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PREPARATION AND CHARACTERISATION OF NOVEL SIX-COORDINATE RUTHENIUM(II) NITROSYL COMPLEXES

BRUNO GIOVANNITTI, OTTAVIO GANDOLFI, MAURO GHEDINI and GIULIANO DOLCETTI *

Department of Chemistry, Università della Calabria, 87030 - Arcavacata (CS) (Italy)

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Summary

The preparation and characterisation of the complexes obtained by oxidation addition reactions between $RuNOCl(PPh_3)_2$ (I) and acyl chlorides, aryl halides, activated olefins, or quinones are described. The high reactivity of complex I is compared with that of the analogous rhodium(I) and iridium(I) carbonyl complexes and the isoelectronic ruthenium(0) complexes. The stereochemistry around the metal is discussed on the basis of the IR spectra. The high reactivity of complex I is accounted for in terms of activation due to the presence of the nitrosyl group.

Introduction

Oxidative addition reactions involving four and five coordinate d^8 metal complexes are of much importance [1], especially in view of the number of homogeneous catalyst d^8 complexes involved in industrial implications [2]. Much emphasis has recently been given to the study of nitrosyl complexes as homogeneous catalysts, and it has been suggested that the ambivalent character of the nitrosyl ligand, usually coordinated as NO^+ or NO^-, and the potential existence of a conformational equilibrium between the two forms [3], are responsible for the unexpected reactivity of the nitrosyl complexes. Nitrosyl complexes are active homogeneous catalysts for the hydrogenation of olefins [4,5], and nitrosyl complexes are usually more reactive than their carbonyl analogues. Of all known d^8 complexes which undergo oxidative addition reactions, none have received more attention than Vaska's compound [1], $IrCl(CO)(PPh_3)_2$. Since the nitrosyl ligand when coordinated in the NO^+ linear situation is isoelectronic with CO, and forms analogues of the carbonyl compounds one triad to the right, we have been interested in the study of the reactivity of the d^8 ruthenium(0)

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* To whom correspondence should be addressed.

complexes $RuCl(NO)(PPh_3)_2$ (I) for which a d^8 configuration and a square planar geometry with a linearly-bonded nitrosyl group have been proposed [6]. Our aim was to examine the ability of the ruthenium nitrosyl to undergo oxidative additions with a variety of reagents and to compare its reactivity with that of the iridium(I) and rhodium(I) carbonyl analogues.

Experimental

All the reactions and subsequent work-up were performed under nitrogen purified by passage through a column filled with R-3-11 BASF deoxygenating catalyst and then dried over calcium chloride. The complexes $RuCl_3(NO)(PPh_3)_2$ and $RuCl(NO)(PPh_3)_2$ (I) were prepared as previously described [6—8]. Nitric oxide was the Matheson Gas 98% commercial product from which NO_2 was removed by passage through a silica gel trap at —78°C [9].

All reagents were reagent grade, and were recrystallized or distilled under nitrogen before use. All solvents were reagent grade and were dried by standard methods and distilled under nitrogen or argon. Solvents were degassed before use.

Infrared spectra were recorded with Perkin—Elmer 180 or 377 instruments. The solid samples were examined as KBr pellets or Nujol mulls.

The analyses were determined by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa (Italy).

In all the reactions described the yields were in the range 40—60%.

Reactions of I with ACOX (II: $A = CH_3$, $X = Cl$; III: $A = C_6H_5$, $X = Cl$)

To a 5 ml benzene solution of 0.200 g (0.298 mmol) of I the stoichiometric amount of freshly distilled appropriate ACOX was added. The brown solution was magnetically stirred at room temperature for 12 hours. The yellow precipitate was filtered off, washed with ether and dried under vacuum. Anal. II: Found: C, 59.59; H, 4.32; Cl, 9.90; N, 1.82; P, 8.40. $C_{38}H_{33}Cl_2NO_2P_2Ru$ calcd.: C, 59.31; H, 4.32; Cl, 9.21; N, 1.82; P, 8.05%. III: Found: C, 61.58; H, 4.16; Cl, 9.02; N, 1.61. $C_{43}H_{35}Cl_2NO_2P_2Ru$ calcd.: C, 62.10; H, 4.24; Cl, 8.52; N, 1.68%.

Reactions of I with AX (IV: $A = CH_3$, $X = I$; V: $A = C_6H_5CH_2$, $X = Cl$)

To a 5 ml benzene solution of 0.200 g (0.298 mmol) of I the stoichiometric amount of the appropriate AX was added. The brown solution was magnetically stirred at room temperature for 24 hours for IV or 3 days for V. The yellow precipitates were filtered off, washed with ether, and dried under vacuum. Anal. IV: Found: C, 53.79; H, 4.06; Cl, 4.64; I, 14.70; N, 1.56. $C_{37}H_{33}ClINOP_2Ru$ calcd.: C, 53.35; H, 3.99, Cl, 4.26; I, 15.23; N, 1.68%. V: Found: C, 63.21; H, 4.63; Cl, 8.96; N, 1.56; P, 8.00. $C_{43}H_{37}Cl_2NOP_2Ru$ calcd.: C, 63.16; H, 4.56; Cl, 8.67; N, 1.71; P, 7.58%.

Reactions of I with olefins (VI, tetracyanoethylene (TCNE) and VII, fumaronitrile (FMN))

To a 5 ml benzene solution of 0.200 g (0.298 mmol) of I the stoichiometric amount of sublimed olefin was added. The red suspension was stirred at room temperature for 2 hours in the preparation of VI or 5 hours in the preparation of VII. The brown precipitates were filtered off, washed with ether, and dried under vacuum. Anal. VI: Found: C, 61.58; H, 3.65; Cl, 4.74; N, 8.49; P, 7.29. $C_{42}H_{30}ClN_5OP_2Ru$ calcd.: C, 61.58; H, 3.69; Cl, 4.33; N, 8.55; P, 7.56%. VII: Found: C, 62.02; H, 4.17; Cl, 5.03; N, 4.98; P, 7.90. $C_{40}H_{32}ClN_3OP_2Ru$ calcd.: C, 62.46; H, 4.19; Cl, 4.61; N, 5.46; P, 8.05%.

Reactions of I with quinones: VIII, tetrachloro-1,2-benzoquinone; IX, tetrabromo-1,2-benzoquinone; X, 1,2-naphthoquinone; XI, 9,10-phenanthrenequinone; XII, tetrachloro-1,4-benzoquinone

To a 5 ml benzene solution of 0.200 g (0.298 mmol) of I the stoichiometric amount of the appropriate recrystallized quinone was added. The brown solution was stirred at room temperature for 5 hours for VIII, IX and XII and for 5 days for X and XI. The brown precipitate was filtered off, washed with ether and dried under vacuum. Anal. VIII: Found: C, 54.51; H, 3.65; Cl, 18.20; N, 1.22. $C_{42}H_{30}Cl_5NO_3P_2Ru$ calcd.: C, 53.83; H, 3.23; Cl, 18.92; N, 1.49%. IX: Found: C, 44.55; H, 2.84; N, 1.32. $C_{42}H_{30}Br_4ClNO_3P_2Ru$ calcd.: C, 45.25; H, 2.71; N, 1.26%. X: Found: C, 64.89; H, 4.53; N, 1.58. $C_{46}H_{36}ClNO_3P_2Ru$ calcd.: C, 65.05; H, 4.27; N, 1.65%. XI: Found: C, 67.69; H, 4.24; N, 1.43. $C_{50}H_{38}ClNO_3P_2Ru$ calcd.: C, 66.77; H, 4.26; N, 1.56%. XII: Found: C, 52.82; H, 3.53; Cl, 19.08; N, 1.37. $C_{40}H_{30}Cl_5NO_3P_2Ru$ calcd.: C, 53.83; H, 3.23; Cl, 18.92; N, 1.49%.

Results and discussion

It is known that complex I undergoes oxidative addition reactions with a number of small molecules [5] such as halogens, oxygen, hydrogen chloride, mercuric halides and fluorocarbons [17]. We have prepared and characterized the novel nitrosyl complexes II—XII by treatment of the ruthenium(0) complex I with activated olefins, alkyl and acyl halides, and quinones, demonstrating the high reactivity of the nitrosyl complex. Selected infrared bands for these complexes are reported in Table 1. Unfortunately, because of the very low solubility of these compounds and the very high oxygen sensitivity of the starting nitrosyl complex I, when the triphenylphosphine was replaced by more soluble phosphines [7], it was impossible to obtain satisfactory ^1H NMR spectra. Thus the stereochemistry around the metal is tentatively based only on the infrared spectra and by analogy with the structures of the rhodium(III) and iridium(III) carbonyl analogues.

Reactions with acid chlorides

Oxidative addition reactions of carboxylic acid chlorides with complexes of metal in d^8 or d^{10} electronic configuration give acylmetal complexes [10]. While five coordinated acyl complexes are obtained in the reaction of acyl halides with chlorotris(triphenylphosphine)rhodium(I) [11], acetyl and benzoyl chloride react with chlorotris(triphenylphosphine)rhodium(I) to give six-coordinate methyl and phenyl carbonyl complexes [12]. Only more basic rhodium(I) complexes react with the more reactive acetyl bromide [13] to give six-coordinate acylated complexes. Similarly, Kubota and Blake [10] have reported that when Vaska's compound is stirred for four days with benzoyl chloride no reaction

TABLE 1

SELECTED INFRARED BAND OF $RuCl(NO)(PPh_3)_2$ ADDUCTS

Compound	ν(NO)[a] (cm^{-1})	Other frequencies[a] ν (cm^{-1})	ν(Ru—Cl)[b] (cm^{-1})
I	1742[c]		
II	1870s	1627m(CO)	335w, 310w, 290w
III	1870s, 1842s	1700w, 1655m(CO)	330w, 300w, 220w
IV	1845s	2910w(CH_3)	300w
V	1868s		331w
VI	1835s	2216m(CN)	320w
VII	1798s	2200m(CN)	310w
VIII	1830s	1432s, 1255m, 975m, 810m, 792w[d]	330w
IX	1829s	1420s, 1259m, 1232m, 930w[d]	325w
X	1802s	1580w, 1455m, 1390m, 1270m, 800w[d]	321w
XI	1795s	1600m, 1580m, 1420m, 1051m, 938w, 790w, 758m[d]	328w
XII	1869s	1680m, 1405s	327w

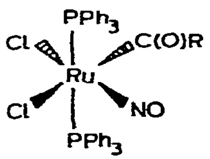
[a] As KBR pelletts. [b] As Nujol mulls. [c] In benzene solution. [d] Characteristic vibration of the o-diolato or quinone ligand.

occurs, but with Vaska-type iridium complexes containing more basic phosphines acylated products are formed. In contrast, I reacts very easily with acetyl and benzoyl chloride to give the six-coordinate acyl complexes II and III.

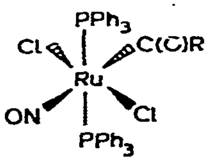
$$I + R(CO)(Cl) \rightarrow RuCl_2(COR)NO(PPh_3)_2 \qquad (1)$$

$$(II, R = C_6H_5;$$
$$III, R = CH_3)$$

The infrared spectra of complexes II and III show a single strong band in the 1800 cm^{-1} region, attributable to a linear nitrosyl stretching frequency. The nitrosyl stretching band is at higher frequency than in the parent complex, and is diagnostic of the reduced back-donation to the NO due to metal oxidation [14]. The far infrared spectra of II and III show 3 bands in the M—Cl region. Assuming the *trans* orientation of the two phosphine groups *, this indicates that at least two isomers, with *cis* and *trans* chlorine atoms, must be formed.



(IIa, R = C_6H_5;
IIIa., R = CH_3)



(IIb, R = C_6H_5;
IIIb, R = CH_3)

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* Unless otherwise specified a *trans* orientation of the two phosphine molecules is supposed in all the proposed structures in this paper.

cis-Chloride atoms have been proposed in the analogous reactions of Vaska's compound [10] on the basis of IR and NMR spectra. In our case the presence of a band around 330 cm^{-1} does not allow us to exclude *trans* orientation of the two chlorine atoms. Thus we suggest structures a and b for these complexes. As shown in Table 1, the benzoyl chloride adduct shows two nitrosyl bands due to the two isomers.

Reactions of I with alkyl halides

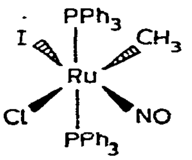
I reacts with methyl iodide and benzyl chloride to give the six-coordinate complexes IV and V (eq. 2). The compounds IV and V have a stretching ν(NO)

$$I + RX \rightarrow RuCl(X)(NO)(PPh_3)_2R \qquad (2)$$

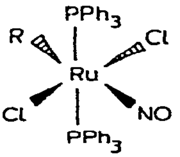
$$(IV, R = CH_3, X = I;$$
$$V, R = C_6H_5CH_2, X = Cl)$$

at 1845 and 1868 cm^{-1}, respectively. Compound IV has a band at 300 cm^{-1} which suggest a Cl *trans* to a CH_3 group [14].

In compound V the ν(Ru—Cl) stretch appears at 330 cm^{-1} which indicates a Cl *trans* Cl situation.



(IV)



(V, R = $C_6H_5CH_2$)

These data would suggest a *cis* addition for these RX reagents. Compound IV and V are formed under very mild conditions when compared to those used by Heck [16] in the case of the iridium carbonyl analogues.

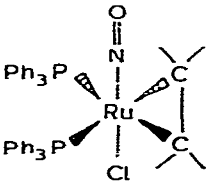
Reactions of I with activated olefins

Tetracyanoethylene (TCNE) and fumaronitrile (FMN) react smoothly at room temperature with a benzene solution of I to give the stable 1 : 1 adducts VI and VII (eq. 3). In both reactions an equimolar amount of cyanoolefin is

$$I + \text{cyanoolefin} \rightarrow RuCl(NO)(PPh_3)_2(\text{cyanoolefin}) \qquad (3)$$

$$(VI, \text{cyanoolefin} = TCNE;$$
$$VII, \text{cyanoolefin} = FMN)$$

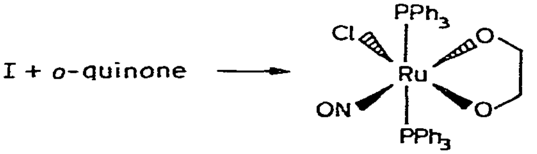
sufficient to obtain high product yields. The infrared spectra of VI and VII as KBr pellets show a sharp band in the CN region, 2216 cm^{-1} (VI) and 2200 cm^{-1} (VII), due to the ν(CN) of the coordinate olefin and a strong band at 1835 cm^{-1} for VI and 1798 cm^{-1} for VII due to the stretching vibration of a linearly bonded nitrosyl ligand. The nitrosyl stretching frequency for the TCNE adduct is higher than that of the FMN adduct, implying a weaker "back-donation" of electronic charge from the metal to the nitrosyl ligand in the adduct. This reflects the known trend in synergic acceptor—donor abilities of the TCNE (stronger acceptor and weaker donor) and FMN (weaker acceptor stronger donor). It is known that the replacement of hydrogen by electronegative groups in the ligand causes a decrease of basicity at the central metal. This has the consequence that the coordination of electron-withdrawing substituting ligands produces a weaking of the metal—nitrogen bond; thus in these nitrosyl complexes the cyanoolefins behave as bond weaking ligands, as in the rhodium and iridium carbonyl analogues [17]. Each of the complexes VI and VII has one band in the far-IR region (VI, 320 cm^{-1}, VII, 310 cm^{-1}) due to Cl *trans* to NO [15,18]. The proposed structure for VI and VII is thus as shown, with a *cis* orientation for the phosphine groups and Cl *trans* to the nitrosyl group, similar to that determined in the case of the Vaska-tetracyanothylene and the rhodium-fumaronitrile adducts [19].



(VI, VII)

Reactions of I with quinones

The novel six-coordinate complexes VIII, IX, X and XI of the type RuClNO(*o*-diolato)$(PPh_3)_2$ have been obtained by reaction of I with *o*-quinones (eq. 4).



(4)

VIII, tetrachloro-1,2-benzoquinone;
IX, tetrabromo-1,2-benzoquinone;
X, 1,2-napthoquinone;
XI, 9,10-phenanthrenequinone

The infrared spectra (Table 1) of the adducts are similar. The ν(NO) band of the parent complex I is shifted by ca. 50—100 cm^{-1} to higher energy upon adduct formation. Such shifts are caused by a reduced metal to nitric oxide donation due to the higher metal oxidation state present in the adducts. The lowering of the NO stretching frequency going from VIII (1975 cm^{-1}) to XI (1790 cm^{-1}) reflects the reduced electron-withdrawing ability of the ligands derived from the parent quinones. Upon adduct formation the quinone—carbonyl stretching vibration is generally lost, an observation that is consistent with ligand reduction upon adduct formation. In Table 1 the vibrational bands which are assigned to *o*-diolato ligands are those which are not obscured by bands due to triphenylphosphine or other entities present in the complexes. The assignments are consistent with the observations reported for similar compounds [20]. The stereochemistry of the addition products has been tentatively determined by examination of their far infrared spectra. The ruthenium—chlorine stretching vibration in the *o*-diolato adducts occurs at about 330 cm^{-1}. Since metal—chlorine stretching vibrations with chlorine *trans* to nitric oxide or phosphine generally appear at a frequency lower than 320 cm^{-1} [20], the chlorine must be situated *trans* to one of the oxygen atoms of the added ligand. An identical situation has been found in the case of *o*-diolato complexes of the rhodium carbonyl analogue [21]. From the literature it is clear that the kinetics of addition of a quinone to a substrate are strongly affected by the oxidizing ability of the quinone and similarly the nature of the complex itself alters the course of the addition [21—24]. As a measure of the oxidizing ability of the quinones, polarographic half-wave potentials [25] for reduction of some quinones to their corresponding semiquinone radical anions are given in Table 2. We do not imply that semiquinone radicals are necessarily intermediates in the mechanism path. Under the mild conditions used for the formation of complexes VIII—XI, the corresponding rhodium and iridium carbonyl complexes behave differently. The tetrahalobenzoquinone adds readily to rhodium(I), iridium(I) and ruthenium(0) carbonyl phosphine complexes [21]. The weaker oxidants 1,2-naphthoquinone and 9,10-phenanthrenequinone add to $Ir(CO)Cl(PPh_3)_2$ under photoactivation [22] or thermal activation [21], and these reactions are not known in the rhodium(I) carbonyl case. The more basic iodo Vaska-type compound reacts easily. Ruthenium(0) carbonyl phosphine complexes react in boiling ethanol [21]. Although the strong oxidizing *p*-quinones are known to form adducts with d^{10} iridium and rhodium nitrosyl [23] and platinum phosphine [24] complexes, they do not react with rhodium(I) and iridium(I) Vaska-type compounds. I react very easily with tetrachloro-1,4-benzoquinone to give the adduct XII, for which we cannot suggest a possible simple stereochemistry.

We previously reported [26] that the ruthenium nitrosyl complex I reacts with carboxylic acid anhydrides to form six coordinate ruthenium(II) nitrosyl complexes. This has been confirmed with fluoro-substituted anhydrides, for which complexes of the type $Ru(COR)(O_2CR)NO(PPh_3)_2$ have been obtained. Further investigation of the reaction with acetic anhydride itself has indicated that the product was incorrectly formulated and the reaction is much more complicated than simple addition of acetic anhydride. Further studies of the reactions with carboxilic anhydrides will be reported later.

TABLE 2

POLAROGRAPHIC HALF-WAVE POTENTIALS FOR REDUCTION OF QUINONES TO SEMI-QUINONES RADICALS

Quinone	$E_{1/2}$ (V) [a]
Tetrachloro-1,2-benzoquinone	+0.14 [b]
Tetrachloro-1,4-benzoquinone	+0.02 [c]
1,2-Naphthoquinone	—0.56 [c]
9,10-Phenanthrenequinone	—0.66 [c]

[a] Measured in acetonitrile solution. [b] Data from ref. 15. [c] Ref. 27.

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