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Intramolecular Double C-H Activation in $FvM_2(en)_4$ (Fv=fulvalene; M=Ir, Rh; en=ethylene)

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Intramolecular Double C-H Activation in $FvM_2(en)_4$ (Fv=fulvalene; M=Ir, Rh; en=ethylene)

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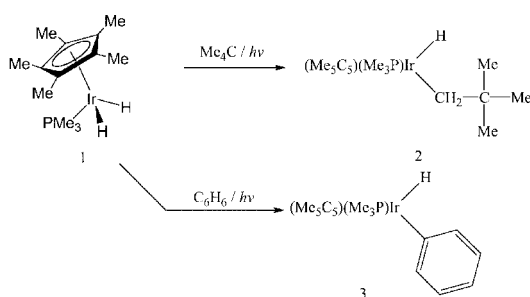
주제어: 분자내 이중 C-H 활성화, 풀발렌 동종이 핵 착분

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Alkanes are among the most abundant and unreactive species in organic compounds. In industry free-radical activation of carbon-hydrogen bonds is often utilized at high temperatures, thereby limiting the selectivities in functionalization reactions. Therefore, it has been of great interest to achieve the selective carbon-hydrogen activation by the appropriate transition metal compounds.¹ Only a few transition metals among the metal complexes have been observed to insert C-H bonds in saturated hydrocarbons through an oxidative addition mechanism. Of those, complexes of rhodium and iridium are found effective for that purpose.

In 1982, Bergman and Janowicz found that dihydrido-iridium(III) complex (**1**) undergoes intermolecular oxidative addition to single C-H bonds in saturated hydrocarbons in high yield in homogeneous solution under UV irradiation as shown in *Scheme 1*.²

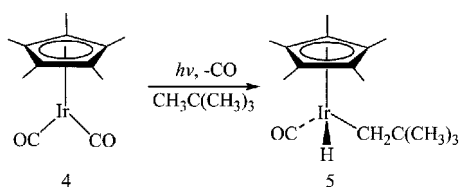
Here, irradiation ($\lambda_{\max} \geq 275$ nm; high pressure Hg lamp, Pyrex filter) of this Ir complex in benzene resulted in loss of dihydrogen, yielding the



Scheme 1.

corresponding hydriodophenyl complex (**3**), which is another example of sp^2 C-H bond activation. Similar stoichiometric oxidative addition of C-H bond of alkanes to a photochemically generated iridium complex was observed by Graham and Hoyano almost at the same time. *Scheme 2* show that irradiation of a solution of $(\eta^5-C_5Me_5)Ir(CO)_2$ (**4**) in neopentane at room temperature leads to the formation of the hydridoneopentyliridium complex (**5**).³

For a multinuclear transition metal complex having strong interaction among metals through either



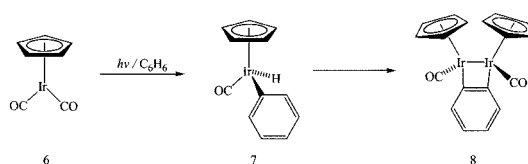
Scheme 2.

direct metal-metal bond or bridging ligands, the substrate can be activated in an efficient and characteristic manner probably due to the cooperative action between metals.¹

In particular, dinuclear organotransition-metal have gained much attention seemingly due to the fact that bimetallic compounds incorporating two reactive metal sites in close proximity may be in easy access to reaction pathways not available to mononuclear systems as a result of mutually beneficial electronic and/or steric effects. However, it seems extremely of import to avoid fragmentation of the polynuclear framework so as to achieve true reactivity.⁵ To circumvent this undesirable process, a wide variety of chelating ligands such as diphosphines,⁶ phosphido bridges,⁷ pyrazolate,⁸ indirectly linked cyclopentadienyl anions,⁹ and cyclic δ -hydrocarbones¹⁰ have been utilized. However, their fundamental drawback has been the relatively weak metal-ligand bond. An exception is the class of linked cyclopentadienyls which offer a very robust framework to attached metals. For example, metal-cyclopentadienyl(M-Cp) bond is quite strong (90–118 kcal/mol)¹¹ and relatively inert.¹²

Fulvalene-bridged dinuclear systems may exhibit different properties from those of Cp analogs, and of analogs based on Cp rings connected by intervening linkages. For the metal-metal bonded complexes with fulvalene ligand, the fulvalene ligands are likely to bend away from planarity to accommodate the metal-metal bonds. This bent fulvalene ligand seems to weaken the metal-metal bond accordingly, resulting in unique reactivity.

In 1977, Rausch and Wood observed the hydrocarbon activation by $\text{CpIr}(\text{CO})_2$ (**6**) under UV irradiation in benzene. The product recovered in low yield (2%) was shown by X-ray crystallographic

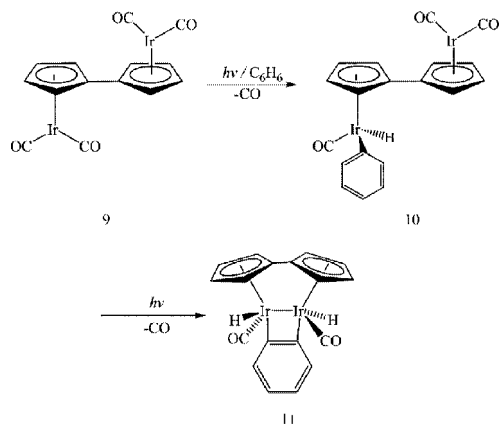


Scheme 3.

analysis to be the diiridium O-phenylene complex (**8**). This product was assumed to be derived from the phenylhydride complex (**7**) which is too thermally unstable to isolate (Scheme 3).¹³

West in Vollhardt research group tried a similar photochemical reaction using fulvalene bisiridium tetracarbonyl (**9**) in benzene. The initial photoproduct would be the phenylhydride complex (**10**), which should be subsequently activated at the 2-position on the phenyl ligand, leading to the doubly C-H activated product (**11**). This photochemical reaction was performed in 1.5 mM solution of the reactant in degassed dry benzene by a broad-band Hanovia 450 W medium Hg-vapor lamp with a water-cooled jacket (Scheme 4).^{14,21,22,23}

In this report, we reveal the first syntheses of $\text{FvIr}_2(\text{en})_4$ (**12**)¹⁵ and $\text{FvRh}(\text{en})_4$ ($\text{en}=\text{ethylene}$) (**13**)¹⁶ so as to explore the possible vinyl C-H activation chemistry therein. Preparation of the fulvalene bisiridium tetraethylene (**12**) began with the degassed ethylene bubbled into the THF solution of $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ for about 10 min. at 0 °C and then the yellow solid dispersion turned light yellow solution. Dilithioful-



Scheme 4.

valene was then introduced into the reaction solution at 0 °C with ethylene bubbling for more than 1hr, leading to a deep orange precipitation. This product solution was passed through Celite column and solvent was removed under vacuum.

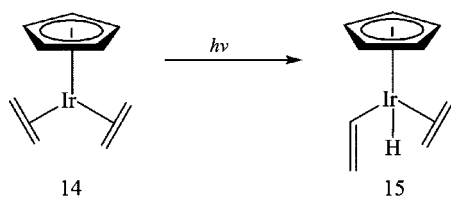
In case of the preparation of fulvalene bisrhodium tetraethylene, $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ was dispersed in THF at 0 °C for about 10 min., followed by addition of DME solution of dithiofulvalene.

The reaction solution was then stirred at ambient temp. for about 40 min. with ethylene purge. The dark solid slurry solution was then passed through alumina column, where only deep yellow solution was collected and solvent was removed under vacuum. Column chromatographic separation of product using the mixed solvent system (pentane: diethyl ether = 1 : 1 by vol.) was employed. Preparation of 12 and 13 afforded the corresponding products in 68% and 37% yields, respectively.

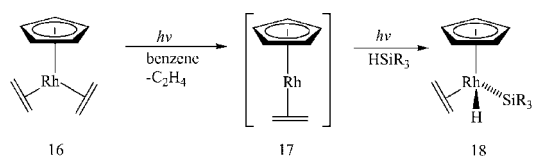
Photolysis of 12 in benzene at 15 °C at N_2 purge for 3hr using broad-band Hanovia 450 W medium-pressure Hg-vapor lamp was performed, leading to the rather surprising product (21)¹⁷, a quadruply intramolecular C-H activation product.

Perutz and Haddleton¹⁸ also observed the similar photochemical conversion of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ (14) into vinylhydride complex (15) (Scheme 5).

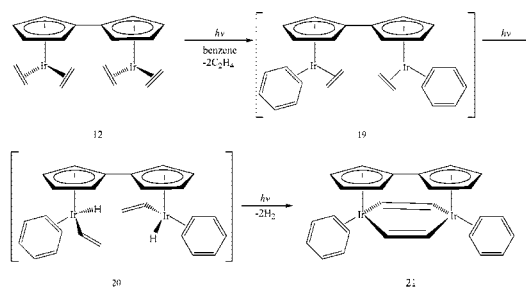
They also reported that 16 at UV irradiation in benzene at 25 °C loses one ethylene to have a reactive intermediate, 17, which eventually undergoes



Scheme 5.



Scheme 6.



Scheme 7.

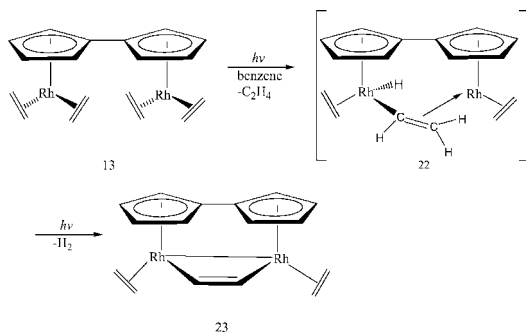
Si-H bond activation (18) (Scheme 6).

Here, the photochemical reaction of 12 in benzene seems to replace two ethylene by two benzene, and then undergo the photochemical conversion of the corresponding ethylene complex (19) into the corresponding vinylhydride complex (20) intermediate, followed by loss 2H_2 , to yield the product (21) (Scheme 7).

During this photoreaction the hydrido ethyl intermediate formation can be evidenced by previous reaction 13, 14, 18.

However, the photochemical reaction of 13 in benzene under the similar reaction condition to the previous one gave a rather unexpected product (23), which may be in part explained by loss of one ethylene on photolysis, followed by the corresponding vinyl hydride complex (22), eventually leading to the doubly C-H activated product (23)¹⁹ with loss of H_2 ¹⁴ (Scheme 8).

However, it seems rather unclear that this photochemical reaction does not afford any benzene coordination after loss of ethylene in contrast to previous



Scheme 8.

photochemical reaction of Ir complex (12).

Here we notice that the sp^2 C-H bond of coordinated ethylene here is already weaker than the free phenyl C-H bond; therefore, intramolecular C-H bond activation takes place to yield the doubly activated product (23).

This result may be also supported by the similar bond dissociation energies of the corresponding sp^2 C-H bond between benzene and ethylene²⁰.

Much more effects in this regard should be directed towards the elucidation of this chemical reaction pathways.

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REFERENCES

- Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22* 91.
- Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.
- Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.
- Tada, K.; Oishi, M.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 2422.
- Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146.
- Huffman, J. C.; Lloyd, B. R. *Inorg. Chem.* **1989**, *28*, 3087.
- Stephan, D. W.; Jenkins, H. A.; Loeb, S. J. *Inorg. Chem.* **1989**, *28*, 1998.
- (a) Sherlock, S. J.; Cowie, M.; Singleton, E.; Steyn, M. V. *J. Organomet. Chem.* **1989**, *361*, 353. (b) Neumann, F.; Suess-Fink, G. *J. Organomet. Chem.* **1989**, *367*, 175.
- Reddy, K. P.; Peterson, J. L. *Organometallics* **1989**, *8*, 547.
- Clode, K. E.; Wright, A. H. *J. Chem. Soc. Chem. Commun.* **1988**, 1463.
- Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 7399.
- Kahn, A. P. Ph. D. Thesis, University of California at Berkeley, **1990**.
- Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 7870.
- West, M. J. Ph. D. Thesis, University of California at Berkeley, **1991**.
- ¹H NMR (C_6D_6) δ 5.00(s, 4H), 4.60(s, 4H), 2.49(d, 8H), 0.94(d, 8H).
- ¹H NMR (C_6D_6) δ 5.18(s, 4H), 4.67(s, 4H), 2.65(d, 8H), 1.25(d, 8H).
- ¹H NMR ($CDCl_3$) δ 6.85(dd, 4H), 6.41(dd, 4H), 6.10(m, 4H), 5.12(m, 4H), 4.89(m, 4H), 4.56(m, 4H), (C_6D_6) δ 7.64(dd, 4H), 7.23(dd, 4H), 6.92(dd, 4H), 6.86(dd, 4H), 5.50(m, 4H), 4.22(m, 4H), 4.03(m, 4H); MS(EI) m/z 720.
- Belt, S. T.; Duckett, S. B.; Haddleton, D. M.; Perutz, R. N. *Organometallics* **1989**, *8*, 748.
- ¹H NMR ($CDCl_3$) δ 5.40(s, 2H), 5.26(t, 4H), 5.15(t, 4H), 3.85(s, 4H), 0.87(s, 4H).
- Bond dissociation energy for sp^2 C-H of ethylene(110 kcal/mol); that of benzene (111 kcal/mol).
- Kenneth B. Capps, Glenn D. Whitener, Andreas Bauer, Khalil A. Abboud, Ian M. Wasser, K. Peter C. Vollhardt and Carl D. Hoff. *Inorg. Chem.* **2002**, *41*, 3212.
- Bernd Kayser, Michael J. Eichberg and K. Peter C. Vollhardt. *Organometallics* **2000**, *19*, 2389.
- Ning-Chou Chen, Michael J. Eichberg, K. Peter C. Vollhardt, Ricardo Sereheli, Ian M. Wasser and Glenn D. Whitener *Organometallics* **2002**, *21*, 749.