Kurzmitteilung / Short Communication

Room-Temperature C−F Bond Activation of Hexafluorobenzene by a Tailor-Made Pt(0) Intermediate, [(dtbpm)Pt(0)]

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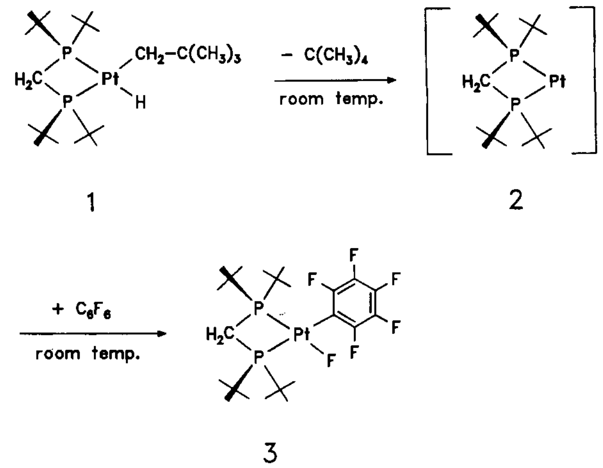
Reductive elimination of neopentane from *cis*-hydridoneopentyl[η^2-bis(di-*tert*-butylphosphanyl)methane]platinum(II), (dtbpm)Pt(Np)(H) (**1**), allows to generate the 14-electron fragment [(dtbpm)Pt(0)] (**2**) at ambient temperature. This highly reactive intermediate is capable of activating C−F bonds of hexafluorobenzene, yielding exclusively the C−F insertion product (dtbpm)Pt(C_6F_5)F (**3**).

Although numerous transition-metal compounds have been shown to cleave C−H and various C−X bonds[1], only a few examples of thermally induced *intra*-[2] and still fewer cases of *inter*molecular[3] C−F bond activations are known. The pronounced inertness of perfluorinated hydrocarbons (e.g. C_6F_6, C_6F_{14}), caused by their high C−F bond-dissociation energies[4] and by the weakness of metal−fluorocarbon interactions[5], has even led to their successful employment as solvents in photochemical C−H activation experiments[6], although some organometallic C−H-activating intermediates seem to react with fluorocarbons in a non-specified way[7]. With hexafluorobenzene, the 16-electron intermediate [Cp(PMe$_3$)Rh] forms a π complex Cp(PMe$_3$)Rh(η^2-C_6F_6), stable towards subsequent thermal or light-induced oxidative addition of a C−F bond to the metal[8], whereas the analogous compound Cp*(PMe$_3$)Rh(η^2-C_6F_6) may be converted into Cp*(PMe$_3$)Rh(C_6F_5)F in a *photochemical* reaction[9]. Neither [Cp*(PMe$_3$)Rh] (when generated in C_6F_6 at 65°C) nor Cp*(PMe$_3$)Rh(η^2-C_6F_6) (up to 110°C), undergo thermal C−F insertion processes[9]. To our knowledge, a quantitative, *inter*molecular, low-temperature C−F activation of C_6F_6, yielding exclusively a stable *cis*-fluoropentafluorophenyl transition-metal complex without consecutive reaction steps, is unprecedented so far. The first such case is reported here.

We have recently shown, that the stereoelectronically unusual 14-electron intermediate [(dtbpm)Pt(0)] (**2**), the four-membered ring-chelate structure of which is stabilized by the particular diphosphanylmethane ligand bis(di-*tert*-butylphosphanyl)methane (dtbpm)[10], can be generated from its precursor **1**[11] at ambient temperature by reductive elimination of neopentane. **2** not only can be trapped by alkenes, alkynes, or other ligands but, presumably due to its extremely small P−Pt−P angle of ca. 75°C [i.e. ca. 105° less than the groundstate-geometry value of linear (PR$_3$)$_2$Pt molecules!] and its steric properties, this high-energy fragment also exhibits novel, quite specific and selective *inter*molecular bond-activation patterns. Thus, **2** has been shown to activate C−Si bonds of tetramethylsilane, tetraethylsilane, hexamethyldisilane, and of related compounds at room temperature, and according to prelimiary mechanistic studies these C−Si bond cleavage reactions seem to take place by primary C−H activation steps of methyl groups[11]. It was in this context that we also investigated the reactivity of **2** towards the strong C−F bonds of hexafluorobenzene.

When **1** is allowed to react with C_6F_6 at room temperature over a period of 8 days (suspension of **1** in an excess of C_6F_6, vide infra), a clean and quantitative conversion into the thermally stable *cis*-fluoropentafluorophenylplatinum(II) complex **3**, accompanied by elimination of neopentane, is observed (Scheme 1).

Scheme 1



Compound **3** is isolated by evaporation of excess C_6F_6 and can be recrystallized from dichloromethane/hexane (1:1), furnishing colorless crystals. As all nuclei of **3** are NMR-active, its structure could be characterized unequivocally by ^{1}H-, ^{19}F-, ^{31}P-, ^{13}C-, and ^{195}Pt-NMR spectroscopy, as well as by IR and by elemental analysis.

Mechanistically, we assume the intermediacy of the "hot", unsaturated 14-electron fragment **2**. For **2** an extremely high-lying d-type HOMO, energetically way above the rest of the platinum d levels, and a rather low-lying σ-acceptor LUMO (mainly an sp hybrid at Pt), are predicted by MO calculations[12a,b]. Energy and shape (hybridization) of both frontier MOs are caused by the constraint of the anomalously small P−Pt−P angle of the four-membered chelate ring. Thus, **2** is expected to be a very strong Lewis acid, but simultaneously its electron-donating (π-donor) capability towards empty σ*- or π*-acceptor levels of substrates should be much more pronounced than for other, less bent or linear dicoordinate Pt(0) complexes[12c], tailoring **2** for oxidative addition (bond-activation) processes. The high kinetic reactivity of **2** is coupled to a large thermodynamic driving force for C – F activation of C_6F_6, because in line with available data for relative Pt – X bond energies[13], the strong Pt – F and Pt – C_6F_5 bonds of product **3** should make the reaction of Scheme 1 very exothermic. We do not know at this point, if π complexation of C_6F_6 precedes the C – F activation step, but certainly (dtbpm)Pt(η^2-C_6F_6) has to be regarded as a reasonable intermediate en route to **3**. If this perfluoroarene π complex, unobserved so far, is involved, it must have a distinctly smaller barrier towards insertion of the coordinated metal fragment (dtbpm)Pt into one of the C – F bonds than e.g. a Cp*(PMe_3)Rh or a Cp(PMe_3)Rh unit, in accord with their different electronic-structure characteristics. At this point, however, we cannot yet rigorously exclude an alternative mechanism with direct formation of **3** from **1**, initiated by an electron-transfer process involving C_6F_6 as a substrate with high electron affinity and the rather electron-rich Pt(II) center of intact **1**, followed by elimination of neopentane in a subsequent step. From a merely steric point of view and in the light of successful trapping experiments[11], which established the formation of **2** from **1**, the latter pathway, requiring an approach of C_6F_6 to the rather crowded Pt center of **1**, seems less attractive than a reaction of hexafluorobenzene with preformed **2**, which has its frontier orbitals[11] pointing precisely towards the "open" metal-coordination site.

Detailed mechanistic studies, also with other fluorocarbon substrates, are necessary to elucidate the exact course and the scope of this unusual C – F activation reaction. Such work, along with experiments aimed towards an isolation of related π complexes of arenes with the (dtbpm)Pt metal fragment is in progress in our laboratory, as well as further studies of the unique bond-activation properties of **2** towards various other C – X bonds.

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Experimental

All manipulations were carried out under dry and oxygen-free nitrogen. Solvents were dried following standard literature procedures and were distilled under N_2 immediately before use. C_6F_6 was dried over P_4O_{10}, distilled under nitrogen, and condensed directly into the reaction vessel. *cis*-Hydridoneopentyl[η^2-bis(di-*tert*-butylphosphanyl)methane]platinum(II) (**1**) was prepared according to ref.[11]. – IR: FT spectrometer Nicolet 5 DX. – ^{1}H NMR (270 MHz, reference CH_2Cl_2 as int. standard, δ = 5.32 rel. to TMS), $^{13}C\{^1H\}$ NMR (67.90 MHz, reference CH_2Cl_2 as int. standard, δ = 53.8 rel. to TMS), $^{31}P\{^1H\}$ NMR (109 MHz, reference 85% H_3PO_4 as ext. standard), $^{195}Pt\{^1H\}$ NMR (57.8 MHz, referenced to 21.4 MHz with a 100-MHz spectrometer[13]): JOEL-JNM-GX 270 FT-NMR spectrometer. – ^{19}F NMR: Bruker AM 360 (338.9 MHz, reference CF_3CO_2H as ext. standard). – Elemental analysis: Microanalytical Laboratory of the Institute. – Melting point (uncorrected): Electrothermal IA 9200 melting-point apparatus, glass capillaries sealed under N_2.

cis-Fluoro(pentafluorophenyl)[η^2-bis(di-tert-butylphosphanyl)methane]platinum(II) (**3**): 6.00 ml (52.1 mmol) of hexafluorobenzene is vacuum-transferred into a Schlenk tube equipped with a magnetic stirring bar and containing 0.31 g (0.54 mmol) of powdered **1**. The colorless suspension is allowed to react at room temperature (ca. 20°C) over a period of 8 d with continous stirring under nitrogen. After this time, the reaction mixture has adopted a pale yellow color, and the original alkyl hydride **1** is quantitatively converted into **3**, which precipitates. The excess hexafluorobenzene is removed under reduced pressure, the off-white solid residue is washed twice with 5-ml portions of hexane and dried in vacuo; yield 0.37 g (99%) of spectroscopically pure material (^{31}P NMR). The compound can be recrystallized from dichloromethane/hexane (1:1) furnishing air-stable, colorless crystals, m.p. 265°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (m), 2908 (m), 2873 (m), 1501 (vs), 1448 (vs), 1397 (w), 1373 (w), 1180 (w), 1058 (m), 952 (vs), 810 (w), 782 (w), 739 (w), 670 (w), 680 (w), 495 (w), 467 (w). – ^{1}H NMR (CD_2Cl_2): δ = 3.43 (t + satellites, $|\,^2J_{P,H} + {}^2J_{P',H}\,|$ = 17.8 Hz, 2H, PCH_2P), 1.56 (d, $^3J_{P,H}$ = 14.5 Hz, 18H, *t*Bu), 1.35 (d, $^3J_{P,H}$ = 15.2 Hz, 18H, *t*Bu). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = –12.2 (m + satellites, $^1J_{Pt,P}$ = 2016 Hz, P *cis* to F), –18.0 (dd + satellites, $^1J_{Pt,P}$ = 3313 Hz, $^2J_{P,P}$ = 25.4 Hz, $^2J_{P,F}$ = 170 Hz, P *trans* to F). – ^{19}F NMR (CD_2Cl_2): δ = –39.56 (m + satellites, $^3J_{Pt,F}$ = 283 Hz, 2F, *ortho*) –84.70 (t, $^3J_{F,F}$ = 22.2 Hz, 1F, *para*), –86.48 (m, 2F, *meta*), –93.95 (dd + satellites, $^2J_{P(cis),F}$ = 25.0 Hz, $^2J_{P(trans),F}$ = 165.8 Hz, $^1J_{Pt,F}$ = 273 Hz, PtF, 1F). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 149.41 (m, C_{ipso}), 146.14 (m, C_{ortho}), 139.33 (m, C_{meta}), 135.68 (m, C_{para}), 37.50 [m, $PC(CH_3)_3$], 36.15 [m, $PC(CH_3)_3$], 31.73 (dd, $^1J_{P,C}$ = 24.2 Hz, $^1J_{P,C}$ = 9.5 Hz, PCH_2P), 31.18 [d, $^2J_{P,C}$ = 4.38 Hz, $PC(CH_3)_3$], 30.59 [d, $^2J_{P,C}$ = 3.66 Hz, $PC(CH_3)$]. – $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ = 1018 ($AMLXY_2$-spin system, $^1J_{Pt,P(trans\ to\ F)}$ = 3293 Hz, $^1J_{Pt,P(cis\ to\ F)}$ = 2044 Hz, $|\,^1J_{Pt,F} + {}^3J_{Pt,F}\,|$ = 282 Hz, $^4J_{Pt,F}$ = 60 Hz).

$C_{23}H_{38}F_6P_2Pt$ (685.59)
Calcd. C 40.07 H 5.67 F 16.20 P 9.35 Pt 28.92
Found C 40.29 H 5.59 F 16.63 P 9.04 Pt 27.46

CAS Registry Numbers

1: 128328-63-2 / **3**: 138407-88-2 / C_6F_6: 392-56-3

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