Characterization of Group VI carbonyls with bidentate phosphines

This literature discussion is based on Özer and Özkar *Turk. J. Chem.* **1999**, *23*, 9-14 and focuses on Group VI metal carbonyl compounds with bidentate phosphine ligands.

1) What is the goal of this paper?

2) The authors describe the phosphine ligands as usually being 'bidentate' and having 'two tertiary phosphorous atoms linked by a flexible hydrocarbon chain'. What does this mean?

3) There are three bidentate ligands in this study, dppm, dppe and dppp. Draw structures of these three ligands being sure to include any lone pair.

4) The other ligand in this study is a carbonyl (CO) ligand. This is not exactly like a carbonyl which you might recall from Organic Chemistry. Draw a Lewis structure of the free carbon monoxide (CO) molecule.

5) Both the phosphine ligands and the carbonyl ligands serve as what we would call L-type ligands meaning that they donate their lone pair to a metal center to make a bond. In the compounds in this study, how many electrons in total are being donated by the ligands to the metal center?

6) The metals of interest in this paper all come from Group 6. How many valence electrons do these metals have?

7) What is known as the electron number for the compound is the sum of the electrons coming from the ligands plus the valence electrons from the metal. What is the electron number for the compounds of interest in this study?

8) The authors characterize these compounds by a variety of spectroscopic techniques. The first is IR spectroscopy. They suggest that the presence of the four absorption bands in the CO-stretching region indicates a *cis*- geometry and that the metal centers are pseudo-octahedral. Using P to indicate the phosphine ligands and M to represent the metal, sketch the two possible isomers of these compounds. You should draw 2 structures and not 18 (two for each compound). Be sure to clearly indicate which is the structure proposed by the authors.

9) The IR is presented in Table 1 and the heading states that these are the CO stretching frequencies. Based on your recollection from Organic Chemistry, is there anything unusual about the stretching frequencies? How might your answer for question 4 help explain this?

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10) Consider your answer from question 8, how many phosphorous atoms are present in both structures? How many unique phosphorous environments are there in those structures?

11) Once again consider your answer from question 8, how many CO ligands are in the structures? How many unique CO environments are there in those structures?

12) For most of the compounds there are 4 CO vibrations in the IR spectrum. Is this because each CO ligand has a unique vibration? In thinking about your answer, you might want to recall what is required for a vibration to be IR active.

13) Would you expect the other isomer you found in question 8 to give the same number of CO vibrations in the IR? Why or why not?

14) The authors are quite convinced that these compounds form only one isomer. Your simplified picture in your answer to question 8 suggests that there are two possible isomers. What is missing from your simplified picture that could be a reason for only forming one isomer and suggest a possible way that you could make a modification to allow for the other isomer.

15) The authors state that the signals for the CO ligands in the ^{13}C NMR spectra appear as triplets. What are these coupling to?

16) In table 2 the authors present all of the ^{13}C NMR chemical shifts for these compounds. Note that the is a typo in the column headings and that column labeled CO_2 should actually be CH_2. The numbers in parenthesis represent the ^{13}C-^{31}P coupling constants. Explain which carbon atoms are being observed in the last five columns for compound **3c**, rationalize the coupling constants and estimate the relative integration for these peaks.

17) The authors state that "The ^{31}P{^{1}H} NMR signals of the tungsten complexes are composed of a very intense singlet accompanied by the tungsten satellites. What do they mean by this?

18) In the last paragraph on page 12, the authors discuss the idea of σ-donation and π-accepting. We previously considered the σ-donation aspect of CO ligands when we considered them as L-type, donating a pair of electrons to the metal. What is meant by CO being a π-acceptor? How does it accomplish this? What impact does it have on the CO bond?