# First example of B–C bond cleavage in the BAr$_F$ (B[C$_6$H$_3$(CF$_3$)$_2$-3,5]$_4$) anion mediated by a transition metal species, *trans*-[(Ph$_3$P)$_2$Pt(Me)(OEt$_2$)]$^+$

**Wayde V. Konze, Brian L. Scott and Gregory J. Kubas***

*Chemical Science and Technology Division, MS J514, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: kubas@lanl.gov*

**The first example of transition metal-mediated decomposition of the widely used BAr$_F$ anion (BAr$_F$ = B[C$_6$H$_3$(CF$_3$)$_2$-3,5]$_4$) has been accomplished by mild heating of the cationic platinum complex *trans*-[(Ph$_3$P)$_2$Pt(Me)(OEt$_2$)]$^+$(BAr$_F$)$^-$ in low-coordinating solvents to form the diarylated product *trans*-(Ph$_3$P)$_2$Pt(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$_6$H$_3$(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$_3$P)$_2$Pt(Me)(OEt$_2$)]$^+$(BAr$_F$)$^-$ **1a**, which decomposes to form the diarylated complex *trans*-(Ph$_3$P)$_2$Pt(Ar$_F$)$_2$ **2** under mild conditions.

The complex *trans*-[(Ph$_3$P)$_2$Pt(Me)(OEt$_2$)]$^+$(BAr$_F$)$^-$ **1a** was prepared by reacting (Ph$_3$P)$_2$Pt(Me)$_2$ with [H(OEt$_2$)$_2$]$^+$BAr$_F^-$ in Et$_2$O at room temperature. Compound **1a** is stable in Et$_2$O 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$_3$P)$_2$Pt(Ar$_F$)$_2$ **2** formed as colorless crystals [eqn. (1)].† The reaction was also more conveniently

**1a** → **2** [eqn. (1)], C$_6$H$_6$ Reflux, 1 h
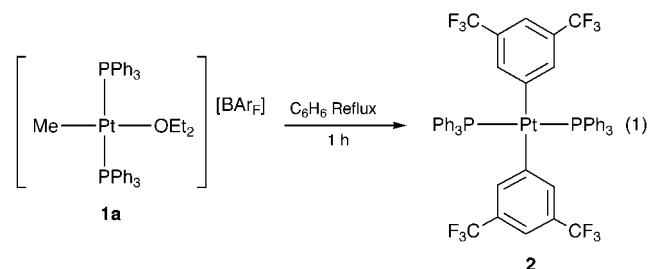
carried out by refluxing **1a** in toluene for 20 min. Complex **2** was characterized by elemental analysis, $^1$H NMR and $^{31}$P{$^1$H} NMR,† and the structure was determined by X-ray diffraction studies.‡ A characteristic feature of the $^1$H NMR spectrum of **2** is the downfield shift of the Ar$_F$ 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).‡

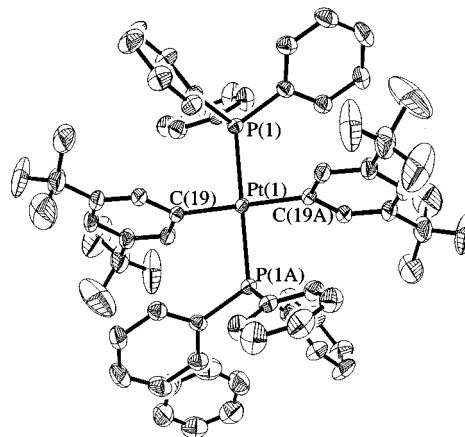**Fig. 1** Molecular structure of **2** showing the atom numbering scheme (50% probability ellipsoids). Selected bond distances (Å) and angles (°): Pt(1)–C(19) 2.083(2), Pt(1)–P(1) 2.3180(5), C(19)–Pt(1)–P(1) 91.73(6), C(19)–Pt(1)–P(1A) 88.27(6).

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$_2$P)$_2$Pt(Me)(solv)]$^+$ with NaBPh$_4$ results in the

[eqn. (2)] Na[BPh$_4$], MeOH
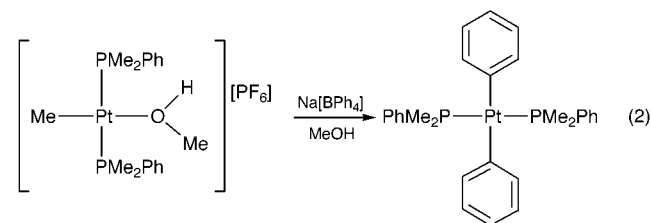
formation of the neutral bis(phenyl)platinum derivative (PhMe$_2$P)$_2$Pt(Ph)$_2$.[5] It was determined from these studies that weakly bound ligands (*e.g.*, F$_2$C=CFH) in place of the coordinated solvent molecules enhanced the phenylation reaction. In a separate study,[6] the mechanism of phenyl transfer 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$_2$O, 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)(O-Et_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 $B[C_6H_3(CF_3)_2-3,5]_3$ **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

1 S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927.
2 M. Brookhart, B. Grant and A. F. Volpe, *Organometallics*, 1992, **11**, 3920; See also: M. D. Butts, B. L. Scott and G. J. Kubas, *J. Am. Chem. Soc.*, 1996, **118**, 11831; P. J. Alaimo, B. A. Arndtsen and R. G. Bergman, *J. Am. Chem. Soc.*, 1997, **119**, 5269; M. W. Holtcamp, L. M. Henling, M. W. Day, J. A. Labinger and J. E. Bercaw, *Inorg. Chim. Acta*, 1998, **270**, 467.
3 J. Powell, A. Lough and T. Saeed, *J. Chem. Soc., Dalton Trans.*, 1997, 4137.
4 M. Aresta, E. Quaranta and I. Tommasi, *New J. Chem.*, 1997, **21**, 595.
5 H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 1226; H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1971, **10**, 2699.
6 K. Siegmann, P. S. Pregosin and L. M. Venanzi, *Organometallics*, 1989, **8**, 2659.
7 R. A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri and R. J. Angelici, *Organometallics*, 1994, **13**, 1341.

*Communication 9/02274K*