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Organometallics in Superacidic Media: Generation of Highly Electrophilic (Fluoroalkyl)phosphine Pt(II) Cationic Complexes

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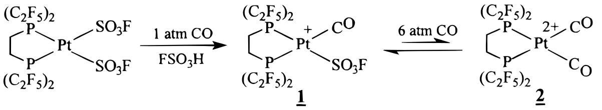
The chemistry of highly electrophilic late transition metal centers has received increasing attention in recent years.[1] In the context of "Shilov chemistry", the involvement of cationic Pt(II) centers in hydrocarbon activation has been recently demonstrated by several groups for $L_2Pt(R)X$ systems.[2,3] A key for electrophilic group 10 studies has been the use of weakly coordinating anions such as $B[3,5\text{-}C_6H_3(CF_3)_2]_4^-$ and $MeB(C_6F_5)_3^-$, which allows the incipient generation of reactive 14-electron metal centers.[2−4] Several years ago we reported the synthesis of very electron-poor (perfluoroalkyl)phosphine complexes (dfepe)Pt(Me)X (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; X = O_2CCF_3, OTf, SO_3H).[5] While these systems could, in principle, afford an extremely electrophilic $(dfepe)Pt(Me)^+$ moiety, simple anion dissociation is greatly disfavored, and ligand association reactions to form $(dfepe)Pt(Me)(L)^+$ products are not observed.[6]

A different approach was suggested by the unusual stabilities of (dfepe)Pt(Me)X and $(dfepe)Pt(X)_2$ compounds in the protic superacids CF_3SO_3H and FSO_3H,[5,7] together with Aubke's novel syntheses of unusual cationic metal polycarbonyl complexes, $M(CO)_n^{m+}$, which exploit the inherently low nucleophilicity of superacidic media.[8,9] In this report we show that well-defined (dfepe)Pt(II) coordination compounds with accessible coordination sites may be generated in superacidic solvent systems, the utility of $SbF_5(SO_2)$ as a stoichiometric reagent for the generation of weakly associated $L_nM^+[(X)(SbF_5)_n]^-$ organometallics, and some initial observations regarding the stabilization of transition metal−carbon bonds in superacidic media.

$(dfepe)Pt(X)_2$ (X = OTf, FSO_3) complexes have very limited solubilities in aprotic solvents and do not react with CO. In fluorosulfonic acid, however, treatment of $(dfepe)Pt(FSO_3)_2$ with 1 atm CO cleanly generates a cationic monocarbonyl product $[(dfepe)Pt(CO)(FSO_3)]^+$ (**1**) ($\nu(CO) = 2214$ cm^{-1}) (eq 1). Under higher pressures of CO (>40 psi), the reversible appearance of an additional single ^{31}P resonance and two new $\nu(CO)$ bands at 2235 and 2222 cm^{-1} are attributed to generation of $[(dfepe)Pt(CO)_2]^{2+}$ (**2**). In triflic acid, only $[(dfepe)Pt(CO)(OTf)]^+$ (**3**) ($\nu(CO) = 2210$ cm^{-1}) is observed under these conditions.[10] Both **1** and **3** in the absence of CO only slowly revert to $(dfepe)Pt(X)_2$ at 20 °C over several days. This acid-dependent carbonylation behavior has been previously attributed to the formation of more weakly coordinating hydrogen-bonded anion aggregates, $X(HX)_n^-$.[11,12]



(1)

Aubke has reported that dissolution of simple transition metal salts in the neat Lewis superacid SbF_5 in the presence of CO leads to X^- abstraction and the formation of novel polycarbonyl polycations such as $Pt(CO)_4^{2+}$, $Ir(CO)_6^{3+}$, and $Fe(CO)_6^{2+}$ with $Sb_2F_{11}^-$ counteranions.[8,13] Treatment of the donor phosphine complex $(dmpe)Pt(Me)_2$ with SbF_5 at 20 °C does not afford any identifiable soluble products. In contrast, both $(dfepe)Pt(Me)_2$ and $(dfepe)Pt(OTf)_2$ dissolve readily in SbF_5 and cleanly generate a common $(dfepe)Pt(X)_2$ solution species **4** exhibiting a single ^{31}P NMR resonance at δ 65.0 ($^1J_{PtP} = 4530$ Hz) (Scheme 1).[14] Although we have not yet directly determined the nature of the counteranion X in this solvent, the $^1J_{PtP}$ for this complex is significantly higher than that observed for $(dfepe)Pt(OTf)_2$ ($^1J_{PtP} = 4210$ Hz) and is clearly indicative of a more weakly coordinating $SbF_6(SbF_5)_n^-$ counteranion such as SbF_6^- or $Sb_2F_{11}^-$.[15] Similar treatment of $(dfepe)Pt(Me)_2$ with FSO_3H:SbF_5 mixtures ranging from 5% to over 90% SbF_5 uniformly produce $(dfepe)Pt(X)_2$ solution species with a slightly lower $^1J_{PtP}$ of 4350 Hz; anions of the general form $(FSO_3)_nSbF_6^{n-}$ are likely under these conditions.[16] The stability of **4** in pure SbF_5 is remarkable; no spectral changes were noted by ^{31}P NMR after 5 h at 120 °C. Complex **4** is exceedingly soluble in both SbF_5 and SbF_5/FSO_3H, and thus far attempts to isolate pure crystalline materials from these solutions have not been successful.

The reactivity of **4** is consistent with its formulation as an incipient source of "$(dfepe)Pt^{2+}$"; treatment with 2 atm of CO at 20 °C produces $(dfepe)Pt(CO)_2^{2+}$ (**2**) ($\nu(CO) = 2235, 2223$ cm^{-1}),

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(10) Selected spectroscopic data for **1**: ^{31}P NMR (FSO_3H, 161.97 MHz, 20 °C) δ 75.4 (pseudo pentet, $^2J_{PF(a)} = {}^2J_{PF(b)} = 52$ Hz, $^1J_{PtP} = 3210$ Hz; P trans to CO), 65.2 (ps p, $^2J_{FP} = 86$ Hz, $^1J_{PtP} = 3490$ Hz; P trans to FSO_3). For **2**: ^{31}P NMR (FSO_3H, 161.97 MHz, 20 °C) δ 80.4 (m, $^1J_{PtP} = 2795$ Hz). For **3**: ^{31}P NMR (HOTf, 161.97 MHz, 20 °C) δ 74.9 (p, $^2J_{PF} = 85$ Hz, $^1J_{PtP} = 3150$ Hz; P trans to CO), 65.3 (p, $^2J_{PF} = 85$ Hz, $^1J_{PtP} = 3500$ Hz; P trans to OTf).

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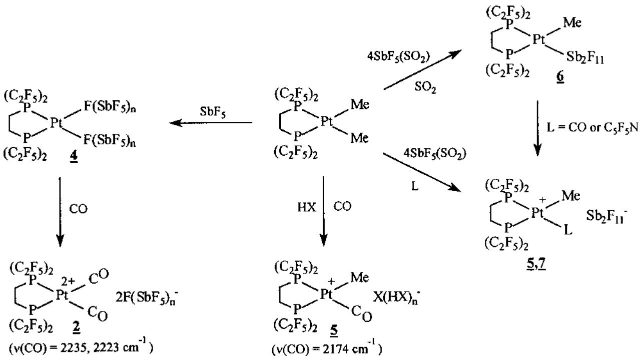
Scheme 1



with no evidence for monocarbonyl formation. The value of ν(CO)$_{ave}$ (2229 cm^{-1}) for this nonclassical[17] dicarbonyl dication is intermediate between ν(CO)$_{ave}$ reported for the neutral Pt(II) complex $(FSO_3)_2Pt(CO)_2$ (2202 cm^{-1}) and the tetracarbonyl dication, $Pt(CO)_4^{2+}$ (2261 cm^{-1}).[8d,18] The electron-poor nature of **2** is further reflected by the unusually high-field ^{13}C NMR carbonyl resonance at δ 152.6, which appears as a doublet due to coupling to the trans phosphorus ($^2J_{PC}$ = 132 Hz).[19] Taken together, the platinum carbonylation data in HOTf, FSO_3H, and SbF_5 are in accord with a relative anion lability ordering $Sb_2F_{11} > SO_3F^- > OTf^-$.

Acid-assisted anion labilization is also observed in (dfepe)Pt(Me)(X) systems: Unlike carbonylations of (dfepe)Pt(Me)(OTf) in aprotic solvents, which result in reduction to give (dfepe)Pt(CO)$_2$,[6,20] exposure of either triflic or fluorosulfonic acid solutions of (dfepe)Pt(Me)(OTf) and (dfepe)Pt(Me)(FSO_3), respectively, to 1 atm CO cleanly generates (dfepe)Pt(Me)(CO)$^+$ (**5**) (ν(CO) = 2174 cm^{-1}). The ν(CO) value for **5** appears to be the highest yet reported for a metal−alkyl complex. The methyl cation **5** also exhibits the highest protolytic stability of any transition metal organometallic system yet reported. Compared to (dfepe)Pt(Me)(FSO_3), which completely converts to (dfepe)Pt(FSO_3)$_2$ in FSO_3H in less than 4 h at 20 °C, FSO_3H solutions of **5** in the absence of ambient CO pressure slowly convert to the monocarbonyl cation **1** with a half-life of approximately 3 days. In a 0.2:0.2:1 mixture SO_2:SbF_5:FSO_3H, ca. 70% unreacted **5** is observed after 1 h.

Identifiable (dfepe)Pt(Me)(X) products were not obtained by treatment of (dfepe)Pt(Me)$_2$ with either $C_5F_5NH^+[B(Ar_f)_4]^{-2}$ or $B(C_6F_5)_3$ in pentafluoropyridine. However, addition of 3 equiv of $SbF_5(SO_2)$,[21] (a convenient crystalline source of antimony pentafluoride) to (dfepe)Pt(Me)$_2$ in SO_2 at −20 °C produces a thermally unstable species tentatively formulated as (dfepe)Pt(Me)(Sb_2F_{11}) (**6**).[22,23] The corresponding reaction in pentafluoropyridine gave (dfepe)Pt(Me)(C_5F_5N)$^+$$Sb_2F_{11}^-$ (**7**), which could be obtained as a pale-violet oily solid. Both **6** and **7** serve as labile sources of (dfepe)Pt(Me) cations; exposure of either **6** or **7** to 1 atm CO results in quantitative conversion to (dfepe)Pt(Me)(CO)]$^+$. No CO insertion into the Pt−Me bond is observed in **5** after hours at ambient temperature and at pressures up to 100 psi. Preliminary ligand exchange studies for (dfepe)Pt(Me)(L)$^+$ give a relative binding affinity ordering of L = MeCN > acetone > CO > C_5F_5N > SO_2.

In summary, by exploiting both superacidic solvent systems and the Lewis superacidic reagent $SbF_5(SO_2)$, we have been able to generate labile, highly electron-poor platinum cationic systems with well-defined (fluoroalkyl)phosphine coordination spheres. The cationic methyl complexes (dfepe)Pt(Me)(L)$^+$ in particular provide an important bridge between purely inorganic metal superacids and true organometallic systems[9b] and afford the opportunity for fundamental studies of metal-mediated hydrocarbon conversions in this extreme medium. Efforts are currently underway to further characterize these and related (fluoroalkyl)phosphine metal complex systems and explore their coordination chemistry.

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(18) Selected spectroscopic data for **2**: ^{13}C NMR (SbF_5, 100.61 MHz, 20 °C) δ 152.6 (d, $^2J_{PC}$ (trans) = 132 Hz, $^1J_{PtC}$ = 1330 Hz; Pt(^{13}CO)), 110−120 (m, P(C_2F_5)), 21.5 (br s; PCH_2). ^{31}P NMR (SbF_5, 161.97 MHz, 20 °C) δ 78.7 (P, $^2J_{PF}$ = 91 Hz, $^1J_{PtP}$ = 2790 Hz).

(19) δ(CO) values as low as 121 ppm have been reported for $M(CO)_n^{m+}$ systems.[8.]

(20) In contrast to CO addition, (dfepe)Pt(Me)(X) complexes react readily with H_2 in both protic and aprotic solvents to form [(dfepe)Pt(μ-H)]$_2$: Bennett, B. L.; Roddick, D. M. *Inorg. Chem.* **1996**, *35*, 4703−4707.

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(22) Solvation to form [(dfepe)Pt(Me)(SO_2)]$^+$ has not been ruled out. Spectroscopy for **6**: ^{1}H NMR (SO_2, 400.13 MHz, 20 °C) δ 2.77 (m, 2H; PCH_2), 2.48 (m, 2H; PCH_2), 1.23 (d, $^3J_{PH}$ = 7 Hz, 3H; $PtCH_3$). {^{1}H}^{13}C NMR (SO_2, 100.61 MHz, −10 °C) δ 107−124 (m; P(C_2F_5)), 25.5 (P(CH_2)), 15.9 ((P(CH_2)), 9.4 (d, $^1J_{PC}$ = 71 Hz, $^1J_{PtC}$ = 1450 Hz; Pt(CH_3)). ^{31}P NMR (SO_2, 161.97 MHz, −10 °C) δ 88.5 (pd, J_{PP} = 27 Hz, $^2J_{PF}$ = 66 Hz,$^1J_{PtP}$ = 1610 Hz; P trans to Me), 54.6 (pd, J_{PP} = 27 Hz, $^2J_{PF}$ = 68 Hz, $^1J_{PtP}$ = 5920 Hz). ^{19}F NMR (SO_2, 376.49 MHz, −65 °C) δ −79.0 (s, 6F; P(CF_2CF_3)), −80.0 (s, 6F; P(CF_2CF_3)), −106 to −110 (m, 8F; P(CF_2CF_3)), −91.2 (br s, 1F; Sb_2(μ-F)), −111.8 (br s, 8F; SbF_{eq}), −133.1 (br s, 2F; SbF_{ax}).

(23) The ultimate fate of the abstracted methyl group has not been determined. ^{13}C NMR spectra indicate no carbon-containing products other than **6** in solution; a small (0.38 H) protic resonance is observed at 13.3 ppm in C_5F_5N which is likely produced by the decomposition of an initial abstraction product such as (Me)SbF_5^-.