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### Nitrido Complexes of Rhenium(V) with 2,2'-Dipyridyl & 1,10-Phenanthroline

D. SEN & N. C. TA

Department of Chemistry, Indian Institute of Technology  
Kharagpur 721302

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$\text{ReNX}_2(\text{PPh}_3)_2$  reacts with N-heterocyclic bases in benzene to give complexes of the composition,  $\text{Re}_3\text{N}_3\text{X}_6\text{L}_3(\text{PPh}_3)$  (L = 2,2'-dipyridyl or 1,10-phenanthroline, X = Cl or Br). The complexes have been characterized on the basis of elemental analysis, IR and magnetic susceptibility data. The IR spectra of the complexes show strong bands in the region 1050-1060  $\text{cm}^{-1}$  indicating the presence of  $\text{Re} \equiv \text{N}$  bond. The complexes are weakly paramagnetic.

LITTLE work has been reported on di- or tri-nuclear nitrido complexes of rhenium(V) having  $d^2$  configuration compared to osmium(IV) and ruthenium(IV)<sup>1,2</sup> complexes having  $d^4$  configuration. Except  $\text{K}_{2n}[\text{ReN}(\text{CN})_4]_n \cdot n\text{H}_2\text{O}$  (ref. 3), no other bi- or tri-nuclear nitrido complex of rhenium with  $d^2$  configuration has been reported. The present note deals with the isolation and characterization of some trinuclear nitrido complexes of rhenium(V) with N-heterocyclic bases, 2,2'-dipyridyl and 1,10-phenanthroline.

$\text{ReNX}_2(\text{PPh}_3)_2$  was prepared by a standard method<sup>4</sup>. 2,2'-Dipyridyl and 1,10-phenanthroline were BDH products. Nitrogen was determined by Dumas semimicro method. Rhenium, halogen and phosphorus were estimated gravimetrically as tetraphenyl arsonium perchlorate complex, silver chloride, and ammonium phosphomolybdate respectively. Magnetic susceptibilities were measured using the Guoy balance. Infrared spectra were recorded in Nujol

mull on a Perkin-Elmer 421 infrared spectrophotometer.

The following general method was employed to synthesize the complexes,  $\text{Re}_3\text{N}_3\text{X}_6\text{L}_3(\text{PPh}_3)$  with minor variations in the actual quantities of the reactants and the solvents.

$\text{ReNX}_2(\text{PPh}_3)_2$  (0.3 g) was dissolved in hot, dried benzene (90 ml). The N-heterocyclic base (0.5 g) in benzene (15 ml) was added to this solution. It was refluxed for 4 hr in nitrogen atmosphere. The volume of the solution was reduced to 20 ml and kept for 24 hr in a refrigerator. The deep violet crystals obtained were filtered, washed with benzene, ether and finally dried *in vacuo*.

The complexes are violet crystalline substances, insoluble in benzene, ethanol, diethyl ether, chloroform and carbon tetrachloride but readily soluble in acetone and nitrobenzene. In nitrobenzene solution the compounds did not show any appreciable dissociation indicating the coordinated nature of the anions. The analytical data are shown in Table 1. The IR spectra of the complexes,  $\text{Re}_3\text{N}_3\text{X}_6\text{L}_3(\text{PPh}_3)$ , show bands in the region 1050-1060  $\text{cm}^{-1}$  which are expected to be due to  $\nu\text{Re} \equiv \text{N}$  vibration as reported in the case of  $\text{ReNX}_2(\text{PPh}_3)_2$  (X = Cl or Br)<sup>2,4</sup>. The complexes  $\text{Re}_3\text{N}_3\text{Br}_6(\text{Phen})_3(\text{PPh}_3)$ ,  $\text{Re}_3\text{N}_3\text{Cl}_6(\text{Phen})_3(\text{PPh}_3)$ ,  $\text{Re}_3\text{N}_3\text{Br}_6(\text{Dipy})_3(\text{PPh}_3)$  and  $\text{Re}_3\text{N}_3\text{Cl}_6(\text{Dipy})_3(\text{PPh}_3)$  show  $\nu\text{Re} \equiv \text{N}$  at 1060, 1055, 1058 and 1054  $\text{cm}^{-1}$  respectively. A band at 1560 or 1558  $\text{cm}^{-1}$  due to  $\nu\text{C} = \text{N}$  in the free bases shifts to  $\sim 1580$   $\text{cm}^{-1}$  indicating coordination through nitrogen<sup>5,6</sup>. The absence of any band, characteristic of free ligands, in the spectra of complexes suggests their bidentate nature. It is difficult to locate the band due to triphenyl phosphine in the spectra of these complexes as both 2,2'-dipyridyl and 1,10-phenanthroline absorb in the region 1090-1100  $\text{cm}^{-1}$ . However, comparing the sharpness of the bands observed in the spectra of free bases and the complexes, it appears that the band characteristic of coordinated triphenyl phosphine<sup>7</sup> may be present around 1095  $\text{cm}^{-1}$ .

The magnetic moments of the complexes are given in Table 1. Very low magnetic moments of the complexes may be attributed to strong metal-metal interaction through magnetic exchange involving nitride bridging.

Further study on the 2,2'-dipyridyl and 1,10-phenanthroline complexes and the isolation of analogous compounds with oxine and pyridine are in progress, details of which will be published elsewhere.

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TABLE 1 — ANALYTICAL AND MAGNETIC MOMENT DATA OF THE COMPLEXES

Compound	Found (%)				Calc. (%)				$\mu_{\text{eff}}^*$ (B.M.)
	Re	N	Halogen	P	Re	N	Halogen	P	
$\text{Re}_3\text{N}_3\text{Br}_6(\text{Phen})_3(\text{PPh}_3)$	29.51	6.72	25.72	1.72	29.65	6.74	25.50	1.65	0.67
$\text{Re}_3\text{N}_3\text{Cl}_6(\text{Phen})_3(\text{PPh}_3)$	34.39	7.89	13.23	1.87	34.55	7.80	13.19	1.92	0.46
$\text{Re}_3\text{N}_3\text{Br}_6(\text{Dipy})_3(\text{PPh}_3)$	30.72	6.84	26.70	1.65	30.83	6.90	26.52	1.71	0.43
$\text{Re}_3\text{N}_3\text{Cl}_6(\text{Dipy})_3(\text{PPh}_3)$	36.08	8.20	13.96	2.09	36.12	8.16	13.82	2.01	0.51

\* $\mu_{\text{eff}}$  values are at 300°K.

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### Preparation & Characterization of Dimethylformamidyl Substituted Titanium(IV) Compounds

R. C. PAUL, B. N. ANAND, S. K. VASISHT & RAMESH KAPOOR  
Department of Chemistry, Panjab University  
Chandigarh 160014

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Dimethylformamidyl substituted titanium(IV) chlorides;  $TiCl_3[CON(CH_3)_2]_2 \cdot 2DMF$ ,  $TiCl_2[CON(CH_3)_2]_2 \cdot DMF$ ,  $TiCl_2[CON(CH_3)_2]_2$ ,  $TiCl[CON(CH_3)_2]_3$  and  $Ti[CON(CH_3)_2]_4$  have been prepared by the reaction of titanium(IV) chloride and dimethylformamidyl sodium. These compounds have been characterized by their elemental analyses, infrared, molar conductance and thermal studies.

IN continuation of our studies on the preparation of dimethylformamidyl substituted metal halides<sup>1</sup>, we now report the results of our investigations on the reactions between titanium(IV) chloride and dimethylformamidyl sodium. Solvolytic reactions of metal halides in dimethylformamide are completely lacking. Only in case of formamide a few partially solvolyzed products involving titanium(IV) chloride<sup>2</sup>, tin(IV) chloride and iron(III) chloride<sup>3</sup> have been reported.

Dimethylformamide (J. T. Baker analysed) was purified as reported in literature<sup>4</sup>. Dimethylformamidyl sodium was prepared as reported earlier<sup>5</sup>. Titanium(IV) chloride (Riedel) was used after distillation in dry nitrogen atmosphere.

*Preparation of compounds* — Titanium(IV) chloride when stirred with the suspension of dimethylformamidyl sodium,  $NaCON(CH_3)_2$  in carbon tetrachloride in different molar ratios (Table 1) for a period ranging between 4 to 24 hr gave yellow voluminous precipitates at 0°. The compounds were filtered and washed with carbon tetrachloride to remove unreacted titanium(IV) chloride. Sodium chloride and any unused dimethylformamidyl sodium were removed by treating the yellow mass with pure DMF. The DMF solution on evacuation yielded solid compounds. The last traces of dissolved sodium chloride were removed by successive treatments with fresh DMF till their solutions gave negative test for chloride ions. Generally three to four such treatments yielded pure products. Finally, the compounds were obtained by repeated washings with carbon tetrachloride and dried by keeping under vacuum ( $10^{-2}$  torr) for several hours.

The completely substituted product,  $Ti[CON(CH_3)_2]_4$  was obtained in small yields by refluxing the mixture in mole ratio 1:6 in methylene chloride for 3-4 days. The mixture was filtered and the filtrate was evacuated to get a white solid. It was purified by recrystallization from carbon tetrachloride-pet. ether. It was then sublimed at 40° at  $10^{-4}$  torr to get colourless crystals.

Complexes of some of these compounds with quinaline (Q) and ethylenediamine (en) were prepared by stirring their suspension in carbon tetrachloride with excess of base at 0°. The compounds were filtered under dry conditions, washed with petroleum ether and dried *in vacuo*.

Titanium was estimated gravimetrically as  $TiO_2$ . Chloride was determined as AgCl after fusing the compounds with  $Na_2CO_3$  and KOH. Carbon, hydrogen

TABLE 1 — ANALYTICAL DATA OF COMPOUNDS

Product	Molar conductance in DMF	Found (%) Calc.**				
		Ti	Cl	C	H	N
$TiCl_3[CON(CH_3)_2]_2 \cdot 2DMF$ (1)*	49.7	13.1 (12.9)	28.2 28.6	28.6 29.0	5.1 5.4	11.5 11.3
$TiCl_3[CON(CH_3)_2]_2 \cdot DMF \cdot Q$ (2)	48.2	11.4 (11.2)	24.3 24.9	42.2 42.0	4.6 4.7	9.5 9.8
$TiCl_3[CON(CH_3)_2]_2 \cdot 3en$ (3)	—	11.3 (11.8)	26.0 26.2	26.1 26.6	7.2 7.4	24.0 24.1
$TiCl_2[CON(CH_3)_2]_2 \cdot DMF$ (4)†	35.7	14.0 (14.3)	21.3 21.1	31.7 32.1	5.4 5.7	12.7 12.5
$TiCl_2[CON(CH_3)_2]_2$ (5)	32.1	18.5 (18.2)	26.8 27.0	27.3 27.4	4.6 4.6	10.2 10.6
$TiCl[CON(CH_3)_2]_3$ (6)‡	24.5	15.7 (16.0)	11.5 11.9	35.7 36.1	6.0 6.0	14.3 14.0
$Ti[CON(CH_3)_2]_4$ (7)‡	0.2§	13.5 (13.9)	—	44.0 42.9	7.3 7.1	17.3 16.6

\*Reactants in the molar ratio 1:1.5 ( $TiCl_4$ -sodium dimethylformamidyl).

†Reactants in the molar ratio 1:3.

‡Reactants in the molar ratio 1:6.

§In nitrobenzene.

\*\*Calculated values are given in the parentheses.