

Preliminary communication

C–H bond activation in functionalized organic compounds with $\text{Cp}^*(\text{PMe}_3)\text{IrMe}(\text{OTf})$: generation, structural characterization and metal-based rearrangement of the acetone activation product $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{OH})\text{CH}_2)^+\text{OTf}^-$

Bruce A. Arndtsen, Robert G. Bergman*

Chemical Sciences Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, CA 94720, USA

Received 6 February 1995; in revised form 2 April 1995

Abstract

The iridium complex $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Me})\text{OTf}$ (**1**) ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$, $\text{OTf} = \text{OSO}_2\text{CF}_3$) reacts cleanly with acetone at room temperature. This reaction results in overall double C–H activation, generating the cationic η^3 -hydroxyallyl complex $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{OH})\text{CH}_2)^+\text{OTf}^-$ (**2**). Complex **2** was characterized by X-ray diffraction and found to contain a hydrogen-bonded triflate anion. The ultimate product formed on reaction with acetone is strongly dependent upon the nature of the counterion present. Replacement of the triflate ion in **2** with other anions leads to the metallacyclobutanone $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^2\text{-CH}_2\text{COCH}_2)$, the η^1 -enolate $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_2\text{COCH}_3)\text{S}(p\text{-tolyl})$ and the free cation salt $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{OH})\text{CH}_2)^+ \text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4^-$.

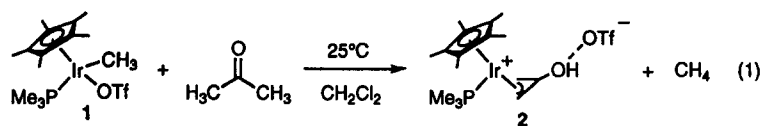
Keywords: Iridium; C–H activation; Metallacycles

Carbon–hydrogen (C–H) bond activation research during the past decade has demonstrated two general processes by which certain transition metal complexes can effect the stoichiometric cleavage of carbon–hydrogen bonds [1–4]. The first involves the oxidative addition of the C–H bond to an unsaturated metal fragment, and is typical of electron-rich late metal systems [5–13]. The second takes place by a 1,2-R–H addition, in which the C–H bond adds across a highly electrophilic d^0 metal M–X bond [14–24]. This dichotomy has led to significant limitations in the scope and chemistry of transition-metal based C–H bond activation. The late metal complexes are often highly reactive, thereby generating complicated mixtures when different types of C–H bond are present in a reacting molecule. Also, the coordinatively saturated products are generally resistant to subsequent reactions and/or rearrangements designed to transform the C–H activated complex into a functionalized organic compound [25–27]. Conversely,

while the σ -bond metathesis systems do generally demonstrate significant bond selectivities (e.g. primary $\gg$ secondary, tertiary) and contain an empty coordination site, the oxophilic metals that typify these complexes are often not compatible with common organic functional groups.

We recently reported that the iridium complex $\text{Cp}^*(\text{PMe}_3)\text{IrMe}(\text{OTf})$ (**1**) ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$, $\text{OTf} = \text{OSO}_2\text{CF}_3$) reacts at ambient temperature with alkanes and arenes R–H to generate methane and the corresponding Ir–R complexes [28]. In contrast to typical bond activations with electron-rich metal fragments, these reactions are relatively mild, requiring neither photolysis nor elevated temperature, and are highly selective for methane primary and/or arene C–H bonds. In addition, the electron-rich metal center appears to be compatible with heteroatom-containing functional groups, allowing the use of methylene chloride as a solvent for these reactions. In an effort to extend the generality of this unusual and selective σ -bond metathesis-like chemistry, we have begun to explore the activation of C–H bonds in organic substrates containing functional groups. Herein we report the clean reaction

* Corresponding author.



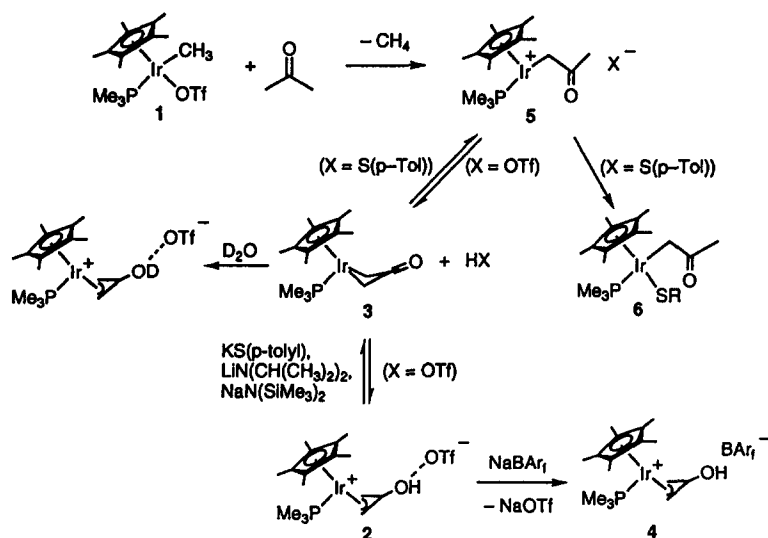
of **1** with a carbonyl-containing substrate, acetone, to generate an η^3 -2-hydroxyallyl iridium complex, as well as its subsequent anion-dependent rearrangement.

The addition of acetone to a methylene chloride solution of **1** at 25 °C leads to gradual lightening of the reaction mixture over the course of 1 day. Examination of the solution by ^1H NMR spectrometry (CD_2Cl_2) reveals the formation of methane and a new iridium-containing product in essentially quantitative yield by NMR. This complex displays one set of Cp^* (δ 1.87 (d, 15H, $J_{\text{P-H}} = 1.9$ Hz)) and PMe_3 (δ 1.39 (d, 9H, $J_{\text{P-H}} = 9.7$ Hz)) signals [29]. However, rather than the methylene and methyl resonances that might be expected for the simple C–H activated product, two sets of doublets were observed [δ 3.26 (dd, 2H, $J_{\text{P-H}} = 1.2$ Hz, $J_{\text{H-H}} = 5.0$ Hz), δ 1.73 (dd, 2H, $J_{\text{P-H}} = 16.0$ Hz, $J_{\text{H-H}} = 5.0$ Hz)], as well as a broad singlet at δ 8.36 (s, 1H). This pattern is consistent with the presence of an η^3 -hydroxyallyl fragment, and is similar to that reported for other transition metal hydroxyallyl complexes [30–33]. The ^{13}C NMR spectrum is also consistent with the presence of a symmetrical allyl-type fragment, showing resonances only for the terminal [δ 8.95 (s)] and internal [δ 130.6 (d, $J_{\text{P-C}} = 3.5$ Hz)] carbons. Based on these data, **2** can be formulated as a cationic η^3 -hydroxyallyl iridium complex as depicted in Eq. (1).

Complex **2** was isolated in 93% yield by precipitation from CH_2Cl_2 with hexane as light yellow crystals, and its formulation as a cationic π -hydroxyallyl com-

plex was confirmed by X-ray diffraction [34]. As shown in the ORTEP diagram (Fig. 1), the complex has a pseudo-three-legged piano stool geometry about iridium with a symmetrically bound η^3 -allyl fragment (Ir–C(14, 16) 2.18 Å, Ir–C(15) 2.21 Å, sum of angles about C(15): 359°) oriented exo to the Cp^* ligand. The C–O bond length (1.35 Å) in **2** is intermediate between that of a normal single and double bond. This, in conjunction with the short hydroxide–triflate bond length (O(1)–O(11) 2.69 Å), suggests hydrogen bonding in **2** that makes it intermediate between a cationic p -allyl complex and metallacyclobutanone (**3**). The IR spectrum of **2** supports this formulation, with a broadened O–H stretching absorption that is shifted into the hydrogen bonding region (3175 cm^{-1}). The hydrogen-bonded complex **2** can be converted completely to the cationic η^3 -hydroxyallyl complex **4** by replacement of the triflate with the non-interacting tetraarylborate anion [$\text{B}(\text{3,5-C}_6\text{H}_3(\text{CF}_3)_2)_4$] $^-$ [35]. The spectroscopic data for **4** are similar to those of **2**, except for a shift in the ^1H NMR hydroxide resonance upfield to 4.13 ppm and a distinct sharpening and shifting of the O–H IR stretch (3553 cm^{-1}).

In analogy to the chemistry of **1** with alkanes, we propose that a critical step in the formation of **2** is the activation of the C–H bond of acetone to eliminate methane and generate a new Ir–C bond, followed by an intramolecular rearrangement to activate the second C–H bond (Scheme 1) [36]. Information about the



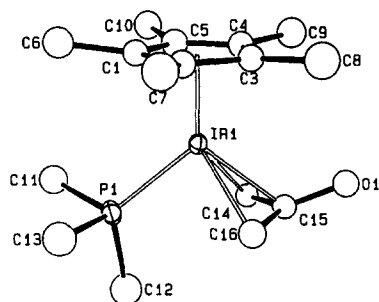


Fig. 1. ORTEP diagram of complex **2** (triflate counterion removed for clarity). Selected bond lengths and angles: Ir–P(1): 2.287 (3) Å; Ir–Cp: 1.872 Å; Ir–C(14): 2.176 (12) Å; Ir–C(15): 2.207 (11) Å; Ir–C(16): 2.187 (12) Å; C(15)–O(1): 1.353 (13) Å; C(14)–C(15): 1.440 (16) Å; C(15)–C(16): 1.432 (16) Å; O(1)–O(triflate): 2.694 (12) Å; P(1)–Ir–C(14): 89.4 (3)°; P(1)–Ir–C(15): 104.9 (3)°; P(1)–Ir–C(16): 86.0 (3)°; C(14)–C(15)–C(16): 118.3 (10)°; O(1)–C(15)–C(14): 122.3 (10)°; O(1)–C(15)–C(16): 118.3 (10)°.

nature of these intermediates as well as their potential interconversion was obtained from reactivity studies on **2**. Addition of D₂O to **2** results in immediate deuteration of the hydroxide but not the allyl C–H bonds. This suggests rapid equilibration between **2** and the metallacyclobutanone structure **3** and triflic acid, from which label can be incorporated via rapid exchange with D₂O to generate DOTf, followed by collapse to deuterated **2**. The lack of detectable deuterium in the allyl positions, even at elevated temperatures, demonstrates that reversion of **2** to **5** (product of protonation at C_α in **3**) does not occur under these conditions.

This equilibrium between **2** and metallacyclobutanone **3** can be shifted by replacement of triflate with more basic anions. Thus, addition of LiN(CH(CH₃)₂)₂ or NaN(Si(CH₃)₃)₂ to a THF solution of **2** results in the immediate generation of amine as well as **3** in 85% isolated yield. Spectroscopic data are consistent with the formulation of **3** as a metallacyclobutanone, as shown in Scheme 1 [37]. Notably, the IR shows the disappearance of an O–H stretch and generation of an organic carbonyl $\nu(\text{CO})$ at 1573 cm^{−1}, and ¹³C NMR analysis reveals a signal at 171.5 ppm for this carbon.

Metallacyclobutanone **3** can also be prepared by addition of potassium thiolate to **2**, but in this case the ketone appears to be only an intermediate along the pathway to non-chelated products. Thus, treatment of **2** with KS(*p*-tolyl) in CH₂Cl₂ leads to the quantitative formation of **3** and (*p*-tolyl)SH, which reacts over the course of 1 day at 25 °C to generate the η^1 -enolate complex Cp*(PMe₃)Ir(CH₂COCH₃)(STol) **6** in 40% yield by NMR. Complex **6** cannot be formed sufficiently cleanly to allow isolation because secondary reaction with thiol liberates acetone and generates the bis-thiolate Cp*(PMe₃)Ir(STol)₂ [38]; nevertheless its formulation as an η^1 -enolate was confirmed by spectral data [39].

The generation of metallacyclobutanone **3** and η^1 -enolate **6** from **2** demonstrates the strong dependence of

the stable iridium–enolate isomers upon the coordinative ability of the anion, and also illustrates (based upon microscopic reversibility) the potential mechanism by which hydroxyallyl complex **2** is formed. Initial C–H activation of acetone by **1** would generate the triflate salt of **5**, whose weak Lewis and proton basicities facilitate conversion to complex **2**. Both amide and thiolate anions convert **2** to metallacyclobutanone **3**, and with thiol a slower secondary reaction proceeds to protonate at C_α and generate **5**, which can then be trapped by the strongly coordinating thiolate anion. This reaction of HSTol at C_α in **3** differs significantly from the deuterium incorporation solely at oxygen with D₂O, which presumably occurs via deuteration of **3** by D₃O⁺ OTf[−], and suggests the nature of counterion X[−] may influence the kinetic as well as thermodynamic characteristics of these isomerizations [40].

In conclusion, we have demonstrated that **1** reacts rapidly with acetone, leading to the hydrogen-bonded η^3 -hydroxyallyl complex **2**. To our knowledge this generation of a π -allyl complex directly from acetone is unique among transition metal complexes, and demonstrates the unusual ability of **1** to undergo σ -bond metathesis with the C–H bonds of functionalized organic substrates. In addition to cleavage of the C–H bond, the empty coordination site on the iridium center formed by ionization provides a site for rearrangement of the activated fragment, and depending upon the anion allows the formation of η^1 -enolate, metallacyclobutanone and cationic π -allyl complexes. Examination of the reaction of **1** with other functionalized organic substrates, as well as their subsequent metal-based rearrangements, is currently under way.

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-7600098. The structural study of **2** was carried out by Dr. F.J. Hollander, director of the U.C. Berkeley X-ray diffraction facility (CHEXRAY).

References and notes

- [1] For reviews of metal mediated C–H activation see Refs. 2–4.
- [2] C.L. Hill, *Activation and Functionalization of Alkanes*, John Wiley, New York, 1989.
- [3] A.E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Boston, 1984.
- [4] J.A. Davies, P.L. Watson, J.F. Liebman and A. Greenberg, *Selective Hydrocarbon Activation*, VCH, Toledo, 1990.
- [5] A.H. Janowicz and R.G. Bergman, *J. Am. Chem. Soc.*, **104** (1982) 352.

- [6] A.H. Janowicz and R.G. Bergman, *J. Am. Chem. Soc.*, **105** (1983) 3929.
- [7] R.G. Bergman, P.F. Seidler and T.T. Wenzel, *J. Am. Chem. Soc.*, **107** (1985) 4358.
- [8] J.K. Hoyano and W.A.G. Graham, *J. Am. Chem. Soc.*, **104** (1982) 3723.
- [9] J.K. Hoyano, A.D. McMaster and W.A.G. Graham, *J. Am. Chem. Soc.*, **105** (1983) 7190.
- [10] W.A. Kiel, R.G. Ball and W.A.G. Graham, *J. Organomet. Chem.*, **383** (1990) 481.
- [11] W.D. Jones and F.J. Feher, *J. Am. Chem. Soc.*, **106** (1984) 1650.
- [12] M. Hackett, J.A. Ibers and G.M. Whitesides, *J. Am. Chem. Soc.*, **110** (1988) 1436.
- [13] T. Gregory, P. Harper, R.S. Shinomoto, M.A. Deming and T.C. Flood, *J. Am. Chem. Soc.*, **110** (1988) 7915.
- [14] P.L. Watson, *J. Am. Chem. Soc.*, **105** (1983) 6491.
- [15] P.L. Watson, *J. Chem. Soc., Chem. Commun.* (1983) 276.
- [16] P.L. Watson and G.W. Parshall, *Acc. Chem. Res.*, **18** (1985) 51.
- [17] M.E. Thompson and J.E. Bercaw, *Pure Appl. Chem.*, **56** (1984) 1.
- [18] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, *J. Am. Chem. Soc.*, **109** (1987) 203.
- [19] C.M. Fendrick and T.J. Marks, *J. Am. Chem. Soc.*, **108** (1986) 425.
- [20] J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz and J.M. Williams, *J. Am. Chem. Soc.*, **110** (1986) 8731.
- [21] C.C. Cummins, S.M. Baxter and P.T. Wolczanski, *J. Am. Chem. Soc.*, **110** (1988) 8731.
- [22] J.L. Bennett and P.T. Wolczanski, *J. Am. Chem. Soc.*, **116** (1994) 2179.
- [23] C.P. Schaller and P.T. Wolczanski, *Inorg. Chem.*, **32** (1993) 131.
- [24] J. de With and A.D. Horton, *Angew. Chem. Int. Ed. Engl.*, **32** (1993) 903.
- [25] A few examples of stoichiometric functionalizations with late metal C–H activation have been observed; see Refs. [6,26,27].
- [26] R.A. Periana and R.G. Bergman, *Organometallics*, **3** (1984) 508.
- [27] M.V. Baker and L.D. Field, *J. Am. Chem. Soc.*, **109** (1987) 2825.
- [28] P. Burger and R.G. Bergman, *J. Am. Chem. Soc.*, **115** (1993) 10462.
- [29] Spectral data for complex 2: ^1H NMR (CD_2Cl_2) δ 8.95 (s) OH, d 3.26 (dd, $^3J_{\text{P-H}} = 1.2$ Hz, $^2J_{\text{H-H}} = 5.0$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 1.87 (d, $^3J_{\text{P-H}} = 1.9$ Hz) $\text{C}_5(\text{CH}_3)_5$, δ 1.73 (dd, $^3J_{\text{P-H}} = 16.0$ Hz, $^2J_{\text{H-H}} = 5.0$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 1.39 (d, $^2J_{\text{P-H}} = 9.7$ Hz) $\text{P}(\text{CH}_3)_3$; ^{13}C NMR (CD_2Cl_2): δ 130.6 (d, $^2J_{\text{P-C}} = 3.5$ Hz) C–OH, δ 96.2 (d, $^2J_{\text{P-C}} = 3.0$ Hz) C_5Me_5 , δ 22.2 (d, $^2J_{\text{P-C}} = 4.2$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 15.0 (d, $^1J_{\text{P-C}} = 39.8$ Hz) $\text{P}(\text{CH}_3)_3$, δ 8.9 (s) $\text{C}_5(\text{CH}_3)_5$; ^{31}P NMR (CD_2Cl_2): δ –36.03 (s) PMe_3 ; ^{19}F NMR (CD_2Cl_2): δ 77.6 (s) OSO_2CF_3 ; IR (CH_2Cl_2) $\nu_{\text{OH}} = 3175\text{ cm}^{-1}$; Anal. Calc. for $\text{C}_{17}\text{H}_{29}\text{F}_3\text{IrO}_4\text{PS}$: C, 33.49; H, 4.79%; Found: C, 33.66; H, 4.68%.
- [30] For examples of metal–hydroxyallyl complexes see Refs. [33–35].
- [31] T.-M. Huang, R.-H. Hsu, C.-S. Yang, J.-T. Chen, G.-H. Lee and Y. Wang, *Organometallics*, **13** (1994) 3657.
- [32] K. Oda, N. Yasuoka, T. Ueki, N. Kasai and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **43** (1970) 362.
- [33] A. Ohsuka, T. Fujimori, T. Hirao, H. Kurosawa and I. Ikeda, *J. Chem. Soc., Chem. Commun.* (1993) 1039.
- [34] Crystal data for 2. $\text{C}_{17}\text{H}_{29}\text{IrSPF}_3\text{O}_2$, Formula weight = 609.7. Crystal parameters at $t = -90^\circ\text{C}$: $a = 12.68(2)$, $b = 13.448(2)$, $c = 14.670(2)$ Å, $\alpha = 64.254(12)$, $\beta = 88.226(13)$, $\gamma = 73.729(14)^\circ$, $V = 2149.0(5)$ Å³; space group: $P-1$, $Z = 4$, $d_c = 1.88\text{ g cm}^{-3}$, $\mu_c = 64.0\text{ cm}^{-1}$; crystal dimensions: $0.20 \times 0.25 \times 0.25\text{ mm}^3$. Data measurement parameters: radiation: Mo K α ($\lambda = 0.71073$ Å); monochromator: highly-oriented graphite ($2\theta = 12.2^\circ$); diffractometer: Enraf–Nonius CAD-4; reflections measured: +H, +/–K, +/–L; 2θ range: $3\text{--}45^\circ$; scan type: theta–2theta; scan width: $\Delta\theta = 0.65 + 0.35 \tan\theta$; scan speed: 5.49 (θ , deg min^{-1}); background: measured over 0.25° ($\Delta\theta$) added to each end of the scan; Vert: aperture = 4.0 mm ; Horiz: aperture = $2.0 + 1.0 \tan\theta\text{ mm}$; reflections collected: 5613. Data reduction and refinement: structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. reflections with $F^2 > 3\sigma(F^2)$: 4674; atoms in least-squares: 54, $R = 4.4\%$, $wR = 5.4\%$.
- [35] Spectral data for complex 4: ^1H NMR (CD_2Cl_2): δ 7.73 (s) *ortho*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$, δ 7.58 (s) *para*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$, δ 4.13 (s) OH, δ 3.08 (dd, $^3J_{\text{P-H}} = 1.5$ Hz, $^2J_{\text{H-H}} = 6.7$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 1.85 (d, $^3J_{\text{P-H}} = 1.9$ Hz) $\text{C}_5(\text{CH}_3)_5$, δ 1.81 (dd, $^3J_{\text{P-H}} = 11.4$ Hz, $^2J_{\text{H-H}} = 1.4$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 1.36 (d, $^2J_{\text{P-H}} = 9.7$ Hz) $\text{P}(\text{CH}_3)_3$; ^{13}C NMR (CD_2Cl_2): δ 162.1 (q, $^1J_{\text{B-C}} = 50.0$ Hz) B–C, δ 135.2 (s) *ortho*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$, δ 129.3 (q, $^2J_{\text{F-C}} = 29.7$ Hz) *meta*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$, δ 125.1 (q, $^1J_{\text{F-C}} = 29.7$ Hz) $\text{C}_6\text{H}_3(\text{CF}_3)_2$, δ 117.9 (qq, $^3J_{\text{F-C}} = 4.0$ Hz) *para*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$, δ 126.1 (d, $^2J_{\text{P-C}} = 3.0$ Hz) C–OH, δ 91.8 (s) C_5Me_5 , δ 23.3 (d, $^2J_{\text{P-C}} = 4.0$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 15.2 (d, $^1J_{\text{P-C}} = 40.1$ Hz) $\text{P}(\text{CH}_3)_3$, δ 9.2 (s) $\text{C}_5(\text{CH}_3)_5$; ^{31}P NMR (CD_2Cl_2): δ –35.04 (s) PMe_3 ; ^{19}F NMR (CD_2Cl_2): δ 61.9 (s) $\text{C}_6\text{H}_3(\text{CF}_3)_2$; IR (CH_2Cl_2) $\nu_{\text{OH}} = 3553\text{ cm}^{-1}$; Anal. Calc. for $\text{C}_{48}\text{H}_{41}\text{BF}_{24}\text{IrOP}$: C43.55; H, 3.12%; Found: C, 43.69; H, 3.07%.
- [36] While the details of the mechanism for C–H bond activation with 1 have not been determined, preliminary kinetic and reactivity data suggest that the 16-electron cation $\text{Cp}^+(\text{PMe}_3)\text{IrMe}^+$ is the reactive substrate: B.A. Arndtsen and R.G. Bergman, unpublished results.
- [37] Spectral data for complex 3: ^1H NMR (CD_2Cl_2): δ 2.37 (d, $^2J_{\text{H-H}} = 5.7$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 1.75 (d, $^3J_{\text{P-H}} = 1.9$ Hz) $\text{C}_5(\text{CH}_3)_5$, δ 1.65 (dd, $^3J_{\text{P-H}} = 15.1$ Hz, $^2J_{\text{H-H}} = 5.0$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 1.35 (d, $^2J_{\text{P-H}} = 9.7$ Hz) $\text{P}(\text{CH}_3)_3$; ^{13}C NMR (CD_2Cl_2): δ 171.5 (s) C–OH, δ 92.5 (d, $^2J_{\text{P-C}} = 3.5$ Hz) C_5Me_5 , δ 18.0 (d, $^2J_{\text{P-C}} = 4.0$ Hz) $\text{CH}_2\text{C}(\text{OH})\text{CH}_2$, δ 15.9 (d, $^1J_{\text{P-C}} = 37.4$ Hz) $\text{P}(\text{CH}_3)_3$, δ 8.9 (s) $\text{C}_5(\text{CH}_3)_5$; ^{31}P NMR (CD_2Cl_2): δ –38.79 (s) PMe_3 ; IR (CH_2Cl_2) $\nu_{\text{CO}} = 1573\text{ cm}^{-1}$.
- [38] Addition of excess *p*-thiocresol to 3 results in the generation of bis-thiolate $\text{Cp}^+(\text{PMe}_3)\text{Ir}(\text{Stol})_2$ and acetone in 76% and 62% NMR yields, respectively.
- [39] Spectral data for complex 6: ^1H NMR (CD_2Cl_2): δ 7.45 (d, 5.0 Hz) *meta*- $\text{C}_6\text{H}_4(\text{CH}_3)$, δ 7.19 (d, 5.0 Hz) *ortho*- $\text{C}_6\text{H}_4(\text{CH}_3)$, δ 2.75 (dd, $^2J_{\text{H-H}} = 7.1$ Hz, $^3J_{\text{P-H}} = 8.1$ Hz) CH_2COCH_3 , δ 2.35 (s) $\text{C}_6\text{H}_4(\text{CH}_3)$, δ 1.89 (s) CH_2COCH_3 , δ 1.64 (d, $^3J_{\text{P-H}} = 1.9$ Hz) $\text{C}_5(\text{CH}_3)_5$, δ 1.52 (d, $^2J_{\text{P-H}} = 10.5$ Hz) $\text{P}(\text{CH}_3)_3$.
- [40] This kinetic barrier to deuteration of complex 3 ($\text{X} = \text{OTf}$) at C_α should theoretically be surmountable at elevated temperatures; however, 2 + D_2O decomposes over time above 75°C .