This paper (*Organometallics* **2016**, *35*, 3163) outlines the reactivity of a zirconium compound with carbon monoxide and isonitriles. Although these molecules are isoelectronic, they give very different products.

1. The zirconium compound (compound 1) studied in this paper contains Cp\* ligands. What is the formula for Cp\*? Depict the orbital interactions between the metal center and a Cp\* ligand.
2. The compound of interest in this paper is Cp\*2Zr(2,3-dimethylbutadiene) (compound 1). Three different depictions of this molecule are shown below (two of which are shown in a generic sense just above the results and discussion section of the paper). Classify each structure using CBC MLlX­xZz classification, determine the ligand bond number, the valence on zirconium and the dn count for zirconium. Note: For clarity, the methyl groups of the Cp\* ligands are not shown.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
| Cp\* |  |  |  |
| C=C |  |  |  |
| Zr-C |  |  |  |
| Classification |  |  |  |
| EN: |  |  |  |
| LBN: |  |  |  |
| Valence: |  |  |  |
| dn |  |  |  |

1. Shown below is the MLX plot for zirconium. Based on this information, rank the structures in question 2 from most common to least common.

|  |  |
| --- | --- |
| **Zr** | **Electron Number** |
| **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** | **16** | **17** | **18** | **T** |
| **Valence** | **0** | ML2 |  | ML3 |  | ML4 |  | ML5 |  | ML6<1% |  | ML7<1% | <2% |
| **1** |  | ML2X |  | ML3X |  | ML4X |  | ML5X |  | ML6X |  |  |
| **2** | MLX2 |  | ML2X2 |  | ML3X2<1% |  | ML4X2 |  | ML5X2<1% |  | ML6X26% | <8% |
| **3** |  | MLX3 |  | ML2X3<1% |  | ML3X3 |  | ML4X3 |  | ML5X32% |  | <3% |
| **4** | MX42% |  | MLX4 |  | ML2X43% |  | ML3X43% |  | ML4X455% |  | ML5X425% | 88% |
| **T** | 2% |  |  | <1% | <4% |  | 3% |  | <57% | 2% | <32% |  |

1. While electron counting is a nice formalism, it is not superior to looking at actual experimental data. The structure of compound 1 was determined in this paper (although it appears in the supporting information). Using the data provided, provide rationale for the structure presented in question 2 that seems to best fit the experimental evidence. All of the bonds of interest are drawn as dashed lines so they do not bias you towards a structure. All distances are in Angstroms (Å).

|  |  |
| --- | --- |
|  | **Additional useful information** |
| Bond | Length (Å) | Reference |
| C-C in C2H6 | 1.532 | Organic Chemistry 6th Ed. by Brown, Foote, Iverson and Anslyn, Brooks/Cole, 2012. |
| C=C in C2H4 | 1.339 | Organic Chemistry 6th Ed. by Brown, Foote, Iverson and Anslyn, Brooks/Cole, 2012. |
| Zr-C in Cp2ZrMe2 | 2.277 | Hunter, Hrncir, Bynum, Penttila, Atwood, *Organometallics*, **1983**, *2*, 750. |

1. The structure of the Cp (C5H5) analog has not been reported, but the structure of a similar compound has. Instead of methyl groups coming off of the carbons of the C=C, the ligand is 2,3-bis(methylene)-bicyclo(2.2.2)octane (Erker, Engel, Kruger, Tsay, Samuel, Vogel, *Z. Naturforsch., B: Chem. Sci.* **1985**, *40*, 150). The relevant bond lengths are presented below. Compare this data to the data presented in question 4 and account for the differences.

|  |  |
| --- | --- |
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| C=C in C2H4 | 1.339 | Organic Chemistry 6th Ed. by Brown, Foote, Iverson and Anslyn, Brooks/Cole, 2012. |
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1. Compound 1 is reacted with carbon monoxide and a variety of isonitriles (sometimes called isocyanides). Compare the structures and electron counts of carbon monoxide to isonitriles (for our purposes HNC will be sufficient). What experimental advantages are there to working with an isonitrile over carbon monoxide?
2. Compound 1 reacts with 1 equivalent of isonitrile, RNC (R = iPr, tBu or Ad) to form a new product, either 5, 2 or 3 respectively. Propose a mechanism for the formation of one of these products. Name the key organometallic reaction that is taking place.
3. With the RNC ligands, when R = iPr, the addition of excess isonitrile results in the formation of compound 4. Why isn’t a similar compound observed when R = tBu or Ad?
4. Compound 2 reacts with iPrNC to initially yield compound A which loses tBuNC to give compound 5. Compound 5 ultimately reacts with a second equivalent of iPr to give compound 4 (Scheme 1). What does this series of reactions tell you about the stability of these compounds and provide some reasoning as to why they occur.
5. Compounds 2-5 depict an interaction between the zirconium and nitrogen. Do you think the bond distances support this interaction? Classify compound 2 using CBC MLlX­xZz classification, determine the ligand bond number, the valence on zirconium and the dn count for zirconium. Clearly indicate how you are classifying the interaction between the zirconium and nitrogen. How does this classification relate to your answer to questions 2 and 4?
6. The reaction of compound 1 with carbon monoxide gives a very different sort of product, compound 7. Scheme 2 proposes that the initial step in this reaction results in the formation of compound B which is similar to what is observed for the reaction with isonitriles. This compound undergoes reductive elimination to give compound C. Compound C undergoes β-hydride elimination to give compound 7. To verify these potential steps classify compounds B, C and 7 using CBC MLlX­xZz classification, determine the ligand bond number, the valence on zirconium in each compound and the dn count for zirconium in each compound. Hint: you may want to consider an alternative structure of compound C, you should clearly indicate any alterations you made.
7. What particular spectroscopic evidence is used to support the formation of compound 7?
8. The reaction of compound 1 with excess carbon monoxide gives an enediolate, compound 8, which is shown in the supporting information. Presumably compound B forms before compound 8. Suggest a mechanism for the formation of compound 8.
9. What reaction is taking place in the conversion of compound 7 to compound 6?