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## C–H Activation

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## Manganese(I)-Catalyzed C–H Activation: The Key Role of a 7-Membered Manganacycle in H-Transfer and Reductive Elimination

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Dedicated to Professors Michael Bruce and Robin N. Perutz

**Abstract:** Manganese-catalyzed C–H bond activation chemistry is emerging as a powerful and complementary method for molecular functionalization. A highly reactive seven-membered  $Mn^I$  intermediate is detected and characterized that is effective for H-transfer or reductive elimination to deliver alkenylated or pyridinium products, respectively. The two pathways are determined at  $Mn^I$  by judicious choice of an electron-deficient 2-pyrone substrate containing a 2-pyridyl directing group, which undergoes regioselective C–H bond activation, serving as a valuable system for probing the mechanistic features of Mn C–H bond activation chemistry.

C–H bond activation–functionalization chemistry is a central arena for catalyst development and synthetic application.<sup>[1]</sup> Transition metals mediate the efficient and selective activation of C–H bonds, with recent attention focusing on environmentally benign and sustainable metals, for example, Mn, Co, Fe, and Cu.<sup>[2]</sup>  $Mn^I$  promotes C–H activation of substrates containing nitrogen-directing groups.<sup>[3]</sup> For example, **1** gives cyclomanganated complex **2**, with subsequent reaction with alkyne **3** forming a proposed 7-membered ring intermediate **4** (Scheme 1).<sup>[4]</sup> Formation of either **5**, **6**, or **7** results from reductive elimination, H-transfer, or dehydrogenative annulation, respectively.

Processes utilizing  $Mn^I$ , particularly  $[Mn(C^{\wedge}N)(CO)_4]$  **2**,<sup>[5,6]</sup> have been of broad interest. The mechanistic features of the remarkable synthetic work of Ackermann and Wang,<sup>[3,4]</sup> where intermediates **4a–c** have been proposed,

prompted us to examine whether they could be detected and characterized and then subsequently be shown to deliver organic products such as **5–7**. Complexes **4d–f**, formed by insertion of internal alkynes are known,<sup>[6,7]</sup> but their competence in terms of a fully connected reaction system, affording organic products, has not been examined. As 18-electron species containing four CO ligands, possessing high thermodynamic stability, they are unlikely to be directly involved in the catalytic cycle.<sup>[8]</sup>

Herein we describe a suitable reaction system (**1g**→**4g**→**5g** or **6g**, Scheme 1) that takes advantage of the exquisite reactivity of an electron-deficient 2-pyrone ring system containing a 2-pyridyl directing group (**1g**). We recognized that the 2-pyrone could act as a hemilabile ligand in 7-membered manganacycle **4g**, potentially providing sufficient stabilisation for observation of this key intermediate. Our findings demonstrate that **4g** acts as a central manifold to reductive elimination and H-transfer, giving products **5g** and **6g**, respectively, with details described herein.

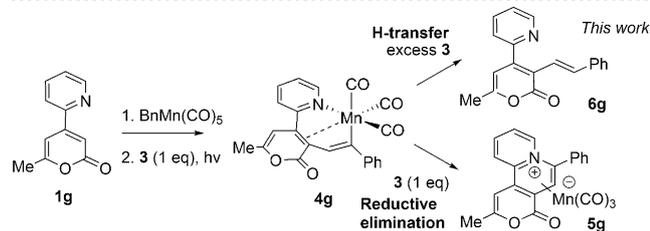
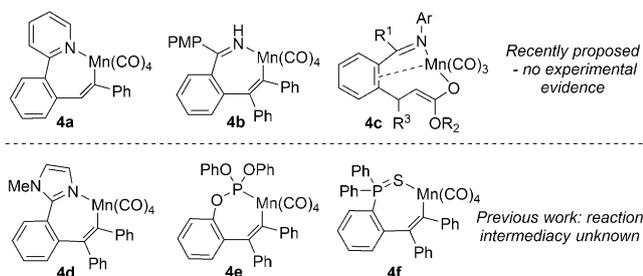
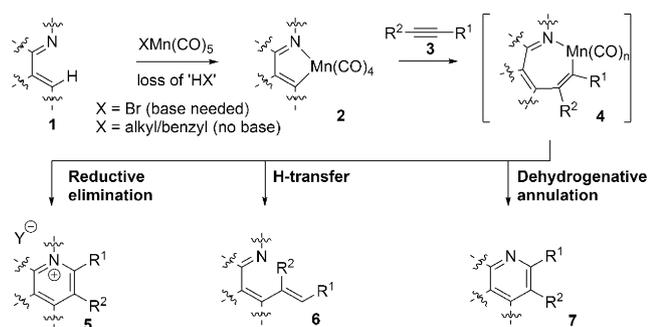
Our study began with the reaction of 2-pyrone **1g** with  $BnMn(CO)_5$  in hexane at 75 °C, which gave cyclometalated **2g** cleanly and in quantitative yield (Scheme 2). Complex **2g** was fully characterized (see the Supporting Information); a single crystal X-ray structure confirmed that regioselective C–H activation occurred at C3, in keeping with  $Pd^{II}$ -direct arylations of 2-pyrones,<sup>[9]</sup> albeit most likely by a  $\sigma$ -CAM-type process.<sup>[10]</sup>

We hypothesized that UV irradiation<sup>[11]</sup> of **2g** would lead to solvated intermediate  $I_{pyr}$  (Scheme 2, middle inset).<sup>[12]</sup> Subsequent alkyne trapping via intermediate  $II_{pyr}$ , would then convert into the alkyne insertion manganacycle **4g**. UV irradiation (Hg/Xe Arc lamp, 200–2500 nm) of a mixture of **2g** and **3** (1.1 equiv) in  $[D_8]THF$  at 240 K (at 5 min intervals), and reaction monitoring by  $^1H$  NMR spectroscopy between intervals, revealed the formation of a new intermediate that grows up to 9.6 % conversion. Further irradiation resulted in spectral broadening (paramagnetic species), but crucially, full NMR analysis of manganacycle **4g** was possible, with HMQC/HMBC correlation methods/n.O.e. experiments. Analysis shows that **4g** formed regioselectively at C3 (Scheme 2, bottom inset). MS analysis also confirmed the presence of **4g** (LIFDI  $m/z$  427 for  $[M]^+$  and ESI  $m/z$  428 for  $[MH]^+$ ) in solution.

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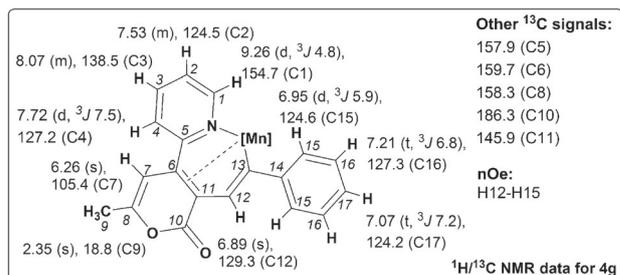
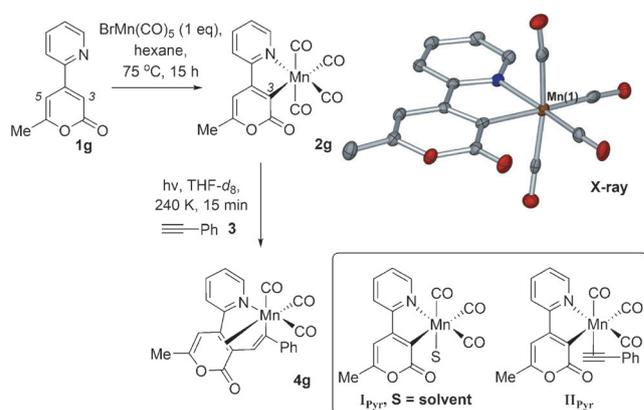


**Scheme 1.** Manganese(I)-catalyzed C–H activation, and potential products and intermediates.

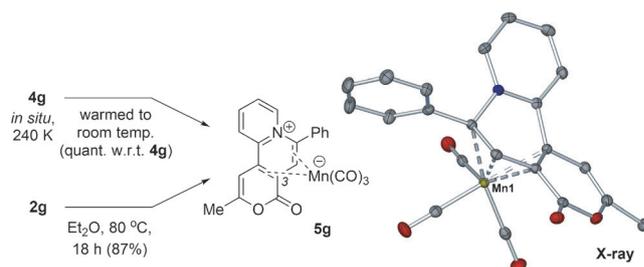
Experimentally there is evidence in **4g** of an interaction between the 2-pyrone olefinic bond (C6–C11) and the Mn<sup>I</sup> center at  $\delta = 159.7$  ppm (C6) and  $\delta = 145.9$  ppm (C11), which stabilizes the tricarbonyl complex. Computational studies (DFT methods) confirm that HOMO–4 within **4g** has 2-pyrone–Mn bonding character (see the Supporting Information), confirming **4g** as a feasible structure. The small coordination shifts in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum imply this interaction is weak, although generation of a vacant site at Mn (**4g'**) and subsequent alkyne coordination (**4g''**) ought to be feasible. The DFT studies for **III<sub>Pyr</sub>** (**4g**) and **III<sub>Ph</sub>** (**4a**) indicate no low-lying vacant orbitals (HOMO–LUMO gap = 1.70154–1.97588 eV), consistent with Mn having an 18-electron count.

Warming of the [D<sub>8</sub>]THF solution of **4g** to room temperature led to the formation of the reductive elimination product **5g** (Scheme 3). Complex **5g** was fully characterized (see the Supporting Information) and confirmed by X-ray analysis to possess a Mn(CO)<sub>3</sub> anion. **5g** was also formed in 87% yield on treatment of **2g** with **3** (1.1 equiv.) at 80 °C, Et<sub>2</sub>O, 18 h (sealed tube). Thus, the same reaction pathway (**2g** + **3** → **5g**) results from either UV irradiation or thermal heating, validating our approach in utilizing UV irradiation to enable detection and characterization of intermediate **4g**.

Interestingly, catalytic reactions of **1g** with **3**, under the reaction conditions reported by Wang et al.<sup>[4]</sup> for 2-phenyl-

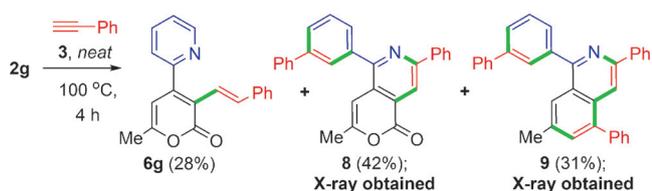


**Scheme 2.** Cyclomanganation of **1g** gives **2g**, which upon photolysis with phenylacetylene **3** gives **4g**. The X-ray structure of **2g** is given (top right, ellipsoids set at 50% probability; H-atoms omitted and Mn atom labeled only for clarity). Insets: proposed transient intermediates on route to **4g** and the key NMR data for **4g**.



**Scheme 3.** Thermally controlled reductive elimination from either **2g** or **4g** to give **5g**. An X-ray structure of a single crystal of **5g** is also shown (ellipsoids set to 50% probability; H-atoms omitted and Mn atom labeled only, for clarity).

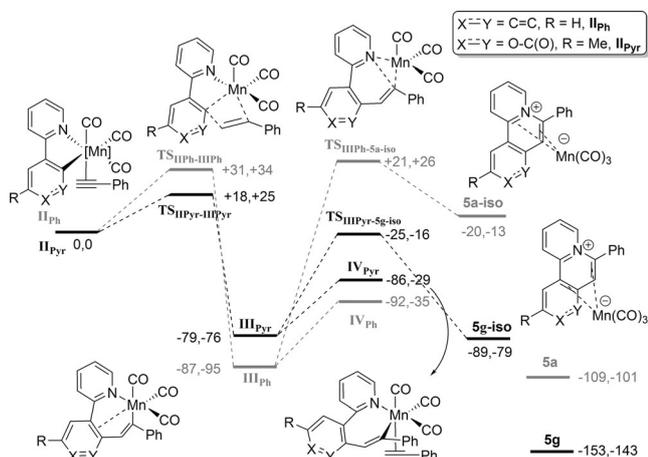
pyridine **1a** (conditions: BrMn(CO)<sub>5</sub>, C<sub>2</sub>NH, Et<sub>2</sub>O, 100 °C for 6–24 h), do not lead to formation of alkenylated products (for example, **6g**). This indicates that the rate of reductive elimination from **4g** to give **5g** is faster than the rate for alkyne H-transfer to give **6g** (see above). We rationalized that reaction of **2g** in neat phenylacetylene **3** would enable H-transfer to become the dominant pathway (Scheme 4), but the reaction afforded three new products. Firstly, the H-transfer product **6g** was formed in 28% yield; an excess of **3** favors H-transfer over reductive elimination. Central to the success of the reaction is coordination of a second molecule of alkyne **3** and subsequent alkyne H-transfer of intermediate **4g**. The other products **8** and **9** were unexpected, resulting from a noteworthy Diels–Alder reaction (DAR) of **3** with the 2-pyridine ring,<sup>[13]</sup> followed by ring fragmentation (single-



**Scheme 4.** Reaction of **2g** in neat phenylacetylene **3**. The green bonds show the newly formed bonds in the organic products, with red showing the insertion location of **3** (**5g** not observed under these reaction conditions).

crystal X-ray structures of **8** and **9** confirmed the molecular connectivity, correlating with NMR spectroscopy, see the Supporting Information). Compound **9** shows that the 2-pyrone participated in a secondary inverse electron demand DAR.<sup>[14]</sup> Along with **6g**, both **8** and **9** derive from **4g**, where the DARs and 2-pyridyl fragmentation are secondary reactions.

To understand the steps leading to the formation of **5g** DFT methods were used (Scheme 5, see the Supporting



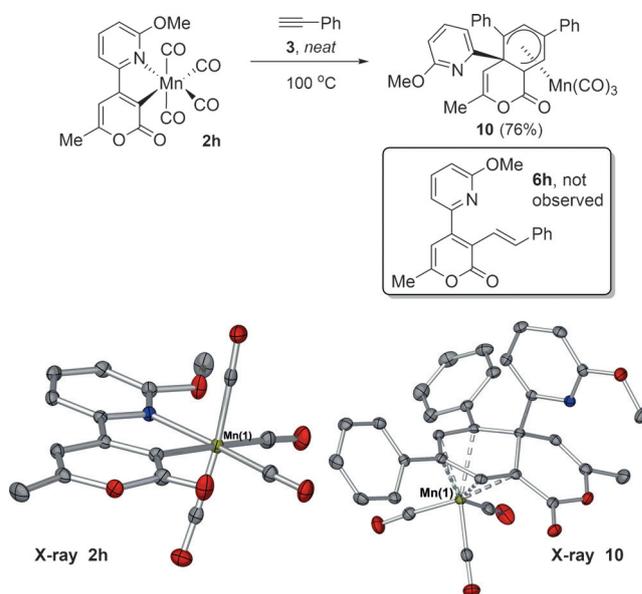
**Scheme 5.** DFT calculations showing the feasibility of reductive elimination from **5a** and **5g**, starting from intermediates **II<sub>Ph</sub>** and **II<sub>Pyr</sub>** respectively. Energies are zero point energy-corrected electronic energies and Gibbs energies at 298.15 K in  $\text{kJ mol}^{-1}$  relative to **II**.

Information for details of DFT calculations). Starting from **II<sub>Pyr</sub>**, formed via loss of CO from **2g** and coordination of **3**, insertion of coordinated alkyne into the Mn–C(pyrone) bond proceeds through a low-energy transition state (**TS<sub>IV<sub>Pyr</sub>-III<sub>Pyr</sub></sub>**) to give **III<sub>Pyr</sub>**. The latter intermediate is equivalent to characterized **4g**. C–N reductive elimination from **III<sub>Pyr</sub>** via transition state **TS<sub>III<sub>Pyr</sub>-5g-iso</sub>**, results in the formation of the 2-methyl-4-oxo-6-phenyl-4*H*-3,7λ<sup>5</sup>-pyrano[4,3-*a*]quinolizin-7-ylidinium ring system (**5g**). A DRC analysis of **TS<sub>III<sub>Pyr</sub>-5g-iso</sub>** revealed that the imaginary eigenvector led to **5g-iso** (the coordination isomer of **5g**); a  $\pi$ -slip then gives **5g**.

The corresponding potential energy surface for the phenyl-substituted system (giving the Chen and Wang product **5a**) revealed that the same reaction pathway was viable (pathway shown in gray in Scheme 5). The barrier to insertion of **3** (**TS<sub>II-III</sub>**) was slightly greater (Gibbs energies at 298.15 K

relative to the respective compound **II** + 25  $\text{kJ mol}^{-1}$  for 2-pyrone versus + 34  $\text{kJ mol}^{-1}$  for phenyl) and that **III<sub>Pyr</sub>** was relatively higher in energy than **III<sub>Ph</sub>** (–76  $\text{kJ mol}^{-1}$  versus –95  $\text{kJ mol}^{-1}$ ). To explain the different outcome from the phenyl and 2-pyrone substituents it is informative to consider the higher energy of **TS<sub>III<sub>Ph</sub>-5a-iso</sub>** (+ 26  $\text{kJ mol}^{-1}$ ) against **TS<sub>III<sub>Pyr</sub>-5g-iso</sub>** (–16  $\text{kJ mol}^{-1}$ ). Therefore, the energetic spans for reductive elimination are 60  $\text{kJ mol}^{-1}$  (2-pyrone) and 121  $\text{kJ mol}^{-1}$  (phenyl). When compared with the formation of **IV<sub>Pyr</sub>** and **IV<sub>Ph</sub>**, which is the next step in forming H-transfer products **5g** and **5a**, respectively, it is evident that the reductive elimination to form **5g** is competitive, but in the case of **5a** the much larger energetic span to reductive elimination allows for productive catalysis via alkyne coordination to give **IV<sub>Ph</sub>**.<sup>[4]</sup>

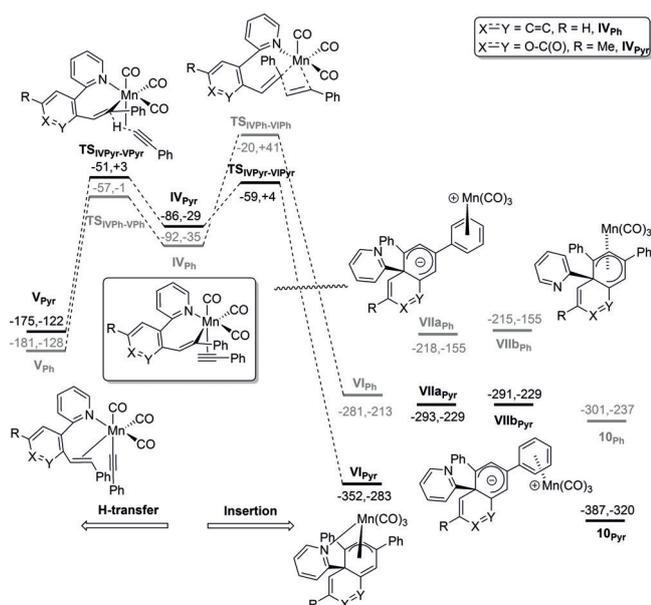
While no double alkyne insertion products were detected in reactions of **2g** with phenylacetylene **3**, the reaction of related derivative **2h** with **3** resulted in exclusive formation of double alkyne insertion product **10** (Scheme 6; the structure



**Scheme 6.** Double alkyne insertion into **2h**. Dotted lines show Mn coordination in complex **10** for clarity (ellipsoids set to 50% probability; H-atoms omitted and Mn atom labeled only, for clarity).

of **6h** is shown as an expected alkenylated product). This remarkable result shows the impact that a subtle change to the pyridyl directing group has on the barriers to these steps.

We rationalized the experimental observations by DFT calculations, which enabled a mechanism for this reaction and the differences between the phenyl- and 2-pyrone-substituted complexes to be proposed (Scheme 7). In the case of the pyrone derivative, coordination of alkyne to **III<sub>Pyr</sub>** results in formation of **IV<sub>Pyr</sub>** having two energetically accessible fates. H-transfer through **TS<sub>IV<sub>Pyr</sub>-V<sub>Pyr</sub></sub>** (+ 3  $\text{kJ mol}^{-1}$ ) results in the formation of alkynyl complex **V<sub>Pyr</sub>** which would liberate **6h**, however insertion of the alkyne into the Mn–C bond of **IV<sub>Pyr</sub>** through **TS<sub>IV<sub>Pyr</sub>-VI<sub>Pyr</sub></sub>** (+ 4  $\text{kJ mol}^{-1}$ ) affords more energetically favourable **VI<sub>Pyr</sub>**. The process seen for reactions of **2h** has



**Scheme 7.** DFT calculations showing the feasibility of a double alkyne insertion pathway to rationalize formation of double alkyne insertion product **10**. Energies are zero point energy-corrected electronic energies and Gibbs energies at 298.15 K in  $\text{kJ mol}^{-1}$  relative to **II**.<sup>[17]</sup>

resulted in the formation of two C–C bonds. Preliminary investigations indicate that this proceeds through a “two-steps no intermediate” pathway<sup>[15]</sup> with the initial insertion into the Mn–C bond, followed by cyclization giving a six-membered ring without an intermediate. However, in **VI<sub>pyr</sub>**, the Mn is  $\eta^3$ -coordinated to the pendant pyridyl group and newly formed ring. To form **10<sub>pyr</sub>**, which is the lowest point on the potential energy surface at  $-320 \text{ kJ mol}^{-1}$ , the Mn needs to migrate to the alternative ring-face. We postulate that this involves migration onto one of the phenyl rings in the ligand, for example, **VIIa<sub>pyr</sub>**. The ring rotates allowing the Mn to migrate to the other face of the pentadienyl system, giving **VIIb<sub>pyr</sub>**. It is reasonable to presume that this proceeds via a low energy ring-walking process.<sup>[16]</sup>

In the case of the phenyl derivative, all of the states predicted for the 2-pyrone system are viable; however, **TS<sub>IVph-VPh</sub>** is far higher in energy than **TS<sub>IVph-VPh</sub>** ( $+41 \text{ kJ mol}^{-1}$  versus  $-1 \text{ kJ mol}^{-1}$ ). Therefore, insertion of the second alkyne is non-competitive, with the H-transfer pathway leading to the alkenylated product, consistent with experimental observations.

In conclusion, we have detected and characterized a commonly proposed 7-membered manganyl cycle **4g** (of direct relevance to generic structure **4**, Scheme 1). Manganyl cycle **4g** sits at the selectivity junction to reductive elimination or H-transfer steps. Depending on the reaction conditions, **5g** or **6g** products form that correspond to reductive elimination and protonation pathways, respectively. Double alkyne insertion to give **10** has also been revealed in these studies. Our observations provide the first clear cut evidence that manganyl cycles such as **4** are key intermediates in Mn<sup>I</sup>-mediated C–H bond activation processes involving substrates containing directing groups.<sup>[3,4,7]</sup> More generally, such intermediates

may be considered as leading to side reactions, but here we have shown that it presents an opportunity to control product selectivity. Serendipitously we have uncovered a rare example of a DAR of a pyridine derivative, where the intermediate fragments to form products such as **8** and **9**. Taken together, our findings provide a unique insight into Mn<sup>I</sup>-mediated C–H bond activation processes, especially how relatively minor changes in substrate structure influence product selection; Mn<sup>I</sup>-based metallocycles clearly offer rich chemistry,<sup>[3]</sup> much potential, and warrant further study more generally in organic and organometallic chemistry.

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