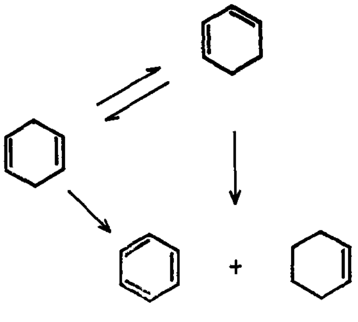
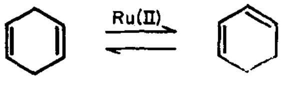
Homogeneous Catalytic Hydrogen Transfer in Cyclic Dienes. Selective Double Bond Migration in the Presence of a Ruthenium(II) Complex

A variety of hydrogen transfer reactions are known to occur when cyclohexadienes are exposed to active Group VIII metal surfaces (*1–4*). Hydrogen transfer results in hydrogen exchange, double bond migration, dehydrogenation, and disproportionation to mixtures of aromatic, olefinic and aliphatic hydrocarbons in the presence of palladium (*1, 2*), platinium (*1, 2*), nickel (*4*), cobalt (*4*) and rhodium (*3*) catalysts. Dehydrogenation and disproportionation occur more readily than double bond isomerization under mild conditions (*3, 4*). Several Group VIII metal complexes in solution have also been found to catalyze hydrogen transfer in cyclohexadienes. Reaction often occurs in a highly selective manner; however, the course of homogeneous catalytic hydrogen transfer in cyclohexa-1,4-dienes, Eq. (1), is highly dependent on the nature of the metal complex and on the reaction medium.


(1)

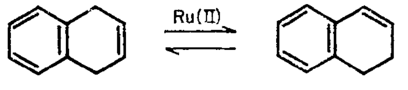
We have found (*5*) that, in the presence of Vaska's complex, $IrCl(CO)(Ph_3P)_2$, 1,4-cyclohexadiene (1,4-CHD) is catalytically disproportionated to benzene and cyclohexene in a selective manner under conditions in which 1,3-cyclohexadiene(1,3-CHD) is unreactive. Mosely and Maitlis (*6*), however, found that the complex, $C_5Me_5Rh(C_8H_8)$, in weakly basic ethanol solution, first isomerized the 1,4-diene to the 1,3-isomer which then underwent facile disproportionation to benzene and cyclohexene. Other metal complexes (*7, 8*) have been shown to catalyze rapid isomerization accompanied by smaller amounts of disproportionation. The ability to control the specific type of hydrogen transfer which occurs in cyclic dienes has found synthetic utility in the catalytic preparation of unconjugated exocyclic olefins using Pt(II) and Ru(II) complexes (*9*), the selective hydrogenation of cyclic dienes without disproportionation in the presence of a Rh(I) complex (*8, 10*) and the isomerization of some substituted cyclic dienes (*7*) with a Rh(I) complex. We report that the ruthenium(II) complex, $RuCl_2(Ph_3P)_3$, is an efficient catalyst for the selective double bond equilibration of cyclic dienes which are highly sensitive to disproportionation over solid metal catalysts. Our results enable us to make preliminary correlations between the type of hydrogen transfer which occurs and the nature of the Group VIII metal complex which is involved.

We found that 1,4-CHD can be equilibrated without disproportionation, Eq. (2), in the presence of $RuCl_2(Ph_3P)_3$ and a suitable co-catalyst whose function is to furnish a CO ligand to the metal to form a catalytically active carbonyl complex (*11*). Benzyl formate was used as a co-catalyst for the ruthenium(II)-catalyzed isomerization of 1,4-CHD in the neat diene at 80°C. The red-brown solution of $RuCl_2(Ph_3P)_3$ gradually became yellow over the first few hours of reaction. A pale yellow complex exhibiting an intense ir absorption at 1990 cm^{-1} due to ruthenium-



(2)

carbonyl (*11*) was precipitated from the reaction mixture using excess pentane at the conclusion of the reaction. The ratio of 1,3-/1,4-isomers at equilibrium was found to be ~2/1 (*12*). Similarly, 1,4-dihydronaphthalene can be selectively isomerized in the presence of $RuCl_2(Ph_3P)_3$ at 80°C in benzene–ethanol solution, Eq. (3), Fig. 1. Tetralin and napthalene were not produced in detectable amounts after long reaction periods. At equilibrium the ratio of 1,2-/1,4-dihydronaphthalene was ~99/1. The osmium(II) complex, $OsHCl(CO)(Ph_3P)_3$, behaved in a similar manner to that of the ruthenium(II) complex. Results of hydrogen transfer reactions of 1,4-CHD in the presence of Vaska's complex and its rhodium analog are contrasted with Ru(II) and Os(II) complexes in Table 1.



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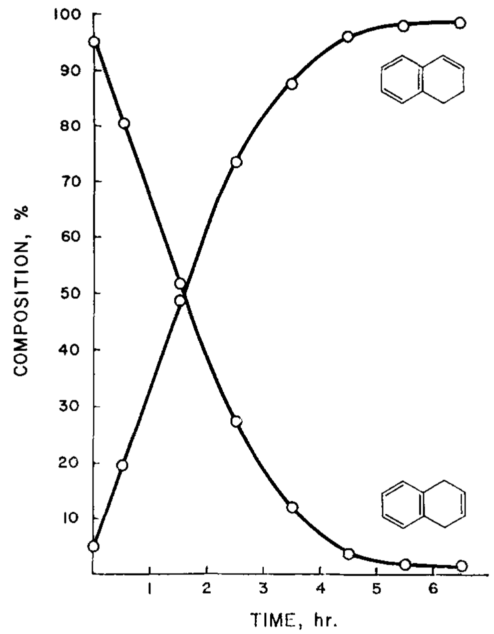


FIG. 1. Isomerization of 1,4-dihydronaphthalene using $RuCl_2(Ph_3P)_3$. Reactions run in 1:1 benzene-ethanol solution which was 2.5 *M* in 1,4-dihydronaphthalene and 3×10^{-3} *M* in $RuCl_2(Ph_3P)_3$ under nitrogen at 80°C.

It is interesting to note that disproportionation is observed in the presence of the coordinatively unsaturated square planar iridium(I) and rhodium(I) complexes, $MCl(CO)(Ph_3P)_2$, which are capable of undergoing oxidative addition of a variety of molecules (*13*) to form octahedral iridium(III) and rhodium(III) complexes. Scheme 1 illustrates two possible reaction pathways (*5*, *14*) which could lead to disproportionation. Both pathways require oxidative addition of 1,4-CHD to form a six-coordinate iridium(III) species. Moseley and Maitlis (*15*) also have proposed a mechanism involving oxidative addition of cyclohexadiene to explain disproportionation in the presence of $C_5Me_5Rh(C_8H_8)$.

TABLE 1

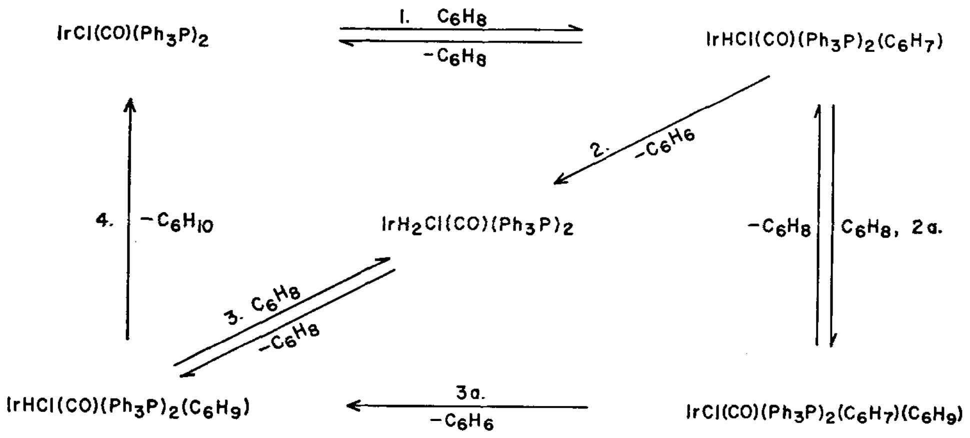
HYDROGEN TRANSFER REACTIONS[a] IN 1,4-CYCLOHEXADIENE

Metal complex	Reaction time (hr)	Components in reaction mixtures (mole %)			
		1,4-CHD	1,3-CHD	Benzene	Cyclohexene
$IrCl(CO)(Ph_3P)_2$	180	33	7	30	30
$RhCl(CO)(Ph_3P)_2$[b]	90	80	1.5	9	9
$RuCl_2(Ph_3P)_3$[c]	45	33	67	—	—
$OsHCl(CO)(Ph_3P)_3$	90	34	65	1	—
$IrH(CO)(Ph_3P)_3$	90	50	50	—	—

[a] The diene (5 ml) was vacuum transferred into the reaction vessel containing 5 mg of the catalyst. Dry nitrogen was then admitted to the system and the solution was stirred magnetically at 80°C for the indicated time. The product mixtures were separated and analyzed by glc using a 150 ft capillary column coated with UCON 550-X. The identity of the products was confirmed by their ir spectra.

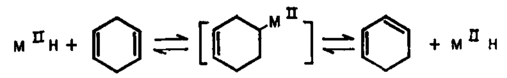
[b] Solution became grey and cloudy after several hours.

[c] Added 50 mg of benzyl formate.



SCHEME 1

The ruthenium(II) and osmium(II) carbonyl complexes, on the other hand, are coordinatively saturated, more sterically hindered than the iridium(I) and rhodium (I) complexes, and may be more resistant to oxidative addition (*16*) of 1,4-CHD to give Ru(IV) and Os(IV) adducts. In these cases, metal hydride (probably generated *in situ* in the ruthenium case) (*9*, *11*) catalyzes isomerization via addition and elimination, Eq. (4), but a pathway for rapid disproportionation does not exist. One might expect, therefore, that an iridium(I) complex having greater steric hindrance, a higher coordination number, and a hydrido-ligand might exhibit enhanced isomerization activity at the expense of disproportionation. Indeed, the complex, IrH(CO)(Ph$_3$P)$_3$, is an effective catalyst for isomerization of 1,4-CHD, but does not cause disproportionation to benzene and cyclohexene.



(4)

In summary, disproportionation may arise via oxidative addition of 1,4-CHD; however, hydrides formed by such oxidative addition could lead to competing isomerization. If the metal involved does not readily undergo oxidative addition, only isomerization can occur. It is expected that further study of this system will result in a more detailed understanding of the mechanisms which are involved.

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Classification of Metal Catalysts Based on Surface *d*-Electrons

A detailed description of the metal surface (*1*) in terms of positive ion cores, localized *d*-electrons on ion cores and interstitial localization of itinerant electron density has been given by the interstitial-electron model for metals (*2*). On the basis of this model, catalytic metals have been divided into 4 classes according to the orientation and occupancy of *d*-orbitals extending above the metal surface (*3*). Class I metals (Mo, W) have a vacant *d*-orbital perpendicular to the metal surface. Class II metals (Rh, Ir, Ru, Os, Tc, Re) have a vacant *d*-orbital at 36–45° to the surface. Class III metals (Fe, Co, Ni, Pd, Pt) have a partially occupied *d*-orbital at 30–36° to the surface. Class IV metals (Zn, Ga, Cd, In, Ge, Sn, Pb) have been shown by Kita (*4*) to differ from other metals with completed *d*-shells and have been characterized (*5*) as having an asymmetry in their *d*-shells. Promotion of a *d*-electron places Cu, Ag and Au with Class III metals. The above classification is based on the 111 surface for CCP and HCP metals and for the 110 surface for BCC metals. Orbital patterns which indicate more complex behavior for Ni, Pt and Rh as well as the minor changes in orbital orientation on other crystal planes are described in detail in a paper (*3*) discussing hydrogenation catalysis. The metal structures used to obtain *d*-orbital orientation and occupancy differ from those used by Goodenough (*6*), Bond (*7*) or Shopov and Andreev (*8*) in that the localization of itinerant electron density in metal interstices is taken to determine *d*-orbital degeneracy (*2*). The electronic structures for metals, so derived, are compatible with known magnetic properties, electronic heat capacity, Hall Coefficients and electrical conductivity of metals (*2*).

Surface complexes of olefins on metals are proposed (*3*) for Class III metals which utilize electrons in the partially filled *d*-orbitals to form σ-bonds and for Class II metals which utilize metal itinerant electrons in a delocalized electron bond. The expected greater ease of forming bonds with Class III metals (and thus, ease of alkyl reversal) is considered to be the basis for the greater exchange and isomerization observed over Class III metals compared to Class II metals. Classification of metals into 4 classes provides a plausible theoretical basis for many of the mechanistic discussions of hydrogenation reactions (*3*). In addition the interstitial-electron model provides a description of the metal surface which facilitates descriptions of surface complexes of hydrocarbons in familiar terms of ion cores and electrons and clearly relates them to transition metal complexes.

This description of the metal surface supplements metal band theory descriptions, but offers a more chemical approach for discussions of catalytic reactions than many current treatments based on concepts such as "*d*-character" or "holes in the *d*-band." Its emphasis on localized electron environment around metal ion cores has