

**Activation of Aldehydes by the
Ir–2,3-Dimethylbutadiene Complex
Tp^{Me2}Ir(CH₂=C(Me)C(Me)=CH₂)**

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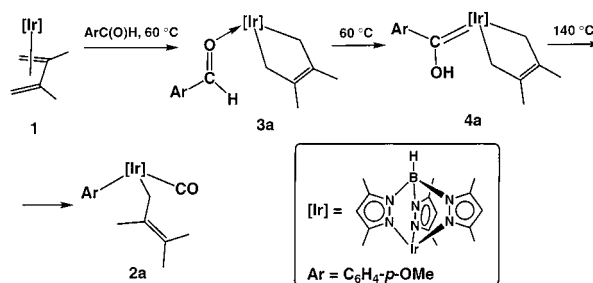
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Transition metal mediated reactions leading to the formation or rupture of the C–H and C–C bonds of organic substrates constitute an area of research of paramount importance.¹ In particular, those involving C–H activation and the decarbonylation of the C(O)H moiety of aldehydes are of considerable interest.² Following earlier work on the activation of the C–H bonds of different organic substrates by Tp^{Me2}Ir^{III} complexes^{3,4} (Tp^{Me2} = hydrotris(3,5-dimethyl)pyrazolylborate⁵) and on the reactivity of the conjugated 2,3-dimethylbutadiene compound Tp^{Me2}Ir(CH₂=C(Me)C(Me)=CH₂) (**1**) toward aromatic C–H bonds,⁶ we wish to present herein preliminary results on the interaction of the latter complex with aromatic and aliphatic aldehydes.

The reaction of compound **1** with an excess (ca. 3 equiv) of MeO-*p*-C₆H₄C(O)H at 135 °C yields ultimately the orange Ir^{III}-carbonyl species **2a**⁷ (Scheme 1) through a series of intermediates. The first of these is the η^1 -aldehyde adduct⁸ **3a**, which can be detected at 60 °C with the appearance of a characteristic C(O)H low-field ¹H NMR signal at δ 9.81. Despite the fact that its concentration in the reaction mixture is never higher than ca. 10% (vide infra), its formulation is secured by the unambiguous

Scheme 1



characterization of the analogous Me₂N-*p*-C₆H₄C(O)H derivative **3b**^{9a} which rearranges more slowly (see below). This is a very rare observation of a coordinated aldehyde in a reaction that ends with the decarbonylation of the organic substrate.^{2a,b,10} Compounds **3** are butadiene derivatives with the very uncommon η^1 : η^1 bonding mode.^{11,12}

In view of literature precedents¹⁰ on the reactivity of aldehydes with transition metal organometallic compounds, the formation of **2a** cannot be considered unusual. Nevertheless, a detailed analysis of this transformation reveals the implication of very unusual intermediates, some of them generated in unexpected and, to the best of our knowledge, unprecedented steps. Thus when the reaction of **1** and an excess of MeO-*p*-C₆H₄C(O)H is carried out at 60 °C, in addition to the η^1 -aldehyde complex **3a**, small concentrations (ca. 10%) of a new compound **4a** can be detected in the reaction mixture at low conversions. As for **3a**, the proposed formulation of the less reactive Me₂N-*p*-C₆H₄C(O)H derivative, **4b**.^{9b} Both **4a** and **4b** exhibit a low-field ¹H resonance in the proximity of 11 ppm. A solid sample of **4b** shows an IR absorption at 3180 cm⁻¹, while in its solution ¹³C{¹H} NMR spectrum a low-field resonance can be found at 241.1 ppm. These and other data support formulation of compounds **4** as Tp^{Me2}Ir(CH₂C(Me)=C(OH)Ar), i.e. as Ir(III) complexes that contain a Fischer's hydroxycarbene, =C(OH)Ar ligand.¹³ NMR studies on the reaction mixture of **1** and Me₂N-*p*-C₆H₄C(O)H prove that

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(7) Selected spectroscopic data: IR (KBr) ν (CO) 2004 cm⁻¹. ¹H NMR (CDCl₃, 25 °C) δ 3.08, 3.05 (AB spin system, ²J_{AB} = 12.0 Hz, IrCH₂). ¹³C-{¹H} NMR (CDCl₃, 25 °C) δ 169.4 (CO), 119.2 (IrC_{ar}), 6.8 (IrCH₂, ¹J_{CH} = 126 Hz).

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(9) (a) Selected spectroscopic data for **3b**: ¹H NMR (CD₂Cl₂, 25 °C) δ 9.33 (s, CHO). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C) δ 200.0 (CHO, ¹J_{CH} = 178 Hz). (b) Selected spectroscopic data for **4b**: IR (Nujol) ν (OH) 3181 cm⁻¹. ¹H NMR (CDCl₃, 25 °C) δ 11.25 (s, 1 H, COH), 3.10, 2.92 (AB spin system, ²J_{AB} = 14.6 Hz, 4 H, 2 IrCH₂). ¹³C{¹H} NMR (CDCl₃, 25 °C) δ 241.4 (Ir=COH), 12.3 (IrCH₂, ¹J_{CH} = 128 Hz).

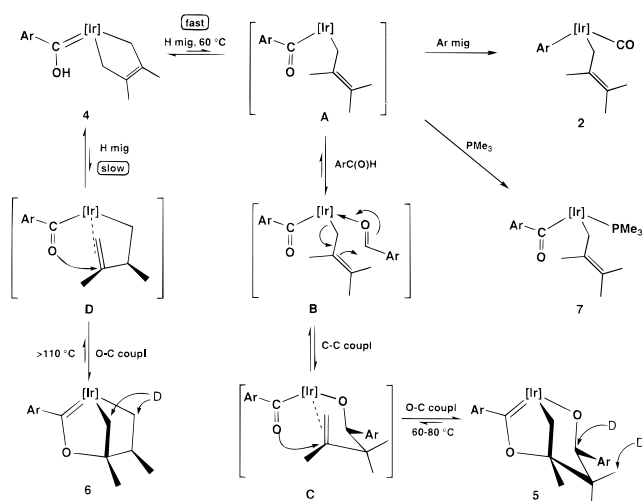
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(11) Even though species of this type have been extensively postulated as intermediates in reactions of η^1 -butadiene complexes (Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723), very few previous reports correspond to compounds of the transition metals (benzoannulated butadiene complexes, i.e. *o*-xylylenes and heterobutadiene species such as perfluorobutadiene complexes are excluded from this discussion).

(12) Compounds of composition Tp^{Me2}Ir(CH₂C(R)=C(R)CH₂)L, therefore related to **3**, are formed when the corresponding η^1 -diene precursors^{6a} are reacted with Lewis bases (R = H, Me; L = PMe₃, CO, NCMe, NC₅H₅ among others). Of these, the PMe₃ adduct (R = H) has been characterized by X-ray studies to be reported elsewhere.

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Scheme 2



complex **3b** is an intermediate in the formation of the Fischer's carbene derivative **4b**. No evidence for a π,η^2 -aldehyde adduct⁸ has been found in this system. To our knowledge, the conversion of an aldehyde into a hydroxycarbene ligand is without precedent in the literature.^{13,14}

Complex **4a** undergoes further reaction at the temperature needed for its formation (Scheme 2). Thus, in the presence of another equivalent of MeO-*p*-C₆H₄C(O)H it converts into the metallacyclic Fischer's carbene derivative **5a**.¹⁵ Only one stereoisomer can be detected in the reaction mixture. Its stereochemistry, deduced from spectroscopic data, has been confirmed by an X-ray study¹⁶ carried out with the analogous benzaldehyde compound **5c** (see Figure 1 of the Supporting Information). As expected, the interaction of an isolated sample of compound **4b** with a second equivalent of Me₂N-*p*-C₆H₄C(O)H produces cleanly species **5b**, *i.e.* the expected new member of this family of compounds.

When complex **5a** is heated in solution for longer periods of time it loses one of the incorporated molecules of the aldehyde (the reaction is complete after 24 h at 60 °C). The presence of 1 equiv of the free aldehyde in the reaction mixture slows down the process, which becomes strongly inhibited when a larger excess of the aldehyde (>5 equiv) is used. NMR monitoring shows the reaction is stereospecific and proceeds through the intermediacy of the hydroxycarbene species **4a**, to give a new Fischer's carbene derivative **6a** (Scheme 2) that contains also a metallacyclic skeleton.¹⁷ Further heating at 135 °C leads to compound **2a**, the thermodynamic product of this transformation.

The mechanism presented in Scheme 2 for the overall process relies upon the hypothesis (supported by deuterium labeling studies, *vide infra*) that the conversion of compounds **4** into intermediates **A**¹⁸ is kinetically favored over their rearrangement to those of type **D**. In the former possibility the H atom of the aldehyde is transferred to one of the CH₂ units, whereas in the

latter it adds to one of the double-bonded carbon atoms. Whereas the migration of the H atom to the C atom occurs directly or through the formation of a hydrido-acyl Ir(V) intermediate, cannot be ascertained.^{3,4} In this regard it is worth noting that Casey and co-workers have recently demonstrated the isomerization of a Re=C(O)R fragment into the corresponding hydrido-acyl complex.^{13c} The addition of a second molecule of the aldehyde to **A** gives the η^1 -aldehyde adducts **B**,¹⁹ which undergo cyclization by a concerted mechanism already advanced for related processes that involve Ti(III)- and Ir(III)-allyl compounds.²⁰ The oxycarbene nature of the Ir^{III}-C(O)Ar functionality (*i.e.* Ir⁺ = C(Ar)O⁻; see ref 21 for some reactivity associated with the somewhat analogous 1,3-dipolar carbenic resonance form Ir⁺=CH-CH₂⁻ in Ir^{III}-CH=CH₂ complexes) would account for the formation of **5**. The use of C₆H₅C(O)D gives complex **5c-d₂** in which the labeling occurs exclusively at the positions shown in Scheme 2.

As mentioned briefly above, heating solutions of **5** for longer periods of time reverses the reaction. Under these conditions, the kinetically less-favored **4** → **D** conversion may take place and compounds **6** may be generated. The use of **5c-d₂** provides complex **6c-d₁**, with the deuterium label exclusively at, and evenly distributed among, the four methylenic sites (within experimental error, no labeling at the CHMe position can be detected). Hence and as our working assumption implies, the **4c** ⇌ **A** equilibrium is attained faster than complex **6c** forms and moreover there is a substantial kinetic isotope effect for the migration of H onto the double-bonded carbon atoms of **4c**.²² Eventually, under more drastic conditions (>130 °C) complex **6** also reverses to **A** to afford, ultimately, the aryl(carbonyl) compounds **2**,²³ *i.e.* the thermodynamic products of the reaction. In accord with this observation, which requires a migratory CO deinsertion step, the thermal decomposition of **6** in the presence of a large excess of PMe₃ (>10 equiv, 120 °C) yields the aryl(phosphine) adducts **7**, which can be alternatively obtained from **5** at a lower temperature (60 °C). Crotonaldehyde and acetaldehyde also give related cyclic carbenes, although the decarbonylation process is complicated by the formation of several byproducts.

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Supporting Information Available: Synthetic procedures and spectroscopic and analytical data for complexes **2a**, **4b**, **5a,c**, **6a,c**, and **7a**; details of the X-ray diffraction study, an ORTEP view, crystal and refinement data, selected bond lengths and angles, and atomic coordinates and anisotropic displacement parameters (15 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(14) The opposite reaction, *i.e.* the decomposition of hydroxycarbene complexes to liberate aldehydes, has been described: (a) Fischer, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1 and references therein.

(15) Selected spectroscopic data for **5a**: ¹H NMR (CDCl₃, 25 °C) δ 4.18 (s, 1 H, CHAr), 4.04, 3.88 (AB spin system, ²J_{AB} = 11 Hz, 2 H, IrCH₂). ¹³C{¹H} NMR (CDCl₃, 25 °C) δ 251.3 (Ir=C).

(16) Crystal data for **5c**: monoclinic, *P*2₁/*c*, *a* = 8.1922(6) Å, *b* = 20.794(1) Å, *c* = 21.859(2) Å, β = 98.922(1)°, *V* = 3678.6(4) Å³, *Z* = 4, *D_c* = 1.492 Mg/m³, *R* = 0.0568 for *I* > 2σ(*I*), *wR*₂ = 0.1658. *R* indices (all data): *R* = 0.0609, *wR*₂ = 0.1706.

(17) Selected spectroscopic data for **6a**: ¹H NMR (C₆D₆, 25 °C) δ 3.72, 2.95 (AB spin system, ²J_{AB} = 10.4 Hz, 2 H, IrCH₂), 2.99 (dd, ²J_{HH} = 10.8, ³J_{HH} = 2.2 Hz, 1 H, IrCHHCHMe), 2.58 (dd, ³J_{HH} = 6.7 Hz, 1 H, IrCHHCHMe). ¹³C{¹H} NMR (C₆D₆, 25 °C) δ 247.5 (Ir=C).

(18) Intermediates of this kind have been proposed in the Ru or Rh catalyzed addition of aldehydes to dienes: Kondo, T.; Hiraischi, N.; Morisaki, Y.; Wada, K.; Watanabe, Y.; Mitsudo, T. *Organometallics* **1998**, *17*, 2013.

(19) Intermediate **A** may be in equilibrium with an η^3 -allyl species. Ir(III) allyls of composition Tp^{Me₂}IrX(η^3 -C₃H₄Me) (X = H, Cl) are known to afford reactive 16e⁻ η^1 -allyls upon thermal treatment. Unpublished results from this laboratory. See also ref 3a.

(20) (a) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: New York, 1986; Chapter 5. (b) CH₃CN adducts of Ir^{III}- η^1 -allyls cyclize in the same way—unpublished results from this laboratory.

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(22) Partial distribution of the CH₂D label into the two diastereotopic Ir-CH₂ protons in **5c-d₂** is observed as the **5c-d₂** → **6c-d₁** reaction progresses. Clearly and as the concentration of free C₆H₅C(=O)D increases, the trapping of fully scrambled **A-d₁** by the aldehyde becomes competitive with respect to the formation of **6c-d₁**.

(23) Tp^{Me₂}Ir^{III}-carbonyls are very stable toward dissociation of CO: Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538.