Table II. Ta_6S

hkl	$\sin^2 \theta_{obsd} \times 10^5$	$\sin^2 \theta_{calcd} \times 10^5$	$I/I_0 \times 100$
002	1,388	1,392	10
200	1,524	1,519	5
−311	4,871	4,867	1
−312		4,886	
004	5,561	5,569	1
311	6,923	6,914	1
020	8,480	8,499	25
021	8,863	8,848	60
312	8,992	8,982	25
−315	9,118	9,123	70
−115	9,508	9,498	20
−513	9,621	9,631	25
204	9,818	9,818	20
022	9,885	9,896	20
−511	10,263	10,258	100
−514	10,375	10,359	80
−602	10,951	10,968	55
−223	11,110	11,104	85
023	11,631	11,636	90
313	11,743	11,748	60
006	12,523	12,529	1
−224	12,854	12,854	1
115	12,919	12,913	50
−423	13,617	13,611	70
−606	13,912	13,906	5
024	14,082	14,069	1

the *b* axes in both Ta_2S and Ta_6S. The average Ta–Ta distance from the central Ta atom to one on the pentagonal antiprisms is 2.91 Å in Ta_2S and 2.93 Å in Ta_6S. The distance from one central Ta atom to the next such atom is 2.79 Å in Ta_2S and 2.64 Å in Ta_6S. Thus, in both structures, each central Ta atom is surrounded by 12 Ta atoms in a slightly distorted icosahedron.

In the Ta_2S structure the chains of Ta antiprisms are bridged in the *a* and *c* directions by two types of sulfur atoms. The first type is bonded to six Ta atoms forming faces of each of two antiprisms with an average Ta–S distance of 2.56 Å. The second type of sulfur atom is bonded to three Ta atoms forming the face of one antiprism and to a Ta atom at the corner of another antiprism with an average Ta–S distance of 2.47 Å.

In Ta_6S, the Ta chains are bridged in the *a* and *c* directions by one sulfur atom bonded to six Ta atoms forming a distorted trigonal prism with an additional Ta atom capping one of the rectangular faces. The average Ta–S distance in Ta_6S is 2.49 Å.

Each of these structures is a new type and exhibits a very different type of metal coordination than is found in other known transition metal sulfides, such as Hf_2S,[3] Ti_2S,[4] V_3S,[5] and $Nb_{21}S_8$[6] or related phosphides such as Ta_2P[7] or Nb_7P_4.[8] In all of these structures, with the exception of Hf_2S, there exist remnants of body-centered structures of the metal.[9] The interpenetrating icosahedral arrangement of Ta atoms in Ta_6S and Ta_2S is unique to these compounds among known structures. These are the only metal-rich compounds of those mentioned above in which there exist metal atoms which do not have nonmetal near neighbors. The coordination about the sulfur in Ta_6S is similar to that found about the nonmetal atoms in Hf_2S, V_3S, Ti_2S, $Nb_{21}S_8$, Ta_2P, and Nb_7P_4, namely trigonal prismatic. However, the two sulfur atoms in Ta_2S are not found in a trigonal-prismatic coordination. A relatively large hole surrounded by sulfur (the shortest S–S distance is 2.86 Å) separates four chains of interpenetrating icosahedra in Ta_2S. This unusual structural feature is unique among the metal-rich sulfides and phosphides.

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[3] H. F. Franzen and J. Graham, *J. Inorg. Nucl. Chem.*, **28**, 377 (1966).

[4] J. P. Owens, B. R. Conrad, and H. F. Franzen, *Acta Cryst.*, **23**, 77 (1967).

[5] B. Pedersen and F. Grønvold, *ibid.*, **12**, 1022 (1959).

[6] H. F. Franzen, T. A. Beineke, and B. R. Conard, *ibid.*, **B24**, 412 (1968).

[7] A. Nylund, *Acta Chem. Scand.* **20**, 2393 (1966).

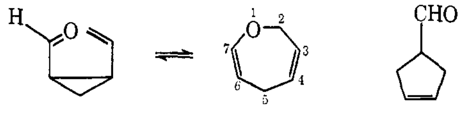
[8] S. Rundquist, *ibid.*, **20**, 2427 (1966).

[9] H. F. Franzen, J. G. Smeggil, and B. R. Conard, *Mat. Res. Bull.*, **2**, 1087 (1967).

Valence Tautomerism in *cis*-2-Vinylcyclopropanecarboxaldehyde. 2,5-Dihydrooxepin

Sir:

Among the valence isomers of *cis*-2-vinylcyclopropanecarboxaldehyde (I), the retro-Claisen rearrangement product, 2,5-dihydrooxepin (II), might reasonably be expected to exist in equilibrium with the parent substance at ordinary temperatures.[1] Earlier workers[2] sought to observe such behavior without success; I was reported to show "surprisingly high thermal stability," resisting change up to 400°, at which temperature it rearranged to 3-cyclopentenecarboxaldehyde (III). We wish to report that I, in fact, is quite thermolabile and may be diverted quantitatively to II under mild conditions.[3]



I II III

Compound I was prepared from *cis*-2-vinylcyclopropanecarboxylic acid chloride[4] by conversion to the acylaziridine and $LiAlH_4$ reduction of the latter.[5] The crude product (bp 40–50° (10 mm)) was purified by preparative glpc. The structure of I follows from its method of preparation and its spectral properties. A molecular weight of 96 is obtained mass spectrally; the infrared spectrum confirms the presence of the

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[1] Evidence for the phenomenon in the closely related system

has been presented by M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **48**, 1985 (1965).

[2] E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

[3] Under more energetic conditions (∼200–300°), I interconverts with its *trans* isomer and with its valence isomer, 2-vinyl-2,3-dihydrofuran, while proceeding irreversibly to III. We hope to report quantitative data on these processes soon (unpublished experiments, R. D. Cockroft).

[4] E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Ann.*, **682**, 1 (1965).

[5] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **80**, 5377 (1958).

aldehyde function (2840, 2760, 1700 cm^{-1}) and the vinyl group (3090, 3010, 1635, 970, 905 cm^{-1}). The 100-MHz nmr spectrum (CCl_4–TMS) shows the following signals: δ 9.37, 1 H, four-line pattern with outer line spacing of 4.5 Hz and inner line spacing of 1.8 Hz (HC=O);[6] δ 5.9–5.5, 1 H, complex multiplet (HC=C); δ 5.24–4.94, 2 H, two overlapping sets of doublets of doublets, corresponding to the AB portion of an ABX pattern (H_2C=C); δ 2.20–1.95, 2 H, and 1.60–1.15, 2 H, complex multiplets assigned to the cyclopropane ring protons.

The behavior of I on glpc analysis offered the first clue to the tautomeric phenomenon. Invariably, under a variety of conditions (column material, temperature, and flow rate) the glpc trace of repeatedly purified I showed the presence of another component which peaked a short time before I and which tailed into the peak of I. Isolation of II in a state of >95% purity was accomplished in the following way: a sample of I, previously enriched in the more volatile component by slow distillation through a spinning-band column at reduced pressure, was injected into a preparative glpc column (10% Carbowax 1500 on Gas-Chrom P) held at 50° and the leading component was trapped. Recycling of the trapped fraction afforded II in increasing purity. The spectral properties of II contrast strongly with those of I and serve to establish its identity as 2,5-dihydrooxepin. The infrared spectrum of II reveals an intense band at 1655 cm^{-1}, characteristic of a vinyl ether, as well as the disappearance of the aldehydic absorptions noted for I. Strong bands at 1270 and 1105 cm^{-1}, attributable to C–O stretching modes, also appear. In the 100-MHz nmr spectrum (CCl_4–TMS), the aldehydic and vinyl signals of I have disappeared and new signals consistent with the dihydrooxepin structure have appeared: δ 6.13, 1 H, doublet of triplets with J values of 7.1, 1.7, and 1.7 Hz (OC^7H=C); δ 6.05–5.80, 2 H, complex multiplet (C^3H=C^4H); δ 4.50–4.15, 3 H, complex multiplets ($-C^2H_2-O$ and HC^6=C); δ 3.00–2.70, 2 H, complex multiplet ($-C^5H_2-$).[7]

At room temperature, II slowly reverts to I with a half-life of about 1 day to form an equilibrium mixture of 95% I and 5% II. Preliminary rate studies in the temperature range of 50–70° yield tentative values of $\Delta H^{\ddagger} = 23$ kcal/mol and $\Delta S^{\ddagger} = -6$ eu for the rearrangement of II to I.

The demonstration of the facile interconversion of I and II adds another example of concerted, bisallylic rearrangements of simple *cis*-disubstituted cyclopropanes to those already recorded.[8] In the present case, however, the cyclopropane derivative is favored at equilibrium, a result which reflects the balance of power when the driving force of carbonyl group formation is pitted against that of relief of cyclopropane ring strain.

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[6] The origin of this peculiar splitting pattern is being investigated. The complexity of the pattern has been found to be solvent, concentration, and temperature dependent. It may further be noted that the corresponding signal in *trans*-2-vinylcyclopropanecarboxaldehyde is a clean doublet with $J = 4.2$ Hz.

[7] These signals and their assignments find close correspondence with those reported for 2-oxabicyclo[3.2.1]octa-3,6-diene in ref 1.

[8] *cis*-Divinylcyclopropane → 1,4-cycloheptadiene (E. Vogel, R. H. Ott, and K. Gajek, *Ann.*, **644**, 172 (1961); W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963)); *cis*-2-vinylcyclopropyl isocyanate → 3,6-dihydro-2H-azepin-2-one (ref 4); Schiff bases of 1,2-diaminocyclopropane → 2,3-dihydro-1,4-diazepins (H. A. Staab and F. Vogtle, *Chem. Ber.*, **98**, 2701 (1965)).

[9] American Chemical Society Petroleum Research Fund Fellow, 1967–1968.

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Preparation and Catalytic Properties of Some Cationic Iridium(III) and Rhodium(III) Dihydrido Complexes[1]

Sir:

Cleavage of the dimeric d^8 complexes, $[M(diene)Cl]_2$ (M = Ir, Rh),[2] with triphenylphosphine has previously led to the isolation of the neutral species, $M(diene)(PPh_3)Cl$.[3] We find that if the reaction is carried out in polar media such as alcohols or nitromethane, the cationic species, $[M(diene)(PPh_3)_2]^+$, are formed and can be isolated as tetraphenylborate or perchlorate salts.[4] We have prepared a series of these complexes with other ligands[5] as well as triphenylphosphine and find that the cationic iridum species are more readily formed and isolated than the corresponding rhodium complexes.

These d^8 complexes undergo a variety of oxidative addition and diene displacement reactions which will be described elsewhere.[6] This communication is concerned only with the interaction of these complexes with molecular hydrogen and the catalytic and related properties of the resultant dihydrido complexes.

The deep red acetone solution of the iridium cation, $[Ir(COD)(PPh_3)_2]^+$, undergoes immediate decolorization when treated with molecular hydrogen, and from the resultant solution, crystals of the cationic complex, $[IrH_2(PPh_3)_2[(CH_3)_2CO]_2]^+$, can be isolated in good yield. The infrared spectrum (Nujol mull) of this complex shows, in addition to triphenylphosphine and uncoordinated anion modes, two bands at 2230 and 2260 cm^{-1} (metal–hydride stretching frequencies) and a strong, sharp doublet at 1650 and 1660 cm^{-1}, which we assign to coordinated acetone.[7] The infrared spectrum in chloroform shows the presence of both free (ν_{CO} ~1710 cm^{-1}) and coordinated (ν_{CO} ~1660 cm^{-1}) acetone, and, on addition of excess triphenylphosphine, the band at 1660 cm^{-1} disappears while the band at 1710 cm^{-1} increases in intensity. Moreover, on concentration of this solution the known cation,

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[1] Work supported by the William F. Milton Fund.

[2] diene refers to 1,5-cyclooctadiene (COD), norbornadiene (NBD), and 1,5-hexadiene.

[3] (a) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610 (1966); (b) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

[4] Ionic species such as $[Ir(COD)(PPh_3)_2]^+$ were detected by conductivity measurements following an nmr study of these reactions: H. C. Volger, K. Vrieze, and A. P. Praat, *J. Organometal. Chem.*, **14**, 429 (1968); see also footnote, p 433. Ionic species in the rhodium system have previously not been observed.

[5] J. A. Labinger and J. A. Osborn, to be submitted for publication.

[6] For example, interaction of these cations with carbon monoxide yields the five-coordinate cations $[M(PPh_3)_3(CO)_2]^+$, $[M(PPh_3)_2(CO)_3]^+$, as well as the solvated carbonyl species, $[Rh_2(PPh_3)_2(CO)_2(S)]^+$.

[7] The shift of ν_{CO} to lower frequency ($\Delta\nu_{CO}$ ~ 50 cm^{-1}) indicates bonding of the keto group *via* oxygen. In the BF_3–acetone adduct, $\Delta\nu_{CO}$ ~ 60 cm^{-1}; see B. F. Susz and P. Chalandan, *Helv. Chim. Acta.*, **41**, 1332 (1958). This can be contrasted with the bonding and spectral changes when perfluoroacetone coordinates to Pt(II); see B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.*, *A*, 167 (1968).