Reading Guide **ANSWER KEY** for
"**Synthesis of Ti Complexes Supported by an *ortho*-Terphenoxide Ligand and Their Applications in Alkyne Hydroamination Catalysis.**" Butler, S. K.; Ashbrook, E. P.; and Tonks, I. A. *Organometallics*, **2023**, *42*, 1732-1739.
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Background
Although it is not stated in the paper, the Tonks research group has pushed the study of group IV, especially titanium, complexes. A) What is the interest in studying titanium as opposed to other elements? B) Why did the authors carry out this study?

Classify complexes **2**, and **4** by the CBC method. Include the VN, LBN, d^n count and total valence electron count of these molecules. Complex **4** is obtained from complex **2** by adding the strong reducing agent KC_8 (essentially potassium metal). Is the valence number of **4** actually lower than that of **2**? In other words, did the strong reducing agent reduce the Ti center?

In the second paragraph of the paper the authors discuss redox "noninnocent" ligands. Using the information in this paragraph and Figure 1A, explain what this term means.

Why are redox noninnocent ligands common in titanium chemistry but less common with "on-time" and "late" metals? The standard reduction potential for Pt(IV)/Pt(II) is on the order of -600-700 mV. The standard reduction potential for Ti(IV)/Ti(II) is approximately -1.5-1.6 V. Use this information to inform your answer. Note, KC_8 has a reduction potential of approximately -2.1 V. You can read more about this reagent here:
https://www.strem.com/catalog/product_blog/140/1/potassium_graphite_kc8-an_excellent_reducing_agent

Synthesis and characterization

The authors claim that the ligand synthesis is a "two-step" procedure (Figure 2). Consult the Supporting Information, pages S7-S15. Evaluate their claim.

On the bottom left of page 1733, the authors state that the ^{t}Bu/Me substituents were chosen to provide "easy-to-interpret" NMR handles and to "increase complex solubility." How do these substituents provide these two outcomes?

In the same paragraph, the free ligand **8** is stated to exist as a mixture of "atropisomers," as determined by variable-temperature ^{1}H NMR (Figure 3). Deprotonation of the ligand forms compound **9** which does not exhibit this behavior "presumably due to Li chelation." What is an atropisomer? Why does **8** exhibit this behavior (your options are steric, electronic, thermodynamic, kinetic, or a complex interplay of several of those factors)? Why does **9** *NOT* exhibit this behavior?

The authors prepare complexes by "salt metathesis" or "protonolysis." Using the information in Figure 4, define these two reactions and provide a balanced chemical reaction for reactions A, B, and C (not all the products are shown; what are the additional products?). What is Bn?

Classify $TiCl_4(thf)_2$, $TiBn_4$, and complexes **10**, **11**, and **12** by the CBC method. Include the VN, LBN, d^n count and total valence electron count of these molecules.

The authors use a τ parameter to describe the geometry of the distorted trigonal bipyramidal complexes (p 1734 just below Table 1). What is this parameter measuring?

At the bottom of page 1734 (last complete paragraph on left side) the authors state that the distance between the Ti and the centroid of the aryl linker is too long to suggest a Ti-π interaction. Discuss this statement, considering also the structures of complexes **4** and **5** in your answer.

There are significant changes in ^{1}H NMR signals for seemingly equivalent protons (see top paragraph on right of page 1734 for one ($\Delta\delta$ = 1.48 ppm for methylene protons), and the following paragraph for another ($\Delta\delta$ = 0.48 ppm for NMe_2 protons)). First, explain the $\Delta\delta$ notation. Second, explain generally why there is such a difference in chemical shift for seemingly similar groups? ^{1}H NMR spectra corresponding to these two structures can be found on page S19 and S21 of the supporting information.

The reaction of **12** with aniline gives a color change with a clean ^{1}H NMR spectrum. Propose the product and a general mechanism (don't try to arrow push) for its formation.

Catalysis

What hypothesis are the authors testing by presenting the results in Table 2? What about Table 3? In other words, explain why they chose the substrates they did for each of the two tables; they did so in order to test reactivity in some way.

Figure 6 shows a “rationale” for regioselectivity. Given this figure and your answer above regarding the reaction of **12** with aniline, propose a complete catalytic cycle starting from **12** to give the hydroamination product. Make sure the elementary steps you propose are reasonable. Everything you need to answer this question is found in the paper, though the authors do not propose a mechanism. What is the “catalyst” for the reaction? is it complex **12**?

In the first full paragraph below Table 2, entry 3 is described as having very low conversion. On the bottom right of page 1735, entry 8 also has a low conversion, while a related catalyst **7** show in in Figure 1 gives a good yield. Given these two statements and the text surrounding them, why is **12** less effective of a catalyst than **7**?

In table 3, the *para*-CF_3 substituted aniline does not give product but instead decomposition. What is a possible reason for why this substrate fails? This question is very much related to the next one… so perhaps consider answering both together.

Organic chemists (and organometallic chemists) like to provide substrate tables to show the scope of the reaction, including the functional group tolerance. If a reaction can be performed with ether, alcohol, ester, and amine substrates, it is going to be more widely applicable for organic synthesis. Given the results in tables 2 and 3, what is your opinion of the substrate scope? Note, this is a general limitation of early metal catalysis in most cases.

Both complexes **11** and **12** were used as precatalysts for hydroamination, but complex **10** was not. What is a possible reason for this?