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Novel η^1-N,η^2-C,C-Binding Mode between Pyridinyl-Functionalized Cyclopentadienyl Ligands and Iridium[†]

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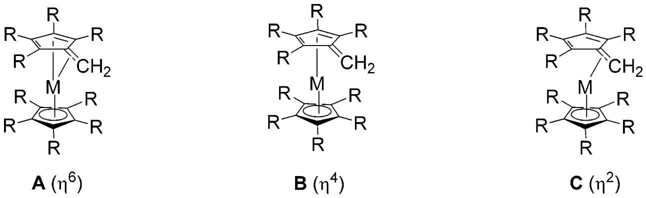
The reaction between 2-(2,3,4,5-tetramethyl-cyclopenta-1,3-dienyl)-pyridine **1** and $IrCl_3$ was performed in an attempt to synthesize a cyclometalated system with decreased π conjugation in the ligand. An unexpected reduction and rearrangement of bis-pyridinyl-cyclopentadienyl cyclometalated Ir(III) intermediate **2** took place yielding bis-pyridinyl-fulvene Ir(I) complex **4**, which exhibits a novel bis-η^1-N,η^2-C,C-binding mode between the pyridinyl-functionalized fulvene ligand and iridium. The iridium atom in **4** is not sandwiched between two cyclopentadienyl moieties; rather, the two cyclopentadienyl groups adopt a π–π stacking arrangement with a centroid–centroid distance of 3.494 Å. The Cl/P^O ligand-exchange reaction between **4** and 2-[(diphenylphosphanyl)-methyl]-1,1,1,3,3,3-hexafluoro-propan-2-ol **5** led to loss of one pyridinyl-functionalized fulvene ligand and produced complex **6**, in which the remaining pyridinyl-functionalized fulvene ligand exhibits the mono-η^1-N,η^2-C,C-binding mode.

1. Introduction

The search for new types of bonding interactions between transition metals and aromatics is of much current interest. Facile dearomatization processes can occur in these systems resulting in unusual coordination modes, for example, the metal/quinone[1] and metal/pentamethylcyclopentadienyl systems.[2] An important reaction pathway for metal complexes bearing pentamethylcyclopentadienyl ligands is the loss of one or two hydrogens from the methyl groups, resulting in cationic or neutral tetramethylfulvene and trimethylallyldiene complexes. In principle, the fulvene ligand $C_5H_4CH_2$ can be coordinated to a metal via η^6, η^4, or η^2-coordination modes (**A**, **B**, and **C** in Scheme 1).

Scheme 1



Complexes of the types shown in Scheme 1 have been prepared for almost all of the Group 4−10 transition metals. They differ from η^6-arene complexes in that the six-electron ligand is generally nonplanar with a substantial deviation of one carbon atom from the plane of the Cp-ring toward the metal atom. The most abundant types are the neutral and cationic η^6-complexes formed by the Group 4−8 metals. Complexes exhibiting η^4-coordination are generally only observed for metals in Groups 9 and 10. η^2-Coordination is encountered only very rarely: mono-η^2-coordination has been observed in one palladium derivative,[3] while the mixed η^1-O,η^2-C,C-coordination mode has been described for a single iridium complex.[4] In this report, we describe the synthesis and structural peculiarities of iridium complexes exhibiting a novel η^1-N,η^2-C,C-binding interaction between the pyridinyl-functionalized fulvene ligand and the metal center.

2. Results and Discussion

As part of a search for cyclometalated aromatic systems with a smaller π system than that of the 2-phenylpyridine ligands,[5] we decided to investigate the cyclometalation of

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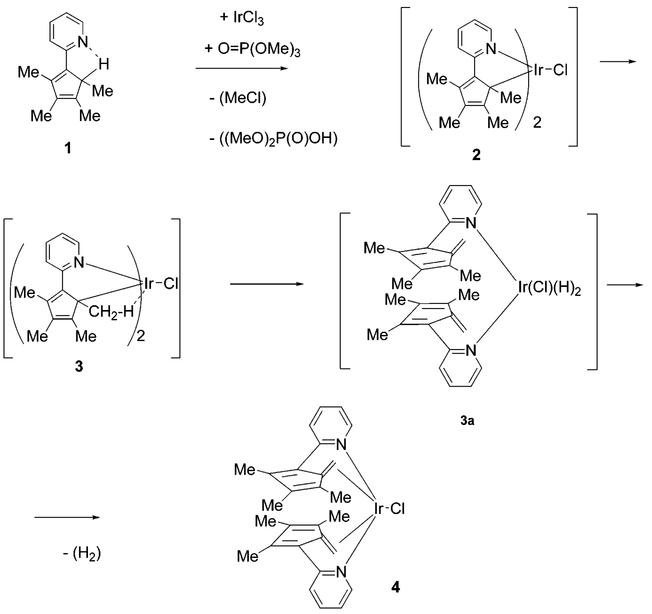
10.1021/ic0505854 CCC: $30.25

Scheme 2



2-(2,3,4,5-tetramethyl-cyclopenta-1,3-dienyl)-pyridine[6] **1** by IrCl$_3$. Ligand **1** has been used previously to synthesize a donor-functionalized pyridine/cyclopentadiene iron complex with the Cp fragment bound in a classical η^5-coordination mode.[6] An intramolecular hydrogen-bond interaction between the allylic hydrogen and the nitrogen atom of the pyridine moiety in ligand **1** was proposed in the above study.[6] This was encouraging because replacement of the allylic hydrogen by iridium would lead to the desired cyclometalated complexes.

The cyclometalation of 2-(2,3,4,5-tetramethyl-cyclopenta-1,3-dienyl)-pyridine **1** with IrCl$_3$ was carried out in trimethyl phosphate (Scheme 2), since electrophilic reactions in trimethyl phosphate often take place under mild conditions.[7] Unexpectedly, univalent iridium complex **4**, in which two pyridinyl-fulvene ligands exhibit a novel η^1-N,η^2-C,C-binding mode, was isolated from the reaction mixture. Apparently, a C−H activation reaction occurs during this process. A plausible mechanism for the formation of **4** likely includes the intermediate formation of the target bis-cyclometalated (C^N) complex **2** containing trivalent iridium. C^N-cyclometalated complexes are the usual products in reactions between 2-phenylpyridine and IrCl$_3$.[5] The loss of two hydrogen atoms from the tetramethyl-substituted cyclopentadienyl ligands of intermediate **2** results in the formation of fulvene moieties.[8] The reduction of **2** to univalent iridium complex **4** and the rearrangement to the η^1-N,η^2-C,C-coordination mode may be facilitated by an Ir−H−C agostic interaction, as depicted for the intermediate **3**; two subsequent hydrogen eliminations would form dihydride intermediate **3a**.[9] The reductive elimination of hydrogen from trivalent **3a** would form the univalent complex **4**. Unfortunately, none of the intermediates formed in the reaction were stable enough to isolate or be monitored by NMR techniques. TLC experiments did not reveal any side products or intermediates.

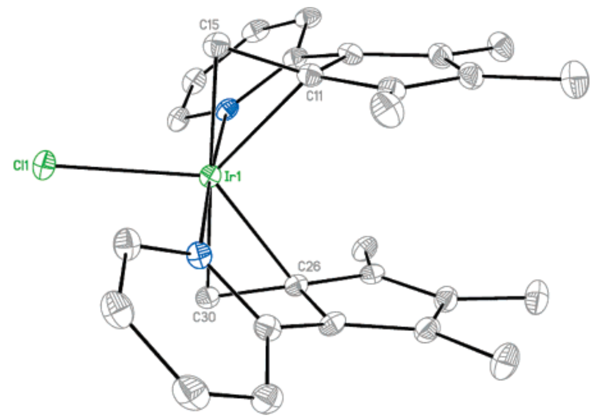


Figure 1. ORTEP drawing of complex **4**.

The X-ray crystal structure of **4** is shown in Figure 1. There is no η^4-coordination between the cyclopentadienyl moieties and iridium, nor is the iridium atom sandwiched between two cyclopentadienyl moieties. Rather, the two cyclopentadienyl moietes adopt a π−π stacking arrangement with a centroid−centroid distance equal 3.494 Å; this is shorter than the average distance of 3.8 Å generally accepted for this phenomenon.[10] The methylene groups of the ligand in **4** are bent 21.0° (0.509 Å) and 18.9° (0.452 Å) from planarity. The deviation from planarity in **4** appears to be the largest yet observed within fulvene−iridium complexes. For example, the deviation in an iridium complex with η^4-coordination was found to be 0.40(1) Å;[9a] the deviation in the only known iridium complex exhibiting the η^1-O,η^2-C,C-coordination mode was found to be 0.02 Å,[7] which is essentially planar. Nevertheless, it should be noted that there is residual double bond character in the *exo*-methylene groups of **4**: the average C═C bond distance of the *exo*-methylene moieties in **4** is 1.438(5) Å, considerably shorter than a normal C−C bond distance of 1.54 Å.

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(8) Analogous transformations of pentamethylcyclopentadienyl methyls to methylenes mediated by iridium are known, see: (a) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862. (b) Fulton, J. R.; Hanna, T. A.; Bergman, R. G. *Organometallics* **2000**, *19*, 602.

(9) Agostic C−H interactions between the methyl groups of various permethylated cyclopentadienyl ligands and metal centers are known and often considered important intermediates in metal-catalyzed dehydrogenation reactions, see: (a) Bouwkamp, M. W.; de Wolf, J.; Del Hiero Morales, I.; Gercama, J.; Meetsma, A.; Troyanov, S. I.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 12956. (b) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc*. **2004**, *126*, 13044. (c) Rodriguez, P.; Diaz-Requejo, M. M.; Belderrain, T. R.; Trofimenko, S.; Nicasio, M. C.; Perez, P. J. *Organometallics* **2004**, *23*, 2162. (d) Van der Boom, M. E.; Iron, M. A.; Atasoylu, O.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Konstantinovski, L.; Martin, J. M. L.; Milstein, D. *Inorg. Chim. Acta* **2004**, *357*, 1854.

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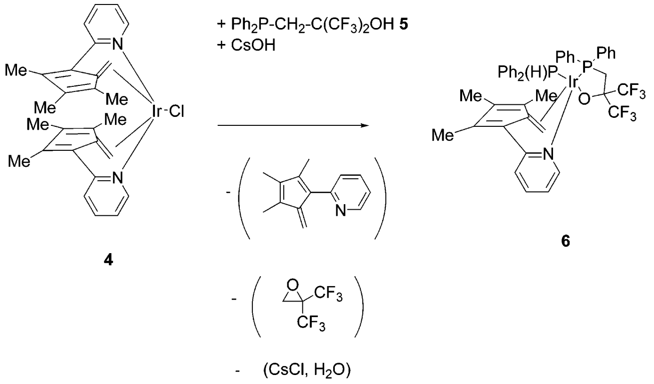
Scheme 3



The ^{1}H NMR spectrum of **4** shows two resonances for the *exo*-methylene protons at δ 2.80 and 3.13, which are comparable to the published chemical shifts for such protons in Pd and Ir complexes.[2−4,9a] The ^{13}C NMR spectrum of **4** shows two characteristic resonances for the *exo*-methylene carbons at δ 31.3 and 71.9, which are again similar to the published values for such carbons in Pd and Ir complexes.[2−4]

A Cl/P^O ligand exchange reaction was carried out between **4** and 2-[(diphenylphosphanyl)-methyl]-1,1,1,3,3,3-hexafluoro-propan-2-ol **5** to test the strength of the interaction between Ir(I) and the two pyridinyl-fulvene ligands in this new bonding mode (Scheme 3).

A red Ir(I) complex, **6**, containing only one pyridinyl-fulvene ligand was isolated from this reaction. That the one pyridinyl-functionalized fulvene ligand was replaced completely is not surprising, given that η^2-coordinated fulvene ligands attached to palladium can be easily replaced by phosphines.[3] However, complex **6** contains two phosphine ligands: the expected P^O-chelating ligand (^{31}P NMR δ 27.63 ($^2J_{PP}$=55.3 Hz)) and a monodentate diphenylphosphine ligand (^{31}P NMR δ −14.7 ($^1J_{PH}$=332.6 Hz, $^2J_{PP}$=55.3 Hz)), which results from the retro-elimination of 2,2-bis-trifluoromethyl-oxirane from the starting β-hydroxyphosphine. The retro-elimination took place to decrease the overall steric hindrance of the complex. The 2,2-bis-trifluoromethyl-oxirane was not isolated from the reaction depicted in Scheme 3. The ^{1}H NMR spectrum of **6** exhibits a broad *exo*-methylene resonance at δ 2.80. The single-crystal X-ray structure of **6** again shows the new chelating η^1-N,η^2-C,C-coordination mode for the pyridinyl-fulvene ligand to Ir(I) (Figure 2).

The C−C bond distance of the *exo*-methylene moiety in **6** is 1.464(4) Å, which is slightly longer than the average of the two *exo*-C−C bonds in **4** (1.438(5) Å) and rather close to the single C−C bond of the permethylated-fulvene ligand (1.498(4)-1.509(4) Å Table 1).[11] This may be attributed to further hybridization of the *exo*-olefinic C atoms toward sp^3 in complex **6** as compared to that in **4**. The *exo*-methylene moiety is again bent out of planarity with the cyclopentadienyl fragment, in this instance by 0.381 Å.

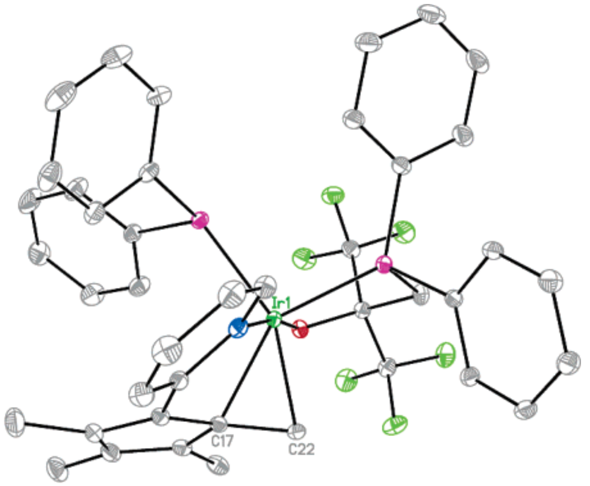


Figure 2. ORTEP drawing of complex **6**.

Table 1. Selected Bond Lengths and Deviations of the *exo*-Methylene Group from Planarity (Å) in Complexes **4** and **6**

complex	C−C	Ir−CH$_2$	Ir−C	deviation
4	1.437(5) C11−C15	2.107(4) Ir−C15	2.157(3) Ir−C11	0.452
	1.439(5) C26−C30	2.117(3) Ir−C30	2.163(3) Ir−C26	0.509
6	1.464(4) C17−C22	2.099(2) Ir−C22	2.188(2) Ir−C17	0.381

In contrast to the η^6-fulvene complexes,[2] in the η^2-coordination mode of complexes **4** and **6**, the shortest bonds are formed between the terminal CH$_2$ moiety and the metal (Table 1), not between the carbon of the cyclopentadienyl ring and the metal. This is a reflection of the fact that iridium is displaced away from the main plane of the fulvene ring by the η^2 coordination of the *exo*-methylene group.

3. Conclusions

Two new Ir(I) complexes containing novel η^1-N,η^2-C,C-chelated pyridinyl-functionalized cyclopentadiene ligands have been isolated. Efforts to prepare cyclometalated Ir and Pt complexes with ligands containing smaller π systems than those of the phenyl-pyridines are underway in our laboratory.

4. Experimental Section

General Procedures. All air-sensitive compounds were prepared and handled under a N$_2$/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. 2,3,4,5-Tetramethylcyclopent-2-enone, *n*-butyllithium, trimethyl phosphate, diphenylphosphine, and 2-bromopyridine were purchased from Aldrich. Iridium (+3) chloride trihydrate was purchased from Alfa Aesar. 2,2-Bis(trifluoromethyl)oxirane is a DuPont product. 2-(2,3,4,5-Tetramethyl-cyclopenta-1,3-dienyl)-pyridine (**1**) was prepared according to the literature.[6] 2-[(Diphenylphosphanyl)-methyl]-1,1,1,3,3,3-hexafluoro-propan-2-ol (**5**) was synthesized by the known addition of diphenylphosphine to 2,2-bis(trifluoromethyl)-oxirane.[12]

Bis{η^1,η^2-[2-(2,3,4-trimethyl-5-methylene-cyclopenta-1,3-dienyl)-pyridine]}Iridium(I) Chloride (4). Five grams (0.025 mol) of 2-(2,3,4,5-tetramethyl-cyclopenta-1,3-dienyl)-pyridine (**1**), 4.42

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Table 2. Summary of Crystal Data, Data Collection, and Structural Refinement Parameters of **4** and **6**

	4	**6**
empirical formula	$C_{28}H_{30}ClIrN_2$	$C_{42}H_{38}F_6IrNOP_2$
fw	622.19	940.87
cryst. color, form	red, irregular block	red/orange, irregular block
cryst. syst.	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	7.9608(15)	10.9554(11)
b (Å)	18.256(4)	17.2237(17)
c (Å)	16.595(3)	20.213(2)
α (deg)	90	90
β (deg)	98.900(3)	96.322(2)
γ (deg)	90	90
V (Å^3)	2382.8(8)	3790.9(7)
Z	4	4
density (g/cm3)	1.734	1.649
abs. μ (mm^{-1})	5.734	3.671
F(000)	1224	1864
cryst size (mm)	.23×.23×.20	.24×.18×.14
temp (°C)	−100	−100
scan mode	ω	ω
detector	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	28.28	28.29
no. observed reflns	15361	69662
no. unique reflns	5637	9337
R_{merge}	0.0286	0.0343
no. params	311	494
S^b	1.03	1.083
R indices [$I>2\sigma(I)$][a]	wR2=0.057 R1=0.025	wR2=0.050 R1=0.023
R indices (all data)[b]	wR2=0.062 R1=0.036	wR2=0.054 R1=0.032
max diff peak, hole (e/Å^3)	1.493, −0.776	2.339, −0.686

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w). [b] $\mathrm{GOF} = S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of refined parameters.

g (0.0125 mol) of iridium(III) chloride trihydrate, and 40 mL of trimethyl phosphate were stirred at 60 °C for 12 h under a flow of nitrogen. The resultant mixture was purified via chromatography on silica with methylene chloride as an eluent. The yield of **4** was 4.38 g (54%) of red crystals with a mp of 314.1 °C (decomp). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 0.63 (s, 3 H, Me), 1.65 (s, 3 H, Me), 1.73 (s, 3 H, Me), 2.80 (s, 1 H, $=CH_2$), 3.13 (s, 1 H, $=CH_2$), 6.75 (m, 1H, Py-H), 7.03 (m, 1H, Py-H), 7.52 (m, 1H, Py-H), 8.56 (m, 1H, Py-H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 11.5, 12.1, 12.6, 31.3, 71.9, 122.0, 122.4, 132.6, 134.5, 136.0, 136.6, 143.2, 155.3, 157.5. Anal. Calcd for $C_{28}H_{30}ClIrN_2$ (mol wt 622.22): C, 54.05; H, 4.86; N, 4.50. Found: C, 54.18; H, 4.96; N, 4.56. The structure was proven by X-ray analysis.

***η*¹,*η*²-[2-(2,3,4-Trimethyl-5-methylene-cyclopenta-1,3-dienyl)-pyridine],(diphenylphosphine),[2-[(diphenylphosphino-*κ*P)methyl]-1,1,1,3,3,3-hexafluoro-2-propanolato-*κ*O]-iridium(I) Chloride (6).** Bis{η^1,η^2-[2-(2,3,4-Trimethyl-5-methylene-cyclopenta-1,3-dienyl)-pyridine]}iridium(I) chloride (**4**) (0.76 g, 0.0012 mol), 2-[(diphenylphosphanyl)-methyl]-1,1,1,3,3,3-hexafluoro-propan-2-ol (**5**) (0.55 g, 0.0015 mol), cesium hydroxide (0.6 g, 0.004 mol) and THF (20 mL) were refluxed under the nitrogen flow for 12 h. The product was purified by chromatography on silica gel with methylene chloride as an eluent. The yield of **6** was 0.68 g (59%) of red crystals with a mp of 100.4 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 0.80 (br, 3 H, Me), 1.85 (br, 3 H, Me), 1.90 (br, 3 H, Me), 2.10 (br, 2H, CH_2-P), 2.80 (m, 2 H, $=CH_2$), 6.50−8.40 (m, 24H, Arom-H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 12.7, 13.4, 14.1, 37.8, 43.6, 76.4, 80.9, 122.43, 123.0, 128.0, 128.4, 129.3, 130.1, 130.4, 131.6, 131.7, 131.8, 134.3, 136.0, 136.4, 138.8, 148.7, 150.9, 157.4. ^{19}F NMR (500 MHz, CD_2Cl_2): δ −78.55 (s, 3F), −76, 54 (br, 3F). ^{31}P NMR (500 MHz, CD_2Cl_2): δ −14.7 (dd, $^1J_{PH}$=332.6 Hz $^2J_{PP}$=55.3 Hz), 27.63 (d, $^2J_{PP}$=55.3 Hz). Anal. Calcd for $C_{42}H_{38}F_6IrNOP_2$ (mol wt 940.91): C, 53.61; H, 4.07; F, N, 1.49. Found: C, 53.64; H, 4.42; N, 1.71. The structure was proven by X-ray analysis.

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Supporting Information Available: Experimental procedures and crystallographic information (CIF file) for complexes **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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