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- (6) Note that the cyclophosphonitrile described in ref 5g coordinates the transition metal via the nitrogen atoms. We do not consider the extra polymethylene chain (to make a ring) in the diphosphines described in ref 5b as a significant factor in metal complexation.
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- (8) With the exception of **4**, all new compounds gave satisfactory spectroscopic and analytical data. Compounds **4** and **6** are both unstable to quaternization reactions at somewhat elevated temperatures (60–80 °C) and short periods of time, or at room temperature over extended periods of time. Consequently, **4** and **6** were routinely stored at –20 °C. We were unable to distill **4**, even using Kugelrohr conditions, and thus were unable to prepare an acceptable analytical sample. The spectroscopic properties of **4** were all consistent with the assigned structure, however.
- (9) Crude **7** was obtained in 35% yield as a white solid, mp 100–130 °C. The material appeared to be homogeneous on TLC (several solvent systems on SiO₂) and gave no extraneous peaks in the mass spectrum.
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- (11) Our experience with these macrocycles is that, at substrate to absorbent ratios of 1:10²; only about one third of the cycle elutes no matter how much care is taken in degassing solvents and silica gel. This observation is true even when material isolated by chromatography is rechromatographed. We suspect that complexation of trace transition metals on the silica gel is the cause of the problem.
- (12) We thank Professor R. E. Davis of this department for the crystal structure determination. The details of this structure, along with others now in progress will be published later.
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- (14) From inspection of CPK models, only the meso-cis isomer, not the meso-trans one shown, or the *dl* isomer can function as a tridentate ligand about a single metal. Since the barrier to inversion of tertiary phosphines is in the range of 30–35 kcal/mol (R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **92**, 3090 (1970)), thermal inversion in refluxing xylene (135 °C) should allow access to the meso-cis isomer from any of the starting isomers.
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- (16) These frequencies are typical of cis-diphosphino metal tetracarbonyls. See, for example, (a) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964); (b) R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967); (c) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).
- (17) The IR CO stretching frequencies were typical of *fac*-tricarbonyl complexes (see ref 16): 7-Mo(CO)₃, ν_{CO} 1940 and 1850 cm⁻¹; 7-Cr(CO)₃, ν_{CO} 1940 and 1860 cm⁻¹. The ³¹P NMR (proton decoupled, 85% H₃PO₄ external standard) spectra for both of these complexes in CDCl₃ solution consisted of a triplet and a doublet (intensity ratio 1:2): 7-Mo(CO)₃, δ –3.76 (t, *J* = 26 Hz) and –52.14 (d, *J* = 26 Hz); 7-Cr(CO)₃, δ –28.33 (t, *J* = 37 Hz) and –79.91 (d, *J* = 37 Hz). The free ligand **7** gave ³¹P NMR resonances at δ 30.56 (s, 2 P) and 25.69 (s, 1 P).
- (18) R. B. King, R. M. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).
- (19) The complex **8**-NiClBF₄ gave a sharp singlet in the ³¹P spectrum (chloroform-*d* solution) at δ –60.62 ppm relative to 85% H₃PO₄ external standard. Uncomplexed **8** exhibited a sharp singlet at δ 28.94 ppm.

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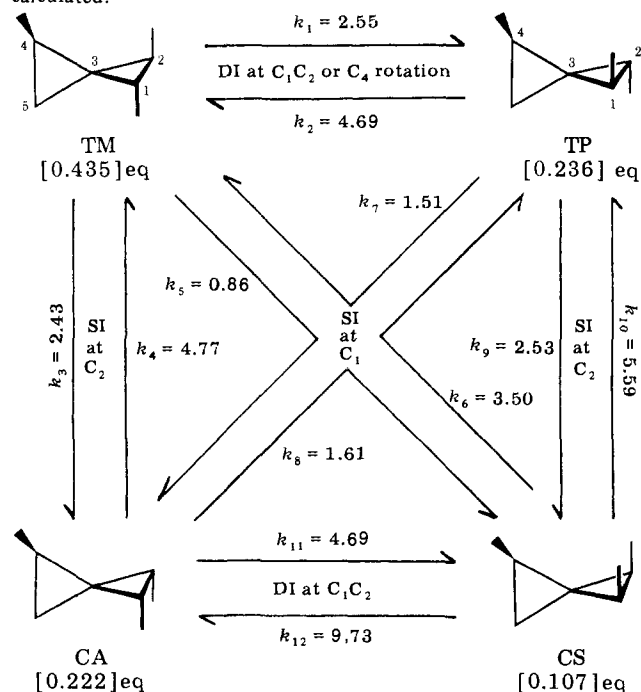
Dominant Double Rotation in the Thermally Induced 1,2,4-Trimethylspiropentane Geometric Isomerization

Sir:

The thermal geometric isomerization of vicinal centers in cyclopropane occurs predominantly by a double inversion process¹ which has been predicted to occur in a conrotatory fashion.² Monosubstitution of both inverting centers by small alkyl groups appears to attenuate the double inversion process such that a near-randomly-closing biradical results.³

Spiropentane undergoes geometric isomerization⁴ by peripheral bond fission⁵ faster than structural isomerization⁶ to methylenecyclobutane. Double inversion has now been observed with 1,2,4-trimethylspiropentane, but a factor analysis

Chart I. Rate constants ($\times 10^6/s$) for the interconversion of the four 1,2,4-trimethylspiropentanes at 561.7 K and 150 Torr: SI = single inversion; DI = double inversion. The equilibrium concentrations are calculated.



suggests that face to face biradicals are being formed and that conrotation occurs with the trans isomers and disrotation occurs with the cis isomers.

The fact is that the four 1,2,4-trimethylspiropentanes⁷ interconvert at 561.7 K with the rate constants ($\times 10^6/s$) indicated in Chart I which in a Runge-Kutta numerical integration of the appropriate differential equations reproduces the experimental data at roughly 20% reaction.⁸ The rate constants satisfy the three microscopic reversibility conditions.⁹

From the data it is clear that both double and single inversion is occurring but trans to trans or cis to cis conversions (double inversion—or, less likely, C₄ epimerization with TM and TP¹⁰) occur as fast as the two single inversion process, in each case suggesting a preference for double inversion.

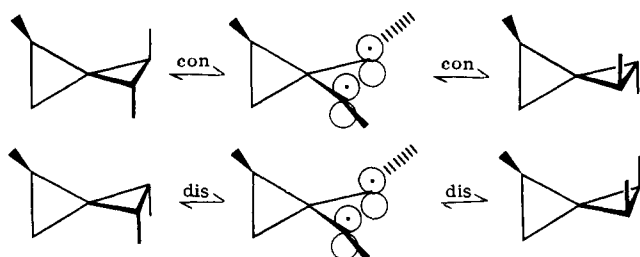
The magnitude of the preference for double inversion is substantial if the data are dissected into contributing factors. A rate retardation factor, f_{+p} , for generating 1,4-proximal, as opposed to medial or distal, methyl relationships is 0.345 ± 0.01 from the rate constant ratio k_5/k_3 or k_8/k_{11} . A rate retardation factor, f_{-p} , for destroying 1,4-proximal, as opposed to medial or distal, methyl relationships is 0.61 ± 0.04 from the rate constant ratio k_7/k_9 or k_6/k_{10} .¹¹ From each spiro-pentane isomer there are two ratios of double to single inversion, and in each case proximal 1,4 relationships are being generated and destroyed, and cis relationships are being generated for which a rate retardation factor, f_{+c} , relative to making a trans relationship may be defined. Any given rate ratio can result from an inherent preference for double vs. single inversion, D/S, modified by the rate-retarding steric factors, f_{+p} , f_{-p} , and f_{+c} .¹³ For any value of f_{+c} , the four D/S ratios from the trans isomers are within 2% of one another, and the same is true of the D/S ratios from the cis isomers (see Table I), lending confidence to the notion that steric factors are being properly considered. The cis factor, f_{+c} , determines the absolute values of the D/S ratios, and Table I gives the D/S ratios for various f_{+c} factors.¹⁴

If the double inversion process is conrotatory, steric effects should favor more double inversion from the trans isomers than from the cis isomers; however, this can be true only if there is a steric preference for generating a cis vicinal relationship, i.e.,

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 $f_{+c} \approx 1$. Since $(D/S)_T \approx (D/S)_C$ when $f_{+c} \approx 1$, 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 Jean¹⁵ 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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- Prepared from previously reported, stereochemically characterized esters, J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, **94**, 8860 (1972), and by base-induced decomposition of methyl *N*-(2-methylcyclopropyl)-*N*-nitrosourethane in neat olefin. These materials were not resolved into enantiomers.
- From TM: $TP_{\text{exptl}} = 0.0871$, $\text{calcd} = 0.0876$; $CA_{\text{exptl}} = 0.0798$, $\text{calcd} = 0.0825$; $CS_{\text{exptl}} = 0.0283$, $\text{calcd} = 0.0332$ at 12 h. From TP: $TM_{\text{exptl}} = 0.1611$, $\text{calcd} = 0.1611$; $CA_{\text{exptl}} = 0.0644$, $\text{calcd} = 0.0650$; $CS_{\text{exptl}} = 0.0677$, $\text{calcd} = 0.0690$ at 12 h. From CA: $TM_{\text{exptl}} = 0.1625$, $\text{calcd} = 0.1619$; $TP_{\text{exptl}} = 0.0680$, $\text{calcd} = 0.0693$; $CS_{\text{exptl}} = 0.1132$, $\text{calcd} = 0.1143$ at 12 h. From CS: $TP_{\text{exptl}} = 0.0723$, $\text{calcd} = 0.719$; $TP_{\text{exptl}} = 0.0943$, $\text{calcd} = 0.0950$; $CA_{\text{exptl}} = 0.1561$, $\text{calcd} = 0.1564$ at 12 h.
- Namely that $k_1 k_9 k_{12} k_4 = k_3 k_{11} k_{10} k_2$ and $k_1 k_{11} k_6 k_7 = k_2 k_{12} k_5 k_8$ and $k_3 k_9 k_6 k_8 = k_4 k_{10} k_5 k_7$.
- We assume that cleavage occurs predominantly at the C₁-C₂ bond rather than at C₄-C₅ owing to the dimethyl substitution.³ Note that in only one of the six interconversions may C₄-C₅ cleavage be of consequence, namely that involving TM and TP.
- 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 (C₂) is retarded by the proximal methyl at C₄.
- (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.
- A sample calculation: for the rate constant k_1/k_5 , k_1 gives TP which has a *trans* C₁C₂ relationship but also a proximal C₁C₄ relationship; k_5 gives CS which has a *cis* C₁C₂ relationship as well as a proximal C₁C₄ relationship. $\therefore k_1/k_5 = (D/S)_T [f_{+p}/(f_{+c} + f_{+p})] = 2.96$. For $f_{+c} = 0.95$, $(D/S)_T = 2.81$.
- A similar analysis of Bergman's data³ 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)ethanorhodium(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 $[\text{Rh}(\text{PR}_3)_2(\text{diene})]^+$ [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 $[\text{Rh}(\text{diphos})(\text{nor})]^+$ (**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., $[\text{Rh}(\text{PPh}_3)_2(\text{nor})]^+$.

In methanolic solution, $[\text{Rh}(\text{diphos})(\text{nor})]^+$,⁹ was found to react rapidly with precisely 2.0 mol of H₂/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) $[\text{Rh}(\text{diphos})]^+$ (**2**) (λ_{max} 432 nm (ϵ_{max}