This paper (*Organometallics* **2016**, *35*, 229) outlines the synthesis and characterization of several [M(CO)3(pincer)] (M = Cr, Mo or W) compounds.

1. Pincer ligands are an important component of this paper. What is a pincer ligand and what are they used for?
2. The compounds in this study have the general formula [M(CO)3(pincer)] (M = Cr, Mo or W). In this study, the pincer ligand is a PNP pincer. Classify the compound [Cr(CO)3(PNP)]. Since all of the metals in this study are Group VI metals, this classification will apply to all of the products reported in this paper. Provide an electron count, the ligand bond number, the valence on chromium and the dn count for chromium. Provide a rationale as to how you assigned the PNP ligand.
3. In addition to the pincer ligands, carbonyl ligands are extremely important in these compounds. Describe/depict the orbital interactions between a metal and a terminal CO ligand.
4. In organic chemistry you likely learned that the νCO band for organic carbonyls (ketones, aldehydes, carboxylic acids, amides, etc.) in the infrared spectrum typically occurs at ~1700 cm-1. The data is table 2 of the paper indicates that the νCO bands occur at significantly high wavenumbers. Account for this difference.
5. What is the boiling point of acetonitrile? You should be sure to cite your source.
6. The reactions are performed under ‘solvothermal’ conditions. Describe the reaction conditions that were used and how these conditions were advantageous to the synthesis of these compounds.
7. In the second paragraph of the introduction, the authors reference another study that prepared similar compounds in low yields. In looking at reference 2, the method used for the synthesis of these compounds is to react the ligand with [M(CO)3(CH3CN)3]. The νCO bands in the IR spectrum of [Cr(CO)3(CH3CN)3] occur at 1910 and 1782 cm-1 (Ross, B.L.; Grasselli, J.G.; Ritchey, W.M.; Kaesz, H.D. *Inorg. Chem.* **1963**, *2*, 1023). Using group theory, determine the isomer of [Cr(CO)3(CH3CN)3] that is formed.
8. The compound [Cr(CO)3(CH3CN)3] is prepared by refluxing [Cr(CO)6] in CH3CN. Considering the nature of the ligands that are being replaced, why is the isomer you found in question 7 the preferred isomer?
9. Based on your answers to questions 7 and 8, can you suggest a possible reason why the synthesis described in question 7 from reference 2 gives low yield?
10. Scheme 3 presents an alternative synthesis for some of the tungsten compounds prepared in this study. List reasons why the synthetic procedure outlined in this paper is superior to the one presented in this scheme.
11. The first step of the reaction presented in scheme 3 shows [W(CO)6] reacting with Br2. Draw a structure for the product of this reaction, [W(CO)4(μ-Br)Br]2 (there appears to be a typo in scheme 3, but the main text confirms this formula). Does the product contain a W-W bond? To help answer that question you may wish to classify the compound, provide an electron count, the ligand bond number, the valence on tungsten and the dn count for tungsten. You should especially account for how you treat the μ-Br ligands.
12. What role does the Br2 play in the reaction mentioned in question 11? To help answer this question you should classify [W(CO)6], provide an electron count, the ligand bond number, the valence on tungsten and the dn count for tungsten. Compare this answer to your answer for question 11.
13. The final step in scheme 3 is the reaction of [W(CO)3(ligand)Br]Br with Na/Hg. What role does the Na/Hg play in this reaction? To help answer this question you should classify [W(CO)3(ligand)Br]Br, provide an electron count, the ligand bond number, the valence on tungsten and the dn count for tungsten. Compare this to your answer for question 2.
14. Table 1 provides NMR data for the compounds reported in this paper. The peaks for the carbon atoms of metal carbonyls are typically shifted downfield (> 200 ppm) in the 13C NMR spectrum. What trend is observed in the chemical shifts for the carbonyl carbons as the metal atom is varied?
15. Two peaks for the carbonyl carbons are reported for each of the compounds in table 1. Why are there two peaks listed? The spectra are shown in the supporting information. Using the spectrum of any one compound, assign the two signals (Note: the spectra were obtained in d6-acetone which is why there is a very large peak at ~206 ppm).
16. What trend is observed for the chemical shift of the phosphorus atoms in the 31P NMR spectrum as the Group VI metal is varied?
17. Why do the peaks for the carbonyl carbons appear as triplets?
18. At the end of the third paragraph and beginning of the fourth paragraph of the results and discussion section, the authors discuss coupling between the phosphorus and tungsten. In your own words, describe what is observed in the 31P NMR spectrum.
19. Why don’t the authors report any coupling between the carbonyl carbons and tungsten?
20. Compare the data for the IR spectra of the [M(CO)3(1a-PNP)] (M = Cr, Mo or W) in table 2. How do the νCO  values change as the metal changes?
21. Using the highest frequency peaks from the νCO data for the chromium compounds presented in table 2, rank the ligands 1a-1e in terms of electron donor ability. You should present some rationale for your ranking as part of your answer and account for any extremely different ligands.
22. Using the highest frequency peaks from the νCO data for the chromium compounds presented in table 2, compare the electron donor ability of the ligands 1a and 1h. Which is more electron donating?
23. Using the highest frequency peaks from the νCO data for the chromium compounds presented in table 2, compare the electron donor ability of the ligands 1b and 1f. Which is more electron donating?
24. Rank the electron donor ability of a series of PNP ligands in which the R groups were the same and the Rʹ = H, Me or Ph, Provide some rationale for your ranking.
25. The bond lengths given below are from the crystal structures for the chromium compounds. Although not given in the paper, these distances can be obtained from the supporting information. The distances are for the carbonyl ligand *trans*- to the nitrogen donor of the PNP ligand. Based on these bond lengths, rank the ligands in terms of electron donor ability. Provide some rationale as to how you came up with this ranking. Does this agree with the ranking you determined from the IR data? Why or why not?

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| **Ligand** | **Cr-C (Å)** | **C-O (Å)** |
| 1a | 1.8295(9) | 1.1653(11) |
| 1b | 1.8128(14) | 1.1731(18) |
| 1d | 1.7927(12) | 1.1861(15) |

1. Beneath table 1 the authors discuss how the steric bulk of the –PR2 group impacts the C-Cr-C angle where the C’s are the carbon atoms of the *trans*- carbonyl ligands. Steric bulk of phosphines is traditionally measured using the cone angle, the large the cone angle the bulkier the phosphine. A newer measurement of steric bulk is the percent buried volume. The C-Cr-C bond angles and steric parameters for the corresponding PR3 ligands are given below. Does the author’s conclusion about steric bulk follow the other steric parameters? Comment on any significant differences you note. The cone angles and percent buried volumes are reported elsewhere (Clavier, H.; Nolan, S.P. *Chem. Commun*. **2010**, *46*, 841).

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| **R group** | **C-Cr-C (˚)** | **Cone angle (˚) PR3** | **Percent buried volume PR3** |
| Et | 166.68(4) | 132 | 32.7 |
| iPr | 164.04(1) | 160 | 37.6 |
| tBu | 155.22(5) | 182 | 42.4 |