1. In the second sentence of the introduction, the authors state "One of the principal goals for such processes has been the conversion of light alkanes into transportable, value-added chemicals". What is meant by 'transportable, value-added chemicals'? This will likely require you to use additional resources, be sure to properly cite them.
2. One of the ligands employed in this study is the nitrosyl ligand (NO). Describe how this ligand interacts with a metal and determine how it impacts the classification and electron count. Including pictures of the orbital interactions might prove useful.
3. In scheme 1, the synthesis of complex 1 is outlined. The starting material in this process is [Cp\*W(NO)(Cl)2]. This reacts with Mg(CH2CMe3)2 to yield [Cp\*W(NO)(Cl)(CH­2CMe3)] which is described as a 16 electron compound in the paragraph beneath the scheme. Classify this compound, provide an electron count, the ligand bond number, the valence on tungsten and the dn count for tungsten. Although in reference to complex 2, you might look beneath Figure 1 for some helpful information.
4. How do these parameters change in going from [Cp\*W(NO)(Cl)(CH­2CMe3)] to complex 1?
5. Describe the bonding on the CH2CH=CMe2 ligand in complex 1.
6. Why is the synthesis of [Cp\*W(NO)(Cl)(CH­2CMe3)] performed in THF while the synthesis of complex 1 is performed in Et2O.
7. Scheme 2 presents the C-H activation of methane using complex 1. What is the other (organic) product of this reaction? You might think of this C-H activation as an oxidative addition of CH4 followed by a reductive elimination of the organic product.
8. Although the previous question told you to think of the C-H activation as oxidative addition followed by reductive elimination, that is completely incorrect. The reaction cannot follow that pathway. Why?
9. Complex 2 exists as a mixture of two isomers. However, there are four possible isomers of this compound. Describe the two missing isomers. Describe the difference between the endo and exo isomers. What rationalization do the authors present for the distribution of the isomers of 2?
10. Describe why the C-H activation of methane shows a dependence on the methane pressure. As part of your discussion you should include a brief description of the formation of complex 3.
11. Complexes 1 and 2 both react with carbon monoxide. What type of reaction is taking place? In your own words describe the steps in the mechanism proposed in Scheme 5. Your description should include a rationale for the significance of step 1 in the mechanism.
12. The prolonged exposure of complex 2 to carbon monoxide results in the formation of two different isomers of a ketone containing product, 6a and 6b. How do the authors propose these isomers form?
13. In describing the characterization of complex 6b the authors mention the presence of 183W satellites, and in particular how these satellites are observed for the signals for the coordinated alkene in the 13C NMR spectrum. What are 183W satellites and why do they occur?
14. In the paragraph above scheme 7, the authors describe the infrared spectrum of complex 6b. Account for the two different CO vibrations in this molecule. The NO vibration occurs at a higher frequency than the NO vibrations in complexes 1-5. The authors briefly describe why this is. Provided a more detailed explanation.
15. The prolonged exposure of complex 1 to carbon monoxide also results in the formation of a coordinated ketone, complex 7. Complex 7 appears to form in only one isomeric form making it different from the reaction of complex 2 which results in two isomers, 6a and 6b. The authors do not offer any suggestions as to why this happens, but perhaps you can.
16. Under higher pressures of CO, both complex 1 and complex 2 react to give [Cp\*W(NO)(CO)2] and free ketone. The carbonylation of complex 1 results in the formation of a single product while the reaction of complex 2 results in three different isomers. Account for this difference.
17. Figure 9 outlines a cycle for the conversion of methane to ketones. How do the authors close the loop in going from compound 8 to the initial starting material mentioned in question 3?