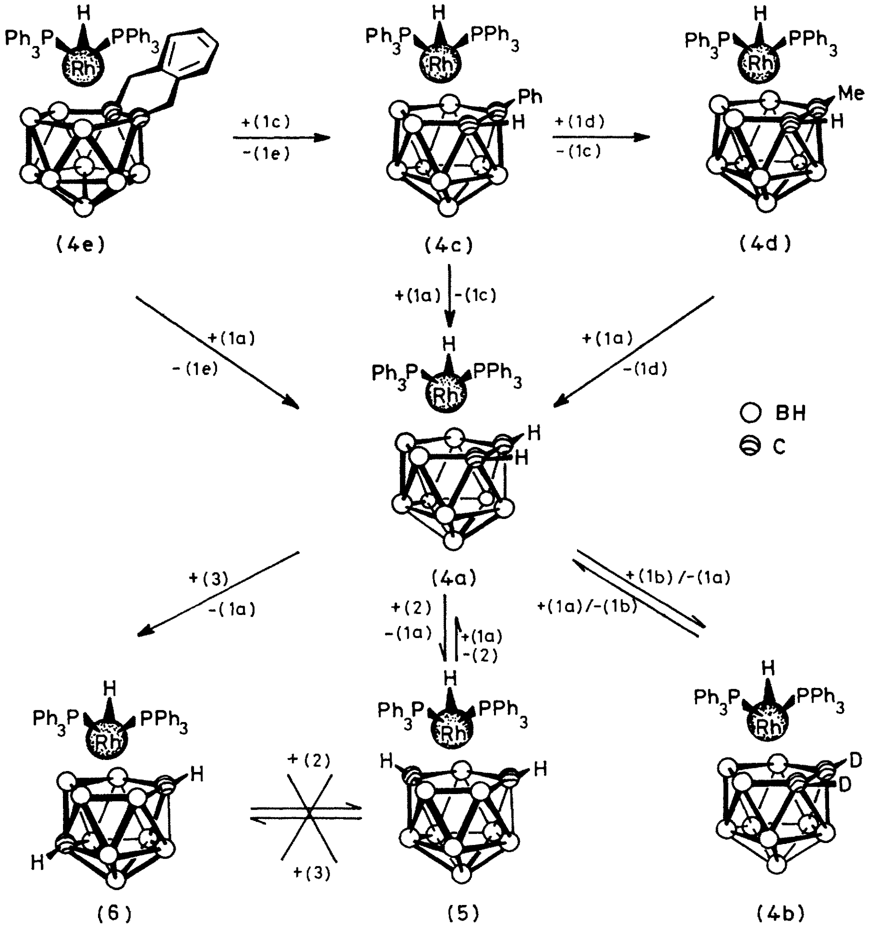
Ready Cage Exchange Reactions of Icosahedral Hydridophosphinorhodacarbaboranes

By Todd B. Marder, Judith A. Long, and M. Frederick Hawthorne*
(*Dept. of Chemistry, University of California, Los Angeles, California* 90024)

Summary Four co-ordination sites of formally six-co-ordinate Rh^{III} carbaborane complexes have been replaced in facile, single-step thermal reactions.

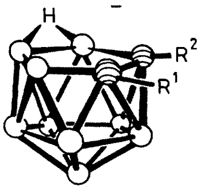
Several reports have appeared concerning thermal ligand exchange reactions of ferrocene and related complexes,[1] arene chromium tricarbonyl complexes,[2] and photolytic exchanges using $[(\eta^5\text{-}C_5H_5)_2MCl_n](M{=}V,Ti,Zr,Hf;\ n = 0,1,2)$.[3] Most of the thermal reactions seem to require vigorous conditions and the yields are in general rather low. However, Khan and Dormond have recently reported facile thermal exchange of cyclopentadienyl rings in certain Ti complexes.[4] In the course of our studies on homogeneous alkene hydrogenation catalysed by phosphinometallocarbaboranes[5] we have discovered a general and facile method for transferring the $(PPh_3)_2Rh$ fragment from one carbaborane cage to another.



Scheme

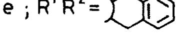
Complex (**4d**) (Scheme) can be prepared by the reaction of the Me$_4$N$^+$ salt of (**1d**) with [(PPh$_3$)$_3$RhCl] in MeOH at room temperature.[6]† The product gradually precipitates as a dark orange powder. Complex (**4a**) can be obtained directly as a yellow-orange powder by the analogous reaction with the anion (**1a**) as well as by the reaction of (**1a**) with previously prepared (**4d**) in refluxing ethanol. These reactions are very clean and the rhodium complexes are isolated in excellent yield. Indeed, in the latter reaction the anion (**1d**) is recovered in good yield. To ensure recovery of pure metal complexes, a *ca.* 10% excess of the anion was used, whereas in order to isolate pure anion, a 10% deficiency of reactant anion was used. The metal complexes were isolated directly, by filtration. The anions were recovered from the filtrate by removal of the solvent *in vacuo*, followed by a benzene wash to remove any remaining rhodium complex. The purity of the rhodium complexes was determined by ^{1}H or $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ n.m.r. spectroscopy.

We have established the following order for ease of displacement of the carbaborane anion: (**1e**)>(**1c**)>(**1d**)>(**1a**)

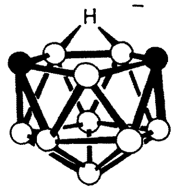


(1)

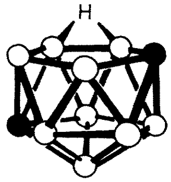
a ; R^1=R^2=H
b ; R^1=R^2=D
c ; R^1=H , R^2=Ph
d ; R^1=H , R^2=Me



e ; R^{1}R^2=



(2)



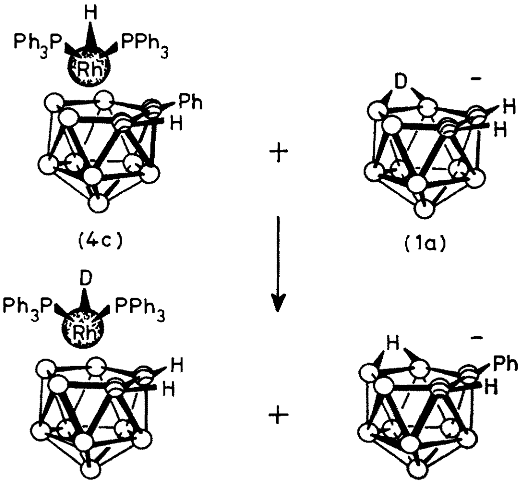
(3)

○ BH
● CH
⊜ C

---

† Compound (**4e**) was characterized by *X*-ray crystallography. Satisfactory analytical data were obtained for all other new compounds.

$>$(**2**) $\sim$ (**3**). Under the conditions employed most of the exchanges are complete in a few hours. However, in the reaction of (**4a**) with (**3**), *ca.* 10% of (**4a**) was present even after 3½ days and in the reaction of (**4a**) with (**2**), trace quantities of (**4a**) were present after 2 days. In the reaction of complex (**5**) with 10 equiv. of (**1a**) for 6 days, the resulting ratio of (**5**) to (**4a**) was *ca.* 7 : 1. *No exchange* was observed in the reactions of either (**5**) with (**3**) or (**6**) with (**2**). Addition of up to 10 equiv. of PPh_3 appeared to have no effect on either the rate or product composition.



The reaction of the carbon-deuteriated analogue of (**4a**), namely (**4b**), with 2 equiv. of the isotopically normal anion (**1a**) showed a significant amount of carbaborane C–H incorporated into the isolated rhodium complex after about one week. A sample of (**4b**) refluxed in ethanol for one week showed no carbaborane C–H in the proton n.m.r. spectrum. When (**4c**) was allowed to react with anion (**1a**), which had been specifically deuteriated at the B–H–B bridging site,[7] the (**4a**) recovered showed Rh–D and no Rh–H.‡ The source of the Rh–H is therefore the acidic B–H–B bridge of the incoming carbaborane anion {as has been shown for the preparation of (**4a**) from $[(PPh_3)_3RhCl]$}.[8] If we assign three co-ordination sites and a formal -2 charge to the carbaborane cage, one site and a -1 charge to the hydride ligand, and one site each to the two PPh_3 groups, then the cage exchange reaction formally replaces four co-ordination sites of a six-co-ordinate Rh^{III} complex in a single clean reaction.

We thank Dr. R. A. Grey for preliminary results, the University of California for a Regents' Fellowship (T.B.M.) and a Chancellor's Fellowship (J.A.L.), and Matthey Bishop Inc. for a generous loan of rhodium trichloride. This work was supported in part by the National Science Foundation and the Office of Naval Research.

(*Received*, 25th *April* 1980; *Com.* 428.)

‡ Determined by ^1H n.m.r. (δ_{Rh-H} $-8{\cdot}40$, CD_2Cl_2) and i.r. (ν_{Rh-H} 2080 and 2120 cm^{-1}; ν_{Rh-D} 1520 cm^{-1}) spectroscopy.

[1] A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Tetrahedron Lett.*, 1963, 1725; *Dokl. Akad. Nauk SSSR*, 1963, **149**, 615; W. H. Morrison, Jr., E. Y. Ho, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1974, **96**, 3603; E. Roman and D. Astruc, *Nouv. J. Chim.*, 1977, **1**, 183; A. N. Nesmeyanov, N. A. Vol'kenau, I. N. Bolesova, and L. S. Shul'pina, *J. Organomet. Chem.*, 1979, **182**, C36.

[2] C. A. L. Mahaffy and P. L. Pauson, *J. Chem. Res.* (*S*) 1979, 126.

[3] E. Vitz and C. H. Brubaker, Jr., *J. Organomet. Chem.*, 1974, **84**, C16; 1976, **104**, C33; J. G-S. Lee and C. H. Brubaker, Jr., *Inorg. Chim. Acta*, 1977, **25**, 181.

[4] O. Khan and A. Dormond, *Bull. Soc. Chim. Fr.*, 1977, **951**; O. Khan, A. Dormond, and J. P. Letourneux, *J. Organomet. Chem.*, 1977, **132**, 149.

[5] T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1974, **96**, 4674; C. W. Jung and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1977, 499; B. A. Sosinsky, W. C. Kalb, R. A. Grey, V. A. Uski, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1977, **99**, 6768; E. H. S. Wong and M. F. Hawthorne, *Inorg. Chem.*, 1978, **17**, 2863.

[6] T. E. Paxson, Ph.D. Dissertation, UCLA, 1974.

[7] D. V. Howe, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, *Inorg. Chem.*, 1971, **10**, 2516.

[8] W. C. Kalb, Ph.D. Dissertation, UCLA, 1979.