1. **Big picture**
   1. In the opening paragraph, the authors briefly mention 'N2 fixation to ammonia'. As this is a communication in *J. Am. Chem. Soc*., the authors are only permitted two pages and therefore do not have a lot of space to write a detailed introduction. Briefly explain the significance of 'N2 fixation to ammonia' and why people are interested in studying this phenomenon. This will likely require you to use additional sources which you must cite.
   2. All of the titanium compounds in this study have derivatives of the cylopentadienyl (Cp – C5H5) ligand. Describe/depict the orbital interactions between a metal and a Cp ligand.
2. **(C5Me4R)2TiCl**

This paper examines reactions with four previously reported titanium sandwich compounds (numbered 1-4) as well as two previously unreported compounds (numbered 5 and 6). Another impact of the page limitation for communications is that almost all of the experimental details are reported in the supporting information. Compounds 5 and 6 are prepared from compounds 5-Cl and 6-Cl. For the purpose of these questions, focus on compound 6-Cl.

* 1. Classify this compound and determine the electron number, ligand bond number, valence and dn count for the Ti.
  2. The 1H NMR data for compound 6-Cl is reported. What are the 1/2 values that are listed for the two peaks?
  3. What do these 1/2 values and the chemical shifts for the two peaks suggest about the electronic structure of this compound? Why? You may need additional sources to fully answer this question, be sure to cite those sources.
  4. Additional characterization for compound 6-Cl includes magnetic susceptibility and EPR data. How does the inclusion of this data relate back to the previous question?
  5. What is suggested by the data from these techniques and why are the numbers different (this may require additional sources which you should cite)?
  6. Estimate the spin-only magnetic moment for this compound.

1. **(C5Me4R)'2Ti**

The syntheses of these compounds are found in the supporting information. To remain consistent with section B above, the focus will be on compound 6.

* 1. Classify this compound and determine the electron number, ligand bond number, valence and dn count for the Ti.
  2. What is sodium amalgam and what purpose does it serve in this reaction?
  3. Is this compound paramagnetic? What experimental evidence did you use to support this conclusion?
  4. How many unpaired electrons does this compound have? Based on your answer estimate the spin-only magnetic moment and compare it to the experimental value.

1. **Comparing the L ligands in (C5Me4R)2TiL2**

The reaction of gaseous species that can act as L-type ligands (CO and N2) results in the formation of compounds of the general type (C5Me4R)2TiL2. Again, the primary focus of these questions will be the derivatives of compound 5, namely 5- (CO)2 and 5-(N2)2.

* 1. Classify these compounds and determine the electron number, ligand bond number, valence and dn count for the Ti in each case
  2. Solutions of 6-(CO)2 in pentane are stable at room temperature based on the reported IR data. Solutions of 6-(N2)2 in pentane at room temperature rapidly release N2. Suggest a reason for this observation.
  3. N2 is isoelectronic to CO which suggests that these two ligands might have similar bonding interactions with a metal center. Does the X-ray crystal structure of 6-(N2)2, in particular the N-N bond length, help support your answer to the previous question? As a point of reference the authors note that the N-N bond length in free N2 is 1.0976 Å.
  4. Using group theory, determine the number of IR active CO vibrations in 6-(CO)2 and N2 vibrations in 6-(N2)2. Include the irreducible representations for these vibrations. In the paragraph above eq 1, the authors suggest descriptions for these vibrations. Assign these descriptions to your irreducible representations and suggest how you made these assignments.

* 1. N2 is not IR active and yet in these compounds vibrations are observed for the N2 ligand. Explain this phenomenon.
  2. Compared to the data provided for the free molecules, CO and N2, does the IR data for 6-(CO)2 and 6-(N2)2 support the conclusion the CO interaction with titanium is stronger than that of the N2? Why or why not? Remember, that although not IR active, the vibrational frequency for N2 can be measured in the Raman spectrum.
  3. Is 6-(CO)2 paramagnetic or diamagnetic? How did you reach this conclusion?

1. **Comparing the R groups in (C5Me4R)2TiL2**
   1. The IR data for the CO compounds can help us in ranking the electron donor ability of the various R groups. Explain how this is possible.
   2. Based on your conclusion in the previous question rank the R groups in terms of electron donor ability.
   3. In the fourth paragraph in the left column of the first page, the authors suggest that when the R was tBu, the electronics would be similar to when the R group is methyl, but the sterics would be similar to when R = SiMe3. Does this logic seem plausable? Why or why not?
   4. How do the authors account for the differences in the reactivity of compounds 1, 4, 5 and 6 with N2.