The bonding arrangement in the O–H–O system is strongly reminiscent of the proton-to-heteroatom attachment in the bifluoride ($F–H–F^-$)[5] and bihydroxide ($H–O–H–O–H^-$)[6] ions, suggesting the designation, "binitrosamine", for ions of the sort described here. The O···O separation of 2.47 (1) Å for the binitrosamine ion is similar to those for other very strong, symmetrical or nearly symmetrical O–H–O bonds (typically 2.4–2.5 Å) and considerably shorter than the 2.6–2.9 Å O···O distances seen for most asymmetric H-bonds.[2,7,8] Additionally, while the graph of O–H distance versus O···O separation for the vast majority of previously studied hydrogen bonds is a monotonically decreasing curve, the plot for those that are very strong and symmetrical is a short line of opposite slope;[8] the measurements for the binitrosamine cation (Figure 1) place it squarely on the latter straight line, indicating that the nitrosamino group belongs with the carboxylates, oximes, *N*-oxides, and a few other (mostly inorganic) species in a select set of functional groups capable of serving as oxygen donors in such very strong hydrogen bonds.[2,7,8]

Isolation of a stable species in which attachment of a proton to such a weak base is strong enough to bind not just one but two nitrosamine molecules is the more remarkable because the mixture from which the 2:1 complex was initially crystallized contained equimolar amounts of *N*-nitrosopyrrolidine and HPF_6, leaving unused acid in the supernatant ether solution. It may also be significant that the isolated salt is much less hygroscopic than the 1:1 acid/nitrosamine adducts we have prepared,[1b] suggesting that water is no more able than ether or excess hexafluorophosphoric acid to dislodge either nitrosamine molecule from its position on the crystal lattice. Added evidence that the binitrosamine cation might exist as such in solution can be found in the chemical shift of the O–H proton, which in dichloromethane-d_2 appeared at 17.0 ppm. This value is at substantially lower field than those of the simple *N,N*-dialkyl-*N'*-hydroxydiazenium ions, whose O–H protons resonate at 13–16 ppm.[9] Such deshielding appears to be characteristic of strongly bonded, biscoordinate hydrogen.[10]

The *N*-nitrosopyrrolidine salt described above is not unique in its stoichiometry. Preliminary results show that hexafluorophosphoric acid also forms a 1:2 complex with *N*-nitrosothiomorpholine. Further study of this novel compound type may provide insight into the origins of the surprising stability that these binitrosamine cation complexes display.

Warning! The strong toxicity of the materials used in this investigation demands that they be handled, stored, and discarded with due respect for the possible hazards involved.[11]

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Supplementary Material Available: Tables of atomic coordinates and full listings of bond lengths and angles (2 pages); listing of observed and calculated structure factors (3 pages). Ordering information given on any current masthead page.

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Ligand Assisted Nucleophilic Additions. Control of Site and Face Attack of Nucleophiles on 4-Oxidoenones†

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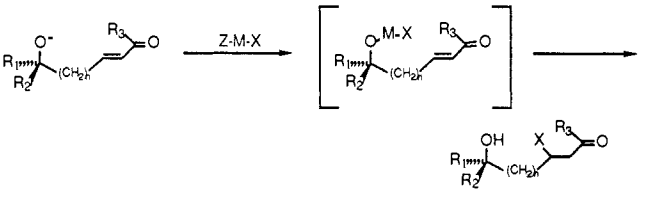
A properly positioned alkoxide–metal complex, possessing a transferable ligand, can exert a high degree of regio- and stereocontrol on the delivery of that ligand to a second reactive site. While the literature is replete with examples of this sort of directing effect where the complex is electrophilic and the second reactive site is electron-rich, little general information is available about the opposite situation, i.e., intramolecular reactions of nucleophilic complexes with electron-deficient functionalities (see generalized depiction in eq 1).[1-6] Herein, we report the results of a systematic study of the latter type of process.[7]



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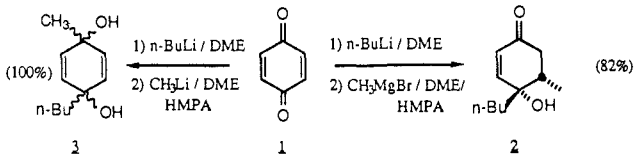
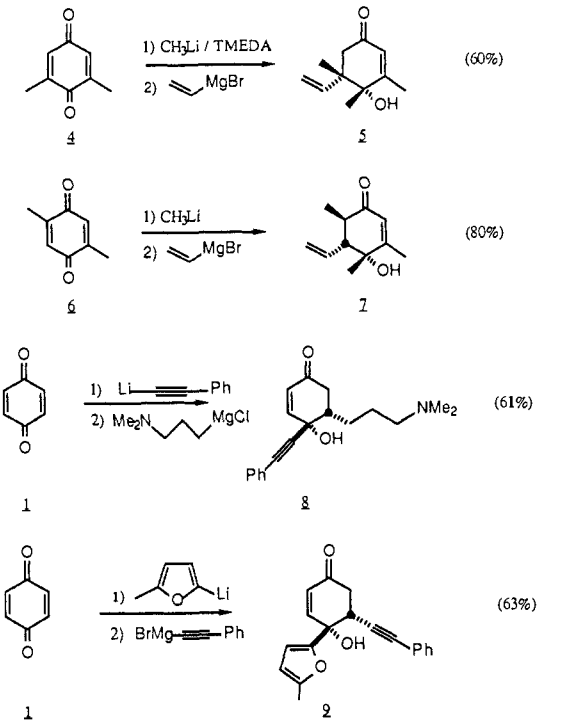
We have discovered that deprotonated *p*-quinols and 4-hydroxyenones undergo diastereofacially specific Michael additions with reagents which typically react intermolecularly in a 1,2-fashion.[8] These results imply a prior complexation of the reagent in question with the alkoxide ion, followed by delivery of the reagent to the β-position of the unsaturated carbonyl functionality. For example, benzoquinone reacts with *n*-butyllithium in 1,2-dimethoxyethane (DME), followed by methylmagnesium bromide/DME/hexamethylphosphoramide (HMPA) or 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) to produce **2** in 82% isolated yield. Interestingly, if methyllithium is used in place of methylmagnesium bromide in the second reaction, only **3** is isolated in quantitative yield.



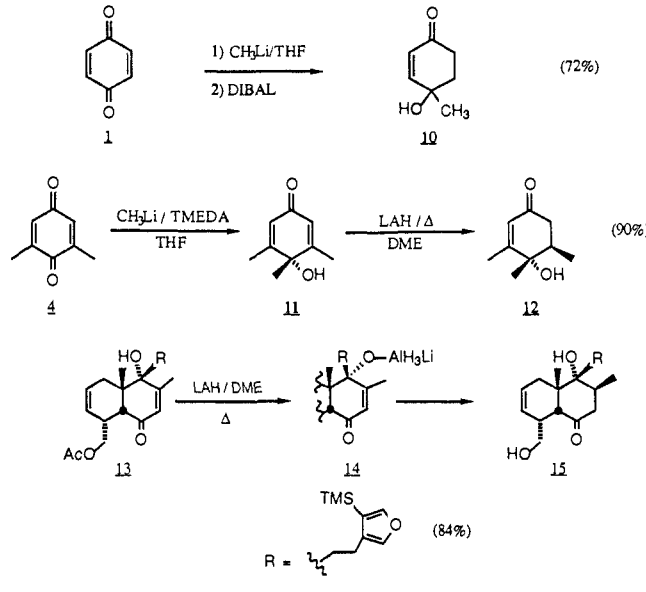
The success of these processes hinges on the rate of exchange of the Z–M–X species with the alkoxide occurring faster than the rate of intermolecular reaction of the reagent with the functional group.[9] We have found that these delivery processes proceed most readily in coordinating solvents, such as tetrahydrofuran (THF) or DME, and, in the case of Grignard reagents, require the addition of HMPA or DMPU. We surmise that these additives facilitate dissociation of the lithium alkoxide from an intimate ion pair to a solvent-separated ion pair and thereby enhance the rate of the metal-exchange process.

At present, we have examined several tandem 1,2/1,4-additions involving carbon nucleophiles, some of which are shown below. On the basis of these results, a number of important observations can be made. (1) In all of the reactions studied, we have never observed the presence of any diastereomeric conjugate addition byproducts. This fact strongly supports the delivery mechanism discussed above. (2) Since the conversions of **4** to **5**,[10] **4** to **12**, and **13** to **15** require extremely hindered alkoxide intermediates, steric factors do not cause significant complications. (3) The conversion of **6** to **7** demonstrates the high regioselectivity which can be expected from substrates which are unsymmetrical with respect to the conjugate addition process. (Note: none of the product derived from conjugate addition to the more-substituted β-carbon was observed.) (4) In the conversion of **1** to **8**, the presence of the chelating dimethylamino group does not adversely affect the outcome of the reaction.[11] (5) These tandem reactions need not be performed together, i.e., the quinol intermediate may be isolated and its lithium alkoxide regenerated by treatment with



lithium diisopropylamide (LDA). As a consequence, this permits the development of optimized reaction conditions for each separate process. Finally, use of these tandem 1,2/1,4-additions permits one to alter normal regioselectivities. For example, although acetylide ions virtually never undergo Michael additions, **1** is converted to **9** in high yield.[12]

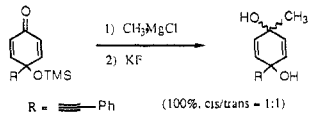
These conjugate addition processes are not restricted to the delivery of carbon nucleophiles. Three examples of this are shown below. In the first example the diisobutylaluminum hydride



(DIBAL) presumably coordinates with the lithium alkoxide intermediate to form an ate complex, which intramolecularly delivers hydride ion to the β-carbon. In the second and third examples (**4** to **12** and **13** to **15**), refluxing solutions of lithium aluminum hydride (LAH) apparently undergo rapid acid–base reactions with the hydroxyl hydrogen, generating mixed alkoxyaluminum hy-

(7) (a) As defined here, ligand assisted nucleophilic additions represent a subset of a more general area referred to recently by Beak and Meyers as Complex Induced Proximity Effects (CIPE). See: Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. (b) Stork[7c] and Evans[7d] have utilized homogeneous hydrogenation catalysts which function by initial coordination with an allylic hydroxyl group, followed by subsequent hydrogen delivery. (c) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072. (d) Evans, D. A.; Morrissey, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3866.

(8) These processes appear to require the presence of an alkoxide ion. As shown below, if the oxygen is protected, no directing effects are observed.



(9) Our current hypothesis attempts to explain our results in terms of monomeric reactants and intermediates. Expanded studies are aimed at sorting out the effects of aggregation and intermolecular versus intramolecular cluster reactions.

(10) We previously reported that regioselective additions of carbanions to unsymmetrical quinones can be achieved by judicious choice of the reaction conditions. See: Liotta, D.; Saindane, M.; Barnum, C. *J. Org. Chem.* **1981**, *46*, 3369.

(11) The stereochemistry of this material was unequivocally determined via X-ray crystallography. Experimental details and full X-ray data are included in the Supplementary Material.

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drides, which then transfer hydride ion intramolecularly. The conversion of **13** to **15** is particularly noteworthy since it involves the formal addition of hydride ion to the concave face of a highly hindered unsaturated ketone.

In summary, we have demonstrated that high degrees of regio- and stereocontrol can be achieved through the use of alkoxide assisted nucleophilic additions. Further mechanistic details about these processes, as well as the application of the ligand assisted nucleophilic additions to the synthesis of complex target molecules, will be the subject of future reports.

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Supplementary Material Available: Experimental details for the preparation of enone **8** including full spectroscopic and X-ray crystallographic data (5 pages). Ordering information is given on any current masthead page.

Insertion of $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$ into the C–H Bonds of Functionalized Organic Molecules: A C–H Activation Route to 2-Oxa- and 2-Azametallacyclobutanes, Potential Models for Olefin Oxidation Intermediates

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Several important transition-metal-based systems are known that are capable of oxidizing alkenes to epoxides and aldehydes.[1] One of the most important is cytochrome P-450; smaller systems involving porphyrins and other chelating ligands have been used as models for these biological oxidations.[2] Several mechanisms have been postulated for such transformations,[3] but one of the most intriguing and often invoked[4] involves four-membered 2-oxametallacyclobutanes as crucial intermediates. In spite of this, and the fact that the oxametallacyclobutane postulate is controversial,[5] only a small number of such metallacycles (or their nitrogen analogues) have been prepared and characterized.[6] We report here a novel route to 2-oxa- and 2-azametallacyclobutanes[7] that has developed from our C–H activation research. This has yielded the first simply substituted members of this class of complexes and has given us an opportunity to begin an investigation of their chemistry.

In studies aimed at determining the relative rate of insertion of the C–H activating species[8] $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$ into C–H versus other types of X–H bonds, we carried out the photolysis of $Cp^*(PMe_3)IrH_2$ (complex **1** illustrated in Scheme I) in *tert*-butylamine. This gives typically 90% conversion (NMR) to the new alkyl hydride $Cp^*(PMe_3)Ir(CH_2CMe_2NH_2)H$ (**2a**). No trace of the amido hydride $Cp^*(PMe_3)Ir(NH\text{-}t\text{-}Bu)H$, which would result from insertion into the N–H bond, was observed. Compound **2a** was too sensitive to isolate in pure form, but it was characterized fully by spectroscopic techniques. In addition to the expected ^1H and ^{13}C signals, it has a characteristic Ir–H resonance at δ −17.81 ppm in the ^1H NMR spectrum. Similarly, irradiation of **1** in *tert*-butyl alcohol gives 95% conversion to the alkyl hydride $Cp^*(PMe_3)Ir(CH_2CMe_2OH)H$ (**2b**, $\delta_{Ir-H} = -17.76$). Once again, only C–H insertion occurs; no formation of the O–H insertion product $Cp^*(PMe_3)Ir(O\text{-}t\text{-}Bu)H$ was detected.

It is possible that the alkoxy hydride $Cp^*(PMe_3)Ir(O\text{-}t\text{-}Bu)H$ and the amido hydride $Cp^*(PMe_3)Ir(NH\text{-}t\text{-}Bu)H$ are being produced, but their formation from $Cp^*(PMe_3)Ir$ is reversible (either thermally or photochemically), and the alkyl hydrides **2a** and **2b** are the thermodynamic rather than the kinetic products of these reactions. Unfortunately, we have not yet been able to prepare these O–H and N–H insertion products independently so that we might test their stability to the reaction conditions. If these species are not being formed, however, we are led to the somewhat surprising conclusion[9] that insertion of $Cp^*(PMe_3)Ir$ into C–H bonds is completely favored over insertion into either O–H or N–H bonds.

Realizing that complexes **2a** and **2b** contain the structural elements needed to form 2-oxa- and 2-azametallacyclobutanes, we sought a method for effecting dehydrogenative ring closure. This was achieved by a chlorination/nucleophilic cyclization sequence. Treatment of the nitrogen compound **2a** with 1 equiv of chloroform in benzene for several days led to the formation of the air-stable cyclic salt **4** in 80% yield. Presumably this reaction takes place via uncyclized precursor **3a**, which rapidly undergoes ring closure under the reaction conditions. Compound **4** is extremely hygroscopic. Crystals of **4** suitable for an X-ray diffraction study were obtained as the dihydrate by crystallization from toluene/hexamethyldisiloxane, and analysis of the data confirmed the proposed structure.[10] An ORTEP diagram of the

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