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Preliminary communication

REACTIVITY OF A d^8 RUTHENIUM(0) NITROSYL COMPLEX

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Summary

The reactivity of the ruthenium(0) nitrosyl complex $RuCl(NO)(PPh_3)_2$ towards a variety of reagents has been examined, and is compared with that of the corresponding carbonyl complexes of rhodium(I) and iridium(I).

Nitrosyl complexes are more reactive than their carbonyl analogues [1], and it has been suggested that the ambivalent character of the nitrosyl ligand, usually coordinated as NO^+(linear) or NO^-(bent), and the possible occurrence of a conformational equilibrium between the two forms is responsible for the unexpected reactivity of the nitrosyl complexes [2]. When the nitrosyl ligand is in the NO^+ linear form it is isoelectronic with the carbonyl group, and forms complexes analogous to the carbonyl compounds one triad to the right. In order to compare the reactivity of the ruthenium(0) nitrosyl complexes [3], $RuCl(NO)(PPh_3)_2$ with those of the isoelectronic carbonyl complexes, $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$, we have studied the reactions of the nitrosyl complex with a variety of reagents; thus we have synthetized several novel nitrosyl complexes by treatment of the ruthenium(0) complex with alkyl and acyl halides, activated olefins, *o*-quinones and carboxylic acid anhydrides, as shown in Scheme 1. In all the reactions the linear coordination mode of the nitrosyl ligand is retained and the ruthenium must be regarded as being in the ruthenium(II) oxidation state.

Elemental analyses for all the complexes are consistent with their being 1:1 adducts. In complex I the nitrosyl stretching frequency is at 1670 cm^{-1}, whereas in all the novel complexes II-XV is in the 1790-1875 cm^{-1} region, as shown in Table 1, indicating a reduced back-donation of electron charge from the metal to the nitrosyl ligand due to the higher oxidation state of the metal.

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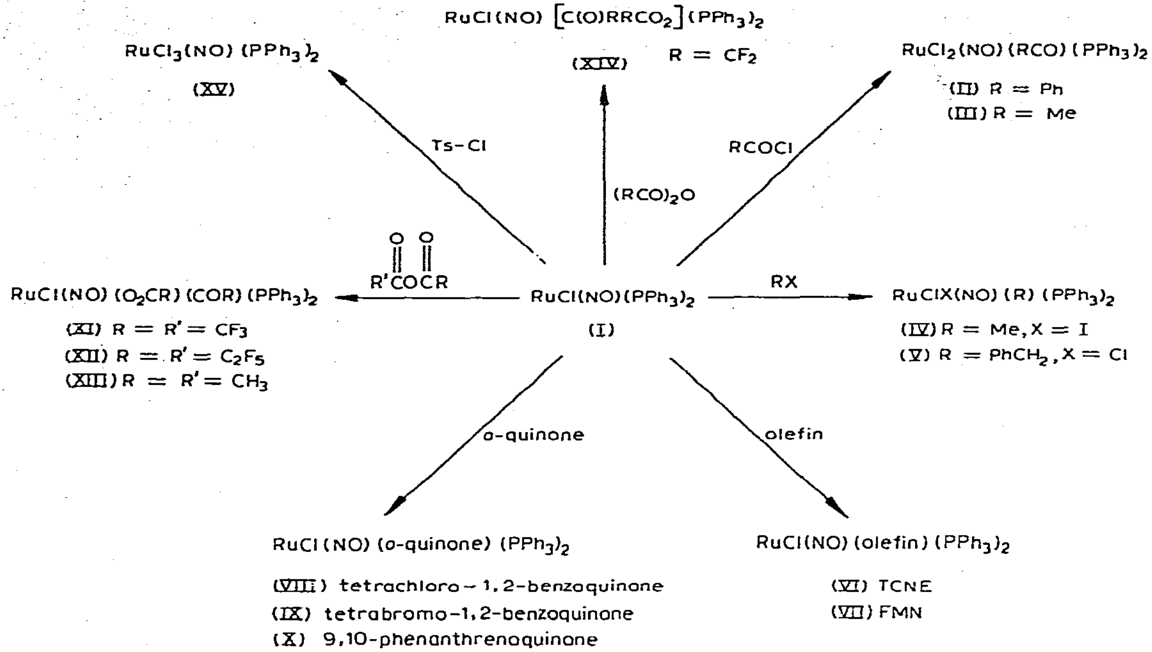

SCHEME 1

TABLE 1

NITROSYL STRETCHING FREQUENCIES (cm^{-1}) (KBr PELLETS)

Complex	$\nu(NO)(cm^{-1})$	Complex	$\nu(NO)(cm^{-1})$
I	1762	IX	1865
II	1850	X	1790
III	1865	XI	1865
IV	1850	XII	1870
V	1845	XIII	1875
VI	1830	XIV	1870
VII	1800	XV	1875
VIII	1875		

The most interesting feature of the reactions is the enhanced reactivity of the nitrosyl complex, the reactions of the nitrosyl complex being carried out under very mild conditions compared to those used for the rhodium(I) and iridium(I) carbonyl analogues.

I undergoes oxidative addition with 9,10-phenanthrenoquinone at room temperature in benzene to give a 6-coordinate complex X having a nitrosyl stretching frequency at 1790 cm^{-1}, which can be associated with the reduced electron-withdrawing ability of the ligand derived from phenanthrenoquinone relative to those from the halogenated *o*-quinones VIII and IX. In contrast it has been reported that 9,10-phenanthrenoquinone adds to the Vaska's compound only under photoactivation [4] or at 80°C [5].

Acetyl chloride does not react with $RhCl(CO)(PPh_3)_2$, though the more basic rhodium(I) complexes do react with the more reactive acetyl bromide [6]. Similarly Kubota [7] has reported that when the Vaska's compound is stirred for 4 days with benzoyl chloride there is no reaction, but with more basic iridium complexes acylated products are formed.

I reacts very easily with alkyl and acyl chlorides to give the very stable 1:1 adducts II and III which are the first stable nitrosyl acyl complexes [1a]. While activated carboxylic acid anhydrides react [8] with $IrCl(CO)(PPh_3)_2$ no such reactions are known for the rhodium analogue. In contrast the ruthenium nitrosyl complex undergoes rapid oxidative addition with acetic anhydride to give the 1:1 adduct XIII. Other reactions have been carried out with fluoro-activated carboxylic acid anhydrides under very mild conditions to give the complexes XI, XII and XIV.

Activated olefins react very smoothly with the ruthenium(0) complex giving the adducts VI and VII in which the nitrosyl stretching frequencies parallel the withdrawing abilities of the electronegative substituted ligands.

It is evident that the ruthenium(0) nitrosyl complex is more reactive than the rhodium(I) and iridium(I) carbonyl analogues and the results confirm that the nitrosyl ligand can activate metal complexes.

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