

Reactions of Trithiazyl Trichloride with Ruthenium, Rhodium & Iridium Complexes

K'C JAIN & U C AGARWALA*

Department of Chemistry, Indian Institute of Technology,
Kanpur 208016

Received 18 September 1982; accepted 23 October 1982

The syntheses of the thionitrosyls and other complexes by the reactions of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{RhH}(\text{PPh}_3)_4$, $\text{Rh}(\text{NO})\text{Br}_2(\text{PPh}_3)_2$ and $\text{IrHCl}_2(\text{PPh}_3)_3$ with trithiazyl trichloride are described. The new complexes obtained have been characterized by elemental analyses, IR, conductivity and magnetic data.

During the past few years a good number of papers have appeared dealing with the various aspects of the thionitrosyl complexes¹, particularly synthetic and structural aspects of terminally bonded- and bridged-thionitrosyls of the transition metal ions². In this note we wish to communicate the results of the reactions of $(\text{NSCl})_3$ with $\text{Rh}(\text{NO})\text{Br}_2(\text{PPh}_3)_2$, $\text{RhH}(\text{PPh}_3)_4$, $\text{IrHCl}_2(\text{PPh}_3)_3$ and $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$.

$(\text{NSCl})_3$, $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{Rh}(\text{NO})\text{Br}_2(\text{PPh}_3)_2$, $\text{RhH}(\text{PPh}_3)_4$ and $\text{IrHCl}_2(\text{PPh}_3)_3$ were synthesized by the methods described elsewhere³. Infrared spectra in the range $4000\text{--}200\text{ cm}^{-1}$, conductivities and room temperature magnetic susceptibilities of the complexes were measured as described in an earlier paper⁴.

Reaction of $[\text{Rh}(\text{NO})\text{Br}_2(\text{PPh}_3)_2]$ with $(\text{NSCl})_3$ —A solution (30 ml) of $(\text{NSCl})_3$ (~3 mmol) in THF was added at 5°C to a stirred solution of $\text{Rh}(\text{NO})\text{Br}_2(\text{PPh}_3)_2$ (0.2 g) in CHCl_3 (30 ml). The stirring was continued at 5°C for another 24 hr, and the resulting solution concentrated to near dryness under reduced pressure. The semisolid residue was extracted with benzene. On adding hexane to the extract, a brown complex, di- μ -thionitrosylbis(dichlorotriphenyl-phosphine)rhodium(III) precipitated out which was centrifuged, washed with hexane, water, dried in air and recrystallized from toluene-dichloromethane (1:1) as brown crystals of $[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$.

Reaction of $\text{RhH}(\text{PPh}_3)_4$ with $(\text{NSCl})_3$ —A solution (30 ml) of $(\text{NSCl})_3$ (~3 mmol) in THF was added dropwise at 5°C with stirring to a solution of $\text{RhH}(\text{PPh}_3)_4$ (0.2 g) in THF (30 ml). Stirring at 5°C was continued for further 2 hr. Brown crystals of $[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ were isolated by the procedure similar to that given above.

Reaction of di- μ -thionitrosyl-bis(dichlorotriphenyl-phosphine)-rhodium(III) with triphenylphosphine—Triphenylphosphine (0.4 g) was dissolved in a solution of $[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ (0.2 g) in CH_2Cl_2 (20 ml). The resulting solution was refluxed for 1 hr and to the reaction mixture was added hexane in excess. A red brown complex, $[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ was precipitated which was centrifuged, washed with ether and dried *in vacuo*.

Reaction of $\text{IrHCl}_2(\text{PPh}_3)_3$ with $(\text{NSCl})_3$ —A solution (30 ml) of $(\text{NSCl})_3$ was added dropwise at 5°C to a stirred solution (20 ml) of $[\text{IrHCl}_2(\text{PPh}_3)_3]$ (0.3 g) in THF. The resulting solution was stirred for 1 hr more and evaporated to near dryness under reduced pressure. The residue was extracted with benzene; on adding hexane to the extract a yellowish brown compound, $[\text{Ir}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ was precipitated which was centrifuged, washed with hexane and dried *in vacuo*.

Reaction of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ with $(\text{NSCl})_3$ —A solution of $(\text{NSCl})_3$ in THF (30 ml) was added dropwise with stirring to a solution (20 ml) of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ (0.5 g) in THF at 10°C . The mixture was further stirred for 1 hr, resulting solution concentrated to about 5 ml and to the residue hexane was added in excess to give a precipitate of $\text{Ru}(\text{CO})_2\text{Cl}(\text{PPh}_3)_2$. It was centrifuged and washed several times with hexane. Tetrasulphurtetranitride was recovered from the filtrate by drying *in vacuo*.

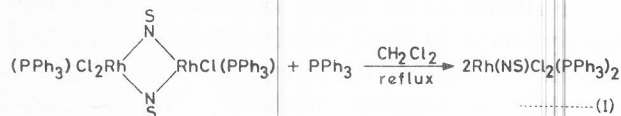
The analytical data of the complexes are given in Table I. They are stable in air, soluble in chloroform, dichloromethane and benzene and are found to be diamagnetic and nonconducting in nitrobenzene.

The reaction of $(\text{NSCl})_3$ in THF with $[\text{Rh}(\text{NO})\text{Br}_2(\text{PPh}_3)_2]$ at 5°C resulted in the formation of the known² brown NS-bridged complex, $[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$. The appearance of a broad band at 830 cm^{-1} [$\nu(\text{NS})$ bridged] in the IR spectrum of the

Table I—Analytical Data of Complexes

Complex	Found (Calc), (%)						
	C	H	N	S	Cl	P	Rh
$[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$	44.6 (44.8)	3.0 (2.9)	3.2 (6.0)	6.7 (14.7)	15.0 (6.4)	6.6 (21.4)	20.8
$[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$	58.5 (58.1)	3.7 (4.0)	2.2 (1.9)	4.5 (4.3)	9.4 (9.5)	8.6 (8.3)	13.2 (13.8)
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$	60.3 (60.6)	3.7 (4.0)	—	—	9.7 (9.4)	8.0 (8.2)	—
$[\text{Ir}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$	51.5 (51.9)	3.3 (3.6)	1.5 (1.7)	3.4 (3.8)	8.6 (8.5)	7.0 (7.4)	—

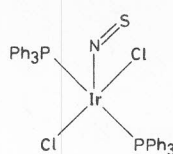
resulting complex in place of the one at 1630 cm^{-1} [$\nu(\text{NO})$ terminal] present in the original compound suggested the substitution of the terminal (NO) by the bridging (NS) group. The presence of NS-bridge was further confirmed by its reaction with $(\text{PPh}_3)_3$ which yielded a monomeric complex $[\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ whose IR spectrum exhibited a shift in 840 cm^{-1} band [$\nu(\text{NS})$ bridged] towards higher wavenumbers (1120 cm^{-1}) a characteristic band of $\nu_{\text{terminal}}(\text{NS})$ ^{1,2}. A new band also appeared at 340 cm^{-1} , which could be assigned to $\nu_{\text{terminal}}(\text{Rh}-\text{Cl})$. It is, therefore assumed that the reaction of the complex with $(\text{PPh}_3)_3$ proceeded according to Eq. (1).



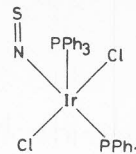
Although two bands due to bridged $\nu(\text{NS})$ should have appeared in the IR spectrum of $[\text{RhCl}_2(\text{NS})(\text{PPh}_3)]_2$ as a result of coupling of the two *cis* (NS) groups, it seems that the interaction between the two (NS) moieties is not large enough to warrant the separation of two bands $\sim 830\text{ cm}^{-1}$; instead the coupling is just enough to broaden the band at 830 cm^{-1} .

Reaction of $(\text{NSCl})_3$ with $[\text{IrHCl}_2(\text{PPh}_3)_3]$ yielded an yellowish brown complex $\text{Ir}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2$ whose IR spectrum displayed a band at 1120 cm^{-1} due to $\nu_{\text{terminal}}(\text{NS})$, in close agreement with the one (1115 cm^{-1}) already reported for $[\text{Ir}(\text{CO})(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$, and a band at 325 cm^{-1} assigned to $\nu(\text{Ir}-\text{Cl})$ (Cl *trans* to Cl^4). It is, therefore, suggested that the compound has presumably one of the two structures (A or B)

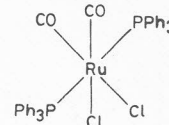
The reaction of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ with $(\text{NSCl})_3$ gave the known *cis*-dicarbonyl complex,



(A)



(B)



(C)

$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2]$, exhibiting characteristic $\nu(\text{CO})$ at 2064 and 2001 cm^{-1} (structure C)⁵, and N_4S_4 which was recovered from the reaction. S_4N_4 has been identified by a direct comparison with a sample synthesized by the literature methods. Interestingly it is the second example⁶ of the use of a complex to synthesize S_4N_4 from $(\text{NSCl})_3$ although recent reports indicate that it can also be synthesized using copper and iron⁷ in place of the complex, $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$.

References

- 1 Jain K C, Pandey K K, Katiyar S S & Agarwala U C, *XXI International conference on coordination chemistry, France*, (1980) 440; Pandey K K, Jain K C & Agarwala U C, *Inorg chem Acta*, **48** (1981) 23; Pandey K K & Agarwala U C, *Z anorg allg Chem*, **461** (1980) 228; Kolthamer B W S & Legzwind P, *J Am chem soc*, **100** (1978) 2247; Bishop M W, Chatt J & Dilworth J R, *J chem Soc Dalton Trans*, (1979) 1.
- 2 Pandey K K & Agarwala U C, *Inorg Chem*, **20** (1981) 1308.
- 3 Jolly W L & Maguire K D, *Inorg Synth*, **9** (1967) 102; Ahmad N, Levison J J, Robinson S D & Uttley M F, *Inorg Synth*, **15** (1974), 58; Osborn J A & Wilkinson G, *Inorg Synth*, **10** (1968) 68.
- 4 Pandey K K & Agarwala U C, *Indian J Chem*, **20A** (1981) 906.
- 5 James B R & Markham L D, *Inorg nucl Chem Lett*, **7** (1971) 373.
- 6 Tiwari R D, Pandey K K & Agarwala U C, *Inorg Chem*, **21** (1982) 845.
- 7 Berthen MP, Vinneht H & Montell Y, *Z Naturforsch*, **B35** (1980) 329.