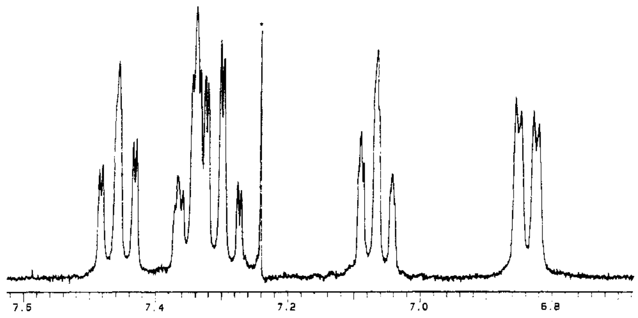

Figure 2. 300-MHz ^1H NMR spectrum ($CDCl_3$) of the phenyl region of **2**. The asterisk denotes residual $CHCl_3$.

temperature, as shown in Figure 2. The coupling pattern and intensity ratios are consistent with the crystal structure of the compound if rotation about the N-phenyl bond is slow on the NMR time scale. The $^{13}C\{^1H\}$ NMR spectrum (25 MHz) up to 100 °C reveals six aromatic resonances and is also consistent with hindered rotation about the N–C bond. Variable-temperature ^{13}C NMR studies in DMSO-d_6 show that the two ortho and two meta aromatic carbon resonances broaden and disappear into the base line at 150 °C. Coalescence of these peaks is not observed even at 175 °C. Use of the two-site-exchange approximation[9] allows estimation of a lower limit for the ΔG^* for N–C bond rotation of ca. 21 kcal mol^{-1}.

This large energy of activation for rotation about an N–C single bond is comparable to the barriers observed for rotation about the N–C bonds of organic amides.[10] However, the crystallographic study revealed a nearly tetrahedral environment around each N in the molecule, suggesting that the hindered rotation is not caused by π bonding between the nitrogen and the phenyl ring. The restricted phenyl ring rotation must therefore arise from the extremely crowded environment of the molecule.

The observation that compound **2** is isolable and stable to 175 °C in DMSO indicates that the Ru–N bond in this amide complex is rather robust. The use of the method of deprotonation of coordinated amines in the synthesis of metal amides is a viable possibility. In this case, its utility is limited by the extreme steric constraints imposed by the C_6Me_6 ligand, which ultimately leads to the formation of dimeric products.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Listings of all bond lengths and angles, thermal parameters, and crystallographic data for $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}NHPh)_3][BF_4]$ (4 pages); a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry
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The Layered, Metallic Scandium Iodide $Sc_{0.93}I_2$: Synthesis, Structure, and Properties

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The scandium halides form a wide variety of novel ternary phases, Sc_5Cl_8C,[2] Sc_4Cl_6B,[3] $Sc_7I_{12}C$,[4] $Sc_6I_{11}C_2$,[5] and $Sc_7I_{12}Co$,[6] for example, in which the third element listed is strongly bonded as an interstitial within each scandium cluster. However, scandium also forms several binary reduced halides that are evidently unique to this element. These include the very fibrous Sc_2Cl_3 and Sc_2Br_3 of unknown structure[7] as well as the off-stoichiometry diiodide detailed here. The last was very briefly described years ago[8] as a metallic phase with a CdI_2-type structure and the composition $ScI_{2.17}$ for samples prepared by equilibration of liquid ScI_3 with excess metal. The composition and structure are unusual since all other metallic iodides appear to be fully reduced diiodides, viz. LaI_2, CeI_2, PrI_2,[9,10] GdI_2,[11] and ThI_2,[12] and to occur principally in other structure types ($TiSi_2$, MoS_2, $Mo_4S_4Br_4$,[13] NbS_2[14]). Although the neighboring TiI_2 and VI_2 exhibit CdI_2-type structures, they are evidently of simple stoichiometry and are semiconductors.[15]

The original studies[16] of this scandium iodide have remained largely unpublished because the structural investigations based on Debye–Scherrer powder diffraction patterns alone had difficulty in resolving the pattern of the reduced product from the very similar overlapping result for ScI_3 (BiI_3-type). The patterns were further complicated by weak extra lines in the patterns of intermediate compositions; these probably arose from ternary phases formed by traces of impurities, carbon for example, that have been discovered since (above). We have now confirmed the stoichiometry and clarified the structure through studies of the synthesis via vapor-phase transport as well as by Guinier powder and single-crystal X-ray diffraction, and we report here the collection of results.

Experimental Section

All compounds were handled in gloveboxes under either dry N_2 or Ar. The scandium metal was an Ames Laboratory product prepared by reduction of ScF_3 with triply distilled Ca. The material used in the later studies had also been vacuum-sublimed, and its typical impurity levels have been described.[3] The earlier investigations of the phase diagram and other properties utilized metal that had higher impurities in some cases (ppm by weight): 0, 300; F, 250; Ta, 1500–2000; Y, 100. Turnings were used in the ScI_3 synthesis and phase studies, while chunks or rolled strips were used in equilibrations. The triiodide was again[4] prepared from the elements in a two-zone silica apparatus with the metal held in a W crucible in the hotter zone. The product was then sublimed three times under high vacuum ($\sim 10^{-5}$ atm) at ~680 °C within a tantalum apparatus contained in a silica jacket. The pure product is bright yellow, not white.[17] We found that the melting point of the product decreased ~10° when the triiodide was sublimed so that it condensed on the SiO_2 jacket rather than in a Ta sleeve, doubtlessly because the former introduces ScOI through a metathetical reaction between ScI_3 and SiO_2.

The so-called diiodide is readily obtained by reaction of liquid or gaseous ScI_3 with excess metal in the range 550–870 °C for about 6 weeks to 4 days, respectively, while contained in welded Ta or Nb containers. The powder patterns obtained with an Enraf-Nonius FR552 Guinier camera show no evidence of ScI_3 in the products, and the analyses (below) by both wet and X-ray methods support the formation of a pure phase.

Thermal analyses of the ScI_3–Sc system out to 35.1 mol % Sc gave

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Table I. Crystal Data for $Sc_{0.92}I_2$

space group, Z	$P\bar{3}m1$, 1	μ (Mo Kα), cm^{-1}	174.6
cell dimens[a]		transm coeff range	0.15–0.96
a, Å	4.0851 (3)	R[b]	0.020
c, Å	6.9824 (7)	R_w[b]	0.026
V, Å^3	100.91 (2)		

[a] Calculated from 22 reflections measured from the Guinier powder pattern with Si as an internal standard ($\lambda = 1.54056$ Å). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$; $w = 1/\sigma(F_o^2)$.

the essential information on the phase relationships of the single intermediate, including the upper temperature limit for the above syntheses, ~892 °C. These analyses were carried out as before[9] in sealed Ta apparatus under vacuum starting with 3.0–4.5 g of sublimed ScI_3. A $^5/_{32}$ in. diameter side tube on this allowed the sequence of metal addition, rewelding, and cooling analysis to be accomplished four to seven times. A portion of the sample was also wet-analyzed after a series as a check; discrepancies were usually less than that corresponding to 0.3 mol % added metal. Equilibrations to measure melt compositions above the diiodide peritectic point were quenched by dropping into silicone oil.[11]

Samples for wet analysis were loaded in the glovebox, weighed in air, corrected for buoyancy, and dissolved and analyzed for both elements as before.[7] Weight recoveries on 10 fully reduced samples of the melt and of the product solid were all in the range 99.3–100.4%, with all but three within ±0.3% of complete recovery.

Four-probe, a.c. resistivity measurements as a function of temperature were made on $^1/_4 \times \sim 3$ in. cast rods of the product by using the apparatus described earlier.[10] The incongruent melting of the $Sc_{0.93}I_2$ (see Results) presented some difficulties in achieving the preparation of completely reduced rod samples. Currents of 0.3–0.75 A at frequencies of 100–500 Hz gave very similar results. The magnetic susceptibilities were briefly surveyed with a Faraday balance,[18] the data being obtained at five fields and the susceptibilities extrapolated to infinite field with the aid of a Honda–Owen plot.

X-ray data for the earlier studies were obtained by the Debye–Scherrer method on samples in 0.3-mm thin-walled capillaries. All critical parameters were later obtained by Guinier methods.[19]

X-ray data on a single crystal 0.1 × 0.2 × 0.3 mm were collected at room temperature and to $2\theta = 70°$ on a Syntex $P2_1$ instrument using monochromated Mo Kα radiation. Some details are given in Table I. The refinement used programs and scattering factors referenced earlier[5,19] and was without incident; residuals on the final difference map were <0.25 e/Å^3. The absorption correction was found to be especially important; this utilized a μr value of 3.4 for a cylindrical correction and Ψ scans collected at two different 2θ values so that interpolation in terms of both θ and ϕ could be secured. Correction for secondary extinction was not significant.

Results and Discussion

The nominal diiodide is the only intermediate in the Sc–ScI_3 system, and it may be secured in quantitative amounts by the reaction of ScI_3 with excess metal over a sizable temperature range, 550–870 °C. Large black hexagonal plate crystals with a blue cast are often formed via an autogeneous vapor-phase transport process, probably via ScI_2(g). All products of such reactions give Guinier powder patterns that are in complete accord with the CdI_2-type structure (below), and lattice constants refined from these were in close agreement. The composition limit is thereby not detectably temperature dependent. Twenty-two lines from the pattern of a sample cooled from 750 to 200 °C over 2 weeks gave $a = 4.0851$ (3) Å and $c = 6.9824$ (7) Å ($V = 100.91$ (2) Å^3), while data from samples brought to room temperature relatively rapidly tended to give slightly (0.002–0.003 Å) smaller and larger values for a and c, respectively, the latter being the stacking direction. The compound behaves as a line phase in a practical synthetic route; that is, a sample containing excess ScI_3 that was equilibrated at 750 °C and then cooled by turning off the power to the (relatively small) furnace gave a powder pattern of a mixture in which the lattice constants of $Sc_{0.93}I_2$ were virtually unchanged ($a = 4.092$ (3) Å, $c = 6.984$ (4) Å). An analogous sample that had been quenched gave parameters within 1σ of those taken as standard (Table I).

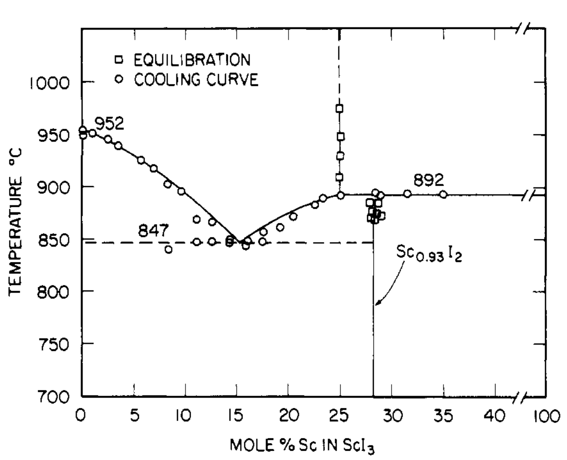

Figure 1. Phase diagram for ScI_3–Sc according to thermal analysis measurements (○) as well as isothermal equilibrations with excess metal followed by analysis of the quenched samples (□).

Table II. Atom Parameters for and Distances in $Sc_{0.92}I_2$

atom	occup	x	y	z	B_{11}[a]	B_{33}
Sc	0.919 (10)	0	0	0	5.91 (9)	3.22 (8)
I	1	$^1/_3$	$^2/_3$	0.25025 (5)	3.84 (2)	3.67 (2)

Distances (Å)

Sc–I	2.934 (1)	I–I	4.208 (1)[b]
I–I, Sc–Sc	4.0851 (3)		

[a] $B_{11} = B_{22} = 2B_{12}$, $B_{13} = B_{23} = 0$, $T = \exp[(-^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Distance across the gap.

The ScI_3–Sc system has been characterized through thermal analysis of samples containing 0–35 mol % metal, that is, over the range of ScI_3 to $ScI_{1.95}$. The results from both cooling-curve analyses and fixed-point equilibrations with excess metal followed by chemical analysis are shown in Figure 1. The 952 °C melting point of ScI_3 that had been sublimed in tantalum is a distinct improvement over the 920 °C value reported earlier.[17] The location of the eutectic point was made somewhat uncertain because of supercooling of the liquidus.

The average of seven equilibrations of salt with excess metal below the melting point gave $Sc_{0.93(0)}I_2$ (or $ScI_{2.15(0)}$) (28.3 mol % Sc) for the composition of the solid phase in equilibrium with scandium, clearly different from a classical diiodide. We prefer the Sc_xI_2 description of the analytic results rather than $ScI_{2/x}$ since the nonintegral composition arises from vacancies on the metal sites (below). The principal limitations of this method are errors caused by fragmentation of the metal, which could leave small pieces within the analytic sample, and by melt that does not reach and equilibrate with the metal. Neither Sc or ScI_3 could be detected in Debye–Scherrer patterns of the products. The reduced phase $Sc_{0.93}I_2$ melts incongruently at ~892 °C to produce the metal and a solution of 25.0 mol % Sc in ScI_3 ($ScI_{2.25}$), this composition being determined by analysis of several quenched samples following 17–25-h equilibrations of the melt with excess metal at higher temperatures, as shown.

We have been further concerned about both the apparent composition of this phase and any possible ordering of the indicated scandium vacancies in the superstructure. A crystal made at 780 °C and furnace-cooled from 702 °C to room temperature was therefore studied by single-crystal X-ray diffraction. Some data collection and refinement conditions are listed in Table I, and the resulting atom parameters and distances appear in Table II. The important result of this fairly routine refinement of the CdI_2-type structure is that the only recognizable defect is in the metal position, its occupancy of 0.92 (1) relative to iodine indicating a composition of $Sc_{0.92(1)}I_2$. This agrees very well with the direct analytical result, $Sc_{0.93}I_2$ (above), showing that the more limited sensitivity of the Debye–Scherrer method did not lead to a serious error in judging the purity of the earlier samples. We adopt the directly measured composition $Sc_{0.93}I_2$ hereafter.

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The data crystal was also examined by the precession method with the cone axis along both $\vec{c}$ and $\vec{a}$, but in neither case was any indication of additional superstructure reflections found. Secondly, a single crystal that had been cooled from 750 to 200 °C over 2 weeks was also checked by long exposures of Weissenberg photographs (Cu Kα) of the $l = 0, 1, 2$ levels as well as precession data (Mo Kα) for the $k = 0, 1$ levels. Both were again negative. Finally, the Guinier pattern of a sample equilibrated for 4.5 months at 550 °C showed nothing new. Evidently an ordering of the 7–8% vacancies in the metal sites on a scale sufficient for coherent X-ray scattering is not present. Smaller domain/twin composites or disorder along $\vec{c}$ could still be involved. This disorder feature (to X-rays) together with the compound's evident fixed composition (above) seems relatively unusual, but the same characteristics have been seen in Lu_3S_4[20] and $Na_{0.6}ScI_3$.[21]

A few other properties of this "diiodide" phase have also been examined. The magnetic susceptibility of a fully reduced sample was examined only briefly. The molar susceptibility corrected only for core diamagnetism is small, 334×10^{-6} emu/mol at room temperature or about 3 times the equivalent value for LaI_2,[10] and this quantity increases only moderately on cooling to 504×10^{-6} emu/mol at 118 K and 465×10^{-6} emu/mol at 77 K, with some possibility of a transition near 103 K. This aspect was not pursued further except to note that the ^{45}Sc NMR spectrum for the compound showed no changes in the 150–77 K range.

A polycrystalline rod of a reduced composition ~0.25 × 3 in. in size was grown in tantalum tubing, and its conductivity was examined by four-probe ac methods. The procedure was only marginally satisfactory for this compound because portions of rods in which crystals of the laminar diiodide grew roughly normal to the rod axis were easily fractured. It was also difficult to achieve complete reduction of such a large sample as it grew away from the metal reservoir. Notwithstanding, a sample with an overall composition corresponding to about 91 mol % $Sc_{0.93}I_2$, the rest ScI_3, was found to exhibit a resistivity of 1.54×10^{-3} Ω cm at 355 K, and this decreased fairly linearly to 0.89×10^{-3} Ω cm at 222 K. This quantity then appeared to increase ~20% on cooling to 160 K, but this may have been spurious as electrical contact was lost at lower temperatures and, shortly thereafter, the sample was lost as well during attempts to adjust the contacts.

The room-temperature resistivity for this sample was about 24 times that for a sample of pure LaI_2 but only about half as large as that obtained for a similarly impure sample containing ~86% of the incongruently melting CeI_2 mixed with $CeI_{2.5}$.[10] Since both the LaI_2 and the "CeI_2" samples showed very similar (positive) temperature coefficients of resistivity, we conclude the impurity level does not seriously hazard the conclusion that $Sc_{0.93}I_2$ is also metallic in character. The compound does not exhibit superconductivity down to 1.5 K. Such a metallic "dihalide" is not found in either the scandium chloride or the scandium bromide systems.[7] We conclude that a π^* description of the conduction band with a significant contribution by the iodide is apt for this phase as well as for LaI_2, CeI_2, etc.[10]

Acknowledgment. We are indebted to Norm Linder for the construction of the thermal analysis apparatus, to R. E. McCarley's group for assistance with the magnetic susceptibility apparatus, and to R. G. Barnes for the NMR examination. The earlier part of this research was supported by Ames Laboratory of the U.S. Atomic Energy Commission, and the later work, by the National Science Foundation, Solid State Chemistry, Grant DMR-8318616.

Supplementary Material Available: A table of information on the single-crystal diffraction study (1 page); a table of observed and calculated structure factors for $Sc_{0.93}I_2$ (1 page). Ordering information is given on any current masthead page.

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Additions and Corrections

1989, Volume 28

Kattesh V. Katti and Ronald G. Cavell*: First Examples of an Isomeric Methylene-Bridged Free Phosphano Phosphoranimine and Metalated Phosphano Phosphoranimine. Synthesis, Characterization, and Isomerization of the Heterodifunctional Ligand $Me_3SiNPPh_2CH_2PPh_2$ and the Transmetalation to the Titanium Derivative $(\eta^5\text{-}C_5H_5)TiCl_2NPPh_2CH_2PPh_2$.

Page 416. In the second column, the heading "Thermal Isomerization of **2R**" and the first sentence of text following should read as follows:

Thermal Isomerization of 2. A sample of **2** (1.512 g, 3.2 mmol) (as the waxy solid recovered from the reaction of dppm and Me_3SiN_3 and *without* recrystallization) was placed in a Schlenk tube and connected to a dynamic vacuum line....

The confusing consequence of this error in the experimental description is that the recrystallized form, **2R**, can be thermally isomerized, which is not the case. In fact, only the isomeric distribution of the waxy solid product **2** can be changed by heating **2** to 160 or 240 °C etc. and this gives the form that we have labeled as **2D**. All statements made in the text with regard to **2D** (and **2** without the modifying label) are correct.—Kattesh V. Katti and Ronald G. Cavell