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Preliminary communication

Trityl tetraphenylborate as a reagent in organometallic chemistry

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Abstract

Trityl tetraphenylborate, prepared from trityl triflate and sodium tetraphenylborate, is shown to be a useful hydride and methyl anion abstraction reagent for organometallic compounds. It reacts with $(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuMe$ to give the fulvene complex $[(\eta^4\text{-}C_5Me_4CH_2)(PMe_3)_2RuMe]BPh_4$, and with $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ in acetonitrile-d_3 to afford the cationic methyl derivative $[(\eta^5\text{-}C_5H_5)_2ZrMe(NCCD_3)]BPh_4$.

Trityl cation (Ph_3C^+) has been widely used as a hydride abstraction reagent in organic [1] and organometallic [2] systems. This reagent is readily available as the perchlorate, hexafluorophosphate or tetrafluoroborate salts. We have had an interest in using hydride abstractions to generate Lewis acidic, cationic transition-metal complexes that could potentially interact strongly with ClO_4, PF_6 or BF_4 counterions. For this reason, we have attempted to develop syntheses to trityl salts that contain other, potentially less reactive anions. In this report we describe the synthesis and characterization of Ph_3C^+ BPh_4^-, and its use in preparing two cationic transition-metal complexes.

The synthesis of trityl tetraphenylborate utilizes as an intermediate trityl triflate (Ph_3C^+ OTf^-, $OTf = OSO_2CF_3$), which has previously been prepared and characterized in solution by NMR and UV-vis spectroscopy [3*]. We have obtained Ph_3C^+ OTf^- by a new method employing the reaction of trityl chloride with trimethylsilyl triflate in dichloromethane at room temperature (eq. 1). By this

$$Ph_3CCl + Me_3SiOTf \xrightarrow{CH_2Cl_2} Ph_3C^+\ OTf^- + Me_3SiCl \qquad (1)$$

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* Reference number with asterisk indicates a note in the list of references.

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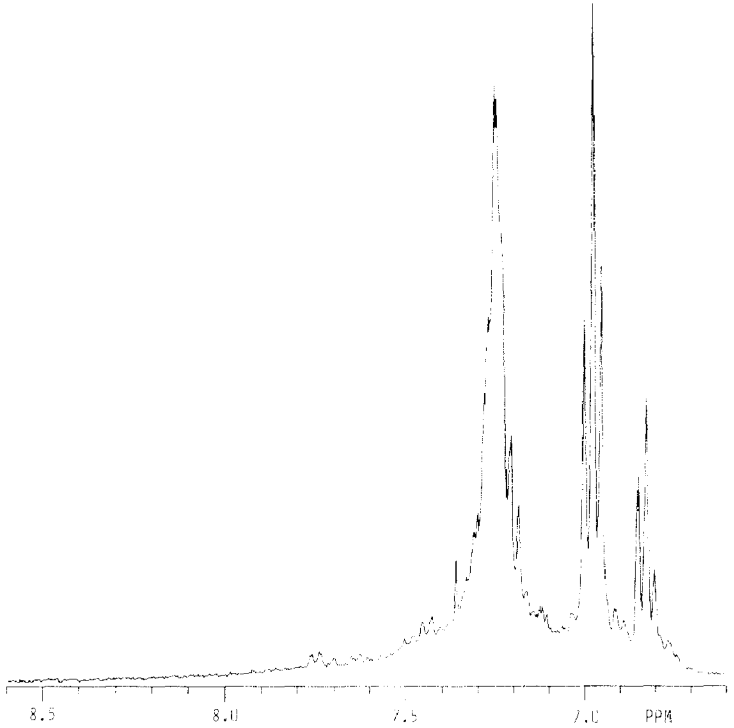


Fig. 1. ^{1}H NMR spectrum of Ph_3C^+ BPh_4^- in acetonitrile-d_3 (aryl region).

procedure Ph_3C^+ OTf^- is obtained as a yellow, microcrystalline solid in 91% yield. Reaction of a slight excess of $NaBPh_4$ (0.73 g, 2.13 mmol) with Ph_3C^+ OTf^- (0.70 g, 1.78 mmol) in acetonitrile (10 ml) at 0 °C produces a dark red solution. This solution was allowed to stand in the dark for ca. 0.5 h at 0 °C, after which dark red needles of Ph_3C^+ BPh_4^- formed. These crystals, obtained in ca. 75% yield, are isolated by filtration and dried under vacuum. It is important to carry out this preparation in the dark and under an atmosphere of nitrogen, since the product is both light and air sensitive. Even in the dark, Ph_3C^+ BPh_4^- decomposes slowly in acetonitrile, and more rapidly in dichloromethane. It can, however, be stored under nitrogen in the dark for several weeks with no apparent decomposition.

Characterization of Ph_3C^+ BPh_4^- is based on elemental analysis (C, H), spectroscopic data, and reaction chemistry. The presence of trityl cation was established with fast atom bombardment mass spectrometry (Found: 243.1169 $C_{19}H_{15}^+$ calcd.: 243.1174). The ^{1}H NMR spectrum in acetonitrile-d_3 (Fig. 1) reveals triplet resonances for the *metal* and *para* protons of BPh_4^-, and an intense, broad peak at ca. δ 7.25. Notably resonances for the trityl protons, expected to be in the region δ 7.6–8.4 [3b*] are not observed. Several lines of evidence point to the fact that these resonances are obscured by the presence of small amounts of trityl radical, which cause delocalization of electron density over all the trityl groups by way of rapid electron transfer between $Ph_3C^{\cdot}$ and Ph_3C^+ centers in solution [4]. Consistent with this, the ^{1}H NMR spectrum of Ph_3C^+ BPh_4^- contained low-intensity resonances due to trityl dimer (A, Fig. 2) [5*]. These signals increase in intensity as Ph_3C^+ BPh_4^- decomposes, indicating that trityl radical is a major decomposition product. Furthermore, upon addition of a small quantity of trityl radical to an acetonitrile-d_3

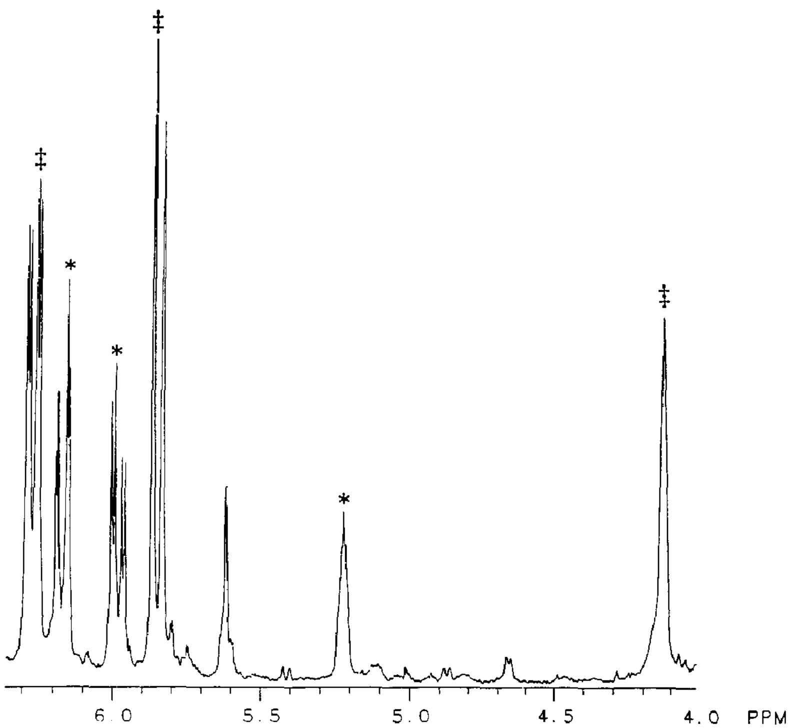
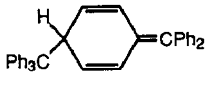


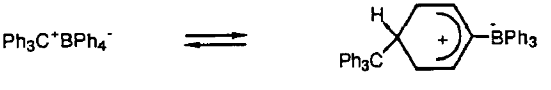
Fig. 2. ^{1}H NMR spectrum of a sample of Ph_3C^+ BPh_4^- in acetonitrile-d_3 showing peaks assigned to trityl dimer (*) and species B (‡). The peak at δ 5.59 is due to Ph_3CH.

solution of Ph_3C^+ OTf^-, the trityl proton resonances disappear. ESR spectroscopy also confirmed the presence of trace amounts of $Ph_3C^{\bullet}$ radical (observed g value 2.003; literature value 2.0026 [6]) in solid samples of Ph_3C^+ BPh_4^-. Variable temperature magnetic susceptibility studies showed that solid samples of Ph_3C^+ BPh_4^- are very weakly paramagnetic, with a magnetism that is consistent with the presence of ca. 0.1% trityl radical.

In addition to signals for BPh_4^- and $(Ph_3C)_2$, ^{1}H NMR spectra of Ph_3C^+ BPh_4^-contain a set of low-intensity peaks that are similar in chemical shifts and overall appearance to the resonances for trityl dimer (Fig. 2). We therefore suggest that these peaks are due to species B [7*], which is in equilibrium with the solvent separated ions and is an intermediate in the decomposition of Ph_3C^+ BPh_4^- to trityl radical and other uncharacterized products (eq. 2). We do not yet understand



A

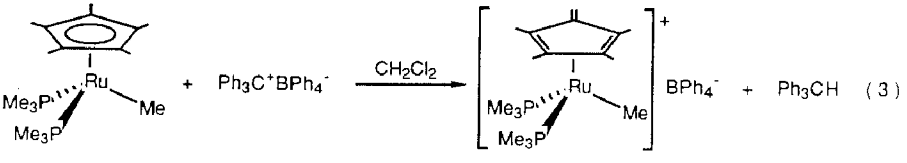


(2)

B

the dark red color of Ph_3C^+ BPh_4^-, but suggest that it may be due to B, or an impurity.

Despite its sensitivity in solution, $Ph_3C^+\ BPh_4^-$ appears to be a useful reagent for carrying out clean abstractions in organometallic systems. This has been illustrated for the two cases shown in eqs. 3 and 4. Reaction of $(\eta^5\text{-}C_5Me_5)(PMe_3)_2$-



1

$$(\eta^5\text{-}C_5H_5)_2ZrMe_2 + Ph_3C^+BPh_4^- \xrightarrow[-Ph_3CMe]{CD_3CN} [(\eta^5\text{-}C_5H_5)_2ZrMe(NCCD_3)]BPh_4 \qquad (4)$$

2

RuMe with $Ph_3C^+\ BPh_4^-$ afforded the cationic fulvene complex **1** [8*] in 45% yield after crystallization from THF/OEt_2. An interesting contrast is the reaction of $(\eta^5\text{-}C_5Me_5)(PMe_3)(CO)FeMe$ with $Ph_3C^+\ PF_6^-$ in THF, which gives Ph_3CH and $[(\eta^5\text{-}C_5Me_5)(PMe_3)(CO)Fe(THF)]PF_6$, apparently via the methylidene complex $[(\eta^5\text{-}C_5Me_5)(PMe_3)(CO)Fe{=}CH_2]PF_6$ [9]. Also note that $(\eta^5\text{-}C_5Me_5)L_2FeMe$ ($L = P(OMe)_3$, $\frac{1}{2}$dppe) react with $Ph_3C^+\ PF_6^-$ to give the cationic iron(III) complexes $[(\eta^5\text{-}C_5Me_5)L_2FeMe]PF_6$ [10]. Reaction of $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ with $Ph_3C^+\ BPh_4^-$ in acetonitrile-d_3 occurred with methyl-group abstraction to give a quantitative yield of the previously reported cationic methyl complex **2** (by ^1H NMR) [11].

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