the krypton fluoride: the third at 82.8 nm, the fifth at 49.7 nm, and the seventh at 35.5 nm. Each successive harmonic was weaker than the preceding one, with about 10^{11} photons per pulse in the third harmonic, 10^{8} per pulse in the fifth, and 10^{5} per pulse in the seventh. The efficiency of the seventh harmonic conversion was estimated to be 3×10^{-9} percent at a helium pressure of about 7 torr. The system operated at 10 pulses per second, as have most of those described previously.

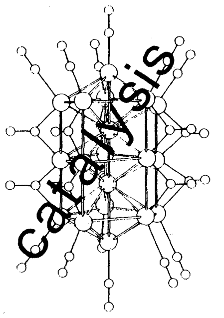
To improve the light output, Bucksbaum speculated, there are several possibilities. One is to increase the density of gas atoms in the jet by a factor of up to 100, which could add a factor of 1000 to the photon flux produced. A nonlinear optical technique called phase matching, if a suitable gas mixture could be found, might increase the flux by another factor of 100. Phase matching means that the incoming light wave and the frequency-converted light wave "stay in step" over a certain distance so that there is time for the short-wavelength wave to build up at the expense of the longer-wavelength light. Shorter pulses would help, as well, because the output of the *n*th harmonic increases with the *n*th power of the intensity of the incoming light. Pulses from krypton fluoride as short as 0.2 picosecond may be possible. Finally, a more efficient collector of the XUV than the diffraction grating used in the experiment is being developed at Bell Laboratories that may gather ten times as many photons, thereby using those that are produced more effectively.

What is all this good for? Many researchers are eyeing a less expensive alternative to synchrotron radiation, which has been the most intense source of tunable XUV light going. Kung says that the 100-nm source there would cost from $75,000 to $100,000 to replicate. Excimer lasers up the ante by $50,000 or more apiece. Bokor says the Bell Laboratories XUV system with one krypton fluoride laser would require $150,000 to construct. And Egger, Pummer, and Rhodes have estimated a cost of about $500,000 for the argon fluoride–based XUV source with three excimer lasers. It is difficult to compare these figures with the price of synchrotron radiation facilities, because these produce light over an extremely wide wavelength range and can serve dozens of researchers simultaneously. A conservative guess is that the two types of light sources will be complementary.

Finally, what are the prospects for even shorter wavelength coherent sources? Bucksbaum predicted that the next likely candidates are the ninth harmonic of krypton fluoride and the seventh of argon fluoride, both of which are close to 27.6 nm. Development of subpicosecond excimer lasers would mean there would be enough intensity to carry harmonic generation of excimer laser light to as short as 10 nm, according to Bokor. Ultimately, the construction of XUV lasers with outputs of the order of 20 nm together with nonlinear optics to shorten their wavelengths could lead to honest to goodness coherent x-ray sources (in marked contrast to what one reads about now).—**ARTHUR L. ROBINSON**

Activating Unreactive C–H Bonds

It is now possible to "get a handle" on hydrocarbons for further reaction by inserting a metal atom in a homogeneous reaction



"One of the most intriguing—and yet elusive—goals of organometallic chemistry has been the use of transition-metal complexes to 'activate' carbon-hydrogen bonds in completely saturated organic compounds," says Robert G. Bergman of the University of California, Berkeley. "Saturated hydrocarbons are among the most ubiquitous, and chemically stable, of all organic materials," he adds. They appear in petroleum, in coal, in synthetic fuels produced by liquefaction of coal and other fossil fuels, and in synthetic fuels produced by Fischer-Tropsch chemistry from syngas.

These hydrocarbons can be burned for their fuel value, but many investigators are now much more interested in their potential as feedstocks for the chemical industry. That use, however, requires that the hydrocarbons be functionalized, given a double bond or some other functional group that serves as a "handle" for further chemical reactions. Those investigators would like to use homogeneous systems to perform that functionalization because they hold the greatest promise of selectivity,* but their research has been, in Bergman's words, "tantalizing and frustrating."

The saturated hydrocarbons are, of course, not completely unreactive. They can be oxidized by heat, free-radical reactions, ozone, hydrogen peroxide, and superacids; but these reactions, says Bergman, "often require large amounts of energy and are usually very unselective." A homogeneous process might well require less energy.

There have been "tantalizing" glimpses that suggest that a homogeneous process is attainable. In the late 1960's, it was shown that acid solutions of certain platinum salts could catalyze the exchange of hydrogen and deuterium in alkanes, a process that requires scission of the carbon-hydrogen bond. This reaction is still controversial, however, because some investigators believe it is heterogeneous. Several investigators have also shown that metal atoms can mediate the oxidation of hydrocarbons through free-radical reactions.

More recently, investigators such as John T. Groves of the University of Michigan and Craig L. Hill of the University of California, Berkeley, have shown that metal-porphyrin complexes can catalyze the oxidation and functionalization of hydrocarbons. These homogeneous complexes are similar to biological cofactors, such as cytochrome P-450, that participate in biological oxidations, and they also operate through free radicals. In contrast, what Bergman and others have been seeking is a so-called oxidative addition in which a metal atom is inserted into a carbon-hydrogen bond in the same manner that has been observed for gases such as hydrogen or chlorine, as well as mercaptans, disulfides, and carboxylic acids.

The prototype for insertion of a metal atom into an alkane carbon-hydrogen bond is the well-known insertion of the

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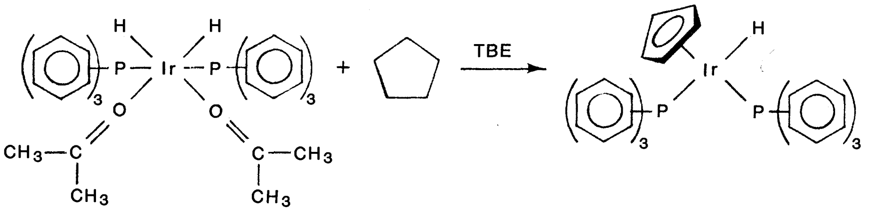
*Selectivity is discussed in earlier articles of this series: 4 February, p. 474; 25 February, p. 944; 25 March, p. 1413; 6 May, p. 592; and 3 June, p. 1032.

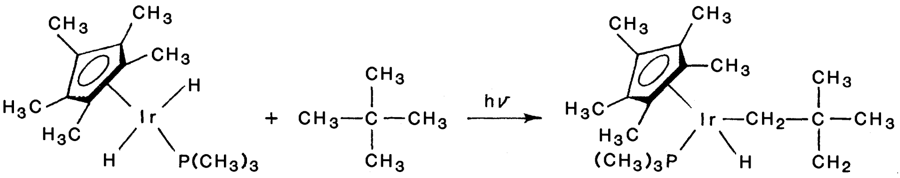
metal atom of many complexes into an arene C–H bond. The existence of the latter and not the former might seem surprising since an arene C–H bond is stronger than an alkane bond, with an energy of about 110 kilocalories per mole compared to energies of about 100 kilocalories per mole for paraffinic bonds. George W. Parshall of the Du Pont Company has suggested that the driving force for the reaction might come from the entropic factor associated with the formation of a complex between the metal atom and the π-electron system of the arene. A partial confirmation of this suggestion is provided by the recent syntheses of metal-arene complexes by William A. G. Graham of the University of Alberta and William D. Jones of the University of Rochester.



The first example

Bergman was able to convert cyclopentane into cyclopentadiene using t*-butylethylene (TBE) as a hydrogen acceptor.*

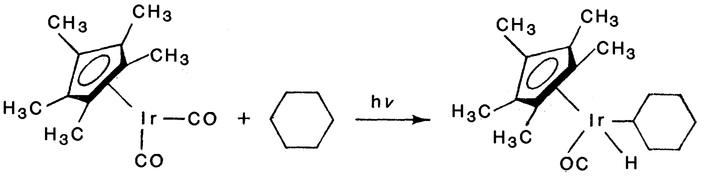
Robert H. Crabtree



A light-initiated reaction

Bergman uses an iridium complex to insert the metal atom into a C–H bond of neopentane.

Robert G. Bergman



Carbonyl instead of phosphine

Graham's iridium complex uses two carbonyl ligands instead of phosphines like Bergman's, but the results are the same.

William A. G. Graham

Further confirmation of this thesis is provided by many observations of intramolecular insertion of a metal atom into a carbon-hydrogen bond of one of its own ligands. This reaction is particularly facile for insertion into aryl C–H bonds, and has been observed for paraffinic C–H bonds. These observations were encouraging because they suggested that the goal of intermolecular oxidative addition was attainable, says Robert H. Crabtree of Yale University, but they were also discouraging: "Even if we were able to make a metal complex reactive enough to cleave paraffinic carbon-hydrogen bonds, how could we hope that the metal would cleave C–H bonds in the substrate paraffin rather than bonds in the solvent or co-ligands?" Fortunately, Crabtree's fears proved unfounded, although for reasons that are not yet clear.

In 1979, Crabtree and Jennifer Quirk reported that a diacetone iridium complex, $[(CH_3COCH_3)_2Ir[P(C_6H_5)_3]_2H_2]^+$, could dehydrogenate certain compounds; the acetone molecules are very weak ligands that presumably dissociate from the complex to form a coordinately unsaturated metal atom. In refluxing methylene chloride, the complex stoichiometrically dehydrogenates cyclooctene to a cyclooctadiene complex, cyclopentene to a cyclopentadienyl complex, and other olefins to diolefin complexes. This reaction was surprisingly selective in that neither the ligands of the complex nor the relatively weak carbon-chlorine bonds of the solvent were attacked. The yields were 80 to 90 percent for alkenes, but less than 10 percent for alkanes.

The yields for alkanes could, however, be vastly improved by adding a hydrogen acceptor to the reaction solution. After many trials, Crabtree's group settled on *t*-butylethylene (3,3-dimethyl-1-butene), which is only weakly complexed by the metal because of its bulk and because it has no allylic hydrogens. This compound strips hydrogen atoms from the metal to open new coordination sites. In its presence, the complex converts cyclopentane to the cyclopentadienyl complex, cyclooctane to the cyclooctadienyl complex, and other alkanes to olefins and diolefins, all in good yields.

Shortly thereafter, Hugh Felkin and his colleagues at the Centre National de la Recherche Scientifique reported similar results with a rhenium complex, $ReH_7[P(C_6H_5)_3]_2$, and *t*-butylethylene as a hydrogen acceptor. This complex converts cyclopentane to the cyclopentadienyl complex and cyclohexane to free cyclohexene (not benzene). In contrast, *n*-hexane is not affected. More recently, Ken Caulton and his colleagues at the University of Indiana have achieved similar results with $ReH_5[P(C_6H_5)_3]_3$; this complex is activated by light, which expels one of the phosphine ligands.

All of these complexes are now thought to act by inserting the metal atom into a carbon-hydrogen bond, then removing a second hydrogen, but many other investigators at the time argued that it was a free-radical or carbonium ion reaction. Notes Crabtree: "We had great difficulty persuading other people that our work was real." In fact it was only after others had isolated intermediates in which the metal was inserted into a C–H bond that the work was finally accepted.

In 1981, Bergman and Andrew H. Janowicz isolated the first such compound. They used an iridium complex, $[\eta^5\text{-}(CH_3)_5C_5]Ir[P(CH_3)_3]H_2$, dissolved in a potential substrate, such as neopentane.† When this complex is irradiated with light, it splits out a hydrogen molecule to become coordinately unsaturated. This intermediate inserts intself into a carbon-hydrogen bond of the solvent to form a new complex, $[\eta^5\text{-}(CH_3)_5C_5]Ir[P(CH_3)_3](H)[CH_2C(CH_3)_3]$. "The intermediate is so reactive," Bergman says, "that we haven't yet found an inert solvent."

Bergman and Janowicz have observed the insertion reaction with normal, iso- and cycloalkanes. At room temperature the reaction is slightly selective for primary bonds, with a primary to secondary

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†The qualifier η^x indicates that x atoms of the ligand are bound to the metal atom.

ratio of about 3 to 2. If the initial product mixture is heated to about 100°C, the complex dissociates and re-forms until only primary insertion is observed. This preference for primary bonds is the opposite of what is observed for free-radical reactions.

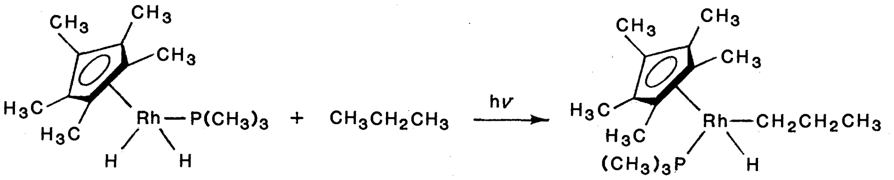
At about the same time, but independently, Graham and James K. Hoyano achieved nearly the same results with a similar iridium complex, $[\eta^5\text{-}(CH_3)_5C_5]Ir(CO)_2$. When this complex is irradiated, it loses a carbonyl moiety before insertion of the metal atom into a C–H bond in the solvent. This complex is also quite reactive, he says: "Any hydrocarbon we've tried undergoes this reaction." Neither Graham's nor Bergman's systems are catalytic, but that "is a rather trivial issue from a fundamental point of view," Bergman says. "The only difference between an ordinary chemical reaction and a catalytic one is that the catalyst is regenerated at the end—all the chemical steps are the same. In fact, if you want to study the mechanism, which we do, it is often easier if the reaction is not catalytic."

More recently, Jones and Frank J. Feher, as well as Bergman and Roy A. Periana-Pillai, have observed insertion reactions with a rhodium complex, $[\eta^5\text{-}C_5(CH_3)_5]Rh[P(CH_3)_3]H_2$. When irradiated, this complex also loses hydrogen, and the metal atom inserts into C–H bonds of both arenes and alkanes. In this case, the reverse reaction is fast, even at −20°C, so the C–H insertion must be done at lower temperatures.

Of all carbon-hydrogen bonds, the most difficult to activate are those of methane, where the bond energy of about 104 kilocalories per mole is nearly as high as that of the arenes. The first unequivocal instance of activation of a methane bond was reported only this April at the American Chemical Society meeting in Seattle. Patricia L. Watson of the Du Pont Company accomplished this formidable feat with a lutetium complex, $Lu[\eta^5\text{-}C_5(CH_3)_5]_2CH_3$. In perdeuterocyclohexane, which is sterically hindered so that it cannot bind to the metal, the complex reacts with labeled methane, $^{13}CH_4$, to give labeled complex and unlabeled methane, indicating that the complex has cleaved a C–H bond of the substrate. The complex also cleaves C–H bonds of ethane and propane, but the metal insertion is followed by β-hydride elimination to give an olefin.

The same types of reactions are observed with the comparable yttrium complex, Watson says, which suggests that lanthanide complexes in general may be useful for this kind of reaction. The lutetium complex can also react with many other species: it can add to the C–H bond of benzene or tetramethylsilane; it forms an adduct with pyridine, followed by *ortho*-metallation of the pyridine ring; it reacts with ylides to form metallacycles; and it splits ethers, such as diethyl ether, to yield a bound ethoxide and free ethane.

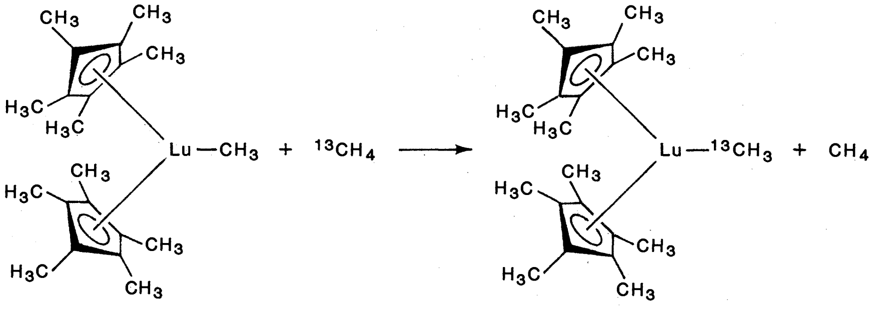
As exciting as these insertion reactions might be to the scientists involved, they are of little practical value if they are dead-end streets. "The question," Bergman says, "is where do we go from here?" Obviously, investigators would like, first, to add some functional group between the metal and the carbon and, second, to make the reaction truly catalytic. So far, they have had more success with the former than with the latter.



William D. Jones

A less stable complex

Rhodium complex can also be used to cleave a C–H bond, but the complex thus formed is less stable and must be isolated at low temperatures.



Patricia L. Watson

A first for methane

Watson used a lutetium complex for the first unequivocal demonstration of activation of a methane C–H bond in a homogeneous reaction.

Graham, for example, has found that carbon monoxide adds between the metal and carbon to form a bound acyl group when carbon monoxide is added to the reaction mixture under pressure. His preliminary results suggest that this occurs by migration of one of the bound carbonyls to the metal-carbon bond, followed by addition of a second carbonyl to the complex. Both Bergman and Jones have also found that the hydrogen in the alkane complexes can be replaced with bromine by reaction with bromoform ($CHBr_3$); Bergman has shown that the bromoalkane can be eliminated from the complex so that the halide provides the desired "handle" for further reactions.

Jones has had more success, albeit with arenes. He and John A. Maguire have shown that irradiation of $[\eta^5\text{-}C_5H_5]Re[P(C_6H_5)_3]_2H_2$ in benzene in the presence of ethylene and hydrogen leads to the catalytic production of ethane, butane, 1-butene, and ethylbenzene. If acetylene is substituted for ethylene, the products are styrene and ethylene. Most of these products involve insertion of ethylene (or acetylene) into an olefin or benzene C–H bond.

Jones and Roger G. Weaving, Jr., have also been successful in inserting an isonitrile into the C–H bond of benzene. The isonitrile is one of the ligands on the complex $Fe[P(CH_3)_3]_2[CNCH_2C(CH_3)_3]_3$. Irradiation of this complex in benzene results in the efficient formation of the aldimine $C_6H_5CH{=}NCH_2C(CH_3)_3$. With added isonitrile, this process is catalytic.

Another issue now is selectivity. "Clearly," says Bergman, "the complexes have already achieved the first and perhaps most crucial type of selectivity—they react more rapidly with C–H bonds in other molecules, even hydrocarbons, than they do with those present in their own ligands. We now also have some information about how effectively the complexes discriminate in reactivity among different types of C–H bonds in reactant molecules. What we still don't understand is the physical basis for that selectivity."—**THOMAS H. MAUGH II**