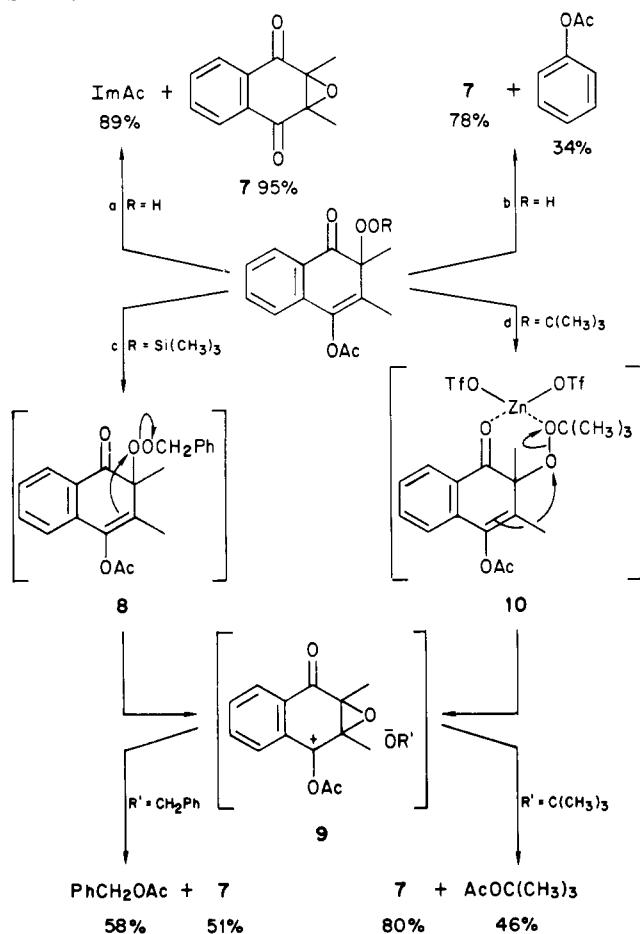


Scheme III^a

^a (a) 1.0 equiv of $(\text{Im})_2\text{CO}$, CHCl_3 , room temperature, 2 h; (b) 1.0 equiv of phenol, $\text{Zn}(\text{OTf})_2$, CH_2Cl_2 , room temperature, 48 h; (c) $n\text{-Bu}_4\text{NF}$, PhCH_2Br , THF , 78°C , 2 h; (d) $\text{Zn}(\text{OTf})_2$, CHCl_3 , room temperature, 48 h.

prepare from **2** by using *tert*-butyl hydroperoxide and cobalt acetate¹² (44%, mp $107.1\text{--}108.1^\circ\text{C}$). With these materials in hand, it became possible to test Suttie's acylation proposal.

In these initial studies we have examined only acetylations at nitrogen and oxygen. The hydroperoxide **3** undergoes an extremely smooth reaction with 1 equiv of carbonyl diimidazole (Scheme III) to form the desired quinone epoxide **7** and acetylimidazole in nearly quantitative yield. Zinc triflate is the most effective Lewis acid catalyst found to date for the formation of phenyl acetate from **3** and phenol.¹³ With other Lewis acids such as boron trifluoride, the hydroperoxide is converted to quinone epoxide **7**, but no acetylation is observed. Thus, the formation of these acetylation products along with the quinone epoxide is good evidence in support of Suttie's mechanism.

It is thought that the key to success in these reactions lies in finding conditions that will restrict the availability of undesired nucleophiles which might react with the activated acetyl group. To this end we have examined conditions that might be expected to generate the desired nucleophile, alkoxide ions, simultaneously with the activated acetyl species. Desilylation of **5** with fluoride ion in the presence of benzyl bromide should lead to the peroxide **8** (Scheme III) and this species might fragment to form an alkoxide ion and active acylating agent as an ion pair **9**, $\text{R}' = \text{CH}_2\text{Ph}$. The feasibility of this ion pair hypothesis is indicated by the

(12) The *tert*-butyl peroxide **6** was prepared using a variation of the procedures of: Kharasch, M. S.; Fono, A. *J. Org. Chem.* **1959**, *24*, 72. Campbell, T. W.; Coppinger, G. M. *J. Am. Chem. Soc.* **1952**, *74*, 1469.

(13) Control experiments have shown that this acetylation is not the trivial result of an imidazole reaction with **3** or a zinc triflate catalyzed reaction between acetic acid and the corresponding alcohol or phenol.

formation of quinone epoxide **7** and benzyl acetate in nearly equivalent yields. Unfortunately, the peroxide **8** could not be detected as an intermediate. Thus, **8** would appear to be very labile in contrast to the *tert*-butyl peroxide **6** which is reasonably stable. The same ion pair model for acetylation succeeds with **6** when zinc triflate is used as a catalyst.¹³ In this reaction the zinc triflate might complex with the α -peroxy ketone unit as shown in **10** and bias the peroxide linkage in favor of a heterolytic cleavage to form the ion pair **9**, $\text{R}' = \text{C}(\text{CH}_3)_3$.¹⁴

In summary, this work has demonstrated that peroxy analogues of vitamin K are readily formed from molecular oxygen under conditions closely approximating those found in biological systems. Further, it has been shown that ionic decomposition of these peroxides does lead to active acylating species. Finally, it must be noted that phenolic esters have previously been converted to active acylating species through electrochemical¹⁵ and chemical¹⁶ means. However, this is the first demonstration of a route for coupling oxidation with molecular oxygen to acylation.

Acknowledgment. We thank Leo Geraci for assistance in the preparation of starting materials and the National Science Foundation for support of this work under Grants CHE-8004235 and CHE-8312691.

(14) The reactions described here afford simple reaction mixtures. Many other conditions examined afford complex mixtures. These intractable mixtures are possibly the result of triggering radical chain modes of peroxide decomposition.

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Lithium-Metalloid Exchange Reactions. Kinetic Evidence for an Intermediate in the Lithium-Iodine Exchange¹

Hans J. Reich,* Nancy H. Phillips, and Ieva L. Reich

*S. M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received January 28, 1985*

The metal-halogen exchanges (Li/Br , Li/I)² are the best known of a family of lithium-metalloid exchange reactions, of which the Li/Sn^3 and Li/Se^4 exchanges are also commonly used members. These reactions have achieved special importance for the preparation of functionalized and/or unstable alkyl-, vinyl-, and aryllithium reagents.^{2b,3b,c,4b} Kinetic studies of the Li/M exchange

(1) For a previous study of hypervalent iodine, see: Reich, H. J.; Cooperman, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 5077.

(2) (a) Gilman, H.; Langham, W.; Jacoby, A. L. *J. Am. Chem. Soc.* **1939**, *61*, 106. Wittig, G.; Pockels, U.; Dröge, H. *Chem. Ber.* **1938**, *71*, 1903. (b) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210. Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. Cooke, M. P., Jr. *J. Org. Chem.* **1984**, *49*, 1144. Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098.

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Table I. Results of Tests 1 and 2

C ₆ H ₅ M	test 1 ^a R ₁ ^b	test 2 ^c R ₂ ^d
(C ₆ H ₅) ₂ Hg	5.7	0.07
C ₆ H ₅ Sn(<i>n</i> -C ₄ H ₉) ₃	2.7	0.97
(C ₆ H ₅) ₃ Sb	2.7	1.03
(C ₆ H ₅) ₃ Bi	3.0	1.03
(C ₆ H ₅) ₂ Te	3.0	1.07
C ₆ H ₅ I	2.9	0.80
	2.9	1.00

^a Comparison of the reactions of a test (C₆H₅Li/C₆H₅M, each 0.2 M) and a control (C₆H₅Li, 0.2 M) solution with chalcone (0.2 M) in THF at -78 °C (eq 2). The control reaction gave 69% 1,2- and 24% 1,4-product. The phenyllithium solution was commercial material (1.8 M in 75:25 ether/benzene, low halide) diluted with anhydrous THF. ^b R₁ = [% 1,2-addition (C₆H₅M)] / [% 1,4-addition (C₆H₅M)]. ^c Comparison of the percent reaction of test and control solutions (as in (a)) with *n*-C₄H₉I (0.2 M) in THF -78 °C for 60 min (eq 2). The control reaction gave 30–32% conversion to *n*-butylbenzene. ^d R₂ = [% *n*-C₄H₉-C₆H₅ (C₆H₅Li/C₆H₅M)] / [% *n*-C₄H₉-C₆H₅ (C₆H₅Li)].

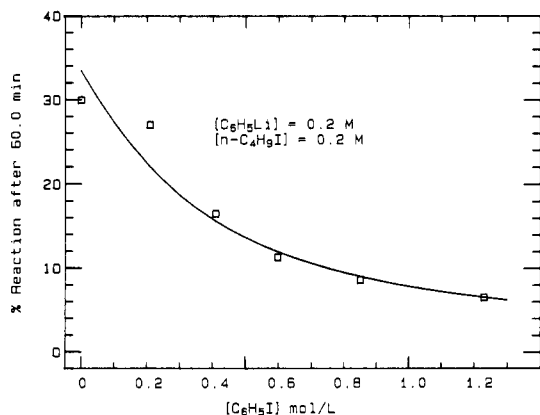


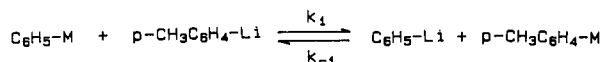
Figure 1. Effect of iodobenzene on the rate of reaction of phenyllithium with 1-iodobutane in THF at -78 °C. The points are experimental, the line was calculated by using $k_2 = 7.0 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ (test 2) and $K = 5.9 \text{ mol L}^{-1}$ (eq 1).

of aryl bromides,^{5a,b} aryl iodides,^{5c} arylstannanes,^{5d} and arylplumbanes^{5e} have generally been interpreted in terms of a four-center transition state (1).^{5b,6a} The possible intermediacy of



transient or even stable "ate" complexes (2) as first suggested by Wittig and Schöllkopf^{6b,4c} has been addressed experimentally for the Li-Sn exchange without definitive results.^{3b} We have undertaken a study of the mechanism of the lithium-metalloid exchange and can now report substantial evidence for an intermediate in the lithium-iodine exchange.

From published results⁵ and our own studies⁷ of PhM/TolLi exchange rates (k_1, k_{-1}), it is clear that (with minor exceptions)



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(7) Unpublished results of I. L. Reich.

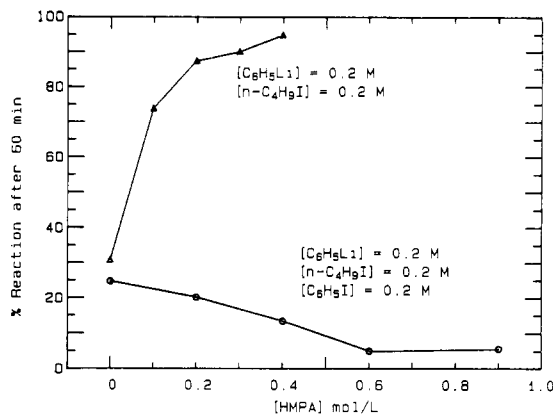
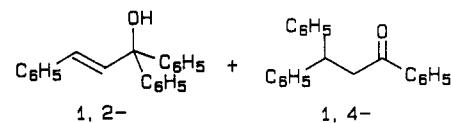
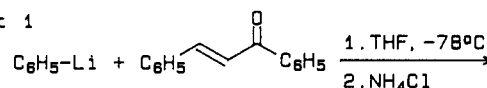


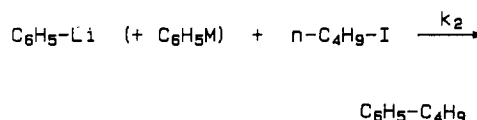
Figure 2. Results of test 2 as a function of HMPA concentration.

the heavier and more electronegative elements exchange most rapidly. We therefore chose the phenyl derivatives of I, Te, Sb, Bi, and Sn, which reach equilibrium at -80 °C in THF in less than 5 min, as the best candidates for more careful scrutiny as to the existence of intermediate "ate" complexes. Tests comparing the reactivity of solutions of C₆H₅Li and 1:1 C₆H₅Li/C₆H₅M were then carried out using these metalloids. Test 1 involved a re-

Test 1

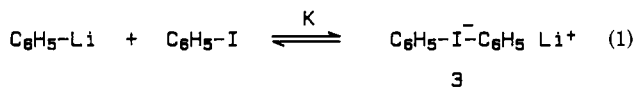


Test 2



gioselectivity comparison, and test 2 a rate comparison (see Table I). Of the main group organometalloids tested only iodine reproducibly showed a significant positive result for either of the tests, although the effect (~15% reduction in rate of reaction with 1-iodobutane) was not large. We therefore chose the phenyllithium-iodobenzene system for more detailed study.

Support for our hypothesis that the rate retardation was caused by the equilibrium of eq 1 was provided by the observation of



further substantial decreases in the rate of alkylation (test 2) when the concentration of iodobenzene was increased.⁸ By assuming that the reaction followed second-order kinetics⁹ and that 3 was unreactive, a reasonable fit of calculated and experimental points was achieved for $K = 5.9 \text{ L mol}^{-1}$ (see Figure 1).

Table I includes an entry for diphenylmercury, which clearly indicates that complexation occurs with phenyllithium in *tetra*-

(8) It should be emphasized that although for both test 2 and test 3 the reactivity of the solution varied as C₆H₅I was added, the titer for active C₆H₅Li [measured by (CH₃)₃SiCl or (CH₃)₂S₂ quench and capillary GC analysis] was always >90% of the initial value when corrected for C₆H₅Li used up in the test reaction.

(9) The reaction of eq 3 follows second-order kinetics at a given concentration of phenyllithium, but the rate constant changes as the [C₆H₅Li] is changed. It is thus not clear whether our method of measuring the "effective" concentration of free phenyllithium from the alkylation rate represents true [C₆H₅Li].

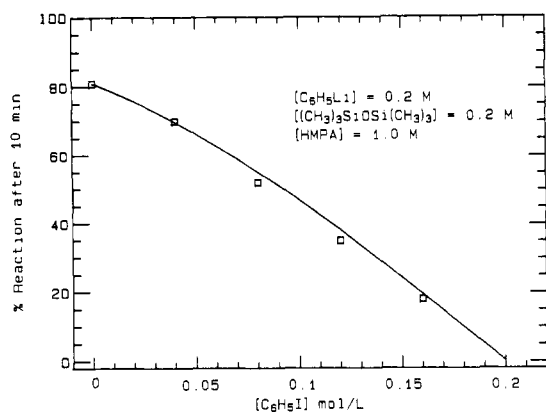
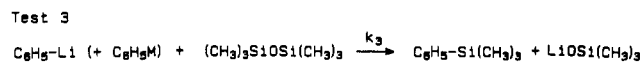


Figure 3. Effect of iodobenzene on the rate of reaction of phenyllithium with hexamethyldisiloxane in THF/1.0 M HMPA at $-78\text{ }^{\circ}\text{C}$ (test 3). The points are experimental, the line was calculated by using $k_3 = 3.55 \times 10^{-4}\text{ L mol}^{-1}\text{ s}^{-1}$ (test 3) and $K = 1.2 \times 10^{-7}\text{ L mol}^{-1}$ (eq 1).

hydrofuran, in contrast to early results of Wittig, Meyer, and Lange, who demonstrated both by vapor pressure osmometry and a metalation test that no interaction occurs in *ether*.¹⁰ This result prompted us to study solvent effects on the iodine system (eq 1) by running test 2 in solutions containing hexamethylphosphoric triamide (HMPA). The small difference between the control and $\text{C}_6\text{H}_5\text{Li}/\text{C}_6\text{H}_5\text{I}$ runs in THF rapidly became very large with increasing HMPA concentration (Figure 2). In fact, the addition of HMPA to a solution of $\text{C}_6\text{H}_5\text{Li}/\text{C}_6\text{H}_5\text{I}$ actually lowers its reactivity. Apparently, increases in concentration of the (presumably unreactive) complex 3 as HMPA concentration was increased more than compensated for the higher reactivity of the remaining free phenyllithium. This dramatic solvent effect can be understood in terms of the differences in solvation requirements for the two sides of eq 1. In contrast to phenyl anion, which binds tightly to lithium in a cyclic dimeric structure,¹¹ the diphenyliodinate anion probably cannot provide a good coordination site for lithium cation, and hence its formation is strongly favored by improved solvation of Li^+ .

To more carefully define the stoichiometry of the interaction between phenyllithium and iodobenzene in solutions containing HMPA, test 3 was developed. Figure 3 presents the results of



this test. The reactivity of the solution decreased monotonically as iodobenzene was added. The complexation is now essentially quantitative and occurs with exact 1:1 stoichiometry.⁸ If the assumption is again made that the reaction follows second-order kinetics and that the complex is unreactive toward hexamethyldisiloxane, a value of $K > 1.2 \times 10^7\text{ L mol}^{-1}$ can be estimated.¹²

Attempts to observe the complex 3 by ^{13}C NMR spectroscopy have been frustrated by the occurrence of rapid exchange processes.

The results presented here demonstrate that phenyllithium and iodobenzene interact reversibly in a strongly solvent-dependent fashion to form a 1:1 complex which we believe is the hypervalent iodine "ate" complex $(\text{C}_6\text{H}_5)_2\text{I}^-\text{Li}^+$ (a 10-I-2 anion¹³). This result has direct bearing on understanding the mechanism of the met-

al-halogen exchange, which we feel is best represented as proceeding via a discrete "ate" complex (e.g. 2, 3) intermediate. Further studies on other lithium-metalloid exchanges are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support. Mark Dorow and Dr. Steven L. Peake performed preliminary experiments and we thank them for their contribution to this project.

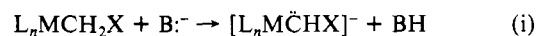
Reaction of Cyanomethyl Complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CN})$ with $n\text{-BuLi}/\text{TMEDA}$; Generation, Stereospecific Alkylation, and Basicity of a Transition-Metal-Substituted Carbanion

Guy L. Crocco and J. A. Gladysz*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received March 4, 1985

Transition-metal alkyls are the cornerstone of organometallic chemistry. However, little is known regarding the acid/base chemistry of the C-H bonds of alkyl ligands. In particular, the deprotonation of neutral metal alkyl complexes at C_α , as depicted in eq i, is to our knowledge unprecedented.¹ We have begun to



probe the acid/base chemistry of chiral cyclopentadienyl rhenium alkyl complexes² and report here (1) the first deprotonation of a neutral metal alkyl complex at the ligating carbon, (2) the stereospecific alkylation of the resulting conjugate base, and (3) a qualitative determination of the effect of the rhenium moiety upon the $\text{C}_\alpha\text{-H}$ ion pair acidity.³

Reaction of cyanomethyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CN})$ (1, in THF)⁴ with $n\text{-BuLi}/\text{TMEDA}$ (1.0 equiv, $-78\text{ }^{\circ}\text{C}$) and then $\text{CH}_3\text{OSO}_2\text{CF}_3$ gave cyanoethyl complex $(SR,RS)\text{-}(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}(\text{CH}_3)\text{CN})$ ($(SR,RS)\text{-}2$) in 75% yield upon workup (eq ii).⁵ The gross structure of $(SR,RS)\text{-}2$ followed readily from its spectroscopic properties,⁵ and its stereochemistry was established by an independent synthesis of the opposite diastereomer, $(SS,RR)\text{-}2$. Diastereomer $(SS,RR)\text{-}2$ was obtained in 91% yield from the reaction of $\text{PPN}^+\text{-CN}^-$ with "kinetic" ethylidene complex $sc\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CHCH}_3)]^+\text{PF}_6^-$ (3, eq iii).⁷ Nucleophilic additions to this⁷ and related⁸ alkylidene complexes have been shown to preferentially occur from a direction anti to the PPh_3 , enabling

(1) Deprotonation of cationic complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_3)_2]^+$: Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

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(3) (a) Acid/base terminology utilized in this manuscript has been recently summarized.^{3b} It must be emphasized that representations of our deprotonated complexes are approximations. For example, we presently have no data on the site or degree of Li^+ ion pairing in 4. (b) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

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(5) Microanalytical, mass spectral, IR, and NMR (^1H , ^{13}C , ^{31}P) data for each new compound are given in the supplementary material. Isotopically labeled compounds were synthesized by modifications of published routes to unlabeled compounds. For all compounds, the absolute configuration at rhenium is specified first.

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(10) Wittig, G.; Meyer, F. J.; Lange, G. *Liebigs Ann. Chem.* **1951**, 571, 167.

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(12) This result is based on the formation of less than 0.04% of $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$ when test 3 was run for 96 h at $-80\text{ }^{\circ}\text{C}$ with 2 equiv of iodobenzene. If the complex (presumably $(\text{C}_6\text{H}_5)_2\text{I}^-\text{Li}^+$) is itself reactive toward hexamethyldisiloxane, then the equilibrium constant would be correspondingly larger. From the results obtained it can be calculated that the "ate" complex is $<10^{-5}$ as reactive as phenyllithium.

(13) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lare, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. Several hypervalent organoiodine compounds have been prepared. Bess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 902.