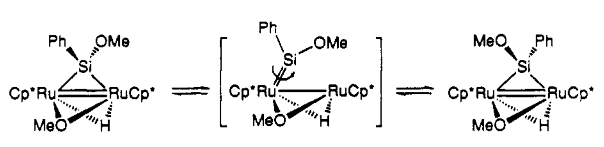
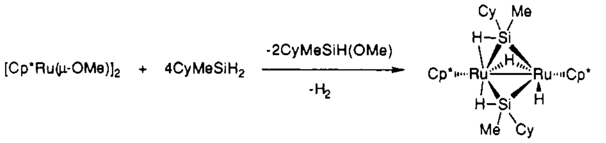


(2)

plex transformation are lacking at this time, but it is conceivable that the Si–O bond is formed via oxidative addition of an H–SiHPh$_2$ bond, followed by Si–O reductive elimination to produce Ph$_2$SiHOMe as an intermediate.[14] Cleavage of an SiPh bond has fewer precedents in stoichiometric processes[15] but is observed in transition-metal-catalyzed reactions that redistribute groups on silicon.[16] The key Si–C bond cleavage step could occur via oxidative addition of the Si–C bond or by α-migration of the Ph group from silicon to ruthenium.

Addition of CyMeSiH$_2$ (Cy = cyclohexyl) to [Cp*Ru(μ-OMe)]$_2$ results in formation of a new complex, isolated as orange crystals from pentane, that does not possess methoxy groups. The elemental analysis and NMR spectra are consistent with a stoichiometry of Cp*Ru(SiMeCy)$_2$H$_2$, and the mass spectrum contains a parent ion peak ([M]$^+$ = 730) which indicates that the compound is dimeric. A ν_{RuH} stretching frequency at 2050 cm^{-1} in the infrared spectrum can be assigned to a terminal Ru–H bond. The ^{29}Si{^{1}H} NMR DEPT spectrum contains a single peak at δ 115.17, which is at relatively low field but considerably upfield of the resonance for silylene-bridged {[(η^5-C$_5$Me$_5$)Ru]$_2$(μ-SiPhOMe)(μ-OMe)(μ-H)}. A highly symmetric structure is suggested by the room temperature ^{1}H NMR spectrum, which displays single sets of resonances for the Cp*, SiMeCy, and hydride ligands. However, the very broad single peak at δ −14.1 for the hydride ligands can be attributed to stereochemical nonrigidity at room temperature. Cooling a toluene-d_8 solution of the complex resulted in decoalescence of the hydride resonances at ca. −15 °C, and the ^{1}H NMR spectrum at −70 °C contains two resonances for the Cp* ligands, and three singlets in the hydride region (δ −12.94, −13.81, and −15.81) in a 1:2:1 ratio. The above data are all consistent with the structure shown in eq 3. Also, the NMR spectra for this compound are remarkably similar to the analogous complex {[Cp*Ru(μ-η^2-H-SiEt$_2$)]$_2$(μ-H)(H)}, which was recently characterized by X-ray diffraction.[4c]



(3)

The above reactions show that the electron-deficient ruthenium methoxide [Cp*Ru(μ-OMe)]$_2$ can serve as a useful starting material for the synthesis of dinuclear ruthenium–silicon compounds. Furthermore, the facile transfer of an alkoxy group from ruthenium to silicon is demonstrated. Related alkoxy-transfer reactions with mononuclear complexes have been reported. For example, silanes HSiR$_3$ react with *trans*-(PR′$_3$)$_2$(CO)IrOR″ (R′ = Me, Ph) to give R$_3$SiOR″ and (PR′$_3$)$_2$(CO)IrH$_2$(SiR$_3$).[17]

Acknowledgment is made to the National Science Foundation for support of this work. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–92), Union Carbide for an Innovation Recognition Program Award (1991–2), and the Mobil Foundation for a financial contribution. We also thank Nora Radu and John Walzer for recording NMR spectra.

Supplementary Material Available: For {[(η^5-C$_5$Me$_5$)Ru]$_2$(μ-SiPhOMe)(μ-OMe)(μ-H)}, tables of crystal data, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates (11 pages). Ordering information is given on any current masthead page.

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$[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$: A Convenient Reagent for Generation and Stabilization of Cationic, Highly Electrophilic Organometallic Complexes

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Summary: A convenient synthesis of the easily handled, crystalline oxonium acid $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$ (**1**) is described. The utility of this reagent for generation and stabilization of highly electrophilic cationic transition-metal complexes through protonation reactions is illustrated by the preparation of stable, ether-free salts of $[C_5Me_5(P(OMe)_3)CoCH_2CH_2(\mu\text{-}H)]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$ from $C_5Me_5(P(OMe)_3)Co(C_2H_4)$. The incorporation of the noncoordinating counterion $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$ in organometallic salts has several advantages relative to $[BF_4]^-$ and $[PF_6]^-$, including high stability and solubility in relatively nonpolar organic solvents.

I. Introduction

The lack of reactivity and non-nucleophilic character of $[BF_4]^-$ and $[PF_6]^-$ have led to their widespread use as noncoordinating (or weakly coordinating)[1,2] counterions supporting cationic organometallic complexes. With the

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[1] For examples of coordinated $[BF_4]^-$ and $[PF_6]^-$ see: (a) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869. (b) Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6056. (c) Beck, W.; Sunkel, K. *Chem. Rev.* **1988**, *88*, 1405.

[2] For descriptions of other noncoordinating counterions see: (a) Shelley, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 3117. (b) Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216 and references therein.

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generation of sufficiently electrophilic complexes, however, the limitations of $[BF_4]^-$ and $[PF_6]^-$ as nonreactive entities are encountered.[3,4] Jordan, for example, has reported the deactivation of the highly reactive d^0 $[Cp_2Zr(CH_3)]^+$ ethylene polymerization catalyst by F^- abstraction from the PF_6^- counterion. To circumvent this problem, $[BPh_4]^-$ was used as a counterion, resulting in a longer lived catalyst.

The susceptibility of tetraarylborates to attack by electrophilic transition-metal complexes has, however, been documented. Hlatky and Turner have isolated a zirconocene tetraarylborate zwitterion derived from attack at the aryl ring by an electrophilic Zr(IV) center.[5] When the non-nucleophilic $[B(C_6F_5)_4]^-$ anion[6] was used, zwitterion formation as well as aryl transfer to the metal center was avoided. Preparation of zirconium and hafnium alkyl cations $[(C_5R_5)_2MCH_3]^+[B(C_6F_5)_4]^-$ was achieved by protonolysis of $(C_5R_5)_2M(CH_3)_2$ with the trialkylammonium salt $[HNBu_3]^+[B(C_6F_5)_4]^-$.[7] Marks has reported a similar preparation of $[Cp^*{}_2ThCH_3]^+[B(C_6F_5)_4]^-$, a highly active olefin polymerization and hydrogenation catalyst, by reaction of $[HNBu_3]^+[B(C_6F_5)_4]^-$ with $Cp^*{}_2Th(CH_3)_2$.[8,9]

In 1984, Kobayashi and co-workers[10] reported the synthesis of the tetraarylborate $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$ ($BAr'_4{}^-$) as its sodium salt. They found that, unlike $[BPh_4]^-$, which is susceptible to protonolysis by H_2SO_4, the presence of the electron-withdrawing CF_3 groups rendered $[BAr'_4]^-$ virtually inert toward degradation by H_2SO_4. Moreover, $NaBAr'_4$ was found to be resistant to a variety of oxidants and extremely lipophilic.

The chemical stability and high solubility of $NaBAr'_4$ led us to consider using $[BAr'_4]^-$ as the counterion for stabilizing cationic electrophilic metal alkyl complexes of the late metals whose catalytic properties we have recently been investigating. A common route for generating such species involves protonolysis of a dialkyl complex or protonation of a neutral olefin complex. In this regard, the aforementioned trialkylammonium salts have limitations in that they are not sufficiently acidic to effect these reactions, particularly in the late-metal systems. Thus, we sought a system which would function as a much stronger Brønsted acid.

In this note we report a convenient synthesis of $[H(OEt_2)_2]^+[BAr'_4]^-$ and illustrate its utility in the generation and stabilization of the highly electrophilic, catalytically active cobalt complex $[C_5Me_5(P(OMe)_3)CoCH_2CH_2(\mu\text{-}H)]^+$.[11,12]

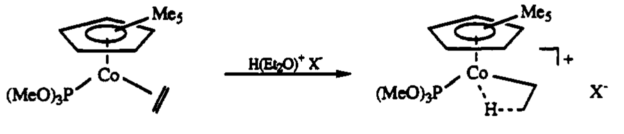
II. Results and Discussion

A. Preparation of $[H(OEt_2)_2]^+[BAr'_4]^-$. Taking advantage of the high solubility of $NaBAr'_4$ in ether, $[H(OEt_2)_2]^+[BAr'_4]^-$ (1) can be prepared in a straightforward manner. Exposure of ether solutions of $NaBAr'_4$ to HCl results in the precipitation of NaCl and the generation of $[HOEt_2]^+[BAr'_4]$. Upon workup, 1 is isolated as an analytically pure, white crystalline solid whose ^1H NMR spectrum and combustion analysis indicated that 1 crystallizes as a dietherate. 1 is very soluble in polar organic solvents (chlorinated hydrocarbons, acetonitrile, ethers) but insoluble in nonpolar solvents. 1 is hygroscopic but, if stored under an inert atmosphere at −20 °C, is stable indefinitely. Solutions of 1, however, decompose slowly ($t_{1/2}$ = ca. 20 h in CD_2Cl_2), giving BAr'_3 and $m\text{-}C_6H_3(CF_3)_2$. Thus, while the $[BAr'_4]^-$ ion is resistant to degradation by H_2SO_4, it is susceptible to protonolysis by the stronger oxonium acid; for this reason solutions of 1 should not be kept at ambient temperatures for prolonged periods of time.

The properties of 1 make it a conveniently handled reagent, especially when compared to $HBF_4{\cdot}Et_2O$. Its crystallinity and high molecular weight allow for accurate weighing of relatively small molar amounts. This plus the high solubility of both 1 *and* salts derived from 1 make it ideally suited for the generation and variable-temperature NMR study of reactive species resulting from protonation or protonolysis.

B. Preparation of $[C_5Me_5(P(OMe)_3)CoCH_2CH_2(\mu\text{-}H)]^+[BAr'_4]^-$. The highly electrophilic Co(III) complex $[C_5Me_5(P(OMe)_3)CoCH_2CH_2(\mu\text{-}H)]^+$ ($[2]^+$) has been shown to catalyze the polymerization of ethylene in a living fashion, but the instability of its $[BF_4]^-$ salt limits its utility. In order to assess the role that the anion plays in the stabilization of these complexes, $[2]^+[BAr'_4]^-$ was prepared and compared to its $[BF_4]^-$ analogue.

The syntheses of $[2]^+[BF_4]^-$ and $[2]^+[BAr'_4]^-$ follow analogous protonations of the neutral ethylene complex 3. As expected, variable-temperature NMR spectra of $[2]^+[BAr'_4]^-$ indicated fluxional behavior identical with that of $[2]^+[BF_4]^-$.[15]



3

2^+ X^- = BF_4, BAr'_4

Whereas $[2]^+[BF_4]^-$ has resisted all attempts of isolation as a stable salt, $[2]^+[BAr'_4]^-$ can be obtained as an analytically pure crystalline solid that can be kept indefinitely under an inert atmosphere. Manipulations involving $[2]^+[BAr'_4]^-$ are thus more convenient than those with its $[BF_4]^-$ analogue. Higher solubility and pure (ether-free) form are advantages $[2]^+[BAr'_4]^-$ holds over $[2]^+[BF_4]^-$, especially for the purposes of NMR studies.

The relative stabilities of $[2]^+[BF_4]^-$ and $[2]^+[BAr'_4]^-$ in CD_2Cl_2 solution have been monitored by ^1H NMR spectroscopy. While $[2]^+[BF_4]^-$ decomposes rapidly at 25 °C ($t_{1/2}$ < 30 min), $[2]^+[BAr'_4]^-$ exhibits much greater stability

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[3] Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* 1986, *108*, 1718.

[4] Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* 1988, *110*, 5902. See also ref 15 in: Ponneson, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. V. *J. Am. Chem. Soc.* 1989, *111*, 6070.

[5] Hlatky, G. C.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* 1989, *111*, 2728.

[6] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* 1962, *2*, 245.

[7] Turner, H. W. European Patent No. 277,004, 1988.

[8] Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* 1991, *10*, 840.

[9] For related reports see: (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* 1991, *113*, 3623. (b) Horton, A. D.; Orpen, A. G. *Organometallics* 1991, *10*, 3910.

[10] Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* 1984, *57*, 2600.

[11] (a) Part of this work, including an abbreviated synthesis of 1, was reported at the 201st Meeting of the American Chemical Society, Atlanta, GA, April 1991: Brookhart, M.; Volpe, A. F., Jr.; DeSimone, J.; Lamanna, W. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, *32*, 461. (b) Following submission of this manuscript, synthesis of 1 using a similar procedure was reported: Taube, R.; Wache, S. *J. Organomet. Chem.* 1992, *428*, 431.

[12] Mann and Lamanna have used $[NBu_4]^+[BAr'_4]^-$ as a noninteracting electrolyte for electrochemical studies: Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* 1991, *30*, 4687.

[13] *Caution!* It has been reported that the solid lithium salt $Li(C_6H_4(CF_3)_2)$ decomposes explosively: Theopold, K. Personal communication.

[14] Hofmann, L.; Werner, H. *J. Organomet. Chem.* 1985, *289*, 141.

[15] (a) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* 1989, *8*, 1212. (b) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horváth, I. T.; Millar, J. M. *J. Am. Chem. Soc.* 1990, *112*, 5634. (c) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* 1985, *107*, 1443.

with $t_{1/2}$ = ca. 7 days. The decomposition products of $[2]^+[BAr'_4]^-$ have not all been identified. However, unchanged aromatic signals of the $[BAr'_4]^-$ ion along with the appearance of CHD_2Cl (δ 2.90 ppm, quintet, J_{HD} = 1.7 Hz) implicate chloride abstraction from the solvent rather than the involvement of $[BAr'_4]^-$ in the decomposition of $[2]^+[BAr'_4]^-$. Accordingly, $[2]^+[BAr'_4]^-$ persists even longer in the less reactive solvent C_6D_5Cl, with $t_{1/2}$ = ca. 30 days at 25 °C.

The greatly enhanced stability of $[2]^+[BAr'_4]^-$ relative to its $[BF_4]^-$ analogue has allowed much broader use of this system in catalysis. Specifically, $[2]^+[BAr'_4]^-$ can now be used to catalyze the living polymerization of ethylene to prepare polyethylene with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.17–1.34) with molecular weights in the range of 13 000–35 000. Other processes catalyzed by $[2]^+[BAr'_4]^-$, including the oligomerization of α-olefins and olefin hydrogenation and hydrolsilation, have also been facilitated by the enhanced catalyst stability and are currently being investigated.

III. Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry, deoxygenated N_2 using standard Schlenk techniques or in a Vacuum Atmospheres drybox, using flame-dried glassware, unless otherwise indicated. Diethyl ether and hexane were distilled from sodium benzophenone ketyl immediately prior to use. Methylene chloride was distilled over P_2O_5. NMR solvents (CD_2Cl_2, C_6D_5Cl) were subjected to three freeze–pump–thaw cycles and stored over 4-Å molecular sieves under a nitrogen atmosphere. 3,5-Bis(trifluoromethyl)bromobenzene was purchased from Aldrich and used as received. NMR spectra were recorded on either a Varian XL-400 or Bruker WM-200 spectrometer. Elemental analyses were performed by Oneida Research Services, Whitesoboro, NY.

$[Na]^+[[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ ($NaBAr'_4$). A modification of the procedure reported by Kobayashi[10] was used. Slow (ca. 2 h) addition of a solution of 50 g (0.17 mol) of 3,5-bis(trifluoromethyl)bromobenzene in Et_2O (250 mL) to Mg turnings (5.1 g, 0.21 mol) in Et_2O (150 mL), followed by refluxing for 30 min, gave a dark gray solution of the aryl Grignard reagent.[13] Upon addition of $NaBF_4$ (3.4 g, 0.03 mol), the heterogeneous reaction mixture was stirred for 48 h, during which time the solution became brown and a fine precipitate formed. (Workup of the reaction mixture did not involve air-free procedures). The reaction mixture was added to Na_2CO_3 (75 g) in water (1 L), stirred for 20 min, and then filtered. Separation and extraction of the aqueous layer with Et_2O (4 × 200 mL) and combining of the Et_2O fractions gave a clear brown solution, which was dried over Na_2SO_4 and treated with decolorizing charcoal. The solution was then filtered, and the solvent was removed under reduced pressure. Prolonged drying under vacuum gives a tan solid (26.4 g, 70%). Washing the crude product with small amounts of cold methylene chloride or chloroform removes traces of colored impurities.

$[H(Et_2O)_2]^+[[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ (1). $NaBAr'_4$ (3.00 g, 3.39 mmol) was dissolved in 75 mL of Et_2O and the solution allowed to stand for 12 h over 4-Å molecular sieves. A 230-mL Schlenk flask fitted with a rubber septum was filled with HCl (g) (6.31 mmol). The $NaBAr'_4$ solution was then added to the flask containing the HCl through the septum via a syringe. (Note: at this and subsequent stages of the procedure, it is recommended to keep solutions of $[H(Et_2O)_2]^+[BAr'_4]^-$ cold; see Results and Discussion.) The reaction flask was then opened to a N_2 atmosphere and allowed to stand at 0 °C while the NaCl precipitate settled. The clear solution was then decanted via a cannula to a separate flask, as were Et_2O washings of the precipitate (2 × 20 mL). The solution was then concentrated to ca. 10 mL and chilled to −78 °C, at which point white crystals of $[H(Et_2O)_2]^+[BAr'_4]^-$ began to form. After this mixture stood for 1 h, hexane (20 mL) was slowly added to further precipitate $[H(Et_2O)_2]^+[BAr'_4]^-$. The supernatant was decanted, and residual solvent was evaporated under reduced pressure to give $[H(Et_2O)_2]^+[BAr'_4]^-$ as white crystals (2.85 g, 84%). ^1H NMR (CD_2Cl_2): δ 11.1 (v br, 1 H Et_2OH), 7.70 (br, 8 H, *o*-H), 7.55 (br, 4 H, *p*-H), 3.85 (br, 8 H, CH_2), 1.32 (t, 12 H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 162.0 (q, J_{BC} = 50 Hz, *i*-C), 135.2 (d, J_{CH} = 163 Hz, *o*-C), 129.0 (q, J_{CF} = 47 Hz, *m*-C), 125.0 (q, J_{CF} = 272 Hz, CF_3), 117.5 (d, J_{CH} = 163 Hz, *p*-C). Anal. Calcd for $C_{40}H_{21}O_2BF_{24}$: C, 47.45; H, 3.29. Found: C, 47.72; H, 3.68.

$[C_5Me_5(P(OMe)_3)CoCH_2CH_2(\mu\text{-}H)]^+[BAr'_4]^-$ ($[2]^+[BAr'_4]^-$). $C_5Me_5(P(OMe)_3)Co(C_2H_4)$ was prepared by following published procedures.[14] A Schlenk flask was charged with $C_5Me_5(P(OMe)_3)Co(C_2H_4)$ (244 mg, 0.705 mmol) and $[H(Et_2O)_2]^+[BAr'_4]^-$ (651 mg, 0.641 mmol, 0.9 equiv). CH_2Cl_2 (2 mL) was added at room temperature, and the flask was gently swirled for 1 min to ensure complete dissolution of the reagents. The resultant deep red solution was then chilled to −78 °C, at which point crystals of $[2]^+[BAr'_4]^-$ began to form. Slow addition of hexane (10 mL) over the course of 2 h resulted in near-complete precipitation of $[2]^+[BAr'_4]^-$. The supernatant was decanted via cannula, and the product was washed with hexane (2 × 5 mL) to remove traces of unreacted $C_5Me_5(P(OMe)_3)Co(C_2H_4)$. The product was dried under vacuum to give $[2]^+[BAr'_4]^-$ as a brick-red, ether-free crystalline solid (722 mg, 93%). Variable-temperature ^1H and ^{13}C NMR spectra of $[2]^+[BAr'_4]^-$ were identical with those of $[2]^+[BF_4]$.[15] Anal. Calcd for $C_{47}H_{41}O_3BCoF_{24}P$: C, 46.63; H, 3.41. Found: C, 46.45; H, 3.38. Half-life determinations were performed by dissolving 20 mg of 1 or $[2]^+[BAr'_4]^-$ in 0.9 mL of CD_2Cl_2 (or C_6D_5Cl) in a 5-mm NMR tube equipped with a side arm, cooling the solution to −78 °C, and flame-sealing the tube under vacuum. Samples were kept in the dark at 25 °C, and ^1H NMR spectra were recorded periodically. The decomposition of 1 was monitored by the decay of aromatic signals from $[BAr'_4]^-$ using Et_2O signals as an internal standard. The formation of $m\text{-}C_6H_3(CF_3)_2$ as a decomposition product of 1 was verified by comparison with the ^1H NMR spectrum of an authentic sample. Half-lives of $[2]^+[BAr'_4]^-$ were estimated by integrating the $P(OMe)_3$ signal from $[2]^+[BAr'_4]^-$ as a fraction of total $(OMe)_3$ signals. $[2]^+[BF_4]^-$ was generated in situ at 25 °C; a ^1H NMR spectrum recorded 30 min later indicated nearly complete decomposition of $[2]^+[BF_4]^-$.

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