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Thionylimide–Transition Metal Complexes

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Recently Turner *et al.* reported the preparation of thionylimide–complexes of platinum [1, 2] by a rather surprising route. $(Ph_3P)_2Pt(OSNH)_2$ was isolated from the reaction of $(Ph_3P)_4Pt$ and $S_4N_4H_4$-$(C_6H_6/(CH_3)_2CO$ as solvent) [1], $Pt(OSNH)_2(S_2N_2H_2)$ [2] was obtained from K_2PtCl_6 and $S_4N_4H_4$ 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 $[Mn(CO)_5SO_2]AsF_6$ (*1a*) or $[Re(CO)_5SO_2]AsF_6$ (*1b*) (or 0.5 mmol $Ni(SO)_2)_2(AsF_6)_2$ (*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 $NH_4^+AsF_6^-$). 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 $[Mn(CO)_5HNSO]AsF_6$ (*2a*), $[Re(CO)_5HNSO]AsF_6$ (*2b*) and $[Ni(HNSO)_4](AsF_6)_2$ (*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*.

$[Mn(CO)_5HNSO]AsF_6$

(*2a*), Dec. 117 °C. *Anal.* Calcd. for $C_5HAsF_6MnNO_6S$: 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.

$[Re(CO)_5HNSO]AsF_6$

(*2b*), Dec. 102 °C. *Anal.* Calcd. for $C_5HAsF_6NO_6ReS$: 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.

$[Ni(HNSO)_4](AsF_6)_2$

(*4*) Dec. 108 °C. *Anal.* Calcd. for $As_2F_{12}H_4N_4NiO_4S_4$: 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:

$$\underset{1}{[MCO)_5SO_2]AsF_6} + HNSO \xrightarrow[-50\,^{\circ}C]{SO_2} \underset{2}{[M(CO)_5HNSO]AsF_6} + SO_2 \qquad (1)$$

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

$$\underset{3}{[Ni(SO)_2](AsF_6)_2} + HNSO_{exc} \xrightarrow[-50\,^{\circ}C]{SO_2} \underset{4}{[Ni(HNSO)_4](AsF_6)_2} + SO_2 \qquad (2)$$

Similar reactions are possible with the hexafluoroarsenates of bivalent transition metals $(M(SO_2)_2(AsF_6)_2$ 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:

$$\underset{5}{[Re(CO)_5NSF]MF_6} + R_3SnOH \xrightarrow[-30\,^{\circ}C]{SO_2} 2b + R_3SnF \qquad (3)$$

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$$5 + H_2O \xrightarrow[-60\,°C]{SO_2} 2b + HF \qquad (3a)$$

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 $(Ph_3P)_2(OSNH)_2$ 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 ν_{as}(NSO) 1261 cm^{-1}, ν_{sym}(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 ν(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), ν(NH) is found at 3222 cm^{-1} (*2a*) and 3180 cm^{-1} (*2b*), ν_{as}(NSO) at 1251/1194 (*1a*) and 1260/1238 cm^{-1} (*1b*). ν_{sym}(NSO) (1048 vs, 1012 sh (*2a*) and 1024 cm^{-1} vs (*1b*)) are the strongest bands in the Raman spectra.

In *4* doubling of ν(NH) (3238 m, 3203 cm^{-1} m) and ν_{as}(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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