

The article furnished for this NMR problem set has for title:

Unusual Ar-H/Rh-H J_{HH} NMR coupling in complexes of Rhodium(III) : Experimental evidence and theoretical support for an η^1 -arene structure.

1. Who are the authors and in which university are they working on?
2. Who is the principal author of the article? If you had a question to ask to the authors of this paper, who would you contact?
3. What do you know on the review it was published on? On the editor?
4. Analyze the structure of the paper and comment.
5. What is J_{HH} ?
6. In the abstract, the authors speak about metallic hydride chemical shift and aromatic chemical shifts. Are the signals of these two features usually downfielded or upfielded?

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7. The authors discuss about a rehybridization of the *ispo* carbon from sp^2 to sp^3 .
How should it modify the J_{CH} value?
8. In the case of π type complexes, the arene ring is unperturbed. What should be the J_{CH} value?
9. Explain Figure 2.
10. What is homonuclear decoupling?
11. What is 1H - 1H TOCSY?
12. The authors comment on a $\Delta\delta$ of 1.75 ppm for the aromatic protons. Try to tell us where it could come from?
13. The authors write about the relaxation of the Rh nucleus. Please explain what this means. Why do they propose to change the field to check on their hypothesis?

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14. What is a 1H - ^{13}C HMQC?
15. Why do you think a reliable indication of the presence of an agostic interaction is a reduction in the coupling constant of the C-H bond?
16. What is T_1 ? How do we measure this value?

17. If a value of T_1 is 962 ms, how long should be the delay between two $\pi/2$ pulses?
18. The T_1 of the hydride is 301 ms that is three times shorter than the one of the aromatic protons. Can you explain where this could come from?
19. What is a crosspeak that is observed in 2D NOE experiments?
20. Describe and analyze Figure 8.

Experimental:

21. Look up at compound 3b and draw a scheme of all attributions of ^1H and ^{13}C .

Supporting:

Homocoupling:

22. What is a relaxation delay of 200 ms. Do you think it is enough?
23. What means that P_1 was calibrated to the $(\pi/4)_x$ pulse?
24. What is a decoupler?

TOCSY:

25. Write the approximate TOCSY sequence.
26. What is the mixing time? And the relaxation delay? Justify the numbers used here
27. What is a dummy scan?
28. The temperature is calibrated to methanol, how does this work?

NOESY:

29. Write an approximate NOESY sequence.
30. Explain all as above.