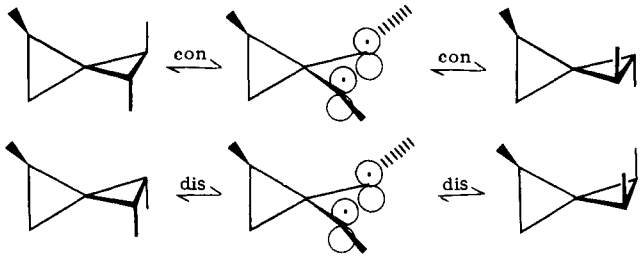
Table I. Ratio of Double to Single Inversion in the Pyrolyses of the Trimethylspiropentanes after Correction for Steric Factors

Starting material	D/S ($f_{+c} = 0.5$)	D/S ($f_{+c} = 0.95$)	D/S ($f_{+c} = 1.5$)
TM → TP/CS	1.48	2.81	4.45
TM → TP/CA	1.52	2.90	4.57
TP → TM/CA	1.55	2.94	4.65
TP → TM/CS	1.52	2.88	4.55
$(D/S)_T$	1.52 ± 0.02	2.88 ± 0.04	4.55 ± 0.05
CA → CS/TM	5.70	3.00	1.90
CA → CS/TP	5.84	3.07	1.95
CS → CA/TM	5.55	2.93	1.85
CS → CA/TP	5.70	3.00	1.93
$(D/S)_C$	5.70 ± 0.07	3.00 ± 0.04	1.91 ± 0.03

$f_{+c} > 1$. It would seem more likely that $f_{+c} \leq 1$ but more like unity since there is only a factor of 0.5 in the thermodynamic preference and the transition state for closure must come early suggesting $f_{+c} \simeq 1$. Since $(D/S)_T \simeq (D/S)_C$ when $f_{+c} \simeq 1$, it appears that the trans isomer undergoes double inversion by conrotation (con) and the cis isomer undergoes double inversion by disrotation (dis). It therefore appears that the propensity for double inversion in the *trans*- and *cis*-dimethylspiropentanes results solely from the sterically most favorable pathway, i.e., outward rotation of both methyl groups in each case. However, in each case these outward rotations should



produce the same π cyclopropane; yet this species must reclose to trans isomers faster when generated from trans isomers or faster to cis isomers when generated from cis isomers. A hypothesis which will rationalize this divergent behavior for the same species is a dynamical one advanced by Jean[15] in calculations on the cyclopropane double inversion process: once the double rotation starts, either con or dis, the motion continues along this trajectory through the past the π biradical to the double inversion product.

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(8) From TM: $TP_{expt'l} = 0.0871$, calcd = 0.0876; $CA_{expt'l} = 0.0798$, calcd = 0.0825; $CS_{expt'l} = 0.0283$, calcd = 0.0332 at 12 h. From TP: $TM_{expt'l} = 0.1611$, calcd = 0.1611; $CA_{expt'l} = 0.0644$, calcd = 0.0650; $CS_{expt'l} = 0.0677$, calcd = 0.0690 at 12 h. From CA: $TM_{expt'l} = 0.1625$, calcd = 0.1619; $TP_{expt'l} = 0.0680$, calcd = 0.0693; $CS_{expt'l} = 0.1132$, calcd = 0.1143 at 12 h. From CS: $TP_{expt'l} = 0.0723$, calcd = 0.719; $TP_{expt'l} = 0.0943$, calcd = 0.0950; $CA_{expt'l} = 0.1561$, calcd = 0.1564 at 12 h.
(9) Namely that $k_1k_9k_{12}k_4 = k_3k_{11}k_{10}k_2$ and $k_1k_{11}k_6k_7 = k_2k_{12}k_5k_8$ and $k_3k_9k_6k_8 = k_4k_{10}k_5k_7$.
(10) We assume that cleavage occurs predominantly at the C_1–C_2 bond rather than at C_4–C_5 owing to the dimethyl substitution.[3] Note that in only one of the six interconversions may C_4–C_5 cleavage be of consequence, namely that involving TM and TP.
(11) The molecular origin of this retardation factor, which runs counter to the expectation that a destabilizing interaction should produce a rate acceleration, appears to be that a face to face biradical is generated, as was suggested for the carbethoxyspiropentane rearrangement,[12a] and the sterically forced[12b] rotation of a methyl outward away from its formerly adjacent carbon (C_2) is retarded by the proximal methyl at C_4.
(12) (a) J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, **94**, 8857 (1972). (b) For examples of outward methyl rotation being preferred over inward rotation, see J. J. Gajewski, *J. Am. Chem. Soc.*, **93**, 4450 (1971); **98**, 5254 (1976); and references contained therein.
(13) A sample calculation: for the rate constant ratio k_1/k_5, k_1 gives TP which has a trans C_1C_2 relationship but also a proximal C_1C_4 relationship; k_5 gives CS which has a cis C_1C_2 relationship as well as a proximal C_1C_4 relationship. $\therefore k_1/k_5 = (D/S)_T\,[f_{+p}/(f_{+c} \times f_{+p})] = 2.96$. For $f_{+c} = 0.95$, $(D/S)_T = 2.81$.
(14) A similar analysis of Bergman's data[3] indicates that for $f_{+c} = 0.95$ D/S for methyl single rotation is 0.93 for both the trans and cis isomers; D/S is 1.09 for ethyl single rotation in the two isomers. For Doering's case,[3] with $f_{+c} = 0.95$ the D/S from the trans isomer when cyano rotates is 1.14 and 2.46 when isopropenyl rotates; from the cis isomer D/S is 0.61 for cyano single rotation and 1.32 for isopropenyl single rotation. Thus Bergman's case appears to be nearly random biradical but Doering's has a significant component of double inversion, at least in the trans case, indicating a preference for conrotation.
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Novel Coordination Chemistry and Catalytic Properties of Cationic 1,2-Bis(diphenylphosphino)ethanerhodium(I) Complexes

Sir:

Considerable interest has recently been focussed on cationic rhodium(I) complexes containing tertiary phosphine ligands, particularly in the context of such complexes as highly effective asymmetric hydrogenation catalysts.[1] While the most extensive studies on the coordination chemistry and catalytic properties relate to such complexes containing *monodentate* tertiary phosphine ligands, for example those derived from $[Rh(PR_3)_2(diene)]^+$ [where diene = norbornadiene (nor) or 1,5-cyclooctadiene],[2-7] the highest optical yields to date (>95% enantiomeric excess in the hydrogenation of prochiral α-acetamidoacrylic acids) have been achieved with cationic rhodium catalysts containing chiral *chelating* diphosphine ligands, notably 1,2-bis(*o*-anisylphenylphosphino)ethane.[8] Accordingly, it seemed of some importance to examine more thoroughly the basic coordination chemistry and catalytic properties of such cationic rhodium–diphosphine chelate complexes. We report here initial results of such studies on [Rh(diphos)(nor)]$^+$ (**1**), where diphos = 1,2-bis(diphenylphosphino)ethane, and on various other cationic rhodium–diphos complexes derived therefrom by hydrogenation. Unexpectedly, the chemistry of these complexes was found to differ in several important respects, including those bearing on their activity as hydrogenation catalysts, from that of the corresponding complexes containing monodentate phosphine ligands, e.g., $[Rh(PPh_3)_2(nor)]^+$.

In methanolic solution, [Rh(diphos)(nor)]$^+$,[9] was found to react rapidly with precisely *2.0* mol of H_2/Rh (confirmed by spectral titration) according to the stoichiometry of eq 1, quantitatively yielding norbornane (confirmed by NMR) and a cationic Rh(I) complex of composition (apart from possible solvent coordination) [Rh(diphos)]$^+$ (**2**) (λ_{max} 432 nm (ϵ_{max}

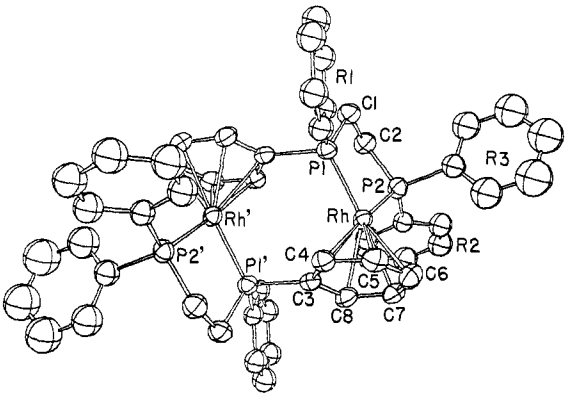


Figure 1. Structure of $[Rh_2(diphos)_2]^{2+}$. Distances (Å): Rh-Rh, 4.275 (1); Rh-P, 2.230 (2), 2.240 (2); Rh-C, range 2.285-2.368, mean 2.33.

$1.49 \times 10^3\ M^{-1}\ cm^{-1}$)). No further uptake of H_2, nor formation of a hydride complex, was detectable (e.g., by NMR). This result is in marked contrast to that reported for $[Rh(PPh_3)_2(nor)]^+$ which reacts with *3* mol of H_2 under the same conditions to form the Rh(III)-hydride complex (**3**) according to eq 2.[4,6,7]

$$[Rh(diphos)(nor)]^+ + 2H_2 \rightarrow [Rh(diphos)]^+ + \text{norbornane} \quad (1)$$
$$\mathbf{1} \qquad\qquad \mathbf{2}$$

$$[Rh(PPh_3)_2(nor)]^+ + 3H_2 \rightarrow [RhH_2(PPh_3)_2(solvent)_2]^+ + \text{norbornane} \quad (2)$$
$$\mathbf{3}$$

$[Rh(diphos)]^+$ was isolated as the BF_4^- salt, *containing no methanol,* and shown by single-crystal x-ray diffraction[10] to have the structure depicted in Figure 1, corresponding to discrete binuclear $[Rh_2(diphos)_2]^{2+}$ ions in which each Rh atom is bonded to two P atoms of a diphos ligand and, through symmetrical π-arene coordination, to a phenyl ring of the diphos ligand of the second Rh atom. Each Rh atom, thus, has an "18-electron valence shell" and the 4.28-Å Rh-Rh separation lies well outside the range of significant metal-metal interaction. Other interatomic distances and bond angles are unexceptional. There are several precedents for π-arene bonding in other cationic Rh complexes, including the structurally characterized compound $Rh[P(OMe)_3]_2BPh_4$.[3,5,11,12]

In methanolic solution, $[Rh_2(diphos)_2][BF_4]_2$ apparently dissociates into mononuclear $[Rh(diphos)]^+$ ions (presumably containing coordinated solvent), as demonstrated by (i) electrical conductance measurements which yielded a slope of $-270\ \Omega^{-1}\ M^{-0.5}$, corresponding to a 1:1 electrolyte,[13] for a plot of equivalent conductance vs. $\sqrt{c}$; (ii) ^{31}P NMR measurements which revealed only a single P signal (d, 2 P, δ 80 (J_{Rh-P} = 203 Hz)); and (iii) measurements on the equilibria for the formation of various 1:1 alkene and arene adducts of $[Rh(diphos)]^+$ (see below). When base (OMe^- or a sterically hindered amine such as triethylamine) was added to a methanolic solution of $[Rh(diphos)]^+$ an irreversible (i.e., not reversed by addition of acid) yellow to red-brown color change was observed, to yield a new species, $[Rh_3(diphos)_3(OMe)_2]^+$ (**4**) (λ_{max} 445 nm (ϵ_{max} $3.3 \times 10^3\ M^{-1}\ cm^{-1}$); ^{31}P NMR, d, 6 P, δ 72 (J_{Rh-P} = 201 Hz)), according to eq 3, the stoichiometry of which was established by spectral titration. The structure of **4**, as deduced from preliminary single-crystal x-ray diffraction data for the PF_6 salt, corresponds to a regular triangular array of Rh atoms, separated by bonding distances of 3.06 Å. Each bidentate diphos ligand is coordinated to one Rh atom (r_{Rh-P} = 2.19 Å) with the P-Rh-P plane perpendicular to the Rh_3 plane. One triply bridging OMe^- ion is symmetrically located on each side of the Rh_3 plane (r_{Rh-O} = 2.15 Å). The $[Rh_3P_6O_2]$ framework thus has D_{3h} symmetry.

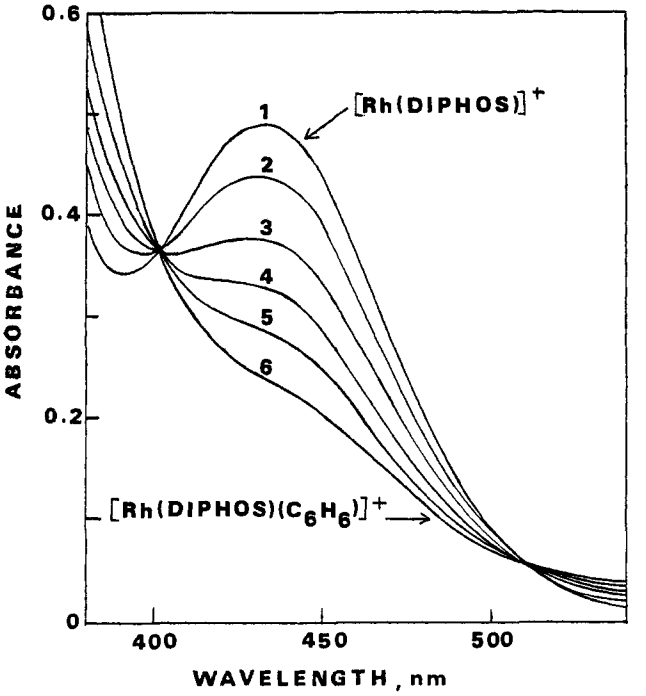


Figure 2. Spectral changes accompanying the addition of benzene to a methanolic solution of $[Rh(diphos)]^+$ (3.3×10^{-4} M) at 20 °C ($10^2[C_6H_6]$, M): **1**, 0; **2**, 2.5; **3**, 5.0 **4**, 7.5; **5**, 12.5; **6**, ≥50.

$$3[Rh(diphos)]^+ + 2OMe^- \rightarrow [Rh_3(diphos)_3(OMe)_2]^+ \quad (3)$$
$$\mathbf{4}$$

In methanol solution, $[Rh(diphos)]^+$ formed 1:1 adducts with a variety of unsaturated substrates (unsat) including alkenes and arenes according to eq 4. Reaction 4 could readily be monitored, and the equilibrium constant K_4 (= $[Rh(diphos)(unsat)]^+/[Rh(diphos)]^+[unsat]$) determined, from the spectral changes accompanying the addition of successive increments of unsat, as exemplified by Figure 2. In the case of benzene the composition of the adduct was confirmed by isolating the salt $[Rh(diphos)(C_6H_6)]BF_4 \cdot C_6H_6$ which dissolved in CD_2Cl_2 to yield a solution whose ^1H NMR spectrum contained two sharp singlets of equal intensity (6 H) corresponding to free (δ 7.4) and coordinated (δ 6.36) C_6H_6. Values of K_4 in methanol, determined for selected substrates, follow: benzene ($18\ M^{-1}$); toluene (97); *o*-, *m*-, or *p*-xylene (~500); 1-hexene (2); styrene (20); methyl acrylate (3). The binding constants of arenes are significantly higher than those of simple alkenes and the binding of styrene is clearly due primarily to the phenyl ring (also reflected in the similarities of the spectra of the benzene (Figure 2) and styrene adducts).

$$[Rh(diphos)]^+ + \text{unsat} \overset{K_4}{\rightleftharpoons} [Rh(diphos)(unsat)]^+ \quad (4)$$

$[Rh(diphos)]^+$ was found to be an effective catalyst for the hydrogenation of simple alkenes as well as various alkene derivatives (styrene, acrylic acid, amidoacrylic acids, etc.). Kinetic measurements on the hydrogenation of 1-hexene (in which the H_2 uptake was monitored), in conjunction with the equilibrium measurements of the type cited earlier, support the mechanistic scheme of eq 5 and 6 which yields the observed rate law, eq 7, where $[Rh]_{tot} = [Rh(diphos)]^+ + [Rh(diphos)(>C{=}C<)]^+$. The kinetically determined values of k_6 and K_4 for 1-hexene in methanol are 0.18 $atm^{-1}\ s^{-1}$ and 1.6 M^{-1}, respectively. The latter value is in good agreement with

$$[Rh(diphos)]^+ + >C{=}C< \overset{K_4}{\rightleftharpoons}$$

$$[Rh(diphos)(>C{=}C<)]^+ \text{ (rapid equilibrium)} \quad (5)$$

$$[Rh(diphos)(>C{=}C<)]^+ + H_2 \xrightarrow{k_6}$$

$$[Rh(diphos)]^+ + H{-}\overset{|}{C}{-}\overset{|}{C}{-}H \text{ (rate determining)} \quad (6)$$

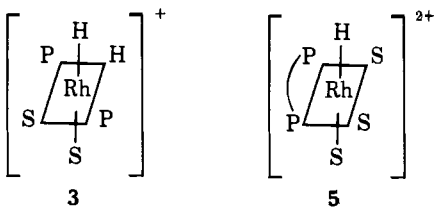
$$\frac{-d[>C{=}C<]}{dt} = \frac{k_6 K_4 [Rh_{tot}][>C{=}C<][H_2]}{1 + K_4[>C{=}C<]} \quad (7)$$

the spectrophotometric value (see above). Kinetic studies on other substrates are in progress.

It should be noted that our mechanism for the $[Rh(diphos)]^+$-catalyzed hydrogenation of alkenes departs significantly from that invoked for the corresponding $[Rh(PPh_3)_2]^+$-catalyzed reaction in which a principal pathway involves the hydrido complex, $[RhH_2(PPh_3)_2(solvent)_n]^+$.[7]

The different reactivities of $[Rh(diphos)(nor)]^+$ and $[Rh(PPh_3)_2(nor)]^+$ toward H_2, reflected in eq 1 and 2, are intriguing as well as being relevant to the mechanistic features of the catalytic hydrogenation reactions of the two species. A possible explanation of this difference is that, whereas $[Rh(PPh_3)_2]^+$ can form an H_2 adduct of structure **3** in which neither H ligand is trans to a phosphine ligand,[4,7] this is not possible (assuming cis disposition of the two H atoms) in the case of a chelating diphosphine ligand in which the two P atoms are constrained to being in mutually cis positions. This is expected to contribute to the instability of the H_2 adduct of $[Rh(diphos)]^+$ and to result in a considerably reduced equilibrium constant for the oxidative addition of H_2 to **2**, apparently to the point where the hydride cannot be detected. This reasoning suggests that $[Rh(diphos)]^+$ should, however, be capable of the facile oxidative addition of *one* hydrogen ligand, i.e., of H^+. In accord with this expectation, it was found that the addition of a noncoordinating acid such as HBF_4, HPF_6, or $HClO_4$ to a methanol or acetonitrile solution of $[Rh(diphos)]BF_4$, reversibly discharged the color of the $[Rh(diphos)]^+$ ion, the spectral changes being *quantitatively* identifiable with the reversible equilibrium of eq 8, with K_8 (MeOH) = 11 ± 2 M^{-1}. The ^1H NMR spectrum of $[HRh(diphos)]^{2+}$ in acetonitrile clearly revealed the hydride ligand coupled to the Rh atom and to two equivalent P atoms (δ −15.7 (J_{Rh-H} = 12.1 Hz, J_{P-H} = 17.2 Hz, also confirmed by ^{31}P NMR), in accord with structure **5**.

$$[Rh(diphos)]^+ + H^+ \overset{K_8}{\rightleftharpoons} [HRh(diphos)]^{2+} \quad (8)$$



3 **5**

These studies, some of which are still being elaborated, have revealed a number of previously unrecognized features of the coordination chemistry and catalytic activity of cationic rhodium complexes containing *chelating* diphosphine ligands which differ strikingly from the chemistry of the corresponding monodentate phosphine complexes. The chemistry of these complexes in relatively poorly coordinating solvents such as methanol, which are typically used for catalytic hydrogenation, appears to be dominated by their "ligand deficiency" as reflected in the formation of unusual polynuclear species such as $[Rh_2(diphos)_2]^{2+}$ and $[Rh_3(dipos)_3(OMe)_2]^+$, and in the strong binding of typically poor ligands such as arenes. It seems likely that the striking stereoselectivity which these catalysts exhibit in the asymmetric catalytic hydrogenation of prochiral olefins such as amidoacrylic and amidocinnamic acids reflects the strong tendency of the functional groups typically present in such substrates (C_6H_5, COOR, NHCOR, etc.) to "coordinate" to the Rh (as has been demonstrated in the comparison of styrene and 1-hexene) and thereby to exert a pronounced "orienting" influence. Our identification of reaction 5 opens up the opportunity for the direct systematic investigation of the effect of various substituents of olefinic substrates both on the equilibrium constants for the binding of the substrate (K_4) and on the structural features (potentially susceptible to elucidation both by NMR and by x-ray diffraction) of the resulting $[Rh(diphos)(>C{=}C<)]^+$ adducts which are key intermediates in the catalytic hydrogenation. Such investigations are in progress.

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(9) $[Rh(diphos)(nor)]BF_4$ was prepared by one of the procedures described by Schrock,[3] namely by reacting $[Rh(nor)Cl]_2$ in acetone with $AgBF_4$, followed by addition of a stoichiometric amount of diphos.
(10) Crystal data of $[Rh_2(diphos)_2][BF_4]_2 \cdot CF_3CH_2OH$ (obtained by recrystallizing $[Rh_2(diphos)_2][BF_4]_2$ from CF_3CH_2OH): space group P_{ccn}; a = 28.528 (7), b = 11.842 (3), c = 15.829 (5) Å; ρ_{obsd} = 1.57 vs. ρ_{calcd} = 1.585 for Z = 4. Data were collected on a Syntex P_{2_1} diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by MULTAN procedure and refined by full-matrix least-squares to R = 0.057, R_W = 0.089, using 3824 reflections with $F^2 \geq 3\sigma_{F^2}$ out of 4726 collected. The uncoordinated phenyl groups and lattice solvent molecule were treated as rigid bodies and the hydrogen atoms as fixed atom contributions at positions corresponding to normal geometries; anisotropic thermal parameters were used for the other atoms. Details of the refinement and structure to be published.
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Models for NADH Coenzymes. Isotope Effects in the *N*-Benzyldihydronicotinamide/*N*-Benzylnicotinamide Salt Transhydrogenation Reaction

Sir:

The study of oxidation-reduction reactions of models for nicotinamide coenzymes has provided a great deal of information about the mechanism of such processes.[1] Perhaps the most fundamental redox reaction involving the dihydropyridine/pyridinium salt redox couple is the transhydrogenation reaction. An in-depth study of the transhydrogenation reaction has special appeal because of the symmetry between reactants