ethane]platinum(0) (**11**).[23] The reaction of **2** with monosubstituted alkynes was more complex: oxidative addition of an alkynyl C–H bond competed with co-

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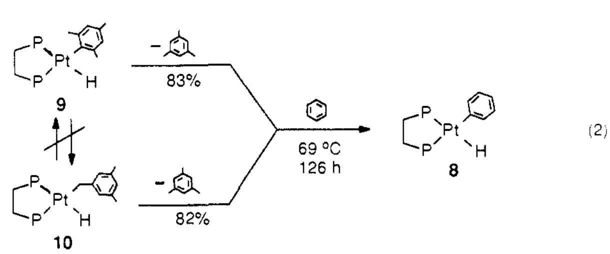
[24] The white precipitate is sparingly soluble in CD_2Cl_2 but virtually insoluble in hydrocarbon solvents. The ^{31}P NMR spectrum shows only a few very small peaks; the ^{1}H NMR spectrum consists of several multiplets in the aliphatic region (δ 2.5–1.0). We have not been able to establish the identity of the precipitate. Note, however, that the ^{31}P NMR spectrum is not consistent with bis[[bis(dicyclohexylphosphino)ethane]platinum(0)]. Similar platinum dimers have been synthesized and fully characterized; the ^{31}P NMR spectra of these complexes are very distinctive. See: Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073.

[25] 1,1,2,2-Tetramethylcyclopropane was chosen as a reactant (instead of cyclopropane, for example) because 1,1,2,2-tetramethylcyclopropane is a commercially available liquid that can be used as a solvent as well as a reactant. Its reactivity with respect to **2** parallels that of cyclopropane; that is, both compounds react with **2** to form *cis*-alkylhydrido[bis(phosphine)]platinum(II) complexes. (The thermolysis of **1** is cleaner in neat 1,1,2,2-tetramethylcyclopropane than in cyclohexane under 1 atm of cyclopropane.) Note that **2** does not insert into a carbon–carbon bond of cyclopropane; thus, the failure of **2** to form platinacyclobutanes upon reaction with 1,1,2,2-tetramethylcyclopropane is not due to the bulk of the alkyl substituents on the cyclopropyl ring.

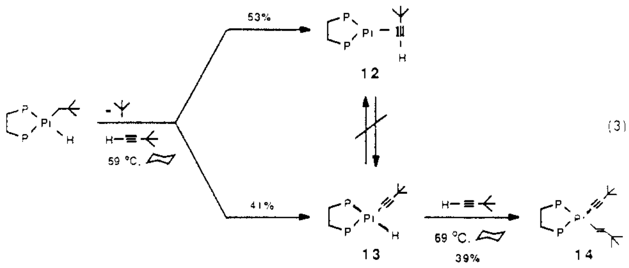
[26] The third product may derive from oxidative addition of a carbon–carbon bond followed by rearrangement to an (olefin)[bis(dicyclohexylphosphino)ethane]platinum(0) complex. Platinacyclobutanes can rearrange to free or coordinated olefins, depending on the experimental conditions. See: Wiberg, K. B.; McClusky, J. V.; Schulte, G. K. *Tetrahedron Lett.* **1986**, *27*, 3083–3086. Hall, P. W.; Puddephatt, R. J.; Seddon, K. R.; Tipper, C. F. H. *J. Organomet. Chem.* **1974**, *81*, 423–430. Al-Essa, R. J.; Puddephatt, R. J.; Tipper, C. F. H.; Thompson, P. J. *J. Organomet. Chem.* **1978**, *157*, C40–C42. Iwanciw, F.; Quyser, M. A.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1976**, *113*, 91–97. Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, *152*, C42–C44. Johnson, T. H.; Cheng, S.-S. *J. Am. Chem. Soc.* **1979**, *101*, 5277–5280.

[27] The reaction of **2** with arylsilanes, e.g. 1,4-bis(trimethylsilyl)benzene and 1,3,5-tris(trimethylsilyl)benzene, is more complex: oxidative addition of a C–H bond competes with insertion into an aryl C–Si bond (Hackett, M., unpublished results).



(2)

ordination of the alkyne. Thus, two products, (3,3-dimethyl-1-butyne)[bis(dicyclohexylphosphino)ethane]platinum(0) (**12**) and *cis*-hydrido(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane] (**13**), were formed in approximately equal amounts. The two products did *not* interconvert upon continued heating. In the presence of excess 3,3-dimethyl-1-butyne, however, **13** was slowly converted to *cis*-[(*E*)-3,3-dimethyl-1-butenyl]-(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]-platinum(II) (**14**) (eq 3).



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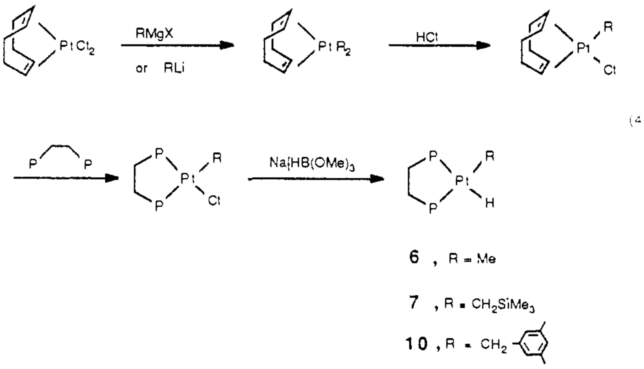
Reaction of 2 with Alkenes. When **1** was heated in cyclohexane solutions of various alkenes, the sole products observed were the (olefin)[bis(phosphine)]platinum(0) complexes **15–17**. The intermediate **2** did **not** add olefin C–H bonds even though the expected product, *cis*-alkenylhydrido[bis(phosphine)]platinum(II), should be thermally stable.[28,29] Allylic carbon–hydrogen bonds were similarly inert with respect to oxidative addition. Prolonged thermolysis of the (olefin)[bis(phosphine)]platinum(0) complexes at 69 °C did not induce oxidative addition; heating the complexes at higher temperatures (110 °C, 165 °C) caused decomposition.

Reaction of 2 with Phosphines. When **2** was generated in the presence of bis(dicyclohexylphosphino)ethane, the product was bis[bis(dicyclohexylphosphino)ethane]platinum(0) (**18**).[23] Similarly, when **1** was thermolyzed in the presence of tricyclohexylphosphine, the product was the coordination complex [bis-(dicyclohexylphosphino)ethane](tricyclohexylphosphine)platinum(0) (**19**).

Reaction Products. The sole gaseous product in the thermolysis of **1** was neopentane, which was identified by its GC retention time and by GC/MS. The yield of neopentane, as quantified by GC with an internal standard of *n*-pentane, varied from 0.85 to 1.0 equiv/mol of **1**.

The identity of the platinum-containing products was established by comparison of the thermolysis products with independently synthesized complexes or by preparative-scale thermolysis of **1** in the presence of the appropriate reactant. In all cases, the platinum complexes were characterized by melting point, ^{1}H and ^{31}P NMR and IR spectroscopies, and elemental analysis and/or mass spectroscopy. (See the Experimental Section.) The independently synthesized complexes were indistinguishable by ^{1}H and ^{31}P NMR spectroscopy from the thermolysis products.

The complexes **6**, **7**, and **10** were synthesized via the route outlined in eq 4. (In principle, **8** is amenable to independent synthesis by this route; in practice, however, an analytically pure sample of **8** was isolated from a completely thermolyzed sample of **1** in benzene.[23]) Treatment of dichloro(1,5-cyclooctadiene)-platinum(II) with excess (2,4,6-trimethylphenyl)magnesium bromide, however, produced chloro(2,4,6-trimethylphenyl)(1,5-cyclooctadiene)platinum(II) directly. Displacement of 1,5-cyclooctadiene by bis(dicyclohexylphosphino)ethane and reduction with sodium trimethoxyborohydride produced **9**.



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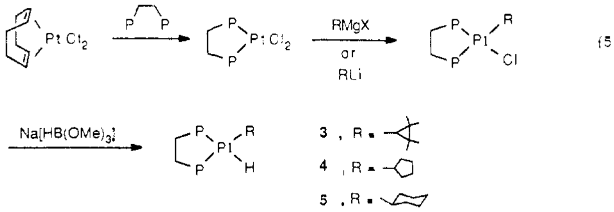
This strategy was not applicable to the preparation of **3–5**. Treatment of dichloro(1,5-cyclooctadiene)platinum(II) with excess (2,2,3,3-tetramethylcyclopropyl)lithium readily afforded bis-(2,2,3,3-tetramethylcyclopropyl)(1,5-cyclooctadiene)platinum-(II),[30] but reaction of this complex with hydrochloric acid yielded chloro(2,2,3-trimethyl-3-methoxybutyl)(1,5-cyclooctadiene)-platinum(II)[30] as the product. The synthesis of chlorocyclopentyl(1,5-cyclooctadiene)platinum(II), a precursor to **4**, was anticipated to be difficult at best because dicyclopentyl(1,5-cyclooctadiene)platinum(II) is known to be stable only at low temperatures.[31] Dicyclohexyl(1,5-cyclooctadiene)platinum(II), which is not a known compound, would probably be at least as unstable as the cyclopentyl complex. Due to these problems, a different strategy, outlined in eq 5, was used to prepare **3–5**. The crucial step in this synthesis was the preparation of the monosubstituted product, *cis*-alkylchloro[bis(dicyclohexylphosphino)-ethane]platinum(II), free from contamination by dialkyl[bis-(dicyclohexylphosphino)ethane]platinum(II) and dichloro[bis-(dicyclohexylphosphino)ethane]platinum(II). In the case of less sterically hindered Grignard or lithium reagents, the reaction with L_2PtCl_2 does not stop at the monosubstituted stage but continues to form L_2PtR_2. Treatment with 1 equiv of Grignard or lithium



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(28) We assume that the thermal stability of the products of oxidative addition to **2** depends on the strength of the platinum–carbon bond in the product. (This assumption is reasonable because the strength of the Pt–P and Pt–H bonds should remain relatively constant for the *cis*-hydridophenyl[bis-(phosphine)]platinum and *cis*-alkenylhydrido[bis(phosphine)]platinum complexes.) The platinum–carbon bond strength in chloro(1,2-(diphenylvinyl)-bis(triphenylphosphine)]platinum(II) (51 ± 6 kcal/mol) is comparable to the platinum-phenyl bond strength in chlorophenyl[bis(triethylphosphine)]platinum(II) (63 ± 4 kcal/mol) and diphenyl[bis(triethylphosphine)]platinum(II) (61 ± 3 kcal/mol). Since **8**, the product of oxidative addition of benzene to **2**, is thermally stable in solution at 69 °C, a *cis*-alkenylhydrido[bis(phosphine)]platinum complex should also be observable. See: Ashcroft, S. J.; Mortimer, C. T. *J. Chem. Soc. A*, **1967**, 930–931. Evans, A.; Mortimer, C. T.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *96*, C58–C60.

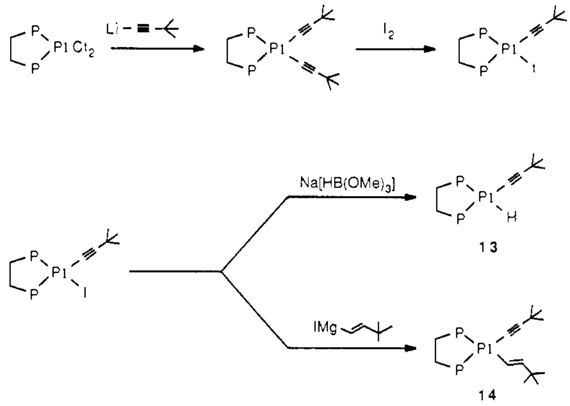
(29) Oxidative addition of an olefinic C–H bond by a transition-metal complex is the exception rather then the rule (coordination). In systems where the transition-metal alkenyl hydride and the transition-metal–olefin complex interconvert, the olefin complex is thermodynamically favored. See: Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582 and Bergman et al.[15] Alkenyl hydrido metal complexes have been implicated in the reaction of $[(i\text{-Pr})_3P]_2IrH_5$ with 3,3-dimethyl-1-butene and isolated from the reduction of $[(Me_2PCH_2CH_2CH_2)_3P]RuCl_2$ in the presence of cyclopentene: Faller, J. W.; Felkin, H. *Organometallics* **1985**, *4*, 1488–1490. Antberg, M.; Dahlenberg, L. *J. Organomet. Chem.* **1986**, *312*, C67–C70. Iron alkenyl hydrides, formed by the photolysis of $(Me_2PCH_2CH_2PMe_2)_2FeH_2$ in the presence of alkenes, isomerize to the corresponding olefin coordination complexes: Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433–7434, 7436–7438.

(30) Spectral and analytical data for this complex are available as supplementary material.

(31) Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Inorg. Chem.* **1981**, *20*, 1312–1314.

reagent yields a mixture of L_2PtCl_2, $L_2Pt(R)Cl$, and L_2PtR_2.[32] Separation of the desired product from the dialkyl- and dichloroplatinum complexes is difficult; *cis*-alkylchloro[bis(dicyclohexylphosphino)ethane]platinum(II) complexes in which the alkyl group contains β-hydrogens are thermally unstable, and few of these complexes (with or without β-hydrogens in the alkyl ligand) survive column chromatography. That the monosubstituted complexes *cis*-chloro(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II), *cis*-chlorocyclopentyl[bis(dicyclohexylphosphino)ethane]platinum(II), and *cis*-chlorocyclohexyl[bis(dicyclohexylphosphino)ethane]platinum(II) were isolated despite the presence of excess lithium or Grignard reagent is probably due to the bulkiness of the alkyl groups.[33]

The platinum acetylide complexes were prepared as described in eq 6. Attempts to prepare bis(3,3-dimethyl-1-butynyl)(1,5-cyclooctadiene)platinum(II) and chloro(3,3-dimethyl-1-butynyl)(1,5-cyclooctadiene)platinum(II) by treatment of dichloro(1,5-cyclooctadiene)platinum(II) with (3,3-dimethyl-1-butynyl)lithium, (3,3-dimethyl-1-butynyl)trimethyltin,[34] or bis(3,3-dimethyl-1-butynyl)mercury[34] were unsuccessful.[35] Treatment of dichloro[bis(dicyclohexylphosphino)ethane]platinum(II) with 1 equiv of (3,3-dimethyl-1-butynyl)trimethyltin[36] or bis(3,3-dimethyl-1-butynyl)mercury[37] failed to yield *cis*-chloro(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II).



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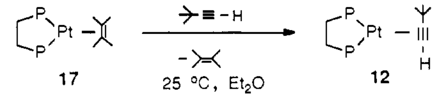
(6)

Reaction[38] of *cis*-bis(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) with iodine was practically instantaneous, to judge from the immediate disappearance of the dark red color of iodine upon addition to a solution of *cis*-bis(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) in THF. The desired product, *cis*-(3,3-dimethyl-1-butynyl)iodo[bis(dicyclohexylphosphino)ethane]platinum(II), can be separated from the inevitable byproduct, diiodo[bis(dicyclohexylphosphino)ethane]platinum(II), and traces of unreacted starting material by column chromatography; diiodo[bis(dicyclohexylphosphino)ethane]platinum(II) could be recycled in the synthesis of bis(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II). Attempts to cleave one acetylide ligand with methylmercury chloride, trimethyltin chloride, or mercuric chloride were unsuccessful;[39] treatment with hydrochloric acid (formed in situ by reaction of acetyl chloride with methanol) caused rearrangement as well as cleavage.[40-42]

The platinum(0) coordination complexes **11** and **15–19** were synthesized by a preparative-scale thermolysis of **1** in the presence of the appropriate reactant. Displacement of 2,3-dimethyl-2-butene from **17** yielded **12** (eq 7).[43] Preparation of these coordination complexes by trapping **2** with olefins, alkynes, or phosphines is preferrable to the more traditional synthetic procedure, that is, reduction of dichloro[bis(phosphine)]platinum(II) complexes with sodium–mercury amalgam, sodium naphthalene, or hydrazine in the presence of the appropriate reactant.[44,45] The insolubility of dichloro[bis(dicyclohexylphosphino)ethane]platinum(II) makes the reduction slow, and the reaction is not amenable to small-scale syntheses.



17

12

(7)

Discussion

The intermediate **2**, generated by reductive elimination of neopentane from **1**, reacts with the C–H bonds of alkanes and

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(32) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705–716, 4020–4033.

(33) We investigated the thermolysis of **1** in the presence of alkyl halides as an alternative route to *cis*-alkylchloro[bis(dicyclohexylphosphino)ethane]platinum(II) complexes. We expected that the reactive intermediate **2** would oxidatively add an alkyl–halide bond. In fact, thermolysis of **1** in cyclohexane containing 1-bromo-2,2,3,3-tetramethylcyclopropane yields *cis*-bromo(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II)[30] as a minor product, but the major product is dibromo[bis(dicyclohexylphosphino)ethane]platinum(II).[30] When **1** is thermolyzed in the presence of cyclopentyl bromide, the sole product is the dibromo[bis(phosphine)]platinum complex. The formation of platinum dihalides from the reaction of platinum(0) complexes with secondary alkyl halides seems to be a general reaction: Pearson, R. G.; Louw, W.; Rajarm, J. *Inorg. Chim. Acta* **1974**, *9*, 251–255.

(34) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 357–368. Segnitz, A.; Kelly, E.; Taylor, S. H.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *124*, 113–123.

(35) Bis(alkylacetylide)(1,5-cyclooctadiene)platinum complexes are considerably more difficult to prepare than bis(phenylacetylide)(1,5-cyclooctadiene)platinum(II): Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987–1992.

(36) Cardin, C. J.; Cardin, D. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 767–779. Sebald, A.; Wrackmeyer, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38*, 1156–1158.

(37) Cross, R. J.; Wardle, R. *J. Chem. Soc. A* **1970**, 840–845.

(38) Iodine selectively cleaves the platinum–acetylide bond without reacting with the carbon–carbon triple bond. Addition of electrophiles such as iodine to alkynes is generally slow. See: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 671–672.

(39) The exchange of halide and acetylide ligands between platinum and mercury or tin is facile.[35,37]

(40) The product appears to be a *cis*-chlorovinyl[bis(dicyclohexylphosphino)ethane]platinum(II) complex, but it was not conclusively identified.

(41) Two alternative routes to monoacetylide complexes were not investigated. Halide abstraction by $AgPF_6$ from a dihalometal complex in the presence of a monosubstituted acetylene yields a halo(acetylide)metal complex: Werner, H.; Weinand, R.; Otto, H. *J. Organomet. Chem.* **1986**, *307*, 49–59. Alternatively, trimethyltin chloride catalyzed ligand exchange produces chloro(acetylide)[bis(phosphine)]platinum(II) complexes from dichloro[bis(phosphine)]platinum(II) and bis(acetylide)[bis(phosphine)]platinum(II): Sebald, A.; Stader, C.; Wrackmeyer, B.; Bensch, W. *J. Organomet. Chem.* **1986**, *311*, 233–242.

(42) As another route to platinum haloacetylides, we investigated the reaction of **2** with haloacetylides. The thermolysis of **1** in a cyclohexane solution of 1-chloro-3,3-dimethyl-1-butyne at 69 °C yielded (1-chloro-3,3-dimethyl-1-butyne)[bis(dicyclohexylphosphino)ethane]platinum(0).[30] Traces of *cis*-chloro(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) are also present. Further thermolysis at 110 °C results in complete conversion of the platinum(0) complex to the platinum(II) compound.[30] The oxidative addition of haloacetylides by platinum(0) complexes seems to be a general reaction; the ease of addition depends on the halide. For example, the reduction of *cis*-dichloro[bis(triphenylphosphine)]platinum(II) in the presence of 1-chloro-2-phenylacetylene produced the coordination complex (1-chloro-2-phenylacetylene)[bis(triphenylphosphine)]platinum(0). On further heating, the coordination complex isomerized to chloro(2-phenylethynyl)[bis(triphenylphosphine)]platinum(II). In contrast, reduction of dichloro[bis(triphenylphosphine)]platinum(II) in the presence of 1-bromo-2-phenylacetylide and 1-iodo-2-phenylacetylide yielded the addition products bromo(2-phenylethynyl)[bis(triphenylphosphine)]platinum(II) and iodo(2-phenylethynyl)[bis(triphenylphosphine)] directly. See: Burgess, J.; Howden, M. E.; Kemmitt, R. D. W.; Sridhara, N. S. *J. Chem. Soc., Dalton Trans.* **1978**, 1577–1581.

(43) Acetylenes readily displace alkenes from $(R_3P)_2Pt$(olefin) complexes. See: Browning, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 97–101. Chatt, J.; Shaw, B. L.; Williams, A. A. *J. Chem. Soc.* **1962**, 3269–3270. Ciriano, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1979**, 1749–1756. Birk, J. P.; Halpern, J.; Pickard, A. L. *J. Am. Chem. Soc.* **1968**, *90*, 4491–4492.

(44) Chatt, J.; Hart, F. A.; Watson, H. R. *J. Chem. Soc.* **1962**, 2537–2545. Hartley, F. R. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 119–137. Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 101–107. Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 107–110.

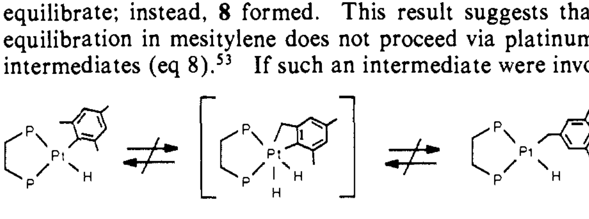
(45) Two alternative routes to platinum(0) coordination complexes were not investigated. The photolysis of (oxalato)[bis(phosphine)]platinum(II) complexes and the electrochemical reduction of dichloro[bis(phosphine)]platinum(II) complexes generate reactive [bis(phosphine)]platinum(0) intermediates that can be trapped by alkynes and phosphines. See: Davies, J. A.; Eagle, C. T.; Otis, D. E.; Venkataraman, U. *Organometallics* **1986**, *5*, 1264–1266. Davies, J. A.; Eagle, C. T. *Organometallics* **1986**, *5*, 2149–2151. Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647–657.

generates platinum alkyl hydrides. The yield of products depends markedly on temperature and concentration: platinum alkyl hydrides are obtained only when dilute (0.015 M) solutions of **1** are thermolyzed at low temperature (45 °C). At higher temperature (69 °C) and concentration, the yields of platinum alkyl hydrides are negligible and insoluble white precipitates form.[24] In fact, at 69 °C cyclohexane is sufficiently inert that it can be used as a solvent for reactions of **1** with other compounds, including tetramethylsilane. Reaction of tetramethylsilane with **2** produces **7**.

The reaction of **2** with alkanes is not quantitative; the complexes **3**–**6** are formed in yields of 12–54%. The low yields may be due to kinetic factors: the platinum alkyl hydrides formed by the reaction of **2** with alkanes may not be thermally stable at the temperatures at which **1** eliminates neopentane to generate **2**. In the absence of accurate values for the bond energies of the various platinum–alkyl bonds, it is difficult to predict whether or not the product of alkane addition will be thermodynamically more stable than **1**. It is possible that the platinum alkyl hydrides are in equilibrium with **2** and alkane, but the equilibrium constant for the formation of the addition product is unfavorable. Furthermore, if **2** is siphoned off irreversibly (by the formation of insoluble precipitates, for example), the equilibrium will be displaced in favor of **2** and alkane to the detriment of the platinum alkyl hydride.[46]

As expected, the electron-rich d^{10} species **2** selects for oxidative addition of a carbon–hydrogen bond of 1,1,2,2-tetramethylcyclopropane in preference to insertion into a carbon–carbon bond. Oxidative addition of a carbon–carbon bond is characteristic of electrophiles such as bis[dichloroethyleneplatinum(II)];[47] nucleophilic or electron-rich species oxidatively add a cyclopropyl C–H bond.[15,16,48,49] Interestingly, singlet methylene, which is isolobal[50] with **2**, inserts into a carbon–hydrogen bond of cyclopropane to form methylcyclopropane.[51]

The intermediate **2** reacts readily with aromatic hydrocarbons to yield *cis*-arylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (aryl = phenyl, 2,4,6-trimethylphenyl) in excellent yield. The driving force for the reaction is presumably the strength of the platinum–aryl bond; previous studies have shown that benzene is not coordinated to the platinum complex before or during reductive elimination of neopentane.[23] The platinum–phenyl bond dissociation energy is 63 ± 4 kcal/mol;[28] the platinum–alkyl bond is probably at least 10 kcal/mol weaker.[52] In the case of mesitylene (1,3,5-trimethylbenzene), the two products of oxidative addition, **9** and **10**, equilibrate. Oxidative addition of an aryl C–H bond is kinetically rapid, but addition of a benzylic C–H bond yields the thermodynamically favored product: for the isomerization of **9** to **10**, $\Delta\Delta G = -0.10 \pm 0.02$ kcal/mol. When the two complexes were heated individually in benzene, they did not equilibrate; instead, **8** formed. This result suggests that the equilibration in mesitylene does not proceed via platinum(IV) intermediates (eq 8).[53] If such an intermediate were involved,



(8)

9 **10**

the equilibration of **9** and **10** in benzene would compete with or preclude the formation of **8**. A more likely pathway for the interconversion of **9** and **10** in mesitylene involves the reductive elimination of mesitylene and oxidative addition of an aryl or benzyl C–H bond with or without the intermediacy of a η^2-mesitylene complex.[54]

The kinetic preference of **2** for oxidative addition of aryl bonds instead of benzyl C–H bonds reflects a surprising lack of steric hindrance at the platinum center in **2**. Sterically encumbered intermediates such as dicyclopentadienetungsten (generated by the thermolysis of dicyclopentadienemethylhydridotungsten[55]) and rhodium octaethylporphyrin (formed by cleavage of the corresponding dimer[56]) insert into benzyl C–H bonds, exclusively; less sterically demanding intermediates, such as those derived from (pentamethylcyclopentadiene)(trimethylphosphine)dihydridoiridium[48] and (pentamethylcyclopentadiene)(trimethylphosphine)dihydridorhodium,[18] react with aryl carbon–hydrogen bonds in competition with or in preference to benzyl C–H bonds. Eventually, **9** does isomerize to **10**, the product of benzylic C–H addition (and the less sterically hindered isomer). Apparently, steric constraints are thermodynamically significant even if they are not kinetically prohibitive.

We attribute the enhanced reactivity of **2** with respect to intermolecular C–H bond activation relative to other coordinatively unsaturated platinum intermediates (e.g. L_2Pt, LPt, and $LPtR_2$) to the bent P–Pt–P configuration dictated by the chelating ligand. Our experimental results agree with the predictions of molecular orbital theory: the bent [bis(phosphine)]platinum(0) complex, **2**, is higher in energy, and hence more reactive, than linear L_2Pt^0.[57] The intermediate **2**, which is too short-lived to be observed even spectroscopically, reacts intermolecularly with carbon–hydrogen

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(46) Halpern has argued that thermodynamic constraints, not kinetic barriers, are the primary obstacle to C–H bond activation: Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41–48.

(47) Puddephatt, R. *Coord. Chem. Rev.* **1980**, *33*, 149–194. McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123–2129. Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045–2046. Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pilbrow, M. F. *J. Chem. Soc. A* **1969**, 1227–1231. Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738–742.

(48) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13–23. Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272–7273.

(49) Exceptions to these generalizations do exist. Highly electrophilic thorium(IV) complexes insert into the C–H bond of cyclopropane.[4] Conversely, nucleophilic L_2Pt^0 species insert into the carbon–carbon bonds of electrophilic cyclopropanes and cyclopropenones such as 1,1,2,2-tetracyano-3-phenylcyclopropane, 1-carbethoxy-1,2,2-tricyano-*trans*-3-phenylcyclopropane, and diphenylcyclopropenone. See: Rajaram, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 829–838. Wong, W.; Singer, S. J.; Pitts, W. D.; Watkins, S. F.; Baddley, W. H. *J. Chem. Soc., Chem. Commun.* **1972**, 672–673. Visser, J. P.; Ramakers-Blom, J. E. *J. Organomet. Chem.* **1972**, *44*, C63–C65. Lenarda, M.; Ros, R.; Graziani, M.; Belluco, U. *J. Organomet. Chem.* **1974**, *65*, 407–416. Yarrow, D. J.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Organomet. Chem.* **1974**, *70*, 133–145.

(50) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724. Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

(51) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971.

(52) Transition-metal–alkyl bond strengths are usually estimated to be ca. 30–40 kcal/mol.[14,18,46]

(53) *cis*-Bis(2-methyl-2-phenylpropyl)[bis(triethylphosphine)]platinum(II) is believed to isomerize to *cis*-(2-*tert*-butylphenyl)(2-methyl-2-phenylpropyl)[bis(triethylphosphine)]platinum(II) via a platinum(IV) intermediate. See: Griffiths, D. C.; Joy, L. G.; Skapski, A. C.; Wilkes, D. J.; Young, G. B. *Organometallics* **1986**, *5*, 1744–1745.

(54) Earlier studies demonstrated that benzene does not coordinate to **1**, but whether or not **2** forms an η^2-coordination complex with arenes is an open question. An η^2-coordinated benzene complex was a possible intermediate in the isomerization of *cis*-hydrido(phenyl-d_5)[bis(dicyclohexylphosphino)ethane]platinum(II) to *cis*-deuterido(phenyl-d_4)[bis(dicyclohexylphosphino)ethane]platinum(II).[23] The facility of aryl C–H bond addition to transition metals is usually rationalized by postulating prior coordination of the arene to the metal: Parshall, G. W. In *Catalysis*; Kemball, C., Senior Reporter; Specialist Periodical Report; The Chemical Society: London, 1977; Vol. 1, Chapter 9. Coordination complexes were implicated in the rearrangements of rhodium and osmium complexes: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819. Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73–93. Admittedly, the ability of mesitylene to form a η^2-complex is questionable.

(55) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35.

(56) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941–7944. In this case, the preference for benzyl instead of aryl hydrogen activation also reflects the fact that benzyl hydrogens are subject to attack by radicals—here, a metalloradical—while aryl hydrogens are relatively inert to radical reactions.

(57) For comparisons of the molecular orbitals and reactivity of bent and linear L_2Pt^0, see: Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115–6128. Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 6928–6937. Low, J. J.; Goddard, W. A., III *Organometallics* **1986**, *5*, 609–622. Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191–205. Zeigler, T. *Inorg. Chem.* **1985**, *24*, 1547–1552. Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482–7492.

bonds; linear [bis(phosphine)]platinum(0) complexes are thermally stable and completely inert with respect to the addition of unactivated C–H bonds.[58,59] In addition, the bent configuration of **2** permits easy access of the solvent molecules to the platinum center and prevents intramolecular C–H activation by precluding any interaction of the cyclohexyl C–H bonds with platinum. In contrast, other coordinately unsaturated species such as $LPtR_2$ fail to react intermolecularly with C–H bonds, presumably because of steric hindrance at the metal center and the facility of competing intramolecular reactions.[60] The ease with which $LPtR_2$ reacts intramolecularly with ligand C–H bonds[61] and intermolecularly with dihydrogen[62] indicates that neither entropic nor enthalpic barriers are intrinsically prohibitive for intermolecular addition of solvent C–H bonds to $LPtR_2$.

Disubstituted alkynes such as diphenylacetylene react with **2** to form coordination complexes. With monosubstituted alkynes, such as 3,3-dimethyl-1-butyne, oxidative addition of the alkyne C–H bond competes with the formation of an η^2-coordination complex. The two complexes, **12** and **13**, do not interconvert, implying that coordination is not a prerequisite to oxidative addition.[63] In a slower, subsequent reaction, excess 3,3-dimethyl-1-butyne inserts into the platinum–hydrogen bond of **13** to form **14**.[64] In contrast, we did not observe *cis*-(3,3-dimethyl-1-butenyl)neopentyl[bis(dicyclohexylphosphino)ethane]platinium(II), the product of the insertion of 3,3-dimethyl-1-butyne into the Pt–H bond of **1**. Reductive elimination of neopentane dominates the chemistry of **1** to the exclusion of other reactions.

The reaction between **2** and olefins produces (olefin)[bis(phosphine)]platinum(0) complexes, exclusively. No *cis*-alkenylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) complexes were detected, despite the fact that the products of oxidative addition of an alkene C–H bond would be expected to be stable.[28,29,65] Allylic carbon–hydrogen bonds are similarly impervious to oxidative addition. The stability of the olefin coordination complexes contrasts with the instability of η^2-arene coordination complexes, which are possible intermediates in the oxidative addition of aromatic hydrocarbons to **2**.[54,63] Olefins are better π-acceptors than arenes; the greater stability of the olefin coordination complexes relative to η^2-arene complexes is not unexpected. Such η^2-arene complexes, is formed, must be unstable with respect to oxidative addition of an aromatic C–H bond.

The reaction of **2** with phosphines yields coordination complexes. Phosphines also trap the isolobal singlet methylene.[51] Importantly, **2** does not react *intra*molecularly with the C–H bonds of the bis(phosphine) ligand. Chelating bis(phosphine) ligands are more resistant to cyclometalation than monodentate phosphines.[66,67]

In conclusion, we note that although this work demonstrates that a soluble platinum complex can react intermolecularly with the carbon–hydrogen bonds of both saturated and unsaturated hydrocarbons, our ultimate goal—the catalytic functionalization of hydrocarbons—remains to be accomplished.[68] Mechanistically important questions, including the factors that govern the selectivity of the reaction, the importance of electron density at the transition-metal center, the preference for inter- vs intramolecular reaction, and the relevance of homogeneous solution chemistry to heterogeneous catalysis, will be the subjects of future investigations.

Experimental Section

General Procedures. Diethyl ether and tetrahydrofuran were distilled from sodium-benzophenone under argon. Cyclohexane (Aldrich HPLC grade, 99.9%) was distilled from Na/K under argon. Cyclopentane and hexanes were stirred over 4/1 v/v sulfuric acid/nitric acid, washed with distilled water, dilute aqueous sodium hydroxide, distilled water, and brine, dried over magnesium sulfate, passed through silica, and finally distilled from Na/K or lithium aluminum hydride under argon. Methane (ultrahigh purity, 99.9%) was purchased from Linde. Benzene was stirred over sulfuric acid and then treated similarly. 1,1,2,2-Tetramethylcyclopropane (Wiley), 3,3-dimethyl-1-butene, 3-methyl-2-(2-propyl)-1-butene (Wiley), 2,3-dimethyl-2-butene (Aldrich), and mesitylene were distilled from calcium hydride. 3,3-Dimethyl-1-butyne (Farchan) was distilled; tetramethylsilane was distilled from lithium aluminum hydride. Triply sublimed magnesium turnings (Alfa) were used in Grignard reactions. Alkyllithium and Grignard reagents were titrated with 2-butanol/toluene under argon with *N*,*N*-naphth-1-ylphenylamine as an indicator.[69] The latter was recrystallized twice from 3/1 v/v distilled water/95% ethanol; any purple oil that fell out of the hot solution was removed via pipet. Diphenylacetylene was recrystallized twice from 95% ethanol. Bis(dicyclohexylphosphino)ethane (Strem) and tricyclohexylphosphine (Strem) were recrystallized from degassed 95% ethanol. 3,5-Dimethylbenzyl bromide was used as received from Lancaster Synthesis. Cyclopentylmagnesium chloride (2.0 M solution in diethyl ether) and (2,4,6-trimethylphenyl)magnesium bromide (1.0 M solution in tetrahydrofuran) were purchased from Aldrich. Dichloro(1,5-cyclooctadiene)platinum(II),[70] chloromethyl(1,5-cyclooctadiene)-

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[58] The [bis(phosphine)]platinum(0) complexes generated by reductive elimination of C–H bonds from platinum(II) complexes are inert to reaction with the C–H bonds of the solvent (toluene, benzene, or THF). See: Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916. Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831–1834. The reactive species LPt^0, presumably an intermediate in the reductive elimination of dimethylcyclopropane from [bis(trialkylphosphine)]-3,3-dimethylplatinacyclobutane, fails to react with cyclohexane: DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601–3607.

[59] [Bis(tricyclohexylphosphine)]platinum(0), the linear analogue of **2**, fails to react with benzene, naphthalene, and toluene; like other L_2Pt^0 complexes, however, it oxidatively adds a variety of substrates. See: Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006–1009. Immirzi, A.; Musco, A.; Zambelli, P.; Carturan, G. *Inorg. Chim. Acta* **1975**, *13*, L13–L14. Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850–5858. Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134–2140.

[60] These two factors are not unrelated; steric congestion at the metal center accelerates the rate of ligand metalation. See: Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 754–763. Shaw, B. L. *J. Organomet. Chem.* **1980**, *200*, 307–318. Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856–3857. Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986–1992.

[61] Brainard, R. L.; Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481–1490. McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403. McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 1676–1678. Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3404–3410. DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–133. Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725.

[62] Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81–85.

[63] Both Bergman[15,29] and Field[29] have presented convincing evidence that a π-complex of ethylene is not an intermediate in the oxidative addition of a vinyl C–H bond. For a theoretical analysis of this reaction, see: Silvestre, J.; Calhorda, M. J.; Hoffmann, R.; Stoutland, P. O.; Bergman, R. G. *Organometallics* **1986**, *5*, 1841–1851. In contrast, coordination of 1-chloro-2-phenylacetylene to platinum is a prerequisite to oxidative addition of the C–Cl bond.[42]

[64] Acetylenes with electron-withdrawing substituents insert readily into platinum–hydrogen bonds; insertion into the platinum–acetylide bonds of neutral complexes is comparatively rare. See: Clark, H. C.; Ferguson, G.f Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961–6972. Hagihara, N.; Sonogashira, K.; Tohda, Y. *J. Organomet. Chem.* **1976**, *110*, C53–C56. Clark, H. C.; Tsang, W. S. *J. Am. Chem. Soc.* **1967**, *89*, 529–533. Clark, H. C.; Wong, C. S. *J. Am. Chem. Soc.* **1977**, *99*, 7073–7074. Attig, T. G.; Clark, H. C.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 189–198. Chisholm, M. H.; Rankel, L. A. *Inorg. Chem.* **1977**, *16*, 2177–2182.

[65] A rigorous proof that the (olefin)[bis(phosphine)]platinum(0) complex is both the kinetic and thermodynamic product of the reaction of **2** with an olefin requires the thermolysis of independently synthesized [bis(phosphine)]alkenylhydridoplatinum(II) complex. If the platinum alkenyl hydride is stable with respect to reductive elimination of the olefin at 69 °C, then the intermediacy of a platinum alkenyl hydride that subsequently isomerizes to the observed platinum olefin complex can be discounted. We thank a reviewer for suggesting this experiment.

[66] Clerici, M. G.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1973**, 516–517.

[67] For reviews of the cyclometalation reaction, see: Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235–271. Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327–352. Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73–86. Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. Constable, E. C. *Polyhedron* **1984**, *3*, 1037–1057.

[68] Crabtree has argued that complexes with multiple labile ligands can provide many sites for substrate binding and are thus the most likely to undergo catalytic, as opposed to stoichiometric, reactions. See: Crabtree, R. H. *Comments Inorg. Chem.* **1985**, *4*, 229–240.

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[70] Drew, D.; Doyle, J. R. *Inorg. Synth.* **1970**, *13*, 52–55. McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.

platinum(II),[71] and bis[(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II)[72] were prepared by literature procedures. The synthesis of *cis*-hydridoneopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**1**) has been previously described.[22,23]

Melting and boiling points are uncorrected. ^1H NMR spectra were recorded at 250, 300, and 500 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 0.0, with shifts downfield of the reference considered positive. Elemental analyses were performed by Spang and Galbraith.

Sealed-Tube Reactions. The general methods used in sealed-tube reactions have been described in detail earlier.[23]

Reactions were carried out in sealed 5-mm-o.d. NMR tubes containing 14–42 mg of **1** and 0.5 mL of solvent that contained the appropriate reactant. The disappearance of **1** was monitored by quantitative ^{31}P NMR spectroscopy for 2–3 half-lives. The 5-mm NMR tubes were positioned coaxially in a 10-mm-o.d. NMR tube containing the lock solvent (C_6D_6) and a sealed capillary of aqueous H_3PO_4 or tetra-*n*-butylphosphonium bromide. A 90° pulse and a relaxation delay of at least $5T_1$ were used to ensure accurate quantitation. The area of the two central peaks of **1** relative to that of the standard was determined by electronic integration. The sample was then thermolyzed to completion (8–10 half-lives), and the yield of the product was determined by integration.

For the reaction of **1** with alkanes, 8-mm-o.d. NMR tubes were used to accommodate the larger volume of solvent (1.5 mL) required to adjust the concentration of **1** (ca. 16 mg) in alkane to 0.015 M. The reference capillary was sealed inside the 8-mm-o.d. NMR tube with the reaction solution. To analyze the sample by ^{31}P NMR spectroscopy, the 8-mm-o.d. NMR tube was positioned coaxially inside a 10-mm-o.d. NMR tube containing D_2O as the lock solvent.

Identification of the Reaction Products. The sole organic product in the thermal decomposition of **1** was neopentane, identified by its GC retention time and by GC/MS; it was quantified relative to a known amount of *n*-pentane added as a GC standard. (These techniques have been described in detail previously.[23]) The solvent was removed either by rotary evaporation or by passing a stream or argon over the sample. The product was dissolved in a deuteriated solvent, analyzed by ^1H and ^{31}P NMR spectroscopies, and tentatively identified. The identity of the product was then confirmed either by an independent synthesis of the complex or by a preparative-scale thermolysis and purification of the product.

Thermolysis of 1 in 1,1,2,2-Tetramethylcyclopropane. An 8-mm-o.d. NMR tube containing ca. 16 mg of **1** in 1.5 mL of 1,1,2,2-tetramethylcyclopropane was thermolyzed at 44.9 °C. The half-life at this temperature was 4.5 h; the disappearance of **1** appeared to obey first-order kinetics. After 10.5 h, 19% of **1** remained; the yield of *cis*-hydrido(2,2,3,3-tetramethylcyclopropane)[bis(dicyclohexylphosphino)ethane]platinum(II) (**3**) was 52%. Small amounts of other products were visible in the ^{31}P NMR spectrum. After 28.5 h, the starting material was completely gone; the reaction solution was pale yellow, and a very thin white film coated the walls of the NMR tube. Three products were visible in the ^{31}P NMR spectrum: **3** (54%), a second platinum alkyl hydride (12%), and a non-hydride complex with inequivalent phosphorus atoms (16%). The sole gaseous product was neopentane.

The thermolysis was repeated at 35.0 °C. At this temperature, the half-life was ca. 22 h. After 154 h, a trace of **1** remained; again, three products were observed: **3** (56%), platinum alkyl hydride (12%), and non-hydride (13%).

The second platinum alkyl hydride was tentatively identified as *cis*-hydrido[(1,2,2-trimethylcyclopropyl)methyl][bis(dicyclohexylphosphino)ethane]platinum(II) on the basis of its ^1H and ^{31}P NMR spectra. A doublet of doublets with platinum satellites was visible in the ^1H NMR spectrum (C_6D_6): δ −0.05, J_{P-H} = 19, $J_{P'-H}$ = 196, J_{Pt-H} = 1203 Hz. The ^{31}P NMR spectrum (C_6D_6) showed two singlets due to two inequivalent phosphorus atoms: δ 75.9 (s with platinum satellites, J_{Pt-P} = 1647 Hz); δ 63.6 (s with platinum satellites, J_{Pt-P} = 1763 Hz). (Note the similarity of the ^{31}P NMR spectrum of this complex to that of **1**.)

The third product was tentatively identified as an (olefin)[bis(dicyclohexylphosphino)ethane]platinum(0) complex on the basis of its ^{31}P NMR spectrum, an AB quartet: δ_A 71.9, δ_B 70.2, J_{AB} = 71 Hz (in 1,1,2,2-tetramethylcyclopropane). (The platinum satellites could not be identified due to the low concentration of this product.) The AB pattern, chemical shifts, and phosphorus–phosphorus coupling constants were typical of the (olefin)[bis(dicyclohexylphosphino)ethane]platinum(0) complexes described in this paper. (Compare these data with the ^{31}P NMR spectra of **15**–**17**.) This spectrum is inconsistent with [bis(dicyclohexylphosphino)ethane]-2,2,4,4-tetramethylplatinacyclobutane(II) and [bis(dicyclohexylphosphino)ethane]-2,2,3,3-tetramethylplatinacyclobutane(II), products derived from the oxidative addition of a carbon–carbon bond. The phosphorus atoms in [bis(dicyclohexylphosphino)ethane]-2,2,4,4-tetramethylplatinacyclobutane(II) are equivalent; the ^{31}P NMR spectrum must consist of a singlet with platinum satellites. The inequivalent phosphorus atoms in [bis(dicyclohexylphosphino)ethane]-2,2,3,3-tetramethylplatinacyclobutane(II) would be expected, by analogy with the other platinum(II) complexes described here, to be weakly coupled (J_{Pt-P} < 5 Hz); in addition, the signals due to phosphorus atoms trans to alkyl groups typically appear at lower field (ca. δ 75; note the ^{31}P NMR spectra of **1** and **3**–**6**). The ^1H NMR spectrum of the reaction mixture (**3**, *cis*-hydridomethyl(1,2,2-trimethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II), and the third product) was too complex to be useful in identifying the third product.

Two (olefin)[bis(dicyclohexylphosphino)ethane]platinum(0) complexes that could form by rearrangement of the 2,2,3,3-tetramethylcyclopropyl ligand without carbon–carbon bond cleavage are (2,4-dimethyl-2-pentene)[bis(dicyclohexylphosphino)ethane]platinum(0) and (2,4-dimethyl-1-pentene)[bis(dicyclohexylphosphino)ethane]platinum(0). These complexes were prepared by the thermolysis of **1** in cyclohexane solutions of 2,4-dimethyl-2-pentene and 2,4-dimethyl-1-pentene, respectively. Neither complex had a ^{31}P NMR spectrum that matched that of the third product, whose identity remains unestablished.

Thermolysis of 1 in Cyclopentane. A sealed 8-mm-o.d. NMR tube containing ca. 15 mg of **1** in 1.5 mL of cyclopentane was thermolyzed at 44.9 °C. The half-life was ca. 4.5 h at this temperature; the disappearance of **1** appeared to obey first-order kinetics. The reaction solution turned pale yellow, and a thin white film coated the walls of the NMR tube. After 11 h at 44.9 °C, the yield of *cis*-cyclopentylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (**4**) was 26%; 18% of **1** remained. After 29 h, the starting material had completely disappeared; the yield of **4** was 25%. Several small, unidentified peaks were present in the ^{31}P NMR spectrum. The sole gaseous product was neopentane.

The thermolysis was repeated at 35.0 °C with a similarly prepared sample. The half-life at this temperature was ca. 18–20 h. The yield of **4** after 48.5 h was 22%; 25% of **1** remained. After 152.5 h, only a trace of **1** was left; the yield of **4** was 22%.

Thermolysis of 1 in Cyclohexane. A sealed 8-mm-o.d. NMR tube containing 16 mg of **1** in 1.5 mL of cyclohexane was thermolyzed at 45.5 °C. At this temperature, the half-life was about 4 h. As the thermolysis progressed, the solution turned slightly red, and a white film coated the sides of the NMR tube. After 21.5 h, the yield of *cis*-cyclohexylhydrido[bis(dicyclohexylphosphino)ethane]platinum(I) (**5**) was 12%; a small amount of **1** (7%) remained. After 43.3 h, **1** had almost completely disappeared; the yield of **5** was 9%. Several small, unidentified peaks were visible in the ^{31}P NMR spectrum. The yield of neopentane was 93%.

When **1** was thermolyzed at 69 °C in cyclohexane, **5** was not observed. The solution turned bright red, and white solids precipitated.[24]

Thermolysis of 1 in Cyclohexane under Methane. A 150-mL beaker equipped with a stirring bar was charged with 46 mg of **1**. The beaker and a Parr bomb were taken into the drybox. The platinum complex was dissolved in 40 mL of cyclohexane that had been subjected to three freeze–pump–thaw degassing cycles. The beaker was placed in the Parr bomb; the bomb was sealed and removed from the glovebox. The bomb was connected to a tank of ultrahigh-purity methane (99.9%); the connecting hose was filled with methane and depressurized several times to remove traces of oxygen. The inlet to the bomb was opened, and the bomb was pressurized to 2050 psi. The bomb was placed in a preheated water bath. After 39 h at 45 °C, the bomb was removed from the bath and allowed to cool to room temperature. The bomb was opened; the beaker was removed, and its contents (pale yellow solution and a small amount of benzene-soluble solid) were transferred to a tared flask. The solvent was removed by rotary evaporation, and the residue, a red oil, was dried in vacuo (0.050 Torr) over KOH. The yield of product was 50 mg.

The contents of the flask were dissolved in 2.0 mL of benzene and transferred to a 8-mm-o.d. NMR tube containing a sealed capillary of aqueous tetra-*n*-butylphosphonium bromide. (The capillary had been previously calibrated relative to 2.0 mL of a 13.2 mM solution of trimethyl phosphite in benzene.) The reaction solution was analyzed by ^{31}P NMR spectroscopy; the yields of the products were determined by comparison of the corresponding peak areas (as determined by electronic integration) relative to that of the reference capillary. The yields reported below are the average of two determinations. The yields of *cis*-cyclohexylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (**5**) and

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[71] Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411–428.

[72] Wozniak, B.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 3116–3120.

cis-hydridomethyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**6**) were 10% and 45%, respectively. A third product, ethylene[bis(dicyclohexylphosphino)ethane]platinum(0), was formed in 23% yield. (Vide infra. Ethylene is a ubiquitous impurity in methane.) A trace (2%) of **1** remained. A few small, spurious peaks were also present.

The contents of the NMR tube were transferred to a recovery flask, and the solvent was removed by rotary evaporation. The flask and its contents were dried in vacuo (0.050 Torr) over KOH. The residue was dissolved in C_6D_6 and analyzed by ^1H NMR spectroscopy.

When the reaction was carried out with 24 mg of **1** in 15 mL of cyclohexane under 2150 psi of methane, the yields of **5** and **6** after 35 h at 45 °C were 16% and 34%, respectively. The yield of ethylene[bis(dicyclohexylphosphino)ethane]platinum(0) was 12%; a small amount (4%) of **1** remained. The relatively low mass balance may be caused by decomposition of the ethylene coordination complex on exposure to oxygen, or it may be due to the small scale of the experiment.

Ethylene[bis(dicyclohexylphosphino)ethane]platinum(0) was independently synthesized by the thermolysis of **1** in C_6D_{12} under 1 atm of ethylene. After 1 h at 69 °C, the sole product was the ethylene coordination complex (quantitative yield). The solvent was removed in vacuo, and the residue, an amorphous white solid, was dissolved in degassed C_6D_6. ^1H NMR (C_6D_6): δ 2.44 ("t" with platinum satellites, $J_{P-H} = 2$, $J_{Pt-H} = 58$ Hz, 4 H), 2.05–1.0 (m, 48 H). ^{31}P NMR (C_6D_6): δ 72.8 (s with platinum satellites, $J_{Pt-P} = 3150$ Hz). The ^{31}P NMR spectrum of the ethylene coordination complex was identical with that of the minor product obtained in the reaction under methane.

Thermolysis of 1 in Hexanes. An 8-mm-o.d. NMR tube charged with ca. 16 mg of **1** and 1.5 mL of hexanes was thermolyzed at 45.5 °C. The half-life was about 4 h at this temperature. As the thermolysis progressed, the solution turned pale red, and a white film coated the sides of the NMR tube. After 38 h, only traces of **1** remained; two products were observed in approximately equal amounts (combined yield, 18%). The ^{31}P NMR spectrum (C_6D_6) showed four peaks (δ 76.6, 76.5, 64.2, and 63.6) in the regions characteristic of platinum alkyl hydrides; several small peaks were also present. (The platinum satellites corresponding to these four peaks could not be assigned unambiguously.) The ^1H NMR spectrum (C_6D_6) showed two doublets of doublets in the hydride range: δ 0.14 (dd, $J_{P-H} = 18$, $J_{P'-H} = 196$ Hz), −0.05 (dd, $J_{P-H} = 18$, $J_{P'-H} = 196$ Hz). (The platinum satellites could not be distinguished from the noise level.) On the basis of the spectroscopic data, the complexes are tentatively identified as isomeric hexylhydrido[bis(phosphine)]platinum complexes; they were not further characterized.

Thermolysis of 1 in Tetramethylsilane/Cyclohexane. Two sealed 5-mm-o.d. NMR tubes, each containing ca. 14 mg of **1** and 0.5 mL of a 1.48 M solution of tetramethylsilane in cyclohexane, were thermolyzed at 69.8 °C. The disappearance of **1** obeyed first-order kinetics for greater than 3 half-lives; $k = 7.0 \times 10^{-4}\ s^{-1}$ (average of two runs). The samples were thermolyzed to completion (ca. 3 h of heating altogether). The sole product was *cis*-hydrido(trimethylsilyl)methyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**7**) (85% yield). The yield of neopentane was 83%.

Thermolysis of 1 in Benzene. The thermolysis of **1** in benzene at 69 °C yielded *cis*-hydridophenyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**8**) in quantitative yield.[23] The sole organic product was neopentane.

Thermolysis of 1 in Mesitylene. Two sealed 5-mm-o.d. NMR tubes, each containing ca. 14 mg of **1** in 0.5 mL of freshly distilled mesitylene, were prepared and thermolyzed at 69 °C. Plots of ln $[1]/[1]_0$ vs time were linear for greater than 2 half-lives; $k = 3.9 \times 10^{-4}\ s^{-1}$ (average of four runs). After 4.2 h (ca. 8 half-lives) at 69 °C, only *cis*-hydrido(2,4,6-trimethylphenyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**9**) (82%) and *cis*-hydrido(3,5-dimethylbenzyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**10**) (14%) were observed. Upon further heating, the two complexes equilibrated. After ca. 40 h, [**9**]/[**10**] = 1.15 (average of two samples); this ratio remained unchanged after an additional 30 h at 69 °C. The rate of approach to equilibrium was not determined because prolonged thermolysis led to some decomposition of **9** and **10**; the reaction solution turned yellow, and the total amount of **9** and **10** decreased. A small amount of an unidentified decomposition product was visible in the ^{31}P NMR spectrum at δ 95.

Equilibration of 9 and 10 in Mesitylene. Two sealed 5-mm-o.d. NMR tubes, each containing ca. 9 mg of either **9** or **10** in 0.5 mL of mesitylene, were prepared. (The platinum complexes **9** and **10** were prepared by independent synthesis; vide infra.) The complexes did not dissolve completely at room temperature; the samples became homogeneous only after several hours of heating at 69 °C. Equilibrium was attained after ca. 60 h; the ratio of **10** to **9** remained unchanged after an additional 30 h. The thermolyzed solutions were yellow and homogeneous; some decomposition had occurred (as evidenced by the appearance of a new peak at δ 95 in the ^{31}P NMR spectrum). For the sample that had originally contained only **9**, K_{eq} = [**10**]/[**9**] = 1.19 (average of three measurements); for the sample that contained only **10** initially, $K_{eq} = 1.14$ (average of three measurements). The average of these values, $K_{eq} = 1.16$, was used to calculate the difference in the platinum–benzyl and platinum–aryl bond strengths at 69 °C. (See Results.) The error limits were determined by the K_{eq} values of 1.19 and 1.14.

Thermolysis of 9 and 10 in Benzene. Two sealed medium-walled 5-mm-o.d. NMR tubes were prepared. One contained ca. 8 mg of **9** in 0.5 mL of benzene; the other contained ca. 8 mg of **10** in 0.5 mL of benzene. The samples were thermolyzed at 69 °C; the reaction progress was monitored periodically by ^{31}P NMR spectroscopy. The sample containing **9** gradually acquired a pale yellow color, but no new signals were observed by ^{31}P NMR spectroscopy. After 126 h, 83% of the platinum complex was present. In contrast, thermolysis of **10** in benzene cleanly produced a new complex whose ^{31}P NMR spectrum was identical with that of **9**. The half-life of **10** at 69 °C was ca. 20 h; after ca. 126 h, no trace of **10** remained. The yield of the new complex was 82%. The solution was pale yellow, and a trace of decomposition product was observed by ^{31}P NMR spectroscopy.

The samples were cracked open; the contents of each tube were transferred to a tared flask. The solvent was removed by rotary evaporation, and the residual colorless oils were dried over KOH in vacuo (0.05 Torr). Analysis of the oils by ^1H NMR spectroscopy revealed the product in each case to be *cis*-hydridophenyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**8**). (The ^{31}P NMR spectrum of **8** in benzene is indistinguishable from that of **9** in benzene.)

Thermolysis of 1 in Diphenylacetylene/Cyclohexane. Thermolysis of **1** in a solution of diphenylacetylene in cyclohexane yielded (diphenylacetylene)[bis(dicyclohexylphosphino)ethane]platinum(0) (**11**) and neopentane as the only products.[23]

Thermolysis of 1 in 3,3-Dimethyl-1-butyne/Cyclohexane. Two 5-mm-o.d. NMR tubes, each containing ca. 21 mg of **1** in a 0.74 M solution of 3,3-dimethyl-1-butyne in cyclohexane (0.5 mL), were thermolyzed at 68.6 °C. The disappearance of **1** obeyed first-order kinetics for greater than 3 half-lives; $k = 5.9 \times 10^{-4}\ s^{-1}$ (average of two runs). On the completion of the thermolysis (ca. 3.5 h), the solutions were completely colorless and homogeneous; the products were (3,3-dimethyl-1-butyne)[bis(dicyclohexylphosphino)ethane]platinum(0) (**12**) (53%) and *cis*-hydrido(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(0) (**13**) (41%). Upon further heating, **13** slowly disappeared (half-life ca. 40 h), and a new product, *cis*-[(*E*)-3,3-dimethyl-1-butenyl](3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**14**), appeared. The yield of **12** remained unchanged. After 270 h at 69 °C, only a trace of **13** remained; the yields of **12** and **14** were 57% and 39%, respectively.

Thermolysis of 1 in 3,3-Dimethyl-1-butene/Cyclohexane. Two sealed 5-mm-o.d. NMR tubes, each containing ca. 20 mg of **1** in a 0.37 M solution of 3,3-dimethyl-1-butene in cyclohexane (0.5 mL), were thermolyzed at 69 °C. Linear first-order kinetics were observed for 3 half-lives; $k = 6.9 \times 10^{-4}\ s^{-1}$ (average of two runs). The samples were thermolyzed to completion (ca. 2.2 h); (3,3-dimethyl-1-butene)[bis(dicyclohexylphosphino)ethane]platinum(0) (**15**) was formed in quantitative yield. The yield of neopentane was 96%.

Thermolysis of 1 in 3-Methyl-2-(2-propyl)-1-butene/Cyclohexane. A sealed 5-mm-o.d. NMR tube containing 21 mg of **1** in a 0.62 M solution of 3-methyl-2-(2-propyl)-1-butene in cyclohexane (0.5 mL) was thermolyzed at 69 °C. The disappearance of **1** followed first-order kinetics for greater than 2 half-lives; $k = 7.0 \times 10^{-4}\ s^{-1}$. The sample was thermolyzed to completion; the sole product was [3-methyl-2-(2-propyl)-1-butene][bis(dicyclohexylphosphino)ethane]platinum(0) (**16**) (97% yield). The only organic product was neopentane (0.92 equiv).

Thermolysis of 1 in 2,3-Dimethyl-2-butene/Cyclohexane. A sealed 5-mm-o.d. NMR tube containing 21 mg of **1** in a 0.62 M solution of 2,3-dimethyl-2-butene in cyclohexane (0.5 mL) was thermolyzed at 69.0 °C. First-order kinetics were observed for greater than 2 half-lives; $k = 7.1 \times 10^{-4}\ s^{-1}$. The sample was thermolyzed to completion; (2,3-dimethyl-2-butene)[bis(dicyclohexylphosphino)ethane]platinum(0) (**17**) was formed in 94% yield. Neopentane was formed in quantitative yield.

Thermolysis of 1 in Bis(dicyclohexylphosphino)ethane/Tetrahydrofuran. The thermolysis of **1** in THF containing bis(dicyclohexylphosphino)ethane yielded bis[bis(dicyclohexylphosphino)ethane]platinum(0) (**18**) and neopentane.[23]

Thermolysis of 1 in Tricyclohexylphosphine/Cyclohexane. Two sealed 5-mm-o.d. NMR tubes, each containing ca. 21 mg of **1** in a 0.31 M solution of tricyclohexylphosphine in cyclohexane (0.5 mL), were thermolyzed at 68.9 °C. The initially colorless solutions became magenta upon heating but remained completely homogeneous. The disappearance of **1** followed first-order kinetics for more than 2 half-lives; $k = 6.9 \times 10^{-4}\ s^{-1}$ (average of two runs). (Tricyclohexylphosphine)[bis(dicyclohexylphosphino)ethane]platinum(0) (**19**) was the sole product (94%

yield). The sole organic product was neopentane (quantitative yield).

Dichloro[bis(dicyclohexylphosphino)ethane]platinum(II). A 100-mL round-bottomed flask with a side arm was equipped with a stirring bar and a pressure-adjusted addition funnel. The flask was charged with dichloro(1,5-cyclooctadiene)platinum(II) (1.50 g, 4.01 mmol) and purged with argon. The platinum complex was then dissolved in ca. 50 mL of degassed CH_2Cl_2; the addition funnel was charged with a solution of bis(dicyclohexylphosphino)ethane (1.88 g, 4.45 mmol) in 40 mL of degassed CH_2Cl_2. The bis(phosphine) solution was added at room temperature. After ca. 4 h, the solvent was removed by rotary evaporation. The residue was recrystallized from hot hexane/$CHCl_3$. Colorless needles formed upon cooling the solution to −10 °C. The crystals were isolated by suction filtration and ground between a mortar and pestle. The white powder was dried in vacuo at 79 °C (0.05 Torr). The yield of white powder, mp (capillary sealed under argon) >250 °C, was 2.37 g (3.44 mmol, 86%). ^{1}H NMR (CD_2Cl_2): δ 2.5–2.1 (m, 8 H), 1.95–1.65 (m, 20 H), 1.65–1.15 (m, 20 H). ^{31}P NMR (CD_2Cl_2): δ 65.1 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 3573 Hz). IR (KBr): 2930 (s), 2855 (s), 1450 (m), 1412 (w), 1350 (w), 1330 (w), 1305 (sh), 1298 (w), 1273 (w), 1210 (w), 1182 (w), 1175 (w), 1118 (w), 1081 (w), 1050 (w), 1008 (m), 920 (w), 891 (w), 870 (w), 852 (m), 822 (w), 799 (w), 755 (sh), 749 (m), 678 (m), 655 (w), 542 (m), 520 (w), 490 (w), 470 (w), 440 (w), 412 (w), 405 (sh), 380 (w), 306 (w), 300 (w), 283 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{48}Cl_2P_2Pt$: C, 45.35; H, 7.03; Cl, 10.30; P, 9.00. Found: C, 45.28; 45.36; H, 6.97, 7.08; Cl, 10.25, 10.36; P, 8.94, 8.92.

1,1-Dibromo-2,2,3,3-tetramethylcyclopropane was prepared from $CHBr_3$ (11 mL, 0.13 mol) and 2,3-dimethyl-2-butene (35 mL, 25 g, 0.29 mol) according to the literature procedure.[73] The product was recrystallized once from 95% ethanol; a small second crop was recovered from the mother liquor. The combined yield of colorless plates, mp 79–80 °C, was 23.0 g (0.092 mol, 73%). ^{1}H NMR (C_6D_6): δ 0.99 (s).

1-Bromo-2,2,3,3-tetramethylcyclopropane was prepared by reduction of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane with tri-*n*-butyltin hydride.[74] The product was isolated in 50% yield after two distillations. ^{1}H NMR ($CDCl_3$): δ 2.73 (s, 1 H); 1.18, 1.08 (two s; combined area, 12 H).

1-Lithio-2,2,3,3-tetramethylcyclopropane was synthesized from 1-bromo-2,2,3,3-tetramethylcyclopropane and lithium powder according to the literature procedure.[75]

***cis*-Chloro-(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II).** A 250-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 *cis*-dichloro[bis(dicyclohexylphosphino)ethane]platinum(II) (0.500 g, 0.727 mmol) and purged with argon. The platinum complex was suspended in 60 mL of THF, and the addition funnel was charged with 1-lithio-2,2,3,3-tetramethylcyclopropane (prepared from 0.55 g of 1-bromo-2,2,3,3-tetramethylcyclopropane and lithium powder) in ca. 75 mL of diethyl ether. The lithium reagent was added at −78 °C, and the mixture was allowed to warm gradually to room temperature. When TLC indicated that the reaction was complete, the homogeneous yellow solution was cooled to 0 °C, and the reaction was quenched with aqueous ammonium chloride. The aqueous layer was extracted with ether; the combined organic extracts were washed with distilled water and brine, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The white solid was recrystallized from warm acetone/hexane; colorless cubes formed upon cooling the solution to −10 °C. The crystals were isolated by suction filtration and dried in vacuo at 79 °C (0.03 Torr). The yield of product, mp (capillary sealed under argon) 211–212 °C dec, was 0.373 g (0.498 mmol, 69%).

The complex appears to be a mixture of rotamers whose relative ratio varies from 1/1 to 4/1, depending on the specific preparation. (We did not determine whether or not the rotamers interconvert upon heating.) Two pairs of peaks are observed in the ^{31}P NMR spectrum; two pairs of methyl signals and two different methine hydrogens, with different coupling constants to platinum, are observed by ^{1}H NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 2.35–2.05 (m, 8 H), 1.9–1.6 (m, 18 H), 1.55–1.15 (m, 28 H; includes two s at δ 1.24 and 1.22), 1.14, 1.12 (two s, 6 H), 0.5–0.3 (two superimposed peaks, each with platinum satellites; δ 0.42, "d" with platinum satellites, $J_{\mathrm{Pt-H}}$ = 60 Hz; 0.40, "q" with platinum satellites, $J_{\mathrm{Pt-H}}$ = 51 Hz; 1 H total). (The major product corresponds to the methyl peaks at δ 1.22 and 1.14 and the methine signal at δ 0.40; the minor product corresponds to the methyl peaks at δ 1.24 and 1.12 and the methine signal at δ 0.42.) ^{31}P NMR (CD_2Cl_2) major product: δ 62.2 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 1694 Hz), 57.5 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 4281 Hz). ^{31}P NMR (CD_2Cl_2) minor product: δ 60.1 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 1687 Hz), 58.6 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 4312 Hz). IR (KBr): 2920 (vs), 2850 (vs), 2705 (sh), 2680 (sh), 1448 (s), 1420 (sh), 1410 (m), 1368 (w), 1345 (w), 1330 (w), 1305 (w), 1298 (w), 1270 (w), 1238 (w), 1210 (w), 1200 (sh), 1182 (w), 1172 (w), 1110 (w), 1081 (w), 1040 (w), 1025 (sh), 1005 (m), 930 (sh), 915 (w), 890 (m), 865 (w), 852 (m), 821 (w), 795 (m), 740 (m), 667 (m), 650 (sh), 538 (s), 518 (w), 485 (w), 470 (w), 440 (w), 405 (w), 372 (w), 350 (w), 286 (m) cm^{-1}. Anal. Calcd for $C_{33}H_{71}ClP_2Pt$: C, 52.82; H, 8.19; Cl, 4.72; P, 8.25. Found: C, 52.73, 52.68; H, 8.51, 8.47; Cl, 4.72; P, 8.19.

***cis*-Hydrido(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (3).** A 100-mL recovery flask equipped with a stirring bar was charged with *cis*-chloro(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (0.200 g, 0.267 mmol) and purged with argon. The complex was dissolved in 20 mL of THF, and a solution of $Na[HB(OMe)_3]$ (0.10 g, 0.79 mmol) in 20 mL of THF was added via cannula. The initially clear solution turned slightly cloudy almost immediately. After 2 h, the reaction mixture was transferred via cannula to a Schlenk flask, and the volatiles were removed in vacuo. The residue was extracted with benzene and filtered through a fine frit. Removal of the solvent by toary evaporation left a colorless oil. This oil was dissolved in the minimum amount of diethyl ether; two volumes of methanol were added, and the colorless solution was cooled to −10 °C. The colorless crystals were isolated by suction filtration and dried over KOH in vacuo (0.05 Torr). The yield of colorless crystals, mp (capillary sealed under argon) 143–145 °C dec, was 0.152 g. Elemental analysis and ^{1}H NMR spectroscopy revealed 0.5 equiv of trimethylborate in the colorless crystals. ^{1}H NMR (C_6D_6): δ 3.01 (s, 5 H), 2.25–1.95 (m, 6 H), 1.95–1.0 (m, 55 H; includes two s at 1.71 and 1.69), −0.37 (dd with platinum satellites, $J_{\mathrm{P-H}}$ = 19, $J_{\mathrm{P'-H}}$ = 196, $J_{\mathrm{Pt-H}}$ = 1165 Hz; 1 H). ^{31}P NMR (C_6D_6): δ 74.1 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 1759 Hz), 64.0 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 1784 Hz). IR (neat): 2920 (vs), 2850 (vs), 2010 (s), 1445 (s), 1415 (sh), 1385 (w), 1368 (m), 1342 (w), 1328 (w), 1300 (sh), 1292 (w), 1268 (m), 1192 (w), 1179 (m), 1172 (m), 1110 (m), 1090 (w), 1040 (w), 1025 (w), 1002 (m), 915 (w), 888 (m), 860 (sh), 850 (m), 820 (sh), 800 (m), 742 (m), 655 (m), 640 (sh), 530 (m), 515 (sh), 500 (w) cm^{-1}. Anal. Calcd for $C_{33}H_{62}P_2Pt\cdot 0.5B(OM)_3$: C, 53.97; H, 8.73; B, 0.70; P, 8.07. Found: C, 54.43, 54.25; H, 9.16, 8.79; B, 0.70, 0.40; P, 8.31.

***cis*-Chlorocyclopentyl[bis(dicyclohexylphosphino)ethane]platinum(II).** A 250-mL round-bottomed flask equipped with a stirring bar, a pressure-adjusted addition funnel, and a reflux condenser topped by an argon inlet was charged with dichloro[bis(dicyclohexylphosphino)ethane]platinum(II) (0.512 g, 0.734 mmol) and purged with argon. The platinum complex was then dissolved in ca. 65 mL of THF; the addition funnel was charged with cyclopentylmagnesium chloride (2.0 M, 2.0 mL, 4.0 mmol; diluted with 20 mL of THF). The Grignard reagent was added at −78 °C; the mixture was allowed to warm gradually to 25 °C, at which temperature the mixture became homogeneous. After 1 h at 25 °C, the reaction was quenched at 0 °C with aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether; the combined organic layers were washed with distilled water and brine, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The residual oil solidified upon addition of pentane; the white solid was dried in vacuo (0.05 Torr) overnight. The crude yield was 0.45 g (0.62 mmol, 84%). Attempts to purify the complex by recrystallization or column chromatography resulted in complete decomposition of the product. ^{1}H NMR (CD_2Cl_2): δ 2.3–1.2 (m). ^{31}P NMR (CD_2Cl_2): δ 66.5 (s with platinum satellites, $J_{\mathrm{Pt-P}}$ = 1578 Hz), 57.1 (s with platinum satellites, $J_{\mathrm{Pt-H}}$ = 4338 Hz).

***cis*-Cyclopentylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (4).** *cis*-Chlorocyclopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) (0.24 g, 0.33 mmol) was dissolved in 10 mL of THF in a 25-mL recovery flask equipped with a stirring bar. The colorless solution was treated at room temperature with a solution of $Na[HB(OMe)_3]$ (0.21 g, 1.6 mmol) in 10 mL of THF. The initially clear solution became cloudy; after ca. 2 h at room temperature, the solvent was removed by rotary evaporation. The residual oil was dissolved in the minimum amount of diethyl ether; then an equal volume of methanol was added, and the solution was cooled to −10 °C. After a second recrystallization, the colorless crystals were dried over KOH in vacuo (0.05 Torr). The yield of 4, mp (capillary sealed under argon) ca. 140 °C dec, was 33 mg (0.048 mmol, 15%). ^{1}H NMR (C_6D_6): δ 2.62 (br s, 5 H), 2.2 (br s, 4 H), 2.06 (br s, 4 H), 1.9–1.0 (m, 44 H), 0.06 (dd with platinum satellites, $J_{\mathrm{P-H}}$ = 19, $J_{\mathrm{P'-H}}$ = 194, $J_{\mathrm{Pt-H}}$ = 1249 Hz, 1 H). ^{31}P NMR (C_6D_6): δ 75.6 (d with platinum satellites, $J_{\mathrm{P-P}}$ = 2, $J_{\mathrm{Pt-P}}$ = 1504 Hz), 63.9 (d with platinum satellites, $J_{\mathrm{P-P}}$ = 2, $J_{\mathrm{Pt-P}}$ = 1793 Hz). IR (neat): 2922 (vs), 2850 (s), 1975 (s), 1450 (m), 1415 (w), 1348 (w), 1332 (w), 1305 (w), 1295 (w), 1272 (w), 1198 (w), 1182 (w), 1173 (w), 1120 (sh), 1110 (w),

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1080 (w), 1050 (w), 1030 (vw), 1005 (w), 915 (w), 880 (w), 852 (m), 821 (w), 792 (w), 745 (w) cm^{-1}. Anal. Calcd for $C_{31}H_{58}P_2Pt$: C, 54.13; H, 8.50; P, 9.01. Found: C, 54.19, 54.27; H, 8.31, 8.37; P, 8.94, 8.89.

***cis*-Chlorocyclohexyl[bis(dicyclohexylphosphino)ethane]platinum(II).** A 250-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 dichloro[bis(dicyclohexylphosphino)ethane]platinum(II) (0.522 g, 0.759 mmol) and purged with argon. The platinum complex was dissolved in 85 mL of THF; the addition funnel was charged with an ethereal solution of cyclohexylmagnesium bromide (0.89 M, 5.0 mL, 4.4 mmol; diluted with 5 mL of THF). The Grignard reagent was added at −78 °C; the initially homogeneous solution became cloudy. The mixture was allowed to warm gradually to room temperature; the cloudy mixture was stirred overnight at 25 °C. The reaction mixture was now homogeneous; TLC (2/1 hexane/THF on silica) showed a single spot at R_f 0.70. The reaction was quenched at 0 °C with aqueous ammonium chloride. The organic and aqueous layers were separated; the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with distilled water and brine, dried over $MgSO_4$, and concentrated to dryness on the rotary evaporator. The residue, an amorphous white solid, was dried in vacuo (0.045 Torr) over KOH. The yield of white solid, mp (capillary sealed under argon) ca. 260 °C dec, was 0.435 g (0.591 mmol, 78%). ^1H NMR (CD_2Cl_2): δ 2.3–1.1 (m). ^{31}P NMR (CD_2Cl_2): δ 64.0 (s with platinum satellites, J_{Pt-P} = 1517 Hz), 55.0 (s with platinum satellites, J_{Pt-P} = 4416 Hz).

All attempts to purify the complex by recrystallization or chromatography caused extensive decomposition; the crude product was sufficiently pure to be used in subsequent reactions.

***cis*-Cyclohexylhydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (5).** A 50-mL recovery flask equipped with a stirring bar was charged with *cis*-chlorocyclohexyl[bis(dicyclohexylphosphino)ethane]platinum(II) (0.305 g, 0.414 mmol) and purged with argon. The complex was dissolved in ca. 10 mL of THF; a solution of Na[HB(OMe)$_3$] (0.211 g, 1.65 mmol) in 10 mL of THF was added via cannula at room temperature. The initially homogeneous solution became cloudy after 30 min. After 3 h, the reaction was quenched at 0 °C with aqueous ammonium chloride. The organic and aqueous layers were separated; the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried with brine and $MgSO_4$; the solvent was removed by rotary evaporation. The residue, an amorphous white solid, was dissolved in the minimum volume of THF at room temperature; two volumes of methanol were added, and the solution was cooled to −10 °C. The white crystals were isolated by suction filtration. After two more recrystallizations, the product was dried over KOH in vacuo (0.10 Torr). The yield of product, mp (capillary sealed under argon) ca. 145 °C dec (without melting), was 0.150 g (0.214 mmol, 52%). ^1H NMR (C_6D_6): δ 3.1–2.4 (m, 5 H); 2.3–1.0 (m, 54 H); 0.02 (dd with platinum satellites, J_{P-H} = 19, $J_{P'-H}$ = 193, J_{Pt-H} = 1260 Hz, 1 H). ^{31}P NMR (C_6D_6): δ 74.9 (s with platinum satellites, J_{Pt-P} = 1451 Hz), 63.1 (s with platinum satellites, J_{Pt-P} = 1811 Hz). IR (neat): 2930 (s), 2859 (s), 1970 (m), 1468 (sh), 1450 (m), 1415 (w), 1348 (w), 1335 (w), 1307 (vw), 1298 (vw), 1272 (w), 1200 (w), 1182 (w), 1175 (w), 1112 (w), 1078 (w), 1005 (w), 920 (w), 890 (w), 822 (w), 793 (w), 745 (w), 660 (w), 645 (sh), 532 (w), 502 (w) cm^{-1}. Anal. Calcd for $C_{32}H_{60}P_2Pt$: C, 54.76; H, 8.62; P, 8.83. Found: C, 54.62; H, 8.77; P, 8.95.

***cis*-Chloromethyl[bis(dicyclohexylphosphino)ethane]platinum(II).** A 100-mL recovery flask equipped with a stirring bar was charged with chloromethyl(1,5-cyclooctadiene)platinum(II).[71] The flask was fitted with a pressure-adjusted addition funnel and purged with argon. The platinum complex was dissolved in 30 mL of degassed CH_2Cl_2; the addition funnel was charged with a solution of bis(dicyclohexylphosphino)ethane (0.424 g, 1.00 mmol) in 30 mL of degassed CH_2Cl_2. The bis(phosphine) was added at room temperature under argon. After 2 h, TLC (2/1 hexanes/THF on silica) showed a single spot at R_f 0.59. The solvent was removed by rotary evaporation. The residue was dissolved in boiling acetone; the volume of the solution was decreased until a few crystals precipitated. The solution was cooled slowly to −10 °C. The crystals were isolated by suction filtration; a second crop of crystals was reclaimed from the mother liquor. After two more recrystallizations, the white crystals were dried in vacuo (0.015 Torr) at 79 °C. The combined yield of white crystals (first, second, and third crops) was 0.427 g (0.639 mmol, 71%). Mp (capillary sealed under argon): 267–278 °C dec. ^1H NMR (CD_2Cl_2): δ 2.3–2.0 (m, 8 H), 1.9–1.6 (m, 18 H), 1.55–1.15 (m, 22 H); 0.42 (dd with platinum satellites, J_{P-H} = 2, $J_{P'-H}$ = 7, J_{Pt-P} = 52 Hz, 1 H). ^{31}P NMR (CD_2Cl_2): δ 66.8 (s with platinum satellites, J_{Pt-P} = 1797 Hz), 57.7 (s with platinum satellites, J_{Pt-P} = 4070 Hz). IR (KBr): 2930 (vs), 2850 (vs), 2800 (sh), 2665 (w), 1448 (s), 1412 (m), 1345 (m), 1330 (w), 1302 (sh), 1298 (m), 1272 (m), 1201 (m), 1180 (m), 1172 (m), 1112 (m), 1080 (w), 1045 (w), 1030 (w), 1005 (s), 918 (m), 890 (s), 870 (m), 852 (s), 822 (m), 800 (m), 748 (s), 735 (sh), 712 (w), 680 (m), 668 nm), 650 (m), 539 (s), 520 (s), 486 (m), 470 (w), 439 (w), 402 (w), 375 (w), 360 (w), 288 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{51}ClP_2Pt$: C, 48.53; H, 7.69. Found: C, 48.42; H, 7.76.

***cis*-Hydridomethyl[bis(dicyclohexylphosphino)ethane]platinum(II) (6).** A 50-mL recovery flask equipped with a stirring bar was charged with *cis*-chloromethyl[bis(dicyclohexylphosphino)ethane]platinum(II) (0.324 g, 0.485 mmol) and purged with argon. The complex was dissolved in 10 mL of THF, and a solution of Na[HB(OMe)$_3$] (0.206 g, 1.61 mmol) in 10 mL of THF was added via cannula. The reaction solution became cloudy immediately. After 3 h at room temperature, the mixture was cooled to 0 °C, and the reaction was quenched with aqueous ammonium chloride. The aqueous and organic layers were separated; the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried with brine and $MgSO_4$. Removal of the solvent by rotary evaporation left an oily solid. The residue was dissolved at room temperature in the minimum volume of THF; four volumes of methanol were added, and the solution was cooled to −10 °C. The crystals that formed after 48 h were isolated by suction filtration. The product was recrystallized a second time. The product was dried over KOH in vacuo (0.08 Torr). The yield of slightly yellow crystals, mp (capillary sealed under argon) ca. 155 °C dec (without melting), was 75.7 mg (0.194 mmol, 25%). ^1H NMR (C_6D_6): δ 2.2–2.0 (m, 6 H), 1.9–1.0 (m, 45 H), 0.53 (dd with platinum satellites, J_{P-H} = 18, $J_{P'-H}$ = 200, J_{Pt-H} = 1154 Hz, 1 H). ^{31}P NMR (C_6D_6): δ 77.4 (s with platinum satellites, J_{Pt-P} = 1823 Hz), 63.4 (s with platinum satellites, J_{Pt-P} = 1746 Hz). IR (neat): 2960 (vs), 2890 (s), 1990 (s), 1482 (sh), 1467 (s), 1438 (m), 1363 (m), 1350 (m), 1322 (w), 1312 (m), 1289 (m), 1220 (m), 1198 (m), 1190 (m), 1130 (m), 1105 (w), 1095 (w), 1069 (w), 1063 (sh), 1046 (w), 1021 (m), 933 (m), 908 (m), 885 (m), 870 (s), 840 (m), 814 (m), 798 (w), 763 (m), 742 (sh), 682 (m), 664 (m), 550 (s), 520 (sh), 500 (w), 480 (w), 455 (w) cm^{-1}. Anal. Calcd for $C_{27}H_{52}P_2Pt$: C, 51.17; H, 8.27; P, 9.77. Found: C, 51.03; H, 8.30; P, 9.47.

***cis*-Bis[(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II)**[72] was prepared by treatment of a suspension of dichloro(1,5-cyclooctadiene)platinum(II) (1.93 g, 5.16 mmol) in diethyl ether with [(trimethylsilyl)methyl]lithium (1.12 g, 11.9 mmol) at −78 °C. The reaction mixture was allowed to warm gradually to 0 °C. The reaction was quenched with 1.0 mL of aqueous methanol at −78 °C, and the product was purified by flash chromatography on silica with petroleum ether as the eluant. The yield of vacuum-dried white solid, mp 63–64.5 °C, was 2.40 g (5.02 mmol, 97%). ^1H NMR (C_6D_6): δ 4.7 (br s with platinum satellites, J_{Pt-H} = 42 Hz, 4 H), 1.95–1.55 (m, 8 H), 1.15 (s with platinum satellites, J_{Pt-H} = 96 Hz, 4 H), 0.3 (s, 18 H).

***cis*-Chloro[(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II)** was prepared by treatment of a solution of *cis*-bis[(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II) (2.34 g, 4.90 mmol) in petroleum ether with concentrated HCl (1.0 mL). After TLC indicated that the reaction was complete, the product was purified by column chromatography with diethyl ether as the eluant. The yield of off-white solid, mp (capillary sealed under argon) 95–96 °C, was 1.82 g (4.27 mmol, 87% yield). ^1H NMR ($CDCl_3$): δ 5.42 (m with platinum satellites, J_{Pt-H} = 37 Hz, 2 H), 4.51 (m with platinum satellites, J_{Pt-H} = 76 Hz, 2 H), 2.6–2.05 (m, 8 H), 1.01 (s with platinum satellites, J_{Pt-H} = 74 Hz, 2 H), 0.10 (s with silicon satellites, J_{Si-H} = 7 Hz, 9 H). IR (KBr): 3020 (w), 3000 (sh), 2945 (s), 2890 (m), 2840 (s), 1475 (w), 1452 (w), 1435 (sh), 1430 (w), 1408 (w), 1360 (w), 1345 (w), 1320 (w), 1308 (w), 1242 (s), 1181 (w), 1165 (w), 1090 (w), 1086 (w), 1040 (w), 1010 (w), 1000 (w), 986 (m), 965 (m), 900 (sh), 840 (vs), 825 (vs), 790 (w), 766 (m), 742 (m), 712 (m), 690 (sh), 679 (m), 613 (w), 578 (w), 540 (w), 504 (vw), 480 (w), 430 (vw), 380 (vw), 320 (sh), 310 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{23}ClPtSi$: C, 33.84; H, 5.44; Cl, 8.32. Found: C, 33.91; H, 5.46; Cl, 8.26.

***cis*-Chloro[(trimethylsilyl)methyl][bis(dicyclohexylphosphino)ethane]platinum(II).** A 100-mL round-bottomed flask with a side arm was charged with *cis*-chloro[(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II) (0.501 g, 1.18 mmol); then the flask was equipped with a pressure-adjusted addition funnel and purged with argon. The platinum complex was dissolved in ca. 50 mL of degassed CH_2Cl_2; the addition funnel was charged with a solution of bis(dicyclohexylphosphino)ethane (0.549 g, 1.30 mmol) in 25 mL of degassed CH_2Cl_2. The bis(phosphine) solution was added at room temperature over a 15-min period; the colorless solution was stirred at 25 °C for 2 h. The solvent was removed by rotary evaporation, and the white solid was recrystallized from hot acetone. Cooling the acetone solution to −10 °C produced colorless prisms. The product was isolated by suction filtration, ground between a mortar and pestle, and dried at 79 °C in vacuo. The yield of white powder, mp (capillary sealed under argon) 214–216 °C, was 0.62 g (0.84 mmol, 71%). ^1H NMR (CD_2Cl_2): δ 2.4–1.95 (m, 8 H), 1.95–1.6 (m, 17 H), 1.6–1.1 (m, 23 H), 0.40–0.0 (overlapping peaks; δ 0.27, dd with platinum satellites, $J_{\mathrm{P-H}} = 4$, $J_{\mathrm{P'-H}} = 9$, $J_{\mathrm{Pt-H}} = 50$ Hz; δ 0.12, s with silicon satellites, $J_{\mathrm{Si-H}} = 6$ Hz; 11 H total). ^{31}P NMR (CD_2Cl_2): δ 66.6 (s with platinum satellites, $J_{\mathrm{Pt-P}} = 1907$ Hz), 58.8 (s with platinum satellites, $J_{\mathrm{Pt-P}} = 4119$ Hz). IR (KBr): 2940 (vs), 2860 (s), 1450 (s), 1420 (sh), 1413 (w), 1348 (w), 1332 (w), 1307 (w), 1298 (w), 1272 (w), 1248 (w), 1232 (m), 1210 (sh), 1203 (w), 1182 (w), 1174 (w), 1114 (w), 1095 (sh), 1090 (sh), 1080 (w), 1050 (w), 1030 (sh), 1008 (w), 942 (w), 920 (w), 890 (w), 852 (s), 825 (s), 800 (w), 749 (m), 721 (w), 670 (m), 650 (w), 540 (m), 520 (w), 490 (w), 472 (w), 438 (w), 410 (w), 402 (w), 380 (w), 358 (w), 288 (m). Anal. Calcd for $C_{30}H_{59}ClP_2PtSi$: C, 48.67; H, 8.03; Cl, 4.79; P, 8.37. Found: C, 48.87, 48.79; H, 7.70, 7.74; Cl, 4.69, 4.73; P, 8.29, 8.36.

***cis*-Hydrido[(trimethylsilyl)methyl][bis(dicyclohexylphosphino)ethane]platinum(II)** (7). A 50-mL recovery flask equipped with a stirring bar was charged with *cis*-chloro[(trimethylsilyl)methyl][bis(dicyclohexylphosphino)ethane]platinum(II) (0.249 g, 0.338 mmol) and purged with argon. The complex was then dissolved in 10 mL of THF and treated with a solution of Na[HB(OMe)$_3$] (0.27 g, 2.1 mmol) in 20 mL of THF. The solution was stirred at room temperature for ca. 6 h, during which time the reaction mixture became quite cloudy. The reaction was quenched at 0 °C with aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether; the combined organic layers were washed with distilled water and brine, dried over $MgSO_4$, and concentrated to a colorless oil by rotary evaporation. The oil was dissolved in the minimum volume of ether; an equal volume of MeOH was added, and the solution was cooled to −10 °C. The colorless crystals so obtained were recrystallized a second time. The product was isolated by suction filtration and dried over KOH in vacuo (0.05 Torr). The yield of colorless crystals, mp (capillary sealed under argon) 141–143 °C dec, was 0.113 g (0.160 mmol, 47%). ^{1}H NMR (C_6D_6): δ 2.2–1.95 (m, 6 H), 1.95–0.90 (m, 44 H), 0.62 (s, 9 H), −0.17 (dd with platinum satellites, $J_{\mathrm{P-H}} = 17$, $J_{\mathrm{P'-H}} = 200$, $J_{\mathrm{Pt-H}} = 1105$ Hz, 1 H). ^{31}P NMR (C_6D_6): δ 76.7 (s with platinum satellites, $J_{\mathrm{Pt-P}} = 1994$ Hz), 63.7 (s with platinum satellites, $J_{\mathrm{Pt-P}} = 1779$ Hz). IR (neat): 2930 (vs), 2850 (vs), 1985 (s), 1448 (s), 1415 (w), 1345 (w), 1330 (w), 1305 (w), 1295 (w), 1270 (w), 1245 (w), 1230 (m), 1195 (w), 1180 (w), 1170 (w), 1110 (w), 1080 (w), 1002 (m), 914 (m), 888 (w), 852 (s), 817 (s), 795 (m), 740 (m), 715 (w), 660 (m), 645 (w) cm^{-1}. Anal. Calcd for $C_{30}H_{60}P_2PtSi$: C, 51.22; H, 8.44; P, 8.79. Found: C, 51.23, 51.19; H, 8.14, 8.23; P, 8.85, 8.76.

***cis*-Hydridophenyl[bis(dicyclohexylphosphino)ethane]platinum(II) (8).** The complex was isolated from a completely thermolyzed sample of **1** in benzene and purified by recrystallization.[23]

***cis*-Chloro(2,4,6-trimethylphenyl)(1,5-cyclooctadiene)platinum(II).**[34] Treatment of dichloro(1,5-cyclooctadiene)platinum(II) (1.061 g, 2.835 mmol) in 75 mL of THF with (2,4,6-trimethylphenyl)magnesium bromide in THF (1.0 M, 12.0 mL, 12 mmol; diluted with 15 mL of THF) at −78 °C, followed by gradual warming to 10 °C, resulted in a homogeneous yellow solution. The reaction was quenched at 0 °C with aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether; the combined organic layers were washed with distilled water and brine, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The product was recrystallized from warm acetone/hexane; cooling the solution to −10 °C produced shiny, colorless needles. After a second recrystallization, the crystals were isolated by suction filtration and dried over KOH in vacuo. A small second crop was isolated from the mother liquors. The yield of colorless crystals, mp 208–212 °C dec, was 0.618 g (1.35 mmol, 48%). ^{1}H NMR (CD_2Cl_2): δ 6.67 (br s, 2 H), 5.73 (m with platinum satellites, $J_{\mathrm{Pt-H}} = 36$ Hz, 2 H), 4.37 (two overlapping m with platinum satellites, $J_{\mathrm{Pt-H}} = 72$, $J_{\mathrm{Pt-H}} = 76$ Hz, 2 H), 2.8–2.1 (m, 17 H). IR (KBr): 3100 (m), 2955 (s), 2920 (s), 2845 (m), 1555 (vw), 1543 (vw), 1482 (m), 1452 (sh), 1430 (s), 1370 (w), 1350 (w), 1340 (w), 1320 (w), 1312 (w), 1290 (w), 1230 (w), 1186 (w), 1168 (w), 1089 (w), 1075 (w), 1041 (s), 1020 (w), 1005 (w), 995 (w), 942 (w), 895 (w), 882 (w), 860 (sh), 850 (m), 820 (w), 798 (w), 765 (m), 717 (m), 578 (w), 560 (w), 504 (w), 478 (w), 422 (w), 360 (w), 312 (m) cm^{-1}.

***cis*-Hydrido(2,4,6-trimethylphenyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (9).** A 100-mL recovery flask equipped with a pressure-adjusted addition funnel and a stirring bar was charged with *cis*-chloro(2,4,6-trimethylphenyl)(1,5-cyclooctadiene)platinum(II) (0.498 g, 1.09 mmol) and purged with argon. The complex was then dissolved in degassed CH_2Cl_2. A solution of bis(dicyclohexylphosphino)ethane (0.515 g, 1.22 mmol) in CH_2Cl_2 was added via the addition funnel. The solution was stirred under argon overnight. Removal of the solvent by rotary evaporation left a yellow oil, which eventually solidified. The crude product, a gummy white solid, was dissolved in 60 mL of THF and treated with a solution of Na[HB(OMe)$_3$] (0.811 g, 6.34 mmol) in 20 mL of THF. The cloudy solution was stirred at room temperature for 4 days; the progress of the reaction was monitored by TLC. The reaction was quenched at 0 °C with distilled H_2O. The aqueous layer was extracted with CH_2Cl_2; the combined organic layers were washed with water, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The product was dissolved in the minimum amount of THF; an equal volume of methanol was layered over the THF solution. White, platelike crystals formed on cooling the solution to −10 °C. After two recrystallizations, the yield of white crystals, mp (capillary sealed under argon) 173 °C dec, was 0.118 g (0.159 mmol, 15%). (This yield includes a second crop isolated from the mother liquors.) ^{1}H NMR (CD_2Cl_2): δ 6.64 ("t", $J = 6$ Hz, 2 H), 2.31 (s with platinum satellites, $J_{\mathrm{Pt-H}} = 5$ Hz, 6 H), 2.19 (s, 3 H), 2.1–0.8 (m, 48 H), −2.30 (dd with platinum satellites, $J_{\mathrm{P-H}} = 15$, $J_{\mathrm{P'-H}} = 182$, $J_{\mathrm{Pt-H}} = 1134$ Hz, 1 H). ^{31}P NMR (CD_2Cl_2): δ 74.3 (s with platinum satellites, $J_{\mathrm{Pt-P}} = 1804$ Hz), 59.4 (s with platinum satellites, $J_{\mathrm{Pt-P}} = 1834$ Hz). IR (neat): 2935 (vs), 2860 (vs), 1998 (s), 1455 (sh), 1450 (s), 1420 (w), 1363 (w), 1349 (w), 1332 (w), 1308 (w), 1298 (w), 1273 (w), 1210 (sh), 1200 (w), 1184 (w), 1175 (w), 1125 (w), 1112 (w), 1095 (vw), 1081 (vw), 1075 (vw), 1025 (w), 1008 (m), 956 (w), 918 (w), 891 (m), 865 (sh), 854 (m), 846 (m), 811 (w), 790 (m), 765 (m), 748 (m), 740 (sh), 709 (m), 665 (m), 645 (w) cm^{-1}. Anal. Calcd for $C_{35}H_{60}P_2Pt$: C, 56.97; H, 8.20; P, 8.40. Found: C, 56.87, 56.82; H, 8.27, 8.29; P, 8.44, 8.37.

(3,5-Dimethylbenzyl)magnesium bromide was prepared by slow (7 h) addition of 3,5-dimethylbenzyl bromide (9.6 mL, 12 g, 0.060 mol) in 50 mL of diethyl ether to a mixture of Mg turnings (4.68 g, 0.192 mol; activated by 1,2-dibromoethane) in 50 mL of ether at reflux temperature. After addition was complete, the mixture was heated under reflux overnight. Titration of the orange solution indicated a concentration of 0.43 M (72%).

***cis*-Bis(3,5-dimethylbenzyl)(1,5-cyclooctadiene)platinum(II).** A 250-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 dichloro(1,5-cyclooctadiene)platinum(II) (1.009 g, 2.70 mmol) and purged with argon. The platinum complex was suspended in 80 mL of diethyl ether, and the Grignard reagent was added at −78 °C over a 30-min period. The reaction mixture was allowed to warm to 15 °C over a 10-h period. (The mixture became homogeneous at ca. −20 °C.) The reaction was quenched at 0 °C with aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether; the organic layers were washed with distilled water and brine, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The residue was dissolved in the minimum volume of ether; an equal volume of methanol was added, and the solution was cooled to −10 °C. The product was isolated as pale yellow plates by suction filtration; a small second crop was isolated from the mother liquor. After a second recrystallization, the crystals were dried over KOH in vacuo (0.05 Torr). The yield of product, mp 145–146 °C dec, was 0.3342 g (0.617 mmol, 23%). ^{1}H NMR (C_6D_6): δ 6.95 ("t", $J = 5$ Hz, 4 H), 6.66 (br s, 2 H), 4.62 (br s with platinum satellites, $J_{\mathrm{Pt-H}} = 29$ Hz, 4 H), 3.30 (s with platinum satellites, $J_{\mathrm{Pt-H}} = 114$ Hz, 4 H), 2.23 (s, 12 H), 1.85–1.65 (m, 4 H), 1.65–1.4 (m, 4 H). IR (KBr): 3100 (sh), 2995 (w), 2970 (sh), 2942 (s), 2910 (s), 2885 (s), 2840 (m), 2730 (w), 1600 (s), 1465 (s), 1450 (s), 1435 (m), 1378 (w), 1342 (w), 1312 (w), 1300 (w), 1230 (w), 1182 (w), 1158 (w), 1038 (w), 1018 (w), 990 (w), 940 (w), 886 (w), 865 (w), 840 (s), 825 (sh), 790 (w), 775 (w), 722 (sh), 708 (m), 620 (w), 520 (w), 465 (sh), 448 (m), 402 (vw) cm^{-1}. Anal. Calcd for $C_{26}H_{34}Pt$: C, 57.66; H, 6.33. Found: C, 57.69, 57.61; H, 6.28, 6.35.

***cis*-Chloro(3,5-dimethylbenzyl)(1,5-cyclooctadiene)platinum(II).** A 100-mL recovery flask equipped with a stirring bar was charged with a solution of *cis*-bis(3,5-dimethylbenzyl)(1,5-cyclooctadiene)platinum(II) in ca. 50 mL of pentane and 2.0 mL of concentrated hydrochloric acid. White precipitate formed rapidly; after 1 h, TLC revealed no trace of the starting material. The solid was dissolved in CH_2Cl_2, and the acid was diluted with distilled water. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The off-white powder was dissolved in CH_2Cl_2 and passed through a column of neutral alumina. The product was recrystallized from warm acetone/hexane; crystals formed upon cooling the solution to −10 °C. The crystals were isolated by suction filtration and dried in vacuo (0.05 Torr) at 79 °C. The yield of white crystals, mp 182–183 °C dec, was 0.138 g (0.302 mmol, 50%). ^{1}H NMR (CD_2Cl_2): δ 6.86 (br s, 2 H), 6.71 (br s, 1 H), 5.55 (m with platinum satellites, $J_{\mathrm{Pt-H}} = 29$ Hz, 2 H), 4.38 (m with platinum satellites, $J_{\mathrm{Pt-H}} = 76$ Hz, 2 H), 3.01 (s with platinum satellites, $J_{\mathrm{Pt-H}} = 102$ Hz, 2 H), 2.6–2.0 (m, 14 H). IR (KBr): 3070 (m), 2955 (s), 2910 (s), 2860 (s), 1592 (s), 1550 (w), 1460 (s), 1427 (m), 1380 (m), 1342 (w), 1318 (w), 1298 (vw), 1235 (w), 1188 (w), 1162 (w), 1145 (vw), 1092 (w), 1075 (w), 1039 (w), 1011 (m), 1000 (w), 988 (m), 935 (w), 901 (w), 868 (w), 842 (s), 810 (m), 795 (w), 768 (m), 650 (s), 476 (w), 430 (w), 310 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{23}ClPt$: C, 44.59; H, 5.06; Cl, 7.74. Found: C, 44.70, 44.61; H, 5.12, 5.08; Cl, 7.88, 7.74.

***cis*-Chloro(3,5-dimethylbenzyl)[bis(dicyclohexylphosphino)ethane]platinum(II).** A 100-mL round-bottomed flask with a side arm was equipped with a pressure-adjusted addition funnel and a stirring bar. The flask was charged with *cis*-chloro(3,5-dimethylbenzyl)(1,5-cyclooctadiene)platinum(II) (0.127 g, 0.278 mmol) and purged with argon. The platinum complex was dissolved in 25 mL of degassed CH_2Cl_2; the addition funnel was charged with a solution of bis(dicyclohexylphosphino)ethane (0.15 g, 0.35 mmol) in 25 mL of CH_2Cl_2. The bis(phosphine) solution was added at room temperature under argon. After 2 h, the solvent was removed by rotary evaporation; the white solid was recrystallized from acetone. Cooling the solution to −10 °C produced colorless crystals. The product was isolated by suction filtration; a small second crop was recovered from the mother liquor. The crystals were ground between a mortar and pestle and dried in vacuo at 69 °C (0.025 Torr). The yield of white powder, mp (capillary sealed under argon) 255–256 °C, was 0.203 g (0.263 mmol, 95%). ^{1}H NMR (CD_2Cl_2): δ 6.93 (br s, 2 H), 6.52 (br s, 1 H), 2.68 (dd with platinum satellites, $J_{P-H} = 3$, $J_{P'-H} = 9$, $J_{Pt-H} = 71$ Hz, 2 H), 2.4–1.0 (m, 54 H; includes s at δ 2.22). ^{31}P NMR (CD_2Cl_2): δ 65.3 (s with platinum satellites, $J_{Pt-P} = 1805$ Hz), 53.7 (s with platinum satellites, $J_{Pt-P} = 4189$ Hz). IR (neat): 2940 (vs), 2862 (vs), 1599 (s), 1452 (s), 1422 (w), 1392 (w), 1380 (w), 1350 (w), 1333 (w), 1310 (sh), 1300 (w), 1275 (w), 1212 (w), 1200 (sh), 1188 (w), 1178 (w), 1165 (w), 1120 (w), 1095 (w), 1080 (w), 1055 (w), 1045 (w), 1030 (vw), 1010 (m), 920 (w), 890 (w), 870 (w), 859 (m), 840 (m), 825 (w), 795 (w), 762 (w), 750 (w), 735 (sh), 703 (w), 670 (m), 652 (w), 610 (w), 555 (m), 520 (w), 490 (w), 475 (w) cm^{-1}. Anal. Calcd for $C_{35}H_{59}ClP_2Pt$: C, 54.43; H, 7.70; Cl, 4.59; P, 8.02. Found: C, 54.53, 54.44; H, 7.69, 7.74; Cl, 4.66, 4.69; P, 7.94, 7.88.

***cis*-(3,5-Dimethylbenzyl)hydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (10).** A 100-mL recovery flask equipped with a stirring bar was charged with *cis*-chloro(3,5-dimethylbenzyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (0.151 g, 0.196 mmol) and purged with argon. The complex was dissolved in 15 mL of THF and treated with a solution of $Na[HB(OMe)_3]$ (0.122 g, 0.955 mmol) in 15 mL of THF. The reaction solution became cloudy almost immediately. After 1 h at room temperature, the reaction was quenched at 0 °C with distilled water. Diethyl ether was added to the solution, and the organic layer was separated. The aqueous layer was extracted with ether; the combined organic layers were washed with water, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The yellow oil was dissolved in the minimum volume of THF; an equal volume of methanol was added, and the solution was cooled to −10 °C. The colorless crystals were recrystallized a second time. The product was isolated by suction filtration and dried over KOH in vacuo (0.025 Torr). The yield of colorless crystals, mp (capillary sealed under argon) 170 °C dec, was 49.2 mg (66.7 μmol, 34%). ^{1}H NMR (CD_2Cl_2): δ 6.76 (br s with platinum satellites, $J_{Pt-H} = 11$ Hz, 2 H), 6.38 (br s, 1 H), 3.05 (dd with platinum satellites, $J_{P-H} = 8$, $J_{P'-H} = 10$, $J_{Pt-H} = 97$ Hz, 2 H), 2.2–1.1 (m, 54 H; includes s at δ 2.19), −1.44 (dd with platinum satellites, $J_{P-H} = 18$, $J_{P'-H} = 190$, $J_{Pt-H} = 1122$ Hz, 1 H). ^{31}P NMR (CD_2Cl_2): δ 73.5 (s with platinum satellites, $J_{Pt-P} = 1852$ Hz), 63.3 (s with platinum satellites, $J_{Pt-P} = 1819$ Hz). IR (neat): 2928 (s), 2860 (s), 1980 (m), 1600 (m), 1450 (m), 1415 (w), 1390 (w), 1375 (w), 1350 (w), 1330 (w), 1298 (w), 1272 (w), 1200 (w), 1185 (sh), 1175 (w), 1115 (w), 1005 (w), 918 (w), 890 (w), 855 (w), 840 (w), 820 (w), 798 (w), 745 (w), 660 (w), 540 (w), 518 (w) cm^{-1}. Anal. Calcd for $C_{35}H_{60}P_2Pt$: C, 56.97; H, 8.20; P, 8.40. Found: C, 57.19, 57.09; H, 7.94, 8.03; P, 8.44, 8.35.

(Diphenylacetylene)[bis(dicyclohexylphosphino)ethane]platinum(0) (11). The complex was prepared by the thermolysis of **1** in cyclohexane containing diphenylacetylene.[23]

***cis*-Bis(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II).** A 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 purged with argon. The flask was charged with a solution of 3,3-dimethyl-1-butyne (3.0 mL, 2.0 g, 24 mmol) in 20 mL of THF; the addition funnel was charged with ethereal methyllithium (11 mL, 1.36 M, 15 mmol). The methyllithium was added at 0 °C; methane evolved immediately. The ice bath was removed, and the colorless solution was stirred at room temperature for 1 h.

A 250-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 dichloro[bis(dicyclohexylphosphino)ethane]platinum(II) (1.04 g, 1.51 mmol) and purged with argon. The platinum complex was suspended in 50 mL of THF; the solution of (3,3-dimethyl-1-butynyl)lithium was transferred via cannula to the addition funnel. The lithium reagent was added at −78 °C, and the reaction mixture was allowed to warm gradually to −20 °C. The mixture became homogeneous at −30 °C and then became slightly cloudy again. The reaction was quenched at −20 °C with aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether; the combined organic layers were washed with distilled water and brine, dried over $MgSO_4$, and concentrated to dryness by rotary evaporation. The residue was recrystallized from warm acetone; cooling the solution to −10 °C produced colorless cubes. The product was isolated by suction filtration; a small second crop was isolated from the mother liquors. The crystals were ground between a mortar and pestle and dried in vacuo at 79 °C (0.030 Torr). The yield of white powder, mp (capillary sealed under argon) ca. 260 °C dec (without melting), was 0.977 g (1.25 mmol, 83%). ^{1}H NMR (CD_2Cl_2): δ 2.28 (m, 4 H), 2.12 (m, 4 H), 1.82 (br s, 8 H), 1.74–1.6 (m, 12 H), 1.54 (m, 4 H), 1.37–1.10 (m, 34 H; includes s at δ 1.25). ^{31}P NMR (CD_2Cl_2): δ 62.0 (s with platinum satellites, $J_{Pt-P} = 2244$ Hz). IR (KBr): 2960 (sh), 2930 (s), 2855 (s), 2120 (w), 1475 (sh), 1465 (sh), 1450 (s), 1422 (w), 1415 (w), 1389 (w), 1360 (m), 1350 (w), 1333 (w), 1308 (w), 1298 (w), 1270 (w), 1250 (s), 1202 (m), 1185 (w), 1175 (w), 1125 (w), 1114 (w), 1080 (w), 1075 (w), 1055 (w), 1045 (w), 1030 (w), 1008 (m), 920 (w), 895 (w), 870 (w), 855 (m), 825 (w), 800 (w), 750 (m), 668 (w), 650 (w), 543 (s), 520 (w), 488 (w), 470 (w), 440 (w), 412 (w), 350 (vw), 300 (w) cm^{-1}. Anal. Calcd for $C_{33}H_{66}P_2Pt$: C, 58.52; H, 8.53; P, 7.94. Found: C, 58.49, 58.40; H, 8.56, 8.61; P, 7.90.

***cis*-(3,3-Dimethyl-1-butynyl)iodo[bis(dicyclohexylphosphino)ethane]platinum(II).** A 100-mL recovery flask equipped with a stirring bar was charged with a solution of bis(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (0.977 g, 1.25 mmol) in 40 mL of THF. The flask was then fitted with a pressure-adjusted addition funnel charged with a solution of iodine (0.322 g, 1.27 mmol) in 40 mL of THF. The iodine solution was added slowly at 0 °C; the red color of the iodine disappeared immediately. The progress of the reaction was monitored carefully by TLC. When ca. 3 mL of the iodine solution remained, TLC indicated that only a trace of starting material remained, and addition was discontinued. The solvent was removed by rotary evaporation, leaving a yellow oil, which solidified upon addition of pentane. The product was purified by flash chromatography on silica using 2/1 hexane/THF as the eluant until TLC indicated that all of the *cis*-(3,3-dimethyl-1-butynyl)iodo[bis(dicyclohexylphosphino)ethane]platinum(II) had eluted. Neat THF was used to elute the byproduct, *cis*-diiodo[bis(dicyclohexylphosphino)ethane]platinum(II). The byproduct was recrystallized from warm $CHCl_3$/hexane; colorless crystals formed upon cooling the solution to −10 °C. Both products were dried over KOH in vacuo at 79 °C (0.05 Torr). The yield of *cis*-(3,3-dimethyl-1-butynyl)iodo[bis(dicyclohexylphosphino)ethane]platinum(II), mp (capillary sealed under argon) ca. 200 °C dec (without melting), was 0.375 g (0.454 mmol, 36%). ^{1}H NMR (CD_2Cl_2): δ 2.55–2.35 (m, 4 H), 2.25–2.1 (m, 4 H), 1.9–1.1 (m, 49 H; includes s at δ 1.25). ^{31}P NMR (CD_2Cl_2): δ 62.7 (s with platinum satellites, $J_{Pt-P} = 3463$ Hz), 61.3 (s with platinum satellites, $J_{Pt-P} = 2274$ Hz). IR (KBr): 2935 (s), 2858 (s), 1450 (m), 1418 (w), 1390 (vw), 1360 (w), 1330 (w), 1308 (w), 1300 (w), 1275 (w), 1250 (m), 1204 (w), 1184 (w), 1176 (w), 1128 (sh), 1118 (w), 1078 (w), 1052 (w), 1045 (w), 1030 (w), 1008 (m), 920 (w), 892 (w), 870 (w), 855 (m), 828 (w), 802 (w), 749 (m), 670 (m), 650 (w), 545 (m), 520 (w), 490 (sh), 474 (w), 440 (w), 410 (w) cm^{-1}. MS (EI) *m/e* (relative intensity): 810 (20), 809 (24), 808 (17; $^{194}M^+ - CH_4$), 730 (17), 729 (20), 728 (22), 727 (12), 726 (13), 685 (19), 684 (22), 683 (21), 606 (14), 605 (47), 604 (64), 603 (94), 602 (80), 601 (100), 600 (76), 599 (74), 598 (40), 597 (37), 596 (13), 594 (23), 580 (17), 534 (39), 523 (17), 522 (16), 521 (16), 520 (11), 519 (10), 516 (11), 513 (13), 452 (10), 441 (10), 440 (15), 439 (12), 438 (14), 436 (11), 360 (12). Anal. Calcd for $C_{32}H_{57}IP_2Pt$: C, 46.55; H, 6.96. Found: C, 46.41; H, 6.99.

The yield of diiodo[bis(dicyclohexylphosphino)ethane]platinum(II), mp (capillary sealed under argon) >260 °C, was 0.289 g (0.331 mmol, 26%). ^{1}H NMR (CD_2Cl_2): δ 2.7–2.5 (m, 4 H), 2.3–2.15 (br s, 4 H), 1.9–1.6 (m, 20 H), 1.6–1.1 (m, 20 H). ^{31}P NMR (CD_2Cl_2): δ 67.9 (s with platinum satellites, $J_{Pt-P} = 3378$ Hz). IR (KBr): 2925 (vs), 2850 (s), 1448 (s), 1420 (w), 1410 (w), 1348 (w), 1330 (w), 1295 (w), 1272 (m), 1210 (sh), 1202 (w), 1181 (w), 1172 (w), 1114 (w), 1080 (w), 1050 (w), 1045 (w), 1028 (w), 1005 (m), 919 (w), 890 (m), 868 (w), 852 (m), 821 (w), 795 (w), 755 (w), 745 (m), 730 (w), 670 (m), 651 (w), 541 (m), 518 (w), 490 (w), 472 (w), 440 (w), 405 (w), 375 (w), 360 (w). Anal. Calcd for $C_{26}H_{48}I_2P_2Pt$: C, 35.83; H, 5.55. Found: C, 35.65; H, 5.66.

(3,3-Dimethyl-1-butyne)[bis(dicyclohexylphosphino)ethane]platinum(0) (12). A 10-mm-o.d. Pyrex thermolysis tube containing **1** (0.101 g, 0.147 mmol) in a 0.72 M solution of 2,3-dimethyl-2-butene in cyclohexane (2.5 mL) was sealed under vacuum and heated at 69 °C for 2.5 h. The tube was cracked open, capped with a septum, and transferred via cannula to a 50-mL Schlenk flask. The solvent was removed in vacuo. The residual white powder was dissolved in 25 mL of diethyl ether; 3,3-dimethyl-1-butyne (0.50 mL, 0.33 g, 4.1 mmol) was added via syringe. The colorless solution was stirred at room temperature for ca. 16 h. The solvent was removed in vacuo, leaving a brittle white solid. The solid was dissolved in the minimum amount of ether; an equal volume of degassed methanol was added, and the solution was cooled to −10 °C. Colorless cubes formed upon cooling. After two more recrystallizations, the yield of colorless crystals, mp (capillary sealed under argon) ca. 180 °C dec, was 9 mg (12 mmol, 8%). ^{1}H NMR (C_6D_6): δ 8.04 (m, 1 H), 2.3–2.2 (m, 2 H), 2.1–1.9 (m, 4 H), 1.9–0.9 (m, 51 H; includes s at δ 1.63). ^{31}P NMR (C_6D_6): ABX spectrum superimposed on an AB spectrum, where X = ^{195}Pt; δ_A 68.4, δ_B 69.0, $J_{AB} = 49$, $J_{AX} = -2959$, $J_{BX} = -3152$ Hz.[76] IR (C_6D_6): 1670 (m), 1390 (m) cm^{-1}.[77] MS (EI) *m/e* (relative intensity): 700 (10), 699 (11), 698 (8; ^{194}M$^+$); 619 (6); 618 (21), 617 (25), 616 (86), 615 (100), 614 (87), 613 (20), 612 (18), 611 (10), 610 (8), 545 (7), 535 (10), 534 (19), 533 (46), 532 (49), 531 (36), 530 (12), 529 (11), 528 (7), 527 (6), 523 (10), 462 (38), 451 (11), 450 (14), 449 (15), 448 (10), 447 (11), 446 (6), 444 (9), 382 (12), 368 (8), 367 (9), 366 (6); 308 (5), 307 (6), 289 (7), 288 (5), 287 (6), 55 (11). Exact mass for $C_{32}H_{58}P_2Pt$ ($^{194.9662}$Pt): calcd, 698.3646; obsd, 698.3677.

***cis*-(3,3-Dimethyl-1-butynyl)hydrido[bis(dicyclohexylphosphino)ethane]platinum(II) (13).** An oven-dried Schlenk flask equipped with a stirring bar was charged with *cis*-(3,3-dimethyl-1-butynyl)iodo[bis(dicyclohexylphosphino)ethane]platinum(II) (0.113 g, 0.137 mmol). The flask was evacuated and back-filled with argon three times; the platinum complex was then dissolved in 10 mL of THF. A solution of Na[HB(OMe)$_3$] (55 mg, 0.43 mmol) in 10 mL of THF was added via cannula, and the slightly cloudy mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo, leaving a gummy solid. The residue was extracted with hexane; the extracts were filtered through a fine frit. The solvent was removed under vacuum, leaving a white solid. Attempts to purify the product by recrystallization caused extensive decomposition, but in the absence of oxygen and protic solvents, the complex is stable indefinitely. Mp (capillary sealed under argon): 185–200 °C dec. ^{1}H NMR (C_6D_6): δ 2.35–2.15 (m, 4 H), 1.95–0.9 (m, 53 H; includes s at δ 1.55), –0.49 (dd with platinum satellites, $J_{P-H} = 17$, $J_{P'-H} = 195$, $J_{Pt-H} = 1072$ Hz, 1 H). ^{31}P NMR (C_6D_6): δ 74.0 (s with platinum satellites, $J_{Pt-P} = 2405$ Hz), 64.6 (s with platinum satellites, $J_{Pt-P} = 1640$ Hz). IR (C_6D_6): 2000 cm^{-1}. MS (CI, isobutane) *m/e* (relative intensity): 702 (24), 701 (39), 700 (93), 699 (100), 698 (75; ^{194}M$^+$), 618 (27), 617 (33), 616 (70), 615 (74), 614 (67), 613 (28), 612 (14), 533 (18), 532 (18), 531 (14), 211 (31), 210 (29), 209 (11). Exact mass for $C_{32}H_{58}P_2Pt$ ($^{194.9662}$Pt): calcd, 698.3646; obsd, 698.3594.

(*E*)-1-Iodo-3,3-dimethyl-1-butene was prepared according to the literature procedure.[78] ^{1}H NMR ($CDCl_3$): δ 6.55 (d, $^{3}J_{H-H} = 15$ Hz, 1 H), 5.93 (d, $^{3}J_{H-H} = 15$ Hz, 1 H), 1.00 (s, 9 H).

[(*E*)-3,3-Dimethyl-1-butenyl]magnesium iodide was prepared by slow addition of a THF solution of the iodide to mixture of magnesium turnings in THF. The reaction mixture was heated under reflux for 3 h after the addition was complete. Titration indicated a yield of 78%.

[(*E*)-3,3-Dimethyl-1-butenyl]lithium was prepared from lithium dispersion and the corresponding iodide in diethyl ether in 38% yield.

***cis*-[(*E*)-3,3-Dimethyl-1-butenyl](3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (14).** A 250-mL three-necked round-bottomed flask equipped with a stirring bar, a Liebig condenser topped by an argon inlet, and a pressure-adjusted addition funnel was charged with *cis*-(3,3-dimethyl-1-butynyl)iodo[bis(dicyclohexylphosphino)ethane]platinum(II) (0.563 g, 0.682 mmol) and purged with argon. The platinum complex was then dissolved in 100 mL of THF; the addition funnel was charged with a solution of [(*E*)-3,3-dimethyl-1-butenyl]magnesium iodide in THF (26 mL, 0.18 M, 4.7 mmol). The Grignard reagent was added at −78 °C; the reaction solution was allowed to warm slowly to 25 °C. The slightly cloudy, pale yellow reaction mixture was stirred at room temperature overnight. The reaction was quenched at 0 °C with aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether; the combined organic extracts were washed with distilled water and brine and dried over $MgSO_4$. Removal of the solvent left a white amorphous solid. The ^{1}H and ^{31}P NMR spectra of the crude product were consistent with *cis*-[(*E*)-3,3-dimethyl-1-butenyl](3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (**14**).

The solid was dissolved in the minimum volume of warm diethyl ether. The volume of the solution was reduced by heating; two volumes of methanol were added, and the solution was cooled to −10 °C. Fine white needles were isolated by suction filtration; a second crop was recovered from the mother liquor. After a second recrystallization, the product was dried over KOH in vacuo. The yield of fine needles, mp (capillary sealed under argon) 239–245 °C dec, was 26 mg; the second crop yielded 28 mg of off-white needles, mp (capillary sealed under argon) ca. 230–240 °C. The mother liquors were concentrated to dryness, and the residue was dissolved in diethyl ether and 95% ethanol. The volume of the solution was reduced with a stream of argon. The white solid that precipitated was collected by suction filtration. The process was repeated; the white crystals were dried over KOH in vacuo. The yield of product, mp (capillary sealed under argon) ca. 245 °C dec, was 55 mg. The combined yield was 0.109 g (0.139 mmol, 20%).

The first crop of crystals proved to be *cis*-[(*Z*)-3,3-dimethyl-1-butenyl](3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II). ^{1}H NMR (CD_2Cl_2): δ 6.88 (ddd, $^{3}J_{H-H} = 13$, $J_{P-H} = 4$, $J_{P'-H} = 6$ Hz, 1 H), 6.62 (ddd with platinum satellites, $^{3}J_{H-H} = 13$, $J_{P-H} = 2$, $J_{P'-H} = 21$, $J_{Pt-H} = 117$ Hz, 1 H), 2.35–1.9 (m, 8 H), 1.9–1.5 (m, 24 H), 1.5–1.15 (m, 34 H; includes two s at δ 1.21 and 1.19). ^{31}P NMR (CD_2Cl_2): δ 62.1 (s with platinum satellites, $J_{Pt-P} = 1621$ Hz), 55.3 (s with platinum satellites, $J_{Pt-P} = 2452$ Hz). IR (KBr): 2920 (vs), 2850 (vs), 2680 (w), 2110 (w), 1472 (sh), 1448 (s), 1420 (sh), 1408 (w), 1385 (w), 1351 (m), 1335 (s), 1305 (sh), 1292 (w), 1270 (w), 1248 (s), 1198 (s), 1190 (w), 1182 (w), 1120 (sh), 1110 (w), 1085 (w), 1048 (w), 1028 (sh), 1004 (m), 915 (w), 890 (m), 860 (sh), 850 (m), 820 (w), 792 (m), 740 (m), 710 (w), 662 (m), 642 (w), 618 (w), 537 (s), 525 (sh), 515 (w), 482 (w), 467 (w), 435 (w), 398 (w) cm^{-1}. Exact mass for $C_{38}H_{68}P_2Pt$ ($^{194.9662}$Pt): calcd, 780.4429; obsd, 780.4403. Anal. Calcd for $C_{38}H_{68}P_2Pt$: C, 58.37; H, 8.76. Found: C, 57.92; H, 8.75.

The second and third crops consisted mainly of *cis*-[(*E*)-3,3-dimethyl-1-butenyl](3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II); a small amount of the *Z* isomer was also present. ^{1}H NMR (CD_2Cl_2): δ 6.94 (ddd, $J_{P-H} = 6$, $J_{P'-H} = 10$, $^{3}J_{H-H} = 17$, 1 H), 6.07 (dd with platinum satellites, $^{3}J_{H-H} = 17$, $J_{P-H} = 9$, $J_{Pt-H} = 75$ Hz, 1 H), 2.3–1.95 (m, 8 H), 1.9–1.5 (m, 22 H), 1.4–1.15 (m, 27 H; includes s at δ 1.24), 1.03 (s, 9 H). ^{31}P NMR (CD_2Cl_2): δ 63.2 (s with platinum satellites, $J_{Pt-P} = 1598$ Hz), 58.8 (s with platinum satellites, $J_{Pt-P} = 2453$ Hz). IR (KBr): identical with the IR spectrum of the *Z* isomer except for an additional peak at 978 cm^{-1} indicative of a trans disubstituted olefin.[79] Exact mass for $C_{38}H_{68}P_2Pt$ ($^{194.9662}$Pt): calcd, 780.4429; obsd, 780.4399.[80]

When *cis*-(3,3-dimethyl-1-butynyl)iodo[bis(dicyclohexylphosphino)ethane]platinum(II) is treated with (3,3-dimethyl-1-butenyl)lithium, the product is *cis*-bis(3,3-dimethyl-1-butenyl)[bis(dicyclohexylphosphino)ethane]platinum(II). The yield of fine white needles, mp (capillary sealed under argon) 147–149 °C, is 25% after three recrystallizations from 1/1 v/v diethyl ether/methanol at −10 °C. ^{1}H NMR (C_6D_6): δ 7.53 (dt, $J_{P-H} = 5$, $^{3}J_{H-H} = 18$ Hz, 2 H), 5.91 (ddd with platinum satellites, $J_{P-H} = 2$, $J_{P'-H} = 9$, $^{3}J_{H-H} = 18$, $J_{Pt-H} = 75$ Hz, 1 H), 2.2–1.95 (m, 8 H), 1.75–1.0 (m, 58 H; includes s at δ 1.35). ^{31}P NMR (C_6D_6): δ 59.1 (s with platinum satellites, $J_{Pt-P} = 1734$ Hz). IR (KBr): 2930 (s), 2855 (s), 1475 (sh), 1450 (m), 1420 (w), 1415 (w), 1388 (w), 1359 (m), 1332 (sh), 1306 (w), 1298 (w), 1271 (w), 1254 (m), 1420 (w), 1415 (w), 1388 (w), 1359 (m), 1332 (sh), 1306 (w), 1298 (w), 1271 (w), 1254 (m), 1210 (sh), 1198 (w), 1182 (w), 1172 (w), 1160 (sh), 1123 (sh), 1112 (w), 1076 (w), 1052 (w), 1045 (w), 1025 (sh), 1005 (m), 980 (m), 915 (w), 891 (w), 869 (w), 852 (m), 821 (w), 794 (w), 776 (sh), 748 (m), 660 (w), 646 (sh), 540 (m), 519 (w), 490 (w), 460 (w), 440 (w), 400 (w), 378 (vw), 355 (vw), 330 (vw) cm^{-1}. Anal. Calcd for $C_{38}H_{70}P_2Pt$: C, 58.22; H, 9.00; P, 7.90. Found: C, 58.57; H, 9.17; P, 7.78.

(3,3-Dimethyl-1-butene)[bis(dicyclohexylphosphino)ethane]platinum(0) (15). A 10-mm-o.d. Pyrex thermolysis tube containing **1** (0.101 g, 0.147 mmol) in a 0.73 M solution of 3,3-dimethyl-1-butene in cyclohexane (2.5 mL) was sealed under vacuum and heated at 69 °C for 3 h. The tube was cracked open and capped with a septum; the colorless solution was transferred to a Schlenk flask, and the solvent was removed in vacuo. The white powder was dissolved in the minimum volume of degassed hexane and cooled to −80 °C. The product precipitated out of solution as a white powder. After three recrystallizations, the complex was dried under vacuum (0.05 Torr). The yield of air-sensitive white powder, mp

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(77) The IR and NMR spectra of **12** are characteristic and diagnostic of alkyne coordination complexes. In particular, the alkyne hydrogen appears as an ABMX pattern in the ^{1}H NMR spectrum and the stretching frequency of the coordinated C–C triple bond (1670 cm^{-1}) is dramatically reduced relative to that of the free alkyne. See: Empsall, H. D.; Shaw, B. L.; Stringer, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 185–188. Nelson, J. H.; Jonassen, H. B.; Roundhill, D. M. *Inorg. Chem.* **1969**, *8*, 2591–2596. Nelson, J. H.; Jonassen, H. B. *Coord. Chem. Rev.* **1971**, *6*, 27–63. Nelson, J. H.; Reed, J. J. R.; Jonassen, H. B. *J. Organomet. Chem.* **1971**, *29*, 163–168.

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(80) The causes of the *E–Z* isomerization are not clear; either heat- or oxygen-promoted reactions may be responsible. The important point is that **14**, the product of **13** and 3,3-dimethyl-1-butyne, is *cis*-[(*E*)-3,3-dimethyl-1-butenyl](3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II).

(capillary sealed under argon) ca. 85 °C, was 33 mg (0.47 mmol, 32%). ^{1}H NMR (C_6D_6): δ 3.03 (m with platinum satellites, J_{Pt-H} = 65 Hz, 1 H), 2.4–2.3 (two overlapping m, each with platinum satellites, J_{Pt-H} = 67, 61 Hz, 2 H), 2.25–2.1 (m, 2 H), 2.05–1.9 (m, 3 H), 1.9–1.5 (m, 19 H), 1.5–1.0 (m, 33 H; includes s at δ 1.43). ^{31}P NMR (C_6D_6): δ 73.1 (d with platinum satellites, J_{P-P} = 71, J_{Pt-P} = 2896 Hz), 68.3 (d with platinum satellites, J_{P-P} = 71, J_{Pt-P} = 3233 Hz). MS (EI) *m/e* (relative intensity): 702 (4), 701 (5), 700 (4; $^{194}M^+$), 619 (7), 618 (26), 617 (30), 616 (90), 615 (100), 614 (87), 613 (20), 611 (34), 534 (16), 533 (36), 532 (39), 531 (29), 530 (11), 528 (19), 462 (27), 451 (9), 450 (10), 449 (11), 448 (8), 447 (7), 368 (5), 367 (6), 308 (9), 307 (17), 84 (26), 69 (11). Exact mass for $C_{32}H_{60}P_2Pt$ ($^{194.9662}$Pt): calcd, 700.3803; obsd, 700.3818.

[2-(2-Propyl)-3-methyl-1-butene][bis(dicyclohexylphosphino)ethane]platinum(0) (16). A 10-mm-o.d. Pyrex thermolysis tube containing **1** (0.104 g, 0.151 mmol) in a 0.74 M solution of 2-(2-propyl)-3-methyl-1-butene in cyclohexane (2.5 mL) was heated at 69 °C for 2.5 h. The tube was cracked open and capped with a septum; the contents of the tube were transferred via cannula to a Schlenk flask, and the solvent was removed in vacuo. The complex was dissolved in the minimum amount of degassed hexane and transferred to a recovery flask. The solvent volume was reduced in a stream of argon until colorless crystals precipitated. Additional crystals formed upon cooling the mixture to −10 °C. The solvent was removed via cannula, and the product was washed with cold hexane. The yield of colorless, air-sensitive crystals, mp (capillary sealed under argon) 177–178 °C dec, was 23 mg (0.032 mmol, 21%). ^{1}H NMR (C_6D_6): δ 3.14 (m, 2 H), 2.42 (dd with platinum satellites, J_{P-H} = 6, $J_{P'-H}$ = 8, J_{Pt-H} = 58 Hz, 2 H), 2.1–1.9 (m, 5 H), 1.9–1.5 (m, 18 H), 1.4–1.0 (m, 37 H; includes a "t" at δ 1.29, J = 6 Hz[81]). ^{31}P NMR (C_6D_6): δ 71.7 (d with platinum satellites, J_{P-P} = 74 Hz, J_{Pt-P} = 2770 Hz), 66.2 (d with platinum satellites, J_{P-P} = 74 Hz, J_{Pt-P} = 3295 Hz). MS (EI) *m/e* (relative intensity): 731 (2), 730 (3), 729 (3), 728 (2; $^{194}M^+$), 716 (2), 715 (3), 714 (3), 713 (2), 691 (2), 690 (2), 689 (2), 640 (6), 639 (6), 607 (7), 606 (24), 605 (33), 604 (91), 603 (100), 602 (89), 601 (25), 600 (21), 599 (12), 598 (10), 524 (12), 523 (21), 522 (52), 521 (59), 520 (43), 519 (14), 518 (16), 517 (8), 516 (13), 453 (34), 442 (13), 441 (17), 440 (17), 439 (12), 438 (12), 437 (6), 436 (5), 332 (13). Exact mass for $C_{34}H_{64}P_2Pt$ ($^{194.9662}$Pt): calcd, 728.4116; obsd, 728.4158. Anal. Calcd for $C_{34}H_{64}P_2Pt$: C, 55.95; H, 8.84. Found: C, 56.03; H, 8.73.

(3,3-Dimethyl-2-butene)[bis(dicyclohexylphosphino)ethane]platinum(0) (17), A 10-mm-o.d. Pyrex thermolysis tube containing **1** (0.106 g, 0.154 mmol) in a 0.77 M solution of 2,3-dimethyl-2-butene in cyclohexane (2.5 mL) was heated at 69 °C for 2.3 h. The tube was cracked open and capped with a septum; the pale red reaction solution was transferred via cannula to a Schlenk flask. The solvent was removed in vacuo, leaving a white powder. The product was dissolved in the minimum volume of diethyl ether; an equal volume of degassed methanol was added, and the solution was cooled to −10 °C. White platelike crystals formed upon cooling. After two more recrystallizations, the yield of air-sensitive white crystals, mp (capillary sealed under argon) 185–188 °C dec, was 10 mg (0.014 mmol, 9%). ^{1}H NMR (C_6D_6): δ 2.34 ("t" with platinum satellites, J_{P-H} = 5, J_{Pt-H} = 47 Hz, 12 H), 2.05–1.5 (m, 24 H), 1.5–1.05 (m, 24 H). ^{31}P NMR (C_6D_6): δ 69.2 (s with platinum satellites, J_{Pt-P} = 2803 Hz). MS (EI) *m/e* (relative intensity): 702 (3), 701 (3), 700 (2; $^{194}M^+$), 619 (7), 618 (27), 617 (31), 616 (86), 615 (100), 614 (86), 613 (22), 612 (20), 611 (11), 535 (12), 534 (23), 533 (55), 532 (63), 531 (47), 530 (14), 529 (15), 523 (11), 462 (41), 451 (14), 450 (17), 449 (18), 448 (11), 447 (11), 382 (19), 368 (10), 367 (10), 307 (10). Exact mass for $C_{32}H_{60}P_2Pt$ ($^{194.9662}$Pt): calcd, 700.3803; obsd, 700.3812.

Bis[bis(dicyclohexylphosphino)ethane]platinum(0) (18). Thermolysis of **1** in a solution of bis(dicyclohexylphosphino)ethane in THF yielded **16** as colorless crystals.[23]

[Bis(dicyclohexylphosphino)ethane](tricyclohexylphosphine)platinum(0) (19). A 10-mm-o.d. Pyrex thermolysis tube containing **1** (0.1035 g, 0.150 mmol) in a 0.093 M solution of tricyclohexylphosphine in cyclohexane (2.5 mL) was heated at 69 °C for 2.5 h. The tube was cracked open and capped with a septum; the magenta solution was transferred via cannula to a Schlenk flask. The solvent was removed in vacuo, and the residual oil was dissolved in the minimum volume of hexane. The solution was transferred to a recovery flask, and the volume of the solution was reduced by passing a stream of argon over the solution. Cooling the solution to −10 °C produced fine magenta crystals. After three recrystallizations, the yield of air-sensitive crystals, mp (capillary sealed under argon) 178–182 °C, was 34 mg (0.038 mmol, 25%). ^{1}H NMR (C_6D_6): δ 2.3–1.0 (m). ^{31}P NMR (C_6D_6): AB_2X spectrum superimposed on an AB_2 spectrum where X = ^{195}Pt; δ_A 78.7, δ_B 93.4, J_{AB} = 161, J_{AX} = 5172, J_{BX} = 3448 Hz.[76] Anal. Calcd for $C_{44}H_{81}P_3Pt$: C, 58.84; H, 9.09; P, 10.35. Found: C, 55.68; H, 8.50; P, 11.07. The discrepancy between the calculated and observed percentages of C, H, and P in **19** is probably due to impurities formed by the reaction of **19** with oxygen or water. Attempts to analyze the complex by mass spectroscopy failed.

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Registry No. **1**, 105373-14-6; **2**, 102286-36-2; **3**, 105373-22-6; **4**, 105373-21-5; **5**, 111848-49-8; **6**, 111848-50-1; **7**, 105373-20-4; **8**, 105373-17-9; **9**, 105373-23-7; **10**, 105373-24-8; **11**, 111848-25-0; **12**, 105399-78-8; **13**, 105373-19-1; **14**, 111848-51-2; **15**, 105373-18-0; **16**, 111848-52-3; **17**, 111848-53-4; **18**, 105373-15-7; **19**, 111848-54-5; CH_4, 74-82-8; $SiMe_4$, 75-76-3; PhC≡CPh, 501-65-5; $(CH_3)_3C{\equiv}CH$, 917-92-0; $CH_2{=}CHC(CH_3)_3$, 558-37-2; $((CH_3)_2CH)_2C{=}CH_2$, 111823-35-9; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; PCy_3, 2622-14-2; neopentane, 463-82-1; 1,1,2,2-tetramethylcyclopropane, 4127-47-3; cyclopentane, 287-92-3; cyclohexane, 110-82-7; benzene, 71-43-2; mesitylene, 108-67-8; *cis*-(hydrido)[methyl(1,2,2-trimethylcyclopropyl)][bis(dicyclohexylphosphino)ethane]platinum(II), 111848-55-6; (ethylene)[bis(dicyclohexylphosphino)ethane]platinum(0), 102286-39-5; dichloro[bis(dicyclohexylphosphino)ethane]platinum(II), 90667-70-2; dichloro(1,5-cyclooctadiene)platinum(II), 12080-32-9; bis(dicyclohexylphosphino)ethane, 23743-26-2; 2,3-dimethyl-2-butene, 563-79-1; 1,1-dibromo-2,2,3,3-tetramethylcyclopropane, 22715-57-7; 1-bromo-2,2,3,3-tetramethylcyclopropane, 3815-06-3; 1-lithio-2,2,3,3-tetramethylcyclopropane, 75135-80-7; *cis*-(chloro)(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-56-7; cyclopentylmagnesium chloride, 32916-51-1; *cis*-(chloro)(cyclopentyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-57-8; *cis*-(chloro)(cyclohexyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-58-9; cyclohexylmagnesium bromide, 931-50-0; chloro(methyl)(1,5-cyclooctadiene)platinum(II), 50978-00-2; *cis*-(chloro)(methyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-59-0; [(trimethylsilyl)methyl]lithium, 1822-00-0; *cis*-bis[(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II), 36223-69-5; *cis*-(chloro)[(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II), 111848-60-3; *cis*-(chloro)-[(trimethylsilyl)methyl][bis(dicyclohexylphosphino)ethane]platinum(II), 111848-61-4; *cis*-(chloro)(2,4,6-trimethylphenyl)(1,5-cyclooctadiene)-platinum(II), 67407-57-2; (2,4,6-trimethylphenyl)magnesium bromide, 2633-66-1; (3,5-dimethylbenzyl)magnesium bromide, 111823-36-0; 3,5-dimethylbenzyl bromide, 27129-86-8; *cis*-bis(3,5-dimethylbenzyl)(1,5-cyclooctadiene)platinum(II), 111848-62-5; *cis*-(chloro)(3,5-dimethylbenzyl)(1,5-cyclooctadiene)platinum(II), 111848-63-6; *cis*-(chloro)(3,5-dimethylbenzyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-64-7; *cis*-bis(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-65-8; *cis*-(3,3-dimethyl-1-butynyl)(iodo)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-66-9; *cis*-diiodo[bis(dicyclohexylphosphino)ethaneplatinum(II), 111848-67-0; [(*E*)-3,3-dimethyl-1-butenyl]magnesium iodide, 111823-37-1; (*E*)-1-iodo-3,3-dimethyl-1-butene, 61382-45-4; [(*E*)-3,3-dimethyl-1-butenyl]lithium, 111823-38-2; *cis*-[(*Z*)-3,3-dimethyl-1-butenyl](3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111954-69-9; (3,3-dimethyl-1-butenyl)lithium, 109050-52-4; *cis*-bis(3,3-dimethyl-1-butenyl)[bis(dicyclohexylphosphino)ethane]platinum(II), 111848-68-1.

Supplementary Material Available; Spectral and analytical data for bis(2,2,3,3-tetramethylcyclopropyl)(1,5-cyclooctadiene)platinum(II), chloro(2,2,3-trimethyl-3-methoxybutyl)(1,5-cyclooctadiene)platinum(II), *cis*-bromo(2,2,3,3-tetramethylcyclopropyl)[bis(dicyclohexylphosphino)ethane]platinum(II), dibromo[bis(dicyclohexylphosphino)ethane]platinum(II), (1-chloro-3,3-dimethyl-1-butyne)[bis(dicyclohexylphosphino)ethane]platinum(0), and *cis*-chloro(3,3-dimethyl-1-butynyl)[bis(dicyclohexylphosphino)ethane]platinum(II) (2 pages). Ordering information is given on any current masthead page.

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(81) This peak appears as a doublet of doublets in CD_2Cl_2 due to coupling to the cis and trans phosphorus atoms. Apparently J_{P-H} and $J_{P'-H}$ are approximately equal in C_6D_6 so the signal appears to be a triplet.