The paper “Palladium(II) and Platinum(II) Compounds of 1,1ʹ-Bis(phosphino)metallocene (M = Fe, Ru) Ligands with Metal-Metal Interactions” (Gramigna, *et. al*, *Organometallics***2013**, *32*, 5966) describes the synthesis and characterization of compounds having an interaction between a group 10 metal and the metal center of a 1,1ʹ-bis(phosphino)metallocene ligand. Structures of a number of these compounds were determined, but we will focus on two in particular, [Pd(dcpf)PPh3]2+ and [Pd(dcpf)PMe3]2+ (dcpf = 1,1ʹ-bis(dicyclohexylphosphino)ferrocene). Find the paper of interest by going to the *Organometallics* homepage (<http://pubs.acs.org/journal/orgnd7>). The crystallographic data can be found in the supporting information in a crystallographic information file (cif). Download the cif and open it using Mercury 3.3 (<http://www.ccdc.cam.ac.uk/Solutions/FreeSoftware/Pages/FreeMercury.aspx>) or Olex2 (<http://www.olex2.org/download/>). It is important to note that these programs display the simplest formula that is repeated in the crystal and not the entire crystal. Address the following questions.

1. Both compounds of interest are cations. Identify the counter anion in both structures.

[Pd(dcpf)PPh3]2+: \_\_BF4-\_ \_\_\_\_\_\_\_\_\_\_

[Pd(dcpf)PMe3]2+: \_\_BF4-\_ \_\_\_\_\_\_\_\_\_\_

1. In growing crystals, sometime solvent molecules can get trapped in the crystal lattice. Identify the solvent(s), if any, in these structures.

[Pd(dcpf)PPh3]2+: \_\_ C2H4Cl2\_\_\_\_ \_\_\_

[Pd(dcpf)PMe3]2+: \_\_CH2Cl2 \_\_\_\_\_\_\_

1. Some crystal structures display disorder which occurs when most of the atoms in the crystal are arranged in exactly the same way but occasionally there is some small difference. This could be the result of an impurity (*e.g.* if in just a few of the cations in the crystal there was Co instead of Fe) or it can be due to a random variation in the way the various pieces fit together (imagine putting 100 coins in a line and having 99 of them being ‘heads up’). In this system we will be more concerned with the second type of disorder. If there is disorder in the structure it is typically represented by atoms not being bonded to any other atoms (Mercury) or atoms overlapping in space (Olex2). What species, if any, are disordered in these structures?

[Pd(dcpf)PPh3]2+: \_\_\_none \_\_\_\_\_\_\_

[Pd(dcpf)PMe3]2+: \_\_ BF4- and CH2Cl2 \_\_\_ \_\_\_\_

1. Measure the following bond lengths (Å) and angles (°).

|  |  |  |
| --- | --- | --- |
|  | **[Pd(dcpf)PPh3]2+** | **[Pd(dcpf)PMe3]2+** |
| Fe-Pd | 2.9340(4)  2.9340(4) | 2.957(1)  2.9566(11) |
| Pd-P(3) | 2.2860(7)  2.2860(7) | 2.271(2)  2.2709(17) |
| P(1)-Pd-P(2) | 156.63(3)  156.63(3) | 157.20(6)  157.20(6) |
| Centroid-Fe-Centroid | 161.19  161.19(6) | 162.76  162.76(15) |
| Angle between C5 planes | 20.41  20.41(15) | 18.94  18.9(3) |

1. The Pd atoms in these compounds should have square planar geometry. Based on your measurements and observations, describe the Pd geometry and account for the structure you observe.
2. Compare the Pd-P(3) bond lengths in these two structures. What might this suggest about the relative electron donor ability of these two phosphines?
3. Look at the space filling versions of these two compounds. Could sterics play a role in the Pd-P(3) bonding?
4. Does the Pd-P(3) bonding impact the Fe-Pd interaction? Why or why not?
5. How is the structure of the ferrocene backbone affected by the strength of the Fe-Pd interaction?