The coordination chemistry of saturated molecules

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Our understanding of bonding in transition metal complexes, as well as our ability to use that understanding in the synthesis and application of new species, has evolved over the last 100 years; and in some sense this special feature on the coordination chemistry of saturated molecules may be considered to represent its culmination. The nature of complexes between transition metal ions and neutral molecules such as ammonia was first correctly described by Werner around the beginning of the 20th century. Interpretations in terms of electronic bonding theories followed soon after. The key feature, of course, is the availability of a low-energy filled "lone pair" orbital available for donation to a vacant orbital on the electron-accepting metal ion.

Next, it was found that molecules containing no lone pair but having a pair of electrons in a π-bond, as in olefins and acetylenes, could also form stable complexes. The first example, Zeise's salt $\{[PtCl_3(C_2H_4)]^-\}$, was actually synthesized more than a century earlier, in 1827, but explanations of structure and bonding in such species were only achieved around the middle of the 20th century. Because the filled orbital is bonding, and hence lower in energy than a lone pair, "back-bonding" (donation of electron density from filled metal d orbitals to vacant ligand π^* orbitals) plays a crucial role.

The logical next step in this progression would be the coordination of molecules having only σ-bonded electrons. Indeed, at about the same time, Halpern and others were accounting for the activation of H_2 at metal centers in terms of interactions between the dihydrogen bonding pair and a vacant metal orbital (for example, see ref. 1). However, these were generally ascribed to transition states rather than intermediates. The implicit concern is that such a species might not be sufficiently stable (relative to dissociation of molecular hydrogen, returning to the reactants, and/or to cleavage of the H–H bond to produce the metal dihydride) to have any significant discrete existence, because the filled σ orbital and vacant σ^* orbital will generally be considerably lower and higher in energy, respectively, than the above π case. The same argument might be thought to apply even more forcefully to C—H bonds: in addition to the unfavorable energetics of donating electrons from a stable bonding orbital, problems of directionality of overlap (compared with

the spherical H $1s$ orbitals) as well as steric repulsion are sure to be worse. Nonetheless, in the early 1970s, Cotton and Trofimenko reported direct crystallographic evidence of a complex containing a coordinated (and chelating) C—H σ bond that was stable under ambient conditions, and vast numbers of many varieties of analogous species have since been discovered. The research articles in this special feature (4–13) comprise a snapshot view of the current state of the art in the field, and the perspective by Kubas (2) and the review by Brookhart *et al.* (3) offer historical perspectives. In the remainder of this introduction, we will highlight just a few of the recent developments.

In the area of dihydrogen complexes, interest is moving beyond structural and spectroscopic characterization, to possible roles as more than simply precursors to metal hydrides. James' classic 1973 monograph on hydrogenation (14) shows a few examples of reactions that suggest the possibility of hydrogen complexes as intermediates rather than transition states (although none are explicitly discussed in such terms), but all proceed to cleave the H—H bond before any subsequent chemistry takes place. However, a number of studies have shown that coordinated dihydrogen can have interesting chemical properties, particularly Brønsted acidity (often stronger than the metal hydrides derived therefrom), and thus could be directly involved in chemical transformations. Relevance to production and oxidation of dihydrogen, either in energy-related processes or in biological hydrogenase enzymes is of particular interest. Papers from the Rakowski DuBois (10) and Sabo-Etienne (9) groups touch on this theme.

C—H coordination and its relevance to C—H activation has been the hottest topic in this field, with obvious potential for applications in energy as well as organic synthesis. The papers in this special feature strikingly demonstrate how the use of a variety of techniques has led to a much more detailed and quantitative understanding of the phenomenon. We have always relied heavily on methods such as kinetics and isotopic labeling, which provide indirect information about σ-bonded intermediates; the work reported by the Jones (11) and Labinger and Bercaw (4) groups illustrate that approach. Powerful spectroscopic methods are also available: we now have several examples of direct observation of coordinated alkane by

NMR, which in combination with time-resolved IR allows definitive identification of structures and generates a considerable amount of data on lifetimes, dynamic behavior, and relative stability of isomers. The papers from the Ball (6) and George (7) groups exemplify this capability.

The interplay between experiment and theory has been effectively exploited for similar purposes, especially where theoretical results are closely tied to experiment and can be used to bridge gaps in the data that cannot be readily obtained experimentally. Two contributions [Eisenstein and Jones group (8) and Bergman and Head-Gordon group (12)] describe such collaborations. Overall a fairly consistent picture is beginning to emerge. Occasionally we find cases (the Re complexes) where the σ complex is more stable than, or in equilibrium with, the product of C—H bond cleavage; more commonly the reverse is true. But the σ complexes are remarkably stable with respect to loss of alkane, which in all cases is found to be much slower than reversible C—H bond cleavage and/or migration from one C—H bond to another. Such a finding, which would have come as a great surprise 20 years ago, strongly implies that the nature of the σ complex will play a major, probably *the* major, role in determining reactivity and especially selectivity in C—H bond activation processes.

At a finer level of detail, complex-specific behavior can be seen. For the Rh system studied by Eisenstein and Jones (8), calculations indicate that coordination of a primary C—H bond is preferred over that of a secondary one, and both experiment and calculations demonstrate that migration from secondary to primary is considerably more rapid than oxidative addition of a secondary C—H bond, so that the latter is not observed at all. However, the (calculated) energy differences are not all that large, so it is perhaps not unexpected that other systems behave differently: Ball's (6) NMR studies show that Re coordinates more strongly to secondary C—H bonds (by a small amount), whereas Labinger and Bercaw's group (4) conclude for their Pt complex that C—H bond cleavage is faster than migration to an adjacent carbon and that reaction at primary and secondary positions is

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roughly comparable. We may anticipate that, as additional systems are examined in similar detail, patterns of variable behavior will begin to emerge, hopefully leading to the possibility of rational design of reactivity.

Moving beyond C—H, a number of examples of coordinated M–H bonds have been reported; the paper from the Carlton group (13) describes some exquisitely detailed multinuclear NMR studies for Rh complexes of Sn–H. And going further, can we see stable examples of coordinated σ X—Y bonds where neither X nor Y is H? These would be expected to be still less favored on the grounds of poorer

overlap and steric hindrance mentioned above. Coordinated C—C bonds would be particularly intriguing, as probable intermediates in the activation of C—C single bonds by transition metals, a well known phenomenon, although mostly restricted to strained molecules such as cyclopropane, or to chelate-assisted cases.¶ The

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¶One interesting example that does not fall into either of these classes is the ''alkane metathesis'' reaction discovered by Basset; early proposals invoked direct interaction of the C—C bond with the metal, in a σ bond metathesis-like mechanism, but more recent studies implicate an alkylidene-based mechanism involving prior C—H activation. See ref. 15.

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contribution from the Green and Weller group (5), which again takes advantage of synergy between experiment and theory, provides a structurally well characterized molecule with a coordinated C—C bond that undergoes C—C activation.

The coordination chemistry of saturated molecules has progressed steadily over the last two or three decades, from a handful of curious examples to a well established and well understood structural paradigm. We confidently expect to see continuing progress as the factors governing stability and reactivity become more thoroughly codified, leading to new and improved applications in synthetic and catalytic chemistry.

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