

## Fischer Carbene Complexes of Iridium(I) for Application in Catalytic Transfer Hydrogenation

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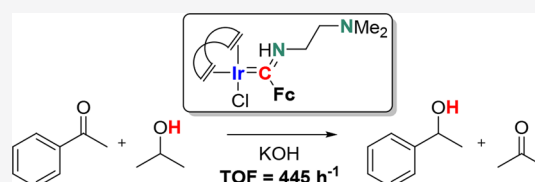
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**ABSTRACT:** New examples of the very rare class of iridium(I) Fischer carbene complexes (FCCs) are reported from the facile transmetalation from group 6 FCCs. Postcomplexation modification of either the carbene ligand or the ancillary coligands results in a tunable Ir<sup>I</sup> metal center, for unprecedented application as a (pre)catalyst in a benchmark transfer hydrogenation reaction. The introduction of an aminocarbene ligand with a pendant N-donor moiety capable of hemilabile coordination yielded the best catalytic results with turnover frequencies reaching 445 h<sup>-1</sup> and requiring 0.1 mol % catalyst and 0.5 mol % base loading, respectively.

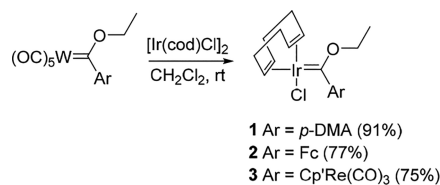


The ability to finely tune the electronic poles of the metal–carbon (double) bond results in unique chemical reactivity. In the case of heteroatom-stabilized Fischer carbene complexes (FCCs),<sup>1</sup> a resurgence in the interest of this versatile chemical bond has been seen to go beyond the traditional applications in template organic synthesis to especially photophysical, optical, and sensing applications.<sup>2</sup> However, applications in catalysis are still lacking due to the inherent difficulties associated with preparing FCCs of the late transition metals. The requirements of low metal oxidation states and the presence of modifiable carbonyl or isonitrile ligands for nucleophilic attack in the preparation of FCCs,<sup>3</sup> often in the presence of halide coligands, are limiting. The use of carbene transfer reactions from group 6 metals have been employed in catalytic transmetalation reactions for alkene and allene cyclization reactions, but reports of isolated late-transition-metal FCCs are rare.<sup>4</sup> This is primarily due to the self-dimerization observed for the electrophilic carbene ligands,<sup>5</sup> although appropriate electron-donating coligands or donating Fischer carbene ligand substituents have enabled the isolation of rhodium(I) FCCs that are stable at room temperature.<sup>6</sup> In this regard, we have reported ferrocenyl Fischer carbene ligands coordinated to rhodium(I) that were stable to both atmospheric conditions and elevated temperatures and pressures.<sup>7</sup> More importantly, we could show that these Rh<sup>I</sup> FCCs were efficient in catalyzing the hydroformylation of 1-octene. In this work, the strategy of transmetalation is extended to the preparation of unprecedented iridium(I) FCC analogues, and the use of these group 9 transition-metal FCCs as catalyst precursors in the transfer hydrogenation reaction is investigated.

Pentacarbonyl tungsten(0) ethoxycarbene complexes, containing the strongly electron donating carbene substituent *p*-*N,N*-dimethylaniline (*p*-DMA)<sup>8</sup> or the organometallic fragment ferrocenyl (Fc),<sup>9</sup> were employed as the precursor

tungsten(0) FCCs for the preparation of the corresponding Ir<sup>I</sup> FCCs **1** and **2** (see Scheme 1), following a methodology

### Scheme 1. Carbene Transfer from Tungsten(0) FCCs for the Preparation of 1–3



similar to that employed for the analogous rhodium(I) FCC with a ferrocenyl (Fc) carbene substituent, [Rh(cod)Cl]{C(OEt)Fc} (cod = 1,5-cyclooctadiene).<sup>7</sup> The carbene transfer reaction ensues with stirring of an equimolar mixture of the group 6 precursor FCC with the dimer [Ir(cod)Cl]<sub>2</sub>, in dichloromethane solvent, at room temperature. The reaction progress was monitored with thin-layer chromatography (tlc), and reaction completion was observed within 24 h. Surprisingly, employing the precursor [W(CO)<sub>5</sub>{C(OEt)-Cp\*Re(CO)<sub>3</sub>}]<sup>10</sup> (Cp\* = cyclopentadienyl), using the same methodology, gave facile access to the FCC **3** (Scheme 1), despite the known electrophilicity of this carbene ligand as a result of the “draining” of electron density by the –Re(CO)<sub>3</sub> moiety.<sup>11</sup> Previously, Fischer carbene ligands containing

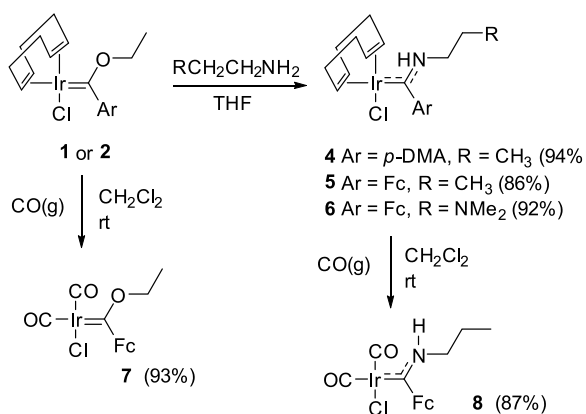
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electron-withdrawing substituents have resulted exclusively in kinetic and thermal decomposition dimerization products.<sup>5–7</sup>

Examples of iridium FCCs are very rare. These include the iridium(III) FCCs generated by C–H bond activation of ethers as reported by the groups of Carmona<sup>12</sup> and Grubbs,<sup>13</sup> respectively. In addition to this class of compounds, two isolated examples of Ir<sup>III</sup> heteroatom-stabilized carbene complexes have been reported,<sup>14</sup> while the use of either a cyclic aminocarbene ligand<sup>15</sup> or an acyclic diaminocarbene ligand<sup>16</sup> has paved the way for free carbene generation and complexation to the only two examples of Ir<sup>I</sup> FCCs preceding this report. In our case, such stringent reaction conditions could be circumvented via direct carbene transfer reactions (see the Supporting Information for complex synthesis and characterization). Simple substitution reactions could be employed to significantly alter the electronic environment around the central Ir<sup>I</sup>, by replacement of the cod ligands with two carbonyl ligands (7, 8) or by aminolysis of the ethoxycarbenes with either *n*-propylamine or *N,N*-dimethyl-1,2-diaminoethane (4–6, 8) (Scheme 2). The latter diamine

### Scheme 2. Postcomplexation Modification to Yield Complexes 4–8



was employed to investigate the possibility of chelation to form a metallacyclic FC ligand. The tertiary amino group remains as an untethered pendant amine, and virtually no difference in the spectroscopic characteristics of complexes 5 and 6 is observed (Supporting Information). Nevertheless, the pendant amine provides the opportunity for hemilabile chelation activity of the FCC ligand during catalysis (*vide infra*). As expected, replacement of the ethoxycarbene substituent with an amino group leads to a significant upfield shift (>40 ppm) in the <sup>13</sup>C NMR resonances of the carbene carbon atoms due to the increased stabilization of the electrophilic carbene carbon by the nitrogen lone pair.<sup>17</sup> The ethoxycarbene complexes 1–3 and 7 display carbene atom chemical shifts in the range of 275.1–286.6 ppm, while the aminocarbene complexes 4–6 and 8 have carbene carbon atoms resonating in the range 232.6–245.5 ppm (see Table 1).

Single crystals suitable for diffraction could be grown for complexes 1–5 and 7 by slow diffusion of hexane/dichloromethane layered solutions, and the molecular structures are shown in Figure 1. Crystallographic data and selected bond lengths and angles are given in Tables S1 and S2 in the Supporting Information. A pseudo-square-planar geometry around the central iridium atom is observed in all cases. The Ir–C<sub>carbene</sub> bond lengths are, in general, shorter for the

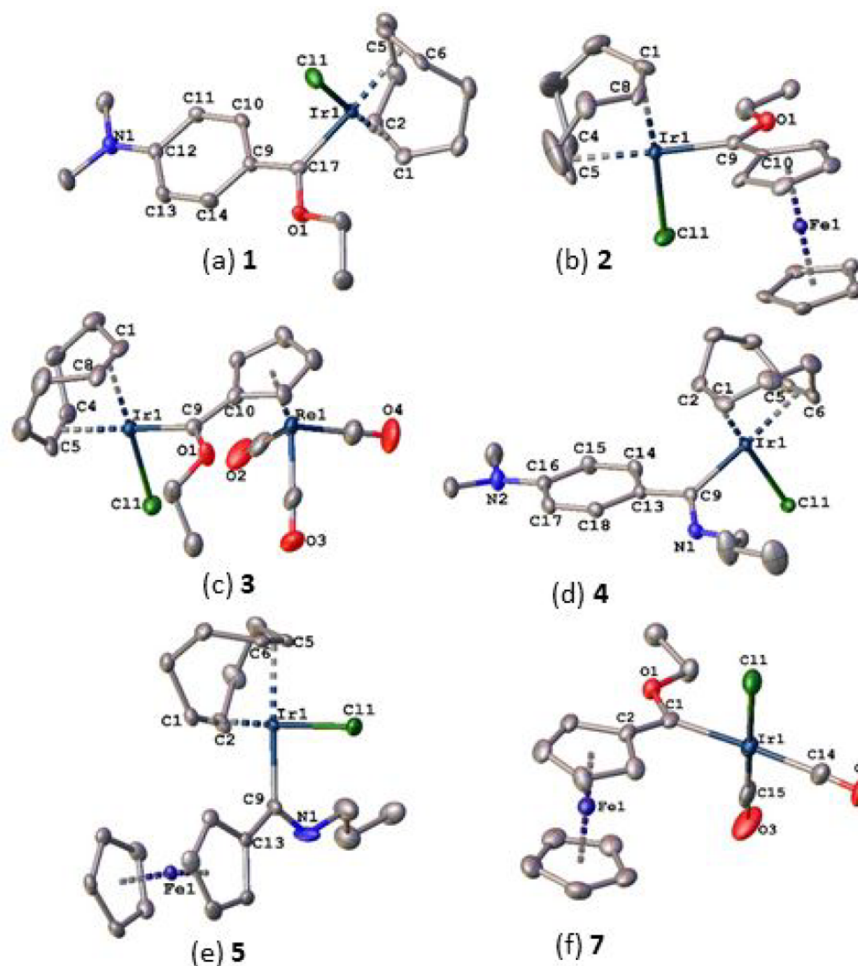
Table 1. Selected Spectroscopic Data for Complexes 1–8

[Ir]	<sup>13</sup> C δ(C <sub>carbene</sub> )	<sup>13</sup> C δ(CO)	IR <sup>f</sup> ν(CO) (cm <sup>-1</sup> )	TEP <sup>g</sup> (cm <sup>-1</sup> )
1	276.7 <sup>a</sup>			2052 <sup>h</sup>
2	286.6 <sup>a</sup>			
3	275.1 <sup>a</sup>			2063 <sup>h</sup>
4	240.3 <sup>a</sup>			2049 <sup>h</sup>
5	245.4 <sup>b</sup>			
6	245.5 <sup>b</sup>			2043 <sup>h</sup>
7	277.4 <sup>c</sup>	184.1, <sup>d</sup> 170.1 <sup>e</sup>	1987, <sup>e</sup> 2069 <sup>d</sup>	2055
8	232.5 <sup>b</sup>	183.6, <sup>d</sup> 170.3 <sup>e</sup>	1980, <sup>e</sup> 2063 <sup>d</sup>	2050

<sup>a</sup>Recorded in CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup>Recorded in CDCl<sub>3</sub>. <sup>c</sup>Recorded in C<sub>6</sub>D<sub>6</sub>. <sup>d</sup>CO ligand *trans* to carbene. <sup>e</sup>CO ligand *trans* to Cl. <sup>f</sup>Recorded in CH<sub>2</sub>Cl<sub>2</sub>. <sup>g</sup>Calculated using the linear regression model TEP = 0.8475·[ν<sub>av</sub>(CO)Ir] + 336.2 cm<sup>-1</sup>.<sup>19</sup> <sup>h</sup>Calculated for the nonisolated dicarbonyl analogues of these complexes; see section S3 in the Supporting Information.

ethoxycarbene complexes, in comparison to the aminocarbene complexes, while the C<sub>carbene</sub>–N bond lengths are indicative of C<sub>carbene</sub>–N bond orders greater than 1 (ranging from 1.315(2) to 1.305(5) Å, respectively, for 4 and 5), commensurate with the upfield <sup>13</sup>C NMR shifts observed for the aminocarbene carbon atoms.<sup>17</sup> Notably, the “electron-sink” cyclopentadienyl rhenium tricarbonyl moiety results in the shortest Ir–C<sub>carbene</sub> bond length for 3 (1.954(7) Å), due to the increased π back-bonding required for the significantly more electrophilic ethoxycarbene ligand in comparison to the *p*-DMA- and Fc-substituted FCCs 1 and 2, with Ir–C<sub>carbene</sub> bond lengths of 1.972(2) and 1.963(9) Å, respectively. In contrast, the cod coligand substitution by two carbonyl ligands has the opposite effect, where introduction of the strongly π acidic CO ligands and competing requirement for π back-donation result in a significantly longer Ir–C<sub>carbene</sub> bond length for 7 (2.065(9) Å), in comparison to the cod analogue 2 (1.963(9) Å). Similarly, the shortest C<sub>carbene</sub>–O bond length is seen for 7 (1.311(10) Å) and is indicative of significant participation of the ethoxy O atom toward carbene carbon stabilization. However, all of the Ir–C<sub>carbene</sub> bond lengths (1.954(7)–2.065(9) Å) are significantly shorter in comparison to those of the only other known structure of an Ir<sup>I</sup> FCC, with Ir–C<sub>carbene</sub> = 2.094(5) Å,<sup>15a</sup> attesting to the greater Ir–C bond order and degree of back-donation. The presence of the coordinated carbonyl ligands also provides the opportunity to calculate Tolman electronic parameters (TEPs) for the carbene ligands as an estimation of the electron-donating ability of the :C(OEt)Fc and :C(NH<sup>*n*</sup>Pr)Fc carbene ligands,<sup>18</sup> in comparison to what is known for a wide range of N-heterocyclic carbenes (NHCs). The TEP values were determined from a linear regression formula<sup>19</sup> and match the values previously obtained for the Rh<sup>I</sup> analogues,<sup>7</sup> to confirm the enhanced donating ability of amino-FCs over that of alkoxy-FCs and generally the strong donating ability of the ferrocenyl-functionalized FCs.<sup>15a</sup> In order to complete the calculated TEPs for a series of carbene ligands, TEPs for the dicarbonyl analogues of complexes 1, 3, 4, and 6 were also determined and the IR spectra measured (section S3 in the Supporting Information). The TEPs range over 20 cm<sup>-1</sup>, from TEP = 2043 cm<sup>-1</sup> for the ligand :C(NH(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>)Fc, indicating that this is the most donating ligand, to TEP = 2063 cm<sup>-1</sup> for the FC :C(OEt)Cp<sup>*r*</sup>Re(CO)<sub>3</sub> as the most electrophilic/least donating carbene ligand.

The ubiquitous NHC ligands are also widely employed as the ligand of choice for both Ir<sup>III</sup>- and Ir<sup>I</sup>-mediated catalytic



**Figure 1.** Ellipsoid plots of complexes 1–5 and 7 (50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): **1**, Ir–C<sub>carbene</sub> 1.972(2), C<sub>carbene</sub>–O 1.349(2), C<sub>carbene</sub>–C<sub>ipso</sub> 1.443(3); **2**, Ir–C<sub>carbene</sub> 1.963(9), C<sub>carbene</sub>–O 1.317(11), C<sub>carbene</sub>–C<sub>ipso</sub> 1.458(13); **3**, Ir–C<sub>carbene</sub> 1.954(7), C<sub>carbene</sub>–O 1.319(10), C<sub>carbene</sub>–C<sub>ipso</sub> 1.449(12); **4**, Ir–C<sub>carbene</sub> 2.0145(17), C<sub>carbene</sub>–N 1.315(2), C<sub>carbene</sub>–C<sub>ipso</sub> 1.475(2); **5**, Ir–C<sub>carbene</sub> 2.029(3), C<sub>carbene</sub>–N 1.305(5), C<sub>carbene</sub>–C<sub>ipso</sub> 1.458(5); **7**, Ir–C<sub>carbene</sub> 2.065(9), C<sub>carbene</sub>–O 1.311(10), C<sub>carbene</sub>–C<sub>ipso</sub> 1.430(12);

hydrogen transfer reactions, although examples of iridium(I) catalysts are less common.<sup>22</sup> However, to our knowledge, only one example of an acyclic carbene Ir<sup>I</sup> complex active in transfer hydrogenation has been reported.<sup>15a</sup> The stability displayed by complexes 1–8 with the electronically modifiable FCC ligands portended their use as catalysts in the transfer hydrogenation of ketones.<sup>20</sup> Acetophenone was employed as the model substrate, with isopropyl alcohol solvent as the sacrificial hydrogen donor. The reaction conditions were optimized by variation of reaction times, catalysts, and base loadings (see Table S4, section S6, in the Supporting Information). Finally, the catalytic experiments were conducted in isopropyl alcohol solvent at reflux temperature, with 0.1 mol % catalyst and 0.5 mol % base loading, with respect to the substrate acetophenone (Table 2). The addition of mercury to the catalytic reaction (entry 11, Table 2) did not result in a variation of either the conversion or calculated TOF in comparison to the mercury-free equivalent entry 6 of Table 2, indicative of a homogeneous mode of action.<sup>21</sup> In addition, a stability test was conducted whereby complex 6 and a stoichiometric amount of base KOH was refluxed in isopropyl alcohol solvent for 16 h. Both the <sup>1</sup>H and <sup>13</sup>C NMR spectra provide clear evidence that the coordinated carbene ligand

remains intact (Figures S22 and S23 in the Supporting Information).

In general, more electron donating carbene ligands, e.g. aminocarbene (entry 4, Table 2) vs ethoxycarbene (entry 1, Table 2) or Fc-FC (entry 2, Table 2) and *p*-DMA-FC (entry 1, Table 2) vs Cp<sup>+</sup>Re(CO)<sub>3</sub>-FC (entry 3, Table 2), perform better, as was also found to be the case for NHCs.<sup>22b</sup> This is also true for the coligands cod (entries 2 and 5, Table 2) vs (CO)<sub>2</sub> (entries 7 and 8, Table 2), where the overall electrophilic nature of the coordination sphere influences the performance of the catalytic metal center. However, the most noteworthy observation is the best performance of complex 6 (entry 6, Table 2), in comparison to not only its ethoxy analogue 2 (entry 2) but also its monoamine analogue 5 (entry 5). Indeed, a yield of 89% is achieved after a reaction time of 2 h, giving rise to a calculated TOF of 445 h<sup>-1</sup>, employing a 0.1 mol % catalyst loading, and a low catalyst/base ratio of 1/5. This result rivals that of the best-performing Ir<sup>I</sup> NHC catalysts previously reported.<sup>22</sup> The excellent performance of this (pre)catalyst 6 can be ascribed not only to the donating ability of the Fc substituent for the electrophilic carbene ligand but possibly also to the synergistic benefits associated with the inclusion of a secondary catalytically active metal center, where Fe<sup>II</sup> is known to be active in transfer hydrogenation.<sup>23</sup> More



**Table 2.** Reduction of Acetophenone with Iridium(I) FCCs 1–8<sup>a</sup>

Entry	[Ir]	Time (h)	% Conversion <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )
1	<b>1</b>	16	22(2.4)	14(1.6)
2	<b>2</b>	16	71(2.4)	45(1.3)
3	<b>3</b>	16	13(1.7)	8(0.8)
4	<b>4</b>	16	87(1.7)	55(1.3)
5	<b>5</b>	16	73(7.8)	45(4.9)
6	<b>6</b>	16	97(1.0)	61(0.6)
7	<b>7</b>	16	23(2.8)	14(1.3)
8	<b>8</b>	16	51(5.4)	32(3.3)
9	<b>4</b>	2	55(6.2)	273(31.2)
10	<b>6</b>	2	89(4.3)	445(22.0)
11	<b>6 + Hg<sup>d</sup></b>	16	98(0.0)	61(0.0)

<sup>a</sup>All reactions were done as triplicate in high-pressure reaction tubes fitted with a greasless high-vacuum stopcock under an argon atmosphere. Optimized reaction conditions: iridium/base/substrate 1/5/1000 in isopropyl alcohol at reflux temperature. Reactions were monitored by gas chromatography using *n*-decane as internal standard. <sup>b</sup>The reactions were performed in triplicate, and standard deviations are indicated in parentheses. <sup>c</sup>Average turnover frequency (TOF) ((mol of product)/(mmol of catalyst h)) determined at the reaction time. <sup>d</sup>Excess Hg(I) was placed in the reaction flask.

importantly, the improved activity of the catalyst **6** in comparison to **5**, where **6** contains an aminocarbene ligand carrying a pendant N-donor moiety, is indicative of the potential hemilabile role of this aminocarbene ligand in the catalytic cycle, as proven for other iridium-mediated transfer hydrogenation catalysts.<sup>22d–f,24</sup>

In summary, rare examples of monoheteroatom-stabilized carbene complexes of Ir<sup>I</sup> are accessible via facile carbene transfer from group 6 FCCs. This paves the way to tunable carbene ligands coordinated to Ir<sup>I</sup>, via simple ligand modification reactions for new examples of catalytically relevant iridium(I) FCCs. Introduction of a donor-functionalized FCC ligand with a pendant N donor yields an Ir<sup>I</sup> (pre)catalyst for the hydrogen transfer reaction from isopropyl alcohol to acetophenone with high efficiency, requiring both a low catalyst and base loading for this benchmark reaction. This work reports but the second example of acyclic carbene complexes of iridium(I) for catalytic application in hydrogen transfer reactions. The catalytic activities of the Ir<sup>I</sup> complexes are largely controlled by the electrophilicity of the Ir<sup>I</sup> metal center.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00079>.

Experimental details, including synthesis, NMR and FT-IR spectra, SC-XRD, and catalysis details (PDF)

## Accession Codes

CCDC 1970902–1970907 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

FCC, Fischer carbene complex; NHC, N-heterocyclic carbene; Fc, ferrocenyl; *p*-DMA, *para*-*N,N*-dimethylaniline; cod, 1,5-cyclooctadiene; tlc, thin-layer chromatography; TOF, turnover frequency

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