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η^2-Coordination and C−H Activation of Electron-Poor Arenes

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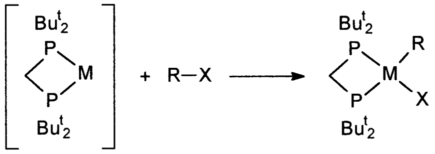
The reductive elimination of neopentane from (dtbpm)Pt(Np)H (dtbpm = bis(di-*tert*-butylphosphino)methane, Np = neopentyl) results in the formation of the highly reactive intermediate [(dtbpm)Pt^0]. This species reacts with a variety of electron-deficient benzenes (1,4-bis(trifluoromethyl)benzene and 1,3,5-tris(trifluoromethyl)benzene) and biphenyls (3,5,4′-tris(trifluoromethyl)biphenyl and 3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl) to form η^2-arene complexes. X-ray crystallography confirms the η^2-bonding motif. The arene complexes all display broad ^{1}H NMR spectroscopic features at room temperature that sharpen considerably at lower temperatures. Thermolysis or photolysis of the arene complexes results in C−H activation and the formation of platinum(II) aryl hydride complexes. The products observed depend on whether the reaction is thermal or photolytic. Reaction with 4,4′-bis(trifluoromethyl)biphenyl yields two C−H activated products directly. Oxidative addition occurs at the 2 and 3 positions of the biphenyl in a 5:1 ratio, respectively. Continued heating of the mixture results in a second C−H activation to form a platinacyclopentane.

Introduction

Bis(phosphino)methanes have long been used in platinum transition metal chemistry.[1] The versions primarily used in the synthesis of most complexes have simple alkyl (methyl, ethyl, or isopropyl) or phenyl substituents on the phosphorus atoms. A notable vacancy in this series is the *tert*-butyl analogue, bis(di-*tert*-butylphosphino)methane (dtbpm). Presumably due to the arduous and unreliable nature of its synthesis, the use of this ligand in inorganic and organometallic syntheses and reactivity has been reported relatively infrequently. Notably, Hofmann and co-workers have made significant contributions to the literature in regards to the use of this ligand in various transition metal systems.[2] On the basis of the theoretical and experimental work published over the past decade we believed that certain systems containing the dtbpm ligand would prove useful in our studies of C−X bond activation processes (eq 1, X = H, C, F, S).



(1)

One report in particular described a platinum compound that appeared to be ideal for our investigations. Reductive elimination of neopentane from (dtbpm)Pt(Np)H (**1**, Np = neopentyl) yields an unsaturated L_2Pt^0 intermediate species.[2c] Theoretical studies predict that the small chelation angle due to a single methylene bridge between two phosphorus atoms will result in a significant increase in the energy of the HOMO and a decrease in the energy of the LUMO of the fragment.[2a] This perturbation of the frontier orbitals leads to the highly reactive nature of the intermediate. The *tert*-butyl substituents on the phosphorus atoms of the dtbpm ligand also provide key benefits: a sterically protected reactive pocket, stronger P−Pt bonds due to the increased basicity at phosphorus (in contrast to other $R_2PCH_2PR_2$ ligands, R = Me, ^{i}Pr, and Ph, which are frequently observed to form A-frame type dimeric compounds[1]), and substituents on phosphorus that disfavor intramolecular C−H activation. Although a definitive example of C−H activation by this intermediate has not yet been realized, insertion of the (dtbpm)-Pt fragment into C−Si, C−F, and C−C bonded substrates has been reported.[2]

Platinum complexes, among many other transition metal compounds, have long been studied in C−H activation processes[3] and C−H and C−C reductive elimination reactions.[4] More recent work has focused

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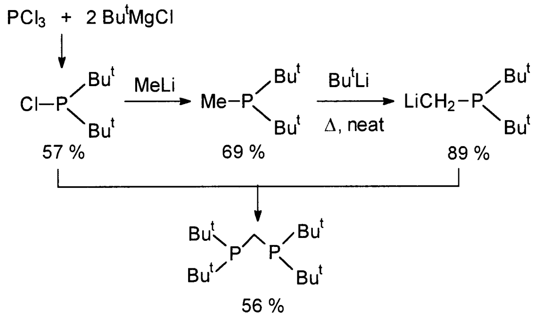
on electrophilic Pt(II) oxidation chemistry;[5–11] however, Pt^0 compounds have been known to activate a variety of hydrocarbons. In seminal work by Whitesides and coworkers in the late 1980s, C−H activation of aromatic and aliphatic alkanes by (dcpe)Pt(Np)H (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) was reported.[12] In the case of aromatic substrates, although not observed, there was clear experimental evidence for η^2-arene intermediates in the formation of aryl hydrides.

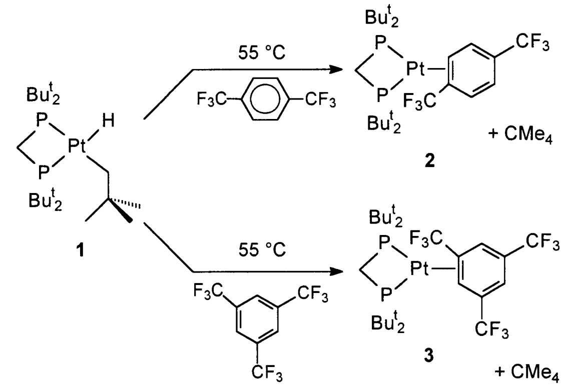
We have recently published accounts utilizing the dtbpm ligand in activating C−C bonds by compound **1**[13a,b] and the functionalization of C−C bonds by $[(dtbpm)RhCl]_2$.[13c] We now wish to report a more convenient synthesis of dtbpm and its application toward C−H bond activation in the L_2Pt^0 system. In particular, we have isolated and characterized an η^2-arene intermediate involved in the stepwise activation of an aryl C−H bond.

Results and Discussion

The reported synthesis of dtbpm requires the addition of excess ^tBuLi to a solution of bis(dichlorophosphino)methane.[14] The reaction is not clean, as a mixture of bis, tris, and tetrakis substituted diphosphinomethanes is formed. A less direct but more selective route employs the combination of $^tBu_2PCH_2Li$[15] and PCl^tBu_2 (Scheme 1), as has been reported in the patent literature.[16] Standard methodologies for the synthesis of (dtbpm)Pt(Np)H were used and have been previously reported.[2c,17]

Scheme 1





(2)

Reaction with Arenes. While the fragment [(dtbpm)Pt] does not react with benzene, trifluoromethyl-substituted benzenes react with (dtbpm)Pt(Np)H to yield η^2-arene or aryl hydride complexes, depending on the reaction conditions.[18] For instance, when compound **1** is heated at 55 °C in the presence of 20 equiv of 1,4-$C_6H_4(CF_3)_2$ or 1,3,5-$C_6H_3(CF_3)_3$ for 90 min, η^2-arene complexes **2** and **3**, respectively, are produced (eq 2). The ^1H NMR spectra of both products featured broad signals at room temperature. Cooling a THF-d_8 solution of compound **2** to −60 °C resolves the aromatic protons into four resonances at δ 7.10 (br s), 6.31 (d), 5.69 (br d with ^{195}Pt shoulders), and 3.72 (br t). The signal at 3.72 ppm has ^{195}Pt satellites that are partially buried by one of the residual solvent peaks and the signal due to the bridging methylene protons. This set of resonances is consistent with the arene being bound to the metal center in an unsymmetrical fashion. ^{19}F NMR and ^{31}P NMR spectroscopy also support this structural assignment. The ^{19}F NMR spectrum has two resonances at δ −61.3 and −65.2. The former has ^{195}Pt satellites ($^4J_{Pt-F}$

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[18] We also examined the reactivity of $C_6H_5CF_3$ and 1,3-$C_6H_4(CF_3)_2$ with (dtbpm)Pt(Np)H. The resulting ^1H and ^{31}P NMR spectra displayed a complex product mixture of Pt−H and Pt−Pt dimeric and monomeric compounds. We have been unable to determine the identity of the products thus far, although it is clear that a small amount of the "simple" C−H activated products, (dtbpm)Pt(aryl)H, have been formed.

= 88 Hz), whereas the latter is a simple singlet. Two signals are also expected in the ^{31}P NMR spectrum, but only a single resonance is observed at 50.4 ppm. Presumably the two phosphorus nuclei are coincidental, as higher order coupling is observed for the ^{195}Pt satellites. The downfield satellite appears as a quartet, and the upfield satellite appears as a singlet.

The aromatic protons in the ^{1}H NMR spectrum of compound **3** resolve into three distinct signals at −20 °C: δ 7.01 (br s), 6.02 (d with ^{195}Pt shoulders), and 3.72 (br d). Again, the ^{195}Pt satellites for the signal at 3.72 ppm are partially obscured. The ^{31}P NMR spectrum yields the expected two doublets at δ 47.9 and 46.7. The value $^{2}J_{\mathrm{P-P}}$ of 91 Hz is unusually large for a cis L_2Pt complex. However, larger J values are often observed when the signals are very close together as in this case. The appearance of the ^{195}Pt satellites is similar to that of compound **2**. Three resonances are observed for the three unique trifluoromethyl groups at δ −59.9, −64.0, and −64.4. Only the signal at −59.9 ppm is coupled to the platinum metal center ($^{3}J_{\mathrm{Pt-F}} = 81$ Hz).

A comparison can be made to the reaction of $C_6(CF_3)_6$ with $(PMe_3)_3$Pt and $(PEt_3)_3$Pt reported by Stone and coworkers nearly three decades ago.[19] An η^2-$C_6(CF_3)_6$ complex was formed and crystallographically characterized in the triethylphosphine complex. On the other hand, C−C activation of the ring structure occurred in the trimethylphosphine complex, resulting in the formation of a platinacycloheptatriene.[20] The authors suggested that a probable intermediate in the second reaction was an η^2-arene complex. Reaction of **1** with $C_6(CF_3)_6$ appears to give a similar fluxional η^2-species.

The proposed η^2 bonding of the arene ring to the metal center in compound **3** was confirmed by X-ray crystallography (Figure 1). The complex adopts a distorted trigonal planar configuration with the bound double bond from the ring (C18 and C19) taking up the third ligand position in addition to the two phosphorus atoms. The plane consisting of the arene double bond and the platinum metal center is distorted from the P1−Pt−P2 plane by 10.8°. Carbon atoms C18 and C19 have bond lengths nearly identical to the metal center at 2.105(5) and 2.119(4) Å, respectively. The P1−Pt−P2 angle of 75.45(5)° is typical for platinum complexes with the dtbpm ligand as a chelate.[2a,c,12a,b] Isolated and structurally characterized complexes featuring an independent arene ring bound in an η^2 fashion are somewhat rare.[19b,21] For platinum in particular, there are an additional five complexes that display *intramolecular* η^2-arene binding with ligands that contain an ancillary phenyl substituent.[22] Both **3** and the other η^2-arene complexes described here (vide infra) all show similar structural features with regard to the aromatic C−C bond distances. A localized diene structure is seen for the nonbound portion of the ring (short−long−short bonds, $\Delta d \approx 0.08$ Å), and the η^2-bound C=C is lengthened to the distance observed for the sp^2-sp^2 C−C bonds (~1.47 Å). In contrast, the other known platinum-η^2-arene complexes in the literature show little or no bond alternation.[22]

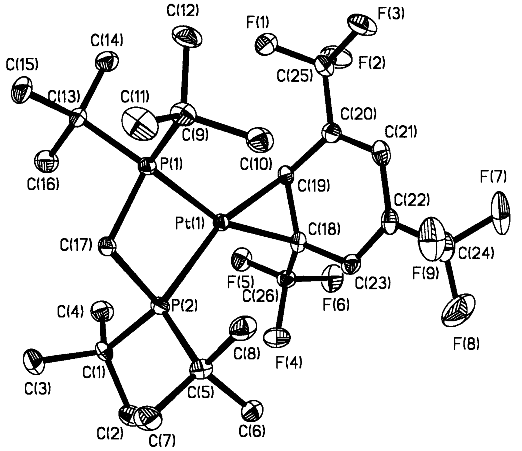
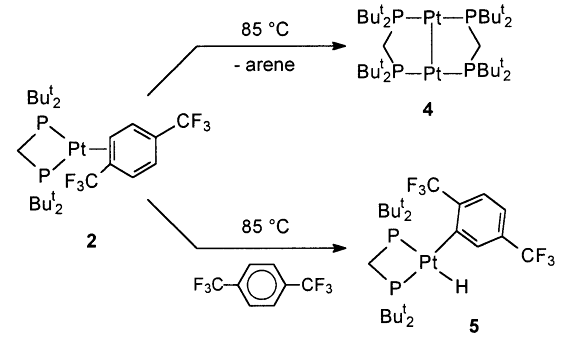


Figure 1. ORTEP diagram for **3**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): C(18)−C(19), 1.472 (7); C(19)−C(20), 1.451 (7); C(20)−C(21), 1.355 (8); C(21)−C(22), 1.433 (9); C(22)−C(23), 1.385 (8); C(23)−C(18), 1.461 (7); Pt(1)−C(18), 2.105 (5); Pt(1)−C(19), 2.119 (4); P(1)−Pt(1)−P(2), 75.45 (5).

The reactivities of compounds **2** and **3** differ when the solutions are heated for longer periods of time. Compound **3** is thermally stable toward C−H activation, whereas compound **2** readily produces an aryl hydride in the presence of excess arene (eq 3). The dimer $(dtbpm)_2Pt_2$ (**4**) is the major product formed when a solution of only compound **2** is heated.[23] Clear evidence



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(20) When a THF-d_8 solution of $C_6(CF_3)_6$ and (dtbpm)Pt(Np)H was heated, ^{31}P NMR spectroscopy indicated that an η^2-arene complex had been formed. The compound was stable toward extended heating, as evidenced by the lack of change in the spectrum. Unfortunately, we were unable to cleanly isolate this compound. For details, see the Experimental Section. It should be noted that C−C cleavage by (dtbpm)Pt(Np)H is not observed for any of the electron-deficient arenes described here.

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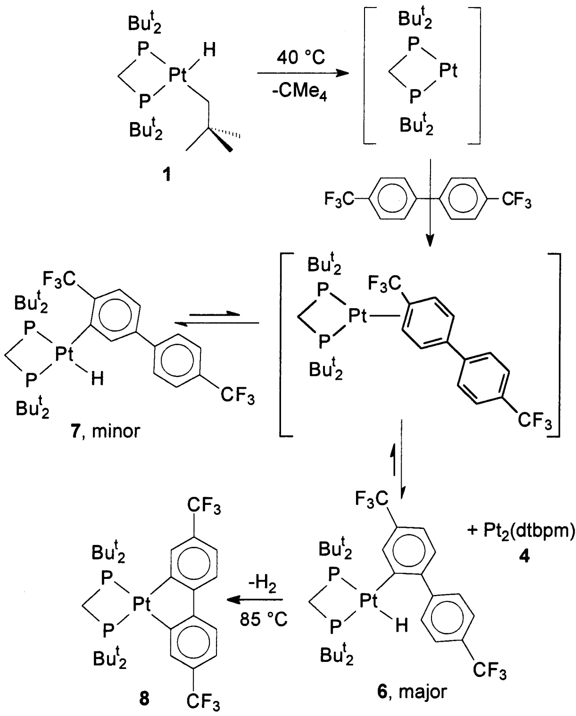
for the formation of the hydride is presented in the ^{1}H NMR spectrum. A doublet of multiplets appears at δ -6.06 ($^1J_{\mathrm{Pt-H}} = 1297$ Hz, $^2J_{\mathrm{P(trans)-H}} = 211$ Hz). Coupling of the hydride to the cis phosphorus is normally easily observed in $L_2Pt(R)H$ complexes, but the resonance is complicated by coupling to the three ^{19}F nuclei of the nearest trifluoromethyl group. Therefore, the combined $^2J_{\mathrm{P(cis)-H}}$ and $^5J_{\mathrm{F-H}}$ values make the peaks appear as sextets with an average value of 3.0 Hz ($J_{\mathrm{P-H}} \approx 2J_{\mathrm{F-H}}$). Sharp resonances are also observed in the aromatic region for the remaining three protons of the arene ring at δ 8.69 (d with ^{195}Pt satellites, $^3J_{\mathrm{Pt-H}} = 68$ Hz), 7.64 (d with ^{195}Pt shoulders), and 7.07 (d). The *tert*-butyl groups emerge as two sharp doublets ($^4J_{\mathrm{P-H}} = 13$ Hz) with an integration of 18 each. In contrast, the *tert*-butyl groups of compounds **2** and **3** both appear as a range of three broad resonances at room temperature. The ^{19}F NMR spectrum displays two resonances at δ -59.7 (s with ^{195}Pt satellites, $^4J_{\mathrm{Pt-F}} = 53$ Hz) and -61.5 (s). The former is on a carbon *ortho* to the Pt−C bond, whereas the latter is *meta* to the Pt−C bond. The ^{31}P NMR spectrum displays two resonances as well, both with ^{195}Pt satellites, at δ 7.5 ($^1J_{\mathrm{Pt-P}} = 1549$ Hz) and -2.5 ($^1J_{\mathrm{Pt-P}} = 1199$ Hz). The NMR data are all consistent with characterization of the product as (dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)](H) (**5**).

The need for electron-withdrawing substituents on the arene is demonstrated by the reaction of compound **1** with benzene. Thermolysis of (dtbpm)Pt(Np)H in the presence of 40 equiv of C_6H_6 in THF-d_8 results in the production of only $(dtbpm)_2Pt_2$. In accordance with Hofmann's results, C−H activation was not observed even in pure benzene solutions.[2c] There appears to be a synergistic effect between the electron-rich [(dtbpm)Pt] moiety and the electron-poor benzenes. Electron-withdrawing groups have been shown to favor the formation of η^2-arene complexes, which should help prevent the [(dtbpm)Pt] moiety from dimerizing to $(dtbpm)_2Pt_2$.[24] Additionally, the oxidative addition of C−H bonds in electron-poor arenes is a favorable exothermic reaction (where sterically feasible) due to the production of a strong metal−aryl bond.[25]

Reaction with Biphenyls. We also examined the reactivity of compound **1** with trifluoromethyl-substituted biphenyls. The reaction of 10 equiv of 4,4′-bis(trifluoromethyl)biphenyl with (dtbpm)Pt(Np)H in THF-d_8 results in the formation of two hydride complexes (Scheme 2). The formation of (dtbpm)Pt(biphenyl)H complexes via C−H activation in this reaction is evident given the observation of two unique platinum hydride resonances in the ^{1}H NMR spectrum at δ -6.21 (major product, **6**) and -6.58 (minor product, **7**). The hydride resonance for the minor product **7** appears as a doublet of sextets with ^{195}Pt satellites and J values consistent with an (dtbpm)Pt(Ar)H formulation ($^1J_{\mathrm{Pt-H}} = 1373$ Hz, $^2J_{\mathrm{P(trans)-H}} = 204$ Hz). Similar to compound **5**, $J_{\mathrm{P(cis)-H}} \approx 2\ J_{\mathrm{C-F}}$, giving rise to a sextet pattern. The hydride resonance for the major product **6** appears as a doublet of doublets with ^{195}Pt satellites also with J values consistent with an (dtbpm)Pt(R)H formulation ($^1J_{\mathrm{Pt-H}} = 1311$ Hz, $^2J_{\mathrm{P(trans)-H}} = 207$ Hz, $^2J_{\mathrm{P(cis)-H}} = 7.6$ Hz). ^{1}H and ^{31}P NMR spectroscopy indicate a 5:1 mixture of compounds **6** and **7**. The ^{31}P NMR spectrum supports the (dtbpm)Pt(Ar)H formulations as well. The major product displays two singlets (with Pt satellites) at δ 12.6 ($^1J_{\mathrm{Pt-P}} = 1648$ Hz) and 2.4 ($^1J_{\mathrm{Pt-P}} = 1296$ Hz), and the minor product also shows two singlets at δ 13.1 ($^1J_{\mathrm{Pt-P}} = 1759$ Hz) and 2.7 ($^1J_{\mathrm{Pt-P}} = 1253$ Hz). Dimer **4** is formed in the reaction as well in approximately 30% yield relative to the combined C−H activated products, as judged by ^{31}P NMR spectroscopy. Compound **6** is identified as the product due to activation of the C−H bond *meta* to the CF_3 group (2 position of the biphenyl ligand), as the corresponding resonances in the ^{19}F NMR are simple singlets in a 1:1 ratio. Compound **7** is therefore characterized as the product due to activation of the C−H bond *ortho* to the CF_3 group (3 or 3′ position of the biphenyl ligand). Confirmation of the minor product's structure, via analysis of the ^{19}F NMR spectrum and/or the aromatic resonances in the ^{1}H NMR spectrum, unfortunately could not be made, as there was too much interference from the excess biphenyl present in solution. Also, we were unable to isolate the minor isomer from the reaction mixture. No evidence characteristic of an η^2-arene complex was observed in either the ^{1}H or ^{31}P NMR spectra during the course of this reaction.

Scheme 2



The major isomer **6** was isolated in 43% yield from a larger scale reaction via fractional crystallization. Reversible C−H activation was observed in this system when a THF-d_8 solution of compound **6** was heated in the presence of 10 equiv of 4,4′-bis(trifluoromethyl)biphenyl, and the reaction was followed by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopies. The reaction was initially heated at 55 °C, but no change was observed after 18

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(23) $(dtbpm)_2Pt_2$ has been reported before as a decomposition product in reactions involving the [(dtbpm)Pt] intermediate by us and Hofmann. See refs 12a and 2c.

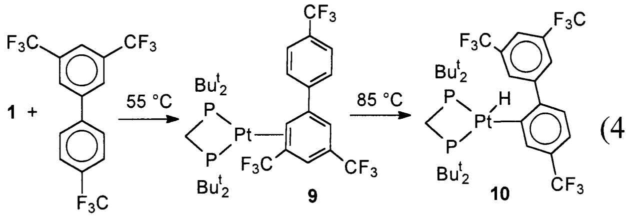
(24) (a) Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 266−269. (b) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685−7695.

(25) Selmeczy, A. D.; Jones, W. D.; Osman, R.; Perutz, R. *Organometallics* **1995**, *14*, 5677−5685.

h. Increasing the temperature to 85 °C resulted in some reactivity as formation of compound **7** was observed. An equilibrium between the two isomers exists, as the 5:1 ratio seen in the initial experiment is reached after approximately 65 h. This ratio stays constant during the course of the reaction. A commonly invoked intermediate in arene isomerizations is an η^2-arene complex.[26] In this case, the biphenyl and hydride ligands reductively eliminate to form an unstable (dtbpm)Pt-[η^2-(4,4′-bis(trifluoromethyl)biphenyl] complex, which then follows one of the subsequent three steps: (1) oxidative addition of biphenyl at the 3 position of the biphenyl to form product **7**, (2) oxidative addition of biphenyl at the 2 position to re-form product **6**, or (3) biphenyl dissociation to form [(dtbpm)Pt].

A new product, most easily seen in the ^{31}P NMR spectrum, started to grow in as well. A sharp singlet at 5 ppm with ^{195}Pt satellites ($^1J_{\mathrm{Pt-P}} = 1523$ Hz) suggested the formation of a symmetric bisphosphine complex with two Pt−C$_{\mathrm{aryl}}$ bonds. A simple doublet in the ^{1}H NMR spectrum for the *tert*-butyl groups of the bisphosphine ligand also reveals the symmetric nature of the product. The aromatic region of the ^{1}H NMR spectrum of the mixture contains three unique resonances for the product, whereas a C−C bond cleavage product would be expected to have only two resonances.[27] The lack of new resonances in the hydride region therefore suggested a second C−H activation. Insertion of the platinum metal center into a C−H bond of the nonbonded ring *ortho* to the C−C bridge would result in formation of a 4,4′-bis(trifluoromethyl) platinacyclopentane complex (**8**) analogous to that of (dtbpm)Pt(2,2′-biphenyl).[12a] Concomitant loss of H_2 would be expected, but gas evolution was not detected during the course of the reaction. Neither was a resonance for H_2 observed in the ^{1}H NMR spectrum. This is perhaps not surprising, as the overall amount of compound **8** formed was relatively small (18% isolated yield in a larger scale reaction). We were able to obtain crystals of the complex, and a single-crystal X-ray analysis confirmed the connectivity of the platinacyclopentane.[28] The overall reaction is shown in Scheme 2.

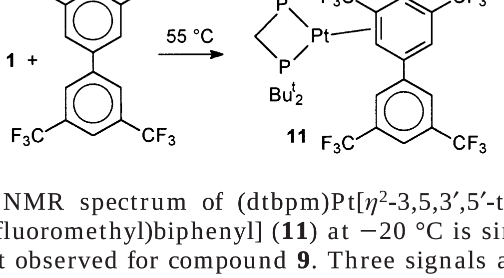
When 5 equiv of 3,5,4′-tris(trifluoromethyl)biphenyl is reacted with compound **1** in THF for 2 h at 55 °C, the η^2 complex (dtbpm)Pt[η^2-(3,5,4′-bis(trifluoromethyl)-biphenyl)] (**9**) is formed exclusively and isolated in 76% (eq 4). As seen in the ^{1}H NMR spectrum for the previously described arene complexes, broad signals are observed for the aromatic protons of the biphenyl ligand at room temperature that sharpen upon cooling (−20 °C). Two doublets due to an AB spin system are observed for the 4′-CF$_3$-substituted ring in addition to three resonances for the 3,5-(CF$_3$)$_2$-substituted ring. One of the latter three signals is relatively far upfield from the others at 4.03 ppm and is coupled to the platinum metal center ($J_{\mathrm{Pt-H}} = 74$ Hz). This points to the biphenyl being bound to the metal through the bis substituted ring and the other ring freely rotating about the C−C bridging bond. Confirming the structural assignment are the three unique resonances in the ^{19}F NMR at δ −61.2, −63.0, and −65.7. The signal at −63.0 is a sharp singlet, whereas the other two are broad resonances with ^{195}Pt shoulders.



(4)

C−H activation occurs when a THF solution of compound **9** is heated at 85 °C. ^{1}H and ^{31}P NMR spectroscopy indicated that the η^2 complex had been converted into an aryl hydride complex (**10**). The reaction was complete after 55 h. A small amount (approximately 10%) of dimer **4** was formed during the course of the reaction. On the basis of NMR spectroscopic data, C−H activation occurs at the 2′ position of the 4′-CF$_3$-substituted phenyl ring. A new set of resonances for the aromatic protons included two singlets at δ 8.39 and 7.82 in a 2:1 ratio and three signals, with an integration of one each, at δ 8.06, 7.24, and 7.09. The signal at 8.06 ppm is assigned as *ortho* to the Pt−C bond. Coupling to the platinum metal center can be seen, although the exact *J* value could not be calculated, as the ^{195}Pt satellites are partially obscured by other resonances. The other two aromatic resonances are doublets and are coupled to each other. The hydride resonance is a doublet of doublets at δ −6.12 with ^{195}Pt satellites ($^1J_{\mathrm{Pt-H}} = 1293$ Hz). Coupling to any of the CF$_3$ groups is not observed. The ^{19}F NMR spectrum reveals only two resonances at δ −62.84 and −62.98 in a 1:2 ratio. Neither peak displays coupling to the ^{195}Pt nucleus. Two doublets with ^{195}Pt satellites are observed in the ^{31}P NMR spectrum for the bisphosphine ligand at δ 6.2 ($^1J_{\mathrm{Pt-P}} = 1680$ Hz) and −3.2 ($^1J_{\mathrm{Pt-P}} = 1291$ Hz). It is interesting to note that indirect C−H bond activation occurs in this case; that is, the *ortho* C−H bond on the ring *not bound* initially to the platinum metal center undergoes oxidative addition. We assume that steric factors discourage insertion into the *ortho* C−H bond of the 3,5-substituted ring.

The reaction of 5 equiv of 3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl with (dtbpm)Pt(Np)H in THF at 55 °C also resulted in the formation of an η^2-biphenyl complex, which was isolated in 57% yield (eq 5). The ^{1}H NMR spectrum of (dtbpm)Pt[η^2-3,5,3′,5′-tetrakis-(trifluoromethyl)biphenyl] (**11**) at −20 °C is similar to that observed for compound **9**. Three signals are seen



(5)

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(26) (a) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647−3648. (b) Gozin, M.; Weisman, A.; Bendavid, Y.; Milstein, D. *Nature* **1993**, *364*, 699−701. (c) Feher, F. H.; Jones, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 4814−4819.

(27) The C−C activated product was independently synthesized. The ^{1}H, ^{19}F, and ^{31}P NMR data of (dtbpm)Pt(4-C$_6$H$_4$CF$_3$)$_2$ does not match that of the product formed. See Experimental Section for the synthesis and NMR spectroscopic data.

(28) Although the platinacyclopentane motif of the compound was verified, there was disorder of the trifluoromethyl groups that we were unable to satisfactorily model during refinement of the structure.

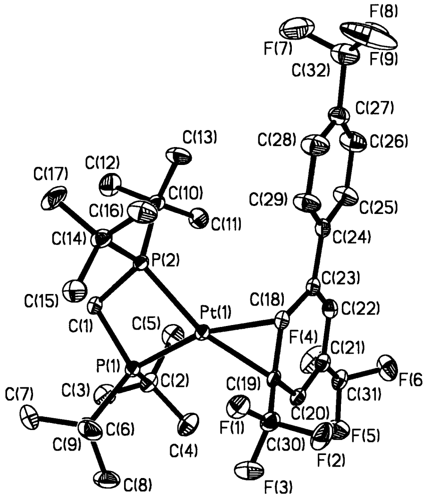


Figure 2. ORTEP diagram for **9**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): C(18)−C(19), 1.472 (6); C(19)−C(20), 1.437 (6); C(20)−C(21), 1.349 (6); C(21)−C(22), 1.428 (6); C(22)−C(23), 1.358 (6); C(23)−C(18), 1.465 (6); Pt(1)−C(18), 2.109 (4); Pt(1)−C(19), 2.121 (4); P(1)−Pt(1)−P(2), 75.53 (4).

for the protons of the bound ring, including the typical upfield resonance for the proton attached to the bound carbon at δ 4.06 ($^2J_{\mathrm{Pt-H}} = 63$ Hz). The resonances for the *tert*-butyl groups of compound **11** are significantly broadened at room temperature, as is seen in all the η-bound arene complexes reported in this study. Three signals are observed in the ^{19}F NMR spectrum at δ −63.10, −65.24, and −67.46 in a 1:2:1 ratio, again indicating free rotation about the C−C bridging bond. The resonances at −63.1 and −67.46 ppm are broad due to ^{195}Pt shoulders. Compound **11** is more robust than its tris(trifluoromethyl) analogue. Thermolysis of this compound did not yield clean C−H activation even after 5 days at 85 °C. Increasing the temperature to 125 °C eventually leads to complete decomposition to (dtbpm)$_2$Pt$_2$ and the free biphenyl.

Compounds **9** and **11** were both characterized by single-crystal X-ray analysis (Figures 2 and 3, respectively). The structural characteristics of both compounds are relatively similar, and the core bonds and angles are nearly identical to those of compound **3**. In both cases the biphenyl ligand is bound to the platinum metal center in an η^2 fashion along the C$_{ortho}$−C$_{meta}$ bond (positions labeled with respect to the C−C bridge) of one ring. For compound **9**, the ligand is bound through the 3,5-bis(trifluoromethyl)-substituted ring, confirming the structural characterization from NMR spectroscopic analysis. The P1−Pt−P2 and C$_{ortho}$−Pt−C$_{meta}$ planes are not quite parallel, being offset by 7.5° and 5.6°, respectively, for compounds **9** and **11**. The rings of the biphenyl ligands also maintain a nearly coplanar orientation with dihedral angles of 5.2° and 6.6°. The CF$_3$ group attached to the carbon atom bound to platinum is bent back from the aromatic ring by 27.5° for compound **9** and 27.9° for compound **11**. Finally, the P1−Pt−P2 angles for **9** and **11** are 75.5° and 75.4°.

Electron-withdrawing substituents are also necessary for the η^2 coordination and C−H activation of biphenyls. The reaction of 4,4′-dimethoxybiphenyl or 3,5,3′,5′-tetramethylbiphenyl with compound **1** leads only to the formation of dimer **4**. Small amounts of C−H activated products (approximately 5%) can be observed in the ^{1}H NMR hydride region when the mixed 4-methoxy-4′-(trifluoromethyl)biphenyl is used. The primary product, however, is again (dtbpm)$_2$Pt$_2$.

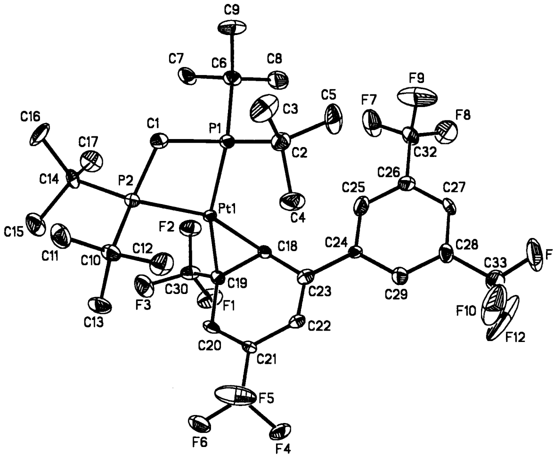
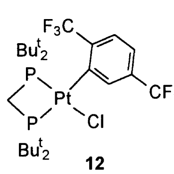


Figure 3. ORTEP diagram for **11**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): C(18)−C(19), 1.452 (13); C(19)−C(20), 1.468 (13); C(20)−C(21), 1.365 (14); C(21)−C(22), 1.421 (14); C(22)−C(23), 1.356 (14); C(23)−C(18), 1.477 (13); Pt(1)−C(18), 2.121 (9); Pt(1)−C(19), 2.117 (9); P(1)−Pt(1)−P(2), 75.42 (9).

The aryl hydrides of [(dtbpm)Pt] react cleanly with halogenated solvents (CDCl$_3$ or CH$_2$Cl$_2$) to effect a halide/hydride exchange. Four distinct doublets with an integration of nine each are observed for the *tert*-butyl groups in the ^{1}H NMR of (dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)]Cl (**12**), (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]Cl (**13**), and (dtbpm)Pt[2′-(3,5,4′-tris(trifluoromethyl)biphenyl)]Cl (**14**). (dtbpm)Pt(2-biphenyl)Cl (**15**), synthesized via reaction of (dtbpm)-Pt(2,2′-biphenyl) with HCl$_{\mathrm{(conc)}}$, displays the same characteristic pattern in its ^{1}H NMR spectrum. This indicates steric interference caused by the chloride ligand with respect to the rotation of the aryl ligand about the Pt−C bond, as only two doublets with an integration of 18 each are observed in each hydride analogue.[29] The structure of compound **12** was determined by single-crystal X-ray analysis and is displayed in Figure 4. The complex adopts a distorted square planar geometry. The aryl ligand is oriented perpendicular to the square plane, and the main distortion is a result of the P1−Pt−P2 angle of 73.95(3)°.



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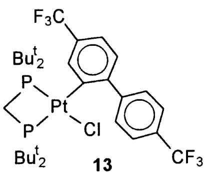

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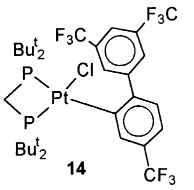

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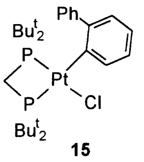

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The chloride-substituted compounds can be labeled via a Cl/D exchange reaction with deuteride reagents.

Table 1. Summary of ^{1}H and ^{31}P NMR Spectroscopic Data for Hydride Complexes

Pt(dtbpm) compound	δ P	$^1J_{\mathrm{Pt-P}}$, Hz	δ H	$^1J_{\mathrm{Pt-H}}$	$^2J_{\mathrm{P-H}}$
Pt(neopentyl)H	9.7	1345 (trans Np)	−4.88	1350	214, 11
(**1**), C$_6$D$_6$	−5.4	1338 (trans H)			
Pt((CF$_3$)$_2$phenyl)H	7.5	1549 (trans Ar)	−6.06	1297	211
(**5**), C$_6$D$_6$	−2.5	1199 (trans H)			
Pt(2-(CF$_3$)$_2$biphenyl)H	7.4	1648 (trans Ar)	−5.78	1311	207, 7.6
(**6**), C$_6$D$_6$	−2.8	1287 (trans H)			
Pt(3-(CF$_3$)$_2$biphenyl)H	13.1	1759 (trans Ar)	−6.58	1373	204
(**7**), C$_6$D$_6$	2.7	1253 (trans H)			
Pt(2′-(CF$_3$)$_3$biphenyl)H	6.2	1680 (trans Ar)	−6.12	1293	204, 7.1
(**10**), THF-d_8	−3.2	1291 (trans H)			
Pt((CF$_3$)$_3$phenyl)H	12.7	2041 (trans Ar)	−8.78	1257	207
(**16**), C$_6$D$_6$	4.13	1339 (trans H)			
Pt(2-(CF$_3$)$_3$biphenyl)H	9.2	1872 (trans Ar)	−7.66	1266	206
(**17**), C$_6$D$_6$	1.6	1237 (trans H)			
Pt(2-(CF$_3$)$_4$biphenyl)H	8.9	1875 (trans Ar)	−7.57	1267	203
(**18**), C$_6$D$_6$	1.8	1242 (trans H)			
Pt(2-biphenyl)H	8.0	1549 (trans Ar)	−5.37	1339	210, 8.8
(**19**), C$_6$D$_6$	−3.2	1381 (trans H)			

Table 2. Summary of Crystallographic Data for 3, 9, 11, and 12

crystal parameter	**3**	**9**	**11**	**12**
emp formula	$C_{26}H_{41}F_9P_2Rh$	$C_{32}H_{45}F_9P_2Pt$	$C_{33}H_{44}F_{12}P_2Pt$	$C_{25}H_{41}ClF_6P_2Pt$
fw	781.62	857.71	925.72	748.06
temperature (°C)	−80	−80	−80	−80
cryst syst	orthorhombic	triclinic	triclinic	orthorhombic
space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
a (Å)	16.0468(8)	9.2656(4)	9.1979(8)	25.2091(10)
b (Å)	10.5316(5)	9.7282(4)	9.8021(9)	12.4820(5)
c (Å)	17.5815(9)	20.1575(9)	21.6730(19)	9.4183(4)
α (deg)	90	91.4580(10)	102.451(2)	90
β (deg)	90	99.3640(10)	90.077(2)	90
γ (deg)	90	107.7850(10)	107.434(2)	90
volume (Å^3), Z	2971.2(3), 4	1701.6(1), 2	1815.8, 2	2963.6(2), 4
density (calc, Mg/m^3)	1.747	1.674	1.693	1.677
abs coeff (mm^{-1})	4.901	4.288	4.036	4.983
F(000)	1544	852	916	1480
cryst size (mm^3)	.15 x 0.12 x 0.10	.18 x 0.02 x 0.24	.16 x 0.08 x 0.08	.04 x 0.22 x 0.40
θ range (deg)	2.25 to 23.25	2.05 to 23.27	2.23 to 23.25	1.62 to 23.26
no. of reflns collected	12755	7648	8302	12622
no. of ind reflns, R_{int}	3633, 0.0318	4815, 0.0206	5164, 0.0313	4020, 0.0316
abs corr	SADABS	SADABS	SADABS	SADABS
no. of data/restraints/params	3633/1/343	4815/0/409	5164/0/433	4020/1/328
GOF on F^2	1.003	1.027	1.320	0.986
R_1, wR_2 (all data)	0.0209, 0.0480	0.0290, 0.0511	0.0699, 0.1091	0.0229, 0.0423
R_1, wR_2 [$I > 2\sigma(I)$]	0.0195, 0.0474	0.0237, 0.0498	0.0623, 0.1070	0.0195, 0.0415
largest diff peak and hole (e/Å^{-3})	1.045 and −0.537	0.931 and −0.716	1.215 and −3.610	0.597 and −0.627

A suspension of compound **13** and dicyclopentadienezirconium dideuteride (Cp_2ZrD_2) was mixed at room temperature for 4 h, and conversion to the deuterium-labeled compound was judged complete by ^{1}H and ^{31}P NMR spectroscopy. The spectra were identical to compound **6** except for the missing hydride resonance at δ −5.78 in the ^{1}H NMR spectrum. Also, the resonance at δ −2.2 in the ^{31}P NMR spectrum appeared as a 1:1:1 triplet, indicating coupling to the ^{2}H nucleus ($^2J_{\mathrm{P(trans)-D}} = 36$ Hz). The mixture was allowed to stand at room temperature for 18 h, and no discernible change in the ^{1}H NMR spectrum was observed. The mixture was then heated at 85 °C for 30 min and again checked by ^{1}H NMR spectroscopy to reveal no discernible H/D exchange. Continued heating at 85 °C resulted in nearly complete reductive elimination of 4,4′-bis(trifluoromethyl)biphenyl-d_1 with concomitant formation of dimer **4** after 16 h. This again is an indication of the instability of the η^2-(4,4′-bis(trifluoromethyl)biphenyl) complex. It appears that without a significant excess of biphenyl in solution the major reaction pathway is dimerization of [(dtbpm)Pt] to $(dtbpm)_2Pt_2$.

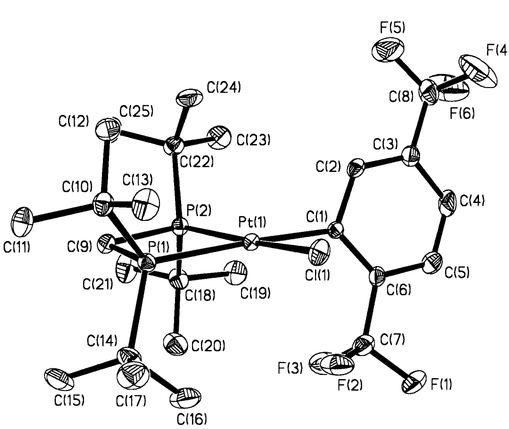

Figure 4. ORTEP diagram for **12**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Pt(1)−C(1), 2.087 (4); Pt(1)−Cl(1), 2.3631 (12); P(1)−Pt(1)−P(2), 75.25 (5); C(1)−Pt(1)−Cl(1), 87.42 (12).

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(29) For other examples of hindered metal−aryl rotation see: Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376.

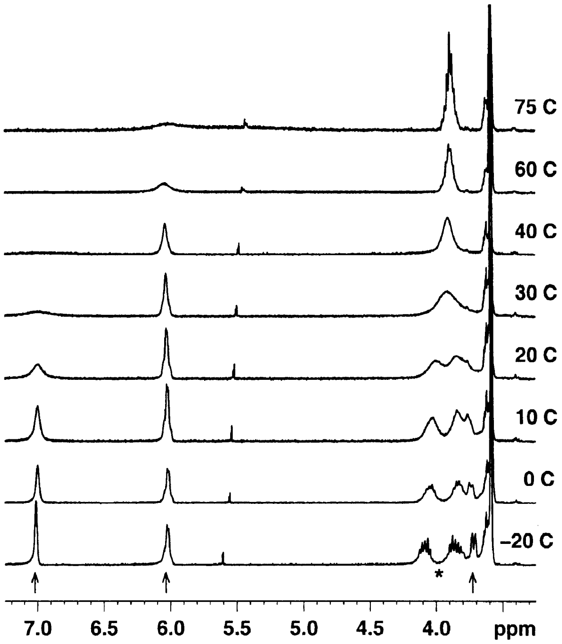

Figure 5. ^{1}H VT NMR spectrum of **3** in THF-d_8. The aromatic resonances are denoted with arrows, and the P−CH$_2$−P resonance by a *. Residual THF protons appear at δ 3.58.

Variable-Temperature NMR Spectra. The appearance at room temperature of several broad resonances in the ^{1}H NMR spectra of the η^2-arene complexes prompted the examination of these compounds for dynamic NMR behavior. Of particular interest are the aromatic resonances for compounds **2**, **3**, **9**, and **11**, although the bridging methylene and *tert*-butyl groups also sharpen and broaden with changes in temperature. At room temperature, (dtbpm)Pt[η^2-1,3,5-$C_6H_3(CF_3)_3$] (**3**) shows a broad signal at δ 3.99 for the hydrogen that is on the C−C double bond of the ring that is bound to the metal center. Two other resonances at δ 6.99 (br s) and 6.02 (br d with ^{195}Pt shoulders) are also observed for the arene ring (Figure 5). Cooling the THF-d_8 solution to −20 °C sharpened the singlet at δ 6.99 considerably. The resonance at δ 3.99 shifted upfield by 0.28 ppm and sharpened into a doublet. The expected coupling to ^{195}Pt was obscured by the bridging methylene protons on one side and the residual THF protons on the other. The resonance at δ 6.02 was not significantly altered. All three signals begin to coalesce toward a single resonance at 40 °C, but the fast-limit structure was not observed below 75 °C.

The room-temperature ^{1}H NMR spectrum of (dtbpm)-Pt[η^2-1,4-$C_6H_4(CF_3)_2$] (**2**) has two broad peaks at δ 6.37 and 5.07 that decoalesce into four broad signals at −20 °C (Figure 6). The slow-limit structure is finally achieved at −60 °C with four resonances at δ 7.10 (br s), 6.31 (d), 5.69 (br d with ^{195}Pt shoulders), and 3.72 (br t). Again, the expected coupling to ^{195}Pt was obscured for the resonance at δ 3.72. Increasing the temperature of the solution caused the pairwise coalescence of the resonances at δ 7.10/5.69 and 6.31/3.72 into two broad singlets, which then coalesced into the baseline at 75 °C. The above data are consistent with migration of the metal around the arene ring, with a slightly higher barrier for migration past a trifluoromethyl group.

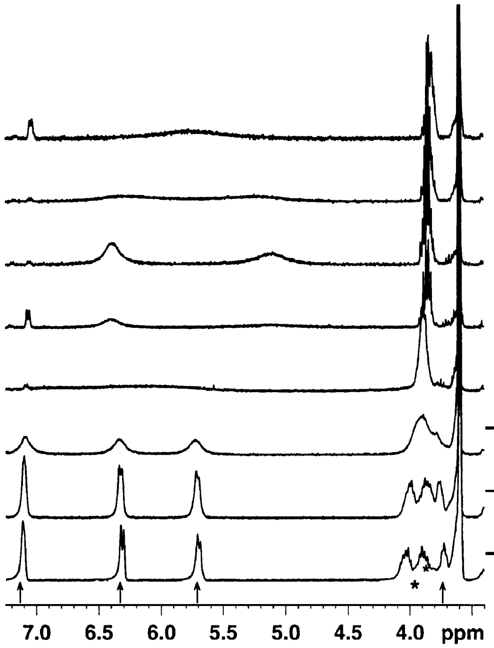

Figure 6. ^{1}H VT NMR spectrum of **2** in THF-d_8. The aromatic resonances are denoted with arrows, and the P−CH$_2$−P resonance by a *. Residual THF protons appear at δ 3.58.

The aromatic protons of the η-bound arene rings in (dtbpm)Pt[η^2-3,5,4′-tris(trifluoromethyl)biphenyl] (**9**) and (dtbpm)Pt[η^2-3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl] (**11**) display behavior similar to that of compound **3**. The resonances are relatively broad at room temperature and resolve nicely at −20 °C (see Supporting Information). An obvious difference between the compounds is that only the two *ortho* hydrogens of the nonbound ring begin to coalescence at higher temperatures for compound **9** and **11** as opposed to all three in compound **3**. However, an interesting observation is made regarding the nonbound ring in compound **9**. In a 1,4-substituted phenyl ring, two doublets would be expected, and this is observed at both the fast- and slow-limit structures. Near room temperature though, the doublet due to the protons at δ 7.99 (*ortho* to the bound ring) undergoes some line broadening. One explanation could be that the ring is not rotating as fast; therefore, the two *ortho* protons are beginning to experience different electronic environments. If this were the case, the doublet due to the *meta* protons should behave similarly, but the appearance of this signal does not change at all. Another explanation may be that the *ortho* protons are experiencing coupling to the platinum metal center. Similar broadening of the *ortho* protons to a ^{195}Pt nucleus are observed in η^2-styrene platinum complexes, yet the crystal structure of compound **9** clearly does not place these hydrogens in an appropriate position for coupling to platinum.[30] Scheme 3 shows a mechanism that allows for an η^2-styrene-like configuration to occur for this compound. The dynamic behavior observed for the protons of the bound ring is consistent with ring-walking, and so access to an η^2-styrene-like compound (structures B and C) is possible.

Photolysis of Compounds. Alternative reactivity patterns are observed when solutions of (dtbpm)Pt(η^2-

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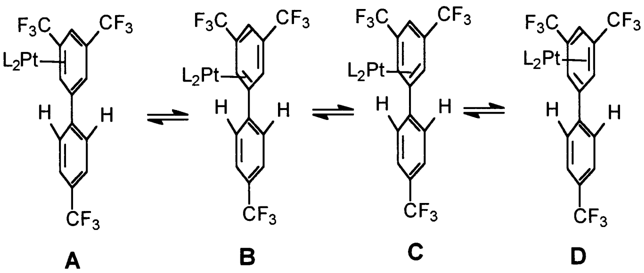
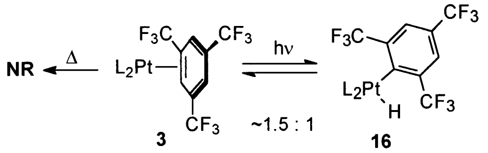
(30) Crascall, L. E.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 3445−3452.

Scheme 3

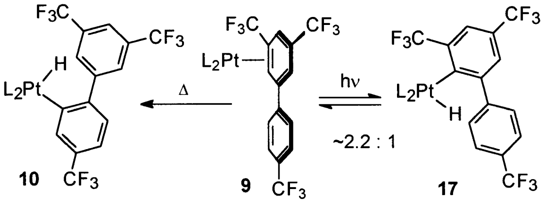


arene) and (dtbpm)Pt(biphenyl)H are irradiated as opposed to thermolysis. The apparent kinetic products of C−H activation are achieved via photolysis. For instance, compound **3**, thermally inert toward C−H activation, is converted to a Pt(II) aryl hydride complex under photolytic conditions in C_6D_6 (eq 6). The sterically hindered product, (dtbpm)Pt[2-(1,3,5-tris(trifluoromethyl)phenyl)](H) (**16**), is formed as judged by ^{1}H, ^{19}F, and ^{31}P NMR spectra. Presumably, the photolytic conditions allows the complex to reach an activated state where C−H bond cleavage is accessible in such a bulky environment. A sharp singlet at δ 8.14 is observed for the two aryl hydrogens as well as a hydride resonance at δ −8.78. The hydride resonance appears as a doublet with ^{195}Pt satellites ($^1J_{\mathrm{Pt-H}} = 1257$ Hz, $^2J_{\mathrm{P(trans)-H}} = 207$ Hz). $^2J_{\mathrm{P(cis)-H}}$, normally observable in these systems, is obscured due to coupling to the six ^{19}F nuclei of the adjacent CF_3 groups. ^{31}P NMR spectroscopy reveals two new resonances with ^{195}Pt satellites at δ 12.7 and 4.13 ($^1J_{\mathrm{Pt-P}}$ = 2041 and 1339 Hz, respectively). Two new signals are also observed in the ^{19}F NMR spectrum in a 2:1 ratio at δ −57.8 and −61.5. The former resonance is coupled to platinum ($^3J_{\mathrm{Pt-F}} = 80$ Hz), whereas the latter is a simple singlet. The reaction does not go to completion, as a photostabilized state is reached after 5.5 h, with the η^2-arene the predominant species (1.5:1).



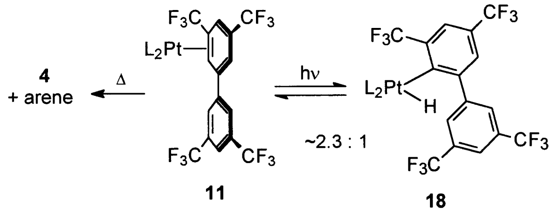
(6)

Photolysis of (dtbpm)Pt(η^2-3,5,4′-tris(trifluoromethyl)biphenyl) (**9**) results in C−H activation as well, albeit with alternate regioselectivity with respect to the thermal activation. The product (**17**) displays a new hydride resonance in the ^{1}H NMR spectrum at δ −7.66 (eq 7). The signal is a doublet of multiplets with ^{195}Pt satellites ($^1J_{\mathrm{Pt-H}}$ = 1266 Hz, $^2J_{\mathrm{P(trans)-H}}$ = 206 Hz). $^2J_{\mathrm{P(cis)-H}}$ is obscured due to coupling to a CF_3 group. Two new resonances with ^{195}Pt satellites at δ 9.2 (s, $^1J_{\mathrm{Pt-P}}$ = 1872 Hz) and 1.6 (second-order multiplet, $^1J_{\mathrm{Pt-P}}$ = 1237 Hz) are observed in the ^{31}P NMR spectrum. In contrast to the thermolytic reaction, where the platinum metal center inserts into the 2′ C−H bond of the mono(trifluoromethyl)-substituted phenyl ring, photolysis induces insertion into the C−H bond of the η^2-C−C double bond of the bis(trifluoromethyl)-substituted phenyl ring. A photostabilized state (2.2:1 preferring compound **9**) is achieved in several hours. Extended photolysis (1 week) did not result in significant decomposition.



(7)

(dtbpm)Pt(η^2-3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl), also inert toward C−H activation under thermolytic conditions, undergoes a similar photochemical transformation, as insertion takes place at the *ortho*-H of the η^2-C−C double bond (eq 8). A hydride resonance at δ −7.57 (d of mult. with ^{195}Pt satellites, $^1J_{\mathrm{Pt-H}}$ = 1267 Hz, $^2J_{\mathrm{P(trans)-H}}$ = 203 Hz) and two resonances in the ^{31}P NMR spectrum at δ 8.9 (s, $^1J_{\mathrm{Pt-P}}$ = 1875 Hz) and 1.8 (second-order multiplet, $^1J_{\mathrm{Pt-P}}$ = 1242 Hz) are observed. ^{1}H and ^{31}P NMR data are consistent with the formulation as (dtbpm)Pt[2-(3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl](H) (**18**). The same product could be formed by activation at the 2′ C−H bond of the nonbound ring; however, given the structural similarities between compounds **9** and **11** it seems reasonable that both reactions occur in an identical fashion. A photostabilized state is once again reached in several hours, where the η^2-biphenyl complex is favored 2.3:1 over the C−H activated complex.



(8)

Compound **4** was the major platinum-containing species formed along with the reductive elimination of 4,4′-bis(trifluoromethyl)biphenyl when a C_6D_6 solution of (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H was photolyzed. The reaction is approximately 38% complete after 4 h of irradiation and completely finished after 16 h. The other platinum(II) isomer, (dtbpm)Pt[3-(4,4′-bis(trifluoromethyl)biphenyl)]H, is formed in a very small amount during the course of the reaction but is eventually converted to $(dtbpm)_2Pt_2$ as well. Photolysis of compound **2** for 90 min in C_6D_6 results in C−H activation similar to that observed in the thermal reaction. Continued exposure for 24 h leads to reductive elimination of the arene and complete decomposition of the platinum-containing species.

Conclusions

We have prepared a number of (dtbpm)Pt(η^2-arene) complexes which are intermediates in the stepwise activation of aromatic C−H bonds. Several direct and nondirect C−H activated products derived from the arene complexes have also been synthesized and characterized. The electronic character of the aromatic ligands has a significant effect on the stability of the arene complexes. Only electron-poor arenes react with the [(dtbpm)Pt^0] intermediate to form new complexes, as electron-rich or neutral arenes result in the formation of the dimer **4**. Additionally, the arene complexes that contain extremely electron-poor benzenes or biphenyls are more stable toward thermal reaction, e.g., compound **3** versus compound **2**. The reactivity of the arene complexes also differs when subjected to thermal versus photolytic conditions. The more accessible C−H bonds are preferentially cleaved when solutions of the arene complexes are heated. In contrast, photolysis yielded complexes that activate C−H bonds in sterically encumbered positions, indicating that the reaction proceeds through a different activated complex under either reaction condition.

Experimental Section

General Considerations. All manipulations were performed using glovebox, Schlenk, or vacuum-line techniques. Diethyl ether, hexanes, toluene, pentane, and benzene were predried over sodium and distilled from sodium/benzophenone ketyl. CH_2Cl_2 was dried over CaH_2 and distilled prior to use. C_6D_6 and THF-d_8 were purchased from Cambridge Isotope Laboratories and dried and distilled from sodium/benzophenone ketyl. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and dried over 3 Å sieves. CD_2Cl_2 was dried over P_2O_5 and vacuum distilled prior to use. (dtbpm)Pt(Np)H,[2c] (COD)Pt(4-$C_6H_4CF_3$)$_2$, $^tBu_2PCl$,[31] $^tBu_2PMe$,[32] and $^tBu_2PCH_2Li$[15] were prepared according to literature methods. dtbpm was prepared as described in the Supporting Information. Biphenyls were purchased from Aldrich or Alfa Aesar or prepared via Suzuki coupling methods.[33]

^{1}H NMR spectra were recorded at ambient temperature (except as noted) on Bruker AMX400 or Avance400 spectrometers and referenced to residual proton solvent signals. ^{31}P NMR spectra were recorded on Bruker AMX400 or Avance400 spectrometers operating at 162 MHz and were referenced to an 85% phosphoric acid external standard set to 0 ppm. ^{19}F NMR spectra were recorded on a Bruker Avance400 spectrometer operating at 376 MHz, and chemical shifts were referenced to a $CFCl_3$ external standard set to 0 ppm. GC/MS was conducted on a 5890 Series II gas chromatograph fitted with an HP 5970 series mass selective detector. Elemental analyses were performed by Desert Analytics. A Siemens SMART system with a CCD area detector was used for X-ray structure determinations.

(dtbpm)Pt(neopentyl)H (1).[2c] ^{1}H NMR (C_6D_6): δ 3.05 (t, $^2J_{P-H} = 6.9$ Hz, 2 H, PCH_2P), 2.64 (dd with ^{195}Pt satellites, $^2J_{Pt-H} = 86$ Hz, $^3J_{P-H} = 7.1$ Hz, $^2J_{P-H} = 8.8$ Hz, 2 H, $CH_2C(CH_3)_3$), 1.62 (s, 9 H, $CH_2C(CH_3)_3$), 1.22 (d, 18 H, $(CH_3)_3CP$, $^3J_{P-H} = 12$ Hz), 1.18 (d, 18 H, $(CH_3)_3CP$, $^3J_{P-H} = 13$ Hz), −4.88 (dd with ^{195}Pt satellites, $^2J_{P(trans)-H} = 214$ Hz, $^2J_{P(cis)-H} = 11$ Hz, $^1J_{Pt-H} = 1350$ Hz, Pt−H). ^{31}P NMR (C_6D_6): δ 9.7 (d with ^{195}Pt satellites, $^1J_{Pt-P} = 1345$ Hz, $^2J_{P-P} = 11$ Hz, trans neopentyl), −5.4 (d with ^{195}Pt satellites, $^1J_{Pt-P} = 1338$ Hz, $^2J_{P-P} = 9$ Hz, trans hydride).

(dtbpm)Pt[η^2-(1,4-bis(trifluoromethyl)benzene)] (2). (dtbpm)Pt(Np)H (115 mg, 0.20 mmol) and 1,4-bis(trifluoromethyl)benzene (861 mg, 4.02 mmol) were dissolved in 40 mL of THF and transferred to a 100 mL Schlenk flask fitted with a reflux condensor. The mixture was stirred at 50 °C for 1.5 h. The volatile material was removed in vacuo and the residue extracted with 5 × 2 mL of hexanes. The remaining material was redissolved in THF, layered with hexanes, and cooled to −25 °C. Orange crystals (20 mg, 14%) deposited after a week. ^{1}H NMR (THF-d_8, rt): δ 6.37 (br s, 2 H, $C_6H_4(CF_3)_2$), 5.07 (br s, 2 H, $C_6H_4(CF_3)_2$), 3.85 (t with ^{195}Pt satellites, $^3J_{Pt-H} = 27$ Hz, $^2J_{P-H} = 7.4$ Hz, 2 H), 1.34 (br m, 36 H, ^{t}Bu). ^{19}F NMR (THF-d_8, rt): δ −61.3 (br s with ^{195}Pt satellites, $^4J_{Pt-F} = 88$ Hz, 3 F, *ipso* CF_3 on Pt−C$_{aryl}$ bond), −65.2 (br s, 3 F). ^{31}P NMR (THF-d_8, rt): δ 50.4 (resonances for the phosphorus atoms are coincidental for this compound, approximate $^1J_{Pt-P} = 3196$ Hz). ^{1}H NMR (THF-d_8, −60 °C): δ 7.10 (br s, 1H, $C_6H_4(CF_3)_2$), 6.31 (br d, $^3J_{H-H} = 9.2$ Hz, 1 H, $C_6H_4(CF_3)_2$), 5.69 (br d, $^3J_{H-H} = 8.7$ Hz, 1 H, $C_6H_4(CF_3)_2$), 3.72 (br m, J_{Pt-H} obscured due to other resonances, 1 H, *ipso* H on Pt−C$_{aryl}$ bond), 4.02 (m, 1 H, PCH_2P), 3.89 (m, 1 H, PCH_2P), 1.42 (br m, 18 H, ^{t}Bu), 1.31 (br d, 9 H, ^{t}Bu), 1.25 (br d, 9 H, ^{t}Bu). For (dtbpm)Pt[η^2-(1,4-bis(trifluoromethyl)benzene)] Anal. Calcd (found): C, 42.07 (42.84); H, 5.93 (6.26).

(dtbpm)Pt[η^2-(1,3,5-tris(trifluoromethyl)benzene)] (3). (dtbpm)Pt(Np)H (80 mg, 0.14 mmol) was dissolved in 25 mL of THF in a 100 mL air-free flask, and 1,3,5-tris(trifluoromethyl)benzene (790 mg, 2.4 mmol) was added to the solution by pipet. The mixture was stirred at 55 °C for 1.5 h. The volatile material was removed in vacuo and the residue extracted with 2 × 2 mL of hexanes. The remaining solids were redissolved in THF, layered with hexanes, and cooled to −25 °C. Orange-yellow crystals (22 mg, 20%) deposited after several days. ^{1}H NMR (THF-d_8, rt): δ 6.99 (br s, 1 H), 6.02 (d with ^{195}Pt shoulders, $J = 4.3$ Hz, 1 H), 3.99 (br s, 1 H, *ipso* H on Pt−C$_{aryl}$ bond), 3.84 (br s, 2 H, PCH_2P), 1.2−1.5 (br resonance, 36 H, ^{t}Bu). ^{19}F NMR (THF-d_8, rt): δ −59.9 (m with ^{195}Pt satellites, $^3J_{Pt-F} = 81$ Hz, 3 F, CF_3 ipso to Pt−C$_{aryl}$ bond), −64.0 (br s, 3 F), −64.4 (br s, 3 F). ^{31}P NMR (THF-d_8, rt): δ 47.9 (d with ^{195}Pt satellites, $^1J_{Pt-P} = 3338$ Hz, $^2J_{P-P} = 91$ Hz), 46.7 (d with ^{195}Pt satellites, $^1J_{Pt-P} = 2967$ Hz, $^2J_{P-P} = 91$ Hz). ^{1}H NMR (THF-d_8, −20 °C): δ 7.01 (s, 1 H), 6.02 (d with ^{195}Pt shoulders, $J = 4.1$ Hz, 1 H), 4.08 (br m, 1 H, PCH_2P), 3.86 (br m, 1 H, PCH_2P), 3.72 (d, ^{195}Pt satellites are obscured by other resonances, 1 H, *ipso* H on Pt−C$_{aryl}$ bond), 1.53 (m, 9 H, ^{t}Bu), 1.46−1.24 (m, 27 H, ^{t}Bu). For (dtbpm)Pt[η^2-(1,3,5-tris(trifluoromethyl)benzene)] Anal. Calcd (found): C, 39.95 (40.05); H, 5.29 (5.53).

(dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)]H (5). (dtbpm)Pt(Np)H (160 mg, 0.28 mmol) was dissolved in 50 mL of THF in a 250 mL round bottom Schlenk flask, and 1,4-bis(trifluoromethyl)benzene (2.2 g, 5.6 mmol) was added to the solution by pipet. The flask was fitted with a reflux condensor and stirred at 55 °C for 2 h and then at 85 °C for 4 h. The volatile material was removed in vacuo. The residue was redissolved in THF, layered with hexanes, and cooled to −25 °C to yield light orange crystals (112 mg, 56%). ^{1}H NMR (C_6D_6): δ 8.69 (d with ^{195}Pt satellites, 1 H, $J = 6.3$ Hz, $^3J_{Pt-H} = 68$ Hz), 7.64 (d with ^{195}Pt shoulders, 1 H, $J_{H-H} = 8.3$ Hz), 7.07 (d, 1 H, $J_{H-H} = 8.3$ Hz), 3.06 (t, $^2J_{P-H} = 8.0$ Hz, 2 H, PCH_2P), 1.13 (d, 18 H, $(CH_3)_3P$, $^3J_{P-H} = 14$ Hz), 1.07 (d, $^3J_{P-H} = 13$ Hz, 18 H, $(CH_3)_3P$), −6.06 (d of sextets with ^{195}Pt satellites, $^1J_{Pt-H} = 1297$ Hz, $^2J_{P(trans)-H} = 211$ Hz, $J = 3$ Hz, 1 H, Pt−H). ^{31}P NMR (C_6D_6): δ 7.5 (s with ^{195}Pt satellites, $^1J_{Pt-P} = 1549$ Hz, trans aryl), −2.5 (second-order multiplet with ^{195}Pt satellites, $^1J_{Pt-P} = 1199$ Hz, trans hydride). ^{19}F NMR (THF-d_8): δ −59.7 (s with ^{195}Pt satellites, $^4J_{Pt-F} = 53$ Hz, 3 F, CF_3 *ortho* to Pt−C$_{aryl}$), −61.5 (s, 3 F, CF_3 *meta* to Pt−C$_{aryl}$). For (dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)]H Anal. Calcd (found): C, 42.07 (41.74); H, 5.93 (6.32).

(dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H (6). (dtbpm)Pt(Np)H (125 mg) and 4,4′-bis(trifluoromethyl)biphenyl (2.03 g, 7.0 mmol) were placed in a 250 mL round bottom flask fitted with a Schlenk adaptor and dissolved in 50 mL of THF. The mixture was stirred at 40 °C for 3 h, at which time a second amount of (dtbpm)Pt(Np)H (75 mg, 0.35 mmol total) in 5 mL of THF was added to the solution via syringe. The solution was stirred at 40 °C for an additional 16 h. The volatile material was removed in vacuo and the residue extracted with 6 × 5 mL of hexanes. Recrystallization from THF/hexanes at −25 °C yielded white crystals (118 mg, 43%). ^{1}H NMR (C_6D_6): δ 8.57 (d with ^{195}Pt satellites, $^4J_{P-H} = 6.0$

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[31] Hoffmann, H.; Schellenbeck, P. *Chem. Ber.* **1967**, *100*, 692−693.

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[33] Cullen, K. E.; Sharp, J. T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2565−2579.

Hz, $^{3}J_{\mathrm{Pt-H}} = 67$ Hz, 1 H, H *ortho* to Pt−C$_{\mathrm{aryl}}$ bond), 8.11 (d, $^{3}J_{\mathrm{H-H}} = 7.9$ Hz, 2 H, $-C_6H_4CF_3$), 7.50 (d, $^{3}J_{\mathrm{H-H}} = 8.0$ Hz, 2 H, $-C_6H_4CF_3$), 7.30 (m, 2 H, H *meta* and *para* to Pt−C$_{\mathrm{aryl}}$ bond), 2.91 (t, $^{2}J_{\mathrm{P-H}} = 7.5$ Hz, 2 H, PCH_2P), 1.04 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 18 H, ^{t}Bu), 0.80 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 18 H, ^{t}Bu), −5.78 (dd with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-H}} = 1311$ Hz, $^{2}J_{\mathrm{P(trans)-H}} = 207$ Hz, $^{2}J_{\mathrm{P(cis)-H}} = 7.6$ Hz, 1 H, Pt−H). ^{31}P NMR (C_6D_6): δ 7.4 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1648$ Hz, $^{2}J_{\mathrm{P-P}} = 7.0$ Hz, trans biphenyl), −2.8 (second-order d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1287$ Hz, $^{2}J_{\mathrm{P-P}} = 7.9$ Hz, trans hydride). ^{31}P NMR (THF-d_8): δ 12.6 (d), 2.4 (d). For (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H Anal. Calcd (found): C, 47.14 (47.31); H, 5.87 (6.05).

(dtbpm)Pt[3-(4,4′-bis(trifluoromethyl)biphenyl)]H (7). Compound **7** was formed in a limited amount in the reaction above and could not be isolated in larger scale reactions. The available ^{1}H and ^{31}P NMR spectroscopic data are given below. ^{1}H NMR (THF-d_8): δ 1.48 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 18 H, ^{t}Bu), 1.38 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 18 H, ^{t}Bu), −6.58 (d of sextets with ^{195}Pt satellites ($^{1}J_{\mathrm{Pt-H}} = 1373$ Hz, $^{2}J_{\mathrm{P(trans)-H}} = 204$ Hz, $J = 3$ Hz, 1 H, Pt−H). ^{31}P NMR (THF-d_8): δ 13.1 ($^{1}J_{\mathrm{Pt-P}} = 1759$ Hz) and 2.7 ($^{1}J_{\mathrm{Pt-P}} = 1253$ Hz).

Thermolysis of (dtbpm)Pt[η^2-(1,4-bis(trifluoromethyl)benzene)]. (dtbpm)Pt[η^2-(1,4-bis(trifluoromethyl)benzene)] (8.3 mg, 0.012 mmol) was placed in a resealable NMR tube and dissolved in 600 μL of THF-d_8. The solution was heated at 55 °C and monitored by ^{1}H and ^{31}P NMR spectroscopy. After 1.5 h 59% of the starting arene remained, 11% had been converted to the C−H activated product **6**, and the balance (30%) had been converted to $(dtbpm)_2Pt_2$ (^{31}P NMR, THF-d_8: δ 84.3, $^{1}J_{\mathrm{Pt-P}} = 4572$ Hz, with higher order couplings. See Supporting Information). After 15.5 h, 13% of the starting arene remained, 35% had been converted to the C−H activated product, and the balance (52%) had been converted to $(dtbpm)_2Pt_2$.

(dtbpm)Pt(2,2′-bis(4,4′-trifluoromethyl)biphenyl) (8). (dtbpm)Pt(Np)H (80 mg, 0.14 mmol) and bis-(4,4′-trifluoromethyl)biphenyl were dissolved in 25 mL of THF in a 100 mL Teflon-stoppered air-free flask. The solution was stirred at 55 °C for 2 h and then at 85 °C for 15 days. The volatile material was removed in vacuo and the residue extracted with 3 × 4 mL of hexanes. The remaining solids were redissolved in CH_2Cl_2 and layered with Et_2O by slow diffusion. Feathery yellow crystals (20 mg, 18%) deposited after several days. ^{1}H NMR (CD_2Cl_2): δ 7.96 (m with ^{195}Pt satellites, $^{3}J_{\mathrm{Pt-H}} = 67$ Hz, 2 H), 7.40 (d, $^{3}J_{\mathrm{H-H}} = 7.6$ Hz, 2 H), 7.21 (d, $^{3}J_{\mathrm{H-H}} = 7.7$ Hz, 2 H), 3.66 (t, $^{3}J_{\mathrm{P-H}} = 7.9$ Hz, 2 H, PCH_2P), 1.51 (d, $^{4}J_{\mathrm{P-H}} = 13.1$ Hz, 36 H, ^{t}Bu). ^{19}F NMR (CD_2Cl_2): δ −62.6 (s). ^{31}P NMR (CD_2Cl_2): δ 4.95 (s with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1523$ Hz). For (dtbpm)Pt(2,2′-bis(4,4′-trifluoromethyl)biphenyl) Anal. Calcd (found): C, 47.27 (47.35); H, 5.63 (5.91).

(dtbpm)Pt[η^2-(3,5,4′-tris(trifluoromethyl)biphenyl)] (9). (dtbpm)Pt(Np)H (71 mg, 0.12 mmol) and 3,5,4′-tris(trifluoromethyl)biphenyl (222 mg, 0.62 mmol) were dissolved in 17.5 mL of THF and transferred to a 100 mL air-free Teflon-stoppered flask. The mixture was stirred at 55 °C for 2 h. The volatile material was removed in vacuo and the residue extracted with 5 × 2 mL of hexanes. The remaining solids were a relatively pure sample of (dtbpm)Pt[η^2-(3,5,4′-bis(trifluoromethyl)biphenyl)]. Recrystallization from THF/hexanes at −25 °C yielded orange-red crystals (73 mg, 68%). An additional crop of crystals was recovered from the mother liquor for a combined yield of 76%. This compound has a complicated ^{31}P NMR spectrum which appears to be typical for the η^2 arene complexes in this system. ^{1}H NMR (THF-d_8, 20 °C): δ 7.99 (br d, $J = 7.9$ Hz, 2 H), 7.64 (d, $J = 8.3$ Hz, 2 H), 6.95 (br s, 1 H), 6.31 (br s, 1 H), 4.08 (br s, 1 H), 3.84 (br m, 2 H, PCH_2P), 1.37 (br m, 27 H, ^{t}Bu), 0.98 (br s, 9 H, ^{t}Bu). ^{19}F NMR (THF-d_8, 20 °C): δ −61.21 (br s with ^{195}Pt shoulders, 3 F), −63.04 (s, 3 F), −65.67 (s with ^{195}Pt shoulders, 3 F). ^{31}P NMR (THF-d_8, 20 °C): δ 44.8 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 3307$ Hz, $^{2}J_{\mathrm{P-P}} = 101$ Hz), 43.9 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 2991$ Hz, $^{2}J_{\mathrm{P-P}} = 101$ Hz). ^{1}H NMR (THF-d_8, −20 °C): δ 8.07 (d, $J = 8.2$ Hz, 2 H), 7.69 (d, $J = 8.4$ Hz, 2 H), 6.96 (s, 1 H), 6.31 (br s with ^{195}Pt shoulders, 1 H), 4.03 (d with ^{195}Pt satellites, $^{2}J_{\mathrm{Pt-H}} = 74$ Hz, $J = 5.6$ Hz, 1 H), 3.88 (m, 2 H, PCH_2P), 1.41 (m, 18 H, ^{t}Bu), 1.31 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, ^{t}Bu), 0.93 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, ^{t}Bu). For (dtbpm)Pt[η^2-(3,5,4′-tetrakis(trifluoromethyl)biphenyl)] Anal. Calcd (found): C, 44.97 (44.81); H, 4.95 (5.35).

Generation of (dtbpm)Pt[2′-(3,5,4′-tris(trifluoromethyl)biphenyl)]H (10). A solution of (dtbpm)Pt[η^2-(3,5,4′-tris(trifluoromethyl)biphenyl)], generated in situ from (dtbpm)Pt(Np)H (8.0 mg, 0.014 mmol) and 3,5,4′-tris(trifluoromethyl)biphenyl (50 mg, 0.14 mmol) in 600 μL of THF-d_8 in a resealable NMR tube, was heated at 85 °C for 37 h. ^{1}H and ^{31}P NMR spectroscopy indicated that the η^2 complex had been converted into an aryl hydride complex. The reaction was nearly complete (∼10% η^2 complex remained) and with a small amount of $(dtbpm)_2Pt_2$ present. Continued heating at 85 °C completed the conversion. ^{1}H NMR (THF-d_8): δ 8.39 (s, 2 H, $C_6H_3(CF_3)_2$), 8.06 (d, $^{4}J_{\mathrm{P-H}} = 6.0$ Hz, ^{195}Pt satellites obscured by other resonances, 1 H, H *ortho* to Pt−C$_{\mathrm{aryl}}$ bond), 7.82 (s, 1 H), 7.24 (d, $^{3}J_{\mathrm{H-H}} = 7.7$ Hz, 1 H), 7.09 (d, $^{3}J_{\mathrm{H-H}} = 8.0$ Hz, 1 H), 3.69 (t with ^{195}Pt shoulders, $^{2}J_{\mathrm{P-H}} = 7.6$ Hz, 2 H, PCH_2P), 1.38 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 18 H, ^{t}Bu), 1.09 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 18 H, ^{t}Bu), −6.12 (dd with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-H}} = 1293$ Hz, $^{2}J_{\mathrm{P(trans)-H}} = 204$ Hz,$^{2}J_{\mathrm{P(cis)-H}} = 7.1$ Hz). ^{19}F NMR (THF-d_8): δ −62.84 (s, 3 F), −62.98 (s, 6 F). ^{31}P NMR (THF-d_8): δ 6.2 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1680$ Hz, $^{2}J_{\mathrm{P-P}} = 5$ Hz), −3.2 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1291$ Hz, $^{2}J_{\mathrm{P-P}} = 5$ Hz).

(dtbpm)Pt[η^2-(3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl)] (11). (dtbpm)Pt(Np)H (85 mg, 0.15 mmol) and 3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl (633 mg, 1.49 mmol) were dissolved in 30 mL of THF and transferred to a 100 mL air-free Teflon-stoppered flask. The mixture was stirred at 55 °C for 2 h. The volatile material was removed in vacuo and the residue extracted with 3 × 3 mL of hexanes. Recrystallization of the insoluble portion from CH_2Cl_2/Et_2O at −25 °C yielded red crystals (55 mg, 40%). An additional crop of crystals (23 mg) was recovered from the mother liquor for a total yield of 57%. ^{1}H NMR (THF-d_8, rt): δ 8.23 (br s, 2 H), 7.90 (s, 1 H), 7.01 (br s, 1 H), 6.39 (br d, $J = 4.2$ Hz, 1 H), 4.08 (br s, 1 H), 3.85 (br m, 2 H, PCH_2P), 1.42 (br d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, ^{t}Bu), 1.34 (br m, 18 H, ^{t}Bu), 0.98 (br s, 9 H, ^{t}Bu). ^{19}F NMR (THF-d_8): δ −63.10 (br s with ^{195}Pt shoulders, 3 F), −65.24 (s, 6 F), −67.46 (d with ^{195}Pt shoulders, $J = 4.5$ Hz, 3 F). ^{31}P NMR (THF-d_8, rt): δ 43.2 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 3318$ Hz, $^{2}J_{\mathrm{P-P}} = 96$ Hz), 41.1 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 2967$ Hz, $^{2}J_{\mathrm{P-P}} = 96$ Hz). ^{1}H NMR (THF-d_8, −20 °C): δ 8.37 (s, 2 H), 8.00 (s, 1 H), 7.02 (br s, 1 H), 6.44 (br d with ^{195}Pt shoulders, $J = 4.8$ Hz, 1 H), 4.06 (dd with ^{195}Pt satellites, $^{2}J_{\mathrm{Pt-H}} = 63$ Hz, $^{2}J_{\mathrm{P-H}} = 10$ Hz, $^{4}J_{\mathrm{H-H}} = 4.4$ Hz, 1 H), 3.90 (m, 2 H, PCH_2P), 1.42 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, ^{t}Bu), 1.37 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, ^{t}Bu), 1.32 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, ^{t}Bu), 0.93 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, ^{t}Bu). For (dtbpm)Pt[η^2-(3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl)] Anal. Calcd (found): C, 42.81 (43.01); H, 4.79 (4.86).

(dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)]Cl (12). (dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)]H (94 mg, 0.13 mmol) was dissolved in 21 mL of THF in a scintillation vial. Then 1 mL CH_2Cl_2 was added and the mixture was stirred at room temperature for 2 h. The volatile material was removed in vacuo and the residue washed with 5 × 2 mL of hexanes. The remaining solids were redissolved in THF, layered with hexanes, and cooled at −25 °C. White crystals (64 mg, 65%) deposited after 3 days. ^{1}H NMR (C_6D_6): δ 8.47 (d with ^{195}Pt satellites, 1 H, $J = 6.8$ Hz, $^{3}J_{\mathrm{Pt-H}} = 45$ Hz), 7.52 (d, 1 H, $J_{\mathrm{H-H}} = 6.0$ Hz), 7.07 (d, 1 H, $J_{\mathrm{H-H}} = 8.0$ Hz), 2.69 (t with ^{195}Pt shoulders, $^{2}J_{\mathrm{P-H}} = 8.2$ Hz, 2 H, PCH_2P), 1.31 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 14$ Hz), 1.20 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 14$ Hz), 1.10 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 14$ Hz), 0.87 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 14$ Hz). ^{31}P NMR (C_6D_6): δ −10.3 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 3518$ Hz, $^{2}J_{\mathrm{P-P}} = 20$ Hz, trans Cl), −16.2 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1519$ Hz, $^{2}J_{\mathrm{P-P}} = 19$ Hz, trans aryl). ^{19}F NMR (C_6D_6): δ −54.7 (br s, 3 F, CF_3 *ortho* to Pt−C$_{\mathrm{aryl}}$), −62.0

(s, 3 F, CF_3 *meta* to Pt$-$C$_{\mathrm{aryl}}$). For (dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)]Cl Anal. Calcd (found): C, 40.14 (40.21); H, 5.53 (5.64).

(dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]Cl (13). (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H (60 mg, 0.076 mmol) was dissolved in 6 mL of toluene in a scintillation vial. Then 50 μL of CCl_4 was added and the mixture was stirred at room temperature for 30 min. The volatile material was removed in vacuo. The remaining solids were dissolved in THF, layered with hexanes, and cooled at -25 °C. White crystals (36 mg, 58%) deposited after 3 days. ^{1}H NMR (C_6D_6): δ 8.42 (d with ^{195}Pt shoulders, 1 H, $J = 8.1$ Hz, $^{3}J_{\mathrm{Pt-H}} = 45$ Hz), 8.39 (d, 2 H, $J_{\mathrm{H-H}} = 8.0$ Hz), 7.49 (d, 2 H, $J_{\mathrm{H-H}} = 8.0$ Hz), 7.26 (d, 1 H, $J_{\mathrm{H-H}} = 7.9$ Hz), 7.14 (d partially obscured by residual solvent peak, 1 H), 2.62 (m, 1 H, PCH_2P), 2.48 (m, 1 H, PCH_2P), 1.22 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 14$ Hz), 1.14 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 14$ Hz), 0.96 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 14$ Hz), 0.38 (d, 9 H, $(CH_3)_3P$, $^{3}J_{\mathrm{P-H}} = 15$ Hz). ^{31}P NMR (C_6D_6); δ -10.1 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 3645$ Hz, $^{2}J_{\mathrm{P-P}} = 2$ Hz, trans Cl), -13.4 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1426$ Hz, $^{2}J_{\mathrm{P-P}} = 2$ Hz, trans aryl). For (dtbpm)Pt[2-(1,4-bis(trifluoromethyl)phenyl)]Cl Anal. Calcd (found): C, 45.17 (45.16); H, 5.50 (5.48).

(dtbpm)Pt[2′-(3,5,4′-tris(trifluoromethyl)biphenyl)]Cl (14). (dtbpm)Pt(Np)H (66 mg, 0.16 mmol) and 3,5,4′-tris(trifluoromethyl)biphenyl (207 mg, 0.58 mmol) were dissolved in 22 mL of THF and transferred to a 100 mL air-free Teflon-stoppered flask. The mixture was stirred at 55 °C for 2 h and then at 85 °C for 40 h. The volatile material was removed in vacuo and the residue washed once with 3 mL of hexanes. The residue was then redissolved in 6 mL of THF. Then 0.5 mL of CH_2Cl_2 was added, and the mixture was stirred at room temperature for 2 h. The solvent was removed under vacuum and the residue washed with 4 × 3 mL of pentane. The remaining solids were dissolved in THF, layered with pentane, and allowed to stand at room temperature. Pale yellow crystals (32 mg, 31%) deposited after several days. ^{1}H NMR ($CDCl_3$): δ 8.57 (s, 2 H, $C_6H_3(CF_3)_2$), 7.98 (d with ^{195}Pt shoulders, $^{4}J_{\mathrm{P-H}} = 7.4$ Hz, 1 H, H *ortho* to Pt$-$C$_{\mathrm{aryl}}$ bond), 7.76 (s, 1 H, $C_6H_3(CF_3)_2$), 7.19 (s, 2 H), 3.33 (m, 1 H, PCH_2P), 3.15 (m, 1 H, PCH_2P), 1.58 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 9 H, ^{t}Bu), 1.37 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 9 H, ^{t}Bu), 1.29 (d, $^{3}J_{\mathrm{P-H}} = 15$ Hz, 9 H, ^{t}Bu), 0.79 (d, $^{3}J_{\mathrm{P-H}} = 15$ Hz, 9 H, ^{t}Bu). ^{31}P NMR ($CDCl_3$): δ -9.3 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 3689$ Hz, $^{2}J_{\mathrm{P-P}} = 16$ Hz), -12.7 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1424$ Hz, $^{2}J_{\mathrm{P-P}} = 16$ Hz). For (dtbpm)Pt[2′-(3,5,4′-tris(trifluoromethyl)biphenyl)]Cl Anal. Calcd (found): C, 43.08 (43.30); H, 4.97 (5.00).

(dtbpm)Pt(2-biphenyl)Cl (15). (dtbpm)Pt(2,2′-biphenyl) (70 mg, 0.11 mmol) was suspended in 8 mL of THF, and 18 μL of concentrated HCl was added via microsyringe. The suspension was stirred for 15 min at room temperature, during which time the yellow crystals dissolved and the solution became colorless. The volatile material was removed in vacuo. The residue was taken up in CH_2Cl_2 and layered with Et_2O. Colorless crystals deposit after several days at -20 °C. ^{1}H NMR ($CDCl_3$): δ 8.13 (d, 2 H, $^{3}J_{\mathrm{H-H}} = 7.4$ Hz), 7.67 (t, 1 H, $J_{\mathrm{H-H}} = 7.3$ Hz, $^{3}J_{\mathrm{Pt-H}} = 39$ Hz), 7.27 (t, 2 H, $J_{\mathrm{H-H}} = 7.5$ Hz), 7.16 (m, 2 H), 7.04 (t, 1 H, $J_{\mathrm{H-H}} = 7.2$ Hz), 6.91 (t, 1 H, $J_{\mathrm{H-H}} = 7.4$ Hz), 3.18 (m, 2 H, PCH_2P), 1.54 (d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 9 H, $(CH_3)_3P$), 1.46 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 9 H, $(CH_3)_3P$), 1.34 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 9 H, $(CH_3)_3P$), 0.76 (d, $^{3}J_{\mathrm{P-H}} = 15$ Hz, 9 H, $(CH_3)_3P$). ^{31}P NMR ($CDCl_3$): δ -8.6 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 3904$ Hz, $^{2}J_{\mathrm{P-P}} = 15$ Hz, trans Cl), δ -9.2 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1328$ Hz, $^{2}J_{\mathrm{P-P}} = 15$ Hz, trans biphenyl). For (dtbpm)Pt(2-biphenyl)Cl Anal. Calcd (found): C, 50.61 (50.45); H, 6.88 (6.87).

Generation of (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]D (6-d_1). (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]Cl (6 mg, 0.0073 mmol) was placed in a resealable NMR tube and dissolved in 600 μL of C_6D_6. Dicyclopentadienylzirconium dideuteride (3.4 mg, 0.015 mmol) was added, and the suspension was mixed at room temperature for 4 h. Conversion to the deuterium-labeled compound was judged complete by ^{1}H and ^{31}P NMR spectroscopy. The spectra were identical to compound (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H except for the missing hydride resonance at δ -5.78 in the ^{1}H spectrum, and the resonance at δ -2.24 revealed coupling to the ^{2}H nucleus in the ^{31}P NMR spectrum. ^{1}H NMR (C_6D_6): δ 8.57 (d with ^{195}Pt satellites, $^{4}J_{\mathrm{P-H}} = 6.0$ Hz, $^{3}J_{\mathrm{Pt-H}} = 67$ Hz, 1 H, H *ortho* to Pt$-$C$_{\mathrm{aryl}}$ bond), 8.10 (d, $^{3}J_{\mathrm{H-H}} = 7.9$ Hz, 2 H, $-C_6H_4CF_3$), 7.50 (d, $^{3}J_{\mathrm{H-H}} = 8.0$ Hz, 2 H, $-C_6H_4CF_3$), 7.31 (m, 2 H, H *meta* and *para* to Pt$-$C$_{\mathrm{aryl}}$ bond), 2.90 (t, $^{2}J_{\mathrm{P-H}} = 7.5$ Hz, 2 H, PCH_2P), 1.04 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 18 H, ^{t}Bu), 0.80 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 18 H, ^{t}Bu). ^{31}P NMR (C_6D_6): δ 7.8 (s with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1649$ Hz, P trans biphenyl), -2.24 (t with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1274$ Hz, $^{2}J_{\mathrm{D-P}} = 36$ Hz, P trans D).

Thermolysis of (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H. (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H (7 mg, 0.0089 mmol) was dissolved in 600 μL of THF-d_8 in a sealable NMR tube and capped. The tube was frozen in liquid N_2 and quickly flame-sealed. The solution was heated at 125 °C for 6 h. Reductive elimination of biphenyl was complete along with concomitant formation of $(dtbpm)_2Pt_2$. Continued heating (14 days) at 125 °C resulted in the eventual decomposition of the platinum dimer.

Thermolysis of (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]D. (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]D was prepared as above in 600 μL of C_6D_6 in a resealable NMR tube. The mixture was allowed to stand at room temperature for 18 h, and no discernible change in the ^{1}H NMR spectrum was observed. The mixture was then heated at 85 °C for 30 min and again checked by ^{1}H NMR spectroscopy to reveal no significant H/D exchange. Continued heating at 85 °C resulted in nearly complete reductive elimination of 4,4′-bis(trifluoromethyl)biphenyl-d_1 with concomitant formation of $(dtbpm)_2Pt_2$ after 16 h, as confirmed in the ^{1}H and ^{31}P NMR spectra.

Generation of (dtbpm)Pt[2-(1,3,5-tris(trifluoromethyl)phenyl)]H (16). (dtbpm)Pt[η^2-(1,3,5-tris(trifluoromethyl)benzene)] (9.8 mg, 0.13 mmol) was dissolved in 0.6 mL of C_6D_6 and transferred to a resealable NMR tube. The tube was photolyzed ($\lambda > 300$ nm) and the reaction monitored by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy. The starting complex was converted to an aryl hydride and reached a photostabilized state after 5.5 h (ratio of η^2 arene to aryl hydride is 3:2). Photolysis for 2 days did not result in any significant decomposition. ^{1}H NMR (C_6D_6): δ 8.14 (s, 2 H), 3.07 (t with ^{195}Pt shoulders, $^{2}J_{\mathrm{P-H}} = 7.9$ Hz, 2 H, PCH_2P), 1.16 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 9 H, ^{t}Bu), 1.05 (br d, $^{3}J_{\mathrm{P-H}} = 13$ Hz, 27 H, ^{t}Bu), -8.78 (d with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-H}} = 1257$ Hz, $^{2}J_{\mathrm{P(trans)-H}} = 207$ Hz, 1 H, Pt$-$H). ^{19}F NMR (C_6D_6): δ -57.8 (t with ^{195}Pt satellites, $^{3}J_{\mathrm{Pt-F}} = 80$ Hz, 6 F, CF_3 *ipso* to Pt$-$C$_{\mathrm{aryl}}$ bond), -61.5 (br s, 3 F). ^{31}P NMR (C_6D_6): δ 12.7 (s with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 2041$ Hz, trans aryl), 4.13 (s with ^{195}Pt satellites, $^{1}J_{\mathrm{Pt-P}} = 1339$ Hz, trans H).

Generation of (dtbpm)Pt[2-(3,5,4′-tris(trifluoromethyl)biphenyl)]H (17). (dtbpm)Pt[η^2-(3,5,4′-tris(trifluoromethyl)biphenyl)] (7.5 mg, 0.0087 mmol) was placed in a sealable NMR tube and dissolved in 600 μL of C_6D_6. The tube was capped, frozen in liquid N_2, and quickly flame-sealed. The tube was photolyzed and the reaction monitored by ^{1}H and ^{31}P NMR spectroscopy. The starting complex was converted to an aryl hydride and reached a photostabilized state after 11 h. Extended photolysis (1 week) did not significantly alter the ratio of η^2 arene to aryl hydride (2.2:1) nor did the reaction mixture decompose. ^{1}H NMR (C_6D_6): δ 8.23 (s with ^{195}Pt shoulders, 1 H, Pt$-C_6H_2(CF_3)_2$), 7.90 (br d, $^{3}J_{\mathrm{H-H}} = 7.8$ Hz, 2 H, $C_6H_4(CF_3)$), 7.61 (s with ^{195}Pt shoulders, 1 H, Pt$-C_6H_2(CF_3)_2$), 7.40 (br d, $^{3}J_{\mathrm{H-H}} = 7.8$ Hz, 2 H, $C_6H_4(CF_3)$), 2.97 (dt, $^{2}J_{\mathrm{H-H}} = 17$ Hz, $^{2}J_{\mathrm{P-H}} = 7.6$ Hz, 1 H, PCH_2P), 2.72 (dt, $^{2}J_{\mathrm{H-H}} = 17$ Hz, $^{2}J_{\mathrm{P-H}} = 7.6$ Hz, 1 H, PCH_2P), 1.17 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 9 H, ^{t}Bu), 0.94 (d, $^{3}J_{\mathrm{P-H}} = 14$ Hz, 9 H, ^{t}Bu), 0.92 (d, $^{3}J_{\mathrm{P-H}} = 13$

Hz, 9 H, ^{t}Bu), 0.45 (d, $^3J_{P-H} = 13$ Hz, 9 H, ^{t}Bu), −7.66 (d of mult. with ^{195}Pt satellites, $^1J_{Pt-H} = 1266$ Hz, $^2J_{P(trans)-H} = 206$ Hz, $^2J_{P(cis)-H}$ is obscured due to coupling to CF$_3$). ^{31}P NMR (C$_6$D$_6$): δ 9.2 (s with ^{195}Pt satellites, $^1J_{Pt-P} = 1872$ Hz), 1.6 (second-order multiplet with ^{195}Pt satellites, $^1J_{Pt-P} = 1237$ Hz).

Generation of (dtbpm)Pt[2-(3,5,3′,5′-tris(trifluoromethyl)biphenyl)]H (18). (dtbpm)Pt[η^2-(3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl)] (7.0 mg, 0.0081 mmol) was placed in a resealable NMR tube and dissolved in 600 μL of C$_6$D$_6$. The mixture was photolyzed and the reaction monitored by ^{1}H and ^{31}P NMR spectroscopy. The starting complex was converted to an aryl hydride and reached a photostabilized state after several hours. An additional 2 days of photolysis did not significantly alter the ratio of η^2-arene to aryl hydride (2.3:1). ^{1}H NMR (C$_6$D$_6$): δ 8.24 (s with ^{195}Pt shoulders, 1 H), 7.76 (s, 1 H), 7.41 (s with ^{195}Pt shoulders, 1 H), (two aromatic H's are obscured by residual C$_6$D$_6$), 2.99 (dt, $^2J_{H-H} = 17$ Hz, $^2J_{P-H} = 8.5$ Hz, 1 H, PCH_2P), 2.69 (dt, $^2J_{H-H} = 17$ Hz, $^2J_{P-H} = 8.5$ Hz, 1 H, PCH_2P), 1.14 (d, $^3J_{P-H} = 14$ Hz, 9 H, ^{t}Bu), 0.95 (d, $^3J_{P-H} = 14$ Hz, 9 H, ^{t}Bu), 0.87 (d, $^3J_{P-H} = 13$ Hz, 9 H, ^{t}Bu), 0.51 (d, $^3J_{P-H} = 13$ Hz, 9 H, ^{t}Bu), −7.57 (d of mult. with ^{195}Pt satellites, $^1J_{Pt-H} = 1267$ Hz, $^2J_{P(trans)-H} = 203$ Hz, $^2J_{P(cis)-H}$ is obscured due to coupling to CF$_3$). ^{31}P NMR (C$_6$D$_6$): δ 8.9 (s with ^{195}Pt satellites, $^1J_{Pt-P} = 1875$ Hz), 1.8 (second-order multiplet with ^{195}Pt satellites, $^1J_{Pt-P} = 1242$ Hz).

Generation of (dtbpm)Pt(2-biphenyl)H. (19) (dtbpm)Pt(2-biphenyl)Cl (7.8 mg, 0.011 mmol) and [Cp$_2$ZrH$_2$]$_2$ (3.8 mg, 0.0085 mmol) were placed in a resealable NMR tube, and 600 μL of C$_6$D$_6$ was added. The mixture was allowed to react at room temperature for 3 h. Conversion to the hydride was judged to be quantitative by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR (C$_6$D$_6$): δ 8.34 (d, 2 H, $^3J_{H-H} = 7.0$ Hz), 8.24 (t with ^{195}Pt satellites, 1 H, $J_{H-H} = 7.0$ Hz, $^3J_{Pt-H} = 68$ Hz), 7.61 (d with ^{195}Pt satellites, 1 H, $J_{H-H} = 7.7$ Hz, $^4J_{Pt-H} = 6.9$ Hz), 7.32 (m, 3 H), 7.20 (t, 1 H, $J_{H-H} = 7.3$ Hz), 7.13 (t obscured by C$_6$D$_5$H resonance, 1 H), 3.01 (t, $^2J_{P-H} = 7.3$ Hz, 2 H, PCH_2P), 1.16 (d, 18 H, (CH_3)$_3$P, $^3J_{P-H} = 13$ Hz), 0.92 (d, 18 H, (CH_3)$_3$P, $^3J_{P-H} = 13$ Hz), −5.37 (dd with ^{195}Pt satellites, $^2J_{P(trans)-H} = 210$ Hz, $^2J_{P(cis)-H} = 8.8$ Hz, $^1J_{Pt-H} = 1339$ Hz). ^{31}P NMR (C$_6$D$_6$): δ 8.0 (d with ^{195}Pt satellites, $^1J_{Pt-P} = 1549$ Hz, $^2J_{P-P} = 11$ Hz, trans biphenyl), −3.2 (d with ^{195}Pt satellites, $^1J_{Pt-P} = 1381$ Hz, $^2J_{P-P} = 9$ Hz, trans hydride).

Thermolysis of (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H in the Presence of 4,4′-bis(trifluoromethyl)biphenyl. (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H (5 mg, 0.0063 mmol) and 4,4′-bis(trifluoromethyl)biphenyl (18 mg, 0.063 mmol) were placed in a resealable NMR tube and dissolved in 600 μL of THF-d_8. The solution was heated at 55 °C and monitored by ^{1}H and ^{31}P NMR spectroscopy. After 3 h, no change was observed. The solution was then heated at 85 °C. After 3 h, 5% of the starting material had been converted to (dtbpm)Pt[3-(4,4′-bis(trifluoromethyl)biphenyl)]H. After 15 h at 85 °C 12% of the starting complex had converted to (dtbpm)Pt[3-(4,4′-bis(trifluoromethyl)biphenyl)]H, 12% had been converted to (dtbpm)Pt[2,2′-(4,4′-bis(trifluoromethyl)biphenyl)], and 2% had been converted to (dtbpm)$_2$Pt$_2$. After 65 h at 85 °C the reaction mixture consisted of 51.6% of the starting complex, 7.9% of (dtbpm)Pt[3-(4,4′-bis(trifluoromethyl)biphenyl)]H, 27.2% of (dtbpm)Pt[2,2′-(4,4′-bis(trifluoromethyl)biphenyl)], and 13.3% of (dtbpm)$_2$Pt$_2$. After 7.5 days at 85 °C the reaction mixture consisted of 24% of the starting complex, 4.5% of (dtbpm)Pt[3-(4,4′-bis(trifluoromethyl)biphenyl)]H, 58% of (dtbpm)Pt[2,2′-(4,4′-bis(trifluoromethyl)biphenyl)], and 13.5% of (dtbpm)$_2$Pt$_2$. The two doublets due to the ^{t}Bu groups of (dtbpm)Pt[2-(4,4′-bis(trifluoromethyl)biphenyl)]H slowly decreased in intensity and gave rise to a single doublet in the same region of the ^{1}H NMR spectrum. A single resonance with ^{195}Pt satellites (δ 4.5, $^1J_{Pt-P} = 1523$ Hz) was also observed to appear in place of the two resonances for the starting complex in the ^{31}P NMR spectra. H$_2$ gas evolution was not observed during the course of the reaction. Once the reaction was complete, the solvent was removed and the residue washed with hexanes to remove (dtbpm)$_2$Pt$_2$ and free biphenyl. The remaining solid was redissolved in CD$_2$Cl$_2$ and ^{1}H, ^{19}F, and ^{31}P NMR were taken. The spectral features indicated a symmetric Pt(II) species. Three aromatic signals, a singlet and two doublets, were observed in a 2:2:2 ratio. The singlet was further downfield than the others and displays ^{195}Pt satellites. The bridging methylene of the diphosphine ligand appeared as a triplet and integrated as two protons, and the doublet for the ^{t}Bu groups integrated as 36 protons. Only one resonance was observed in the ^{19}F NMR. The ^{31}P NMR spectrum showed the same resonance as previously observed. All the NMR evidence indicated that a second C−H activation process had occurred resulting in the formation of a 4,4′-bis(trifluoromethyl)-substituted analogue of (dtbpm)Pt(2,2′-biphenyl). The structure of this complex was confirmed by X-ray crystallography.

Thermolysis of (dtbpm)Pt[η^2-(3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl)]. (dtbpm)Pt[η^2-(3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl)] (10.5 mg, 0.011 mmol) was placed in a resealable NMR tube and dissolved in 600 μL of C$_6$D$_6$. The mixture was heated at 85 °C for 5 days and the reaction monitored by ^{1}H and ^{31}P NMR spectroscopy. Although a biphenyl hydride was formed in the reaction, the transformation was not clean and other products were formed, including the free biphenyl and (dtbpm)$_2$Pt$_2$. Continued heating at 125 °C resulted in nearly quantitative formation of the dimer after 16 h.

Reaction of (dtbpm)Pt(neopentyl)H with C$_6$H$_6$ in THF-d_8. (dtbpm)Pt(neopentyl)H (8 mg, 0.014 mmol) was placed in a resealable NMR tube and dissolved in 1 mL of THF-d_8. Then 40 equiv of C$_6$H$_6$ (50 μL, 0.56 mmol) was then added to the solution via microsyringe, and the mixture was heated at 55 °C for 90 min. The ^{1}H and ^{31}P NMR spectra of the mixture revealed that (dtbpm)$_2$Pt$_2$ was the primary product (>95%) and C−H activation of benzene had not occurred.

(dtbpm)Pt[η^2-hexakis(trifluoromethyl)benzene)]. (dtbpm)Pt(Np)H (8.0 mg, 0.014 mmol) and hexakis(trifluoromethyl)benzene (34 mg, 0.070 mmol) were placed in a resealable NMR tube and dissolved in 0.6 μL of THF-d_8. The mixture was heated at 55 °C and monitored by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy. After 1 h, the starting platinum complex had been consumed. Two broad resonances were observed in the ^{1}H NMR spectrum at δ 2.45 and 1.52 for the methylene and ^{t}Bu hydrogens, respectively. The ^{31}P NMR spectrum revealed an asymmetric bisphosphine complex with multiplet resonances at δ 75.3 and 69.6 with accompanying ^{195}Pt satellites. The ^{19}F NMR spectrum was a single, very broad resonance at −54.55. The solution was then heated at 125 °C for 48 h. Neither the ^{31}P nor ^{19}F NMR spectra changed, but significant sharpening of the resonances was observed in the ^{1}H NMR spectrum. ^{1}H NMR (THF-d_8): δ 2.44 (t with ^{195}Pt shoulders, $^2J_{P-H} = 7.6$ Hz, 2 H, PCH$_2$P), 1.52 (quartet, $J = 6.9$ Hz, 36 H, ^{t}Bu). ^{19}F NMR (THF-d_8): δ −54.55 (br singlet). ^{31}P NMR (THF-d_8): δ 75.3 (m with ^{195}Pt satellites, $^1J_{Pt-P} = 3279$ Hz), 69.6 (m with ^{195}Pt satellites, $^1J_{Pt-P} = 2741$ Hz).

(dtbpm)Pt(4-C$_6$H$_4$CF$_3$)$_2$. A solution of bis(di-*tert*-butylphosphino)methane (47 mg, 0.15 mmol) in 2 mL of THF was added to a solution of (COD)Pt(4-C$_6$H$_4$CF$_3$)$_2$ (83 mg, 0.14 mmol) in 8 mL of THF in a Schlenk round-bottom flask. The flask was fitted with a reflux condensor and heated at 85 °C for 4 days. The volatile material was removed in vacuo and the residue recrystallized from CH$_2$Cl$_2$/Et$_2$O at −25 °C. Two crops of a white crystalline material (70 mg, 64% total) were collected. ^{1}H NMR (C$_6$D$_6$): δ 7.75 (t with ^{195}Pt satellites, $J = 7.0$ Hz, $^3J_{Pt-H} = 60$ Hz, 4 H, H *ortho* to Pt−C$_{aryl}$ bond), 7.39 (d, $^3J_{H-H} = 7.6$ Hz, 4 H, H *meta* to Pt−C$_{aryl}$ bond), 2.85 (t, $^2J_{P-H} = 7.5$ Hz, 2 H, PCH$_2$P), 1.00 (d, $^3J_{P-H} = 13$ Hz, 36 H, ^{t}Bu). ^{31}P NMR (C$_6$D$_6$): δ −6.1 (s with ^{195}Pt satellites, $^1J_{Pt-P} = 1426$ Hz. Anal. Calcd (found): C, 47.15 (47.11); H, 5.87 (6.19).

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Supporting Information Available: Summary of crystallographic procedures, data, intramolecular distances and angles, and positional and thermal parameters for compounds **3**, **9**, **11**, and **12**. Data for the preparation of dtbpm, and the reaction of **1** with 1,4-bistrifluoro-methylbenzene are also included. Figures for the higher order ^{31}P NMR spectrum of **4** and the VT NMR of **9** and **11** are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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