they can be converted onto olefin by heating the reaction mixture at reflux. The stoichiometry of the reaction is unusual; depending on the substrate it varies from about 1.5 to 2.0 mol of I per mole of epoxide. Hence, we generally use a mole ratio of 2. Although the tungsten reagents show high stereoselectivity in reducing the isomeric cyclododecene oxides, only limited stereoselectivity is observed for reduction of acyclic disubstituted and trisubstituted epoxides. Reagent V is unique in showing high stereoselectivity even with acyclic epoxides. This is probably due to contamination by unreacted lithium iodide used in the preparation of V. Addition of lithium iodide to reagent II results in stereospecific reductions and the iodohydrin[6] can be detected in hydrolyzed aliquots of this reaction. Thus, in the presence of iodide, the process resembles mechanistically the Cornforth procedure[10] for stereospecific reduction of epoxides with the advantage that the tungsten reductions do not require separate preparation of the iodohydrin. With regard to reactivity, yield, and, in some cases, stereoselectivity (Table II), the tungsten reagents are generally superior to other reagents[11] for carrying out this same conversion in one reaction vessel.

Using only enough I to reduce one of the oxide functions, clean, selective reduction of the nuclear epoxide function of stigmasterol acetate bisepoxide was observed. We are investigating other selective reductions of polyepoxides.

Acknowledgment. We are grateful to Dr. Ferdinand Wirtz-Pietz and Brian D. Andresen of Professor Klaus Biemann's group for obtaining gc-mass spectral data and to Donald Patrick of our group for carrying out the tube furnace preparations of the tungsten reagents V and VI. We thank the National Science Foundation (GP-30485X), Eli Lilly and Company, and Hoffmann-La Roche, Inc., for support of this research.

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iodohydrins were rapidly and stereospecifically reduced, suggesting that the sluggishness of the reduction of chlorohydrins could not be attributed to rate-determining formation of the alkoxytungsten intermediate.

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[11] Other procedures for direct reduction of epoxides to olefins: (a) S. M. Kupchan and M. Maruyama, *J. Org. Chem.*, **36**, 1187 (1971); (b) K. B. Sharpless, *Chem. Commun.*, 1450 (1970); (c) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968); (d) E. Vedejs and P. L. Fuchs, *J. Amer. Chem. Soc.*, **93**, 4070 (1971). The procedure of Vedejs and Fuchs is stereospecific, giving the olefin of geometry opposite to that of the starting epoxide.

[12] Supported in 1971–1972 by the Epworth Fund.

[13] Fannie and John Hertz Foundation Fellow, 1969–1972.

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Stereochemically Nonrigid Binuclear Acetylene Complexes of Rhodium

Sir:

Complexes of formula $Co_2(CO)_6(ac)$ and $Co_2(CO)_4(ac)_3$ have been isolated from reactions of acetylenes (ac) with dicobalt octacarbonyl.[1] We find that $Rh_2(PF_3)_8$, which resembles $Co_2(CO)_8$ in many chemical respects,[2] reacts with a variety of acetylenes (C_2H_2, $C_6H_5C_2H$, $C_6H_5C_2C_6H_5$, $CH_3C_2CH_3$, $C_6H_5C_2CH_3$, $CH_3C_2CO_2CH_3$, $n\text{-}C_4H_9C_2H$, $t\text{-}C_4H_9C_2H$, and $CF_3C_2CF_3$) to give volatile, red to yellow solids or oils of formula $Rh_2(PF_3)_6(ac)$. The structural analogy between $Rh_2(PF_3)_6(ac)$ and $Co_2(CO)_6(ac)$ has been confirmed by a three-dimensional single-crystal X-ray structural analysis of burgundy-colored $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)\cdot(C_2H_5)_2O$, obtained from $Rh_2(PF_3)_6(C_6H_5C_2C_6H_5)$ and triphenylphosphine in ether (Figure 1).

Crystal Data. triclinic space group $P\bar{1}$; $a = 21.19$ Å, $b = 12.99$ Å, $c = 12.94$ Å; $\alpha = 114.11°$, $\beta = 64.36°$, $\gamma = 115.33°$; $D_m = 1.57$, $D_c = 1.59$ (assuming 1 mol of ether per mole of complex); $Z = 2$.

The present structural determination is based on 5765 independent reflections, with $I/\sigma(I) \geqslant 6.0$, collected on a Picker FACS-I automatic diffractometer, using crystal monochromated Cu Kα radiation. With isotropic thermal parameters for all atoms, block diagonal least-squares refinement has converged to a conventional R factor of 0.091. Data have still to be corrected for absorption effects.

The molecule consists of two $Rh(PF_3)_2[P(C_6H_5)_3]$ moieties symmetrically bridged by diphenylacetylene, the C≡C bond of which is above and normal to the Rh–Rh axis; the triphenylphosphine ligands are on the same side of the molecule as the bridging acetylene. The overall geometry of the molecule is similar to those of $Co_2(CO)_6(C_6H_5C_2C_6H_5)$,[3] $Co_2(CO)_6(C_6F_6)$,[4] and related molecules,[5–8] and the Rh–Rh distance [2.741 (2) Å] indicates a metal–metal interaction [*cf.* $Rh_4(CO)_{12}$ (2.73 Å),[9] $Rh_6(CO)_{16}$ (2.78 Å),[10] and $(C_5H_5)_2Rh_2(CO)_3$ (2.68 Å)[11]]. The Rh–C distances [av 2.112 (14) Å] are equal within experimental error, and the acetylenic C–C distance [C(1)–C(2), 1.36 (2) Å] agrees well with previous values.[3–8] The Rh–PF_3 distances [av 2.216 (4) Å] are significantly shorter than the Rh–$P(C_6H_5)_3$ distances [av 2.391 (4) Å], which is consistent with the strong π-bonding ability of PF_3.

The proton resonances of the ≡CH and ≡CCH_3 groups in the appropriate $Rh_2(PF_3)_6(ac)$ complexes are downfield from those of the corresponding free acetylenes and are split into symmetrical septets by coupling to six apparently equivalent ^{31}P nuclei ($^3J_{PH} \sim 7.5$ Hz; $^4J_{P-CH_3} \sim 6.5$ Hz).

Assuming that all the $Rh_2(PF_3)_6(ac)$ complexes are structurally analogous to $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ and to $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)$, it is predicted

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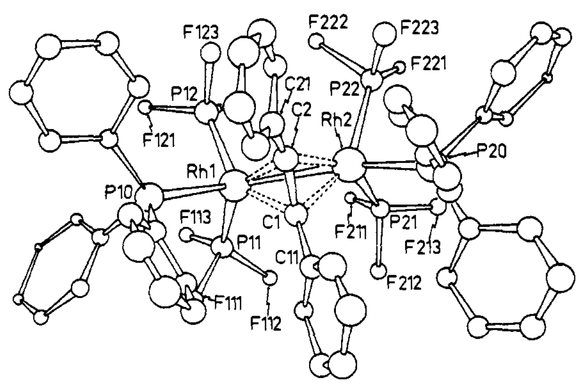

Figure 1. Stereochemistry of $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)$.

that complexes containing unsymmetrically disubstituted acetylenes should have three nonequivalent PF_3 groups (see inset, Figure 2); two of these become equivalent when the acetylene is symmetrically disubstituted. At room temperature, the high-resolution ^{19}F nmr spectrum of all the compounds in $CFCl_3$ consists of a doublet with separation about 1400 Hz, due to $^1J_{PF}$ and $^3J_{PF}$. Each peak is broad and without fine structure, presumably because of the large number of coupled nuclei with $I = {}^1/_2$. On lowering the temperature, each peak broadens and then separates into two or three peaks which sharpen on further cooling. As expected, complexes containing symmetrically disubstituted acetylenes give two peaks (ratio ~2:1), whereas those containing unsymmetrically disubstituted acetylenes give three peaks (ratio ~1:1:1) (Figure 2);[12] the changes are reversible with temperature. These observations, and the fact that the spectra are unaffected by the presence of free PF_3,[13] are consistent only with intramolecular exchange of coordinated PF_3 groups; *i.e.*, the molecules are stereochemically nonrigid. This exchange is fast on the nmr time scale at room temperature and slow at low temperatures (−50 to −147°). The magnitude of the barrier to exchange depends critically on the acetylene substituents and varies from $CF_3C_2CF_3$ [$\Delta G^{\ddagger}$ (−56°) ~ 10 kcal/mol] to $n\text{-}C_4H_9C_2H$ [$\Delta G^{\ddagger}$ (−138°) ~ 6 kcal/mol] in the complexes so far studied. In contrast, even at −90°, the carbonyl ^{13}C nmr spectrum of $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ is a relatively sharp singlet, suggesting that at this temperature the intramolecular exchange of CO groups is still rapid on the nmr time scale.

The stereochemical nonrigidity of these rhodium complexes can be explained by assuming a propeller-like rotation of the PF_3 ligands about the Rh–Rh bond with the acetylene remaining stationary. Alternatively, or in addition, there could be a concerted rotation of the $Rh_2(PF_3)_6$ unit with respect to the acetylene. These possibilities, and the effect of aceylene stubstituents on the activation barrier, will be discussed in detail in a forthcoming publication.

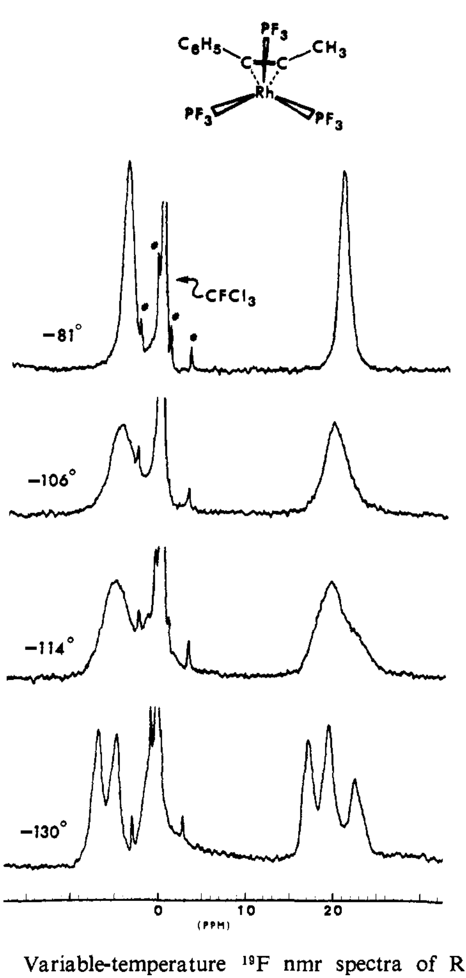

Figure 2. Variable-temperature ^{19}F nmr spectra of $Rh_2(PF_3)_6(C_6H_5C_2CH_3)$ in $CFCl_3$ measured at 56.45 MHz. At −130° one peak is obscured by the $CFCl_3$ resonance. The inset is a projection of the molecule along the Rh–Rh bond not including the eclipsed Rh and PF_3 groups. (#) indicates spinning side bands of $CFCl_3$ and $^{13}CFCl_3$ resonances.

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[12] The ratio is only approximately 1:1:1 owing to overlap of the separate resonances arising from the complex spin system. We have recently found that the ^{31}P-decoupled ^{19}F nmr spectra of $Rh_2(PF_3)_6(CH_3C_2\text{-}n\text{-}C_3H_7)$ in CHF_2Cl at −142° and of $Rh_2(PF_3)_6(p\text{-}NO_2C_6H_4C_2CO_2C_2H_5)$ in CHF_2Cl at −103° consist of three singlets of equal intensity which coalesce to a singlet as the temperature is raised.

[13] We thank a referee for pointing out that CO exchange with the analogous $Co_2(CO)_6(ac)$ complexes is also very slow [G. Cetini, O. Gambino, P. L. Stanghellini, and G. A. Vaglio, *Inorg. Chem.*, **6**, 1225 (1967)].

9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide

Sir:

The 1,4 cycloaddition of SO_2 to 1,3-dienes is a well-known reaction.[1] Cyclooctatetraene sulfone **4**, however, is not formed from **1** in liquid SO_2 even after 30 days at 20°. Paquette, *et al.*, have prepared derivatives of **4** by a bishomoconjugative Ramberg–Bäcklund rearrangement of thiapropellane dioxides.[2]

We found that on treatment of **1** in liquid SO_2 at −70° with 1.0 equiv of antimony pentafluoride in SO_2, evaporation of the solvent, and work-up with dichloromethane–water, the colorless leaflets of the sulfone **4**, mp 192.5–193° dec, were obtained in 95% yield; ir

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