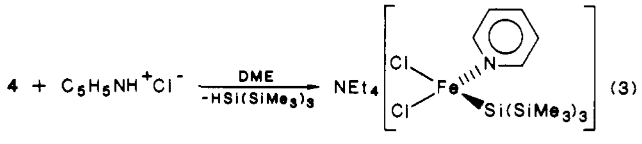
Treatment of **3** with NEt_4Cl in 1,2-dimethoxyethane results in cation exchange to give $NEt_4[(TTSS)_2FeCl]$ (**4**), which has been structurally characterized.[5] An ORTEP view of the anion in **4** (Figure 1) shows the unusual three-coordinate geometry for the d^6 Fe(II) center. The steric bulk of the TTSS ligands results in a Si(1)–Fe–Si(5) angle of 136.9 (2)°, significantly larger than the Si–Fe–Cl angles (av 111.4 (4)°). These differences in bonding angles about iron are probably responsible for the observed deviations from tetrahedral environments about Si(1) and Si(5). Other metrical parameters associated with the TTSS ligation in **4** do not differ markedly from those found in $(CO)_5Mn(TTSS)$[6] and $(CO)_5Re(TTSS)$.[7] The Fe–Si bond distances (av 2.490 (6) Å) appear to be the longest yet observed for an iron silyl complex. Other reported Fe–Si distances range from 2.22 to 2.46 Å.[8]

The reaction chemistry of compounds **1–4** has been briefly surveyed. Acidolysis of **4** with 1 equiv of pyridinium hydrochloride gives the anionic pyridine complex **5** (eq 3), which may be crystallized from diethyl ether/1,2-dimethoxyethane. The chloride ligand in **4** may be abstracted by $Me_3SiOSO_2CF_3$ in toluene giving Me_3SiCl and $NEt_4[(TTSS)_2FeOSO_2CF_3]$ (**6**), isolated as purple crystals from pentane/toluene. The triflate ligand in **6** is weakly coordinated and is readily displaced by ethers (eq 4). Neutral complexes **7** and **8** are crystallized from pentane. Manganese silyl complex $(TTSS)_2Mn(DME)$ (**9**), obtained similarly from the lithium salt **2** and $Me_3SiOSO_2CF_3$, presumably has a four-coordinate structure analogous to **8**. Mass spectra of **8** and **9** contain no parent ions but feature strong peaks due to $M(TTSS)_2^+$. Exact mass measurements gave values of 550.1724 for **8** (calcd: 550.1729) and 549.1764 for **9** (calcd: 549.1760) for the $M(TTSS)_2^+$ ions.



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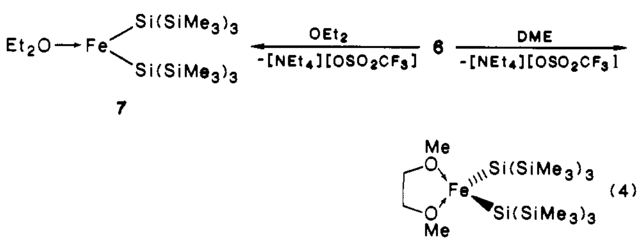

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We are presently examining the chemistry of these and related low-coordinate transition-metal silyl complexes. Initial results indicate that coordinative unsaturation in these systems provides a high degree of reactivity toward unsaturated substrates.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant AFOSR-85-0228. The U.S. Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation thereon.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and positional and thermal parameters for **4** (4 pages); tables of observed and calculated structure factors for **4** (12 pages). Ordering information is given on any current masthead page.

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(5) $C_{26}H_{74}ClNFeSi_8$: monoclinic, $P2_1/c$, $a = 14.943$ (3) Å, $b = 21.198$ (3) Å, $c = 15.291$ (4) Å, $\beta = 99.16$ (2)°, $V = 4782$ (2) $Å^3$, $Z = 4$, $\mu = 5.83$ cm^{-1}, Mo Kα ($\lambda = 0.71073$ Å), 23 °C, Nicolet R3 diffractometer, graphite monochromator, purple crystal (0.35 × 0.30 × 0.25 mm) from 1,2-dimethoxyethane/diethyl ether, sealed in glass capillary. Of 5425 reflections collected ($4° \leq 2\theta \leq 42°$), 5181 were unique ($R_{int} = 1.77\%$), and 1957 with $F_o \geq 5\sigma(F_o)$ were considered observed. No absorption correction was needed. A model for disorder found in NEt_4^+ was constructed by constraining the NC_4 fragment to tetrahedral symmetry and refining the C–C distances as a common variable. The overall temperature factor, $U_{iso} = 0.068$, obtained from a Wilson plot is large and reveals that the structure is unusually thermally active. Absence of diffraction data beyond $2\theta = 42°$, the disordered NEt_4^+ ion, and the low density (D(calcd) = 1.00 g cm^{-3}) are in keeping with a very loose lattice packing. Solution by direct methods (SOLV), blocked cascade refinement, non-hydrogen atoms anisotropic, hydrogen atoms (except for those of NEt_4^+ which were ignored) isotropic (fixed and idealized positions): $R_F = 9.6\%$, $R_{wF} = 10.3\%$, data/parameter = 6.7, GOF = 1.58, highest peak = 0.61 $e^-/Å^3$ (within NEt_4^+).

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Synthetically and Biologically Interesting *N*-Acylquinone Imine Ketals and *N*-Acylquinol Imine Ethers from Anodic Oxidation of Anilides

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The electrochemistry of aromatic amines has been extensively studied;[1] however, less is known about the electrochemical oxidation of the corresponding amides.[2-4] Several types of reactions have been reported, but most involved poor yields and/or material balances and no synthetic use has been made of this chemistry. Thus, the anodic oxidation of simple anilides in acetonitrile/pyridine gives pyridination products,[2b,3a,b] while amide derivatives of *p*-anisidine in nucleophilic solvents (water, methanol) afford mixtures of benzoquinone, benzamide, or methyl benzoate, depending on the reaction conditions.[2a,3a,c] Unstable intermediates have been detected in the anodic oxidations[3c] of *N*-aryl amides by cyclic voltammetry and ultraviolet spectroscopy, but these compounds were not isolated or characterized. Finally, anodic oxidation of the anilide of *N*-methyl-*p*-anisidine affords the corresponding *N*-methylbenzoxazolium perchlorate,[3c] and various dimeric products are formed under other reaction conditions.[3d,4]

The extensive biological interest in the oxidation products derived from acylated aromatic amines[5,6] and the synthetic po-

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(5) (a) Calder, I. C.; Creek, M. J.; Williams, P. J.; Funder, C. C.; Green, C. R.; Ham, K. N.; Tange, J. D. *J. Med. Chem.* **1973**, *16*, 499. (b) Calder, I. C.; Creek, M. J. *Aust. J. Chem.* **1976**, *29*, 1801. (c) Hinson, J. A.; Nelson, S. D.; Gillette, J. R. *Mol. Pharmacol.* **1979**, *15*, 419. (d) Calder, I. C.; Caciolli, S. *Aus. J. Chem.* **1979**, *32*, 1301. (e) Gemboys, M. W.; Mudge, G. H.; Gribble, G. W. *J. Med. Chem.* **1980**, *23*, 304.

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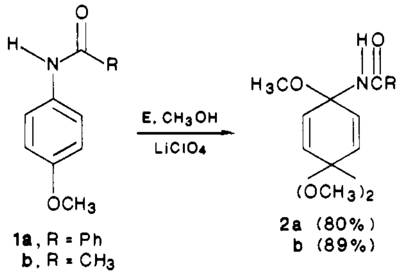
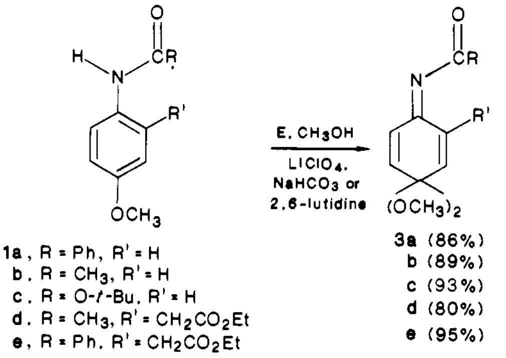
tential of stable products derived from oxidation of anilides prompted our examination of the anodic oxidation of simple amides of aromatic amines. We report herein a facile method for the preparation of *N*-acyl derivatives of quinone imine monoketals[7] and quinol imine ethers[8,9] by anodic oxidation of readily available aromatic amide derivatives and useful carbon–carbon bond-forming reactions of these compounds.

Initially, the anodic oxidations of a number of amides of *p*-methoxy anilines were conducted in methanolic potassium hydroxide, conditions employed in the high-yield preparations of quinone bis-ketals from the corresponding 1,4-dimethoxy benzene derivatives.[10,11] However, our results paralleled much of the earlier observations in the literature:[2-4] complicated reaction mixtures and low material balance. By contrast, anodic oxidation of **1a** at constant current in 2% methanolic lithium perchlorate at 0 °C followed by conventional workup and recrystallization gave **2a** (80% yield, 71% current efficiency). Similarly, **1b** afforded **2b**.

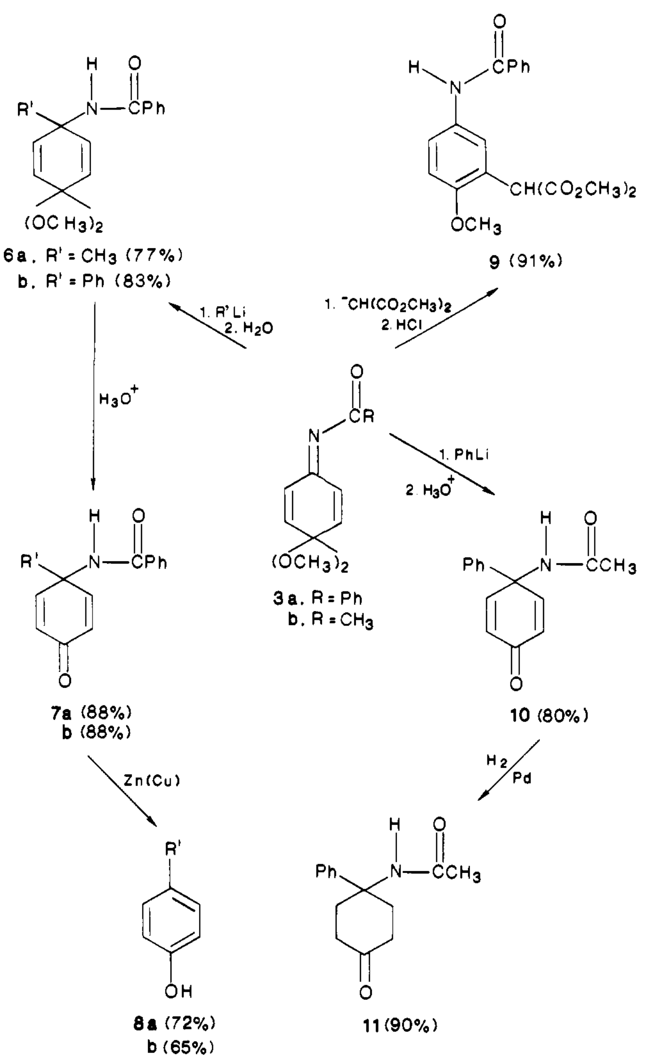


These compounds are the first examples of a doubly protected quinone imine moiety. Reaction of **2a** with sodium hydride in tetrahydrofuran afforded the *N*-acylquinone imine ketal **3a** (86% yield).



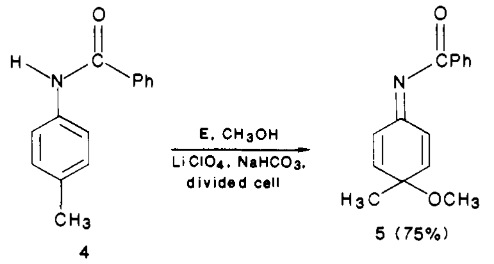
Because the quinone imine ketals were of major synthetic interest, a one-step approach to these compounds was developed. Anodic oxidation of the benzoyl, acetyl, and *tert*-butoxycarbonyl derivatives of *p*-anisidine, **1a–c**, in a single cell at constant current in 1–2% methanolic lithium perchlorate containing either finely divided sodium bicarbonate or 2,6-lutidine was found to be a convenient, efficient procedure for preparation of **3a–c**. The majority of this was done with sodium bicarbonate as base; however, under these conditions, workup of the reaction mixture must be done carefully and rapidly to avoid deacylation of **3**. When 2,6-lutidine was employed as the base in the anodic oxidation, the yield of product was generally superior to the method using sodium bicarbonate since deacylation does not occur in the workup procedure. Presumably, this fast deacylation of the *N*-aryl amide oxidation products was at least part of the complication in the earlier oxidations[2b,3a,c] in solvent systems containing water or methanol.

Scheme I. Representative Reactions of *N*-Acylquinone Imine Ketals



The products obtained from simple workup of the oxidation reaction mixture were yellow to light red oils which were judged to be greater than 95% pure by ^{1}H and ^{13}C NMR spectroscopy. The products can be further purified by silica gel chromatography, but all of the chemistry reported herein has been performed on material obtained directly from workup of the electrolysis solution. The compounds are stable for at least several days when stored under nitrogen at −10 °C. However, they undergo rapid deacylation in aqueous base to afford the unstable imine derivative.

Although the generality of the anodic oxidation has not been extensively explored for substituted systems, anodic oxidation of **1d** and **1e** afforded **3d** and **3e** in 80% and 95% yields, respectively. Thus, even systems having somewhat acidic benzylic hydrogens undergo the oxidation in good yield. Furthermore, the reaction is not limited to *p*-methoxyaniline derivatives since **4** gives on anodic oxidation the *N*-acylquinol ether imine **5**[12] in 75% yield.



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[8] The *N-tert*-butyl imines of quinol ethers have been prepared from the *N*-chloro derivatives of anilines,[9] but their chemistry has not been extensively studied.

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[12] Compound **5** in which the *N*-benzoyl group is replaced by *N*-acetyl is known.[6c] The ^{1}H and ^{13}C NMR data for these compounds are in qualitative agreement.

This chemistry affords a convenient route to *N*-acylquinone imine ketals from the readily available aromatic amides. Although oxygen nucleophiles effect deacylation of **3a**,**b**, organolithium reagents and malonate anion react to give good yields of the 1,2- and 1,4-addition products (see Scheme I). Furthermore, hydrolysis followed by reduction allows either replacement of the original amino group with an alkyl or aryl residue (**7a**,**b** → **8a**,**b**) or preparation of a 4,4-disubstituted cyclohexanone (**10** → **11**). Thus *N*-acylquinone imine ketals offer opportunities for functionalization of certain aniline derivatives in the same manner that quinone monoketals serve as intermediates for oxygenated aromatic systems.[11] Future publications will deal with synthetic applications of this chemistry.[13]

Acknowledgment. We thank the National Science Foundation for partial support of this study.

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[13] Anodic oxidations were conducted on 0.3–1.0 g of compound in 100–200 mL of reagent grade methanol by using a cylindrical platinum gauze anode and a platinum sheet cathode. Typically twice the amount of finely divided sodium bicarbonate relative to the compound or 1 equiv of 2,6-lutidine was employed as indicated. Compounds not previously reported showed exact mass or combustion analysis in agreement with the assigned structures. The products obtained as solids had the following melting points: **2a**, 113–114 °C; **6a**, 89–90 °C; **6b**, 151–154 °C; **7a**, 178–180 °C; **7b**, 180–182 °C; **10**, 155–157 °C; **11**, 136–138 °C.

Reverse Transmetalation: A Strategy for Obtaining Certain Otherwise Difficultly Accessible Organometallics

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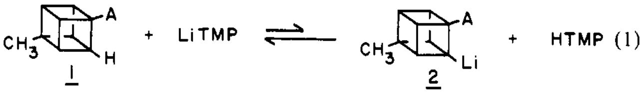
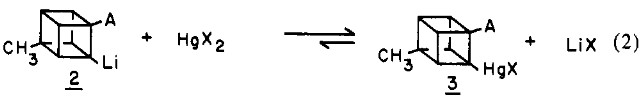
An amide group provides a small but useful activation for ortho-lithiation on the cubane nucleus. For example, reaction of the *N*,*N*-diisopropylcubanecarboxamide **1** with 8 equiv of lithium tetramethylpiperidide (LiTMP) under equilibrating conditions in THF at 0 °C gives about 3% of the lithium derivative **2** (eq 1).[1] The low conversion and the large excess of base make it difficult to use **2** directly.[2] However, if its generation is carried out in the presence of mercury salts, transmetalation occurs easily (eq 2), and the equilibrium of eq 1 is drawn effectively to the right.



(1)



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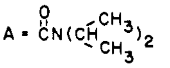
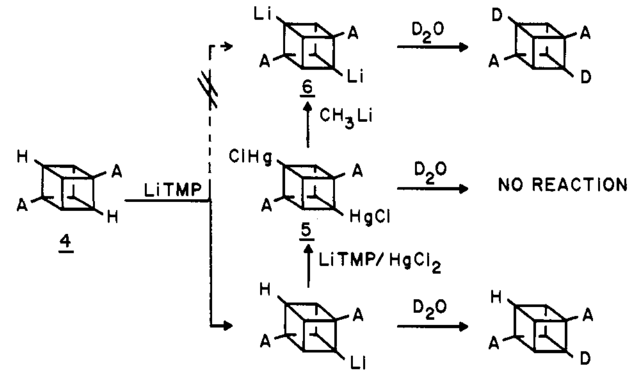


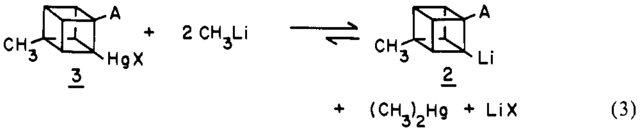
$A = \overset{O}{\overset{\|}{C}}N(CH(CH_3)_2)_2$

Nearly complete conversion of **1** to the organomercury **3** occurs. Such cubyl mercuries are readily isolable pure as their chlorides and are excellent progenitors for cubyl halides,[1] but they do not have the broad reactivity spectrum of organolithiums and Grignards. We report now on the successful implementation of an idea for obtaining these more reactive metallocubanes at substantial concentrations, in good yields, and free of interfering reagents.

Scheme I



Seyferth and others have shown that tetraorganostannanes and organolithiums undergo equilibrium transmetalation.[3,4] There are a few reports of similar exchanges between diorganomercuries and organolithiums or Grignards.[5] We expected that an equilibrium among various cubyl and alkyl metallics would favor cubyl attached to the more electropositive metal. The higher s character in an exocyclic cubane carbon orbital[6] over that of a typical alkane carbon would better accommodate the more polar C–metal bond. Additionally, in the amide-substituted cubanes dealt with here, intramolecular amide–metal interactions would shift the equilibrium in the same direction. Indeed, we find that when pure **3** (X = Cl) in THF at −20 °C is reacted with CH_3Li (2 equiv; 1.7 M in diethyl ether) the cubyllithium **2** is formed in high yield by lithium-for-mercury exchange (eq 3).[7] As **3** was originally



(3)

made by mercury-for-lithium transmetalation on **2**, we call the process "reverse transmetalation". It is very efficient. If after 5 min at −20 °C the reaction is quenched with CH_3OD, less than 5% of starting **3** can be found, but **1** is regenerated (>95%) with at least 95% monodeuterium incorporation.

The ortholithiated cubane amide **2** prepared by reverse transmetalation is very useful. For example, it has been successfully carbonylated (CO_2), phenylselenenylated (PhSeCl), and oxygenated. Interestingly, although cubane amides like **1** are attacked readily by alkyllithiums, **2** is stable, at least for 30 min at 0 °C, to itself and to excess CH_3Li. Apparently, the interaction between the amide and the ortho metal stabilizes both.

We demonstrated previously that reaction of cubanediamide **4** with LiTMP/$HgCl_2$ gives by sequential lithiation/transmetalation the dimercury compound **5** (chloride workup).[1] There is evidence against the intermediacy of the dilithiated cubane **6** in this process, *but such a dilithiated cubane can be formed in high yield by double-reverse transmetalation* (Scheme I). Treatment

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[1] Eaton, P. C.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724.

[2] Achieving stoichiometric deprotonation by using alkyllithiums is not feasible; nucleophilic attack on the amide occurs preferentially. We shall report later on the use of other activating groups.

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[4] For some further examples and other leading references, see: (a) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. (b) Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277.

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[6] (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157. (b) Stock, L. M.; Luh, T.-Y. *J. Am. Chem. Soc.* **1974**, *96*, 3712. (c) So, S. P.; Wong, M. H.; Luh, T.-Y. *J. Org. Chem.* **1985**, *50*, 2632.

[7] The other product is $(CH_3)_2Hg$. It does not interfere with further conversions of **2**. It is, however, volatile and toxic. Due caution is called for. It can be destroyed by adding iodine after **2** has been used, but before the reaction mixture is worked up.

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