

Multiple Coordination and Activation of Lewis Bases by Multidentate Lewis Acids

JAMES D. WUEST

*Département de Chimie, Université de Montréal,
Montréal, Québec, H3C 3J7 Canada*

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Introduction

Mercury is the hottest, the coldest, a true healer, a wicked murderer, a precious medicine, and a deadly poison, a friend that can flatter and lie.

J. Woodall

*The Surgeon's Mate or
Military & Domestic Surgery (1639)*

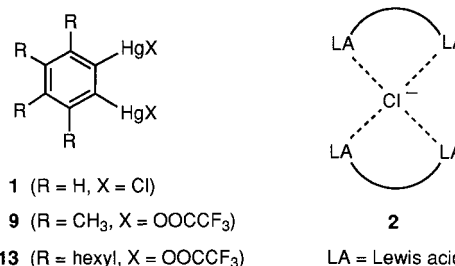
The coordination chemistry of compounds that have multiple sites of Lewis basicity has been studied intensively, and multidentate reagents of this type are familiar and widely used.¹ In contrast, the coordination chemistry of analogues that have multiple sites of Lewis acidity is still largely unexplored, even though multidentate Lewis acids promise to be useful for many purposes. Multidentate Lewis acids remain esoteric not because they lack potential utility, but rather because they are typically more reactive and difficult to make than their multidentate Lewis basic counterparts.

The first systematic studies of the synthesis and coordination chemistry of multidentate Lewis acids were published more than 30 years ago by Shriver and Biallas.² Their pioneering work, which explored the coordination chemistry of 1,2-ethanediylbis[difluoroborane] and related bidentate Lewis acids, provided important preliminary information about the ability of two adjacent sites of Lewis acidity to interact simultaneously with basic sites in other molecules. Surprisingly, their results did not immediately prompt other chemists to study multidentate Lewis acids, and only recently have we and others begun to give the subject the further attention it deserves.^{3–13}

In our studies of multidentate Lewis acids, we have made extensive use of derivatives of 1,2-phenylenedimercury such as dichloride **1**, which holds two nearby Lewis acidic atoms of mercury in a well-defined orientation. Although these organomercury compounds are typically weak Lewis acids,¹⁴ they offer compensating advantages

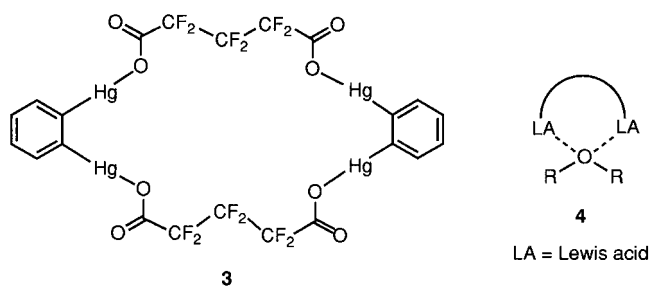
that have proved to make them uniquely suitable for exploring the coordination chemistry of multidentate Lewis acids. In particular, (1) effective and convenient methods exist for their synthesis, (2) they are easy to manipulate because they are not highly sensitive to H₂O or O₂, and (3) their two sites of Lewis acidity are oriented in a way that favors simultaneous binding to basic sites in a variety of guests. Our intent has been to use derivatives of 1,2-phenylenedimercury to acquire a fundamental understanding of the coordination chemistry of multidentate Lewis acids, and then to develop more reactive analogues designed to be of greater practical value.

In our initial work, we found that 1,2-phenylenedimercury dichloride (**1**) forms adducts with halides in solution and in the solid state.³ An X-ray crystallographic study established that the reaction of dichloride **1** with tetraphenylphosphonium chloride produces an anionic 2:1 chloride adduct that can be represented by structure **2**, in



which chloride is simultaneously bound by four Lewis acidic atoms of mercury provided by two molecules of bidentate host **1**. Simple organomercury compounds do not normally form stable anionic adducts, so this observation shows that multidentate binding can exert special thermodynamic and kinetic effects with important chemical consequences, including the stabilization of unusual structures.

Multidentate Lewis acids derived from 1,2-phenylenedimercury can also form novel adducts with neutral organic bases. For example, macrocyclic perfluoroglutarate **3** yields a crystalline 1:2 complex with tetrahydrofuran (THF) in which the basic oxygen atom of each molecule of THF is doubly coordinated in the manner represented by structure **4**.⁴ In this adduct, both lone pairs



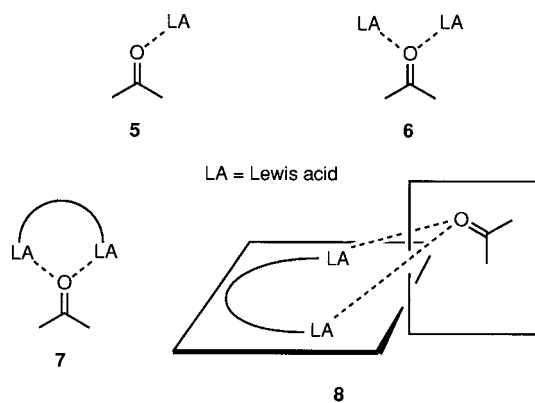
Jim D. Wuest received his A.B. in 1969 from Cornell University and his Ph.D. in 1973 from Harvard University, where he was a student of R. B. Woodward. After serving as an assistant professor of chemistry at Harvard, he moved to the Université de Montréal in 1981. He is broadly interested in synthesis, structure, and reactivity in organic, organometallic, and inorganic chemistry. One of his principal goals in research is to learn how chemists can put noncovalent interactions to more effective use.

of the ether oxygen atom interact simultaneously with the two Lewis acidic atoms of mercury in each 1,2-phenylenedimercury unit incorporated in perfluoroglutarate **3**.

Monodentate analogues do not normally form stable adducts with ethers, so multidentate binding again has chemically significant effects.

Structural Studies of the Intermolecular Multiple Coordination of Carbonyl Compounds by Multidentate Lewis Acids

The unusual behavior of derivatives of 1,2-phenylenedimercury encouraged us to explore the coordination chemistry of multidentate Lewis acids in greater depth. Simple monodentate Lewis acids are broadly useful in chemistry because they can bind complementary Lewis bases and thereby modify their reactivity. An example of great practical importance is the activation of carbonyl compounds by the formation of complexes **5**.¹⁵ By reducing the electron density on the carbonyl carbon, further polarizing the carbon–oxygen double bond, and lowering the energy of the lowest unoccupied molecular orbital, the complexation of carbonyl compounds by simple monodentate Lewis acids can have dramatic kinetic effects. For example, the Diels–Alder reaction of methyl acrylate with butadiene at 20 °C in benzene is 10⁵ times faster in the presence of an equimolar amount of AlCl₃.^{16,17} Furthermore, Lewis acids can also have beneficial effects on regioselectivity and stereoselectivity. For all of these reasons, Lewis acids play a major role as catalysts and stoichiometric reagents in contemporary organic synthesis.



The precise geometries of adducts **5** vary, depending on the Lewis acid and the substrate. In general, neutral main-group Lewis acids favor η^1 (σ) complexes in which the Lewis acid lies close to the carbonyl plane along the direction of one of the formal sp^2 lone pairs on oxygen.^{15,18} In principle, this leaves the other sp^2 lone pair free and available for binding a second Lewis acid, which would produce doubly coordinated termolecular complexes **6**. Such adducts are potentially valuable in synthesis because they promise to be even more highly activated than their singly coordinated analogues **5**.

Unfortunately, doubly coordinated termolecular adducts **6** are presently unknown.^{19,20} However, we reasoned that closely related doubly coordinated bimolecular complexes **7** might be formed if the two sites of Lewis acidity were connected to create a single bidentate reagent. In

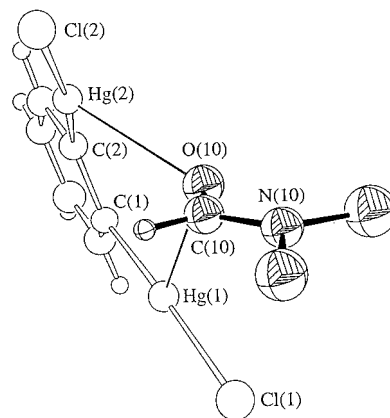


FIGURE 1. ORTEP drawing of the structure of the 1:1 complex of 1,2-phenylenedimercury dichloride (**1**) with dimethylformamide (DMF) viewed along the carbonyl C(10)–O(10) axis from slightly above the carbonyl plane. All atoms of dichloride **1** and the formyl hydrogen atom appear as spheres of arbitrary size. Other non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability, and other hydrogen atoms are omitted for simplicity. Dative interactions with mercury are indicated by narrow lines, and bonds in DMF are drawn using solid lines. Important interatomic distances (Å) and angles (deg) include Hg(1)···O(10) = 2.78(1), Hg(2)···O(10) = 2.68(1), C(10)–O(10)···Hg(1) = 116(1), C(10)–O(10)···Hg(2) = 120(1), N(10)–C(10)–O(10)···Hg(1) = 109(2), and N(10)–C(10)–O(10)···Hg(2) = –152(2).

fact, crystallization of 1,2-phenylenedimercury dichloride (**1**) from *N,N*-dimethylformamide (DMF) yields a 1:1 adduct of this general type (Figure 1), which is the first unambiguous example of a carbonyl compound doubly coordinated by two sites of Lewis acidity.²¹ In this adduct, both carbonyl O···Hg distances are significantly shorter than the sum of the van der Waals radii of oxygen (1.40 Å)²² and mercury (1.73 Å).²³ The two sites of Lewis acidity do not both lie in the carbonyl plane, but instead occupy widely varying positions with respect to the plane, as represented by noncoplanar structure **8**. This observation and related data suggest that carbonyl oxygen atoms do not have strong steric or electronic preferences for bonding to organomercury compounds along specific directions, presumably because dative bonds between oxygen and mercury are characteristically long, weak, and deformable.^{4–8} In this way, dative O···Hg interactions can be considered to resemble hydrogen bonds.²⁴

For the following reasons, the special structural features of doubly coordinated bimolecular adducts **7** and **8** promise to make them even more useful in synthesis than their doubly coordinated termolecular analogues **6**. Rotation around the dative oxygen–Lewis acid bond in singly coordinated adducts **5** normally gives complex mixtures of activated conformers. As a result, chiral nonracemic monodentate Lewis acids often fail to promote reactions with high degrees of enantioselectivity. Doubly coordinated termolecular analogues **6** should behave similarly. In contrast, doubly coordinated adducts **7** and **8** derived from chiral nonracemic bidentate Lewis acids are intrinsically better designed for use in asymmetric synthesis because double coordination imposes additional conformational constraints.

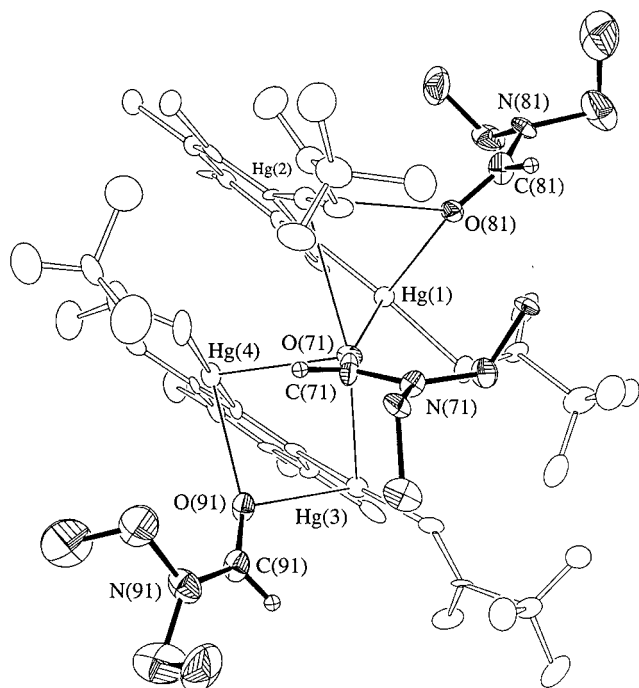


FIGURE 2. ORTEP view of the structure of the 2:3 complex of 3,4,5,6-tetramethyl-1,2-phenylenedimercury bis(trifluoroacetate) (**9**) with diethylformamide (DEF). Non-hydrogen atoms are represented by ellipsoids corresponding to 30% probability, formyl hydrogen atoms appear as spheres of arbitrary size, and other hydrogen atoms are omitted for simplicity. Dative interactions with mercury are indicated by narrow lines, and bonds in DEF are drawn using solid lines.

Formation of the doubly coordinated 1:1 adduct of 1,2-phenylenedimercury dichloride (**1**) with DMF can be considered to involve the creation of a three-center, two-electron bond that results from the interaction of two empty orbitals contributed by mercury with one of the two lone pairs of the carbonyl oxygen atom. In principle, the second lone pair remains free and available for further complexation, which would produce unprecedented adducts in which the carbonyl oxygen atom is surrounded by more than two sites of Lewis acidity. We have found that such adducts are formed when 3,4,5,6-tetramethyl-1,2-phenylenedimercury bis(trifluoroacetate) (**9**) is crystallized from DMF or *N,N*-diethylformamide (DEF).⁶ In both cases, analogous 2:3 adducts are obtained, and the structure of the DEF adduct is shown in Figures 2 and 3. Two of the three bound amides are doubly coordinated in the manner of structure **8**. However, the carbonyl oxygen atom of the third amide is simultaneously bound by four sites of Lewis acidity provided by two molecules of bidentate host **9**, thereby creating the remarkable quadruply coordinated termolecular structure **10**.

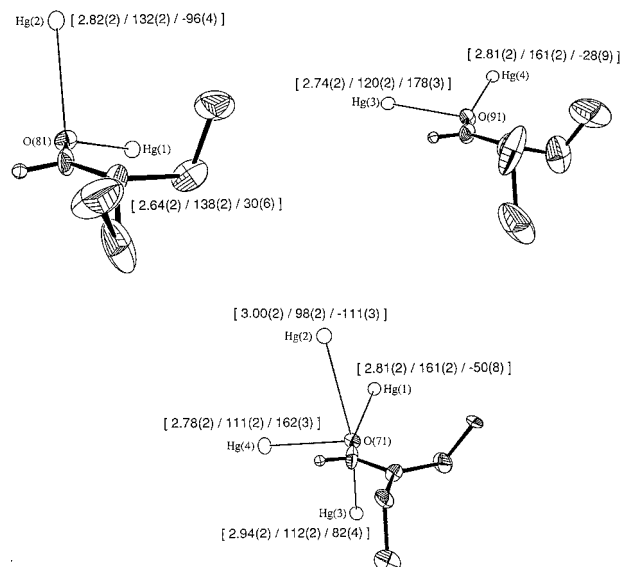
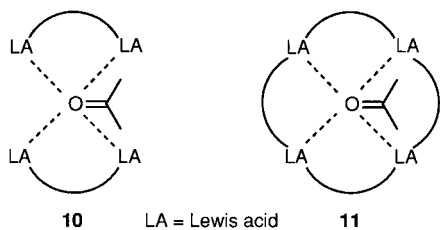
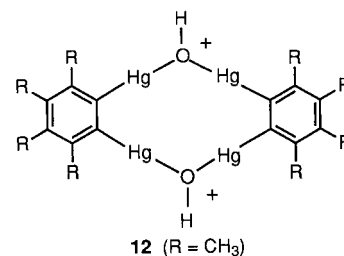


FIGURE 3. ORTEP views of the structure of the 2:3 complex of 3,4,5,6-tetramethyl-1,2-phenylenedimercury bis(trifluoroacetate) (**9**) with diethylformamide showing only the three bound amides and the associated atoms of mercury when viewed along the carbonyl C=O axes from slightly above the carbonyl planes. The three geometric parameters that appear next to each atom of mercury correspond to the carbonyl O...Hg distance (Å)/C=O...Hg angle (deg)/N-C=O...Hg dihedral angle (deg).

Again, the Lewis acidic atoms of mercury occupy widely varying positions with respect to the carbonyl planes. The existence of the quadruply coordinated adduct **10** provides a dramatic illustration of the ability of carbonyl oxygen atoms to coordinate simultaneously to multiple sites of Lewis acidity when they are linked appropriately in multidentate reagents. Furthermore, a striking analogy exists between quadruply coordinated adduct **10** and the structure of crystalline urea, in which each carbonyl oxygen atom accepts four hydrogen bonds.²⁵

An even more impressive quadruple coordination of carbonyl compounds, represented by bimolecular structure **11**, results when two 1,2-phenylenedimercury units are connected to create a single cyclic tetradentate Lewis acid. For example, crystallization of the bis(trifluoromethanesulfonate) salt of cyclic μ -hydroxide **12** from



DEF yields a 1:2 adduct of this type,⁷ and its structure is shown in detail in Figure 4. The carbonyl C(11)-O(11) bond length in each quadruply bound amide (1.24(1) Å) is somewhat longer than the generally accepted value for free tertiary formamides (1.22 Å), and the N-C(O) bond length (1.31(2) Å) is slightly shorter than the normal value (1.35 Å).²⁶ The observed changes in bond lengths are

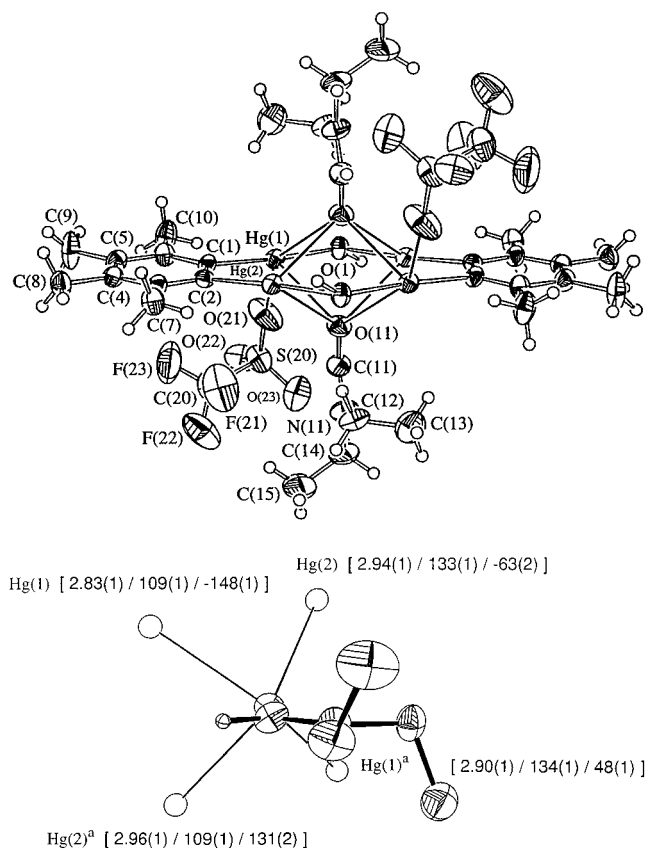


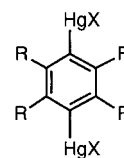
FIGURE 4. ORTEP views of the structure of the 1:2 complex of the bis(trifluoromethanesulfonate) salt of cyclic μ -hydroxide **12** with diethylformamide. The upper view provides the atomic numbering scheme. Non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability, hydrogen atoms are shown as spheres of arbitrary size, and dative and ionic interactions with mercury are indicated by narrow lines. The lower drawing shows one of the equivalent bound amides and the four associated atoms of mercury when viewed along the carbonyl C=O axis from slightly above the carbonyl plane. In this view, the formyl hydrogen atom appears as a sphere of arbitrary size, and the other hydrogen atoms are omitted for simplicity. The three geometric parameters that appear next to each atom of mercury correspond to the carbonyl O(11)···Hg distance (Å)/C(11)–O(11)···Hg angle (deg)/N(11)–C(11)–O(11)···Hg dihedral angle (deg).

consistent with weakening of the carbon–oxygen double bond, but they are not large enough to be considered crystallographically significant. However, the unusual quadruple coordination causes an important shift in the carbonyl stretching frequency, which moves from 1689 cm^{-1} (Nujol) in free DEF to 1648 cm^{-1} (Nujol) in the adduct. This marked shift suggests that multiple coordination may weaken the carbon–oxygen double bond and enhance its reactivity.

Thermodynamic Effects of the Double Coordination of Carbonyl Compounds by Bidentate Lewis Acids

Our initial studies of the coordination chemistry of multidentate Lewis acids derived from 1,2-phenylenedimercury are noteworthy because they established for the first time that the multiple coordination of carbonyl com-

pounds and other basic substrates is possible and may cause useful chemical activation. However, our studies focused on association in the solid state and left unanswered many fundamental questions about multiple coordination in solution. In particular, our work provided no detailed thermodynamic comparison of single and double coordination, and in no chemically well-defined case had the double coordination of carbonyl compounds been shown to accelerate subsequent chemical transformations.^{27,29} We have recently acquired this important information by comparing the thermodynamic and kinetic effects of the coordination of amides by 3,4,5,6-tetrahexyl-1,2-phenylenedimercury bis(trifluoroacetate) (**13**) and its 1,4-isomer **14**,³⁰ two bidentate Lewis acids designed to be



14 (R = hexyl, X = OOCF₃)

significantly more soluble than previously known derivatives of phenylenedimercury. The Lewis acidic sites in both compounds are sterically and electronically similar, so any differences in their interactions with carbonyl compounds must result largely from the fact that 1,2-isomer **13** can form doubly coordinated adducts, whereas 1,4-isomer **14** can only form singly coordinated adducts. We chose amides as the carbonyl substrates in these studies primarily because they are among the most basic carbonyl compounds,³¹ allowing them to associate with Lewis acids that are intrinsically weak.

The association of bidentate Lewis acid **13** and its 1,4-isomer **14** with amides was most conveniently studied by IR spectroscopy, using solutions in CH_2Cl_2 containing DEF. The carbonyl regions of typical spectra showed peaks at 1668 cm^{-1} for free DEF, at 1633 cm^{-1} for DEF bound by 1,2-isomer **13**, and at 1647 cm^{-1} for DEF bound by 1,4-isomer **14**. The distinctly different stretching frequencies observed for bound DEF immediately suggested that 1,2-isomer **13** forms a doubly coordinated complex in solution, as related compounds do in the solid state, whereas 1,4-isomer **14** forms a singly coordinated complex. Double coordination causes a significantly larger shift relative to free DEF (35 cm^{-1}) than single coordination does (21 cm^{-1}), suggesting that double coordination is stronger than single coordination and that it weakens the carbon–oxygen double bond more substantially. Related studies confirmed that more highly substituted amides such as *N,N*-dimethylpivalamide are bound similarly, whereas ketones and other less basic carbonyl compounds are bound more weakly or not at all.

Quantitative analysis of variable-temperature IR spectra yielded association constants for the binding of DEF by bidentate Lewis acids **13** and **14**, and van't Hoff plots revealed that for the double coordination of DEF by 1,2-isomer **13**, $\Delta H^\circ = -4.5 \pm 0.2 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -6.9 \pm 1.0 \text{ eu}$, whereas for the single coordination of DEF by

1,4-isomer **14**, $\Delta H^\circ = -3.4 \pm 0.2$ kcal mol⁻¹ and $\Delta S^\circ = -8.1 \pm 1.0$ eu. As expected, both values of $|\Delta H^\circ|$ are very small, and they confirm quantitatively that the association of carbonyl compounds with Lewis acidic organomercury compounds is inherently weak. The strength of the interactions is similar to that of typical hydrogen bonds. Nevertheless, our measurements are noteworthy because they have provided the first quantitative demonstration that double coordination is significantly more exothermic than single coordination. Specifically, our results suggest that conversion of a singly coordinated complex into a doubly coordinated complex is exothermic by 1.1 ± 0.2 kcal mol⁻¹ in this particular system, or approximately 32% as exothermic as initial formation of the singly coordinated adduct itself. This provides strong experimental confirmation of earlier ab initio calculations of ΔH° for formation of the singly and doubly coordinated 1:1 and 1:2 σ complexes of formaldehyde with BH₃ in the gas phase, which suggested that ΔH° for addition of the second equivalent of BH₃ (-2.3 kcal mol⁻¹) is 32% of the value of ΔH° for addition of the first (-7.3 kcal mol⁻¹).³² It is remarkable that a similar thermodynamic relationship between single and double coordination governs two widely different carbonyl substrates and two dissimilar Lewis acids that form complexes likely to have distinctly different geometries. Although the strikingly close agreement may be partly fortuitous, we believe that it supports the following generalization: The double coordination of carbonyl compounds by two sites of Lewis acidity is enthalpically feasible, and ΔH° for coordination of the second site is a significant fraction of ΔH° for coordination of the first. Furthermore, the close convergence of theoretical and experimental results in two different systems suggests that our thermodynamic and kinetic studies of the effects of double coordination are likely to have general significance, even though they are based on the behavior of special organomercury compounds with unique structures and weak Lewis acidity.

As expected, the observed values of ΔS° for single and double coordination are both consistent with the formation of 1:1 complexes. The two values are not significantly different, even though it is likely that the doubly coordinated adduct is somewhat more highly ordered. In part, the similarity of the values is presumably due to the rigid orientation of the Lewis acidic atoms of mercury in 3,4,5,6-tetrahexyl-1,2-phenylenedimercury bis(trifluoroacetate) (**13**). In addition, dative bonds between oxygen and mercury are long, weak, and deformable,⁴⁻⁸ so the values of $|\Delta S^\circ|$ associated with their formation should be unusually small.

Kinetic Effects of the Single and Double Coordination of Carbonyl Compounds by Lewis Acids

Collectively, our studies suggest that the double coordination of amides by bidentate Lewis acids derived from 1,2-phenylenedimercury is a general phenomenon and that it weakens the carbon–oxygen double bond more than

single coordination does. If so, double coordination should have unique effects on the reactivity of bound amides. Because bidentate Lewis acids derived from 1,2-phenylenedimercury are weak, however, any special kinetic effects of double coordination will be small and hard to detect. We decided to compare the effects of bidentate Lewis acids **13** and its 1,4-isomer **14** on barriers for rotation around the N–C(O) bond in amides, using values of ΔG^\ddagger determined by variable-temperature ¹H NMR spectroscopy.

Coalescence of the methyl signals of *N,N*-dimethylpivalamide (DMP) occurred at $T_c = -1.5, -14, \text{ or } -16 \pm 1$ °C, respectively, in solutions containing an equimolar amount of 1,2-isomer **13**, an equimolar amount of 1,4-isomer **14**, or DMP alone (0.093 M in CDCl₃). The corresponding values of ΔG^\ddagger are 12.9, 12.3, and 12.2 \pm 0.1 kcal mol⁻¹. As expected, the differences are small; nevertheless, they are significant, and they have established for the first time that the double coordination of carbonyl compounds can have measurable effects on the rates of subsequent chemical transformations. In this particular case, the effects presumably arise because the association constant for double coordination is higher than that for single coordination, and because double coordination further weakens the carbon–oxygen double bond of amides, further strengthens the N–C(O) bond, and thereby inhibits rotation more effectively.³³

An Effective Strategy for Making Strong Multidentate Lewis Acids

The deceitful interpreters of nature assume mercury to be the common germ of all the metals, forgetting that nature varies its seeds according to the different things the seeds are meant to bring forth.

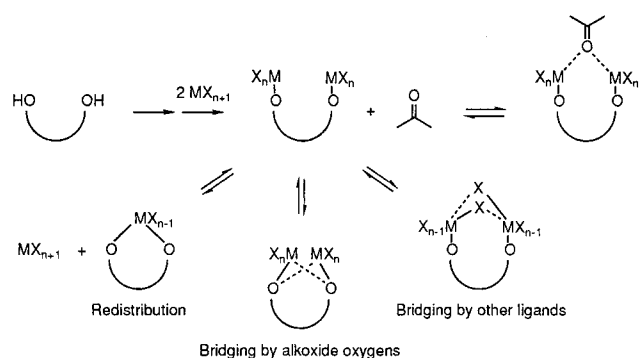
Leonardo da Vinci

Codex atlanticus

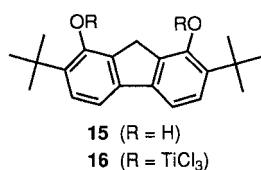
As we had hoped, derivatives of 1,2-phenylenedimercury served well in our initial exploratory studies of the coordination chemistry of multidentate Lewis acids. However, their Lewis acidity is intrinsically weak and soft, so they are not ideal for the multiple coordination and activation of carbonyl compounds and other basic guests of substantial practical importance in organic synthesis. In general, the multidentate Lewis acids studied so far by our group and others are conceptually important but unlikely to become useful reagents, and we expect them to remain exotic curiosities of the laboratory. To help bring multidentate Lewis acids further into the mainstream of chemistry, we have set two goals: (1) Develop an effective strategy for making strong multidentate Lewis acidic reagents that are more suitable for the multiple coordination and activation of common basic substrates. (2) Establish that these reagents are superior to conventional monodentate analogues in applications of genuine practical importance.

We have shown that a particularly convenient method for making strong multidentate Lewis acids is to convert

Scheme 1

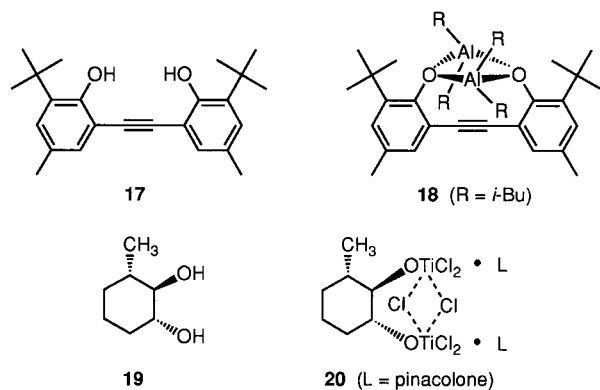


organic compounds with multiple hydroxyl groups or similar sites into the corresponding metal hydroxides or related derivatives.^{9–12} For example, treatment of diphenol **15** with 2 equiv of TiCl_4 yields bis(trichlorotitanium phenoxide) **16**,¹⁰ in which two strongly Lewis acidic atoms



of titanium are held in close proximity in a potentially convergent manner. This general strategy is attractive for the following reasons: (1) The syntheses are typically simple, and many require only a single step. (2) The sites of Lewis acidity are oriented by using heteroatoms, rather than carbon atoms, to attach them to a suitable framework, so the resulting reagents are intrinsically more Lewis acidic than their organometallic counterparts. (3) In principle, a wide variety of multidentate Lewis acids containing different elements can be prepared from a single precursor. (4) Suitable precursors are widely available, and many are chiral molecules that can easily be obtained in nonracemic form.

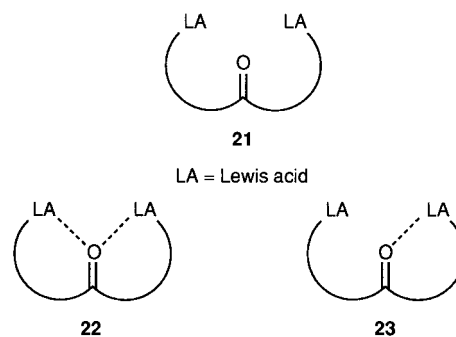
Although our strategy has numerous attractive features, using it to construct useful multidentate Lewis acids is not a trivial exercise. The hydroxyl groups in the precursor must be held close together so that the resulting sites of Lewis acidity can operate in conjunction to bind and activate basic substrates. At the same time, however, the sites cannot be so close together that they interact directly in an unproductive way. The importance of a judicious compromise is illustrated by Scheme 1, which shows the synthesis of a hypothetical bidentate Lewis acid suitable for the double coordination of carbonyl compounds, along with potential obstacles caused by (1) redistribution to give metal dialkoxides, (2) bridging by alkoxyde oxygens, and (3) bridging by other ligands. All of these vexing problems have been encountered. For example, diphenol **17** reacts with 2 equiv of $\text{Al}(i\text{-Bu})_3$ to give oxygen-bridged derivative **18**,¹¹ and the addition of 2 equiv of TiCl_4 to diol **19** in the presence of pinacolone yields the chloride-bridged adduct **20**.¹² We have begun to learn how to avoid these obstacles by selecting precursors with more suitably oriented hydroxyl groups. Although we have not yet been



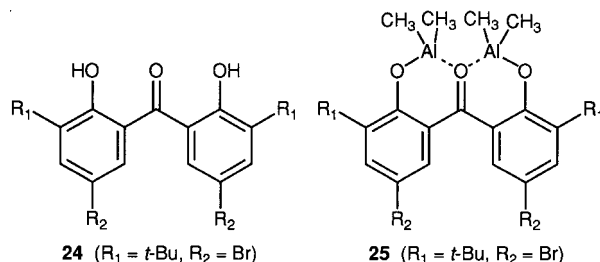
able to use our general strategy to make strong bidentate Lewis acids that doubly coordinate simple carbonyl compounds in the manner of Scheme 1, we are optimistic that this goal is feasible.

Intramolecular Double Coordination of a Ketone by Two Sites of Lewis Acidity

Our optimism is based in part on the behavior of specialized molecules **21** in which a carbonyl group is flanked by two intramolecular sites of Lewis acidity. If double coordination of the carbonyl oxygen atom is enthalpically feasible, then symmetric structure **22** should be favored; if not, then asymmetric singly coordinated structure **23**



will be preferred. The required molecules **21** can be synthesized conveniently by converting carbonyl compounds with flanking hydroxyl groups or similar sites into the corresponding metal alkoxides or related derivatives. For example, treatment of 2,2'-dihydroxybenzophenone **24** with 1 equiv of $\text{Al}_2(\text{CH}_3)_6$ yields the corresponding aluminum phenoxide **25**,⁹ in which both Lewis acidic



atoms of aluminum interact intramolecularly with the carbonyl oxygen atom. The structure of compound **25**, which is shown in Figure 5, incorporates several interest-

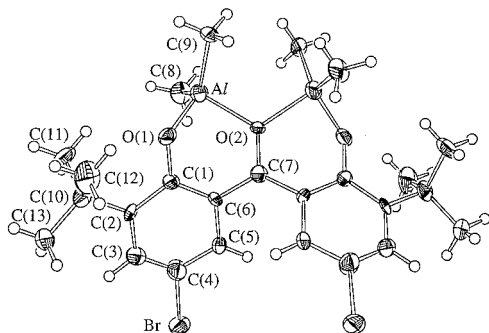
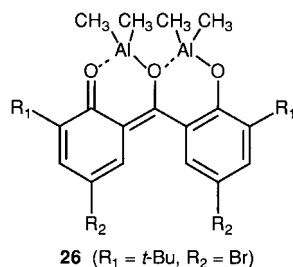


FIGURE 5. ORTEP drawing of the C_2 -symmetric structure of aluminum phenoxide **26**. Hydrogen atoms are shown as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 50% probability. Important interatomic distances (Å) and angles (deg) include O(2)–C(7) = 1.34(2), Al–O(2) = 1.96(1), Al–O(1) = 1.78(1), O(1)–C(1) = 1.32(2), C(1)–C(6) = 1.44(3), C(6)–C(7) = 1.44(2), O(1)–Al–O(2) = 92(1), O(1)–Al–C(8) = 112(1), O(1)–Al–C(9) = 110(1), C(8)–Al–C(9) = 124(1), and C(1)–O(1)–Al = 122(1).

ing features. In particular, the two dative O(2)···Al bonds are longer (1.96(1) Å) than the corresponding distance (1.91(1) Å) in the singly coordinated benzophenone complex of an analogous monodentate Lewis acid,³⁴ presumably because the carbonyl oxygen atom in doubly coordinated compound **25** is shared by two atoms of aluminum. In addition, the carbonyl C(7)–O(2) bond is markedly longer (1.34(2) Å) than those in singly coordinated analogues (1.24(1) Å)³⁴ or in uncoordinated benzophenones (1.22–1.23 Å). These striking geometric deformations can be attributed jointly to the effects of double coordination and to the contribution of resonance hybrid **26** to the structure of aluminum phenoxide **25**.



Preferred formation of symmetric structure **25** indicates that the double coordination of simple carbonyl compounds by two sites of strong Lewis acidity is enthalpically feasible and may have useful chemical consequences, including enhanced reactivity of the carbonyl group. As a result, further study of strong multidentate Lewis acids prepared by our general strategy is likely to be rewarding.

Conclusions

Our research has established that (1) the double coordination of carbonyl compounds by two sites of Lewis acidity is enthalpically feasible in the solid state and in solution, (2) ΔH° for coordination of the second site is a significant fraction of ΔH° for coordination of the first, and (3) double coordination can have important effects on the structure, spectroscopic properties, and reactivity of bound carbonyl compounds. Our results are based in part on the special

case of the complexation of amides by weak Lewis acids derived from phenylenedimercury; nevertheless, we are optimistic that our conclusions will prove to have general validity and that significant effects will be observed whenever basic molecules of any type are bound by suitable multidentate Lewis acids.

Multidentate Lewis acids remain poorly studied, but they can no longer be dismissed as esoteric reagents of mere academic interest. Recent studies have shown that bidentate Lewis acids can bind and activate organic substrates in genuinely useful ways,^{27,29} and our present results provide fundamental new information that should accelerate development of this promising field of research. Moreover, strongly encouraging analogies exist between the activation induced by bidentate Lewis acids and catalytic processes that are already known to play important roles in nature. In particular, double coordination of the oxygen atom of carbonyl groups is conceptually similar to double coordination of the oxygen atom of phosphoryl groups by two metal cations, which is believed to be a crucial step in various enzyme-catalyzed phosphoryl transfers.^{35,36} For these reasons, we expect multidentate Lewis acids to become increasingly useful to chemists as the special features of their coordination chemistry are revealed, and as simple ways to make them are devised.

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