

Thionylimide–Transition Metal Complexes

G. HARTMANN, R. HOPPENHEIT and R. MEWS*

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, F.R.G.

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Recently Turner *et al.* reported the preparation of thionylimide–complexes of platinum [1, 2] by a rather surprising route. $(\text{Ph}_3\text{P})_2\text{Pt}(\text{OSNH})_2$ was isolated from the reaction of $(\text{Ph}_3\text{P})_4\text{Pt}$ and $\text{S}_4\text{N}_4\text{H}_4$ ($\text{C}_6\text{H}_6/(\text{CH}_3)_2\text{CO}$ as solvent) [1], $\text{Pt}(\text{OSNH})_2(\text{S}_2\text{N}_2\text{H}_2)$ [2] was obtained from K_2PtCl_6 and $\text{S}_4\text{N}_4\text{H}_4$ in aqueous solution. According to these investigations the OSNH-ligand is connected to Pt *via* oxygen. Preparation of HNSO, which is rather unstable in the condensed phase, is described in the literature by three different methods (a) the reaction of OSCl_2 and NH_3 in the gas phase [3, 6], (b) from SO_2 and NH_3 [4], and (c) by hydrolysis of NSF [5]. We report here two different methods for the synthesis of HNSO–transition metal complexes: (a) exchange of coordinated SO_2 with preformed HNSO, and (b) substitution of the sulfur-bonded fluorine of coordinated NSF by OH nucleophiles.

Experimental

Method (a)

On to 1 mmol $[\text{Mn}(\text{CO})_5\text{SO}_2]\text{AsF}_6$ (1a) or $[\text{Re}(\text{CO})_5\text{SO}_2]\text{AsF}_6$ (1b) (or 0.5 mmol $[\text{Ni}(\text{SO})_2]_2(\text{AsF}_6)_2$ (3)), 20 ml SO_2 were condensed then a twofold excess of HNSO [3] was slowly added (the condensed HNSO has to remain colorless, if it turns yellow, the product will be contaminated with $\text{NH}_4^+\text{AsF}_6^-$). The reaction mixture was warmed to -80°C and stirred between -70 and -50°C till a clear solution resulted. Solvent and excess of ligand was removed at low temperature under vacuum. The analytically pure complexes $[\text{Mn}(\text{CO})_5\text{HNSO}]\text{AsF}_6$ (2a), $[\text{Re}(\text{CO})_5\text{HNSO}]\text{AsF}_6$ (2b) and $[\text{Ni}(\text{HNSO})_4](\text{AsF}_6)_2$ (4) remain as residues in quantitative yield.

Method (b)

To 0.7 mmol 5 in 20 ml SO_2 the stoichiometric amount Me_3SnOH was condensed at -196°C . The reaction mixture was warmed to -30°C and stirred at this temperature for 2 hours. The insoluble Me_3SnF was filtered off and the solvent removed at 20°C . According to IR-spectroscopy the residue is pure 2b, in a quantitative yield, direct hydrolysis of 5 will give impure 2b.

*Author to whom correspondence should be addressed.

 $[\text{Mn}(\text{CO})_5\text{HNSO}]\text{AsF}_6$

(2a), Dec. 117°C . Anal. Calcd. for $\text{C}_5\text{HASF}_6\cdot\text{MnNO}_6\text{S}$: S, 7.17; N, 3.13. Found: S, 6.92; N, 3.18. IR (Nujol): 3222m, 2170m, 2075vs, 2055vs, 1251m, 1194w, 1020vw, 768w, 705vs, 677s, 627vs, 585w, 562w, 533w, 398 cm^{-1} vs.

 $[\text{Re}(\text{CO})_5\text{HNSO}]\text{AsF}_6$

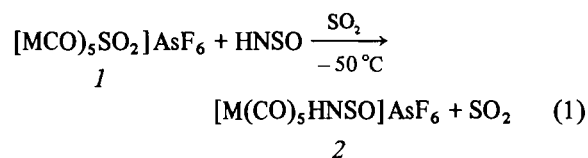
(2b), Dec. 102°C . Anal. Calcd. for $\text{C}_5\text{HASF}_6\cdot\text{NO}_6\text{ReS}$: S, 5.54; N, 2.42. Found: S, 5.52; N, 2.49. IR (Nujol): 3180m, 2175m, 2068vs, 2007vs, 1260m, 1238m, 1023w, 712sh, 700vs, 680m, 613m, 589s, 575sh, 544m, 470w, 397 cm^{-1} s. Ra: 2172m, 2166m, 1996w, 1260vw, 1237vw, 1024vs, 684w, 614w, 572w, 476m, 428w, 370vw, 340m, 272 cm^{-1} vw.

 $[\text{Ni}(\text{HNSO})_4](\text{AsF}_6)_2$

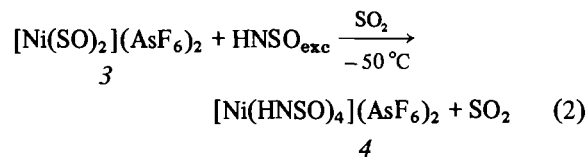
(4) Dec. 108°C . Anal. Calcd. for $\text{As}_2\text{F}_{12}\text{H}_4\text{N}_4\text{NiO}_4\text{S}_4$: S, 18.62; N, 8.13. Found: S, 18.50; N, 7.92. IR (Nujol): 3238m, 3203m, 1252m, 1237m, 1169m, 1145m, 701vs, 677sh, 397 cm^{-1} s.

Results and Discussion

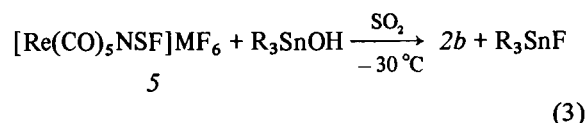
Displacement of SO_2 in pentacarbonyl–sulfur dioxide complexes gives the corresponding thionylimide derivatives in quantitative yield:



1a, b, 2a, b, M = Mn, Re



Similar reactions are possible with the hexafluoroarsenates of bivalent transition metals ($\text{M}(\text{SO}_2)_2(\text{AsF}_6)_2$ M = Co, Ni, Cu); these reactions are more difficult to control because side reactions and polymerisations occur. To date only 4 has been isolated in a pure state. A second route to complexes of type 2 is *via* a nucleophilic substitution at coordinated thiazyl fluoride:





The last reaction is difficult to control because HF will further attack *2b*. Because the products of reactions (1) and (3) are identical according to IR-spectroscopy, we assume that in both cases the HNSO ligand is present and not the isomer HOSN. From the last reaction it might also be concluded that the ligand is coordinated *via* nitrogen. The spectroscopic properties of the HNSO ligand in *2a* and *2b* differ markedly from those reported for coordinated HNSO in the literature [1, 2]. Although the bond lengths determined for the OSNH ligand in $(\text{Ph}_3\text{P})_2(\text{OSNH})_2$ are not very reliable (the SO distances were given as 1.341(17) Å and 1.258(11) Å, the SN distances as 1.452(19) Å and 1.485(19) Å, respectively), they seem to be rather short. Therefore it is surprising that in these compounds no absorption bands due to the OSN system above 1040 cm^{-1} were assigned.

(For HNSO (gas) is reported $\nu_{\text{as}}(\text{NSO})$ 1261 cm^{-1} , $\nu_{\text{sym}}(\text{NSO})$ 1090 cm^{-1} [6] for the solid 1248.7 and 1082.7 cm^{-1} , respectively [7]; d (SN) 1.512 Å, d (SO) 1.451 Å [8]). In the $\nu(\text{CO})$ region, *2a* and *2b* show the pattern expected for C_{4v} symmetry (*2a*) (IR): A_1 2170 E 2075 A_1 2055 cm^{-1} ; *2b*: A_1 2175 (IR) 2172 (Ra) B_1 2166 (Ra) E 2068 (IR) A_1 2007 (IR) cm^{-1} 1996 (Ra), $\nu(\text{NH})$ is found at 3222 cm^{-1} (*2a*) and 3180 cm^{-1} (*2b*), $\nu_{\text{as}}(\text{NSO})$ at 1251/1194 (*1a*) and 1260/1238 cm^{-1} (*1b*). $\nu_{\text{sym}}(\text{NSO})$ (1048 vs, 1012 sh (*2a*) and 1024 cm^{-1} vs (*1b*)) are the strongest bands in the Raman spectra.

In *4* doubling of $\nu(\text{NH})$ (3238 m, 3203 cm^{-1} m) and $\nu_{\text{as}}(\text{NSO})$ (1252 m, 1237 m, and 1169 m, 1145 cm^{-1} m) is observed, suggesting the presence of two different types of HNSO ligands. Because the AsF_6^- ions show no distortion, and because the central Ni atom is expected to be hexacoordinated, two of the HNSO ligands might act as bidentate ligands.

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