of the crystallographic data and ^{1}H NMR spectral data, both isomers appear to be classical dihydrides. The H–H distances and H–Re–H angles[14] are normal for classical hydrides.[15]   In addition, T_1 measurements for both isomers are consistent with this conclusion.[16]   The ^{1}H NMR spectrum of the *trans*-[ReHD(mhp)$_2$(PPh$_3$)$_2$]${}^+$ cation[17] shows a hydride resonance that has shifted approximately 0.1 ppm downfield from that of the dihydride complex. As expected, the hydride–deuteride complex does not exhibit resolvable H–D coupling, which would be characteristic of η^2-HD bonding.[18]

We observe an exceedingly slow conversion of the trans isomer to the cis in CD$_2$Cl$_2$ at room temperature. The isomerization appears to be an intramolecular process that is independent of added ligand (PPh$_3$, Hmhp, or Li(mhp)). It proceeds cleanly at room temperature (there are no observable side products) and can be followed conveniently by either ^{1}H or ^{31}P{^{1}H} NMR spectroscopy.[19]   A zero-order rate constant $k = (7.9 \pm 0.2) \times 10^{-9}$ M s^{-1} at 20 °C was determined from the ^{31}P{^{1}H} spectra.[20]   One possible explanation for the remarkable stability of the trans isomer is that the mhp ligands, which lie essentially in a plane with their methyl groups projecting toward each other, provide a barrier to the rotation of the ReH$_2$ unit that may be necessary to convert it to the cis isomer. This process can only be accomplished by a concomitant twisting of the mhp ligands from this planar arrangement, a process that apparently is not very favorable energetically. We find that the analogous complexes with ligands that do *not* contain methyl groups, i.e., [ReH$_2$(L)$_2$(PPh$_3$)$_2$]PF$_6$, where L is the anion of 2-hydroxypyridine or 2-mercaptopyridine, appear to exist exclusively in the cis form.[21]   Efforts are now being directed toward designing other mixed-ligand sets that will display similar stereochemical characteristics in polyhydride systems.

Supplementary Material Available: A listing of atomic positional parameters for the structures of *cis*-[ReH$_2$(mhp)$_2$(PPh$_3$)$_2$]PF$_6$·(CH$_3$)$_2$CO and *trans*-[ReH$_2$(mhp)$_2$(PPh$_3$)$_2$]PF$_6$·C$_2$H$_4$Cl$_2$ and a figure (Figure S1) showing the ^{1}H NMR of spectra of these two complexes (9 pages). Ordering information is given on any current masthead page.

(14) Cis isomer: H(1)–H(2) distance 1.6 (1) Å; H(1)–Re–H(2) angle 61 (3)°. Trans isomer: H(1)–H(2) distance 1.53 (5) Å; H(1)–Re–H(2) angle 56 (2)°.

(15) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989,** *111,* 5757.

(16) Over the temperature range +25 to –80 °C the Re–*H* resonances remained essentially unchanged although they broadened slightly at the lower temperature limit. For the cis isomer the observed T_1 (min) at 200 MHz was 59 ± 7 ms (–74 °C) while for the trans isomers the observed T_1 (min) was 52 ± 11 ms (–76 °C). For a recent discussion of the T_1 method, see: Crabtree, R. H.; Luo, X. *Inorg. Chem.* **1990,** *29,* 2788.

(17) The deuteride was prepared by the addition of a 10-fold excess of CF$_3$CO$_2$D to a CD$_2$Cl$_2$ solution of ReH(mhp)$_2$(PPh$_3$)$_2$ in a sealed NMR tube, under N$_2$ gas. Both the acid and the CD$_2$Cl$_2$ were deoxygenated prior to use.

(18) For data on a similar shift in a hydride resonance, see: Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989,** *8,* 1824.

(19) A comparison was made of the trans → cis isomerization at three temperatures (0, 20, and 40 °C). No detectable amount (by NMR) of the cis isomer had formed after 4 days at 0 °C, while at 20 °C under these conditions the trans to cis isomer distribution was ca. 90:10. After 4 days at 40 °C (refluxing CH$_2$Cl$_2$) the cis isomer was now the dominant species (there was very little trans left), but a considerable quantity (ca. 30%) of the deprotonated complex ReH(mhp)$_2$(PPh$_3$)$_2$ had also formed under these conditions.

(20) A CD$_2$Cl$_2$ solution of the trans isomer was sealed in an NMR tube (under N$_2$ atmosphere), and the integrated intensity of the ^{31}P{^{1}H} signal was monitored over a period of several weeks to ca. 90% conversion. A CD$_2$Cl$_2$ solution of PPh$_3$ was used as an external standard.

(21) Leeaphon, M.; Walton, R. A., unpublished results. The mechanism of this zero-order isomerization is under further study, but it does not appear to be photochemical in origin.

Nb$_{1.72}$Ta$_{3.28}$S$_2$: A Novel Phase in the Ta–Nb–S Ternary System with a Layered Structure

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The structures of the metal-rich sulfides of Nb and Ta differ markedly. In Nb$_{21}$S$_8$[1] and Nb$_{14}$S$_5$,[2] the metal coordinations are capped pentagonal prisms and capped distorted cubes, while Ta$_2$S[3] and Ta$_6$S[4,5] contain linear chains of facing-sharing Ta pentagonal antiprisms.

High-temperature preparative studies have recently yielded two compounds: Nb$_{4.92}$Ta$_{6.08}$S$_4$[6] and Nb$_{6.74}$Ta$_{5.26}$S$_4$.[7]   Both ternaries have unique structure types with coordinations similar to the Nb-rich sulfides. Here we report a new compound Nb$_{1.72}$Ta$_{3.28}$S$_2$ (*I4/mmm a* = 3.320 Å, *c* = 21.619 Å), with a layered structure reminiscent of Ta$_2$Se[8] found by high-temperature techniques.

The initial reactant, Ta$_2$S, was synthesized from the elements in an out-gassed silica tube at 800 °C for 3 days. By the same procedure "Nb$_2$S" was synthesized. A pellet of Ta$_2$S and "Nb$_2$S" (n_{Ta_2S}:n_{Nb_2S} = 3:1) was arc-melted on a copper plate under Ar by using a tungsten electrode. The arc-melted sample exhibits the facile shearing characteristic of layered compounds. The powder pattern of the arc-melted sample arose principally from the title compound. The full width of the 002 diffraction ($2\theta = 8.17°$) in the Guinier pattern is 0.13°. The widths of the diffraction lines indicated that the sample was poorly crystallized. When the sample was annealed at 1350 °C for several hours the new phase disproportionated. The major remaining phase was Nb$_x$Ta$_{11-x}$S$_4$ ($x \simeq 5$).[6]

Intensity data were obtained from a crystal (0.02 × 0.02 × 0.25 mm^3) obtained from the arc-melted sample by using a Rigaku AFC6 single-crystal diffractometer employing monochromatic Mo Kα radiation and the 2θ–ω scan technique up to 60° (2θ). Data were obtained for 124 unique reflections with $F^2 > 3\sigma(F_o{}^2)$. Calculations were performed with the program package TEXSAN. The crystal was also examined by the Weissenberg technique and some streaking was observed. Thus, the crystal was not of optimum quality for refinement and the precision of the results could be adversely effected. However, the R factor was indicative of satisfactory refinement.

The structure was solved in the space group *I4/mmm* by the direct method. The formula was determined from the refinement to be Nb$_{1.72}$Ta$_{3.28}$S$_2$. The DIFABS absorption correction was applied. The results are given in Table I. Each metal position is occupied by both Nb and Ta. The arc-melted sample was checked by EDAX. The major phase consists of Ta, Nb, and S elements with minor amounts of W and Cu originating from the arc-melting and therefore probably on the sample surface.

The structure (Figure 1) can be viewed as *bcc*-type elemental Nb or Ta structure in which two neighboring layers in every seven are replaced by sulfur and thus some distortions relative to *bcc* are observed; e.g., the cube consisting of eight M2 contracts along the *c* axis while the cube of four M1 and four M3 expands along the *c* axis, with M2 deviating slightly from the center of the cube. This novel layered structure is reminiscent of Ta$_2$Se,[8] which is composed of six layers in the sequence Se–Ta–Ta–Ta–Ta–Se, also in *bcc*-type packing. In ZrCl[9] the sequence of the layers is Cl–

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Table I. Final Cell, Refinement, and Atom Parameters for $Nb_{1.72}Ta_{3.28}S_2$[a]

	occupancy, %	z	B_{eq}, Å²	U_{11}	U_{33}
M1 2a	88.3 Ta + 11.7 Nb	0	0.98 (9)	0.011 (1)	0.015 (2)
M2 4e	82.6 Ta + 17.4 Nb	0.4248 (1)	0.68 (5)	0.0098 (7)	0.006 (1)
M3 4c	37.3 Ta + 62.7 Nb	0.1560 (1)	0.74 (8)	0.009 (1)	0.010 (2)
S 4e		0.3024 (4)	0.7 (2)	0.011 (4)	0.005 (6)

[a] Tetragonal, space group $I4/mmm$, a = 3.3203 (9) Å, c = 21.619 (12) Å, Z = 2. 124 unique reflections ($I \geq 3\sigma I$), 15 variables, R = 0.035, R_W = 0.038. x, y = 0 for all atoms; $U_{22} = U_{11}$, U_{ij} = 0. B_{eq} = $8\pi^2/3$ ($U_{11} + U_{22} + U_{33}$).

Figure 1. Picture of one unit cell for $Nb_{1.72}Ta_{3.28}S_2$. Larger circle represents S.

Zr–Zr–Cl and the homoatomic analogue structure is *ccp*-type.

The coordination of M1 is as follows: eight M2 (2.856 Å) at the corners of a distorted capped cube, four M1 (3.320 Å) and two M3 (3.373 Å) as capping atoms. Around M2 there are four M1 (2.856 Å) and four M3 (2.926 Å) at the corners of a distorted capped cube, five M2 (four at 3.320 Å and one at 3.251 Å), and one S (2.646 Å) as capping atoms. The corners of the distorted capped cube around M3 are four M2 (2.926 Å) and four S (2.514 Å) while the capping atoms are one M1 (3.373 Å) and four M3 (3.320 Å), respectively.

As the identifying number of the metal increases, the Nb/Ta ratio on that position also increases. The number of coordinating sulfurs for M1, M2, and M3 are 0, 1, and 4, respectively; i.e., the more Nb in the position, the more S bonded to this position. This is the fourth example supporting the suggestion[7] that Nb–S binding energy is greater than that of Ta–S in the metal-rich sulfides. The shortest distance between sulfur atoms (3.26 Å) in neighboring layers indicates interlayer van der Waals interactions, consistent with the graphitic character and the tendency of the compound to disorder.

The layered disulfides (TiS_2, MoS_2, NbS_2, etc.) have been studied extensively[10] because they intercalate both organic and inorganic substances into the interlayer van der Waals gap between adjacent sulfur layers. The compound reported here introduces

the possibility of studying intercalates in a new setting, namely, in a compound with a robustly metallic region separating the van der Waals layers. This compound also raises again the intriguing chemical question posed previously by $Nb_{4.92}Ta_{6.08}S_4$[6] and $Nb_{6.74}Ta_{5.26}S_4$,[7] namely: what are the properties of mixed Nb–Ta that cause compounds of the mixed metals to differ substantially in M/S ratio and structure from the binary sulfides of Nb and Ta?

Supplementary Material Available: Tables of crystal data and bonding distances for $Nb_{1.72}Ta_{3.28}S_2$ (3 pages); table of observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

Total Synthesis of Deoxybouvardin and RA-VII: Macrocyclization via an Intramolecular Ullmann Reaction

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Bouvardin (**8**, NSC 259968) and deoxybouvardin (**2**), bicyclic hexapeptides isolated initially from *Bouvardia ternifolia* (Rubiacea) and identified by single-crystal X-ray structure analysis (bouvardin) and chemical correlation (deoxybouvardin),[1] represent the initial members of a growing class of potent antitumor antibiotics now including the bicyclic hexapeptides RA-I – RA-VII.[2-7] Synthetic efforts on **1–8** have been characterized by the

	R¹	R²	R³	R⁴	R⁵	
1	H	CH₃	CH₃	H	H	O-methyl deoxybouvardin, (RA-VII)
2	H	H	CH₃	H	H	deoxybouvardin, (RA-V)
3	H	H	CH₃	OH	H	RA-I
4	H	CH₃	H	H	H	RA-II
5	H	CH₃	CH₃	OH	H	RA-III
6	H	CH₃	CH₃	H	OH	RA-IV
7	OH	CH₃	CH₃	H	H	O-methyl bouvardin, (RA-VI)
8	OH	H	CH₃	H	H	bouvardin

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