Synthesis of Tertiary and Other Sterically Demanding Alkyl and Aryl Complexes of Iridium by Aldehyde C−H Bond Activation

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The first syntheses of transition metal complexes containing tertiary alkyl ligands were reported as late as 1972.[1−3] Since then, very few tertiary alkyl complexes of transition metals have been described.[4−9] Such complexes have been difficult to synthesize and isolate due to their propensity to undergo further reactions such as β-elimination, giving stable transition metal hydrides.[10] In group 9, we are aware of a handful that have been isolated,[11−14] but none of iridium.[15] Herein, we report a method for the synthesis of two cationic tertiary alkyl (and other highly hindered) carbonyl complexes of iridium which are quite stable; thus far, none has been observed to decompose at room temperature. This work represents an example[16] of the rational application of C−H bond activation[17−19] to the synthesis of a class of complexes of chemical or structural interest. During the course of this work we have also examined the reactions of α,β-unsaturated aldehydes. These lead to isolable π-complexes as kinetic products which, upon thermolysis, undergo subsequent C−H bond activation and migratory deinsertion to give thermodynamically more stable (carbonyl)(vinyl)iridium complexes.

In earlier studies, we showed that the iridium(III) complexes $Cp^*(PMe_3)Ir(Me)(OTf)$ (**1a**) and $[Cp^*(PMe_3)Ir(Me)(CH_2-Cl_2)][BAr_f]$ (**1b**) ($Cp^* = \eta^5\text{-}C_5Me_5$, OTf = OSO_2CF_3, BAr_f = $B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$) intermolecularly activate C−H bonds in a number of alkanes, arenes, and functionalized organic

Scheme 1
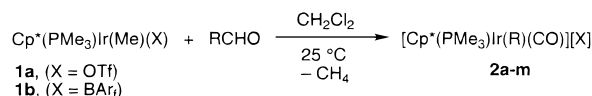
2a, R = Me, X = OTf⁻; **2b**, R = Et, X = OTf⁻; **2c**, R =*n*-Pr, X = OTf⁻; **2d**, R = *c*-Pr, X = OTf⁻; **2e**, R = *t*-Bu, X = OTf⁻; **2f**, R = *t*-Bu, X = BPh₄⁻; **2g**, R = 1-adamantyl, X = OTf⁻; **2h**, R = 1-adamantyl, X = BAr_f⁻; **2i**, R = 1-ethylpropyl, X = OTf⁻; **2j**, R = Ph, X = OTf⁻; **2k**, R = *p*-tolyl, X = OTf⁻; **2l**, R = 2,4,6-trimethylphenyl, X = OTf⁻; **2m**, R = 2-(*Z*)-1-phenylpropenyl, X = OTf⁻

compounds.[16,19−21] Here we report that reactions between **1a,b** and aldehydes (RCHO) occur rapidly with decarbonylation at room temperature to produce methane and iridium salts of the general formula $[Cp^*(PMe_3)Ir(R)(CO)][X]$ (**2a−e, g−m**) (X = OTf, BAr_f) (Scheme 1). In spite of the fact that these reactions usually occur within minutes at 25 °C and in most cases at reasonable rates even at −60 °C, the reactions are exceptionally clean and selective. High yields (quantitative by NMR; 63−87% following two recrystallizations) are obtained with a variety of aldehydes, and no evidence for attack of Ir at any hydrogen other than that attached to the carbonyl carbon atom is observed. Most unusual is the fact that even when the alkyl group is tertiary or highly hindered, the reaction still proceeds cleanly to the metal alkyl (or aryl) product **2**. Such selectivity for the aldehyde C-H bond has been observed in other decarbonylation systems.[22−24]

Following anion metathesis of **2e** to form **2f**, single-crystal X-ray diffraction studies were performed on tertiary alkyl complexes **2f** and **2h**. The structures of **2f** and **2h** clearly show the proposed formulation; however, both were plagued by severe disorder, resulting in geometric data that should be considered with care. For this reason, a single-crystal X-ray diffraction study was performed on mesityl carbonyl complex **2l**. Although this too was successfully modeled with 5% disorder in the cation, these data are significantly more reliable than the other two structures. ORTEP diagrams of each of these cations are illustrated in Figure 1 and full crystallographic data may be obtained from the Supporting Information.

The ³¹P{¹H} NMR chemical shifts of complexes **2a−m** in CD_2Cl_2 depend to some extent upon the nature of the group coordinated to the metal. They appear at about −34 ppm except for bulky R groups (e.g., 2,4,6-trimethylphenyl, 1-adamantyl, *tert*-butyl). For complexes containing such sterically demanding ligands, the ³¹P{¹H} NMR shifts appear further upfield (ca. −45 ppm). The terminal carbonyl stretching frequencies vary little in these compounds, appearing between 1997 and 2035 cm⁻¹, typical for late transition metal η^1-carbonyl complexes.[25] Full spectroscopic data are consistent with the formulations given.

Treatment of methyl triflate complex **1a** with α,β-unsaturated aldehydes was explored to determine whether π-coordination of the double bond is competitive with activation of the aldehydic C−H bond. Reaction of **1a** with α-methylcinnamaldehyde, $((E)\text{-PhC(H)}=\text{C(Me)CHO})$, once again leads to decarbonylation of the organic reactant, affording the vinyl carbonyl complex $[Cp^*Ir(PMe_3)(CO)(2\text{-}(Z)\text{-}1\text{-phenylpropenyl})]$-$[OTf]$ **2m**. However, upon treatment of **1a** with acrolein

(1) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512−2514.
(2) Kruse, W. *J. Organomet. Chem.* **1972**, *42*, C39−C42.
(3) Gill, D. F.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1972**, 65−66.
(4) Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600−4601.
(5) Noth, H.; Schmidt, M. *Organometallics* **1995**, *14*, 4601−4610.
(6) Bougeard, P.; McCullough, J. J.; Sayer, B. G.; McGlinchey, M. J. *Inorg. Chim. Acta* **1984**, *89*, 133−138.
(7) Girolami, G. S.; Howard, C. G.; Wilkinson, G.; Dawes, H. M.; Thornton-Pett, M.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 921−929.
(8) Giering, W. P.; Rosenblum, M. *J. Organomet. Chem.* **1970**, *25*, C71−C73.
(9) Schumann, H.; Jeske, G. Z. *Naturforsch. B: Chem. Sci.* **1985**, 1490−1494.
(10) Ogoshi, H.; Watanabe, E.; Koketsu, N.; Yoshida, Z. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2529−2536. (b) A referee has emphasized that some of these are quite stable; see ref 1.
(11) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Summers, M. F.; J. H. Ramsden, J.; Marzilli, P. A.; Marzilli, L. G. *Organometallics* **1985**, *4*, 2086−2090.
(12) Giese, B.; Hartung, J.; Kesselheim, C.; Lindner, H. J.; Svoboda, I. *Chem. Ber.* **1993**, *126*, 1193−1200.
(13) Eckert, H.; Lenoir, D.; Ugi, I. *J. Organomet. Chem.* **1977**, *141*, C23−C27.
(14) Jensen, F. R.; Buchanan, D. H. *J. Chem. Soc., Chem. Commun.* **1973**, 153−154.
(15) Our group prepared a tertiary cubyliridium species, but did not isolate it: Sponsler, M. B.; Weiller, B. H.; Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 6841−6843.
(16) Luecke, H. F.; Arndtsen, B. A.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2517−2518.
(17) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240−4242.
(18) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352−354.
(19) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162.
(20) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462−10463.
(21) Arndtsen, B. A.; Bergman, R. G. *J. Organomet. Chem.* **1995**, *504*, 143−146.
(22) Abu-Hasanayn, F.; Goldman, M. E.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 2520−2524.
(23) Gomez, M.; Kisenyi, J. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *296*, 197−207.
(24) Lehmkuhl, H.; Schwickardi, R.; Mehler, G.; Kruger, C.; Goddard, R. Z. *Anorg. Allg. Chem.* **1991**, *606*, 141−155.
(25) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; pp 768−775.
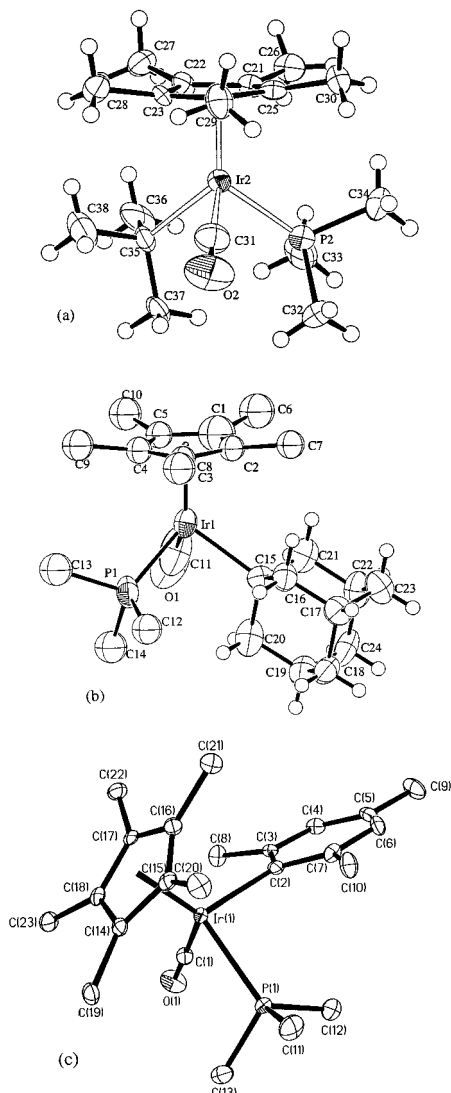
Figure 1. ORTEP diagrams of (a) [Cp*(PMe3)Ir(tBu)(CO)][BPh₄] **2f**, (b) [Cp*(PMe3)Ir(1-adamantyl)(CO)][BAr$_f$] **2h**, (c) [Cp*(PMe3)Ir-(mesityl)(CO)][OTf] **2l** showing the major component in each.

Scheme 2
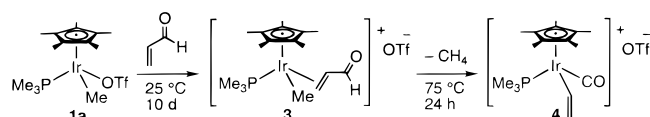
(CH₂=CHCHO), slow reaction over 10 days at room temperature results in formation of π-complex **3**, which is easily isolated in 63% yield (Scheme 2). A new aldehyde proton resonance for this species is seen at 8.23 ppm (cf. 9.55 ppm in free acrolein), which appears as a broad doublet, as it is coupled both to the α-proton of acrolein and to the ^{31}P nucleus on the iridium center. Also indicative of the structure illustrated for **3** is the ^{1}H NMR resonance for the iridium-bound methyl group which appears as a doublet ($^3J_{PH}$ = 6.4 Hz) at 0.81 ppm (cf. 0.92 ppm in **1a**) indicating that loss of methane has not occurred. The difference between these two reactions is presumably due to the reduced steric hindrance about the C−C double bond of acrolein compared to that in α-methylcinnamaldehyde, resulting in the observed competition between alkene coordination and C−H activation. The π-complex **3** is found to be the kinetic product of the reaction, as subsequent thermolysis in CH₂Cl₂ (75 °C, 24 h) affords the expected vinyl carbonyl product **4** (Scheme 2) in 57% isolated yield. It is possible, therefore, that the π-complex is also formed with α-methylcinnamaldehyde,

Scheme 3
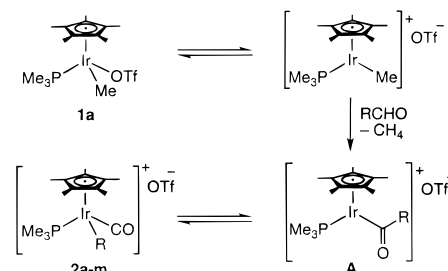
but in that case may rearrange more rapidly to the C−H activation product. The reaction with acrolein is the first case in our Ir(III) C−H activation systems in which we have observed formation of an adduct that continues on to a C−H activation product.

We believe that formation of complexes **2a**−**m** proceeds by initial C−H activation of the aldehydic proton to afford acyl intermediate Cp*(PMe₃)Ir(COR)(OTf) (complex **A** in Scheme 3). This may occur by oxidative addition to give an iridium-(V) intermediate, followed by reductive elimination of methane.[26] Iridium(V) compounds are not common, but a few have been isolated including (Cp*)Ir(H)₂(SiEt₃)₂[27] and (Cp*)Ir(Me)₄[28] synthesized by Maitlis and co-workers, which are surprisingly stable, lending credence to the intervention of an intermediate of this type. The reaction could alternatively occur by σ-bond metathesis between the iridium−methyl and the aldehydic C−H bonds, giving the same acyl intermediate **A**, as is common in many early transition metal d⁰ systems.[29] Demonstrating that the aldehydic proton is indeed the one being activated, reaction between **1a** and [1-D₁]acetaldehyde results in quantitative production of CH₃D and no detectable CH₄ by ^{1}H NMR spectroscopy.[30] Rearrangement of **A** by carbonyl migratory deinsertion would give observed products **2a**−**m**.

In conclusion, we have found a mild route to a variety of cationic alkyl and aryl carbonyl complexes of iridium by the C−H bond activation of aldehydes. This reaction demonstrates a high degree of selectivity for the aldehydic C−H bond and allows the formation of complexes having stable bonds between a metal and several extremely sterically demanding alkyl and aryl ligands. While most aldehydes react immediately to form products **2**, the reaction with acrolein provides us with an example of a substrate that first coordinates to the cationic iridium starting material and subsequently undergoes C−H activation.

Supporting Information Available: Spectroscopic and analytical data for complexes **2a**−**m**, **3**, and **4** and X-ray structural data for **2f**, **2h**, and **2l** (44 pages). See any current masthead page for ordering and Internet access instructions.

JA970245K

(26) Strout, D. L.; Zaric, S.; Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 6068−6069.

(27) Fernandez, M.-J.; Maitlis, P. M. *Organometallics* **1983**, *2*, 164−165.

(28) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 808−809.

(29) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley and Sons: New York, 1989.

(30) This experiment demonstrates that these reactions do *not* proceed by a so-called "dissociative" reaction involving initial cyclometallation in solution, cf.: Hinderling, C.; Plattner, D. A.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 243−244.