

placed atoms or molecules with cylindrical charge distribution. The *tiara* or girdle of nickel-sulfur atoms may be regarded as a cylindrical "mousetrap" waiting to devour any suitably electron-rich or clathrate-prone "mouse." The hexameric association of $[\text{Ni}(\text{SC}_2\text{H}_5)_2]_6$ in solution is consistent with our belief that no significant change in molecular conformation (such as nickel-sulfur bond breaking to give noncyclic chains) occurs on dissolution of the molecular crystal in organic solvents.

Analogous polymeric palladium mercaptides have been prepared^{2,6} and are believed to be similarly hexameric. On the basis of the work described here, it is highly probable that these latter complexes with the congener element palladium will be isostructural with the corresponding nickel complexes. Noteworthy is that the structure of $[\text{Ni}(\text{SC}_2\text{H}_5)_2]_6$ is one of the two models put forward by Hayter and Humiec² for the palladium *n*-propyl mercaptide. Further chemical investigations are in progress.

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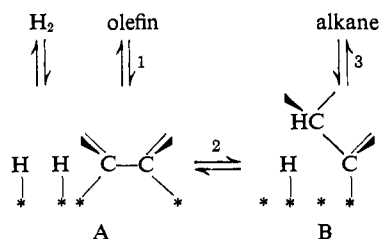
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The Nature of the Diadsorbed Intermediate in Hydrogenation of Olefins

Sir:

The classical Horiuti-Polanyi mechanism for the hydrogenation of olefins on metals of group VIII



is also applied to isotopic exchange between deuterium and alkane¹: the sequence, reaction -3, alternation between di- and monoadsorbed alkane (B and A), reaction 3. If A is diadsorbed alkane, its conformation must be eclipsed.²

It has been argued recently that olefin π -bonded to a single surface atom³ is the preferable form of A. In

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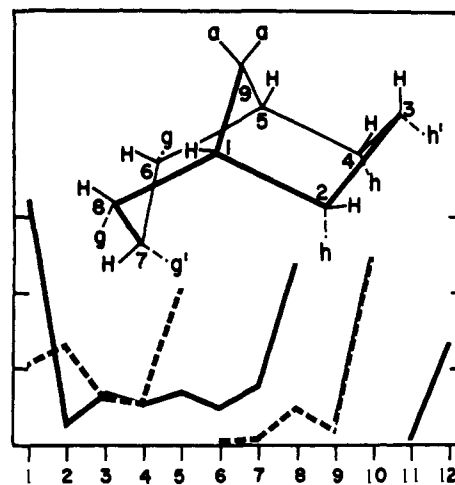


Figure 1. Initial isotopic exchange patterns of bicyclo[3.3.1]nonane at 70° (full line) and cyclopentane at 60° (dashed line).

isotopic exchange of cyclopentane^{1,2} (Figure 1), both forms of intermediate A predict a maximum at d_5 ($\text{C}_5\text{H}_5\text{D}_5$), and both require some additional process to account for initial product more exchanged than d_5 . Indeed, the merely geometrical difference between the two forms is small. Are there molecules which permit a distinction?

In small bicyclic hydrocarbons, neither double bonds (Bredt's rule) nor eclipsed conformations can exist at bridgeheads. As the ring sizes increase, the prohibition against eclipsed conformations relaxes before that against double bonds, for example, bicyclo[3.3.1]nonane, shown in Figure 1 as one of the more favorable conformations of cyclooctane⁴ bridged by methylene. The two hydrogen atoms of the H set at carbon atoms 1 and 2 are eclipsed. Thus, alternation between mono-adsorbed and eclipsed diadsorbed bicyclononane (A and B) permits the exchange of all eight atoms of the H set. If A were π complex one could get from one trimethylene ring to the other only *via* a π -bonded bridgehead olefin. This would be of much too high an energy to function as intermediate A. As shown in Figure 1, the first large maximum in exchange on palladium-on-alumina occurs at d_8 . Thus, at least on palladium, the geometry of eclipsed diadsorbed alkane is acceptable for A; that of a species at all close to olefin is not. Of course, the π complex might be the form in which olefin is first adsorbed.

The argument above specifies geometry but the details of the bonding of A remain unknown. The arguments favoring the π complex depend largely upon the existence of molecular π complexes of olefins, but those are mononuclear, and adsorbed species may well be bonded to several surface atoms as in metallic carbides and nitrides. It has been proposed³ that dialkylacetylenes hydrogenate *via* initial adsorption of acetylene as a linear complex (C') with π bonding to two surface atoms. Here, there are molecular, polynuclear anal-

(3) (a) J. J. Rooney and G. Webb, *J. Catalysis*, **3**, 488 (1964); (b) G. C. Bond and P. B. Wells, *Advan. Catalysis*, **15**, 91 (1964).

(4) Conformation II in K. B. Wiberg, *J. Am. Chem. Soc.*, **87**, 1070 (1965). However, in the solid state, both cyclohexane rings are almost surely in the chair conformation: M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964).

ogies,⁵ and the geometry of the acetylenic portion resembles that of diadsorbed ethylene (C).



Here again, diadsorbed seems preferable to π complex,⁶ but good evidence supports surface intermediates which resemble π -bonded diene and allyl.^{3,6}

We suggest that bicyclononane- d_{10} and - d_{12} result from exchange of h,h and g,g. Adamantane (bicyclononane with carbon atoms 3 and 7 bridged by methylene) exchanges only one hydrogen atom per period of adsorption. Since all of its vicinal hydrogen atoms are rigidly staggered, this accords with predictions.² Accordingly, the atoms at carbon atom 9 in bicyclononane will not exchange in conjunction with others barring some transannular reaction. In exchange of 1,1,3,3-tetramethylcyclohexane on palladium,⁷ there is a maximum at d_5 in addition to one at d_3 which results from alternation between A and B. Formation of bicyclononane- d_{10} and - d_{12} is consistent with the proposal⁷ that d_{10} in cyclopentane and d_5 in tetramethylcyclohexane result from alternation between π -bonded olefin and π -bonded allyl. This cannot exchange h' and g'.

These experiments were run in a flow apparatus with 5% palladium-on-alumina catalyst² previously reduced in hydrogen at 350°. The partial pressures were cyclopentane, 93 mm.; bicyclononane, 8 mm.; adamantane, 5 mm.; and deuterium to 1 atm.

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(7) F. C. Gault, J. J. Rooney, and C. Kemball, *J. Catalysis*, **1**, 255 (1962).

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Volatile Rare Earth Chelates

Sir:

We have synthesized and characterized volatile chelates of 15 trivalent rare earths and have separated mixtures of the complexes by gas chromatography. The ligand employed in this study was 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane), hereafter abbreviated H(thd). The chelates are thermally stable, anhydrous, unsolvated compounds of the formula $M(\text{thd})_3$. Molecular weight measurements on the lanthanum, samarium, gadolinium, terbium, thulium, and ytterbium complexes indicate that the compounds are monomeric in benzene. Infrared measurements showing the absence of O-H stretching vibrations and the close agreement of elemental analyses have proved that the crystalline compounds are anhydrous.

The complexes readily undergo vacuum sublimation without apparent decomposition at temperatures between 100 and 200°. Differential thermal analyses and visual observations of melting behavior indicate that most of the complexes can be heated above 300° and then cooled and remelted at the original melting point. Thermal gravimetric analysis of $\text{Er}(\text{thd})_3$ in a helium atmosphere showed that *ca.* 99% of the sample sublimed below 230°.

Efforts to synthesize the rare earth chelates by a previously reported method¹ produced only poor yields. It was reasoned that perhaps the low yields were caused by destructive air oxidation of the complexes in solution during the syntheses and subsequent recrystallizations. Oxidation of $\text{Ni}(\text{thd})_2$ in solution has been found to occur readily.² A method in which air was excluded wherever possible was developed, and this has permitted the synthesis of the trivalent rare earth complexes in yields of 90–97%. The general method is illustrated by the preparation of $\text{Tb}(\text{thd})_3$. Sixty mmoles of H(thd) (Pierce Chemical Co.) was dissolved in 30 ml. of 95% ethanol in a thick-walled flask fitted with a stopcock connected to a vacuum system. NaOH (2.4 g.) dissolved in 50 ml. of 50% ethanol was added. The reactants were continuously stirred with a magnetic stirrer. $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (20 mmoles, prepared from 99.9% Tb_4O_7) dissolved in 50 ml. of 50% ethanol was added. Immediately the flask was evacuated, sealed, and stirred for 2 hr. The volume of the solution was reduced by 50% by reduced pressure distillation, and 350 ml. of distilled water was added. The $\text{Tb}(\text{thd})_3$ which separated was quickly vacuum filtered, dried, and sublimed at 180° *in vacuo*. The yield of sublimed product was 13.17 g. (92.9%). The sublimed crystals were recrystallized from *n*-hexane *in vacuo* and vacuum dried (m.p. 177–180°). The crystals of $\text{Tb}(\text{thd})_3$ emit brilliant green fluorescence when irradiated at 3660 Å. with an ultraviolet lamp. Table I shows the melting points, elemental analyses, and, for the diamagnetic complexes, the proton n.m.r. spectra in carbon tetrachloride relative to internal tetramethylsilane.

One of the objectives of this study was to separate rare earth complexes by gas chromatography. All previous efforts have failed owing to the lack of volatility and the thermal instability of the other rare earth chelates examined.^{3,4} Gas chromatographic experiments have shown that all of the thd chelates can be chromatographed without decomposition. Benzene solutions of each of the complexes were injected into the chromatographic column at 200°; the chromatogram of each complex showed a single peak well separated from the solvent peak. The crystalline complexes collected from the effluent carrier gas stream were shown to have been eluted without decomposition by comparison of melting points and ultraviolet and visible spectra with those of each complex before injection.

There appear to be appreciable and significant differences in the volatilities of the rare earth complexes

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(3) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Ltd., Oxford, 1965, pp. 23, 36.

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