

Alkenyl-Assisted C³-C Bond Activation of Acetylacetonate Coordinated to Iridium

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Supporting Information Placeholder

ABSTRACT: The cleavage of a C³-C bond of the acetylacetonate (acac) ligand of the complexes Ir{(E)-CH=CHR}{κ²-N,C-(quin-C₆H₄)}(acac)(PⁱPr₃) (R = H (**1**), Ph (**2**)) has been achieved by reaction with an acid and subsequently with a base. The rupture is assisted by the alkenyl coligand. The latter reacts with the acid to be coupled with the acac group, in order to weaken the C³-C bonds. Then, the base removes an acylium group from the resulting intermediates [Ir{κ²-N,C-(quin-C₆H₄)}{κ³-O,O,C-(acac-C₂H₂R)}(PⁱPr₃)]⁺ (R = H (**3**), Ph (**4**)) to afford Ir{κ²-N,C-(quin-C₆H₄)}{η⁴-CH(R)CHC(Me)O}(PⁱPr₃) (R = H (**5**), Ph (**6**)).

The rupture of C-C bonds is the least frequent among the metal-mediated σ-bond activation processes.¹ The noticeable inertia of C-C bonds is mainly a consequence of two characteristic of these bonds; the orbital directionality which is little favorable for interacting with the transition metals and their low polarity which prevents the heterolytic activation.² Thus, often, the metal-mediated C-C cleavage relies on ring strain,³ attainment of aromaticity,⁴ and stabilization of the resulting metal species by chelate or pincer effects.⁵ There is also a handful of examples in which C(sp²)-C(sp) and C(sp³)-C(sp) bonds of alkynes and nitriles are cleaved by transition metal fragments, previous coordination of the multiple bond. Jones has shown the oxidative addition of a C(sp²)-C(sp) bond of diphenylacetylene to Pt(0) under photolysis.⁶ In contrast to the alkyne, nitriles undergo thermal oxidative addition of the R-CN bond to Rh(0),⁷ Rh(I),⁸ Ni(0),⁹ and Pt(0).¹⁰ Some ligands facilitate the cleavage, without changes in the oxidation state of the metal, participating directly in the process. Bergman, Brookhart, and co-workers have shown that the Rh(III) cation [Rh(η⁵-C₅Me₅)(SiPh₃)(CH₂Cl₂)(PMe₃)]⁺ activates the R-CN bond of aryl and alkyl nitriles to form complexes of general formula [Rh(η⁵-C₅Me₅)(R)(CNSiPh₃)(PMe₃)]⁺.¹¹ We have reported that the square planar Rh(I) boryl complex Rh(Bpin){xant(PⁱPr₃)₂} (HBpin = pinacolborane, xant(PiPr₂)₂ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) promotes the cleavage of the R-CN bond of aryl nitriles to give the square planar aryl derivatives Rh(R){xant(PⁱPr₂)₂} and [CNBpin]_n, via Rh{C(R)=NBpin}{xant(PⁱPr₂)₂} intermediates.¹²

Transition metal acetylacetonate complexes are traditional compounds in coordination chemistry with notable applications in organometallics, catalysis, material science and medicine, among other fields.¹³ A characteristic of this class of compounds is their high stability and the robustness of the acetylacetonate (acac) ligand, which is related to electron delocalization. The latter

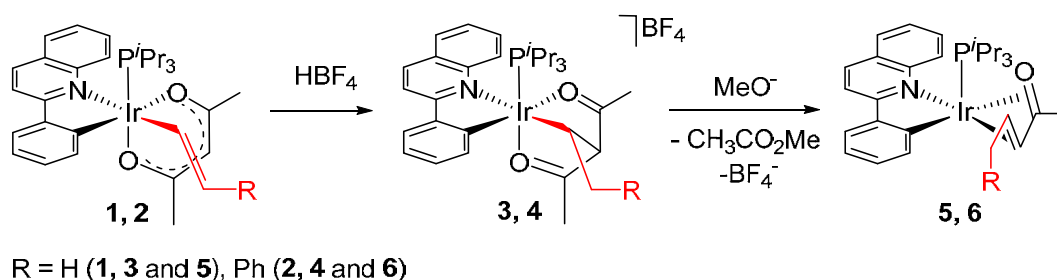
strengthens the C³-C bonds, which become shorter and more stable than a single bond. In spite of its robustness, we here show that the C³-C bonds of the acac group can be broken with the assistance of an alkenyl ligand.

The alkenyl-acetylacetonate complexes Ir{(E)-CH=CHR}{κ²-N,C-(qui-C₆H₄)}(acac)(PⁱPr₃) (R = H(**1**), Ph(**2**)) are phosphorescent yellow Ir(III) emitters. The X-ray structure of **2** has revealed that the acac C³-C distances are 1.390(5) and 1.396(5) Å,¹⁴ i.e., about 0.15 Å shorter than the expected one for a C-C single bond (1.54 Å) and only about 0.05 Å longer than that expected for a C-C double bond (1.34 Å). Although these bond lengths suggests strong C-C bonds, one of them is easily broken by means of the sequential addition of an acid and a base (Scheme 1).

Treatment of dichloromethane solutions of **1** and **2** with 1.1 equiv of HBF₄·OEt₂ leads to the salts [Ir{κ²-N,C-(qui-C₆H₄)}{κ³-O,O,C-(acac-C₂H₂R)}(PⁱPr₃)]BF₄ (R = H (**3**), Ph (**4**)), as a result of the addition of the proton of the acid to the C_β atom of the alkenyl ligand and the intramolecular coupling between the C_α atom of the latter and the C³-atom of the acac group. The reactions are consistent with the known nucleophilicity transfer from C_α to C_β in alkenyl ligands attached to third row late transition metals.¹⁵ The reactions between acac groups and coordinated carbon skeletons are rare. They include the nucleophilic attack to π-alkynes,¹⁶ the external addition to the central position of an allyl,¹⁷ the addition of the C³-H bond to the C-C double bond of an alkenyl,¹⁸ and the exchange between the C³H-hydrogen atom and a substituent of an alkylidene.¹⁹

Salts were isolated in high yields, 93% (**3**) and 80% (**4**), and characterized by X-ray diffraction analysis. Figures 1 and 2 show a view of the cations of **3** and **4**, respectively. Both structures prove the formation of an O,O,C-terdentate ligand, which is fac-coordinated in an octahedral environment with the C(1) atom disposed *trans* to the N atom of the orthometalated heterocycle and the oxygen atoms O(1) and O(2) situated *trans* to the phosphine and the metalated phenyl group of the chelate. The Ir-C(1) bond lengths of 2.103(2) (**3**) and 2.099(5) (**4**) Å and the Ir-C(3) distances of 2.011(2) (**3**) and 2.004(5) (**4**) Å are consistent with Ir-C(sp³) and Ir-C(sp²) single bonds. As expected for the presence of a Ir-C(sp³) bond, the ¹³C{¹H} NMR spectra, in dichloromethane-*d*₂, at room temperature show a doublet (²J_{C-P} = 6 Hz) at 28.6 ppm for **3** and at 34.1 ppm for **4**. The resonance corresponding to the metalated carbon atom of the phenyl group appears at 133.9 ppm for **3** and at 132.6 ppm for **4** also as a doublet (²J_{C-P} = 8 Hz).

Scheme 1. Cleavage of a C³-C of Acetylacetonate by Sequential Addition of an Acid and a Base



The C_α-C³ coupling produces the elongation of the C³-C bonds of the acac moiety, which display bond lengths of 1.519(3) (C(18)-C(19)) and 1.513(3) (C(18)-C(21)) Å in **3** and 1.497(8) (C(18)-C(19)) and 1.513(7) (C(18)-C(21)) Å in **4**; i.e., about 0.1 Å longer than in the starting compounds. The elongation facilitates the heterolytic cleavage of one of them by means of a process resembling the retro-Claisen condensations.²⁰ Thus, the addition of 1.0 equiv of KOH or Et₃N to methanol solutions of **3** and **4** leads to the neutral compounds Ir{κ²-N,C-(quin-C₆H₄)}{η⁴-CH(R)CHC(Me)O}(PⁱPr₃) (R = H (**5**), Ph (**6**)) and methyl acetate (δ_H, 1.95 and 3.57). Chan and co-workers have achieved the C-CO cleavage of ketones using Rh(II) porphyrins derivatives in water. However, in contrast to the cleavage here shown, the resulting acyl fragment stays attached to the metal center.²¹

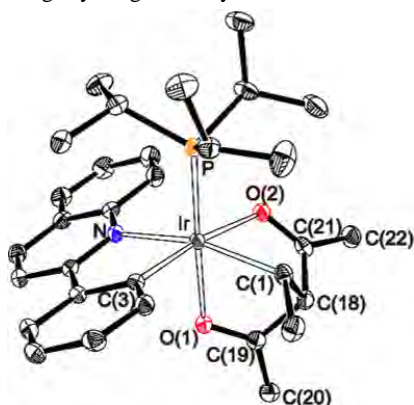


Figure 1. ORTEP diagram of complex **3** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected angles (deg): C(1)-Ir-N = 161.47(8), O(1)-Ir-P = 178.19(4)°, O(2)-Ir-C(3) = 171.32(7).

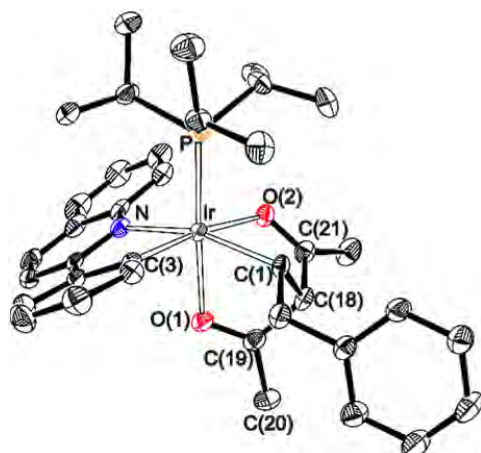


Figure 2. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected angles (deg): C(1)-Ir-N = 159.92(18), O(1)-Ir-P = 177.64(10)°, O(2)-Ir-C(3) = 170.58(17).

Complexes **5** and **6** were isolated as orange solids in 61% and 57% yield, respectively. The rupture of the acac moiety of the terdentate ligand of **3** and **4**, with formation of an α,β-unsaturated ketone, was confirmed by means of the X-ray diffraction structure of **5**, which proves the coordination of both C-C and C-O double bonds. Figure 3 shows a view of the molecule. The coordination of the C(4)-C(3) bond is asymmetrical; the iridium-carbon (terminal) distance of 2.126(4) Å (Ir-C(4)) is about 0.06 Å shorter than the iridium-carbon (central) bond length of 2.191(4) Å (Ir-C(3)). The latter is about 0.08 Å shorter than the Ir-CO distance of 2.270(4) Å (Ir-C(1)), whereas the C(4)-C(3) bond length of 1.465(6) Å is about 0.05 Å longer than the C(3)-C(1) distance of 1.412(5) Å. These structural data strongly support a significant contribution of the σ²-π resonance form to the Ir-ketone bonding. The coordination polyhedron around the metal center can be rationalized as a distorted square pyramid with the phosphine in the apex. At the base, the C(4) atom lies *trans* to the N atom of the heterocycle whereas the oxygen atom is disposed *trans* to the metalated phenyl group. The ¹³C{¹H} NMR spectra of **5** and **6**, in benzene-*d*₆, also support a significant contribution of the σ²-π resonance form to the ketone coordination. In agreement with similar cases,²² the CO, CH, and CHR resonances respectively appear at 150.1, 73.3, and 20.6 ppm for **5** and at 151.4, 71.5, and 27.8 ppm for **6**.

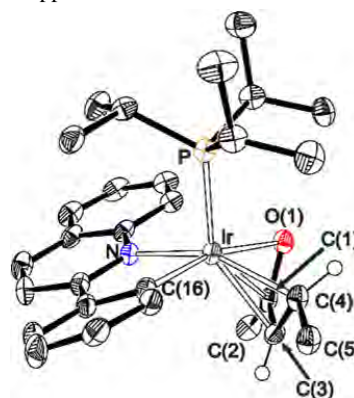


Figure 3. ORTEP diagram of complex **5** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected angles (deg): C(4)-Ir-N = 152.15(15), O- Ir-C(16) = 164.52(14).

In conclusion, the cleavage of a robust C³-C bond of the stable acetylacetonate group of complexes alkenyl-iridium-acetylacetonate has been achieved by reaction with an acid and subsequently with a base. The rupture is assisted by the alkenyl ligand, which undergoes the attack of the acid and couples with

the acac group to weaken the C³-C bonds. Then, the base removes an acylium group. These results revealed that the presence of a carbon skeleton acting as co-ligand in acetylacetonate complexes is a risk for the acetylacetonate integrity, since it can help to the cleavage of one of the C³-C bonds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental section, ¹H, ³¹P{¹H} and ¹³C{¹H} spectra of **3-6** (Figures S1 – S13), details of the structural analysis of **3**, **4**, and **5** (PDF).

Accession codes

CCDC 1561716-1561718 contain the crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interests

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