prepared by anation of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}0.5H_2O$ with ammonium chloride in methyl alcohol. Thus the reaction in all probability proceeded through a square-pyramidal intermediate.

Similar studies at elevated temperatures also clearly indicated the first step in the dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}0.5H_2O$ to be the formation of *trans*-$[Cr(en)(tn)FCl]Cl$. Continued heating of the product resulted in a new material, the electronic spectrum of which indicated that another reaction had taken place. The product could be predominately *cis*-$[Cr(en)(tn)FCl]Cl$ that was formed as the result of a trans → cis isomerization of the original dehydration product. Such a product could arise either via a dissociative type mechanism that involved a trigonal-bipyramidal intermediate or via Cr–N bond rupture and the opening of a chelate ring as described by Mitra.[21] On the basis of the data currently available it is not possible to establish which of these mechanisms is most nearly correct. A coordinating anion is apparently necessary for the second reaction since *trans*-$[Cr(en)(tn)FCl]ClO_4$ is stable under the conditions where *trans*-$[Cr(en)(tn)FCl]Cl$ reacts. If the second product is the result of a trans → cis isomerization, the reaction does not apear to be complete since the molar absorptivities of the final product are lower than expected for a pure cis isomer.

Studies similar to those carried out for *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}0.5H_2O$ indicated that *trans*-$[Cr(en)(tn)F(OH_2)]Br_2$ did not lose any coordinated water when dried for 7 days over magnesium perchlorate. When the dehydration was carried out at elevated temperatures, it was not possible to detect the presence of any *trans*-$[Cr(en)(tn)FBr]Br$. The dehydration reaction, which appears to occur via a different mechanism, is thought to yield *cis*-$[Cr(en)(tn)FBr]Br$ as the major product.

Reaction of an aqueous solution of the dehydration product with silver sulfate appears to yield predominately *cis*-$[Cr(en)(tn)F(OH_2)]^{2+}$. The electronic spectrum of the product is similar to that reported[6] for *cis*-$[Cr(en)_2F(OH_2)]^{2+}$. However, the molar absorptivities appear to be lower than expected for a pure cis isomer.

Reaction of a methyl alcohol solution of the product, obtained by the prolonged dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Br{\cdot}0.5H_2O$ at 140 °C, with ammonium fluoride or ammonium thiocyanate was the basis for the preparation of (±)-*cis*-$[Cr(en)(tn)F_2]Br$ and (±)-*cis*-$[Cr(en)(tn)FNCS]Br$. The cis geometry of the difluoro complex was confirmed by the isolation of $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]Br$. Since it has been well established that anation reactions of Cr(III) complexes are stereoretentive, the resolution of the product of such a reaction serves to confirm the presence of a cis isomer in the starting material. From a comparison of the optical rotatory dispersion curves of $(-)_{546}$-*cis*-$[Cr(en)_2F_2]^+$,[22] $(-)_{546}$-*cis*-$[Cr(en)_2FNCS]^+$,[6] $(-)_{546}$-*cis*-$[Cr(en)_2F(OH_2)]^{2+}$,[23] and $(-)_{546}$-*cis*-$[Cr(en)_2FNH_3]^{2+}$,[1] the absolute configuration of $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]Br$ was assigned as Δ. The isolation of one of the chiral forms of *cis*-$[Cr(en)(tn)F_2]^+$ also serves to confirm the trans geometry of those complexes whose cations contain the identical ligands but whose electronic spectra exhibit more than two absorption bands. Apparently *cis*-$[Cr(en)(tn)F_2]^+$ is the first fluoro-containing complex of Cr(III) of its type to be resolved.

Although the geometry of the complex identified as *cis*-$[Cr(en)(tn)FNCS]Br$ was not established via resolution techniques, the assigned geometry is well supported by the electronic spectral data.

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Notes

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Two More Space Group Changes

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$TaCl_2H_2(PMe_3)_4$. The crystal structure of this paramagnetic hydride complex of Ta^{IV} was described[1] in space group *Cc* (monoclinic; $a = 15.127$ (3) Å, $b = 12.005$ (3) Å, $c = 12.410$ (2) Å, $\beta = 92.49$ (1)°, $Z = 4$). It should be described, instead, in space group $C2/c$, with the molecule lying on a site of crystallographic symmetry C_2.

After the coordinates in Table II of ref 1 were adjusted by $\Delta x = 0.0214$, $\Delta z = 0.1462$ (placing the Ta atom on a twofold axis) and the coordinates of pairs of symmetry-related atoms were averaged, three full-matrix least-squares refinement cycles led to an R of 0.0303 and a goodness-of-fit of 2.61 for the 2514 F_o and $\sigma(F)$ values recovered from the supplementary material; in the third cycle no shift was greater than 0.19σ (a hydrogen atom). The $C2/c$ coordinates for the Ta, Cl, P, and C atoms are given in Table I; their U_{ij} values and the coordinates and isotropic B's of the hydrogen atoms are included as supplementary material.

It is somewhat surprising that the R index and (particularly) the goodness-of-fit are slightly higher than the values 0.0285 and 2.56 reported for the *Cc* model.[2] Accordingly, we attempted to repeat the *Cc* refinement, beginning with the parameters of ref 1. (Such a refinement cannot begin with the $C2/c$ parameters, because of exact singularities.) After small adjustments of the scale factor (to 0.993) and the U_{ij} values—perhaps due to slightly different form factors—we obtained essentially the same indexes: $R = 0.0288$, GOF = 2.60. However, continued refinement through four full-matrix least-squares cycles gave no hint of convergence; while the agreement indexes stayed effectively constant, many parameter shifts were appreciably larger than their esd's—up to 3.4σ for two hydrogen atoms and 1.8σ (0.05 Å) for a carbon atom.[3]

Table I. Coordinates ($\times 10^4$) for $TaCl_2H_2(PMe_3)_4$, Space Group $C2/c$

atom	x	y	z	B_{eq}[a]
Ta	0	−2710.1 (2)	2500	1.10 (1)
Cl(2,3)	−1079.6 (7)	−1103.9 (9)	2152.8 (9)	1.94 (2)
P(4,7)	224.7 (7)	−2307.6 (9)	446.1 (9)	1.60 (2)
P(5,6)	−1494.5 (7)	−3719.4 (9)	2467.6 (9)	1.56 (2)
C(8,19)	730 (3)	−3357 (4)	−401 (4)	2.21 (8)
C(9,18)	886 (3)	−1077 (4)	182 (4)	2.18 (8)
C(10,17)	−779 (3)	−2035 (4)	−395 (4)	2.41 (8)
C(11,14)	−2452 (3)	−3121 (4)	3120 (4)	2.38 (8)
C(12,16)	−1477 (3)	−5129 (4)	3006 (4)	2.10 (8)
C(13,15)	−2014 (3)	−3959 (5)	1123 (4)	2.52 (8)

[a] $(8\pi^2/3)\sum_{i,j}U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

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(2) The "goodness of fit" reported in ref 1 is 1.083. However, using the values of F_o and $\sigma(F)$ in the supplementary material and 2514 and 325 for the numbers of observations and parameters, we obtain 2.56 for the quantity $[\sum(F_o - F_c)/\sigma(F)]^2/2189]^{1/2}$.

Table II. Coordinates (×10^4) for 1,5-$(Ph_2PN)_2(NSBr)_2$, Space Group $P2_1/n$

atom	x	y	z	B_{eq}[a]
Br(1,2)	−306 (1)	−3190 (1)	1228.1 (5)	4.48 (2)
S(1,2)	−672 (2)	−2670 (3)	−253 (1)	2.76 (4)
P(1,2)	−1766 (2)	898 (3)	−96 (1)	2.74 (4)
N(1,3)	−1657 (6)	−1175 (9)	−442 (3)	3.24 (14)
N(2,4)	−546 (5)	2035 (9)	345 (3)	3.02 (13)
C(11,41)	−2568 (7)	756 (12)	663 (4)	2.84 (17)
C(12,46)	−2412 (8)	2061 (12)	1281 (5)	4.35 (19)
C(13,45)	−3082 (9)	1953 (16)	1832 (6)	5.97 (24)
C(14,44)	−3922 (9)	574 (16)	1781 (5)	5.23 (23)
C(15,43)	−4071 (8)	−710 (14)	1182 (6)	4.59 (21)
C(16,42)	−3413 (8)	−629 (12)	619 (5)	3.87 (18)
C(21,31)	−2690 (7)	2143 (11)	−961 (5)	3.03 (18)
C(22,32)	−3054 (8)	1378 (12)	−1741 (5)	4.02 (19)
C(23, 33)	−3763 (9)	2364 (16)	−2392 (5)	5.18 (24)
C(24,34)	−4091 (10)	4134 (19)	−2273 (7)	6.62 (30)
C(25,35)	−3719 (10)	4947 (14)	−1507 (8)	6.36 (32)
C(26,36)	−3008 (9)	3941 (14)	−849 (5)	4.60 (23)

[a] See footnote *a* of Table I.

Moreover, many bond lengths became disparate; for example, the P–C distances ranged from 1.74 (3) to 1.90 (2) Å and the Ta–H distances were 1.86 (11) and 1.16 (12) Å. These sorts of difficulties (which were not noted in ref 1) are typical of attempts to refine an approximately centrosymmetric model in a noncentrosymmetric space group.[4]

As usual,[5] refinement in the centrosymmetric space group $C2/c$ has led to equality of some bond lengths that appeared to be unequal in Cc; for instance, the Ta–Cl distance is now 2.551 (1) Å rather than 2.542 (5) and 2.563 (5) Å.[1] The two Ta–P distances remain unequal, at 2.564 (1) annd 2.631 (1) Å, but the P–C distances are statistically equal at 1.830 (3) Å. The Ta–H distance is 1.69 (6) Å, appreciably shorter than the values 1.94 (11) and 1.85 (11) Å reported in ref 1; as noted there, the most accurate Ta–H bond length available, from a neutron diffraction study[6] of Cp_2TaH_3, is 1.774 (3) Å.

1,5-$(Ph_2PN)_2(NSBr)_2$. The structure of this 8-membered-ring compound was described[7] in space group Pn (monoclinic; a = 11.476 (3) Å, b = 7.240 (1) Å, c = 16.914 (4) Å, β = 106.42 (1)°, Z = 2). It should be described in $P2_1/n$, with the molecule lying on a crystallographic center of symmetry.

After the coordinates in Table II of ref 7 were decremented so that the origin lay at the approximate center of symmetry (x = 0.655, y = 0.25, z = 0.665) and the coordinates of symmetry-related atoms were averaged,[8] full-matrix least-squares refinement quickly converged at an R of 0.042, a weighted R of 0.046, and a goodness-of-fit of 1.33 for 1199 observed reflections and 154 parameters; corresponding values reported for the Pn structure are 0.043, 0.047, and 1.34 for 185 parameters. Our refinement included anisotropic U_{ij}'s for the Br, S, P, and C atoms; in the earlier Pn refinement the C atoms were treated as isotropic.[9] In both refinements the hydrogen sites were assumed. The $P2_1/n$ parameters are given in Table II.

The $P2_1/n$ refinement has led to coordinate esd's about one-third as large as reported previously, presumably as a result of removing the near-singularities associated with refining an approximately centrosymmetric structure in a noncentrosymmetric space group.[4] It has again led to considerably more reasonable molecular geometry. For example, whereas the Pn model resulted in P–N distances ranging from 1.54 (2) to 1.68 (2) Å and S–N distances from 1.47 (2) to 1.57 (2) Å, the $P2_1/n$ refinement results in essentially equal values P–N = 1.613 (6), 1.629 (6) Å and S–N = 1.521 (6), 1.532 (6) Å. Even more dramatic are the changes in C–C distances (ref 1, supplementary material), which ranged from 1.12 (3) to 1.79 (3) Å for the Pn description but now range only from 1.351 (14) to 1.386 (15) Å.

The additional 2_1 axis requires the systematic extinction of reflections $0k0$ with k odd. Of the five such reflections included in the supplementary material, three are coded as "unobserved" and the other two as "$I_o < 0$".

Concluding Remarks. We can hear faint voices saying, "So what?"—the original, noncentrosymmetric descriptions of these two compounds showed the same atom connectivities as the revised centrosymmetric descriptions, and the average bond lengths are little changed. To many, these may be the only important considertions. But *reliable* bond lengths and angles are vital to many fields of chemistry. Refinement of a centrosymmetric structure in a noncentrosymmetric space group can well lead to inequalities in bond lengths so large (P–N, 1.54 (2) and 1.68 (2) Å, e.g.) as to invite fancy explanations when none is warranted. Moreover, the "wolf" syndrome is to be feared: if the reported accuracies of diffraction results cannot be trusted, further developments in such areas as bonding theory will surely be delayed. The centrosymmetric–noncentrosymmetric ambiguity is a particularly bothersome one, and we urge continual awareness of it and of its possible consequences.

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Registry No. $TaCl_2H_2(PMe_3)_4$, 85939-38-4; $(Ph_2PN)_2(NSBr)_2$, 90133-20-3.

Supplementary Material Available: Listings of anisotropic U_{ij} values and of hydrogen parameters for both compounds (Tables S1 and S2) (2 pages). Ordering information is given on any current masthead page.

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(3) The esd's were considerably larger than for the $C2/c$ refinement and varied greatly among atoms of the same type. These are manifesttions of the near-singularities (see ref 4).

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(8) There appear to be two misprints in Table II of ref 7: the y coordinate of N(2) should probably be 0.456 rather than 0.656, and the z coordinate of C(21) should probably be about 0.570 rather than 0.500. Also, the U values in the supplementary material (Table S1) are ×10^3 rather than ×10^4.

(9) Near-singularities in the least-squares matrix would presumably have led to severe convergence problems in the Pn refinement; the final shift-to-esd ratios are not given. Including anisotropic U_{ij}'s for the C atoms would probably have made the problem more severe.

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Surface-Selective Dispersion of $Os_3(CO)_{12}$ on Layered Silicate Clay. Reaction of $HOs_3(CO)_{12}^+$ with Hectorite

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A variety of metal complex catalysts may be immobilized by intercalation in smectite clays.[1,2] Oftentimes, the intercalated complex catalyst is more selective than the analogous complex in homogeneous solution. The steric requirements of surface transition states[3] or the position of surface equilibria[4] can provide the basis for enhanced catalytic selectivity.

Metal carbonyl cluster complexes represent a potentially important class of compounds for intercalation in clays, because they may exhibit interesting catalytic properties in their own right or they may serve as precursors for the formation of atomically dispersed metal centers.[5] Although metal carbonyls can be readily

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