negative sign for both complexes corresponds to the $A_1 \rightarrow E_a$ electronic transition. Our structural data clearly show that $(-)_D$-tris(biguanide)chromium(III) has the same absolute configuration as the $(+)_D$-tris(ethylenediamine)cobalt(III) ion; Λ with respect to the threefold axis.[9,10] Thus, in contrast with the cobalt(III) system, the *negative* E_a component of the CD spectrum of trigonal chromium(III) corresponds to the $\Lambda(C_3)$ configuration.

Turning our attention to the anomaly reported by Michelsen[1] in the CD spectra in the region of the ligand internal transitions, we believe that the enantiomeric character of the tris(biguanide)cobalt(III) and -chromium(III) CD spectra arises from the opposite absolute configurations of these complexes. We note that the chelate rings in the biguanide complexes are planar, and that the bond lengths suggest a high degree of electronic delocalization. We suggest, therefore, that the CD spectra in the region of the ligand electronic transitions be interpreted using the exciton model recently described by Bosnich and by Mason.[11] The exciton theory predicts that complexes with the $\Lambda(C_3)$ configuration will exhibit a positive (E) CD band followed, at higher energy, by a negative (A_2) band in the region of the internal ligand electronic transitions. Our experimental results verify this relationship for the chromium(III) ion and for the biguanide ion, which is among the few ligands which forms resolvable complexes and has isolable electronic transitions within the range of practical instrumentation.

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[9] K. Nakatsu, *Bull. Chem. Soc. Jap.*, **35**, 832 (1962).

[10] Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *ibid.*, **30**, 795 (1957).

[11] B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969); S. F. Mason, *Inorg. Chem. Acta Rev.*, **2**, 89 (1968).

George R. Brubaker, Lawrence E. Webb
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616

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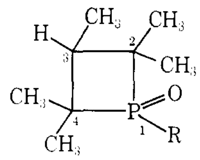
Stereochemistry of Nucleophilic Attack on a Cyclic Phosphinate Ester[1]

Sir:

Nucleophilic displacement reactions at a phosphoryl center generally proceed with inversion of configuration at phosphorus.[2] We wish to report a noteworthy exception to this: namely, attack of methoxide ion on either the *cis* or *trans* isomers of 1-methoxy-2,2,3,4,4-pentamethylphosphetane 1-oxide (**1**) takes place with retention of configuration.



1, R = CH_3O
2, R = Cl
3, R = OH

The pure *trans* (1-Cl and 3-CH_3) isomer[3] of the acid chloride **2** was prepared by treatment of 2,4,4-trimethyl-2-pentene with PCl_3–$AlCl_3$ according to the procedure of McBride.[4] Subsequent reaction of the recrystallized product with sodium methoxide–methanol[4] or triethylamine–methanol gave a single isomer of **1** (*trans*).[5] A predominance (3:2) of the *cis* ester was obtained by heating the acid **3** with thionyl chloride in benzene (5 hr at reflux temperature) followed by esterification with triethylamine–methanol.[6] Use of deuteriomethanol–triethylamine gave the labeled ester (R = CD_3O) in each case above.

Clear distinction between the isomers was apparent in the nmr[7] spectra (60 MHz, benzene, TMS): **1** (*trans*) τ 8.86 (d, 6 H, J_{PCCH_3} = 18.5 Hz), 8.92 (d, 6 H, J_{PCCH_3} = 18.0 Hz), 6.37 (d, 3 H, J_{POCH_3} = 10.1 Hz); **1** (*cis*) τ 8.75 (d, 6 H, J_{PCCH_3} = 18.3 Hz), 8.97 (d, 6 H, J_{PCCH_3} = 18.0 Hz), 6.42 (d, 3 H, J_{POCH_3} = 10.1 Hz); **2** (*trans*) τ 9.32 (dd, 3 H, J_{HCCH_3} = 7.0 Hz, J_{PCCCH_3} = 1.5 Hz), 8.83 (d, 6 H, J_{PCCH_3} = 21.4 Hz), 8.88 (d, 6 H, J_{PCCH_3} = 23.0 Hz); **2** (*cis*) τ 9.28 (dd, 3 H, J_{HCCH_3} = 7.0 Hz, J_{PCCCH_3} = 1.0 Hz), 8.77 (d, 6 H, J_{PCCH_3} = 21.5 Hz), 8.97 (d, 6 H, J_{PCCH_3} = 23.8 Hz).

An aliquot from a solution of 400 mg of *trans*-**1** (R = CD_3O) in 1.0 ml of 0.65 *N* $NaOCH_3$–CH_3OH was placed in a sealed, evacuated nmr tube; a similar aliquot was prepared from a mixture of **1** (*trans*:*cis*, 2:3; R = CD_3O). Exchange of CD_3O by CH_3O took place in each isomer; for example, after 3 hr at 25° the *trans*–*cis* mixture (2:3) had undergone about 30 and 70% exchange, respectively. After 48 hr, exchange (under these conditions) for both isomers was about 90% complete. The pure sample of **1** (*trans*) showed 80% exchange after 11 hr at 50°. Control runs in each of the above cases were performed under identical conditions using **1** (*trans*) and **1** (*trans*:*cis*, 2:3) in which R = CH_3O; no isomer interconversion was

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[1] We wish to thank the National Institutes of Health for support of this research under Grant CA-11631.

[2] M. J. Gallagher and I. D. Jenkins in "Topics in Stereochemistry," Vol. 3, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, pp 31-38 and 82-85.

[3] The stereochemistry and detailed geometrical structure of **2** (*trans*) has been determined by X-ray work by Dr. M. Haque of Montana State University, Department of Chemistry (unpublished results).

[4] J. J. McBride, Jr., E. Jungermann, J. J. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962).

[5] Since this communication was submitted, W. Hawes and S. Trippett, *J. Chem. Soc., C*, 1455 (1969), showed that treatment of the acid chloride with sodium methoxide proceeds with retention.

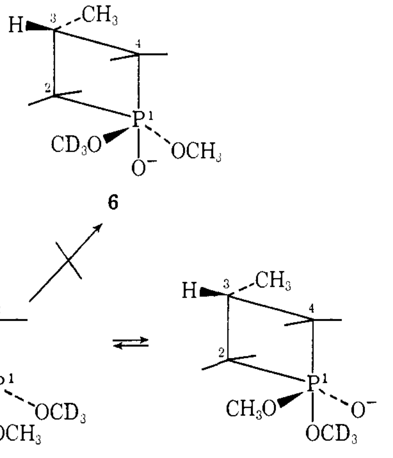
[6] There is some confusion in the literature on the preparation of the isomers of **2** and **3**. McBride[4] has implied that thionyl chloride treatment of **3** (from aqueous hydrolysis of **2**) gave back the starting isomeric acid chloride; repetition of this work in our laboratory revealed that both *cis*- and *trans*-**2** are formed and that each is clearly distinguishable in the nmr (see text). Moreover, K. Bergesen, *Acta Chem. Scand.*, **21**, 1587 (1967), claimed to have isolated *cis*- and *trans*-**3**; there is obvious uncertainty concerning this point [see W. H. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968); P. Haake, R. D. Cook, W. Schwarz, and R. D. McCoy, *Tetrahedron Lett.*, 5251 (1968)].

[7] The interpretation of chemical shifts and coupling constants for these compounds is parallel to that of analogs whose spectra have been discussed elsewhere [S. E. Cremer, and R. J. Chorvat, *J. Org. Chem.*, 32, 4066 (1967)]. The ^{31}P–^{1}H coupling constants were verified by decoupling experiments. The nmr of pure **1** (*trans*) and **2** (*trans*) enabled the assignment of peaks for **1** (*cis*) and **2** (*cis*) in which each was the predominant component in an isomeric mixture.

observed (within the error limits of nmr integration, about ±5%).[8] Indeed no interconversion of the isomers was observed after 24 hr at 60°. Thus exchange occurs in each isomer with retention of configuration[9] and without isomer crossover.

Attack of CH_3O^- along an apical coordinate (*i.e.*, the P–C_2 bond[10]) of **1** (*trans*, R = CD_3O) gives intermediate[11] **4** which leads to **5** by pseudorotation (using O^- as a pivot group).[12] Displacement of CD_3O^- from an apical position in **5** (requirement of microscopic reversibility[11b]) yields the *trans* ester. Alternatively, pseudorotation of **4** to give **6** is unlikely for the electron-donating O^- is in an energetically unfavorable position.[11b,13] Also, **6** would ultimately lead (by further pseudorotation) to isomer crossover, which was not observed.

Equatorial attack by methoxide on **1** (*trans*) can occur from the same or opposite side of the 3-methyl group to give the mirror image of **6** and **5**, respectively. Pseudorotation of the mirror image of **5** (O^- pivot) gives the mirror image of **4** which produces **1** (*trans*) on equatorial departure of CD_3O^-; however, as the group leaves, the apical CH_3O undergoes a 65–70° angle change[14] in going to **1** (*trans*). This angle change does not apply to the "apical-in-out" mechanism (**4** → **5** → **1** (*trans*)) which may therefore be regarded as the energetically favored process.[11b,13]



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4 **5**

Sheldon E. Cremer, Bhupendra C. Trivedi
Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233

Received August 12, 1969

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[8] The per cent deuterium exchange and lack of isomer crossover was followed in the nmr. In $NaOCH_3$–CH_3OH solution pure **1** (*trans*) showed peaks (TMS reference) at τ 6.21 (d, CH_3O), 8.60 (s, 6 H, $PCCH_3$), and 8.92 (s, 6 H, $PCCH_3$); the last two values occur from overlap of two doublets (in benzene all four lines are evident; see text). Thus, the per cent exchange in *trans*-**1** (R = CD_3O) was followed by integration of the area in the methoxy region (initially zero) relative to either and/or both of the upfield methyl peaks at τ 8.60 and 8.92. No detectable amount of **1** (*cis*) appeared in this or the control run (R = CH_3O) in either the methoxy or upfield methyl region (see below). The *cis* ester (in a mixture of isomers in $NaOCH_3$–CH_3OH) showed characteristic peaks at τ (center) 8.69 (d, 6 H, $PCCH_3$), 8.82 (d, 6 H, $PCCH_3$), and 6.30 (d, CH_3O). The ^{31}P–^{1}H coupling constants in $NaOCH_3$–CH_3OH were nearly the same (within ±1 Hz) as in benzene. At 100- and 250-Hz sweep width the CH_3O peaks from **1** (*cis*) and **1** (*trans*) in a mixture were separable to the base line; likewise the peak at τ 8.60 (s, *trans*) was flanked on each side by the lower field half of the doublet at τ 8.69 (*cis*) and the lower field half of the doublet at 8.82 (*cis*); separation was very close to the base line. The per cent exchange in the *cis* isomer was followed by integration of the CH_3O doublet (τ 6.30) relative to the methyl region (either and/or both τ 8.69 and 8.82); the analogous ratio for the *trans* ester in the mixture was also determined in a similar manner. In the exchange study, the area ratio of τ 8.69 (or 8.82) to 8.60 remained constant; this also held for the control mixture of **1** (R = CH_3O). Moreover, the area ratio of the *cis*:*trans* esters in the methoxy region of the control remained constant and provided an additional check on the lack of isomer interconversion.

[9] Similarly, treatment of **2** (*trans*) with phenyllithium to give the 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide,[5,7] mp 127°, must also go with predominant (minimum of 90%)[7] retention. This is now *unambiguously* established since the X-ray of the above oxide has been carried out [C. N. Caughlan and M. Haque, *Chem. Commun.*, 1228 (1968)]; Professor Caughlan has informed us that the *trans* structure (1-phenyl and 3-methyl) is correct and that the word "*cis*" in his manuscript was in error and should be "*trans*."

[10] Attack along the P–C_4 bond produces the mirror image of **4**.

[11] The ring spans the equatorial–apical positions in a trigonal bipyramid. An equatorial–equatorial relation (120°) would be highly strained. For pertinent references see: (a) P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, **90**, 6722 (1968); (b) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (c) K. E. DeBruin, K. Nauman, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7031 (1969).

[12] Although the *trans* isomer is used as an illustration, the *cis* compound can be used with parallel conclusions.

[13] P. C. Van der Voorn and R. S. Drago, *ibid.*, **88**, 3255 (1966); D. S. Frank and D. A. Usher, *ibid.*, **89**, 6360 (1967); D. B. Boyd, *ibid.*, **91**, 1200 (1969), and references cited therein.

[14] This is an approximation based on X-ray data from 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide,[9] the acid **3** [D. D. Swank and C. N. Caughlan, *Chem. Commun.*, 1051 (1968)], and a related phosphonium salt [C. Moret and L. M. Trefonas, *J. Am. Chem. Soc.*, **91**, 2255 (1969)].

Characterization of $C_4H_6Fe(CO)_3\cdot SO_2\cdot BF_3$, the Product of an Arrested Friedel–Crafts Sulfination of Butadieneiron Tricarbonyl[1]

Sir:

Recent studies on the protonation of diene complexes of iron tricarbonyl using HSO_3F–SO_2 at low temperature[2] have prompted us to investigate systems in which Lewis acids other than the proton are present.

BF_3 gas was bubbled into a yellow solution of butadieneiron tricarbonyl (2.00 g) in 3.5 ml of liquid SO_2 under nitrogen at −30°. A brown coloration and a precipitate were produced; excess BF_3 and solvent were then allowed to escape while the mixture was slowly warmed to room temperature. Pumping at 0.5 Torr left an essentially quantitative yield (3.39 g) of the title compound (I) as a yellow solid,[3] mp 136–140° dec.

Crystals of I were grown under nitrogen from a solution in 1:2 nitromethane–dichloromethane over which was placed a layer of *n*-hexane. The slow diffusion of the latter into the solvent mix, accompanied by gradual cooling (+25 to −10° over 24 hr), provided the necessary controlled lowering of solubility. Yellow needle-like parallelepipeds, crystallizing in the noncentrosymmetric monoclinic space group $P2_1$ (C_2^2; no. 4) were obtained. Unit cell data are: a = 6.58 Å, b = 11.78 Å, c = 7.40 Å, β = 92.41°, ρ_{obsd} = 1.79 ± 0.05 g cm^{-3},[4] ρ_{calcd} = 1.886 g cm^{-3} for M = 325.84 and Z = 2.

Complete X-ray diffraction data to $\sin\theta$ = 0.40 (Mo Kα radiation, $\bar{\lambda}$ 0.7107 Å) were collected with a 0.01° incrementing Supper-Pace Buerger automated diffractometer, using a stationary background, ω-scan, stationary-background counting sequence. The structure was solved by a combination of Patterson, Fourier,

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[1] This work was supported by NSF Grant GP-8077, ARPA Contract SD-88 (M. R. C.), and USPHS Grant GM-14336 (H. D. K.).

[2] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Am. Chem. Soc.*, **91**, 6968 (1969), and references cited therein.

[3] *Anal.* Calcd for I: C, 25.80; H, 1.86. Found (Miss Heather King, Microanalyst, Department of Chemistry, UCLA): C, 26.02; H, 2.05%.

[4] The density was measured by flotation in a bromoform–hexane mixture.