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Sequential C−H Activation and Dinuclear Insertion of Ethylene Promoted by a Diiridium Complex

Yaofeng Yuan, M. Victoria Jiménez, Eduardo Sola, Fernando J. Lahoz, and Luis A. Oro*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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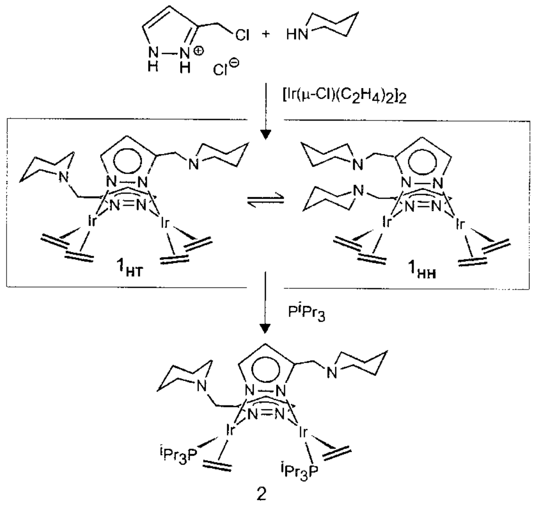
The exploitation of cooperative reactivity among metals in polynuclear complexes constitutes an attractive alternative to attempt challenging catalytic transformations.[1] The multimetallic reaction sites often present in di- and polynuclear compounds have been found to be efficient in substrate activation reactions, such as those leading to C−H,[2] Si−H,[3] C−C,[4] C=C,[5] C−Si,[6] and C−S bond cleavages.[7] Also, such multimetallic sites have been shown to favor constructive reactions affording new C−H,[8] C−N,[9] C−Si,[10] and C−C bonds.[11,12] Some of the latter processes were found to involve alkenyl ligands, and elementary steps such as reductive eliminations and migratory couplings with methylene or vinylidene bridges.[11,12] This communication illustrates that, in addition to the aforementioned elementary reactions, dinuclear complexes are also efficient to promote dinuclear olefin insertions into metal−alkenyl bonds. Through this C−C bond-forming step, two ethylene molecules, formerly bonded to different metal atoms, could be converted into a terminal hydride and a bridging 3-buten-1-yl ligand. The understanding of this behavior has been facilitated by the use of diiridium complexes containing piperidine-substituted pyrazolate bridges, since the presumably more simple analogues with non-substituted pyrazolate ligands[13] gave in fact more unstable and complicated reaction mixtures.

The diiridium tetrakis-ethylene complex **1**, doubly bridged by 3-(piperidinemethyl)pyrazolate ligands, has been prepared by treatment of a THF solution of 3-(chloromethyl)pyrazole hydrochloride[14] with an excess of piperidine, and subsequent addition of the complex $[Ir(\mu\text{-}Cl)(C_2H_4)_2]_2$.[13] Blue crystals of **1** were obtained in 76% yield after extraction of the reaction residue with hexane and subsequent cooling to 233 K. The toluene-d_8 NMR samples of these crystals prepared and measured at 213 K were found to contain exclusively the isomer $\mathbf{1_{HT}}$ (head-to-tail isomer of C_2 symmetry) (Scheme 1). When warming up to room temperature, these samples readily developed an equilibrium distribution of isomers, consisting of a 60:40 mixture of $\mathbf{1_{HT}}$, and its head-to-head isomer of C_s symmetry $\mathbf{1_{HH}}$, respectively.[15,16] This thermodynamic isomer distribution, indicative of the similar energy of both isomers, seems to rule out any strong coordination of the piperidine arms to the metals in the ground state of complex **1**, thus supporting the proposed structures. Nevertheless, the possibility of a weak piperidine interaction that could influence the kinetic behavior of these isomeric complexes appears very likely.

To enhance the C−H activation capabilities of the iridium centers of **1**, partial substitution of the ethylene ligands by the basic P^iPr_3 was attempted. In toluene at 283 K, the substitution reaction required up to 4 days, and afforded a sole HT isomer of complex **2**, both in solution and in solid state (Scheme 1, Figure 1).

Scheme 1



Complex **2** was found to be stable in solution below 293 K. However, C−H activation of an ethylene ligand could be promoted either thermally or by UV irradiation. Interestingly, each procedure led to a different reaction product. UV irradiation of **2** in C_6D_6 solution afforded the hydride-vinyl complex **3** (Figure 1). The compound maintains the HT arrangement of the pyrazolate bridges, with one of the piperidine arms completing a distorted octahedral coordination around the formally Ir(III) center.[17] The vinyl ligand resulting from the ethylene oxidative addition bridges the metals in an asymmetric $\mu,\eta^1{:}\eta^2$-coordination mode.[18] As a result of this coordination mode, the ligand distribution around the Ir(I) center resembles a trigonal bipyramid, with the two C=C moieties contained in the equatorial plane. Although such cis and coplanar arrangement of the two C=C fragments appears to be suitable for an insertion process, **3** did not evolve insertion products, even under harsh reaction conditions.

The slow isomerization of **2** into **4** could already be detected in C_6D_6 solutions of **2** at room temperature. Quantitative isomerization was achieved after heating these solutions to 333 K for a few minutes. In this case, the isomerization involves the rearrangement of the ligand environment from HT to HH, as well as the transformation of the two ethylene ligands into a terminal hydride and a bridging 3-buten-1-yl. Formally, the complex contains Ir(I) and Ir(III) centers which, with regard to the short intermetallic distance and the descriptions given to closely related analogues,[19] are likely connected by an Ir(I)−Ir(III) dative metal−metal bond.

The formation of **4** most likely occurs through a reaction sequence consisting of an ethylene C−H activation step followed by the insertion of the second ethylene into a metal-bridging vinyl bond. Given that the hydride−vinyl complex **3** did not show any thermally induced evolution, this reaction sequence leading to **4** should be initiated by the reorganization of the dinuclear frame from HT to HH. The exclusive formation of **4** upon the thermal evolution of **2** would indicate that the unobserved HH isomer of **2** activates ethylene faster than the observable HT species.

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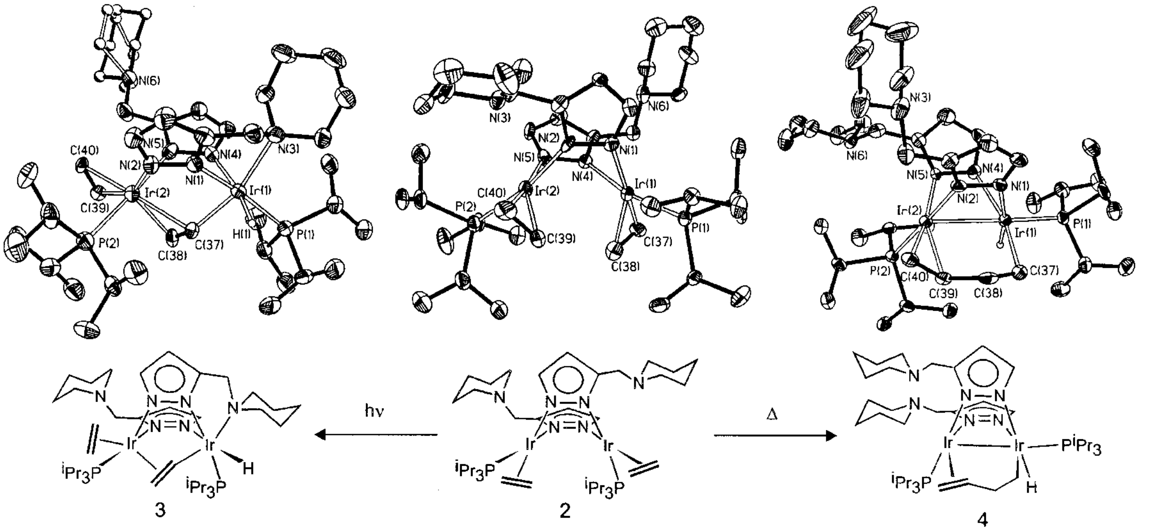

Figure 1. C−H activations of ethylene in complex **2**. Thermal ellipsoid plots of the crystal structures are drawn at the 50% probability level. Atoms involved in disorder have been isotropically refined. Selected bond lengths (Å) and angles (deg) are as follows: **2**: Ir(1)···Ir(2) 3.3029(3), Ir(1)−C(37) 2.093(10), Ir(1)−C(38) 2.073(10), Ir(2)−C(39) 2.117(9), Ir(1)−C(40) 2.153(8), C(37)−C(38) 1.327(11), C(39)−C(40) 1.360(11). **3**: Ir(1)···Ir(2) 3.5036(2), Ir(1)−C(37) 2.017(9), Ir(1)−N(3) 2.390(7), Ir(2)−C(37) 2.287(8), Ir(2)−C(38) 2.178(8), Ir(2)−C(39) 2.004(7), Ir(2)−C(40) 2.022(7), N(3)−Ir(1)−C(37) 156.7(3), N(1)−Ir(1)−P(1) 170.6(2), N(4)−Ir(1)−H(1) 170(3), N(5)−Ir(2)−P(2) 177.5(2), N(2)−Ir(2)−C(37) 82.0(3), N(2)−Ir(2)−C(40) 107.8(3), C(38)−Ir(2)−C(39) 91.1(3). **4**: Ir(1)−Ir(2) 2.7492(5), Ir(1)−C(37) 2.090(9), Ir(2)−C(39) 2.187(8), Ir(2)−C(40) 2.115(8), C(37)−C(38) 1.527(11), C(38)−C(39) 1.488(12), C(39)−C(40) 1.375(12), Ir(2)−Ir(1)−P(1) 172.96(6), N(1)−Ir(1)−H(1) 170(3), N(4)−Ir(1)−C(37) 162.4(3), Ir(1)−Ir(2)−P(2) 109.05(6), N(2)−Ir(2)−P(2) 176.6(2), C(37)−C(38)−C(39) 117.7(7), C(38)−C(39)−C(40) 126.5(8).

These considerations suggest a significant dependence of the C−H activation behavior of **2** on the orientation of the piperidine substituents, although they do not coordinate to the metal centers in the ground state of the complex. Thus, the structure of **4** indicates that the C−H activation step occurs preferentially at the iridium atom which is not protected by piperidine arms. This may indicate that piperidine nitrogen can effectively compete with the C−H bonds for the empty orbitals of the iridium atoms, disfavoring the transition state required for the C−H activation. Moreover, a disfavoring role of the piperidine moiety for the insertion reactions seems apparent from the structure of **3**, not only because of its contribution to stabilize the vinyl intermediates by coordination, but also because its presence in the vicinity of the metal atom may hinder the shift of the phosphine to an axial coordination position, which seems to be a requirement for the stabilization of the insertion product.

The results described herein indicate that dinuclear complexes may constitute adequate environments to promote and support reaction sequences of substrate functionalization through C−H activation. In the present case, the functionalization step has been found to involve a dinuclear insertion of ethylene into a bridging vinyl moiety, which takes place under mild reaction conditions. The possibility of exploiting this elementary reaction in catalytic applications such as olefin polymerization is under current investigation.

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Supporting Information Available: Synthetic procedures and spectroscopic and analytical data for complexes **1**−**4** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org

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