Ligand Metalation in Triisopropylphosphine−Platinum(II) Compounds†

David L. Thorn

Central Research and Development Department, Central Science and Engineering Laboratory, Experimental Station P.O. Box 80328, Wilmington, Delaware 19880-0328

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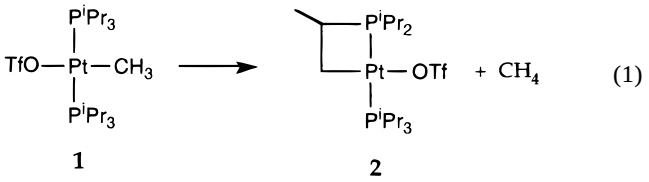
The compound *trans*-(methyl)(trifluoromethanesulfonato)(bis(triisopropylphosphine))-platinum(II) (**1**) is stable in solution at room temperature, but when treated with a catalytic amount of HCl, it undergoes rapid loss of methane and forms the metalated compound (triisopropylphosphine)(trifluoromethanesulfonato)(2,2-diisopropyl-3-methyl-1-platina-2-phosphacyclobutane) (**2**). The key intermediate is *trans*-chloro(trifluoromethanesulfonato)(bis-(triisopropylphosphine))platinum(II) (**3**), which rapidly undergoes metalation with loss of trifluoromethanesulfonic acid.

While ligand metalation is a very well-known reaction and there are many examples in platinum−phosphine chemistry,[1] ligand metalation usually requires either vigorous conditions, e.g., prolonged heating, or extremely bulky tertiary alkyl groups on the ligand. One interesting exception to this generalization is provided by van der Boom et al.,[2] who showed that the ligand (diisopropylphosphino)isodurene—bulky but without tertiary alkyl groups—undergoes facile metalation on Pt(II) centers. Another exception, facile "platination" of a triisopropylphosphine ligand (eq 1),



1 **2** (1)

was recently discovered in our laboratory. The reaction of eq 1 is especially interesting because, when first encountered, the reaction was erratic: Sometimes the reaction was rapid at room temperature, reaching completion in 1 h or less, but sometimes the reaction was unobservably slow, with solutions of (methyl)-platinum compound **1** in CD_2Cl_2 persisting unchanged for more than 24 h at room temperature. Evidently this reaction was catalyzed by small and variable amounts of some unknown component. As described below, HCl serves as such a catalyst; after the deliberate addition of small amounts of HCl, the metalation reaction (eq 1) reaches completion in as little as a few minutes at room temperature.

It was suspected initially that chloro compounds were involved in the erratic promotion/catalysis of eq 1, because the solvent used, CD_2Cl_2, can easily contain (or react with low-valent transition metals to provide) small amounts of chloride. On the basis of that suspicion we worked out the chloro/trifluoromethanesulfonato ("triflato")/acid chemistry summarized in Scheme 1. All of the compounds in Scheme 1 have been characterized by NMR spectroscopy; all but **3** and **4** have been isolated, and **1**, **2**, and **5** have been characterized by C, H analysis. In the course of this work it was established that, while chloride does play a key role in the promotion/catalysis of eq 1 by the probable mechanism discussed below, CD_2Cl_2 itself does not serve as a chloride source. Rather, adventitious chloride and residual HOTf were responsible for the initially erratic nature of the reaction of eq 1; pure **1** in pure CD_2Cl_2 is stable for several days at room temperature.

Most of the reactions in Scheme 1 are familiar but two are noteworthy. The first noteworthy reaction is between **1** and trifluoromethanesulfonic acid (HOTf, "triflic acid"). At room-temperature methane is *not* evolved, provided there is no available chloride present.[3,4] Signals in ^{1}H and ^{31}P NMR spectra shift when HOTf is added, indicating some interaction between **1** and HOTf, but the Pt−CH_3 group remains intact, and **1** is partially

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(1) See, for example: Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. Chem. Commun.* **1970**, 1176−1177. Al−Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972−1982. Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59−63. Clark, H. C.; Goel, A. B.; Goel, R. G.; Goel, S. *Inorg. Chem.* **1980**, *19*, 3220−3225. Goel, A. B.; Goel, S.; Vanderveer, D. *Inorg. Chim. Acta* **1981**, *54*, L267−L269. Goel, R. G.; Ogini, W. O.; Srivastava, R. C. *Organometallics* **1982**, *1*, 819−824. Simms, B. L.; Shang, M.; Lu, J.; Youngs, W. J.; Ibers, J. A. *Organometallics* **1987**, *6*, 1118−1126. Alyea, E. C.; Malito, J. *J. Organometal. Chem.* **1988**, *340*, 119−126. Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Organometallics* **1989**, *8*, 1188−1191. Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A.; Manassero, M. *J. Chem. Soc., Dalton Trans.* **1995**, 777−781.

(2) Van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 2562−2568.

(3) Probably, when HCl (or HOTf and a chloride source) is added to alkyltriflatoPt **1** or **2**, the reaction actually proceeds by Cl/triflate exchange to first make the corresponding chloro(alkyl)platinum compound and HOTf, which then react.

(4) When **1**, **2**, or **3** is treated with stoichiometric HOTf there is a *slow* reaction to form $HP^iPr_3^+$ along with several unidentified Pt compounds (however, hydrido signals are not observed at room temperature). With excess HOTf, the formation of $HP^iPr_3^+$ becomes rapid and often dominates. Among the resulting unidentified Pt compounds there may be monophosphine species such as $\{Pt(CH_3)(P^iPr_3)(OTf)\}_x$ similar to the (monophosphine)(methyl)palladium compounds described by Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1141−1147.

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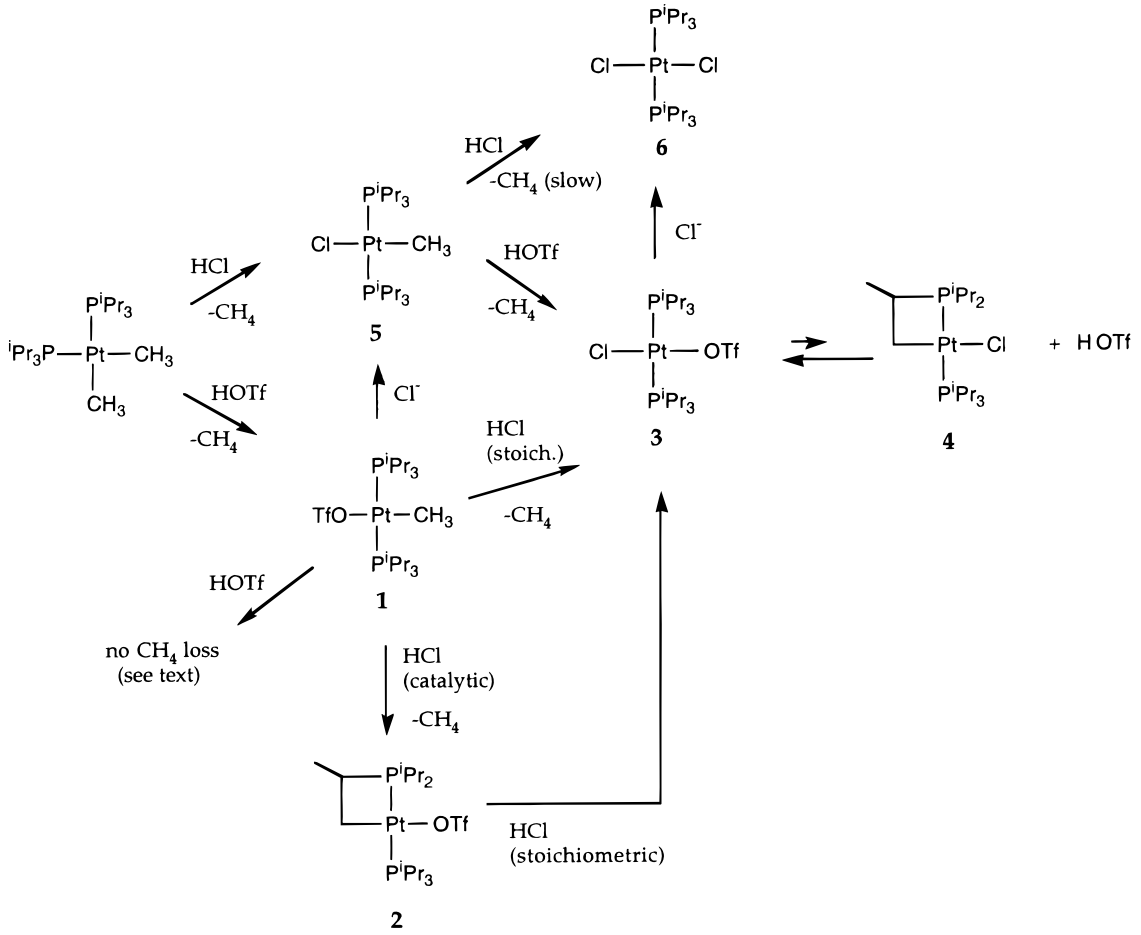
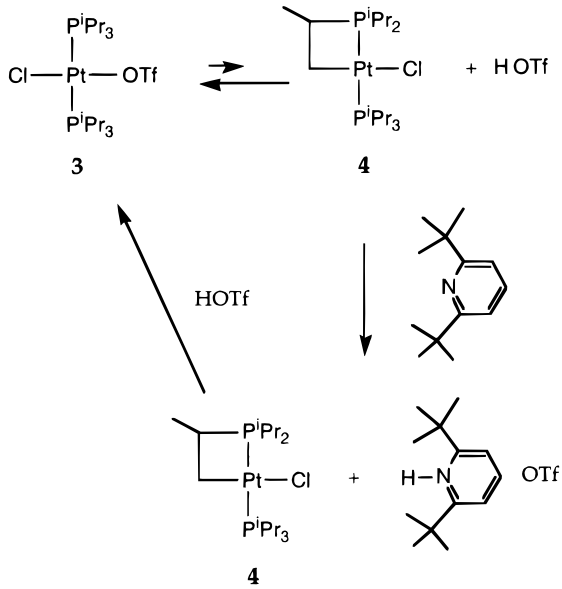
Scheme 1



restored by addition of noncoordinating base (e.g., 2,6-di-*tert*-butylpyridine).[4] Compound **1** does react with HCl to form methane (with stoichiometric HCl, the major Pt-containing product is **3**), suggesting some critical role played by the chloride in promoting the protonolysis of the Pt−CH_3 bond.[3] Like **1**, **2** does not react rapidly with stoichiometric HOTf [4] but does react with stoichiometric HCl [3] to form the C−H bond and make **3.** Evidently the Pt−C bonds of triflato(alkyl)-platinum compounds **1** and **2** are extremely robust; their reluctance to undergo room-temperature protonolysis with HOTf may result from the Pt−C bonds being trans to a ligand (triflato) having poor trans influence. The Pt−C bonds of chloro(alkyl)platinum compounds **4** and **5** do readily undergo protonolysis with HOTf.[5]

The second noteworthy reaction in Scheme 1 is the rapid, reversible metalation of chloro(triflato)platinum compound **3**. In CD_2Cl_2 solution **3** is converted largely to **4** within a few minutes at room temperature when treated with 2,6-di-*tert*-butylpyridine, and **4** is converted back largely to **3** comparably rapidly when treated with HOTf (eq 2). But attempts to isolate **3** have failed, as it is vulnerable to several additional reactions, including irreversible chloride redistribution according to the



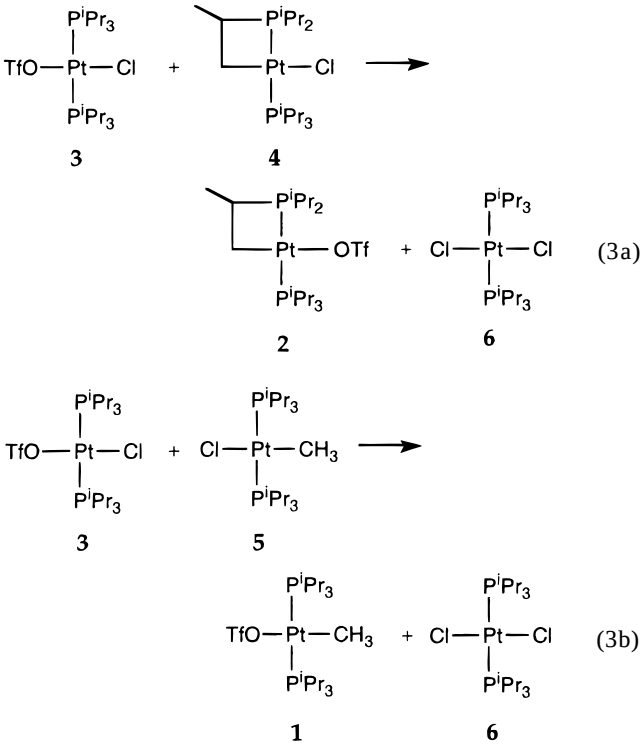
(2)

reactions of eqs 3a,b.[6] Thus, even without added reagents, **3** is unstable in CD_2Cl_2 solution and gradually reacts to form **2**, **6**, HOTf, $HP^iPr_3^+$, and at least one additional Pt compound not yet identified.[4]

Exactly why **3** so readily undergoes metalation is not known for certain. A likely mechanism is electrophilic

(5) The mechanism of protonolysis of Pt(II)−CH_3 bonds has been discussed recently by: Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966−4968. Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371−9372. Stahl, S. S.; Labinger, J. A.; Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 5961−5976. There has been some controversy over the precise mechanism and earlier articles are referenced therein.

(6) The chloride redistribution reaction, eq 3b, is observed whenever significant concentrations of **3** and **5** are simultaneously present. The successful preparation of **3** from **5** (Scheme 1) requires the rapid addition of stoichiometric HOTf; if less than 1 equiv of HOTf is used, **1** and **6** become major products.

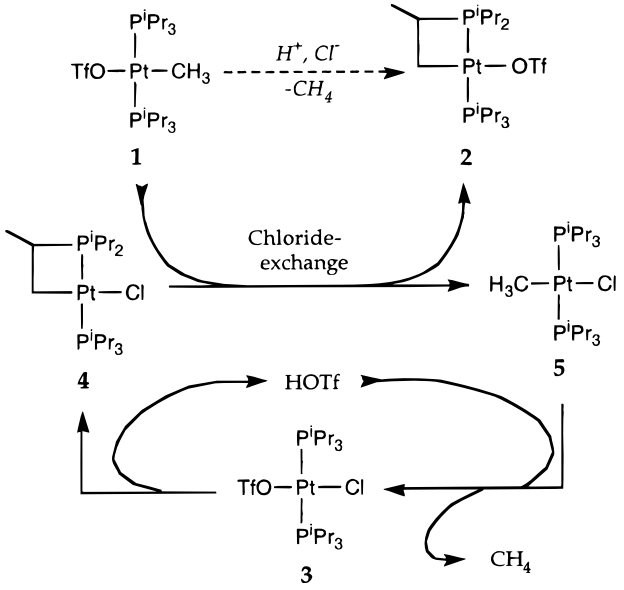


attack on the ligand alkyl groups by a transient three-coordinate outer-sphere triflato species $[Cl(^iPr_3P)_2Pt]^+OTf^-$, in which case, there are at least three contributing factors. First, the triflato ligand is especially labile in **3** owing to the steric bulk of the phosphine ligands cis to it, thus making the hypothetical three-coordinate outer-sphere triflato form $[Cl(^iPr_3P)_2Pt]^+OTf^-$ unusually easy to attain. Second, this same steric bulk ensures that whenever the triflato ligand is separated from the Pt center, there are 36 equivalent ligand C−H bonds immediately available to undergo metalation. And third, the Pt−C bond that results from metalation is very robust, as four-member rings in (metalla)phosphacyclobutanes and (metalla)azacyclobutanes are often quite stable.[1,7]

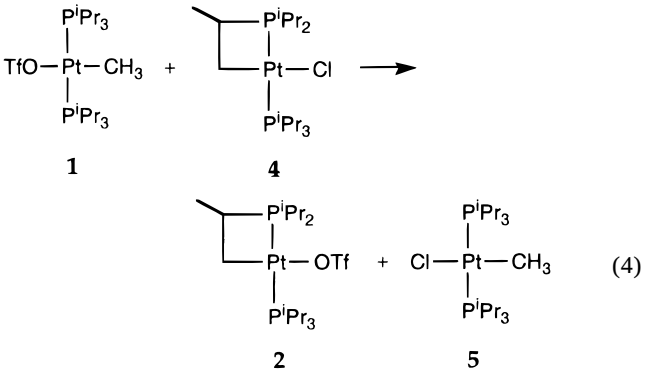
Given the facile metalation observed for **3** (eq 2), we are convinced it is the crucial intermediate in the chloride-mediated metalation reaction of **1**. In the overall reaction (Scheme 2), the equilibrium metalation of **3** is driven to completion by removing the metalated chloroplatinum **4** via chloride exchange with **1**, as indicated in eq 4. This reaction completes the catalytic cycle for the conversion of **1** into **2** using small amounts of HOTf/Cl^- or HCl as given in the overall scheme of Scheme 2. Thus, when a solution of methylplatinum triflato compound **1** in CD_2Cl_2 is treated with ~5 mol % HCl (in ether or dioxane), forming a small amount of **3** in situ, the metalated **2** is formed in >90% yield within 10 min at room temperature. With less HCl, the reaction requires more time for completion but results in a higher yield of **2**.

Note that chloride *exchange* between **1** and **4** (eq 4) is a vital component of this catalytic cycle, but chloride *redistribution*, which converts monochloro compounds into dichloro compound **6** (eqs 3), does not occur to a significant extent in this catalytic cycle. This is because

Scheme 2



chloride redistribution (eqs 3) is a bimolecular reaction between two chloro-containing compounds, while chloride exchange (eq 4) involves only one chloro-containing



compound. By keeping only a very small overall concentration of chloro-containing compounds, chloride redistribution becomes slow relative to chloride exchange, **6** does not accumulate as a significant reaction product, and the H^+Cl^--catalyzed conversion of **1** to **2** is observed as a very clean reaction. If a higher concentration of chloro-containing compounds is present, chloride redistribution becomes a significant reaction and dichloro **6** becomes a significant reaction product.[6]

In the cycle of Scheme 2 both chloride and acid are essential catalytic components and exhibit an interesting theme of mutual activation: The $Pt-CH_3$ group is activated toward acidolysis by triflic acid when "promoted" by a trans-chloride ligand (e.g., **1** → **5**), and the chloride ligand in turn is labilized in **4** by the trans alkyl group thus available to exchange with **1** and continue the catalytic cycle. Without chloride, acid alone (e.g., HOTf) does not convert **1** to **2**, as discussed above; without H^+, chloride alone simply converts **1** to **5** (Scheme 1) and metalation is not observed at room temperature. The combined role of H^+Cl^- is to cleave a Pt(II)−C bond and generate a metalation-prone electrophilic metal center and is very like the role played by HBF_4 or HOTf in the exchange of cycloplatinated dimethylbenzylamine with azobenzene, reported by

(7) Zhang, L.; Zetterberg, K. *Organometallics* **1991**, *10*, 3806−3813.

Ryabov and van Eldik.[8] In their work, protonolysis of the aryl−Pt(II) bond is promoted by other electron-donating aryl−Pt(II) and amine−Pt(II) groups, and added chloride is unnecessary.

Superficially, the overall transformation of **1** into **2** plus methane is reminiscent of "σ-bond metathetical exchange" of alkyl groups on late transition metal centers.[9] But the H^+Cl^--catalyzed ligand metalation reaction **1** → **2** proceeds via discrete intermediate **3** having no Pt−C bonds, by what is probably an electrophilic mechanism. It is likely that ligand metalation chemistry observed for many other phosphine−Pt compounds[10,11] proceeds through electrophilic intermediates similar to **3** and that whatever forcing conditions may be required to observe metalated products actually reflect the difficulty in making such electrophilic intermediates. Once the intermediate is available, making the Pt−C bond may be a relatively fast reaction.[9,12,13]

Experimental Section

Reactions were carried out in an atmosphere of dry N_2 using solvents dried over molecular sieves. NMR spectra were recorded using QE300 (^{1}H, ^{31}P) and Bruker 500 (^{13}C, ^{1}H of **2** and **4**) instruments; data for unmetalated compounds are summarized in Table 1. C, H analyses were performed by Galbraith Laboratories. The compounds *cis*-dimethyl(bis(triisopropylphosphine))-platinum(II)[14] and *trans*-dichlorobis(triisopropylphosphine)platinum(II)[15] (compound **6**) were prepared following literature methods.

***trans*-(Methyl)(trifluoromethanesulfonato)(bis-(triisopropylphosphine))platinum(II) (1).** To a stirred suspension of *cis*-dimethyl(bis(triisopropylphosphine))platinum(II) (1.21 g (2.22 mmol) in 10 mL of ether) was added, slowly, 0.35 g of trifluoromethanesulfonic acid (2.33 mmol). The material dissolved and a precipitate formed. The suspension was stirred 30 min at room temperature and filtered, yield 1.18 g (1.74 mmol, 78%). An analytically pure sample was obtained by recrystallization from concentrated toluene solution. Anal. Calcd for $C_{20}H_{45}O_3F_3P_2S_1Pt_1$: C, 35.34; H, 6.67. Found: C, 35.37; H, 6.86.

Table 1. ^{1}H, ^{31}P NMR Data for Unmetalated Compounds[a]

compound, L_2PtXY[b]	Pt-CH_3[c]	isopropyl H	^{31}P[d]
1, X = CH_3, Y = triflate	0.81 t (6; 96)	1.37 quart (7), 2.68 m	42.0 (2896)
3, X = Cl, Y = triflate		1.47 quart (7), 2.85 m	31.6 (2377)
5, X = CH_3, Y = Cl	0.47 t (5; 83)	1.38 quart (7), 2.89 m	32.9 (2850)
6, X = Cl, Y = Cl		1.44 quart (7), 2.95 m	27.8 (2415)

[a] Measured in CD_2Cl_2 solution at ambient probe temperature, ~24°C. Chemical shifts in ppm downfield from external Me_4Si (^{1}H), H_3PO_4 (^{31}P); coupling constants in Hertz. [b] L = triisopropylphosphine. [c] Coupling constants (Hz) in parentheses: First number, J_{31P}; second number, J_{195Pt}. [d] Coupling constant J_{195Pt} in parentheses.

(Triisopropylphosphine)(trifluoromethanesulfonato)(2,2-diisopropyl-3-methyl-1-platina-2-phosphacyclobutane) (2). Compound **1** (0.33 g (0.49 mmol) in 1 mL of CD_2Cl_2) was treated with 0.01 g of HCl/ether solution (~0.1 M) (~0.001 mmol of HCl, 0.2 mol % of **1**) and allowed to stand at room temperature. Bubbles of methane gas were observed and methane was detected in solution (NMR δ 0.2 [5]). After 4 h at room temperature, the reaction was complete by NMR analysis and the formation of **2** was essentially quantitative. The solution was evaporated and the residue redissolved in ~5 mL of warm pentane. After 2 days at −25 °C, the crystalline deposit was collected, yield 0.22 g (0.33 mmol, 68%). Anal. Calcd for $C_{19}H_{41}O_3F_3P_2S_1Pt_1$: C, 34.39; H, 6.23%. Found: C, 34.25; H, 6.45. NMR (CD_2Cl_2): δ {1H}^{31}P, −20.0 (d, 376, J_{Pt} 2238), 41.8 (d, 376, J_{Pt} 3009) ^{1}H (500 MHz) PtC**H**H′ 1.94 (d, 18, of t, 10, of d, 7; J_{Pt} 105), PtCH**H**′ ~1.16 obsc; $PtCH_2C$**H**Me, $PtCH_2CHMeP(C$**H**$Me_2)_2$, 2.63 (m), 2.68 (m), 3.03 (m); $PtCH_2CH$**Me**, $PtCH_2CHMeP(CH$**Me**$_2)_2$ 1.12 (dd, 7, 14), 1.17 (dd, 7, 14),1.37 (dd, 7, obsc), 1.44 (dd, 7, 19), 1.48 (dd, 7, 17); $PtP(C$**H**$Me_2)_3$ 2.36 (m); $PtP(CH$**Me**$_2)_3$ 1.33 (dd, 7, 14), 1.35 (dd, 7, 14); ^{13}C, −18.4 (d, 23, J_{Pt} 636; Pt**C**), 18.2 (dd, 5, 5), 35.9 (d, 30, J_{Pt} 68), plus complex pattern of isopropyl C signals (18−25 ppm).

***trans*-Chloro(methyl)(bis(triisopropylphosphine))platinum(II), (5).** Compound **1** (0.50 g, 0.74 mmol) was added to a methanol solution (10 mL) of tetramethylammonium chloride (0.5 g). A white precipitate formed immediately and was collected after the mixture had been stirred for 30 min, yield 0.40 g (95%). Anal. Calcd for $C_{19}H_{45}P_2Cl_1Pt_1$: C, 40.32; H, 8.01. Found: C, 40.22; H, 8.15.

***trans*-Chloro(trifluoromethanesulfonato)(bis-(triisopropylphosphine))platinum(II) (3) and (Triisopropylphosphine)(chloro)(2,2-diisopropyl-3-methyl-1-platina-2-phospha-cyclobutane) (4).** Compound **5** (0.13 g, 0.23 mmol) in 2 mL of CD_2Cl_2 was treated with 0.034 g (0.23 mmol) of trifluoromethanesulfonic acid, and the solution was separated into two

(8) Ryabov, A. D.; van Eldik, R. *Angew. Chem.* **1994**, *106*, 798; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 783−784.

(9) Exchange with alkanes is exhibited by (solvento)(methyl)Ir (Luecke, H. F.; Arndtsen, B. A.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2517−2518. Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970−1973. Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462−10463) and (solvento)(methyl)Pt (Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848−849). In these compounds of the late transition metals, the actual mechanism of such alkyl group exchange is likely to be oxidative addition/reductive elimination of H−C bonds. Alkyl compounds of the early transition metals exchange with alkanes by mechanisms more closely approximating true σ-bond metathesis.

(10) Other routes to metalated triisopropylphosphine−platinum compounds include chloride abstraction from the dichloro **6** using AgOTf, which results in several compounds including the metalated triflato compound **2**. That the reaction is relatively slow arises from the difficulty in abstracting the relatively nonlabile chloride from **6**, since metalation is rapid once the chlorotriflato compound **3** is formed. There are also reactions of the dichloro compound **6** with $AlCl_3$ in CD_2Cl_2; the resulting complex mixture has ^{31}P NMR signals consistent with the presence of metalated compounds.

(11) Tricyclohexylphosphine-platinum and tricyclopentylphosphine-platinum compounds analogous to the triisopropylphosphine-platinum compounds described herein behave similarly, except the cyclohexyl group provides a more complex set of metalated products (not fully characterized), some of which eventually lead to hydridoplatinum compounds.

(12) This is fully consistent with recent studies of methane activation by (triflato)(methyl)(Ir) compounds.[9] In this reaction, loss of the triflato ligand is a critical component, as the reaction occurs much more rapidly when the triflato ligand is replaced by solvent.

(13) Rapid ligand metalation by electrophilic Ir(III) compounds has been demonstrated; see: Simpson, R. D. *Organometallics* **1997**, *16*, 1797−1799. Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974−1978.

(14) Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81−85.

(15) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorganic Syntheses;* Wiley-Interscience: New York, 1979; Vol. 19, pp 107−110.

portions. The NMR spectra of one portion (recorded within 10 min) indicated the formation of **3** along with small amounts of dichloro **6** and metalated **2**. The second portion of the solution was treated with 0.05 g of 2,6-di-*tert*-butylpyridine, and NMR spectra (recorded within ~15 min) indicated the formation of metalated **4** (and protonated 2,6-di-*tert*-butylpyridine) along with small amounts of **2** and dichloro compound **6**. NMR data for **4**: $\{^1H\}^{31}P$, −27.9 (d, 403; J_{Pt} 2208), 36.2 (d, 403; J_{Pt} 2906); $\{^1H\}^{13}C$, Pt*C* −14.1 (d, 26, J_{Pt} 580).

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