diacyl derivatives could be even more stable.

Registry No. 1a, 7746-94-3; **1b**, 21303-80-0; **1c**, 1008-76-0; **2a**, 88730-03-4; **2b**, 88730-04-5; **2c**, 51800-35-2; **3a**, 88730-05-6; **3b**, 88730-06-7; **3c**, 88730-07-8; **4a**, 88730-08-9; **4b**, 88730-09-0; **5**, 1011-46-7; **6**, 88730-10-3; **7**, 88730-11-4; **8**, 88730-12-5.

Protonation of Organometallic Hydrides with Fluorochemical Acids[†]

Allen R. Siedle* and Richard A. Newmark

Science Research Laboratory
3M Central Research Laboratories
St. Paul, Minnesota 55144

Louis H. Pignolet

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Richard D. Howells

3M Commercial Chemicals Division Laboratory
St. Paul, Minnesota 55144

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We wish to report some results of a comprehensive investigation of bis((perfluoroalkyl)sulfonyl)alkanes and -amines and of perfluoroalkanesulfonic acids which presage a substantial scope and diversity for the chemistry of these materials. This is exemplified here by their reactions with organometallic hydrides. Protonation is, in principle, one of the most elementary reactions of such hydrides and is a key step in numerous catalytic and synthetic processes. Idealized protonation proceeds in two steps: proton transfer then, in some cases, reductive elimination of dihydrogen. If, however, a nucleophilic solvent or counterion is present, either of the cationic products, M^+ or MH_2^+, may be captured and neutralized or coordinated. Described in this work is the protonation of a wide variety of transition-metal hydrides under conditions in which noncoordinated M^+ or MH_2^+ salts may be easily isolated in highly soluble forms.

For this purpose, the novel fluorochemical acids bis((trifluoromethyl)sulfonyl)methane (**1**); bis((trifluoromethyl)sulfonyl)phenylmethane (**2**),[1] and bis((trifluoromethyl)sulfonyl)amine (**3**) were employed.

$$\underset{\mathbf{1}}{(CF_3SO_2)_2CH_2} \qquad \underset{\mathbf{2}}{(CF_3SO_2)_2CHPh} \qquad \underset{\mathbf{3}}{(CF_3SO_2)_2NH}$$

These acids possess a combination of properties that make them virtually unique in the context of their organometallic chemistry. All are volatile, crystalline solids; **1** and **2** are not hygroscopic and may be easily handled in air. They are strong nonoxidizing acids (pK_a of **1** was estimated to be about −1 in water). All are soluble in apolar, nondonor solvents such as dichloromethane or toluene, and, finally, their conjugate bases are essentially noncoordinating. The reactions described below were effected by combining equimolar amounts of **1**–**3** with a suspension of the metal hydride in dry, deoxygenated toluene. The fluorochemical acid salts formed as products are only sparingly soluble and, after stirring for ca. 8 h, were isolated in analytically pure form.

Cobalt(I) and iridium(I) hydrides are protonated to give cationic dihydrides (eq 1). The stereochemistry of $L_4MH_2^+$ (M = Co, Ir) appears to be cis, as, for example, in $(diphos)_2IrH_2^+HC(SO_2CF_3)_2^-$ (**4**), ν_{IrH} 2060, 2080 cm^{-1}, $\delta(^1H)$ −11.7 ($J_{PH\,trans}$ = 114 Hz).

$$L_4MH + H_2C(SO_2CF_3)_2 \rightarrow L_4MH_2^+HC(SO_2CF_3)_2^- \qquad L = Ph_3P,\ diphos/2 \qquad (1)$$

Rhodium(I) hydrides are protonated but then undergo reductive elimination of H_2, consistent with Vaska's observation that Rh(I) undergoes oxidative addition reactions less readily than the Co(I) or Ir(I) analogues.[2] Protonation of $(Ph_3P)_4RhH$ is distinctive in that 1 equiv of Ph_3P is also lost to provide in high yield salts of the red, 14-electron Rh(I) cation $(Ph_3P)_3Rh^+$. In contrast, $[(PhO)_3P]_4RhH$ affords $[(PhO)_3P]_4Rh^+$.

Bau, Reed, et al. first prepared $(Ph_3P)_3Rh^+ClO_4^-$ from $(Ph_3P)_3RhCl$ and thallium(I) perchlorate, but the synthetic route proceeding from the rhodium hydride avoids toxicity and explosion hazards associated with $TlClO_4$.[3] The crystal structure of the ClO_4^- salt revealed a slightly distorted T-shaped P_3Rh geometry in the solid. We find that, in CH_2Cl_2 solution, $(Ph_3P)_3Rh^+$ is fluxional. At 35 °C, the $\{^1H\}^{31}P$ NMR spectrum of $(Ph_3P)_3Rh^+HC(SO_2CF_3)_2^-$ (**5**) comprises a doublet at δ 38.1 (J_{PRh} = 172 Hz)[4] while at −50 °C, the A_2B portion of an A_2BX pattern is observed with δ_A 31.5 (dd, J_{PRh} = 133, J_{PP} = 32 Hz) and δ_B 50.1 (dt, J_{PRh} 245, J_{PP} = 32 Hz). This agrees with the results of Albright, Hoffman, and Kochi[5] which indicate that a C_{3v} P_3Rh configuration should be Jahn–Teller unstable and distort toward a T-shaped geometry. In **5**, ΔH_{act} for the process that permutes the ^{31}P environments is ~11.6 kcal/mol at 2 °C.

Fluorochemical acid salts in which the CF_3 groups are replaced by larger fluoroalkyl groups have significantly greater solubility in aromatic hydrocarbons. Thus, $H_2C(SO_2C_8F_{17})_2$ and the nonhygroscopic, easily handled sulfonic acids $C_8F_{17}SO_3H$ and $C_8F_{15}SO_3H$ may be used to prepare highly soluble, catalytically active (vide infra) transition-metal salts. Exemplary are $(Ph_3P)_3Rh^+HC(SO_2C_8F_{17})_2^-$ (**6**) and $(Ph_3P)_3Rh^+C_8F_{17}SO_3^-$ (**7**) whose saturated solutions in toluene are ca. 0.4 M. Evidence for the noncoordinating nature of the anion in **6** was obtained from the ^{13}C NMR spectrum in toluene where the methine carbon appears at δ 61.2 (J_{CH} = 186 Hz) with no evidence of ^{13}C–^{103}Rh coupling.[6,7]

The congruence of S–O stretching frequencies in **5** (1345, 1100 cm^{-1}) and $c\text{-}C_5H_{12}N^+HC(SO_2CF_3)_2^-$ (1330, 1085 cm^{-1}) indicates that rhodium is not coordinated to the SO_2CF_3 oxygen atoms.

These new $(Ph_3P)_3Rh^+$ derivatives have an extensive chemistry, which is under study. Although no complex between **5** and 1-pentene is detectable by ^{31}P NMR, this olefin is quantitatively isomerized to 2-pentene (trans:cis = 9:1). Further, **5** catalyzes the cyclotrimerization of hexafluoro-2-butyne and hydroformylation of 1-hexene. Reaction of solid **5** with ≥1 atm of CO provides $(Ph_3P)_3Rh(CO)_2^+HC(SO_2CF_3)_2^-$ (**6**) ν_{CO} 2019, 1988 cm^{-1}. In the solid state, **6** is indefinitely stable but CH_2Cl_2 solutions, when evaporated or purged with nitrogen, form $(Ph_3P)_3Rh(CO)^+HC(SO_2CF_3)_2^-$ (**7**), ν_{CO} 2026 cm^{-1}.

Hydrides of Fe(II), Ru(II), and Os(II) are protonated with loss of hydrogen (eq 2 and 3). In **8** and **9**, the hydride occupies an axial position and the CO ligand an equatorial site in a trigonal-bipyramidal coordination geometry as the high-field regions of the ^1H NMR spectra comprise doublets of triplets: **8**, δ −7.4

$$(Ph_3P)_3MH_2(CO) + H_2C(SO_2CF_3)_2 \rightarrow (Ph_3P)_3MH(CO)^+HC(SO_2CF_3)_2^-\cdot PhCH_3 + H_2 \qquad (2)$$

$$\mathbf{8},\ M = Ru;\ \mathbf{9},\ M = Os$$

$$(diphos)_2FeH_2 + H_2C(SO_2CF_3)_2 \rightarrow \underset{\mathbf{10}}{(diphos)_2FeH^+HC(SO_2CF_3)_2^-\cdot PhCH_3} + H_2 \qquad (3)$$

[†] Dedicated to E. L. Muetterties.

(1) Practical syntheses of **1** and **2** were first reported by: Koshar, R. J.; Mitsch, R. A. *J. Org. Chem.* **1973**, *38*, 3358.

(2) Vaska, L.; Chen, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671.

(3) Yared, Y. W.; Miles, S. L.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7176.

(4) ^1H, ^{13}C, and ^{31}P chemical shifts are expressed relative to internal $(CH_3)_4Si$ and external 85% H_3PO_4. Negative shifts are to higher field of the reference.

(5) Komiya, S.; Albright, T. A.; Hoffman, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

(6) Wilkinson (Wilkinson, G. U.S. Patent 3 794 671, 1974) reported the synthesis of $(Ph_3P)_3RhBF_4$. This compound was insoluble in most organic solvents, and the electrical conductivity in nitromethane was too low for a 1:1 electrolyte. It was formulated as a monomer Rh(I) species with the fourth Rh coordination position occupied by fluorine from the BF_4^- counterion.

(7) Cf. $H_2C(SO_2CF_3)_2$, $\delta(^{13}C)$ (benzene-d_6) 64.0, J_{CH} = 144 Hz; NH_4^+-$HC(SO_2CF_3)_2^-$, $\delta(^{13}C)$ (D_2O) 52.8, J_{CH} = 186 Hz.

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($J_{\mathrm{PH\,trans}} = 100$, $J_{\mathrm{PH\,cis}} = 25$ Hz); **9**, δ −7.0 ($J_{\mathrm{PH\,trans}} = 82$, $J_{\mathrm{PH\,cis}} = 25$ Hz). In contrast, **1** and **2** react with $(Ph_3P)_3RuHCl(CO)$ in toluene at 60 °C to form $(Ph_3P)_4Ru_2HCl_2(CO)_2{}^+$, purified as the Ph_4B^- salt **11**. The ^{1}H NMR spectrum of this compound reveals a triplet of triplets, δ −13.2, $J_{\mathrm{PH}} = 43$, 11 Hz, indicative of a hydride bridging two $(Ph_3P)_2RuCl(CO)$ units. Protonation of the polyhydride $(Ph_3P)_3OsH_4$ with **1** produces stereochemically nonrigid $(Ph_3P)_4OsH_3{}^+HC(SO_2CF_3)_2{}^-$ (**12**), $\delta(^1H)$ (27 °C) −9.83 ($J_{\mathrm{PH}} = 20$ Hz, binomial pentet). Its $\{^1H\}^{31}P$ NMR spectrum at $\leq$−80 °C discloses two resonances at δ −9.4 and 40.7 in a 3:1 ratio, consistent with a static structure in which osmium is surrounded by a tetrahedron of phosphorus atoms with terminal hydride ligands positioned on the triangular faces of the OsP_4 core.[8]

In conclusion, we find that bis((perfluoroalkyl)sulfonyl)alkanes and -amines are unique and useful reagents for the synthesis of cationic organometallic compounds. Sulfonic acids having long perfluoroalkyl groups are especially useful in preparation of salts that have high solubility in aromatic hydrocarbons. Extension to other classes of organometallic compounds is under investigation as is the chemistry of the cationic materials reported here.

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(8) The crystal structure of **12** will be reported elsewhere. Preliminary results confirm the presence of a slightly distorted OsP_4 tetrahedron.

Mechanism of Amination of Organolithiums by Alkoxyamines: Use of a Geometrical Test for Displacements on Heteroatoms

Peter Beak,* Anwer Basha, and Bruce Kokko

Department of Chemistry
University of Illinois at Urbana—Champaign
Urbana, Illinois 61801

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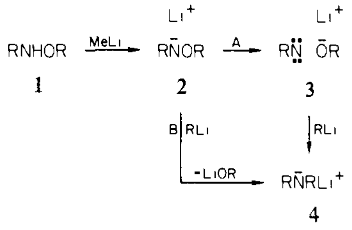
Alkoxyamine derivatives bearing at least one proton on nitrogen can be activated by methyllithium to give species that react with organolithium reagents to provide amines in synthetically useful yields as shown in eq 1.[1-3] The mechanism of the reaction has

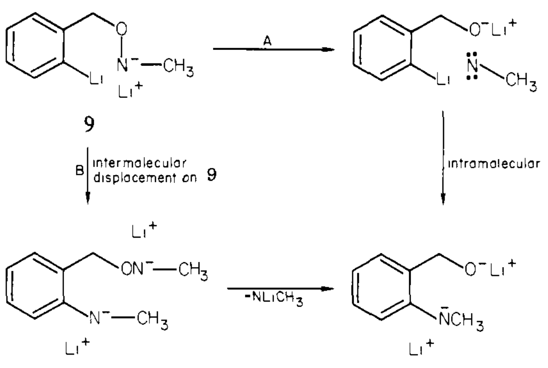
$$\mathrm{RLi} \xrightarrow[2.\ \mathrm{H_3O^+}]{1.\ \mathrm{RONHR\text{-}CH_3Li}} \mathrm{RNHR} \qquad (1)$$

not been determined. In this communication we report observations that support a process of displacement by the nucleophilic organolithium on the nitrogen of a lithium alkoxyamide in a transition state that has bond angles characteristics of an S_N2 reaction. The present results illustrate an approach, suggested by work done by Eschenmoser on nucleophilic displacements on carbon and by Kampmeier on radical displacements on sulfur, that should be generally useful for establishing the stereochemistry of displacements on atoms that do not maintain chirality.[4-6]

Scheme I

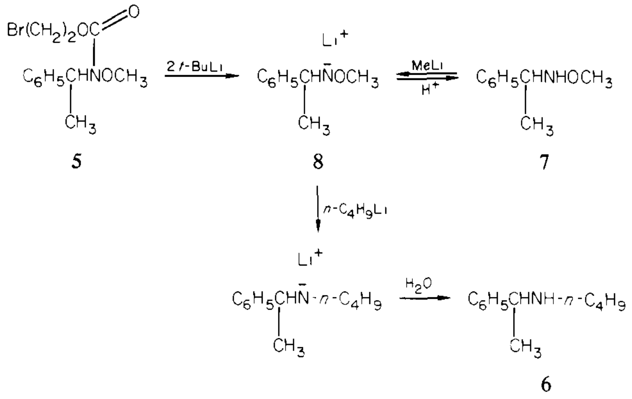


Scheme II



Two possible mechanisms for the amination are outlined in Scheme I. Initial deprotonation of the alkoxyamine **1** to **2** could be followed by loss of lithium methoxide to produce a nitreneoid **3**, which, by addition of an organolithium, would give the lithium amide product **4** as illustrated for pathway A. Alternatively, direct displacement on the initially formed anion **2** by the organolithium could be envisioned as shown for pathway B.

We have confirmed that reaction proceeds via a lithium alkoxyamide by formation of that intermediate by two different paths. Treatment of the bromocarbamate **5** with 2 mol of *tert*-butyllithium at −78 °C followed by *n*-butyllithium, warming to −15 °C, and addition of water provides the amine **6** in 64% yield. If



an acid quench is added after the reaction with *tert*-butyllithium, the alkoxyamine **7** is obtained in 80% yield. The amine **6** is also obtained in 68% yield when **7** is treated with methyllithium prior to addition of *n*-butyllithium. These results rule out direct reaction of **7** and support the intermediacy of **8**.[7]

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(1) Sheverdina and Kocheshkov (Sheverdina, N. I.; Kocheshkov, Z. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1938**, *8*, 1825) first reported the use of methoxyamine with 2 equiv of organolithium to provide amines. For representative cases, see: Gilman, H.; Ingham, R. *J. Am. Chem. Soc.* **1953**, *75*, 4843. Acton, E. M.; Silverstein, R. M. *J. Org. Chem.* **1959**, *24*, 1487. Silver, M. W. *J. Am. Chem. Soc.* **1961**, *83*, 3487. Yamada, S. I.; T.; Shiorri, Oguri, T. *Chem. Pharm. Bull.* **1975**, *23*, 167. Erdik, E. **1975**, *Commun. Fac. Sci. Univ. Ankara, Ser. B.* **1980**, *26*, 83; *Chem. Abstr.* **1981**, *95*, 115634*p*. Wakefield, B. J. "Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; p 215.

(2) (a) Beak, P.; Kokko, B. J. *J. Org. Chem.* **1982**, *47*, 2822. (b) Beak, P.; Kokko, B. J. *Tetrahedron Lett.* **1983**, 561. (c) Quirk, R. P.; Chung, P. L. *Polymn. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, in press.

(3) For recent developments with other aminations, see: Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1983**, 3795. Boche, G.; Bernheim, M.; Niessner, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 53. Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 1054.

(4) Tenud, L.; Faroog, S.; Seible, J.; Eschenmoser, A.; *Helv. Chim. Acta.* **1970**, *53*, 2059.

(5) Kampmeier, J. A. *ACS Symp. Ser.* **1978**, *No.* **69**. Kampmeier clearly noted the potential of this approach for determining the geometry of displacement at heteroatoms that do not maintain chirality.

(6) For generalizations, see: Baldwin, J. E.; Lusch, M. J. *Tetrahedron* **1982**, *19*, 2939 and references cited therein.

(7) The conversion of **5** to **8** presumably involves bromine lithium exchange followed by loss of ethylene and carbon dioxide. The later loss could occur slowly to release small amounts of **8** for reaction during the warming period.

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