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THE SYNTHESIS OF THIONITROSODIMETHYLAMINE ($Me_2NN{=}S$) COMPLEXES OF RUTHENIUM, OSMIUM, AND IRIDIUM

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Summary

Neutral hydrido complexes $[ML]ClH(PPh_3)_3$ ([ML] = Ru(CO), Os(CO) and Ir(Cl)] react with thionitrosodimethylamine, $Me_2NN{=}S$, to give $[ML]ClH(SNNMe_2)(PPh_3)_2$ with H *trans* to $Me_2NN{=}S$, while the hydrido cations *cis,trans*-$[[ML]H(SNNMe_2)_2(PPh_3)_2]^+$ are obtained from $Me_2NN{=}S$ and $[Ru(NCMe)_2(CO)(PPh_3)_2]^+$, $[OsH(OH_2)(CO)(PPh_3)_3]^+$ and $[IrClH(NCMe)_2(PPh_3)_2]^+$, respectively. The coordinatively unsaturated aryl complexes $[ML']Cl(p\text{-tolyl})(PPh_3)_2$ ([ML'] = Ru(CO), Os(CO) and Os(CS)) coordinate one molecule of $Me_2NN{=}S$ to give $[ML']Cl(p\text{-tolyl})(SNNMe_2)(PPh_3)_2$, the chloride ligands of which are labile. Spectroscopic data suggest that in all these complexes the $Me_2NN{=}S$ ligand adopts a $\eta^1(S)$ coordination mode.

Introduction

Multiple bonding between carbon and divalent sulphur provides the basis for a rich and diverse organic chemistry, which has been extended to organometallic complexes, e.g., thiocarbonyl (MCS), thioformyl (MC(S)H) and dithiocarboxylate ester ($MC(S)SCH_3$) compounds. In contrast, the analogous chemistry involving multiple bonding between nitrogen and divalent sulphur has proved particularly elusive. Compounds containing a free N=S functionality are rare, thionitrosoamines, $R_2NN{=}S$ ($R_2N = Me_2N$ [1], $[CH_2]_5N$ [1] and Ph_2N [2]) being the only stable organic examples besides transition metal–thionitrosyl complexes [3,4]. Sulphur imides (i.e. thionitroso compounds), RNS, have been generated as ligands in coordination complexes by fragmentation of sulphur diimides, $S(NR)_2$, but the bonding to the metal in these complexes (e.g., $Fe_2(CO)_6(RNS)$, R = H [5], $SiMe_3$ [5], CMe_3 [6], tolyl [6]; $Fe_2(CO)_7(RNS)$, R = CMe_3 [6]; $Fe_3(CO)_9(S)(RNS)$, R = CMe_3 [6]; $Ru_2(CO)_6(RNS)$, R = CMe_3 [7])) always involves the N=S linkage, thereby significantly reducing the bond multiplicity [cf. 7].

We describe here the syntheses of a number of six-coordinate thionitrosodimethylamine complexes of ruthenium, osmium and iridium in which the $Me_2NN{=}S$

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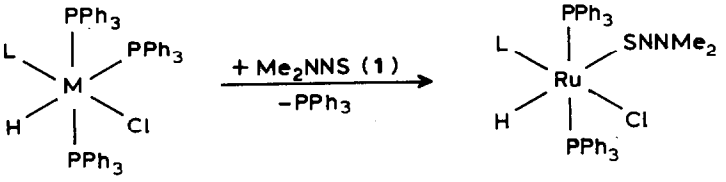
ligand is present along with migratory-active ligands, e.g., hydrido and aryl groups. Thionitrosoamine complexes of chromium [2,8], palladium and platinum [9,10] have been described previously; in all the cases studied up till now the thionitrosoamine (R_2NNS) ligand was apparently coordinated via the sulphur atom in a monodentate manner.

Results and discussion

Hydrido complexes

The compounds $MClH(CO)(PPh_3)_3$ (M = Os, Ru) display a reactivity associated with the sterically congested *mer*-tris(phosphine) arrangement, the initial substitution usually occurring *trans* to the hydrido ligand and is followed in some cases by rearrangement. Thus, the addition of an ethereal solution of $Me_2NN{=}S$ (**1**) to a suspension of $MClH(CO)(PPh_3)_3$ in toluene results in rapid formation of $MClH(CO)(SNNMe_2)(PPh_3)_2$ (M = Ru (**2**) and Os (**3**)) as bright orange crystals. Similar treatment of $IrCl_2H(PPh_3)_3$ (Ir(Cl) being isolelectronic with Os(CO)) gives yellow $IrCl_2H(SNNMe_2)(PPh_3)_2$ (**4**).



(**2** : ML = Ru(CO) ;
3 : ML = Os(CO) ;
4 : ML = Ir (Cl))

The *trans*-bis(phosphine) arrangement in **2–4** is confirmed by the appearance of the hydride resonances in the ^1H NMR as triplets (Table 1) whilst the *trans*-dichloride geometry in **4** is supported by the far-infrared spectrum (a single band, $\nu_{as}(IrCl_2)$, at 318 cm^{-1}). The $\nu(CO)$ frequencies of **2** and **3** are similar to those observed in the starting materials, suggesting that the net donor ability of $Me_2NN{=}S$ (**1**) is comparable to that of triphenylphosphine. According to the ^1H NMR data, the dimethylamino groups in **2–4** (as in complexes described later) adopt a conformation in which the two methyl groups are in quite different chemical environments. This indicates that the ligand is planar, with a high barrier to rotation about the nitrogen–nitrogen bond. The canonical form **B** (Scheme 1) suggested by Middleton [1] for free $Me_2NN{=}S$ is presumably even more relevant to a description of **1** as a ligand in transition metal complexes.

The infrared spectra of complexes **2–4** show bands at 1352m, 1261w, 1120m, 837w and 790w cm^{-1} together with an enhancement of the triphenylphosphine-associated bands at 1084 and 1020 cm^{-1}, presumably due to coincident $Me_2NN{=}S$ modes. These absorptions correspond to the bands noted for $(CO)_5Cr(SNNMe_2)$ [2], with some differences in relative intensities. In addition, weak bands were found at 932 and 898 cm^{-1}. The band at 790 cm^{-1}, which has been attributed to NS stretching in the chromium complex (785 cm^{-1}) [2], is particularly weak, and cannot

TABLE 1

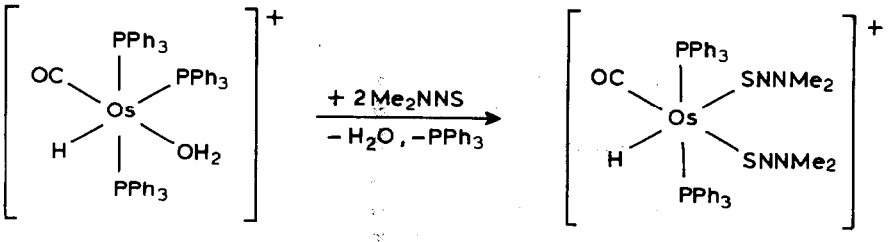
SPECTROSCOPIC DATA FOR HYDRIDO-THIONITROSODIMETHYLAMINE COMPLEXES

Compound	Infrared [a]		^{1}H NMR [d]		
	ν(CO)	ν(MH)	δ(NMe$_2$)	δ(MH) (Triplet)	^2J(PH)
RuClH(CO)(SNNMe$_2$)(PPh$_3$)$_2$ (2)	1922	[c]	3.48, 3.07	−8.97	19.8
OsClH(CO)(SNNMe$_2$)(PPh$_3$)$_2$ (3)	1919 1905 [b]	2041	3.31, 2.91	−9.43	19.0
IrCl$_2$H(SNNMe$_2$)(PPh$_3$)$_2$ (4)	–	2104	3.34, 3.06	−16.93	13.6
[OsH(CO)(SNNMe$_2$)$_2$(PPh$_3$)$_2$]$^+$ (5)	1924	2039	3.41, 3.36 3.22, 2.81	−9.63	18.0
[RuH(CO)(SNNMe$_2$)$_2$(PPh$_3$)$_2$]$^+$ (6)	1936	[c]	3.48, 3.39 3.29, 2.85	−9.62	18.0
[IrClH(SNNMe$_2$)$_2$(PPh$_3$)$_2$]$^+$ (7)	–	[c]	3.73, 3.53, 3.34, 2.53	−15.75	12.7

[a] Data for Nujol mulls between KBr discs and shown in cm^{-1}. [b] Solid state splitting, ν(CO) 1905 cm^{-1} in CH_2Cl_2 solution. [c] Not observed. [d] Data determined with saturated solutions of the complexes in $CDCl_3$ at 25°C (90 MHz) and shown in δ(ppm) relative to internal Me_4Si $\delta = 0.00$. Coupling constants ^2J(PH) given in Hz.

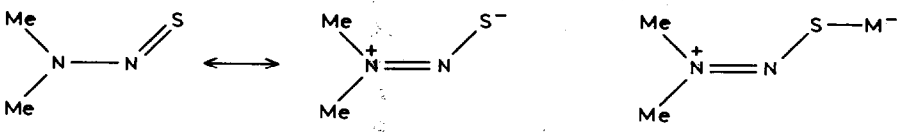
be unambiguously distinguished from M–H deformation modes, also expected in this area, in the absence of isotope studies.

Treatment of a tetrahydrofuran solution of $[OsH(OH_2)(CO)(PPh_3)_3]^+$ BF_4^- with an excess of **1** gives (following chromatographic purification) the bis(thionitrosoamine) complex cation $[OsH(CO)(SNNMe_2)_2(PPh_3)_2]^+$ (**5**), which was characterised as both the BF_4^- and PF_6^- salts because some IR bands of the counter-anion and the ligand coincide.



(5)

The stereochemistry of **5** follows from the observation of four methyl resonances of equal intensity in the ^{1}H NMR along with a triplet resonance for the hydride

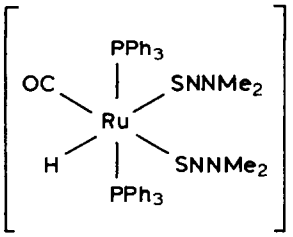


(A) (B)

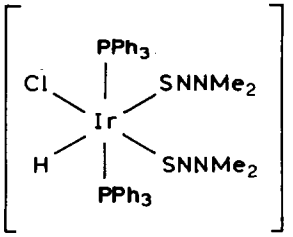
SCHEME 1

ligand; a *trans*-bis(thionitrosoamine) stereochemistry would give only two methyl resonances. A similar pattern is observed in the spectrum of the product of the reaction of $[RuH(CO)(NCMe)_2(PPh_3)_2]^+$ SbF_6^- with **1**, indicating an analogous cation **6**.

Similarly, $[IrClH(SNNMe_2)_2(PPh_3)_2]^+$ (**7**) is obtained from the reaction of $[IrClH(NCMe)_2(PPh_3)_2]^+$ with an excess of **1**, but the yields were lower than those of **5** and **6**. It is assumed that **5–7** are isostructural on the basis of their very similar IR and NMR spectroscopic data.



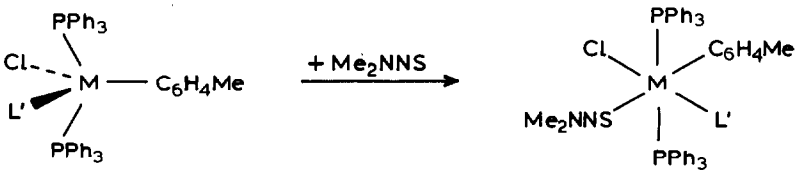
(6)



(7)

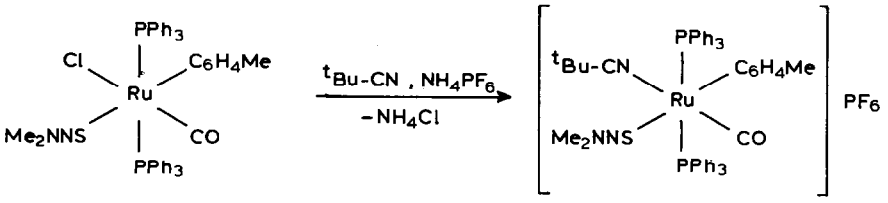
Aryl complexes

The 16-electron aryl complexes $[ML']Cl(p\text{-tolyl})(PPh_3)_2$ ([ML'] = Os(CO), Os(CS) and Ru(CO)) react smoothly with **1** to afford the 18-electron complexes **8–10** in excellent yield.



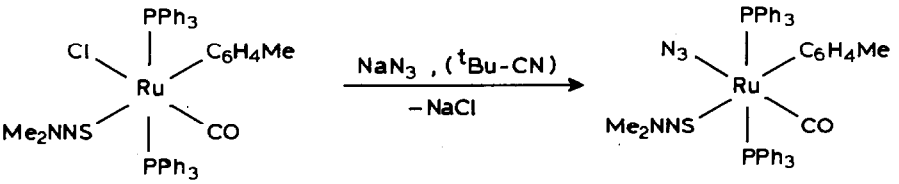
(**8** : ML' = Os(CO) ;
9 : ML' = Os(CS) ;
10 : ML' = Ru(CO))

It proved necessary to prepare $RuCl(phenyl)(CO)(SNNMe_2)(PPh_3)_2$ (**11**) in a similar manner from $RuCl(phenyl)(CO)(PPh_3)_2$ in order to provide unambiguous assignment of the tolyl and dimethylamino methyl resonances in the ^1H NMR spectra. All the aryl complexes form brightly coloured air-stable crystalline solids. The tolyl-carbonyl complexes show solid-state splitting of the $\nu(CO)$ absorptions, but in solution (CH_2Cl_2) single bands are observed. The stereochemistry expected to arise from nucleophilic attack *trans* to the apical aryl group in the square-pyramidal precursors is as shown, and it has been shown to be present by a single crystal X-ray structural analysis of **8** [11]. The chloride ligands in **8–10** are labile; thus, e.g., **10** in the presence of t-butyl cyanide (pivalonitrile) and a non-coordinating anion provides the salt **12** · PF_6 derived from substitution of chloride by a nitrile.



(10) (12) · PF_6

Alternatively, when a solution of **10** is treated with sodium azide and a catalytic amount of t-butyl cyanide the azido complex **13** is formed in good yield.



(10) (13)

Experimental

All reactions were carried out under prepurified nitrogen using conventional Schlenk techniques. Unless otherwise stated, work-up was carried out in the open air.

The ligand $Me_2NN{=}S$ was prepared as described previously [1] and used in all experiments as a 0.20 mol/l solution in diethyl ether. This solution was stored at −30°C for 5 months with no apparent decomposition. No information is available concerning the toxicity of thionitrosoamines, but in view of the high carcinogenity of nitrosoamines, $Me_2NN{=}S$ and its solutions should be used in an efficient hood.

The starting complexes $MClH(CO)(PPh_3)_3$ (M = Ru [12], Os [13]), $IrCl_2H(PPh_3)_3$ [14], $[OsH(H_2O)(CO)(PPh_3)_3]BF_4$ [13], $[RuH(CO)(CH_3CN)_2(PPh_3)_2]SbF_6$ [cf. 15], MCl(*p*-tolyl)$(CO)(PPh_3)_2$ (M = Ru, Os [16]) and OsCl(*p*-tolyl)$(CS)(PPh_3)_2$ [17] were obtained by published procedures. RuCl(phenyl)$(CO)(PPh_3)_2$ was prepared by the method used for the analogous *p*-tolyl complex [16] but with diphenyl- in place of di-*p*-tolyl-mercury.

The IR spectrometers used were Perkin–Elmer 297 and 983 G, as well as Beckman 4240. The ^1H NMR spectra were measured on a JEOL FX 90 Q instrument.

$RuClH(CO)(SNNMe_2)(PPh_3)_2$ (2)

A suspension of $RuClH(CO)(PPh_3)_3$ (0.30 g, 0.32 mmol) in toluene (5.0 ml) was treated with an ethereal solution of $Me_2NN{=}S$ (3.0 ml of 0.20 mol/l; 0.60 mmol). The mixture was stirred for 4 h, then hexane (5 ml) was added to effect complete separation of the orange product. The mixture was stirred for a further 30 min and the crystals were filtered off, washed with hexane (2 × 10 ml), and recrystallised from dichloromethane/ethanol. Yield 0.24 g (97%). M.p. 173°C (dec.).

$OsClH(CO)(SNNMe_2)(PPh_3)_2$ (3) and $IrCl_2H(SNNMe_2)(PPh_3)_2$ (4)

Treatment of $OsClH(CO)(PPh_3)_3$ and $IrCl_2H(PPh_3)_3$ in a manner similar to that described for the synthesis of **2** gave **3** (yield 96%, m.p. 196°C (dec.). Anal. Found: C, 54.60; N, 3.58. $C_{39}H_{37}ClN_2OOsP_2S$ calcd.: C, 53.88; N, 3.22%) and **4** (yield 96%, m.p. 157°C), respectively.

$[OsH(CO)(SNNMe_2)_2(PPh_3)_2]^+ BF_4^-$ (5 · BF_4)

A suspension of $[OsH(OH_2)(CO)(PPh_3)_3]^+ BF_4^-$ (0.30 g, 0.27 mmol) in tetrahydrofuran (10 ml) was treated with a solution of $Me_2NN{=}S$ in ether (3.0 ml of 0.20 mol/l; 0.60 mmol). The complex slowly dissolved and stirring was continued for 2 h, after which a yellow solid had separated. Toluene (30 ml) was added and the volume of the solution was reduced in vacuo to ca. 15 ml. The yellow solid was filtered off, washed with cold (0°C) toluene (10 ml) and hexane (2 × 10 ml), then dissolved in a minimum of dichloromethane and chromatographed on silica gel with dichloromethane as eluant (yellow zone). The complex was crystallised by the addition of t-butanol and slow removal of dichloromethane under reduced pressure then filtered off, washed with diethyl ether (2 × 10 ml), and dried in vacuo. Yield 0.22 g (83%). The PF_6^- salt of **5** was prepared by recrystallising **5** · BF_4 twice in the presence of a four-fold excess of NH_4PF_6. M.p. 184°C (decomp.).

$[RuH(CO)(SNNMe_2)_2(PPh_3)_2]^+ SbF_6^-$ (6 · SbF_6)

A suspension of $[RuH(CO)(NCMe)_2(PPh_3)_2]^+ SbF_6^-$ (0.27 g, 0.28 mmol) in tetrahydrofuran (5.0 ml) was treated with an ethereal solution of $Me_2NN{=}S$ (3.0 ml of 0.20 mol/l; 0.60 mmol). The mixture was stirred for 2 h then toluene (50 ml) added and the volume of the mixture reduced slowly to ca. 20 ml on a rotary evaporator. The yellow crystals were filtered off, washed with toluene (10 ml) and hexane (10 ml), and dried in vacuo. Yield 0.26 g (87%). M.p. 139°C. Anal. Found: C, 46.22; H, 4.22; N, 5.26. $C_{41}H_{43}F_6N_4OP_2RuS_2Sb$ calcd.: C, 46.00; H, 4.05; N, 5.23%.

$[IrClH(SNNMe_2)_2(PPh_3)_2]^+ BF_4^-$ (7 · BF_4)

A suspension of $IrCl_2H(PPh_3)_3$ (0.30 g, 0.29 mmol) in acetonitrile (10 ml) was treated with a solution of silver tetrafluoroborate in acetonitrile (3.0 ml of 0.10 mol/l; 0.30 mmol). The suspension was refluxed for 15 min, cooled, diluted with dichloromethane (20 ml) and filtered through Celite, and the filtrate was evaporated under reduced pressure. The residue was suspended in tetrahydrofuran (15 ml) and treated with a solution of $Me_2NN{=}S$ in ether (3.5 ml of 0.20 mol/l; 0.70 mmol), the mixture then stirred for 15 h. Work-up and chromatographic purification as described for the synthesis of **5** · BF_4 gave yellow crystals of **7** · BF_4. Yield 0.15 g (52%). M.p. 155°C (decomp.).

Complexes **2**–**7** are described in Table 1.

$OsCl(tolyl)(CO)(SNNMe_2)(PPh_3)_2$ (8)

A suspension of $OsCl(tolyl)(CO)(PPh_3)_2$ (0.055 g, 0.063 mmol) in toluene (3.0 ml) was treated with a solution of $Me_2NN{=}S$ in ether (0.70 ml of 0.20 mol/l; 0.14 mmol). The red suspension was stirred for 20 min and then hexane was added to complete the precipitation of the scarlet product, which was filtered off, washed

TABLE 2

SPECTROSCOPIC DATA FOR σ-ARYL-THIONITROSODIMETHYLAMINE COMPLEXES [a]

Compound	Infrared ν(CO) [b]	^{1}H NMR	
		δ(NMe_2)	δ(CH_3) (tolyl)
OsCl(tolyl)(CO)(SNNMe$_2$)(PPh_3)$_2$ (**8**)	1921, 1908 (1910)	3.40, 2.61	2.18
OsCl(tolyl)(CS)(SNNMe$_2$)(PPh_3)$_2$ [c] (**9**)	–	3.49, 2.78	2.19
RuCl(tolyl)(CO)(SNNMe$_2$)(PPh_3)$_2$ (**10**)	1929, 1898 (1924)	3.51, 2.68	2.16
RuCl(phenyl)(CO)(SNNMe$_2$)(PPh_3)$_2$ (**11**)	1915	3.57, 2.72	–
[Ru(tolyl)(NC^{t}Bu)(CO)(SNNMe$_2$)(PPh_3)$_2$]$^+$ (**12**)	1960	3.65, 3.01	2.23 [d]

[a] For conditions see footnotes of Table 1. [b] Where there was solid-state splitting the corresponding ν(CO) value obtained in a dichloromethane solution is given in parentheses. [c] ν(CS) 1279, 1268 in Nujol. [d] δ(^{t}Bu) 0.90 ppm.

with hexane (2 × 10 ml), recrystallised from dichloromethane/ethanol, and dried in vacuo. Yield 0.055 g (91%). M.p. 183°C. The complex was characterized by X-ray crystallography [11].

OsCl(tolyl)(CS)(SNNMe$_2$)(PPh_3)$_2$ (9), RuCl(tolyl)(CO)(SNNMe$_2$)(PPh_3)$_2$ (10) and RuCl(phenyl)(CO)(SNNMe$_2$)(PPh_3)$_2$ (11)

Treatment of OsCl(tolyl)(CS)(PPh_3)$_2$, RuCl(tolyl)(CO)(PPh_3)$_2$ and RuCl(phenyl)(CO)(PPh_3)$_2$ similar to that described for the synthesis of **8** gave **9** (yield 91%, m.p. 161°C), **10** (yield 98%, m.p. 160°C. Anal. Found: C, 62.34; H, 5.01; N, 3.18. $C_{46}H_{43}ClN_2OP_2RuS \cdot 0.25\ CH_2Cl_2$ (solvent evident in ^{1}H NMR), calcd.: C, 62.23; H, 5.02; N, 3.14%) and **11** (yield 94%, m.p. 159°C) respectively.

[Ru(tolyl)(NC^{t}Bu)(CO)(SNNMe$_2$)(PPh_3)$_2$]$^+$ PF_6^- (12 · PF_6)

A solution of RuCl(tolyl)(CO)(SNNMe$_2$)(PPh_3)$_2$ (0.13 g, 0.15 mmol) in dichloromethane (10 ml) was treated with a solution of NH_4PF_6 (0.20 g, 1.23 mmol) in water (3 ml) and ethanol (20 ml) then with pivalonitrile (0.30 ml). The orange solution immediately became bright yellow and the product was isolated as yellow crystals by the slow removal of dichloromethane under reduced pressure followed by decantation of the mother liquor. The solid was washed with cold ethanol (10 ml) and dried in vacuo. Yield 0.14 g (90%). M.p. 158°C (dec.).

Complexes **8–12** are described in Table 2.

Acknowledgements

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