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Reactions of N,N-Bis(trifluoromethyl)hydroxylamine with Sulfur and Nitrogen Halides

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A study of the reactions of $(CF_3)_2NOH$ with several sulfur- and nitrogen-containing halides in the presence of cesium fluoride has resulted in the preparation and characterization of several previously unreported compounds of the general formula $(CF_3)_2NOX$ where X = SO_2F, $SO_3N(CF_3)_2$, $S(O)ON(CF_3)_2$, $SON(CF_3)_2$, $S(O)F$, and $SSON(CF_3)_2$. These have been isolated and identified by infrared, nmr, and mass spectra, molecular weight determinations, and elemental analyses. An unstable compound of the formula $(CF_3)_2NONF_2$ is reported as is a convenient method for the preparation of $(CF_3)_2NON(CF_3)_2$.

Fluoroorganic and organic compounds which contain the bis(trifluoromethyl)nitroxide moiety have been prepared recently in several ways. The stable free radical $(CF_3)_2NO\cdot$ has been shown to add to fluoroolefinic and olefinic double bonds[1,2] and to abstract protons to produce substitution products with toluene[1] and benzene.[2] Reactions of the radical also produce inorganic compounds, *e.g.*, with metallic tin and lead to give the respective $M(ON(CF_3)_2)_2$ compounds and with NO to give the yellow dimer $(CF_3)_2NONO$.[3] Use of $(CF_3)_2NONa$ in tetrahydrofuran[4] provides a route for the preparation of carbon or silicon compounds such as $CH_3ON(CF_3)_2$ or $(CH_3)_3SiON(CF_3)_2$ from CH_3I or $(CH_3)_3SiCl$.

In our laboratory, it has been possible to prepare a series of bis(trifluoromethyl)nitroxides of general formula $(CF_3)_2NOC(O)X$ through the reaction of bis(trifluoromethyl)hydroxylamine with perfluoroacyl and carbonyl halides as well as acyl and allyl halides in the presence of CsF or KF.[5,6]

In the present investigation we have extended the reactions of N,N-bis(trifluoromethyl)hydroxylamine in the presence of cesium fluoride to include several inorganic halides. Compounds of the general formula $(CF_3)_2NOX$ (where X = SO_2F, $SO_3N(CF_3)$, $SON(CF_3)_2$, $S(O)F$, $SSON(CF_3)_2$, and NF_2) which result from reaction with SO_2F_2, SOF_2, SCl_2, S_2Cl_2, and NF_2Cl have been prepared and characterized. All are obtained at room temperature or below. Derivatives of SO_2F_2 and SOF_2 are thermally and hydrolytically stable.

Experimental Section

Reagents.—Cesium fluoride (99%), sulfur tetrafluoride (95%), and disulfur dichloride (practical) were obtained from American Potash and Chemical, Co., K & K Laboratories, and the Eastman Chemical Co., respectively. Sulfinyl fluoride was prepared by heating sulfinyl chloride with an excess of CsF. Sulfonyl fluoride,[7] chlorodifluoramine,[8] N,N-bis(trifluoromethyl)hydroxylamine,[9,10] and sulfur dichloride[11] were prepared by literature methods. Prior to reaction, disulfur dichloride, sulfinyl fluoride, chlorodifluoramine, sulfonyl fluoride, and N,N-bis(trifluoromethyl)hydroxylamine were purified by distillation. Acetonitrile was dried over calcium hydride at room temperature.

General Methods.—All reactions were carried out in 100-ml Pyrex bulbs connected to a stopcock through a 19/38 ₸ joint. Gases and volatile liquids were handled in conventional glass vacuum apparatus under conditions of high vacuum. Prior to reaction, finely divided cesium fluoride (about 2 g) was placed in the bulb and heated at 200° for 10 min under dynamic vacuum to remove traces of water. The $(CF_3)_2NOH$–CsF adduct was formed by condensing the $(CF_3)_2NOH$ (usually 3–7 mmol) onto the CsF at $-183°$ and allowing the mixture to warm to room temperature over a period of 30 min. No effort was made to determine the exact stoichiometry of the adduct formed.[5]

Infrared spectra (Table I) were recorded using a Beckman IR5A infrared spectrophotometer. All spectra were obtained in the gas phase with a Pyrex cell of 25-mm path length and fitted with sodium chloride windows. Nuclear magnetic resonance spectra (Table II) were determined with either a Varian Model DP-60 (56.4 Mc) or a Varian Model HA-100 (94.1 Mc). Trichlorofluoromethane was used as an internal standard. Mass spectra were recorded using a Consolidated Engineering Corp. Type 21-103 mass spectrometer or a Hitachi Perkin-Elmer RMU-6E.

Vapor pressure data for the relatively volatile compounds $(CF_3)_2NOS(O)F$ and $(CF_3)_2NOSO_2F$ were obtained by holding the compounds in a liquid state at various low temperatures and reading the pressure on a mercury manometer. For the remaining compounds, vapor pressures were measured in an apparatus similar to that described by Kellogg and Cady.[12] Molecular weights of pure compounds were determined by Regnault's method using a bulb fitted with a Fischer and Porter Teflon stopcock.

Elemental analyses (Table III) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or Alfred Bernhardt Mikroanalytisches Laboratorium, Mulheim, Germany.

Sulfonyl Bis(trifluoromethyl)nitroxide, $((CF_3)_2NO)_2SO_2$.—SO_2F_2 (2.25 mmol) remained in contact with the adduct (5 mmol of $(CF_3)_2NOH$ and 2 g of CsF) for 3 hr at 25°. The reaction mixture was separated by gas chromatography utilizing a 2-ft column packed with Kel-F Oil No. 3 (3M Co.) on Chromosorb P (F & M Scientific Corp.), and 1.6 mmol of $((CF_3)_2NO)_2SO_2$ and 0.3 mmol of $(CF_3)_2NOSO_2F$ were obtained. Sulfonyl bis(tri-

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TABLE I

INFRARED SPECTRA (CM^{-1})

$(CF_3)_2NONF_2$	$((CF_3)_2NO)_2SO$	$(CF_3)_2NOS(O)F$	$(CF_3)_2NOSO_2F$
1320 vs	1318 vs	1308 vs	1510 vs
1270 vs	1268 vs	1247 vs	1326 vs
1228 vs	1238 vs	1227 vs	1280 vs
1045 m	1192 s	1196 s	1257 vs
980 s	1027 s	1032 s	1239 vs
893 s	976 s	977 s	1193 s
848 s	803 w	786 w	1023 s
792 s	781 m	750 m	980 s
729 s	752 m	713 m	862 vs
685 w	715 s	632 m	821 s
	694 s		740 w
			719 m
			635 m

$((CF_3)_2NO)_2S_2$	$((CF_3)_2NO)_2S$	$((CF_3)_2NO)_2SO_2$
1319 vs	1307 vs	1490 vs
1265 vs	1271 vs	1323 vs
1235 vs	1228 vs	1273 vs
1030 s	1024 s	1247 vs
977 s	972 s	1226 vs
802 w	796 s	1190 s
780 w	783 m	1020 s
753 w	758 m	976 s
716 w	712 s	811 s
694 w	691 m	739 w
		716 s
		632 m

TABLE II

^{19}F NMR SPECTRA

	Chem shift, ppm			
Compound	C–F	S–F	N–F	Area ratio
$(CF_3)_2NONF_2$[a]	+66.3		−122.0	3.0:1.0
$(CF_3)_2NOS(O)F$[b]	+67.49	−59.52		6.0:1.0
$(CF_3)_2NOSO_2F$[c]	+67.76	−37.37		6.0:1.0
$((CF_3)_2NO)_2SO_2$[a]	+69.6			
$((CF_3)_2NO)_2SO$	+67.68			
$((CF_3)_2NO)_2$	+67.76			
$((CF_3)_2NO)_2S_2$	+67.66			

[a] Denotes sample run using the Varian DP-60. [b] J_{SF-CF} = 4 cps. [c] J_{SF-CF} = 7 cps.

TABLE III

ELEMENTAL ANALYSES

	Mol wt		% C		% F		% S		% N		Log $P_{mm} = (-X/T(°K)) + Y$		
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	X	Y	Bp, °C
$((CF_3)_2NO)_2SO_2$	400	398	12.00	12.18	57.00	56.83	8.00	7.86	7.00	7.06	2172	8.88	95.7[a]
$(CF_3)_2NOSO_2F$	251	248	9.53	9.68	53.40	52.87	12.75	12.52	5.57	5.46	2981	12.51	57.0 ± 0.2
$((CF_3)_2NO)_2SO$	384	383	12.50	13.03	59.37	59.29	8.34	8.17					79 ± 2 (692 mm)[b]
$(CF_3)_2NOS(O)F$	235	237	10.21	10.33	56.50	56.40	13.61	13.47	5.95	5.80	1479	7.48	48.2
$((CF_3)_2NO)_2S_2$	400	398	12.00	12.15	57.00	56.59	16.00	15.84	7.00	7.15	2633	9.88	102.0 ± 0.2
$((CF_3)_2NO)_2S$	368	364	13.02	13.23	62.00	61.85	8.69	8.60			2099	8.96	72.8 ± 0.3[c]

[a] Slight decomposition above 80°. [b] Slight decomposition above this point. [c] Slight decomposition above 58°.

fluoromethyl)nitroxide is stable to hydrolysis by water or 0.2 *M* NaOH for periods up to 12 hr and temperatures as high as 80°.

Bis(trifluoromethyl)nitroxosulfonyl Fluoride, $(CF_3)_2NOSO_2F$.—The reaction between SO_2F_2 (4 mmol) and the adduct (4 mmol of $(CF_3)_2NOH$ and 2 g CsF) was allowed to proceed for 1 hr at 25°. The $(CF_3)_2NOSO_2F$ was purified by gas chromatography utilizing a 2-ft column described above, and 1.4 mmol of $(CF_3)_2NOSO_2F$ and 0.3 mmol of $((CF_3)_2NO)_2SO_2$ were obtained.

Sulfinyl Bis(trifluoromethyl)nitroxide, $((CF_3)_2NO)_2SO$.—A 7-mmol sample of $(CF_3)_2NOH$ and 5 ml of dry acetonitrile were condensed onto 2 g of CsF. After approximately 2 hr at room temperature, the mixture was decanted under an atomosphere of dry nitrogen, and the solution was placed in a Pyrex bulb. After the acetonitrile was removed under vacuum, six 0.5-mmol portions of SOF_2 were added to the adduct. Each portion was allowed to remain in contact with the adduct for 15 min. As much as 2 mmol was added before any unreacted SOF_2 could be detected in the infrared spectrum of the volatile products. Sulfinyl bis(trifluoromethyl)nitroxide was purified by fractional codistillation;[13] an over-all yield of 1.9 mmol was obtained. The compound is stable to water at room temperature for at least 18 hr.

Bis(trifluoromethyl)nitroxosulfinyl Fluoride, $(CF_3)_2NOS(O)F$.—A mixture of the adduct (3 mmol of $(CF_3)_2NOH$ and 2 g of CsF) and SOF_2 (5 mmol) was allowed to react for 20 min at −100°. The mixture was then allowed to warm to room temperature and separation of the products, using a 6-ft column packed with silicon gum (Dow Chemical Co.) on Chromosorb P, yielded the following products which were identified by infrared and nmr spectra: $(CF_3)_2NOS(O)F$ (40%), SOF_2, and $((CF_3)_2NO)_2SO$ (30%).

Bis(trifluoromethyl)nitroxodisulfide, $((CF_3)_2NO)_2S_2$.—To the adduct (6 mmol of $(CF_3)_2NOH$ and 2 g of CsF) was added a 3-mmol portion of S_2Cl_2, and the reaction vessel was held at −20° for 18 hr. The reaction products were fractionated initially through 0, −25, and −183° traps. The disulfide and other impurities were collected at −25°. The disulfide was purified by several passes through a 12-ft column packed with Kel-F Oil No. 3 on Chromosorb P. A yield of 0.75 mmol was obtained. Other products identified included $((CF_3)_2N)_2S$[14,15] and $((CF_3)_2NO)_2S$.

Bis(trifluoromethyl)nitroxosulfide, $((CF_3)_2NO)_2S$.—A 3-mmol sample of SCl_2 was condensed onto the adduct (6 mmol of $(CF_3)_2NOH$ and 2 g of CsF) and held at −20° for 18 hr. The mixture was warmed to −10° and the volatile products were removed under dynamic vacuum. $((CF_3)_2NO)_2S$ was purified by gas chromatography using a 6-ft silicone gum column. A 1.25-mmol sample was obtained.

The compound can also be obtained in lower yield by the reaction of the adduct (5 mmol of $(CF_3)_2NOH$ and 2 g of CsF) with S_2Cl_2 (3 mmol). After 18 hr at −20° and separation by trap-to-trap distillation, impure $((CF_3)_2NO)_2S$ was found at −25°. A yield of 10–20% was obtained after gas chromatographic separation with a Kel-F column.

Bis(trifluoromethyl)nitroxodifluoramine, $(CF_3)_2NONF_2$.—A 4-mmol sample of $(CF_3)_2NOH$ and 10 ml of acetonitrile were condensed onto dry CsF (1.5 g). The acetonitrile solution was decanted from the CsF and 2 mmol of NF_2Cl was condensed onto the solution at −183°. The contents were allowed to warm to and remain at room temperature for about 10 min. The mixture was held at −95° and unreacted NF_2Cl, N_2F_4, and a small amount of SiF_4 were removed. When the reaction mixture was warmed to −30°, $(CF_3)_2NONF_2$, contaminated with $(CF_3)_2NO\cdot$,[3] was removed from the solvent. $(CF_3)_2NONF_2$ is thermally unstable at room temperature and could not be separated from the bis(trifluoromethyl)nitroxide. Thus, the characteriza-

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tion of this compound depended, at least in part, on indirect methods and the yield can only be estimated to be about 50–70%. Separation of $(CF_3)_2NO\cdot$ and $(CF_3)_2NONF_2$ *via* fractional codistillation yielded SiF_4, N_2F_4, $(CF_3)_2NO\cdot$, and $(CF_3)_2NONF_2$. Continued codistillation resulted in the same compounds until all the $(CF_3)_2NONF_2$ was consumed. If the $(CF_3)_2NONF_2$ and $(CF_3)_2NO\cdot$ mixture was allowed to remain in glass for about 30 min, separation gave SiF_4, N_2F_4, $(CF_3)_2NO\cdot$, and $(CF_3)_2NONO$. Further decomposition could be prevented by holding the mixture of $(CF_3)_2NONF_2$ and radical at −183° after removal from the solvent.

Reaction with SF_4.—A 3-mmol sample of SF_4 was condensed onto the adduct (6 mmol of $(CF_3)_2NOH$ and 2 g of CsF), and the contents of the vessel were allowed to warm from −183 to −100° over a 15-min period. Separation of the products using a silicone gum column gave no bis(trifluoromethyl)nitroxo derivatives of SF_4. Products isolated were $(CF_3)_2NON(CF_3)_2$[16] (65%), $(CF_3)_2NOS(O)F$, SOF_2, and $(CF_3)_2NO\cdot$.

Reaction with CF_3OSO_2F.—A 2-mmol sample of CF_3OSO_2F[17] was condensed onto an equivalent quantity of adduct. The mixture was held at 0° for 2 hr. Products identified by infrared analysis after separation using a Kel-F on Haloport F column were $((CF_3)_2NO)_2CO$, $(CF_3)_2NOSO_2F$, $((CF_3)_2NO)_2SO_2$, SO_2F_2, and COF_2. None of the desired compound, $CF_3OSO_2ON(CF_3)_2$, was observed.

Results and Discussion

The infrared spectra of these compounds have many characteristic bands for which assignments can be made. As is to be expected the C–N stretching frequency is essentially nonvariant and appears between 972 and 980 cm^{-1}; this agrees well with $(CF_2)_2NOH$. The shift of the N–O frequency (1023–1045 cm^{-1}) from that of $(CF_3)_2NOH$ (1042 cm^{-1}) is diagnostic of compound formation. While bands in the 712–729-cm^{-1} region are assigned to CF_3 deformation for all compounds and those between 1190 and 1280 cm^{-1} to CF stretch for $(CF_3)_2NONF_2$ and $((CF_3)_2NO)_2S_x$ ($x = 1, 2$), the CF stretching assignments in the remaining molecules are complicated by the presence of S=O stretch and SO_2 symmetric stretch. For $((CF_3)_2NO)_2SO_2$ and $(CF_3)_2NOSO_2F$, asymmetric SO_2 stretches occur at 1490 and 1510 cm^{-1},[18,19] respectively. The latter is very high even when compared with F_2NOSO_2F (1492 cm^{-1})[20] or SO_2F_2 (1502 cm^{-1}).[21]

The infrared and nmr spectra of $(CF_3)_2NONF_2$ were obtained by maintaining the sample at −183° until just prior to recording the spectra. The former is the result of subtraction of bands assigned to $(CF_3)_2NO\cdot$[3] which is the only significant impurity. While the symmetric N–F stretch is likely associated with the band at 1045 cm^{-1} which also must be assigned to N–O stretch, the band at 893 cm^{-1} may be assigned to N–F asymmetric stretch.[20,22]

At room temperature, the ^{19}F nmr spectrum of $(CF_3)_2NONF_2$ was not well defined, presumably because of the influence of the paramagnetic radical, $(CF_3)_2NO\cdot$. However, when the tube was cooled prior to recording the spectrum, two well-defined peaks were recorded. The NF shift is similar to other NF_2 compounds, *e.g.*, F_2NOSO_2F (ϕ^* −128.8)[23] and CF_3ONF_2 (ϕ^* −124).[24] The CF resonance in all of the compounds is essentially nonvarying.[5,6] Interaction occurs between the trifluoromethyl groups and fluorine atoms bonded to the central atom in $(CF_3)_2NOS(O)F$ and $(CF_3)_2NOSO_2F$.

The mass spectra of these compounds do not show molecule ions and in every case the CF_3^+ species is the predominant one. The spectra are, however, consistent with the structures reported. For example, a peak at 96 assigned to $S_2O_2^+$ in $((CF_3)_2NO)_2S_2$ is useful in seconding the elemental analysis for this compound.

A possible route for the production of $((CF_3)_2N)_2O$ in the reaction of $(CF_3)_2NOH$ with SF_4 involves the initial formation of an unstable intermediate, $(CF_3)_2NOSF_2ON(CF_3)_2$, which subsequently decomposes to SOF_2 and $((CF_3)_2N)_2O$. The largest yield of $((CF_3)_2N)_2O$ is obtained when a $(CF_3)_2NOH$ to SF_4 molar ratio of 2:1 is used. The SOF_2 which is formed reacts with any remaining $(CF_3)_2NOH$ to give $(CF_3)_2NOS(O)F$. When the reactants are combined in a 1:1 ratio, the yield of $((CF_3)_2N)_2O$ is greatly reduced. Sulfinyl bis(trifluoromethyl)nitroxide is recovered as one of the major products when a 4:1 ratio is used. That the SF_4 had been hydrolyzed to SOF_2 prior to reaction is precluded by the presence of $((CF_3)_2N)_2O$ since none is observed when the initial reactant is SOF_2. In view of the stability of other SF_2 compounds (*e.g.*, $(i\text{-}C_3F_7)_2SF_2$),[25] the apparent brief existence in this case of a $-SF_2-$ species is unexpected. The $(CF_3)_2NO$ group would not shield the sulfur atom from attack as is the case with the perfluoroisopropyl derivative. Also, the lower energy of the O–S bond and the great stability of the resulting product would contribute to the lack of stability of the postulated intermediate.

That the reaction of trifluoromethyl fluorosulfate and $(CF_3)_2NOH$ yielded no $CF_3OSO_2ON(CF_3)_2$, but instead gave products which would result from reaction of $(CF_3)_2NOH$ with COF_2 and SO_2F_2, is explained by the fact that CF_3OSO_2F, in the presence of CsF, undergoes defluorosulfurylation to give COF_2 and SO_2F_2.[26]

The reactivity of SO_2F_2 seems to be enhanced in the presence of an alkali metal fluoride for, whereas SO_2F_2 approaches SF_6 in its lack of reactivity, in this case reaction occurs readily with $(CF_3)_2NOH$ at 25°. The mono- and disubstituted sulfinyl and sulfonyl products which are formed have hydrolytic stability comparable to that of R_fSO_2F and $(R_f)_2SO_2$.[18,19]

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Preparation and Properties of Some Ternary Selenides and Tellurides of Rhodium[1]

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The compounds MRh_2X_4 (M = Cr, Co, Ni; X = Se, Te) and Rh_3Te_4 have been prepared and found to have the monoclinic Cr_3S_4-type structure (space group I2/m) except for $CoRh_2Te_4$, and $NiRh_2Te_4$ which are trigonal (space group $P\bar{3}m1$). The symmetry of these compounds with defect NiAs structure depends upon whether the metal ion vacancies are ordered or randomly arranged in alternate metal layers. Electrical resistivity and Seebeck coefficient measurements reveal metallic behavior. This may arise from partially filled σ^* conduction bands formed as a result of interactions between the metal e_g and anion s,p_σ orbitals.

Introduction

The monoclinic defect NiAs structure (space group I2/m) was first proposed by Jellinek[2] for Cr_3S_4. This structure is intermediate between the NiAs ($B8_1$) and CdI_2 (C6) types. The idealized packing sequence of the cations and vacancies in this ordered structure with AB_2X_4 stoichiometry is shown in Figure 1. The transition metal cations, A and B, occupy three-fourths of the octahedral sites between the layers of hexagonal close-packed anions. The packing sequence is such that B^{3+} layers alternate with layers containing the A^{2+} cations and vacancies. It can be seen that ideally the A^{2+} cations are ordered with respect to the vacancies.

A large number of sulfides,[3-7] selenides,[5-9] and tellurides[10,11] of the type AB_2X_4 have since been reported to be isostructural with Cr_3S_4. Structural, electrical and magnetic properties have been investigated for many of these compounds. All these compounds with the monoclinic defect NiAs structure, however, contain only the first transition series metals Ti, V, Cr, Fe, Co, and Ni.

The present investigation was undertaken to determine whether the Cr_3S_4-type structure could also accommodate the second transition series metal, rhodium. Both the ionic radius of octahedrally coordinated Rh^{3+} and the stability of this oxidation state appeared to favor the existence of compounds such as $NiRh_2Se_4$ and $NiRh_2Te_4$. In addition to their preparation, the structural and electrical properties of these new compounds were also studied.

Experimental Section

Preparation.—Attempts were made to prepare the compositions MRh_2Se_4 (M = Cr, Fe, Co, Ni) and $M'Rh_2Te_4$ (M' = Ti, V, Cr, Fe, Co, Ni, Rh). High-temperature reactions of stoichiometric amounts of the high-purity elements were carried out in evacuated silica tubes. The sources of supply and purity of the starting materials were as follows: Fe, Co, Ni, Cr (all 99.99+%), Se, and Te (99.999%) were obtained from Gallard-Schlesinger Corp.; Ti (99.9%) was obtained from Metal Hydrides, Inc.; and Englehard supplied the Rh (99.9+%). The iron, cobalt, and nickel were freshly reduced prior to use. The reactants were heated at 600 and 800° for 3 days with intermediate grinding under dry nitrogen. When X-ray diffraction analysis indicated other than a single phase following this treatment, additional grindings of the products and firings at temperatures from 900 to 1000° were performed. All final products were studied by X-ray diffraction.

X-Ray Measurements.—Crystallographic parameters were determined on powder samples of the single-phase products using a Norelco diffractometer. Radiation was obtained from a high-intensity copper source (λ(Cu Kα_1) 1.5405 Å) and monochromatized with an AMR-202 focusing monochromator. Cell parameters were calculated and refined using an IBM 360 computer program of a modified Cohen's least-squares method.[12]

Chemical Analysis.—Each of the elements was determined for two of the single-phase tellurides, Rh_3Te_4 and $NiRh_2Te_4$. Samples weighing approximately 50 mg were dissolved by refluxing several hours with concentrated sulfuric acid, the only effective solvent. After the solution was made 2 *N* in hydrochloric acid in a total volume of 200 ml and heated to boiling, tellurium was quantitatively precipitated with sulfur dioxide and hydrazine, dried, and weighed according to standard techniques.[13,14] Rhodium was determined on aliquots of the filtrate by a spectrophotometric tin(II) chloride method,[15] employing a Bausch and

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