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- 7. The solenoidal microcoil was made from 50-µm diameter wire composed of 99.99% Cu (California Fine Wire, Grover Beach, CA) and coated with  ${\sim}6.4~\mu\text{m}$ of polyurethane. The fused silica capillary (Polymicro, Phoenix, AZ) was used without removing its polyimide coating. Coil fabrication was monitored with a dissecting stereomicroscope. By using a procedure modified from a previous approach (3), the coil was wound (with no gap between turns) past the number of turns desired (17 here), and cyanoacrylate adhesive (Ross, Conros Corp., Taylor, MI) was applied at points 17 turns apart. After the glue dried, excess turns were removed from each end to yield the final 17-turn coil. The polyurethane coating on the coil leads was removed with Strip-X (GC Electronics, Rockford, IL) followed by concentrated H<sub>2</sub>SO<sub>4</sub>. The leads were soldered to a 3-cm long, semirigid coaxial cable (UT85SS; Rosenberger Micro-coax, Collegeville, PA) and wired to the circuit as shown in Fig. 1. The nonmagnetic, tuning and matching variable capacitors (1 to 30 pF, Johansen 5641; Boonton, NJ) and the fixed capacitor (2.2 pF; Non-Mag 100 B 2R2 PN; American Technical Ceramics, Huntington Station, NY) complete the transmit/receive circuit. The unit was connected to the NMR by using a lowmagnetic, coaxial cable (Belden MIL-C-17G; Richmond, IN). Both transmission line and cable have a 50-ohm impedance. The coil and capillary are situated horizontally in the static magnetic field (Fig. 1) and are housed in an AI tube inserted into the widebore magnet.
- 8. Fluorinert FC-43 (3M, St. Paul, MN) was contained in a 20-ml, low-density polyethylene bottle fitted and epoxied to the circuit board. Once the fluid was applied to the coil region, the NMR signal took about 3 hours to stabilize. Shimming was performed only after application of the FC-43 yielded a stable signal. Teflon tubing (30 gauge) was attached to the capillary with a shrink-melt Teflon sleeve (Small Parts, Inc., Miami Lakes, FL). Samples were injected into the capillary via the Teflon tubing by using a syringe and needle connection. For data acquisition, the syringe was left in place and the outlet end of the tubing was closed off with another needle attached to a cutoff valve. All spectra and NMR data were obtained and analyzed on General Electric 300-MHz (7.05 T) spectrometers. The 89-mm wide-bore (WB) magnet (GN-300WB) and a custom probe stand (made inhouse) were used for all microcoil experiments. The GN-300WB and a similar narrow-bore (NB) unit (GN-300NB) were both used for studies with 5-mm spinning tubes (Wilmad 528-PP, Buena, NJ). Both spectrometers are equipped with their own 10-mm, highresolution, broad-band solution probes. The WB probe has an observe coil length of 20 mm that encloses within a 5-mm tube a sample volume of 278  $\mu\text{l};$  the NB probe has a coil length of 18 mm that encloses a volume of 250  $\mu$ l within a 5-mm tube (15). All experiments were run at ~18.5°C within the magnet bore. Neither NMR magnet was vibrationally isolated, nor were the magnet, console, or software modified to accommodate the microcoil probe. The 5-mm spinning tube was shimmed in a conventional manner with a deuterated lock solvent. The microcoil, however, was shimmed on the free induction decay (FID) signal of a protonated compound, usually neat acetone, or the compound of interest in a particular experiment. Solvent locking was not used for the microcoil, as the present circuit was only designed for tuning to protons at 300 MHz. Tuning and matching was performed with the circuit board and microcoil outside the magnet; otherwise, the procedure was conventional. A new microcoil is automatically placed in the axial center of the shims by the design of the probe stand. The probe was moved to the vertical shim center by adjustment of the vertical position until a significant change in the Z1 coarse shim shifted the position of a reference peak less than 1 Hz [W. W. Conover, in Topics in C-13 NMR Spectroscopy, G. C. Levy, Ed. (Wiley-Interscience, New York, 1984), vol. 4, p. 37]. The micro-

coil was then manually shimmed by using the five coarse adjustments for Z1, Z2, Z3, X, and Y. A simplex-based, Conover-derived macro optimized the remaining fine shim settings. After manual and auto shimming, Z2 and Z4 sometimes require manual adjustment based on the appearance of the final signal. A new microcoil is shimmed in <3 hours. The sample injection arrangement allows samples to be loaded without moving the probe.

- 9. The volume magnetic susceptibility of FC-43,  $\chi_v = -0.655 \times 10^{-6}$ , is within 15% of the  $\chi_v$  for Cu of  $-0.768 \times 10^{-6}$  and within 7% of the  $\chi_v$  for D<sub>2</sub>O of  $-0.705 \times 10^{-6}$ , compared to  $\chi_v = +0.030 \times 10^{-6}$  for air and  $\chi_v = -1.084 \times 10^{-6}$  for silica. The magnetic susceptibility of FC-43 was measured on a 1.0 T magnetometer (Quantum Design, Model MPMS, San Diego, CA). Other values from D. R. Lide, Ed., *CRC Handbook of Chemistry and Physics* (CRC Press, Ann Arbor, MI, ed. 74, 1993). All  $\chi_v$  values are dimensionless but computed using cgs units.
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- 11. Ethylbenzene, 2,3-dibromopropionic acid, sucrose, D<sub>2</sub>O, and acetone-d<sub>6</sub> (99.5 atom-%), were purchased from Aldrich (Milwaukee, WI). L-Arginine-HCI was obtained from Sigma (St. Louis, MO). Peptide was obtained from American Peptide, Sunnyvale, CA. Spectra are referenced to either 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt (aqueous solutions; Aldrich), or tetramethylsilane (organic solutions; Aldrich).
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- 13. The 90° pulse width (PW) for both arginine and sucrose was 1.6  $\mu$ s for the capillary and 210  $\mu$ s for the 5-mm tube for the same transmission power setting. Data acquisition parameters were established by adjustment of the spectral width and number of data points to yield an FID that was nearly completely relaxed in the first half of the pulse repetition time ( $T_p$ ). The spectral resolution,  $1/T_p$ , was always <1 Hz per

data point. Data were acquired for 1 and 10 min for both compounds. The line broadening value was set equal to the linewidth (12) but used only for the determination of S/N ratios in the computation of LODs. For the microcoil, the line broadening was 0.6 Hz, and for the 5-mm tube, 0.3 Hz. Data acquisition parameters for arginine HCI (60 scans/min): data points, 4096; spectral width, ±1004 Hz; pulse repetition time, 1.02 s; resolution, 0.98 Hz per point. For sucrose (48 scans per minute): data points, 2048; spectral width, ±400 Hz; pulse repetition time, 1.28 s; resolution, 0.78 Hz per point. For peptide: 256 scans in 11.8 min; data points, 8192; spectral width, ±2674 Hz; pulse repetition time, 0.77 s; 1.3 Hz per point; recycle delay, 1.0 s; line broadening 0.6 Hz; the water signal at 4.8 ppm was presaturated for 1.0 s per scan

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## Unusually Mild and Selective Hydrocarbon C–H Bond Activation with Positively Charged Iridium(III) Complexes

Bruce A. Arndtsen and Robert G. Bergman\*

Certain transition metal complexes can react to break normally inert carbon-hydrogen (C–H) bonds, but these metal-based processes typically require photochemistry or elevated temperatures. In addition, most are unselective toward complicated functionalized substrates, which has limited their synthetic usefulness. The cationic iridium complex Cp\*(P(CH<sub>3</sub>)<sub>3</sub>)Ir(CH<sub>3</sub>)(CICH<sub>2</sub>CI)<sup>+</sup>BAr<sub>f</sub><sup>-</sup> [Cp\* =  $\eta^5$ -C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>, BAr<sub>f</sub> = B(3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] can thermally activate methane and terminal alkanes at unprecedentedly mild temperatures (10°C). This complex will also induce C–H activation reactions in various functionalized substrates at ambient temperatures. High steric and electronic selectivity is observed, leading invariably to only one reaction product; the initial C–H activation reaction is typically followed by rapid metal-based rearrangements (that is, functionalization).

In synthetic chemistry, methods exist to transform nearly every organic functional group into another, thereby making many natural and unnatural compounds accessible to laboratory synthesis. Perhaps the most glaring exceptions to this rule involve saturated

\*To whom correspondence should be addressed.

carbon-hydrogen (C-H) and carbon-carbon (C-C) bonds in alkanes or alkyl groups, where current techniques typically require these groups to be considered untouchable to selective synthetic reagents. Although the necessity for transforming these compounds and groups can sometimes be avoided by altering the choice of starting materials, the ubiquitous nature of saturated C-H bonds (in hydrocarbon fuels and the alkyl groups of useful organic molecules) implies that the ability to

Chemical Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA 94720, USA.

selectively convert alkane C-H bonds into other functional groups would not only greatly enhance synthetic capabilities but would also significantly multiply the potential uses of hydrocarbon feedstocks. Our ability to manipulate C-H bonds has remained limited, however, because of the high homolytic bond strengths and low polarity of these bonds, which have made them inert to all but the most reactive substances (such as highly reactive organic free radicals, carbenes, and super acids). Under such reaction conditions, other functionalities either present or generated in the substrate can undergo unwanted transformation, so the selective functionalization of alkanes has remained difficult to achieve.

Studies in our research group (1) as well as those of Graham (2) and Jones (3) more than a decade ago showed that certain transition metal complexes can react stoichiometrically with alkanes to break their C-H bonds, suggesting that metal complexes might be used to effect alkane functionalization. Since then, several general classes of metal-based C-H bond activation reactions have emerged (4). The first to be identified, typically occurring with "late" transition metals (those located on the right side of the transition series in the periodic table), oxidatively add a C-H bond to a metal center to form (hydrido)(alkyl) metal complexes (Eq. 1, where L is a ligand on the metal and R is an alkyl group) (1-3, 5, 6). Recent



evidence suggests that these reactions often proceed through short-lived "alkane complex" intermediates in which the alkane is





**Fig. 1.** An ORTEP diagram of complex **2** (borane counterion removed for clarity). Selected bond lengths and angles: Ir–P: 2.276 (3) Å; Ir–Cp: 1.857 Å; Ir–C(15):2.105 (12) Å; Ir–Cl(1): 2.462 (3) Å; Cl(1)–C(14): 1.820 (15) Å; C(14)–Cl(2): 1.730 (15) Å; P(1)–Ir–Cl(1): 85.4 (3)°; P(1)–Ir–Cl(1): 88.97 (13)°; C(15)–Ir–Cl(1): 92.2 (4)°; Cl(1)–C(14)–Cl(2): 110.7 (8)°.

weakly associated with the metal center (7). In a second process, now referred to as  $\sigma$ -bond metathesis (Eq. 2), the alkane C–H bond adds across a bond to an electropositive metal (usually an "early" metal, lanthanide or actinide), leading to a different hydrocarbon and a new metal alkyl complex (8). Of these two processes, the early metal  $\sigma$ -bond metathesis reactions typically proceed under milder conditions, allowing the thermal activation of methane and terminal alkanes at temperatures occasionally as low as 45°C, and display a higher degree of selectivity.

We recently reported an unusual example of alkane activation by a late metal (Ir(III)) complex that in its overall character is more closely related to early-metal  $\sigma$ -bond metathesis processes: the reaction at 45°C of Cp\*(PMe<sub>3</sub>)IrMe(OTf) (1) (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>, Me = CH<sub>3</sub>, and OTf = OSO<sub>2</sub>CF<sub>3</sub>) with alkanes (R–H) to eliminate methane and generate Cp\*(PMe<sub>3</sub>)IrR(OTf) (9). The mild conditions for this C-H activation suggests that in this system an unsaturated Ir fragment can be formed readily, probably through loss of the OTf<sup>-</sup> ("triflate") ligand. We report here the results of our effort to prepare and isolate this presumed intermediate by exchange of triflate with the noncoordinating counterion  $BAr_{f}^{-}[BAr_{f} = B(3,5 C_6H_3(CF_3)_2)_4$ ]. This work has led to the generation of  $Cp^*(PMe_3)IrMe(ClCH_2Cl)^+$ - $BAr_{f}^{-}$  (2), which undergoes an unprecedented C–H activation of methane and other organic compounds below room temperature. In addition to its high activity, **2** also displays significant selectivities in the C–H bond that is activated, and can form single products from complicated substrates.

The addition of  $Na^+BAr_{c}^-$  (10) to an orange CH<sub>2</sub>Cl<sub>2</sub> solution of 1 leads to gradual darkening of the mixture over the course of 30 min and the precipitation of NaOTf. Analysis of the reaction mixture by proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectrometry shows the quantitative conversion of 1 to the tetraarylborate salt 2 (Eq. 3 and Fig. 1). Attempts to precipitate this polar compound with pentane or diethyl ether led to the isolation of cationic olefin hydride complexes (see below), suggesting its ability to activate aliphatic C-H bonds. Careful evaporation of the CH<sub>2</sub>Cl<sub>2</sub> solution of 2 allowed its isolation as an orange solid, although prolonged exposure to reduced pressures or room temperature resulted in decomposition to a number of uncharacterized compounds.

Examination of the <sup>1</sup>H NMR spectrum of isolated **2** in CD<sub>2</sub>Cl<sub>2</sub> showed that it coprecipitates with two CH<sub>2</sub>Cl<sub>2</sub> molecules [chemical shift  $\delta$  5.32 (4H)] which exchange rapidly with CD<sub>2</sub>Cl<sub>2</sub> at -90°C. The spectra of both tetraarylborate [<sup>1</sup>H NMR  $\delta$  7.72 (s, 8H),  $\delta$  7.56 (s, 4H); <sup>19</sup>F NMR  $\delta$  -60.91 (s)] and Cp\*(PMe<sub>3</sub>)IrMe [<sup>1</sup>H NMR  $\delta$  1.68 (15H),  $\delta$  1.58 (9H),  $\delta$  1.23 (3H); <sup>31</sup>P NMR  $\delta$  -23.0 (s)] fragments are relatively simple even at low temperature. These observations suggest that if there is any association of a ligand (such as CH<sub>2</sub>Cl<sub>2</sub> or BAr<sub>f</sub><sup>-</sup>) with the prochiral Cp\*(PMe<sub>3</sub>)IrMe cation, adduct formation must be rapid and reversible on the NMR time scale in solution.

Complete characterization of 2 in the solid state was afforded by x-ray diffraction. Cooling a concentrated  $CH_2Cl_2$  solution of 2 to  $-40^{\circ}C$  for 1 day led to the precipitation of orange crystals that were unstable at temperatures above 0°C. Collection and careful mounting of the crystals at temperatures lower than this, followed by a low-temperature x-ray diffraction study, confirmed the presence of two molecules of  $CH_2Cl_2$  per Ir complex in the crystal lattice, with one of these molecules bound to the



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metal center (Fig. 1). The complex has a pseudo three-legged piano stool geometry, with a chloride-bound  $CH_2Cl_2$  molecule occupying one site. Both the borane and second  $CH_2Cl_2$  fragment are located well outside bonding distances to the Ir cation.

Because of its poor ligating ability, CH<sub>2</sub>Cl<sub>2</sub> complexes are relatively rare, and to our knowledge 2 represents the first structurally characterized example of an  $\eta^1$ -bound  $CH_2Cl_2$  unit to a transition metal (11). The weak interaction between CH<sub>2</sub>Cl<sub>2</sub> and Ir is illustrated by a long Ir-Cl distance [2.462(3) Å; numbers in parentheses are in standard errors in the last digit or digits]. Consistent with this, the effect on the  $CH_2Cl_2$ unit upon bonding is minimal. There appears to be a slight lengthening of the C(14)-Cl(1) distance [1.820 (15) Å] and the Cl(1)–C(14)–Cl(2) bond angle of 110.7(8)° is normal. These values can be compared to the spectroscopically determined (12) values for gas phase  $CH_2Cl_2$ , which has a C-Cl bond length of 1.772 Å and a Cl-C-Cl angle of 111.8°.

Complex 2 is extremely reactive toward hydrocarbon C–H bonds. The addition of benzene to a  $CH_2Cl_2$  solution of 2 results in immediate effervescence, due to methane loss, and the generation of the phenyl-substituted complex 5 (Fig. 2). This process proceeds rapidly even at temperatures as low as  $-30^{\circ}$ C, which is substantially faster than the analogous reaction of triflate complex 1, which reacts in a similar manner with arenes at a reasonable rate only above 10°C. Complex 2 also undergoes below-ambient temperature methane activation, as demonstrated by the incorporation of label from <sup>13</sup>CH<sub>4</sub> at 10°C (*13*). Terminal alkanes such as pentane and methylcyclohexane can be activated over the course of minutes at room temperature to ultimately generate terminal ole-fin complexes, a process which likely proceeds through initial C–H activation followed by rapid β-hydride elimination.

The activation of hydrocarbons by 2 represents the most facile general C-H activation by a metal complex observed to date. The only other stoichiometric thermal alkane activation at ambient temperatures we are aware of is that of Wavland's tethered bis-Rh(II) porphyrin complex, which reacts at appreciable rates only with methane (14). Other late metal unsaturated fragments, such as Cp(L)Ir, Cp(L)Rh, or Tp(L)Rh, oxidatively add C–H bonds extremely rapidly; however these all require generation by high-energy thermal or photochemical events (1-5, 7). We believe the high activity of **2** is due to the lability of the  $CH_2Cl_2$ ligand, whose dissociation allows low-temperature access to the 16-electron Ir cation 7 (Fig. 3), although the exact mechanism of the reaction (whether it involves initial associative or dissociative replacement of



Fig. 3. Proposed mechanisms for C-H bond activation by 2.



 $\rm CH_2\rm Cl_2$ , and oxidative addition–reductive elimination or a concerted 4-center transition state for the C–H activation step) are still issues that must be resolved by further experimentation. The weak interaction between Ir and  $\rm CH_2\rm Cl_2$  can be confirmed by more conventional transformations: the coordinated  $\rm CH_2\rm Cl_2$  ligand undergoes immediate displacement at  $-80^{\circ}\rm C$  by a variety of other dative ligands, such as CO and acetonitrile, generating adducts that are unreactive toward alkanes.

With more complicated molecules, preliminary experiments have demonstrated that, even in the presence of other functionalities, complex 2 reacts cleanly at ambient temperatures to break specific C-H bonds. The activation is followed invariably by rapid rearrangement or secondary coordination to the metal center to form saturated 18-electron complexes. For example, diethyl ether (which does not react with triflate 1 at 25°C) reacts with the  $CH_2Cl_2$  complex 2 at room temperature in  $CH_2Cl_2$  in a manner similar to its reaction with terminal alkanes, leading to the vinyl ether complex 4 (Fig. 4). Reaction with methyl acetate gives acetoxymethylene complex 8, a rare example of a transformation in which a methyl hydrogen in a carboxylic acid methyl ester, rather than the substantially more acidic  $\alpha$ -carbonyl hydrogen, is selectively activated. This reaction suggests a strong electronic influence on the C-H activation, in addition to the steric requirements previously observed, with the more electron-rich site being exclusively activated.

Metathesis of the triflate in 1 with the noncoordinating counterion BAr<sub>f</sub><sup>-</sup> leads to the generation of a highly reactive C-H activating, CH<sub>2</sub>Cl<sub>2</sub>-solvated Ir cation. These C-H activations proceed with high steric and electronic selectivities and are often followed by metal-based rearrangements, all of which represent further steps toward the selective low-temperature functionalization of organic substrates through C-H bond activation. The high activity of complex 2 is undoubtedly related to the lability of the CH<sub>2</sub>Cl<sub>2</sub> unit, suggesting that more weakly solvated forms of  $[Cp^*(L)Ir(CH_3)]^+$  (such as by hydrocarbons) should show even higher reactivity toward organic compounds.

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- 13. A 0.010 M solution of **2** in  $CD_2CI_2$  under 1 atm of  ${}^{13}CH_4$  was monitored by <sup>1</sup>H NMR spectrometry at 10°C. Conversion to an equilibrium mixture of **2** and  ${}^{13}C$ -**2** followed pseudo-first-order kinetics (observed rate constant  $k_{obs} = 2.40 \times 10^{-4} \text{ s}^{-1}$ ; half-life = 50.1 min).
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## Direct Perception of Three-Dimensional Motion from Patterns of Visual Motion

Cornelia Fermüller and Yiannis Aloimonos\*

Measurements of retinal motion along a set of predetermined orientations on the retina of a moving system give rise to global patterns. Because the form and location of these patterns depend purely on three-dimensional (3D) motion, the effects of 3D motion and scene structure on image motion can be globally separated. The patterns are founded on easily derivable image measurements that depend only on the sign of image motion and do not require information about optical flow. The computational theory presented here explains how the self-motion of a system can be estimated by locating these patterns.

To detect the image of movement is the first task of all systems with vision, and to reach an understanding of movement is a primary goal of all later perceptual analysis (1), for animals as well as in robots. Although an organism or a mechanism may move in a nonrigid manner as a whole, with the head, arms, legs, wings, or wheels undergoing different motions, the eyes move rigid-ly—that is, as a sum of an instantaneous translation and rotation. Thus, the images perceived on the retina of the eye (or on the film in a camera) originate from a rigid motion.

The fundamental, abstract geometric concept used to describe the computational analysis of visual motion is that of the twodimensional (2D) motion field: As a system moves in its environment, every point of the environment has a velocity vector with respect to the system. The projection of these 3D velocity vectors on the retina of the system's eye constitutes the so-called motion field. This field depends on the 3D motion and the structure of the scene in view. If a spherical eye moves with a translation **t**, the motion field is along the great circles containing the vector **t** (Fig. 1A), pointing away

Computer Vision Laboratory, Center for Automation Research, Department of Computer Science and Institute for Advanced Computer Studies, University of Maryland, College Park, MD 20742–3275, USA.

\*To whom correspondence should be addressed.

**Fig. 1.** Motion fields on a spherical retina. The image **r** of a scene point with position vector **R** (with regard to an orthonormal coordinate system fixed to the center *O* of the unit sphere) is formed by perspective projection through *O*.





ward the focus of contraction (FOC). The points FOE and FOC are the points where t cuts the image sphere. If the eye rotates with a velocity  $\omega$  (Fig. 1B), the motion field is along the circles resulting from the intersection of the image sphere with planes perpendicular to the rotation axis; this axis cuts the sphere at points AOR (axis of rotation) and -AOR. For general rigid motion, the motion field on the sphere is the addition of a translational field and a rotational field (Fig. 1C). In this case, the motion field does not have a simple structure, and it becomes difficult to locate the points FOE and AOR, that is, to solve the problem of determining a system's 3D motion (its egomotion) with the 2D motion field as input (2).

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This difficulty is compounded because the information that can be derived from the sequence of images sensed by the moving retina is not the exact projection of the 3D motion field, but rather only information about the movement of light patterns. The exact movement of every point on the image is termed the optical flow field. In general, accurate values of the optical flow field are not computable; the so-called normal flow, the component perpendicular to the edges, is the only component of the optical flow that is well defined on the basis of local information. This is the well-known aperture prob-