ChemComm

First example of B–C bond cleavage in the BAr_F ($B[C_6H_3(CF_3)_2$-3,5$]_4$) anion mediated by a transition metal species, *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)]^+$

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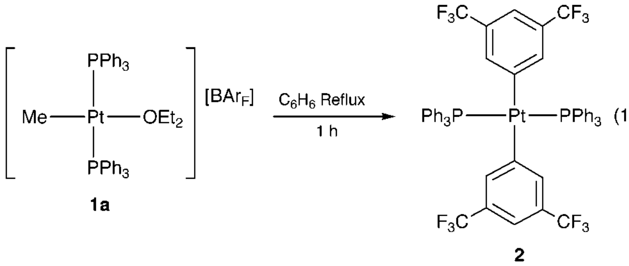
Received (in Bloomington, IN, USA) 22nd March 1999, Revised version received 26th July 1999, Accepted 28th July 1999

The first example of transition metal-mediated decomposition of the widely used BAr_F anion (BAr_F = $B[C_6H_3(CF_3)_2$-3,5$]_4$) has been accomplished by mild heating of the cationic platinum complex *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)]^+(BAr_F)^-$ in low-coordinating solvents to form the diarylated product *trans*-$(Ph_3P)_2Pt(Ar_F)_2$ in good yield, thus demonstrating that such non-interacting anions can react with electrophilic transition metal complexes.

The incorporation of non-coordinating, low-interacting anions for the stabilization of reactive transition metal cations has proven to be very useful for carrying out interesting bond-cleavage reactions, catalytic polymerization reactions and for stabilizing weakly coordinating ligands.[1] In order for these reactions to be successful, the anion must not coordinate to the vacant site, and must not react with the metal center. The BAr_F ($B[C_6H_3(CF_3)_2$-3,5$]_4$) anion has been used widely in this respect because of its ease of preparation and extremely robust character toward a variety of reactive transition metal cations.[2] Recently, however, the BAr_F anion was found to coordinate to various metal complexes in either η^3-, η^4- or η^6-fashion,[3] indicating that this anion can coordinate to suitable transition metal fragments.

Although the non-fluorinated BPh_4^- anion has been shown to be relatively reactive, displaying a marked tendency to act as a phenylating agent toward transition metal cations,[4] there have been no reported examples of arylation reactions between the BAr_F anion and transition metal centers. We herein report the first example of the reaction of the BAr_F anion with a transition metal cation in the complex *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)]^+(BAr_F)^-$ **1a**, which decomposes to form the diarylated complex *trans*-$(Ph_3P)_2Pt(Ar_F)_2$ **2** under mild conditions.

The complex *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)]^+(BAr_F)^-$ **1a** was prepared by reacting $(Ph_3P)_2Pt(Me)_2$ with $[H(OEt_2)_2]^+BAr_F^-$ in Et_2O at room temperature. Compound **1a** is stable in Et_2O solution for several weeks at −30 °C, and is stable indefinitely at −30 °C as an isolated solid. However, when **1a** was placed in benzene and allowed to stand at room temperature for 5 days, the compound *trans*-$(Ph_3P)_2Pt(Ar_F)_2$ **2** formed as colorless crystals [eqn. (1)].† The reaction was also more conveniently carried out by refluxing **1a** in toluene for 20 min. Complex **2** was characterized by elemental analysis, ^1H NMR and $^{31}P\{^1H\}$ NMR,† and the structure was determined by X-ray diffraction studies.‡ A characteristic feature of the ^1H NMR spectrum of **2** is the downfield shift of the Ar_F resonances and the change in relative peak heights; the BAr_F anion has peaks at δ 7.73 and 7.58 in a 2 : 1 ratio, while the coordinated Ar_F group in **2** exhibits peaks at δ 8.25 and 8.05 in a 1 : 2 ratio. The molecular structure of **2** (Fig. 1) shows that the platinum is in a square planar environment, with the bis(trifluoromethyl)phenyl groups located *trans* to each other and at an angle of 72.6° to the plane defined by Pt(1), P(1), P(1A), C(19) and C(19A).‡



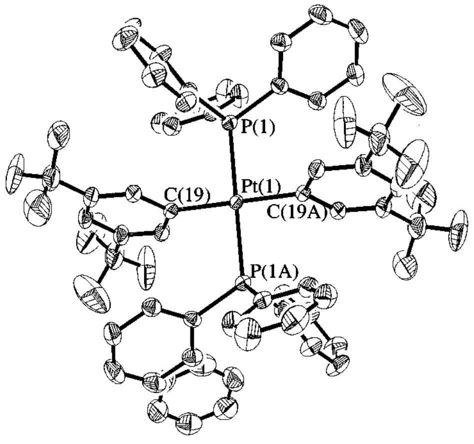
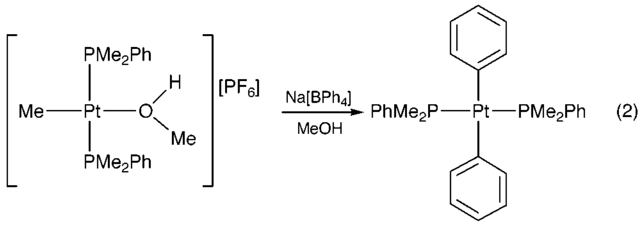


Fig. 1 Molecular structure of **2** showing the atom numbering scheme (50% probability ellipsoids). Selected bond distances (Å) and angles (°): Pt(1)–C(19) 2.083(2), Pt(1)–P(1) 2.3180(5), C(19)–Pt(1)–P(1) 91.73(6), C(19)–Pt(1)–P(1A) 88.27(6).

The formation of **2** entails the net transfer of two 3,5-bis(trifluoromethyl)phenyl groups from the BAr_F anion to the platinum center, constituting the first example of aryl group transfer from the BAr_F anion. Although this reaction is unprecedented for the BAr_F anion, similar reactions have been carried out with the BPh_4 anion; the metathesis reaction [eqn. (2)] of $[(PhMe_2P)_2Pt(Me)(solv)]^+$ with $NaBPh_4$ results in the formation of the neutral bis(phenyl)platinum derivative $(PhMe_2P)_2Pt(Ph)_2$.[5] It was determined from these studies that weakly bound ligands (*e.g.*, F_2C=CFH) in place of the coordinated solvent molecules enhanced the phenylation reaction. In a separate study,[6] the mechanism of phenyl transfer from the BPh_4 anion to the dicationic platinum species $[Pt(solv)_2(L)_2]^{2+}$ (L = PMe_3, PEt_3, PPh_3; solv = H_2O, MeOH) to form $[Pt(Ph)(solv)(L)_2]^+$ was investigated. It was found that



the actual phenylating species is BPh_3, which was formed from proton-induced decomposition of the BPh_4 anion to form BPh_3 and PhH. The coordinated solvent molecules in $[Pt(solv)_2(L)_2]^{2+}$ were assumed to be acidic enough to cause the decomposition of the BPh_4 anion. It is doubtful that a similar mechanism is occurring in the decomposition of **1a**, as the coordinated Et_2O molecule does not contain acidic protons which could cause the decomposition of the BAr_F anion. Instead, this reaction most likely proceeds through an initial step that involves electrophilic attack of the platinum cation on one of the aryl groups of the BAr_F anion. The fate of the methyl ligand is not known, but no methane was evolved during the reaction.

In order to determine the effects of the ligands on the arylation reaction, both the coordinated solvent and the phosphine ligands were varied in **1a**. Complexes containing both coordinated MeCN and MeOH were prepared by dissolving **1a** in MeCN and MeOH, respectively, and precipitating out *trans*-$[(Ph_3P)_2Pt(Me)(NCMe)]^+(BAr_F)^-$ **1b** and *trans*-$[(Ph_3P)_2Pt(Me)(MeOH)]^+$ $(BAr_F)^-$ **1c** as solids.† The ^1H NMR spectrum of **1b** was almost identical to the known compound *trans*-$[(Ph_3P)_2Pt(Me)(NCMe)]^+(BF_4)^-$,[7] and exhibited a singlet at δ 1.157 corresponding to coordinated MeCN, which disappeared when CD_3CN was added. Complex **1c** exhibited a signal at δ 2.684 corresponding to coordinated MeOH, which disappeared when CD_3OD was added. When **1b** was refluxed in either benzene or toluene under identical conditions to that of **1a**, there was no evidence for formation of **2**. However, when **1c** was refluxed in toluene under identical conditions, **2** formed in roughly the same yield as from the reaction of **1a**. Evidently, the more weakly bound Et_2O and MeOH ligands allow the aryl group transfer to occur in order to form **2**, while the more stongly bound MeCN ligand prevents this reaction from taking place.

In order to examine the effects of the phosphine ligand on the aryl group transfer, the complexes *trans*-$[(Pr^i{}_3P)_2Pt(Me)(OEt_2)]^+(BAr_F)^-$ **1d** and *trans*-$[(Et_3P)_2Pt(Me)(OEt_2)]^+(BAr_F)^-$ **1e** were synthesized analogously to the preparation of **1a**. After refluxing **1d** in toluene for several hours, there was no evidence of B–C bond cleavage. However, the less sterically encumbered **1e** reacted after refluxing for 10 min in benzene. A mixture of platinum complexes formed which could not be identified, but clear crystals were obtained from benzene which were characterized by X-ray diffraction to be $B[C_6H_3(CF_3)_2\text{-}3,5]_3$ **3**, the structure of which has not been previously reported.‡ Although this reaction gave different results than the decomposition of **1a**, it still indicates that B–C cleavage takes place with this more basic, less steric phosphine. Evidently, bulky phosphines do not allow this reaction to take place, which is consistent with the transition metal cation attacking the bulky BAr_F anion.

The aryl group transfer from the BAr_F anion to the platinum metal center in *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)]^+(BAr_F)^-$ **1a** represents the first example of a transition metal-mediated decomposition of the normally non-interacting BAr_F anion and serves to alert those who use this anion to the possibility of its reactivity. The mechanism of this reaction is unclear, but we have found that the coordinated solvent must be a weak ligand (Et_2O, MeOH), the solvent for the decomposition reaction must be non-coordinating, and the phosphine ligands must not be too bulky in order for this reaction to proceed. Preliminary results indicate that analogs of **1a** containing isocyanides instead of phosphines allow similar B–C bond cleavage reactions to proceed immediately at room temperature. These results indicate that the initial step of this reaction is electrophilic attack of the platinum cation on an aryl group of the BAr_F anion, which is consistent with the fact that both a sterically accessible metal center and a weakly occupied coordination site are necessary for aryl group transfer to occur.

Notes and references

† *Experimental procedures*: **1a:** to a stirred Et_2O solution (10 mL) of $[H(OEt_2)_2]^+BAr_F^-$ (0.135 g, 0.133 mmol) at room temp. was added $(Ph_3P)_2Pt(Me)_2$ (0.100 g, 0.133 mmol) as a solid. Evolution of methane began immediately, and after 5 min the solution was clear and colorless. The volume was reduced to 3 mL, and 10 mL of hexanes was then added. The volume was reduced to *ca.* 8 mL and placed in a −30 °C freezer for 1 day to obtain a white, crystalline solid. The filtrate was decanted off, the solids were washed with 3 × 5 mL of hexanes at −30 °C and dried under vacuum to give **1a** (0.195 g, 87%). ^1H NMR (CD_2Cl_2, −80 °C): δ 7.73 (s, 8H, BAr_F), 7.21–7.62 (34H, Ph + BAr_F), 3.53 (br, 4H, ether CH_2), 1.16 (t, J_{HH} = 7.05 Hz, 6H, ether CH_3), 0.73 (t, J_{HP} 6.75, J_{HPt} 71.0 Hz, 3H, Pt–Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ 31.3 (s, J_{PPt} 3195 Hz). Anal. Calc. for $C_{75}H_{55}BF_{24}OP_2Pt$: C, 52.44; H, 3.32. Found: C, 52.43; H, 3.59%.

1b and **1c:** complex **1a** (0.100 g, 0.0598 mmol) was dissolved in 10 mL of either MeCN (for **1b**) or MeOH (for **1c**) at room temp. and stirred for 15 min. The solvent was removed under vacuum, the oily residue was dissolved in 2 mL of CH_2Cl_2 and 15 mL of hexanes was then added. After cooling overnight at −30 °C, off-white crystals formed which were isolated by removing the filtrate and drying under vacuum to give **1b** (0.0905 g, 92%) or **1c** (0.0854 g, 90%). For **1b**: ^1H NMR (CD_2Cl_2, 25 °C): δ 7.53–7.75 (42H, Ph + BAr_F), 1.16 (br, 3H, MeCN), 0.28 (t, 3H, J_{HP} 7.05, J_{HPt} 78.3 Hz, Pt–Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 27.2 (s, J_{PPt} 3008 Hz). Anal. Calc. for $C_{71}H_{48}BF_{24}NP_2Pt$: C, 52.03; H, 2.95; N, 0.85. Found: C, 52.41; H, 3.04; N, 0.84%. For **1c**: ^1H NMR (CD_2Cl_2, 25 °C): δ 7.53–7.75 (42H, Ph + BAr_F), 2.68 (br, 3H, CH_3OH), 0.612 (t, 3H, J_{HP} 6.90, J_{HPt} 87.6 Hz, Pt–Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 32.4 (s, J_{PPt} 3114 Hz). Anal. Calc. for $C_{70}H_{49}BF_{24}OP_2Pt$: C, 51.58; H, 3.03. Found: C, 51.63; H, 3.03%.

2: complex **1a** (0.200 g, 0.120 mmol) was dissolved in toluene (5 mL) and heated to reflux for 20 min. The solution turned orange during this time. The solution was cooled, the solvent was removed under vacuum and 5 mL of MeOH was added. The mixture was cooled to −30 °C for 4 h, the white precipitate was collected on a frit, washed with cold MeOH and dried in vacuum to yield pure **2** (0.0875 g, 63%). ^1H NMR (CD_2Cl_2, 25 °C): δ 8.25 (s, 2H, BAr_F), 8.05 (s, 4H, BAr_F), 7.35–7.18 (30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 20.6 (s, J_{PPt} 2998 Hz). Anal. Calc. for $C_{52}H_{36}F_{12}P_2Pt$: C, 54.51; H, 3.17. Found: C, 54.47; H, 3.28%.

‡ *Crystal data*: for **2**: $C_{52}H_{36}F_{12}P_2Pt\cdot 2\ C_6H_6$, M = 1302.05, triclinic, space group $P\bar{1}$, a = 11.3973(6), b = 11.4539(5), c = 12.8260(6) Å, α = 105.675(1), β = 111.466(1), γ = 103.393(1)°, V = 1394.5(1) Å^3, Z = 1, T = 203 K, μ = 2.654 mm^{-1}, wR_2 = 0.0473 (5227 independent reflections), R = 0.0186 [$I > 2\sigma(I)$].

3: $C_{24}H_9BF_{18}$, M = 650.12, triclinic, space group $P\bar{1}$, a = 9.5433(9), b = 11.656(1), c = 12.775(1) Å, α = 100.544(2), β = 110.146(1), γ = 97.299(2)°, V = 1283.4(2) Å^3, Z = 2, T = 203 K, μ = 1.89 cm^{-1}. The final refinement (5459 reflections collected, 4206 independent) included anisotropic temperature factors on all non-hydrogen atoms and converged to R_1 = 0.0628 and wR_2 = 0.1820.

CCDC 182/1365. See http://www.rsc.org/suppdata/cc/1999/1807/ for crystallographic files in .cif format.

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Communication 9/02274K