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Oxotrichlorobis(alkylcyanide)tungsten(V) Complexes; Precursors to Schiff Base Complexes

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Preparative routes to a number of high valent molybdenum and tungsten complexes are extremely difficult when simple highly insoluble salts, *e.g.* $MoCl_3$, are used. However, some donor solvents allow the isolation of soluble adducts which afford good starting materials for the preparation of a range of metal complexes. Thus we have previously found that $MOCl_3(THF)_2$ (M = Mo, W) reacts with phosphines and arsines [1], thioethers [2], Schiff's bases containing O-, S-, and N-donors [3, 4], and quinolines [5]. Similarly $WOCl_3(MeCN)_2$ has been found to have utility as a starting material and was first prepared by direct reaction of acetonitrile with $WOCl_3$ [6]. We wish to report an alternative preparative method here and the characterization of $WOCl_3(RCN)_2$ ($R = CH_3, C_2H_5, C_3H_7$).

Experimental

To $WOCl_3(THF)_2$ [7] (10 g), in a 3-necked 500 cm^3 flask under a dinitrogen atmosphere, was added freshly distilled acetonitrile (50 cm^3) and the resulting solution was refluxed for 2 h. The solution was then concentrated to 30 cm^3, cooled and a small amount of diethyl ether was added to induce precipitation. The product was collected by vacuum filtration using a Schlenk apparatus, washed with diethyl ether (10 cm^3) and dried *in vacuo.* The yield was quantitative and the product was stored in dry N_2 ampoules. A similar method was used to prepare $WOCl_3(RCN)_2$ ($R = C_2H_5, C_3H_7$).

Results and Discussion

The deeply coloured microcrystalline complexes, $WOCl_3(RCN)_2$ ($R = CH_3, C_2H_5, C_3H_7$) (Table I) are all extremely soluble in alkylcyanides but insoluble in toluene or dichloromethane; they appear to be sensitive to moist air in the order n-PrCN > EtCN > MeCN. The $WOCl_3(RCN)_2$ (R = Me, Et) are indefinitely stable when stored in ampoules under N_2, but this method of storage did not inhibit the decomposition of $WOCl_3$ (n-PrCN)$_2$ to a dark blue tar within a few days. Sufficient solubility in dichloromethane allowed EPR spectra to be obtained. These spectra, see Fig. 1, show one broad central line. The reflec-

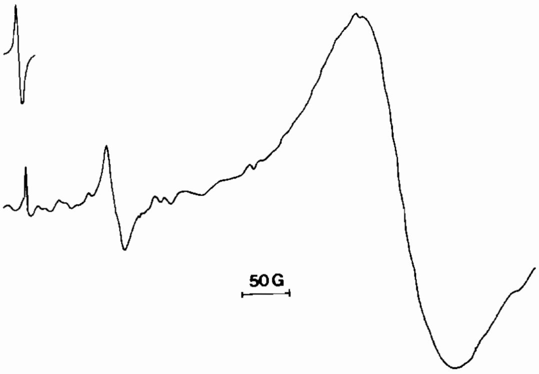

Fig. 1. ERP spectra.

TABLE I. Colour, Analytical Results, EPR, IR and Diffuse Reflectance Spectra of $WOCl_3(RCN)_2$ Complexes.

Compound	colour	Analysis Found (calcd.)			EPR g-value	E_{max} (cm^{-1})	IR (cm^{-1})
		%C	%H	%N			
$WOCl_3(CH_3CN)_2$	purple	12.4(12.4)	1.5(1.5)	7.3(7.2)	1.75	23,800 17,241	980 2270
$WOCl_3(EtCN)_2$	purple	17.3(17.3)	2.4(2.4)	6.9(6.7)	1.75	23,250 18,939	970 2270
$WOCl_3(Pr^nCN)_2$	purple	21.4(21.6)	1.4(1.6)	6.1(6.3)	1.76	–	980 2260
WOCl(salphen)	dark green	43.5(43.7)	2.9(2.6)	5.0(5.1)	1.76	23,520 16,949	1605 980 318

tance spectra exhibit several ill-defined absorptions, one at 17,000–19,000 cm^{-1}, retentatively assigned to $^2B_2 \rightarrow {}^2B_1$. The infrared show ν(W=O) at 970–980 cm^{-1} and coordinated nitrile is indicated by ν(CN) at ~2270 cm^{-1}.

It is thought that these complexes will serve as convenient starting materials for the preparation of other oxotungsten(V) complexes. For example, we have been able to isolate [WOCl(salphen)] {salphen is the dianion of the tetradentate N_2O_2 Schiff base *o*-phenylenebis(salicylideneimine)}, by the reaction of $WOCl_3(MeCN)_2$ with H_2salphen in freshly distilled acetonitrile. This complex (Table I) appears to be structurally similar to its molybdenum(V) analogue [3], exhibiting ν(CN) at 1605 cm^{-1}, shifted to lower energy from that in H_2salphen, 1615 cm^{-1}, and thus indicative of anionic bonding of salphen [4]. The ν(W=O) at 970 cm^{-1} may be compared with ν(Mo=O) at 948 cm^{-1} in [MoOCl(salphen)] [3] and suggests stronger metal–oxygen bonding in the tungsten complex. A single ν(W–Cl) band is observed at 318 cm^{-1}, almost identical to that in the [MoOCl(salphen)] compound. This insensitivity of the ν(M–Cl) as M changes from molybdenum to tungsten in [MOCl(salphen)] is in keeping with the *cis* structure proposed for the molybdenum complex [3].

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