Cyclopentadienyl Complexes of Ir(III) For Attempted C-H Bond Activation

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Dedication ((optional))

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**Abstract:** The complexes Cp(MeIm)IrI2 and CpMe4(MeIm)IrCl2 have been prepared and subsequently methylated to form Cp(MeIm)IrMe2 and CpMe4(MeIm)IrMe2. (Cp = η5-C5H5 , CpMe4 = η5-C5HMe4, MeIm = 1,3-dimethylimidazol–2–ylidene). Protonation with one equivalent of weak acid such as 2,6-dimethylpyridinium chloride affords methane and the Ir(III) methyl chloride complexes. 1H NMR experiments show addition of pyridinium [BArF20]- (BArF20 = [B(C6F5)4]- to the dimethyl species forms [Cp(MeIm)IrMe(py)]+[BArF20]- (py = pyridine) or [CpMe4(MeIm)IrMe(py)]+[BArF20]- respectively alongside methane, while use of the [BArF20]- salts of more bulky 2,6-dimethylpyridinium, and 2,6-bis(*tert*-butyl)pyridinium gave an intractable mixture. Likewise, generation of 16e- species [CpMe4(MeIm)IrMe]+[BArF20]- or [Cp(MeIm)IrMe]+[BArF20]- at low temperature using 2,6-dimethylpyridinium or 2,6-bis(*tert-*butyl)pyridinium in thawing C6D6 or toluene*d8* formed an intractable mixture and did not lead to C-D bond activation. X-ray structures of several Ir(III) complexes show similar sterics as that found for the previously reported Cp\* analogue.

Introduction

Methane represents a large potential resource for the synthesis of higher value liquids such as methanol, which is currently made indirectly via syngas.[1] A practical process for the direct catalytic oxidation of methane to methanol has yet to be realized, despite a great deal of research having been focused on homogenous catalysis in the hope that insight can be gained to better design an industrially applicable heterogenous catalyst. Most attention has been directed towards soluble complexes of platinum,[2–12] with iridium complexes receiving less attention. An iridium system reported to functionalize methane to form methyltrifluoroacetate utilizes an iridium(III) pincer complex and the oxidants MIO4 or MIO3 (M = Na, K).[13] This system cannot utilize O2 as the oxidant, nor is it as efficient as previously reported catalysts of Pt[14] and Pd.[15–17]

A catalyst capable of oxidizing alkanes utilizing O2 as the oxidant is desired, but this is a challenging problem. Bergman and coworkers demonstrated that [Cp\*Ir(PMe3)Me(CH2Cl2)]+(Cp\* = η5-C5Me5) reacts with alkane C–H bonds, including methane, under mild conditions,[18] but this system is unsuitable for oxidative functionalization as the phosphine ligand is incompatible with oxidative conditions.

Preparation of an analog to Bergman’s system where an N-heterocyclic carbene (NHC) ligand was used in place of the PMe3 ligand was undertaken reasoning the former would be more tolerant of oxidative conditions. Abstraction of a methyl group from Cp\*(MeIm)IrMe2 (MeIm = 1,3-dimethylimidazol-2-ylidine) using B(C6F5)3 in the presence of C6H6 or C6H5F resulted in formation of methane and new Ir-Ar species (Ar = C6H5, C6H4F), though the observed C-H bond activation by was quite sluggish. DFT calculations attributed this outcome to a sterically congested Ir(V) intermediate.[19] This result lead us to explore the chemistry of analogous compounds supported by the Cp and CpMe4 ligands. We hypothesized that reduction in the steric demands of the cyclopentadienyl moiety would relieve the steric congestion of a hypothetical Ir(V) intermediate identified by DFT calculations, resulting in greater reactivity towards C-H bonds than observed with [Cp\*(MeIm)IrMe(solv)]+.

Results and Discussion

Air stable Cp(MeIm)IrI2 (**1**) was prepared by reaction of (MeIm)Ag-I in CH2Cl2 with polymeric (CpIrI2)n as previously reported for Cp(PMe3)IrI2 to give Cp(MeIm)IrI2 in 76.5% yield.[20] The 1H NMR spectrum of this material reveals three resonances in CD2Cl2 at 7.02, 5.54, and 4.00 ppm integrating for a ratio of 2:5:6 consistent with the formulation Cp(MeIm)IrI2. (Figure S1). The 1H signals at 7.02 and 4.00 ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety while that at 5.54 ppm is ascribed to the cyclopentadienyl moiety. The 13C{1H} NMR reveals four resonances at 144.40, 123.93, 80.18, and 44.51 ppm ascribed to the carbenic, imidazolylidene backbone, cyclopentadienyl, and imidazolylidene N-methyl positions respectively. Single crystals of **1** were grown from slow vapor diffusion of pentane into a CH2Cl2 solution to provide red-orange blocks suitable for XRD analysis. The solid-state structure reveals Ir in a piano-stool geometry (Figure S25) Examination of the crystal structure shows bond distances for the Ir(1)-C(6), Ir(1)-I(1) and Ir(1)-I(2) bonds of 2.036(5)Å, 2.7260(4)Å, and 2.7221(4)Å and distortion about the “legs” from idealized 90° as exemplified by the C(6)-Ir(1)-I(1), C(6)-Ir(1)-I(2), and I(1)-Ir(1)-I(2) bond angles of 97.00(14)° 96.05(14) ° and 86.44(11) ° respectively.

**Scheme 1.** Preparation of complexes **3**-**8** reported in this study.



Methylation of a solution of **1** in THF with methylmagnesium bromide was sluggish, requiring 36 equivalents as a 3M ethereal solution in diethyl ether to give good yields (88%) of Cp(MeIm)IrMe2 (**2**) after sublimation (Scheme 1). The 1H NMR spectrum of this material reveals four resonances in CD2Cl2 at 6.87, 4.94, 3.70 and 0.56 ppm integrating for a ratio of 2:5:6:6 consistent with the formulation Cp(MeIm)IrMe2 (Figure 1). The 1H signals at 6.87 and 3.70 ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety, that at 4.94 ppm is ascribed to the cyclopentadienyl moiety while that at 0.56 ppm is assigned to the iridium-bound methyl groups. The 13C{1H} NMR reveals five resonances at 161.96, 121.25, 80.89, 38.79, and -33.11 ppm (Figure S4). These resonances are ascribed to the carbenic, imidazolylidene backbone, cyclopentadienyl, imidazolylidene N-methyl, and iridium-bound methyl positions respectively. Reliable elemental analysis could not be obtained for this sample over multiple attempts despite exhibiting a high degree of purity by 1H NMR.

**Figure 1.** ORTEP plot of the molecular structure of complex **2** grown from slow evaporation of a pentane solution at -20 oC with thermal ellipsoids plotted at the 50% probability level. Hydrogen atoms are omitted for clarity.

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Single crystals suitable for XRD studies were grown by slow evaporation of a pentane solution at -20 °C. The solid-state structure of complex **2** shows a three–legged piano stool geometry with the Cp ligand acting as a capping group (Figure 1). Examination of the crystal structure shows bond distances for the Ir(1)-C(6), Ir(1)-C(11) and Ir(1)-C(12) bonds of 1.985(6)Å, 2.102(7)Å, and 2.121(7)Å and distortion about the “legs” from idealized 90° as exemplified by the C(6)-Ir(1)-C(11), C(6)-Ir(1)-C(12), and C(11)-Ir(1)-C(12) bond angles of 89.8(3)° 89.0(3) ° and 81.2(3) ° respectively.

Attempts to convert the dimethyl complex **2** to a cationic mono-methyl complex by reaction with B(C6F5)3 proved unsuccessful, yielding intractable mixtures under various reaction conditions by 1H NMR. In contrast, protonation with [LutH]Cl (Lut =2,6-dimethylpyridine) in CH2Cl2 cleanly formed methane and the corresponding iridium methyl chloride complex **3** in93% yield, demonstrating that protonation is a viable avenue for methyl abstraction (Scheme 1). The 1H NMR spectrum of this material reveals four resonances in CD2Cl2 at 6.93, 5.12, 3.81, and 1.35 ppm integrating for a ratio of 2:5:6:3 consistent with the formulation Cp(MeIm)Ir(Me)Cl (Figure S5). The 1H signals at 6.93 and 3.81

ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety, that at 5.12 ppm is ascribed to the cyclopentadienyl moiety while that at 1.35 ppm is assigned to the iridium-bound methyl group. The 13C{1H} NMR reveals five resonances at 155.67, 122.67, 79.44, 39.38, and -25.54 ppm (Figure S6). These resonances are ascribed to the carbenic, imidazolylidene backbone, cyclopentadienyl, imidazolylidene N-methyl, and iridium-bound methyl positions respectively. Elemental analysis was found to be consistent with the formulation C11H16N2ClIr, and single crystals suitable for XRD analysis were grown from a vapor diffusion of pentane into CH2Cl2 at -20 °C. The solid-state structure of **3** shows a three-legged piano stool geometry with the Cp ligand acting as a capping group (Figure S27.) Examination of the crystal structure shows bond distances for the Ir(1)-C(6), Ir(1)-Cl(1) and Ir(1)-C(21) bonds of 1.999(6)Å, 2.4052(14)Å, and 2.167(5)Å and distortion about the “legs” from idealized 90° as exemplified by the C(6)-Ir(1)-C(21), C(6)-Ir(1)-Cl(1), and Cl(1)-Ir(1)-C(21) bond angles of 88.1(2)° 92.43(17) ° and 81.7(3) ° respectively.

The complex [Cp(MeIm)Ir(Me)CO][BArF20] (**4**), is readily generated in CH2Cl2 at low temperature by reaction of [PyrH][BArF20]with **2** in thawing CH2Cl2 under an atmosphere of CO to give an air stable colorless solid in 91% yield (Scheme 1). The 1H NMR spectrum of this material reveals four resonances in CD2Cl2 at 7.12, 5.77, 3.69, and 1.18 ppm integrating for a ratio of 2:5:6:3 consistent with the formulation [Cp(MeIm)Ir(Me)CO]+ (Figure S7). The 1H signals at 7.12 and 3.69 ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety, that at 5.77 ppm is ascribed to the cyclopentadienyl moiety while that at 1.18 ppm is assigned to the iridium-bound methyl group. The 13C{1H} NMR reveals ten resonances, four of which are ascribed to the [BArF20]- counter-anion (Figure S8). Resonances at 165.61, 133.47, 125.14, 89.52, 40.28, and -37.10 ppm are ascribed to the carbenic, carbonyl, imidazolylidene backbone, cyclopentadienyl, imidazolylidene N-methyl, and iridium-bound methyl positions respectively. The 19F NMR of this material reveals three resonances at -167.60, -163.71, and -133.21 ppm (Figure S9) and 11B NMR reveals one resonance at -16.67 ppm (Figure S10); both of which are consistent with the [BArF20]- counter-anion. Reliable elemental analysis could not be obtained for this sample over multiple attempts because of residual pyridine that persisted through recrystallization. A vapor diffusion of pentane into a CH2Cl2 at -20 °C provided single crystals suitable for XRD analysis. The solid-state structure of **4** shows a three-legged piano stool geometry with the Cp ligand acting as a capping group (Figure S28.) Examination of the crystal structure shows bond distances for the Ir(1)-C(1), Ir(1)-C(11) and Ir(1)-C(12) bonds of 2.036(2)Å, 1.841(3)Å, and 2.120(3)Å and distortion about the “legs” from idealized 90° as exemplified by the C(1)-Ir(1)-C(11), C(1)-Ir(1)-C(12), and C(11)-Ir(1)-C(12) bond angles of 93.45(14)° 88.07(19) ° and 85.6(2) ° respectively.

The IR spectrum of **4** reveals a single carbonyl band at 2042 cm-1 (Figure S23). This stretching frequency compares well to that found for cationic [Cp\*(MeIm)Ir(Me)CO]+ (vCO 2024 cm–1), [Cp\*(PMe3)Ir(Me)CO]+ (vCO 2035 cm–1),[21–23] and [Cp(PMe3)Ir(Me)CO]+ (2041 cm-1)[24] (Table 1) showing that

**Table 1.** Carbonyl stretching frequency of cationic Ir(III) compounds measured by IR spectroscopy.

|  |  |
| --- | --- |
| Compound | vCO (cm-1) |
| **4**[a] | 2042 |
| **8**[a] | 2028 |
| [Cp\*(MeIm)Ir(Me)CO]+ [b] | 2024 |
| [Cp(PMe3)Ir(Me)CO]+ [c] | 2041 |
| [Cp\*(PMe3)Ir(Me)CO]+ [d] | 2035 |

[a] this work. [b] ref #. [c] ref #. [d] ref #.

compound **4** is less electron rich than [Cp\*(MeIm)Ir(Me)CO]+ and similar to the PMe3 ligated complex.[24]

Generation of a cationic Ir(III) monomethyl complex from **2** was attempted at low temperature in thawing CD2Cl2 in a J-Young NMR tube employing pyridinium, 2,6-dimethylpyridinium, or 2,6-bis(*tert*-butyl)pyridinium as their [BArF20]- salts. 1H NMR spectroscopy reveals that **2** can be protonated with pyridinium to cleanly form the monomethyl species. The pyridine ligand is tightly bound to the iridium center, with two sets of pyridine resonances observed, corresponding to free and bound pyridine (Figure S21). Protonation of **2** with more sterically demanding 2,6-dimethylpyridinium or 2,6-bistertbutylpyridinium results in formation of an intractable mixture by 1H NMR.

In light of the sluggish reactivity of [Cp\*(MeIm)IrMe]+ [19] and the seeming self-immolation at the sterically unincumbered but more electron-poor [Cp(MeIm)Ir(Me)]+ (*vide supra*) we undertook preparation of the tetramethylcyclopentadienyl analog to **2**, reasoning it to be an assessable derivative to test if a subtle reduction in sterics about the Ir center may lead to improved reactivity vis-a-vi the Cp\* derivative while avoiding the decomposition seen at the Cp derivative. We reasoned the CpMe4 moiety would have donor-ability near that of Cp\*, leading to similar stabilization of the proposed IrV intermediate while having slight reduction of steric demands vis-a-vi Cp\* The complex CpMe4(MeIm)IrCl2 served as an entry-point to test this hypothesis, and was prepared by reaction of [CpMe4IrCl2]2[25] with (MeIm)Ag-I in CH2Cl2 to provide **5** in 82% yield. The 1H NMR spectrum of this material reveals five resonances in CD2Cl2 at 6.96, 4.77, 3.94, 1.65, and 1.57 ppm integrating for a ratio of 2:1:6:6:6 consistent with the formulation CpMe4(MeIm)IrCl2 (Figure S11). The 1H signals at 6.96 and 3.94 ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety, that at 4.77 ppm is ascribed to the C-H of the tetramethylcyclopentadienyl moiety while those at 1.65 and 1.57 ppm are assigned to two magnetically inequivalent sets of methyl groups on the tetramethylcyclopentadienyl moiety. The 13C{1H} NMR reveals eight resonances at 156.16, 123.78, 95.48, 90.81, 66.98, 39.30, 10.94, and 9.03 ppm. The resonances at 156.16, 123.78, and 39.30 ppm are ascribed to the carbenic, imidazolylidene backbone, and N-methyl positions respectively; those at 95.48, 90.81, and 66.98 are assigned to the C-atoms of the CpMe4 ring and those at 10.94 and 9.03 ppm assigned to the CH3 groups of the CpMe4 ring (Figure S12). A vapor diffusion of pentane into a CH2Cl2 solution at -20 °C provided single crystals suitable for XRD analysis. The solid-state structure of **5** shows a three-legged piano stool geometry with the CpMe4 ligand acting as a capping group (Figure S29.) Examination of the crystal structure shows bond distances for the Ir(1)-C(10), Ir(1)-Cl(1) and Ir(1)-Cl(2) bonds of 2.024(13)Å, 2.411(3)Å, and 2.410(3)Å and distortion about the “legs” from idealized 90° as exemplified by the C(10)-Ir(1)-Cl(1), C(10)-Ir(1)-Cl(2), and Cl(1)-Ir(1)-Cl(2) bond angles of 90.5(3)° 91.1(3) ° and 85.40(11) ° respectively.

**Figure 2.** ORTEP plot of the molecular structure of complex **6** grown from slow diffusion of pentane into a CH2Cl2 solution at -20 oC with thermal ellipsoids plotted at the 50% probability level. Hydrogen atoms are omitted for clarity.

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Alkylation of a solution of CpMe4(MeIm)IrCl2 in diethyl ether with methylmagnesium bromide was sluggish, requiring 30 equivalents as a 3M ethereal solution in diethyl ether to give CpMe4(MeIm)IrMe2 **6** in moderate yield (61%) after sublimation (Scheme 1). The 1H NMR spectrum of this material reveals six resonances in CD2Cl2 at 6.81, 4.30, 3.61, 1.66, 1.60, and 0.04 ppm integrating for a ratio of 2:1:6:6:6:6 consistent with the formulation CpMe4(MeIm)IrMe2 (Figure S13). The 1H signals at 6.81 and 3.61 ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety, those at 4.30, 1.66, and 1.60 ppm are ascribed to the C-H and CH3 protons of the tetramethylcyclopentadienyl moiety, while that at 0.04 ppm is assigned to the iridium-bound methyl groups. The 13C{1H} NMR reveals nine resonances at 165.33, 121.13, 94.13, 86.86, 73.58, 37.93, 10.65, 8.38, and -22.19 ppm (Figure S14). The resonances at 165.33, 121.13, and 37.93 ppm are ascribed to the carbenic, imidazolylidene backbone, and N-methyl positions respectively; those at 94.13, 86.86, and 73.58 ppm are assigned to the C-atoms of the CpMe4 ring, those at 10.65 and 8.32 ppm are assigned to the CH3 groups of the CpMe4 ring, and that at -22.19 ppm attributed to the iridium-bound methyl groups. Elemental analysis was found to be consistent with the formulation C16H27N2Ir, and single crystals suitable for XRD analysis were provided by diffusion of pentane into a CH2Cl2 solution at -20 °C The solid-state structure of complex **6** shows a three–legged piano stool geometry with the CpMe4 ligand acting as capping group (Figure. 2). Examination of the crystal structure shows bond distances for the Ir(1)-C(10), Ir(1)-C(15) and Ir(1)-C(16) bonds of 1.991(3)Å, 2.107(3)Å, and 2.108(3)Å and distortion about the “legs” from idealized 90° as exemplified by the C(10)-Ir(1)-C(15), C(10)-Ir(1)-C(16), and C(15)-Ir(1)-C(16) bond angles of 88.66(14)° 90.39(13)° and 80.57(14)° respectively.

Protonation was demonstrated as a viable method to remove an iridium-bound methyl group analogous to the chemistry described for **2**. Protonation of **6** with [LutH]Cl in CH2Cl2 cleanly formed methane and the corresponding iridium methyl chloride complex **7** in90% yield (Scheme 1). The 1H NMR spectrum of this material reveals eight resonances in CD2Cl2 at 6.91, 4.42, 3.79, 1.70, 1.65, 1.60, 1.53, and 0.90 ppm consistent with the formulation CpMe4(MeIm)Ir(Me)Cl (Figure S15). The 1H signals at 6.91 and 3.79 ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety, that at 4.42 ppm is ascribed to the C-H of the tetramethylcyclopentadienyl moiety those at 1.70, 1.65, 1.60, and 1.53 ppm are assigned to magnetically inequivalent CH3 groups of the tetramethylcyclopentadienyl moiety and that at 0.90 ppm assigned to the iridium-bound methyl group. The 13C{1H} NMR reveals eleven resonances at 160.55, 122.52, 97.92, 90.96, 89.45, 87.38, 71.01, 38.66, 10.77, 8.54, and -16.73 ppm. (Figure S16). The resonances at 160.55, 122.52, and 38.66 ppm are ascribed to the carbenic, imidazolylidene backbone, and N-methyl positions respectively; those at 97.92, 90.96, 89.45, 87.38, and 71.01 ppm are assigned to the C-atoms of the CpMe4 ring, those at 10.77 and 8.54 ppm are assigned to the CH3 groups of the CpMe4 ring, and that at -16.73 ppm is attributed to the iridium-bound methyl group. Elemental analysis was found to be consistent with the formulation C15H24N2ClIr, and single crystals suitable for XRD analysis were provided by diffusion of pentane into a CH2Cl2 solution at -20 °C (Figure S31) The solid-state structure of **7** shows a three-legged piano stool geometry with the CpMe4 ligand acting as a capping group (Figure S31.) Examination of the crystal structure shows bond distances for the Ir(1)-C(10), Ir(1)-C(15) and Ir(1)-Cl(1) bonds of 2.021(10)Å, 2.17(4)Å, and 2.360(6)Å and distortion about the “legs” from idealized 90° as exemplified by the C(10)-Ir(1)-C(15), C(10)-Ir(1)-Cl(1), and C(15)-Ir(1)-Cl(1) bond angles of 87.3(12)° ~~90.39(13) ° and 80.57(14)~~ ° respectively.

Cationic [CpMe4(MeIm)Ir(Me)CO][BArF20](**8**), is readily generated by protonation of **6** with [PyrH] [BArF20]in thawing CH2Cl2 under an atmosphere of CO to give an air stable colorless solid in 93% yield (Scheme 1). The 1H NMR spectrum of this material reveals seven resonances in CD2Cl2 at 7.11, 5.07, 3.68, 2.07, 2.00, 1.90, and 0.84 ppm integrating for a ratio of 2:1:6:3:3:6:3 consistent with the formulation [CpMe4(MeIm)Ir(Me)CO]+ (Figure S17). The 1H signals at 7.11 and 3.68 ppm are assigned to the backbone C-H and N-CH3 protons of the imidazolylidene moiety, that at 5.07 ppm is ascribed to the C-H of the tetramethylcyclopentadienyl moiety, those at 2.07, 2.00, and 1.90 ppm are assigned to the CH3 groups of the tetramethylcyclopentadienyl moiety while that at 0.84 ppm is assigned to the iridium-bound methyl group.

The 13C{1H} NMR reveals eighteen resonances, four of which are ascribed to the [BArF20]- counter-anion (Figure S18). The resonances at 168.42, 125.01, and 39.55 ppm are ascribed to the carbenic, imidazolylidene backbone, and N-methyl positions respectively. The resonance at 136.23 is assigned to carbonyl group, and those at 107.09, 106.75, 102.31, 100.06, and 80.41 ppm are assigned to the C-atoms of the CpMe4 ring. The resonances at 10.87 10.54, 9.68, and 9.41 ppm are assigned to the CH3 groups of the CpMe4 ring, and that at -22.77 ppm attributed to the iridium-bound methyl group. The 19F NMR of this material reveals three resonances at -167.59, -163.74, and -133.12 ppm (Figure S19) and 11B NMR (Figure S20) reveals one resonance at -16.66 ppm; both of which are consistent with the [BArF20]- counter-anion. Elemental analysis was found to be consistent with the formulation C40H24N2BOF20Ir, and single crystals suitable for XRD analysis were provided by diffusion of pentane into a CH2Cl2 solution at -20 °C. The solid-state structure of **8** shows a three-legged piano stool geometry with the CpMe4 ligand acting as a capping group (Figure S32.) Examination of the crystal structure shows bond distances for the Ir(1)-C(10), Ir(1)-C(15B) and Ir(1)-C(16B) bonds of 2.027(4)Å, 2.17018(15)Å, and 1.979(15)Å and distortion about the “legs” from idealized 90° as exemplified by the C(10)-Ir(1)-C(15B), C(10)-Ir(1)-C(16B), and C(15)-Ir(1)-C(16B) bond angles of 87.9(12)° 92.9(8) ° and 82.3(2) ° respectively. IR spectroscopy of **8** reveals one CO band at 2028 cm-1 (Figure S24), demonstrating it to be nearly as rich as [Cp\*(MeIm)Ir(Me)CO]+ (*v*CO 2024 cm–1),[19] and more-so than both the Cp derivative **4** (vCO 2042 cm-1) and Bergman’s PMe3 derivative (*v*CO 2035 cm–1).[26]

Generation of a cationic Ir(III) monomethyl complex from **6** was similarly attempted at low temperature in thawing CD2Cl2 in a J-Young NMR tube employing pyridinium, 2,6-bistertbutylpyridinium or 2,6-dimethylpyridinium as their [BArF20]- salts. 1H NMR spectroscopy reveals that **6** can be protonated to cleanly form the monomethyl cation with pyridinium. The pyridine ligand is tightly bound to the iridium center, with two sets of pyridine resonances observed, corresponding to free and bound pyridine (Figure S22). Protonation of **6** with 2,6-dimethylpyridinium or 2,6-bistertbutylpyridinium, results in formation of an intractable mixture by 1H NMR analogous to the chemistry observed with **2** indicating the cationic 16e- Cp and CpMe4 are unstable in the absence of a trapping ligand.

Bergman and coworkers previously showed that [Cp\*(PMe3)IrMe(CH2Cl2)]+ readily activates the C–H bonds of alkanes and arenes.[27] Likewise, related cationic Ir(III) methyl complexes of the formulation [Cp\*(NHC)IrMe]+ exhibited modest reactivity towards C-H bonds.[19] We anticipated that the sterically less-hindered, 16e- complexes generated *in situ* from the protonation of **2** and **6** with bulky acids would similarly exhibit C-H bond activation. To test this hypothesis, the cationic monomethyl complexes were generated by protonation of **2** and **6** with the [BArF20]- salt of 2,6-dimethylpyridinium, or 2,6-bis(*tert*butyl)pyridinium in thawing benzene-*d­*6 or toluene-*d*8 in a J-Young NMR tube. We reasoned that if active 16e– species are formed activation of abundant C-D bonds of solvent would form some CDH3, which would be readily observable as a triplet in the 1H NMR spectra.[28] Disappointingly, no CDH3 was detected, rather intractable mixtures were formed by 1H NMR analogous to the protonation experiments in CD2Cl2.

The absence of C–D activation at electron-deficient Ir(III) centers generated from **2** or **6** may be understood by considering the potential reaction mechanisms for C-H bond activation proposed for the analogous compound [Cp\*(PMe3)IrMe(CH2Cl2)]+. Two mechanisms have been proposed: oxidative addition/reductive elimination (OA/RE) and sigma–bond metathesis (SBM)[29–32]. Both mechanisms begin with dissociation of CH2Cl2 to form [Cp\*(PMe3)IrMe]+, a 16 e– species possessing an open site for reactivity. An OA mechanism would involve formation of a seven–coordinate IrV complex; several reports of such complexes containing the Cp\*(PMe3)Ir unit have been made.[33–37] Alternatively, a SBM mechanism for [Cp\*Ir(PMe3)Me]+ would involve formation of an agostic bond between substrate (R–H) and the 16 e- Ir(III) center prior to formation of a four–centered Ir(III) metallocycle transition state. SBM reactivity is characteristic of electron deficient d0 early transition metals,[38] and seems less likely for a late transition metal d6 complex with strongly donating ligands such as PMe3 or MeIm. Both the OA and SBM regime rely upon *1)* the stabilization of a coordinatively unsaturated 16 e- Ir(III) species and *2)* a sufficiently assessable Ir(III) center to allow association of R-H substrate to the metal center, a prerequisite for either oxidative addition or formation of an agostic bond and 4-centered metallocycle. Electron density at Ir(III) as measured by the carbonyl stretching frequency of Ir(Me)CO compounds (Table 1) indicates that a 16 e- species generated from **8** should be more stabilized than that formed from [Cp\*(PMe3)IrMe(CH2Cl2)]+, and nearly as stabilized as that formed from Cp\*(MeIm)IrMe2 while that generated from **4** should be significantly less stabilized than the 16 e- species formed from both [Cp\*(PMe3)IrMe(CH2Cl2)]+ and Cp\*(MeIm)IrMe2. In light of these measurements attributing the absence of C-D bond activation at the Cp derivative to insufficient stabilization from donor ligands may be rational, but a similar argument for the CpMe4 derivative is dubious.

A comparison of the Me-Ir-Me bond angles for **2**, **6**, and Cp\*(MeIm)IrMe2 provides a rough evaluation of steric demands at the Ir centers imposed by the cyclopentadienyl derivatives. Increased steric congestion due to the demands of Cp derivatives are reasoned to influence Me-Ir-Me bond angles to be more acute. A comparison finds Me-Ir-Me bond angles of 81.2(3)°, 80.57(14)°, and 80.8(3)° for the Cp, CpMe4, and Cp\* derivatives respectively, indicating CpMe4 and Cp\* to be roughly equivalent and slightly more demanding than Cp. Taken together, the absence of C-D bond activation at the Cp derivative could be attributed to a sterically assessable but electronically destabilized Ir(III) center, but a similar argument cannot explain the absence of C-D bond activation at the CpMe4 derivative that is nearly equivalent, both electronically and sterically, to the Cp\* derivative.

Conclusion

Attempts to improve upon the sluggish C-H bond activation observed at a 16 e- Ir(III) center generated by methyl-abstraction from Cp\*(MeIm)IrMe2 by making structural modifications at the cyclopentadienyl moiety proved unsuccessful, leading instead to rapid decomposition of the 16 e- species in the absence of a trapping-ligand. The donor ability of the Cp and CpMe4 ligands as measured by vCO indicate the Ir(III) center of the Cp derivative is significantly less stabilized vis-a-vi Cp\* while the CpMe4 derivative is nearly equivalent to Cp\*. Examination of the Me-Ir-Me bond angle in the solid-state structures provides a rough measure of the sterics imposed by Cp and CpMe4 in comparison to Cp\*, indicating the steric demands about the Ir(III) centers ligated by CpMe4 and Cp\* to be nearly equivalent and greater than for the Cp derivative. Simply replacing one CH3 group on the Cp\* moiety with a C-H group renders these complexes susceptible to rapid decomposition.

Supporting Information ((optional))

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