Bis(silylenyl)- and bis(germylenyl)-substituted ferrocenes

This literature discussion is in honor of the work of Shigeyoshi Inoue, winner of the 2026 Frederic Stanley Kipping Award in Silicon Chemistry for "groundbreaking contributions to the synthesis and reactivity of low-valent silicon compounds, and advancing the potential of silicon in metal-free catalysis and small-molecule activation" (https://cen.acs.org/articles/104/web/2026/01/Meet-ACS-National-Award-winners-part-4.html accessed 02/05/2026). While there are many possible papers to choose from, the author of this learning object just could not resist one that incorporates ferrocene (*Angew. Chem. Int. Ed.* **2012**, *51*, 6167 DOI: 10.1002/ange.201202175)

1) In your own words, why did the authors perform this work?

2) Scheme 2 presents the synthesis of the ligands. The first step involves a reaction of ferrocene. Using Covalent Bond Classification (CBC), classify the iron center in ferrocene. Determine the valence number, ligand bond number, electron number and d^n count for the iron.

3) What is TMEDA? What role does it serve in this reaction? You likely will need to use some other resource, be sure to cite it appropriately.

4) The Si (**1**) and Ge (**2**) starting materials are drawn above the arrow. Using standard Lewis structure rules, what would the formal charge on the E atom be?

5) There is no net charge indicated on compounds **1** and **2**. Based on your answer to question 4, what is required for there to be no net charge?

6) The chemical formulae for compounds **1** and **2** are $C_{15}H_{23}ClN_2Si$ and $C_{15}H_{23}ClGeN_2$ respectively. What is the significance of the arc that appears to connect the two nitrogen atoms and how does this relate to your answer to question 5? As part of your answer, you should include relevant resonance structures.

7) The authors present limited $^{13}C\{^1H\}$ NMR data for compound **3** in the paper. In the supporting information, there are additional peaks reported at 160.4, 134.9, 130.5, 129.4, 128.9, 53.0 and 31.8 ppm. Provide general assignments for these peaks.

8) The authors describe the Si and Ge atoms in compounds **3** and **4** as being divalent (Si(II) or Ge(II)). How do you rationalize this assignment?

9) The structure of compound **4** is presented in Figure 1. One would think that the four-membered ring would be a square, but from the figure it appears to be more like a kite. In looking at the bond angles, this is a bit more apparent. The N-Ge-N angle is approximately 65˚. The C-N-Ge angles are approximately 93˚. Finally,

the N-C-N angle is approximately 109˚. How do you account for the drastic distortion in this ring?

10) Scheme 3 presents the synthesis of the cobalt compounds **5** and **6**. What is the valence of the cobalt in the starting material?

11) Using CBC, classify the cobalt center in compound **5** being sure to indicate what type of donor ligand **3** is (note, the picture gives you a hint). Determine the valence number, ligand bond number, electron number and d^n count for the cobalt.

12) Compare your answers to questions 10 and 11. What role is KC_8 likely playing in this reaction? Describe how you arrived at this conclusion.

13) The catalytic activity of **5** and **6** was examined. Compound **5** exhibited catalytic activity but compound **6** did not. The authors offer the rationale "because of a stronger coordination of the Ge^{II} donor centers to Co, which consequently hampers the formation of an active site for substrate coordination." Consider your answer to question 11 and explain why the authors might make this statement.

14) While the authors do not examine the mechanism for this catalysis, there have been numerous studies on related compounds. Shown is a proposed mechanism for this system. Note that ligand **3** is not drawn but instead is represented as Si atoms. Indicate the reaction taking place for each step in the process. Also clearly indicate the metal valence and electron count for each structure shown.

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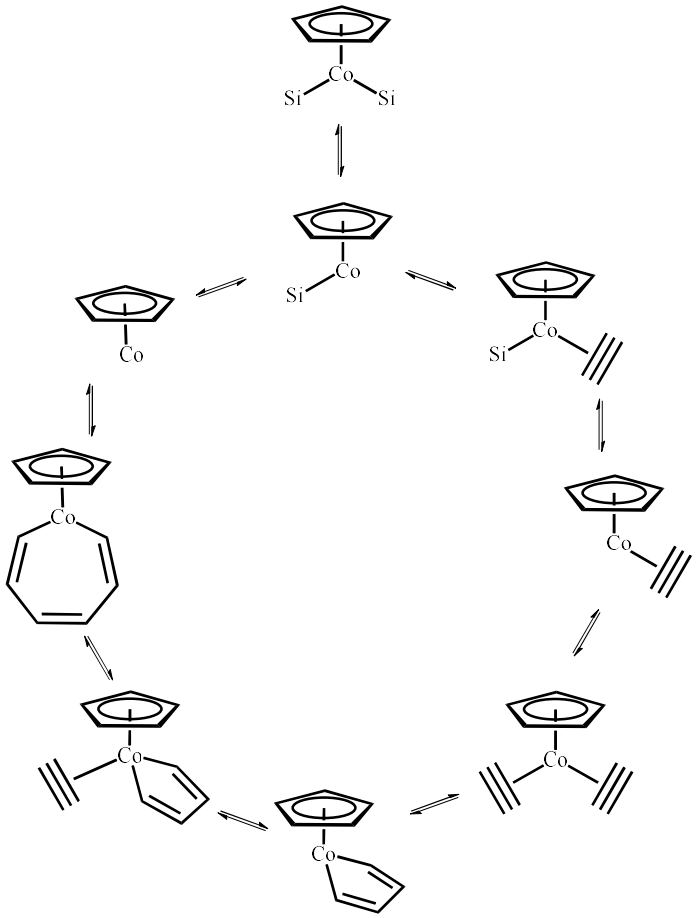

15) Unfortunately, the authors did not prepare the Ge analogue of compound **7**. If they had, how would you expect the IR spectrum, in particular the ν_{CO}, to compare to that of compound **7**? Why?