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]

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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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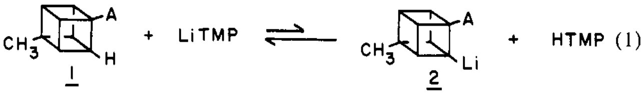
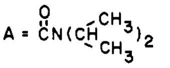
An amide group provides a small but useful activation for ortho-lithiation on the cubane nucleus. For example, reaction of the *N*,*N*-diisopropylcubanecarboxamide **1** with 8 equiv of lithium tetramethylpiperidide (LiTMP) under equilibrating conditions in THF at 0 °C gives about 3% of the lithium derivative **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)

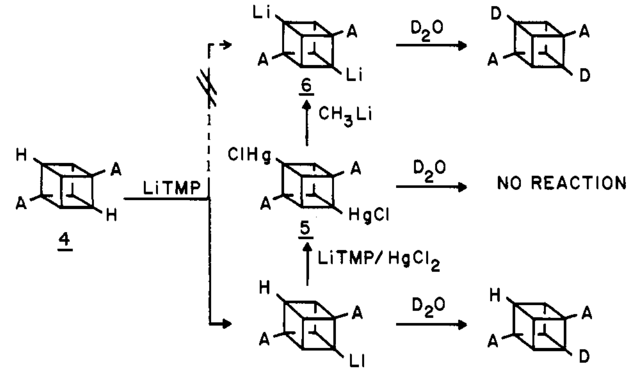
(2)



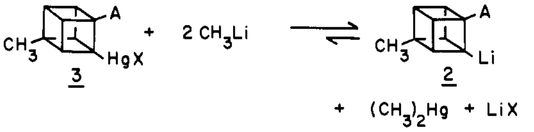
$A = \overset{O}{\overset{\|}{C}}N(CH(CH_3)_2)_2$

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.

[3] (a) Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883. (b) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1962**, *84*, 361.

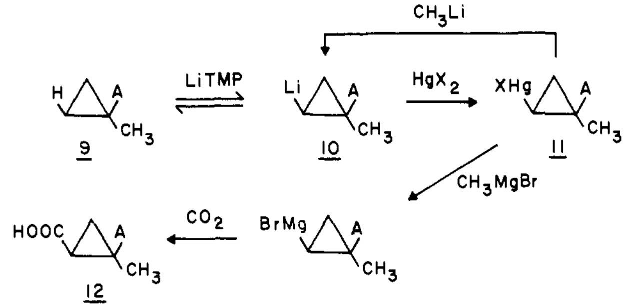
[4] For some further examples and other leading references, see: (a) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. (b) Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**,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

[5] (a) Gilman, H.; Yale, H. L. *J. Am. Chem. Soc.* **1950**, *72*, 8. (b) Curtin, D. Y.; Koehl, W. J. *J. Am. Chem. Soc.* **1962**, *84*, 1967. (c) Burdon, J.; Coe, P. L.; Fulton, M.; Tatlow, J. C. *J. Chem. Soc.* **1964**, 2763. (d) Cohen, S. C.; Massey, A. G. *J. Organomet. Chem.* **1968**, *12*, 341. (e) Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1982**, *104*, 6848.

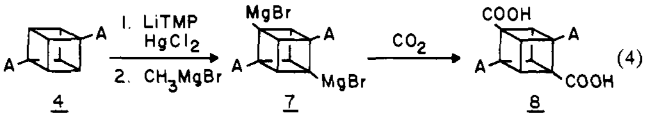
[6] (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157. (b) Stock, L. M.; Luh, T.-Y. *J. Am. Chem. Soc.* **1974**, *96*, 3712. (c) So, S. P.; Wong, M. H.; Luh, T.-Y. *J. Org. Chem.* **1985**, *50*, 2632.

[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.

Scheme II



of **5** with CH$_3$Li in THF at -78 °C gives **6** cleanly, as demonstrated by high-yield formation of dideuteriated **4** on quenching the reaction mixture with CH$_3$OD. Following a similar path (eq 4), and particularly usefully, conversion of **4** to **5** (not isolated), its reaction with CH$_3$MgBr in THF at -20 °C to form the di-Grignard **7**, and subsequent carboxylation gives the cubane tetraacid derivative **8** in 60% yield *overall.*



Use of the reverse-transmetalation procedure is not limited to the cubane system. It should in principle pertain to other systems of relatively high C–H acidity. We have not yet pursued this extensively, but we can give two examples now, one using cyclopropane C–H and the other, aromatic C–H. On treatment with LiTMP/HgCl$_2$ the cyclopropyl amide **9** is converted, by way of ortho-lithiated amide **10**, to the ortho-mercuriated derivative **11**,[8] isolable pure as its chloride in 85% yield (Scheme II). Upon reverse transmetalation with a stoichiometric amount (2 equiv) of CH$_3$Li, conversion to **10** is essentially quantitative, as shown by high-yield formation of monodeuteriated **9** on quenching with CH$_3$OD. In this particular case, the amide group is susceptible to attack by excess CH$_3$Li, and it is better to use CH$_3$MgBr instead. This modification of reverse-transmetalation methodology gives the corresponding cyclopropyl Grignard, which upon carboxylation yields the *cis*-1,2-dicarboxycyclopropane **12** in 90% isolated yield from **11**.

2,6-Dilithio-*N,N*-diethylbenzamide is also readily available by the double transmetalation approach.[9] Treatment of *N,N*-diethylbenzamide with LiTMP/HgCl$_2$ gives in 60% isolated yield the *o,o′*-dimercuriated compound by iterative lithiation/mercuriation. Reverse transmetalation with *n*-BuLi followed by addition of CH$_3$OD produces the *o,o′*-dideuteriated benzamide. If CH$_3$I is added, 2,6-dimethyl-*N,N*-diethylbenzamide is formed in good yield.

We are extending this work to include the preparation of yet more highly metalated cubanes, to the use of these compounds in synthesis, and to application of these techniques to other saturated, strained systems.

Acknowledgment. This work was supported by the Office of Naval Research, the Army Research Office, and the Army Research and Development Command. Funds for major instruments were provided by the NSF and NIH (CA 14599), the latter by way of the University of Chicago Cancer Center. We are grateful to Dr. Michele Maggini for his help working out detailed experimental procedures.

Supplementary Material Available: Experimental details for dimercuriation and dicarboxylation of cubane diamide and the associated characterizations (2 pages). Ordering information is given on any current masthead page.

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(8) Eaton, P. E.; Casucci, M.; Cunkle, G. T., submitted for publication in *J. Org. Chem.*

(9) Cf.: Mills, R. J., Horvath, R. F., Sibi, M. P., Sniekus, V. *Tetrahedron Lett.* **1985**, *26*, 1145.

Local Electron Distribution of Individual Molecular Orbitals Studied by Penning Ionization Electron Spectroscopy: Iron Phthalocyanine

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Recently we have shown that Penning ionization electron spectroscopy, which utilizes metastable rare gas atoms as the excitation source, is a unique technique to provide direct information on the outer spatial electron distribution of individual molecular orbitals.[1] In this paper, we demonstrate that the local distribution of π, σ, and $3d_{\perp}$-like MO's of iron phthalocyanine (FePc) at different parts of the molecule can be probed by applying this technique to a monolayer film and a crystalline one.

When Penning spectroscopy is applied to a gas-phase sample, in which molecules are randomly oriented, it is its "averaged" orbital distribution that is reflected in the Penning ionization electron spectrum (PIES). If we wish to probe the "local" distribution of an MO at a definite part of a molecule, we should control the orientation of target molecules with respect to the metastable beam. Experimentally, this can be effectuated by introducing the beam onto ordered molecules in solid phase. Unlike photons or electrons used for photoelectron, Auger electron, or electron impact spectroscopy, metastables do not penetrate into the solid and hence interact with the outermost surface layer selectively.[2,3] If we expose various parts of molecules to metastables, controlling their arrangement on a substrate, we can probe the distribution of MO's from various directions. Thus, the whole picture or the "shape" of each MO can be obtained. As the first approach from this standpoint, the local distribution of MO's of FePc is investigated here by PIES.

We prepared two kinds of vapor-deposited FePc films. Film I was prepared on a graphite substrate (cleavage plane) held at 213 K and was a monolayer, in which molecules lie flat on the substrate.[3] Film II was formed on a stainless steel substrate at room temperature and was crystalline with tilted molecular orientation.[4] Since FePc molecules are held together by weak van der Waals forces, the electronic structure of molecules in each film is essentially unchanged from that in gas phase. When surface molecules lie flat on the substrate (see the bottom of Figure 1a), π-type MO's spreading normal to the molecular plane (xy plane) exclusively interact with metastables, whereas σ MO's distributed within the plane and shielded by π-type MO's are hardly attacked by metastables. Among π-type MO's, those mainly originated from the iron $3d_{xz}$, $3d_{yz}$, or $3d_{z^2}$ AO (the $3d_{\perp}$-like MO) should interact with metastables more effectively than those derived from the carbon and nitrogen $2p_z$ AO's because the former orbitals protrude outside the molecular (van der Waals) surface more prominently than the latter ones. On the other hand, in the tilted molecular orientation (see the top of Figure 1a), the σ MO's as well as the π are effectively attacked by metastables, but the $3d_{\perp}$-like MO's with little distribution outside the film surface can be scarcely attacked.

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