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THE ACTIATION OF C-H BONDS WITH INTERMEDIATES PRODUCED  
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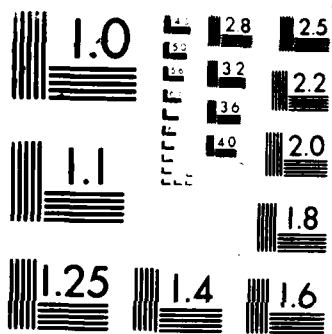
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TECHNICAL REPORT NO. 126

The Activation of C-H Bonds with Intermediates  
Produced by Mild Thermal and Photochemical Decomposition  
of the Metallacycle  $(C_5Me_5)Ir[C(p-ClC_6H_4)=NOC(=O)](CO)$   
in Hydrocarbon Solvents

by

Peter A. Chetcuti and M. Frederick Hawthorne\*

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Abstract

Thermolysis of the metallacycle  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}[\text{C}(\text{p-ClC}_6\text{H}_4)=\text{NOC}(=\text{O})](\text{CO})$  (**1**) at 50°C in benzene or cyclohexane leads initially to the formation of the side-bonded nitrile complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^2\text{-NCC}_6\text{H}_4\text{Cl})(\text{CO})$  (**5**) which has been isolated and characterized. Upon further heating at 50°C loss of the nitrile ligand from **5** results in C-H bond activation of benzene solvent to generate  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{H})(\text{C}_6\text{H}_5)(\text{CO})$  (**2**) in 90% yield. These reactions presumably proceed through the 16-electron metal fragment " $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})$ ". Decomposition of **1** and **5** under mild photolytic conditions in both benzene and cyclohexane also led to C-H activation of the hydrocarbon solvents, generating **2** and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})(\text{H})(\text{C}_6\text{H}_{11})$ , **6**.

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In recent years a number of transition metal complexes have been found to undergo photochemically induced intermolecular C-H bond activation of their hydrocarbon solvents.<sup>1-6</sup> The aryl and alkyl metal hydride products of these reactions are believed to result from the oxidative addition of the 16-electron coordinatively unsaturated metal fragments, "ML<sub>n</sub>", generated by the photolytically induced loss of H<sub>2</sub> or CO, into the C-H bonds of hydrocarbons (Scheme 1). Insertion into C-H bonds also occurs with thermal activation, suggesting that these reactions do not specifically require the reactive metal fragment to be in a photoexcited state.<sup>1a,4,7-18</sup> A preponderance of the previously reported examples of thermal C-H bond activation, in which the products of direct

[Scheme 1]

oxidative addition are observed, involve the reductive elimination of an alkyl or aryl metal hydride, to apparently produce the reactive species "ML<sub>n</sub>", followed by its oxidative addition into the C-H bond of another hydrocarbon.<sup>1b,4,7-9,15-18</sup> In effect, these reactions require as a reactant a metal center which has already undergone C-H activation into a C-H bond and constitute hydrocarbon exchange reactions.

We now wish to report the thermal activation of C-H bonds of hydrocarbons using the precursor metallacycle  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}[\overline{\text{C}(\text{p-ClC}_6\text{H}_4)=\text{NOC}(=\text{O}))}(\text{CO})$  (**1**).<sup>19,20</sup> Thermolysis of **1** would be expected to generate the 16-electron four-coordinate species " $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})$ " (Scheme 2)

[Scheme 2]

which is presumed to be responsible for the activation of a number of hydrocarbons when generated photolytically from  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ .<sup>2</sup> When the metallacycle **1** was maintained in the dark at 50°C in benzene solution for four weeks, a hydride resonance at -15.07 ppm was observed and attributed to the product  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})(\text{H})(\text{C}_6\text{H}_5)$  **2a** (**2**) formed by the oxidative addition of " $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})$ " into the C-H bonds of benzene;<sup>21</sup> addition of  $\text{CCl}_4$  converted **2** to the known  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})(\text{Cl})(\text{C}_6\text{H}_5)$  **22,2a** (**3**) in 90.4% overall yield while the known dimer  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-CO})]_2$  (**4**),<sup>23</sup> identified by its <sup>1</sup>H NMR resonance at 1.58 ppm in  $\text{C}_6\text{D}_6$ , was produced in 8.6% yield as determined by NMR. When the reaction of **1** was carried out in 100% deuterated benzene and monitored by <sup>1</sup>H NMR, two sets of doublets at  $\delta$  7.71 ( $J = 8.3$  Hz) and 7.01 ( $J = 8.3$  Hz) appeared;<sup>24</sup> as the reaction proceeded these resonances decreased in intensity as the resonances due to the free  $\text{p-ClC}_6\text{H}_4\text{CN}$  increased. The same intermediate resonances were observed when the reaction was carried out in cyclohexane and the <sup>1</sup>H NMR of the reaction products obtained before the reaction had gone to completion, thus suggesting the existence of a common intermediate which is formed before oxidative addition of the solvent occurs. In order to isolate the intermediate, a THF solution of (**1**) was stirred at 50°C for 14 hours in the dark. Upon removal of the THF under *vacuo* and extraction of the residue with pentane, a yellow solution was obtained which on cooling afforded a yellow crystalline product in 66% yield. The complex obtained is a side-bonded nitrile complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^2\text{-NCC}_6\text{H}_4\text{Cl})\text{CO}$  **24** (**5**) identified by its characteristic low CN stretching frequency observed at  $1781\text{ cm}^{-1}$  in the IR spectrum.<sup>25,26</sup> Complex **5** was also characterized by <sup>1</sup>H NMR spectroscopy, complete elemental analyses and its molecular structure has been determined by a single-crystal X-ray diffraction study.<sup>27</sup> The resonances in the <sup>1</sup>H NMR spectrum of **5** <sup>24</sup> coincide with those of the intermediate observed when the thermolysis of **1** was monitored by <sup>1</sup>H NMR as described above. In order to confirm that **5** independently activates C-H bonds of hydrocarbons, a 0.07 M solution of **5** in benzene was

maintained in the dark at 50°C for 36 hours, generating the phenyl hydride product, **2**, and the dimer, **4**, in 76.2% and 18.4% yield, respectively. A mechanism consistent with these observations involves the loss of CO<sub>2</sub> from **1** to generate the nitrile complex **5** which at 50°C is labile and loses the coordinated nitrile to release the metal fragment "(C<sub>5</sub>Me<sub>5</sub>)Ir(CO)" which then undergoes C-H bond activation (Scheme 3). The metallacycle **1** was also found to be very photosensitive; when a

[Scheme 3]

sample of **1** was maintained in benzene at 50°C and photolyzed<sup>28</sup> for 36 hours, **2** was obtained in 75.4% yield and **4** in 7.5% yield. The side-bonded nitrile **5** was observed when the <sup>1</sup>H NMR spectrum of the reaction mixture was obtained before the reaction had gone to completion although the steady state concentration of **5** was low since this compound was particularly photosensitive. When **5** was photolyzed<sup>28</sup> in benzene for 12 hours at 50°C, **2** was obtained in 80.6% yield by <sup>1</sup>H NMR; compound **4** was obtained in 4.7% yield. Photolysis of metallacycle **1** in cyclohexane for 13 days under the same conditions yielded the cyclohexylhydride product, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ir(CO)-(H)(C<sub>6</sub>H<sub>11</sub>) (**6**); addition of CCl<sub>4</sub> converted **6** to the known (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ir(CO)(Cl)(C<sub>6</sub>H<sub>11</sub>) (**7**) **2a** in 48.6% overall yield. The dimer **4** was obtained in 33.7% yield. When the side-bonded nitrile complex **5** was photolyzed for 24 hours in cyclohexane at 50°C, **6** was obtained which was converted to the chloride derivative to yield **7** in 67.1% overall yield; compound **4** was obtained in 13.1% yield.

The rhodium metallacycle (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(PMe<sub>3</sub>)Rh{C(*p*-FC<sub>6</sub>H<sub>4</sub>)=NOC(=O)} demonstrates a reactivity similar to that of **1** since the formation of a side-bonded nitrile complex and thermal C-H activation of hydrocarbon solvents are observed. Full details concerning this reaction will be reported shortly.

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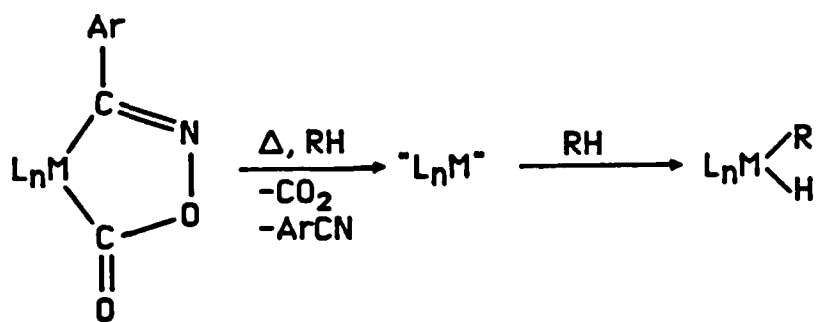
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19. We have synthesized a number of metallacycles by cycloaddition of aryl nitrile oxides with low valent metal carbonyl complexes. A preliminary communication has been published (Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3370) and a complete report will be submitted shortly.
20. Selected data for **1** (full details will be reported elsewhere<sup>19</sup>).  
**1**: Anal. Calcd. for C<sub>19</sub>H<sub>19</sub>ClIrNO: C, 42.57; H, 3.58; Ir, 35.85; N, 2.61. Found: C, 42.12; H, 3.64; Ir, 35.88; N, 2.40. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.39 (d, 2H, J = 8.5 Hz), 7.10 (d, 2H, J = 8.4 Hz), 1.23 (s, 15H).
21. The reactions were carried out in NMR tubes using dried and degassed solvents. In a typical experiment 0.8 mL of reactant solvent was vacuum transferred into 8 mg of the metallacycle **1** and the reactants maintained at a constant temperature. When the reaction was complete the reactant solvent was removed under vacuum and deuterated benzene was then vacuum transferred in and the tube sealed. The alkyl and aryl metal hydrides formed were identified by matching the <sup>1</sup>H NMR chemical shifts with the reported values published by other workers or by conversion to the chloro derivatives by addition of CCl<sub>4</sub>.<sup>2a</sup> Relative yields were measured by <sup>1</sup>H NMR integration.
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24. **5**: IR (nujol): 1949 (br, ν<sub>CO</sub>), 1781 (m, ν<sub>CN</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.72 (d, 2H, J = 8.3 Hz), 7.01 (d, 2H, J = 8.3 Hz), 1.69 (s, 15H).
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26. Side-bonded nitrile complexes have been isolated and characterized as the major products in the thermolysis of the metallacycles  $(C_5H_5)Ir[C(Ar)=NOC(=O)](PPh_3)$ , ( $Ar = p-ClC_6H_4^-$ ,  $p-FC_6H_4^-$ ); Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1986**, *5*, 1913.
27. Complete details on the X-ray crystal structure of **5** will be given in a full report discussing the reactivity of metallacycles of rhodium and iridium.
28. Photochemical experiments were carried out using a 100-W bulb which was supported six inches above an oil bath in which the NMR tubes were maintained at constant temperature. The radiated light was contained within the system by aluminum foil and a stream of cold nitrogen gas was used to cool the system to the desired temperature.





Scheme 2

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