

# Oxidative reactions of “half-sandwich” ruthenium compounds: formation of cationic nitrosyl ruthenium(II) derivatives

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## Abstract

The electrochemical behaviour of the ruthenium(II) alkyl complexes  $[\text{Ru}(\text{Me})\text{Cp}^*(\text{L})_2]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{L} = \text{PMe}_3$  **2a**,  $\text{PMe}_2\text{Ph}$  **2b**),  $[\text{Ru}(\text{CH}_2\text{CMe}_3)\text{Cp}^*(\text{PMe}_3)_2]$  (**3a**), and the related  $[\text{Ru}(\text{Me})\text{Cp}(\text{PPh}_3)_2]$  (**4d**) ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) in  $\text{CH}_2\text{Cl}_2$  involves a one-electron process, yielding the corresponding ruthenium(III) paramagnetic cations, as shown by coupled electrochemical–EPR studies. Compounds **2–4** are oxidised by  $[\text{FeCp}_2]^+$  in benzene to unidentified paramagnetic products which may decompose giving the corresponding alkane. The  $\text{Cp}^*$  compounds react with  $\text{NOBF}_4$  affording the monocationic alkylnitrosyl derivatives  $[\text{Ru}(\text{R})\text{Cp}^*(\text{NO})(\text{L})]\text{BF}_4$  ( $\text{R} = \text{Me}$ ;  $\text{L} = \text{PMe}_3$  **7a**,  $\text{PMe}_2\text{Ph}$  **7b**;  $\text{R} = \text{CH}_2\text{CMe}_3$ ;  $\text{L} = \text{PMe}_3$ ) and, when in excess of  $\text{NO}^+$ , the ruthenium(II) dicationic complexes  $[\text{RuCp}^*(\text{NO})(\text{L})_2](\text{BF}_4)_2$  ( $\text{L} = \text{PMe}_3$  **5a**,  $\text{PMe}_2\text{Ph}$  **5b**). The chloro complexes  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{L})_2]$  ( $\text{L} = \text{PMe}_3$  **1a**,  $\text{PMe}_2\text{Ph}$  **1b**,  $\text{PPh}_3$  **1d**) react analogously with  $\text{NO}^+$  to give  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{L})]\text{BF}_4$  ( $\text{L} = \text{PMe}_3$  **6a**,  $\text{PMe}_2\text{Ph}$  **6b**,  $\text{PPh}_3$  **6d**) and  $[\text{RuCp}^*(\text{NO})(\text{L})_2](\text{BF}_4)_2$  ( $\text{L} = \text{PMe}_3$  **5a**,  $\text{PMe}_2\text{Ph}$  **5b**). In contrast  $[\text{Ru}(\text{Me})\text{Cp}(\text{PPh}_3)_2]$  gives only  $[\text{Ru}(\text{Me})\text{Cp}(\text{NO})(\text{PPh}_3)]\text{BF}_4$ . EPR spectroscopy suggests that these nitrosylation reactions are also oxidative in character proceeding through ruthenium(III) intermediates. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Nitrosyls; Ruthenium–carbon bond cleavage; Electrochemistry; EPR spectroscopy

## 1. Introduction

Reactions involving the cleavage of metal–carbon bonds, which are very important in organometallic chemistry and catalysis, are oxidative in nature and are promoted by electrophiles and oxidant agents [1]. In particular the iridium(III) dimethyl complexes  $[\text{Ir}(\text{Me})_2\text{Cp}^*(\text{L})]$  ( $\text{L} = \text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$ ) have been found to give a rich variety of reactions under oxidative conditions [2]. Electrochemical oxidation in  $\text{CH}_2\text{Cl}_2$  involves a one-electron process, yielding the corresponding iridium(IV) paramagnetic cations, as shown by coupled electrochemical–ESR studies.  $\text{AgBF}_4$  oxidation in  $\text{CH}_2\text{Cl}_2$  gives instead  $\text{MeH}$  and radical species, having a “tucked-in” structure. Such species

have been proved to be involved as intermediates in the intra- and inter-molecular arene C–H activation by the above iridium complexes in the presence of catalytic amounts of one-electron oxidants (ETC catalysis). In contrast the  $\text{PPh}_3$  derivative reacts in the polar acetonitrile solvent with  $[\text{FeCp}_2]^+$  to give methane and  $[\text{Ir}(\text{Me})\text{Cp}^*(\text{PPh}_3)(\text{MeCN})]^+$ , no C–H bond activation of the phosphine being observed [3]. Reaction of the same iridium dimethyl complexes with  $\text{NOBF}_4$  affords interesting cationic alkylnitrosyls [4], which form through a mechanistic pathway involving a one-electron oxidation step. We have found, moreover, that the ruthenium(II) dimethyl complexes  $[\text{Ru}(\text{Me})_2(\eta^6\text{-C}_6\text{Me}_6)(\text{L})]$  are also able to activate the aromatic C–H bonds in the presence of one-electron oxidants [5].

In this paper we describe the results obtained by studying the reactivity, in particular the electrochemical and chemical oxidation, of other “half-sandwich” systems, the alkyl ruthenium(II) compounds  $[\text{Ru}(\text{Me})\text{Cp}^*$

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(L)<sub>2</sub>] (L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph) [6]. As far as we know, only the redox behaviour of the related [RuRCp(PPh<sub>3</sub>)<sub>2</sub>] (R = Me, CH<sub>2</sub>Ph; Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) was explored in the 1980s [7]. Since it was already known that such systems are able to thermally activate arene C–H bonds [6c], we reasoned that the presence of one-electron oxidants could catalyse arene activation analogously to what had been observed for the above-cited iridium and ruthenium complexes [M(Me)<sub>2</sub>(η<sup>n</sup>-C<sub>n</sub>Me<sub>n</sub>)(L)] (M = Ir, n = 5; M = Ru, n = 6; L = phosphine) [2,5]. An encouragement in this direction was provided by Tilset et al. [8] where the oxidation of the related [Ru(Me)Cp\*(CO)(PPh<sub>3</sub>)] is reported to give MeH by hydrogen abstraction from a ligand spectator. While our original hopes eventually proved misplaced, since no ETC catalysis was observed, we have found that these ruthenium alkyls show an interesting chemistry and in particular react with NOBF<sub>4</sub> giving a variety of cationic nitrosyls. The results of these studies are reported below.

## 2. Results and discussion

### 2.1. Preparation of the ruthenium(II) alkyl derivatives [Ru(R)Cp\*L<sub>2</sub>] (R = Me; L = PMe<sub>3</sub> **2a**, PMe<sub>2</sub>Ph **2b**; R = CH<sub>2</sub>CMe<sub>3</sub>; L = PMe<sub>3</sub> **3a**)

The alkyl ruthenium(II) complexes of general formula [Ru(R)Cp(L)<sub>2</sub>] and [Ru(R)Cp\*(L)<sub>2</sub>] (R = Me, CH<sub>2</sub>CMe<sub>3</sub>, L = phosphine) [6] have been prepared by alkylation of the corresponding chlorocompounds, for which several synthetic methods are available in the literature [9] depending on the nature of the phosphine and cyclopentadienyl ligands.

In particular [Ru(Me)Cp\*(PMe<sub>3</sub>)<sub>2</sub>] (**2a**) and [Ru(CH<sub>2</sub>CMe<sub>3</sub>)Cp\*(PMe<sub>3</sub>)<sub>2</sub>] (**3a**) have been prepared (73–76%) [6b] by using equimolar amounts of the appropriate Grignard reagent. [Ru(Me)Cp\*(PMe<sub>2</sub>Ph)<sub>2</sub>] (**2b**) has been synthesised (78%) by employing an excess of LiMe (3:1) [6c]. In all the above cases hydrolysis of the

reaction mixture is avoided and the alkyl derivative is isolated by extraction and crystallisation.

We have obtained [Ru(Me)Cp\*(PMe<sub>3</sub>)<sub>2</sub>] (**2a**) (70%), [Ru(Me)Cp\*(PMe<sub>2</sub>Ph)<sub>2</sub>] (**2b**) (68%) and [Ru(CH<sub>2</sub>CMe<sub>3</sub>)Cp\*(PMe<sub>3</sub>)<sub>2</sub>] (**3a**) (40%) carrying out the alkylation reactions with an excess of Grignard (6–10 per mole of ruthenium), and by treating the reaction mixture with 1,4-dioxane in order to precipitate the magnesium salts prior the hydrolysis. On carrying out the hydrolysis without this pre-treatment it came out that the isolated product is the iodo derivative [Ru(I)-Cp\*(L)<sub>2</sub>], probably obtained by further reaction of the ruthenium alkyl complex with iodo salts, as it had been previously observed [6a]. The yields are in general comparable to those reported in the literature.

### 2.2. Electrochemical oxidation of the ruthenium(II) alkyl derivatives [Ru(R)Cp\*L<sub>2</sub>] (R = Me, L = PMe<sub>3</sub> **2a**, PMe<sub>2</sub>Ph **2b**; R = CH<sub>2</sub>CMe<sub>3</sub>, L = PMe<sub>3</sub> **3a**) and [Ru(Me)Cp(PPh<sub>3</sub>)<sub>2</sub>] **4d**

Fig. 1 shows the cyclic voltammetric behaviour of **2b** in dichloromethane solution, at low temperature (0°C) [10].

Two oxidation processes are displayed, only the first of which exhibits features of chemical reversibility. Controlled potential coulometry (*E*<sub>w</sub> = 0.0 V) shows that the first oxidation consumes one electron/molecule. As a consequence of the exhaustive oxidation, the original pale-yellow solution turns pale-pink and gives rise to a cyclic voltammogram quite complementary to the original one, thus confirming the chemical reversibility of the Ru(II)–Ru(III) **2b**/**2b**<sup>+</sup> process. Based on the relative peak-heights, we assume that also the second oxidation process is a one-electron process likely involving the irreversible Ru(III)/Ru(IV) oxidation.

Complex **4d** exhibits a voltammetric profile substantially similar to that of **2b**, but for the presence of a minor spurious peak between the two main oxidation processes, due to some impurity of [Ru(X)Cp(PPh<sub>3</sub>)<sub>2</sub>] (X = Cl or I) (as proved by the <sup>1</sup>H-NMR spectrum). Also in this case exhaustive one-electron oxidation followed by cyclic voltammetric tests confirms the reversibility of the **4d**/**4d**<sup>+</sup> process. As a consequence of the one-electron removal the original yellow solution turns orange.

Fig. 2 shows the cyclic voltammogram of **3a**, recorded at low temperature.

As seen, in this case the first oxidation step is followed by a series of minor peaks, which cannot be attributed to impurities, in that they arise from decomposition of the electrogenerated monocation **3a**<sup>+</sup>. As a matter of fact the **3a**/**3a**<sup>+</sup> process is not completely reversible since in controlled potential electrolysis it leads to the formation of new products just coincident with the above spurious processes. As a proof of the

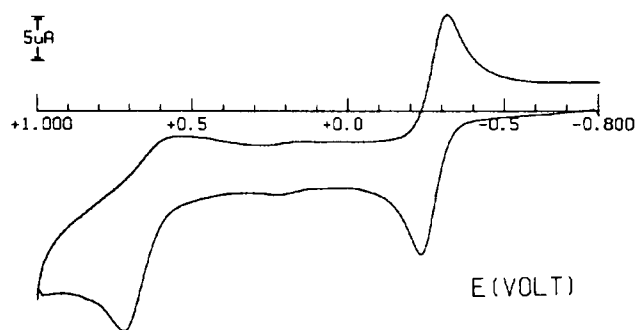


Fig. 1. Cyclic voltammogram recorded at a platinum electrode on CH<sub>2</sub>Cl<sub>2</sub> solution containing **2b** ( $2.4 \times 10^{-3}$  dm<sup>-3</sup>) and [NBu<sub>4</sub>]PF<sub>6</sub> (0.2 dm<sup>-3</sup>). Temperature = 0°C. Scan rate: 0.2 V s<sup>-1</sup>.

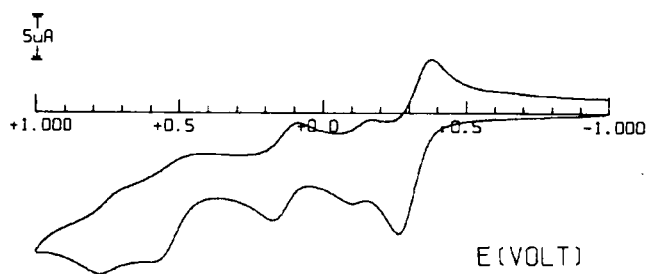


Fig. 2. Cyclic voltammogram recorded at a platinum electrode on  $\text{CH}_2\text{Cl}_2$  solution containing **3a** ( $1.0 \times 10^{-3} \text{ dm}^{-3}$ ) and  $[\text{NBu}_4]\text{PF}_6$  ( $0.2 \text{ mol dm}^{-3}$ ). Temperature =  $0^\circ\text{C}$ . Scan rate:  $0.2 \text{ V s}^{-1}$ .

Table 1

Formal electrode potentials (in V vs. SCE) and peak-to-peak separations (in mV) for the oxidation processes of the Ru(II) complexes under study in  $\text{CH}_2\text{Cl}_2$  solution

Compound	$T$ ( $^\circ\text{C}$ )	$E_{(0/+)}$	$\Delta E_p^a$	$E_{p(+2+)}^{a,b}$
<b>2a</b>	20	-0.34		
<b>2b</b>	0	-0.27	95	+0.72 <sup>b</sup>
<b>2b</b>	20	-0.27	92	+0.69 <sup>b</sup>
<b>4d</b>	20	+0.09	90	+0.91 <sup>b</sup>
<b>3a</b>	20	-0.34 <sup>c</sup>	134 <sup>c</sup>	
<b>3a</b>	0	-0.34	105	

<sup>a</sup> Measured at  $0.2 \text{ V s}^{-1}$ .

<sup>b</sup> Peak potential for irreversible processes.

<sup>c</sup> Measured at  $1 \text{ V s}^{-1}$ .

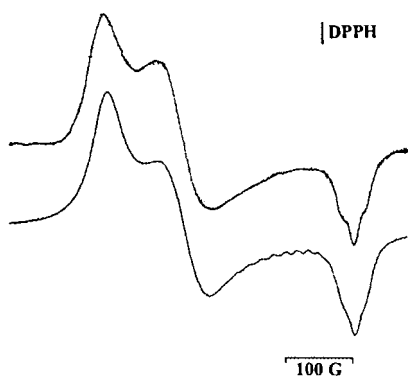


Fig. 3. Experimental (upper) and simulated (lower) EPR spectra of  $4d^+$  at 100 K.

instability of the monocation  $3a^+$ , the voltammogram at room temperature of the  $3a/3a^+$  process appears irreversible and the associated reduction peak can be detected only at high scan rate.

Finally, complex **2a** undergoes an oxidation process which is only in part chemically reversible, but the electrochemical results are not completely reliable because of the low stability of the starting complex.

The redox potentials for all the above processes are reported in Table 1.

The electrode potentials for the oxidation processes are consistent with the electronic characteristics of the ligands with the exception of **2a** and **3a**, for which they are identical (as above discussed, the figure for **2a** might be affected by error). The partial chemical reversibility of the Ru(II)–Ru(III) process of some of the present complexes is in agreement with previous findings on related derivatives [7].

The Ru(III) systems  $2b^+$  and  $4d^+$ , generated by electrolysis at  $-20^\circ\text{C}$  in solution of  $\text{CH}_2\text{Cl}_2$  under inert atmosphere, have been characterised by EPR spectroscopy at different temperatures. Fig. 3 shows the X-band spectra at 100 K of  $4d^+$  as an example.

The X-band EPR spectra of  $2b^+$  and  $4d^+$  at 100 K exhibit an  $S = 1/2$  well-resolved rhombic structure ( $g_x > g_y > g_{\text{electron}} = 2.0023 > g_z$ ) typical of low-spin Ru(III) paramagnetic complexes [11]. The  $4d^+$  species evidences a significant superhyperfine resolution in the  $g_z$  area, with a triplet of relative intensity 1:2:1, deriving from the coupling of the unpaired electron with two magnetically equivalent phosphorus nuclei. The relevant hyperfine couplings reported in Table 2 are computer evaluated [12]. There is no evidence for Ru satellite hyperfine couplings arising from the magnetic interaction of the unpaired electron with the magnetically active ruthenium nuclei.

Table 2 compiles the X-band EPR parameters as derived from computer simulation of the corresponding experimental parameters.

For both the electrogenerated  $2b^+$  and  $4d^+$  complexes, the anisotropic lineshape disappears at the transition temperature from frozen to fluid solution ( $T = 178 \text{ K}$ ).  $4d^+$  exhibits, up to 200 K, the corresponding broad and unresolved isotropic signal, with  $g_{\text{iso}} = 2.126(5)$  and  $\Delta H_{\text{iso}} = 95(6) \text{ G}$ , without any evidence for the relevant phosphorus nuclei superhyperfine splittings. This is a consequence of the overall  $\Delta H_{\text{iso}} = 105(5) \text{ G}$  broadening largely overlapping the relevant  $^{31}\text{P}$  couplings, so that an upper limit for such a magnetic interaction can be evaluated:  $\Delta H_{\text{iso}} \geq 2a_{\text{iso}}(2P)$ . Temperatures higher than 200 K induce the isotropic signal disappearing, and the solution remains EPR mute in the whole temperature range explored (200–300 K). This derives from the increase of the inter/intramolecular dynamics which become extremely rapid, rising the temperature, and results in a dramatic broadening of the fluid solution signal [12]: actually refreezing the solution below the fluid/glassy temperature restores quantitatively the original signal. The related  $g_{\text{iso}}$  and  $\langle g \rangle$  values are in good agreement, suggesting that the main geometry of the electrogenerated  $4d^+$  complex is maintained in different experimental conditions. On the contrary, in the case of the electrogenerated complex  $2b^+$ , the rhombic spectrum drops out at the glassy-fluid transition phase and the paramagnetic solution becomes EPR mute. The lineshape analysis of

the two electrogenerated  $2b^+$  and  $4d^+$  complexes strongly points out the large metal-in character of the actual EPR features and reflects the significant Ru(III) spin-orbit contribution in the present spectra. Accordingly, for both the complexes the singly occupied molecular orbital (SOMO) results from the significant participation of the atomic orbitals of the two phosphorus atoms but has a fundamental ruthenium 4d orbital character, as indicated by the actual  $g_{\text{iso}}$  values and the relevant linewidth  $\Delta H_{\text{iso}}$ . It is also to be noted that the nature of the cyclopentadienyl ligand does not influence substantially the shapes of the signals, the corresponding  $\Delta H_{\text{iso}}$ ,  $g_{\text{iso}}$  and  $a_{\text{iso}}$  values being only slightly affected.

*2.3. Chemical oxidation of the ruthenium(II) alkyl complexes [RuRCp\*(L)<sub>2</sub>] (R = Me, L = PMe<sub>3</sub> **2a**, PMe<sub>2</sub>Ph **2b**; R = CH<sub>2</sub>CMe<sub>3</sub>, L = PMe<sub>3</sub> **3a**) and [Ru(Me)Cp(PPh<sub>3</sub>)<sub>2</sub>] **4d***

When **2a** and **3a** were reacted with equimolar amounts of [FeCp<sub>2</sub>]PF<sub>6</sub> in C<sub>6</sub>D<sub>6</sub>, a gradual change in the colour of the solution from yellow to maroon and formation of a maroon solid was observed. The spectrum recorded after a few hours revealed the formation of methane ( $\delta = 0.14$ ) (**2a**) or neopentane ( $\delta = 0.89$ ) (**3a**) and ferrocene ( $\delta = 4.00$ ), both of them corresponding to 15–20% of the starting product. No signals attributable to new soluble organometallic products were observed.

Compounds **2b** and **4d** react quite slowly with ferrocenium as shown by the rate of formation of ferrocene. Neither methane nor new soluble organometallic products was observed.

These data, together with the electrochemical results, suggest that the compounds undergo one-electron oxidation reactions to give the corresponding radical cations [Ru(R)Cp'(L)<sub>2</sub>]<sup>+</sup> (Cp' = C<sub>5</sub>Me<sub>5</sub>, C<sub>5</sub>H<sub>5</sub>) which, depending on their thermal stability, may decompose to R–H through the homolysis of the Ru–C bond. Then the unstable **2a**<sup>+</sup> and **3a**<sup>+</sup> decompose to give methane and neopentane, respectively, while **2b**<sup>+</sup> and **4d**<sup>+</sup> are further oxidised to give insoluble dicationic species.

In the case of **2a** and **3a**, since decomposition to alkane occurs without incorporation of deuterium when

the reaction is carried out in deuteriated solvents, hydrogen abstraction has to occur from one of the ligands. This behaviour is analogous to that observed, in the presence of catalytic amounts of one-electron oxidants, for the related iridium and ruthenium systems [Ir(Me)<sub>2</sub>Cp\*(PMe<sub>3</sub>)] [2] and [Ru(Me)<sub>2</sub>Cp\*(PMe<sub>3</sub>)] [5], which, however, are able to activate aromatic C–H bonds yielding intermolecular activation products. This difference is perplexing, unless steric factors are crucial: actually it is possible that the presence of two phosphines in the coordination sphere of the ruthenium centres in the [Ru(R)Cp\*(phosphine)<sub>2</sub>] systems, instead of only one in the case of the iridium [2] and ruthenium [5] cases cited above, inhibits the interaction with the arene. In the thermal activation presumably this is overcome by preliminary phosphine dissociation [6c].

*2.4. Synthesis of cationic nitrosyl derivatives by reaction of the chloro and alkyl ruthenium complexes [Ru(X)(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(phosphine)<sub>2</sub>] (X = Cl, Me, CH<sub>2</sub>CMe<sub>3</sub>) with NOBF<sub>4</sub>*

We have recently reported [4] that the iridium(III) dimethyl derivatives [Ir(Me)<sub>2</sub>Cp\*(L)] (L = PMePh<sub>2</sub>, PMe<sub>2</sub>Ph, PMe<sub>3</sub>) react with NOBF<sub>4</sub> to give the cationic methylnitrosyl compounds [Ir(Me)<sub>2</sub>Cp\*(NO)]BF<sub>4</sub> or [Ir(Me)Cp\*(NO)(L)](BF<sub>4</sub>)<sub>2</sub> (L = PMePh<sub>2</sub>, PMe<sub>2</sub>Ph, PMe<sub>3</sub>) depending on the NO<sup>+</sup>/Ir molar ratio employed. We have now studied the reaction of the alkyl ruthenium derivatives **2a**, **2b** and **3a** with NOBF<sub>4</sub> and we have found an analogous behaviour: the nitrosyl complexes [Ru(R)Cp\*(NO)(L)]BF<sub>4</sub> or a mixture of [Ru(R)Cp\*(NO)(L)]BF<sub>4</sub> and [RuCp\*(NO)(L)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> form depending on the phosphine and on the NO<sup>+</sup>/Ru ratio (Scheme 1).

Some previous work had been reported in the literature for the reaction of the chloro complexes [M(Cl)Cp(PR<sub>3</sub>)<sub>2</sub>] (M = Ru, Os; R = Me, Ph) [13] and [Ru(Cl)Cp\*(PPh<sub>3</sub>)<sub>2</sub>] [9e] with NO<sup>+</sup> to give the corresponding dicationic [M(η<sup>5</sup>-C<sub>5</sub>R'<sub>5</sub>)(NO)(L)<sub>2</sub>]<sup>2+</sup> (R' = H, Me; L = Me, Ph) by replacement of the chloride ion. However nothing has been reported, as far as we know, on the reaction of the corresponding alkyl compounds with NO<sup>+</sup>.

Table 2

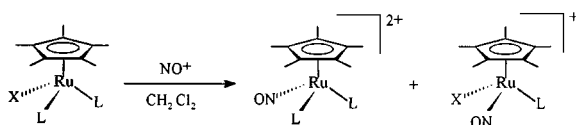
X-band EPR parameters of the electrogenerated compounds **2b**<sup>+</sup> and **4d**<sup>+</sup>, recorded at liquid nitrogen temperature ( $T = 100$  K)

Species	$g_x$	$g_y$	$g_z$	$\langle g \rangle^a$	$g_{\text{iso}}$	$a_x^b$	$a_y^b$	$a_z^b$	$\langle a \rangle^{b,c}$
<b>2b</b> <sup>+</sup>	2.256	2.111	1.982	2.116		23	26	31	27
<b>4d</b> <sup>+</sup>	2.230	2.145	1.984	2.120	2.126	19	21	24	21

<sup>a</sup>  $\langle g \rangle = (g_x + g_y + g_z)/3$ .

<sup>b</sup> In Gauss.

<sup>c</sup>  $\langle a \rangle = (a_x + a_y + a_z)/3$ .

NO<sup>+</sup>/Ru = 1

L	X			
PMe <sub>3</sub>	Cl	<b>1a</b>	<b>5a</b> (26%)	<b>6a</b> (50%)
PMe <sub>3</sub>	Me	<b>2a</b>		<b>7a</b> (76%)
OPMe <sub>2</sub> Ph	Cl	<b>1b</b>		<b>6b</b> (92%)
OPMe <sub>2</sub> Ph	Me	<b>2b</b>		<b>7b</b> (50%)
PPh <sub>3</sub>	Cl	<b>1d</b>		<b>6d</b> (80%)

NO<sup>+</sup>/Ru = 2

L	X			
PMe <sub>3</sub>	Cl	<b>1a</b>	<b>5a</b> (26%)	<b>6a</b> (51%)
PMe <sub>3</sub>	Me	<b>2a</b>	<b>5a</b> (30%)	<b>7a</b> (50%)
PMe <sub>3</sub>	CH <sub>2</sub> CMe <sub>3</sub>	<b>3a</b>	<b>5a</b> (29%)	(40%)
OPMe <sub>2</sub> Ph	Cl	<b>1b</b>	<b>5b</b> (10%)	<b>6b</b> (70%)
OPMe <sub>2</sub> Ph	Me	<b>2b</b>	<b>5b</b> (15%)	<b>7b</b> (50%)
PPh <sub>3</sub>	Cl	<b>1d</b>		<b>6d</b> (80%)

Scheme 1.

In a typical experiment an equimolar amount of NOBF<sub>4</sub> was added to **2a** in CH<sub>2</sub>Cl<sub>2</sub>. The reactant dissolved causing gas evolution (NO) and rapid colour change from maroon to deep-red. From this solution an oil (**7a**) was obtained which is soluble in dichloromethane, acetone, nitromethane, acetonitrile and methanol. The <sup>1</sup>H-NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> showed the presence of an organometallic product characterised by a C<sub>5</sub>Me<sub>5</sub> group ( $\delta = 1.94$ ,  $J_{\text{HP}} = 1.7$  Hz), a  $\sigma$ -bonded methyl group ( $\delta = 0.85$ ,  $J_{\text{HP}} = 6.2$  Hz) and one PMe<sub>3</sub> ligand ( $\delta = 1.64$ ,  $J_{\text{HP}} = 10.9$  Hz). Trimethylphosphine oxide (d,  $\delta = 1.85$ ,  $J_{\text{HP}} = 13.5$  Hz) was also found. The IR spectrum shows two strong bands at 1800 and 1059 cm<sup>-1</sup>, which indicate the presence of coordinated NO and BF<sub>4</sub><sup>-</sup>, respectively. In particular the value of the NO stretching indicates a linear coordination of the nitrosyl ligand. The MS-IS spectrum presents the typical isotopic cluster of peaks ( $m/e$  358 for the <sup>102</sup>Ru isotope) corresponding to [Ru(Me)Cp\*(NO)(PMe<sub>3</sub>)]<sup>+</sup> and a signal at  $m/e$  87 for BF<sub>4</sub><sup>-</sup>. Moreover the fragmentation of the molecular ion indicates the loss of CH<sub>4</sub> ( $m/e$  342). On the basis of all these data **7a** has been formulated as [Ru(Me)Cp\*(NO)(PMe<sub>3</sub>)]BF<sub>4</sub>, which results from the displacement of trimethylphosphine by NO<sup>+</sup>.

When two moles of NO<sup>+</sup> per mole of complex were used, the reaction followed a different course: methane (CH<sub>4</sub>) was immediately formed ( $\delta = 0.20$ , CD<sub>2</sub>Cl<sub>2</sub>), the colour of the solution changed from maroon to deep-red and a light-orange solid precipitated. From the solution **7a** was recovered. The precipitate, which is soluble in acetone, nitromethane, acetonitrile, methanol, analysed correctly for [RuCp\*(NO)(PMe<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**5a**). The MS-IS spectrum indicates a bivalent cation, showing a parent ion at  $m/2$  (209.5 = 419/2)

together with other peaks for the isotopic cluster of ruthenium, characterised by a mass difference of  $\Delta m/2$ . The <sup>1</sup>H-NMR spectrum in CD<sub>3</sub>NO<sub>2</sub> shows the presence of C<sub>5</sub>Me<sub>5</sub> as a triplet ( $\delta = 2.23$ ,  $J_{\text{HP}} = 2.0$  Hz) and two PMe<sub>3</sub> groups as a virtual triplet ( $\delta = 2.0$ ,  ${}^2J_{\text{HP}} + {}^4J_{\text{HP}} = 11.2$  Hz). The presence of a linear terminally bonded NO ligand is indicated by a strong IR absorption at 1845 cm<sup>-1</sup>. The spectrum contains also a large IR band at 1060 cm<sup>-1</sup> indicative of the presence of the BF<sub>4</sub><sup>-</sup> anion.

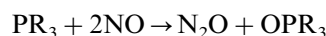
An analogous behaviour was observed in the case of **2b** which reacts with equimolar amounts or with an excess of NOBF<sub>4</sub> giving [Ru(Me)Cp\*(NO)(PMe<sub>2</sub>-Ph)]BF<sub>4</sub> (**7b**) or **7b** and [RuCp\*(NO)(PMe<sub>2</sub>Ph)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**5b**), respectively. OPMe<sub>2</sub>Ph (d,  $\delta = 2.06$ ,  $J_{\text{HP}} = 13.5$  Hz) was also formed.

Changing the nature of the alkyl group does not alter the reaction course: **3a** gives in fact [RuCp\*(NO)(PMe<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**5a**) and [Ru(CH<sub>2</sub>CMe<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(NO)(PMe<sub>3</sub>)]BF<sub>4</sub>. Monitoring the reaction by <sup>1</sup>H-NMR spectroscopy revealed the formation of OPMe<sub>3</sub> and neopentane ( $\delta = 0.91$ ).

In general the dicationic salt precipitates from the dichloromethane solution and may be easily separated from the soluble monocationic one. However in the case of **5b** and **7b** the solubilities are not different enough to allow their separation by simple decantation. Only after several crystallisations from CH<sub>2</sub>Cl<sub>2</sub>/pentane it was possible to obtain the two compounds in a pure form.

In all the above reactions formation of the alkanes (methane, neopentane) occurs without incorporation of deuterium, then apparently the alkyl group extracts a hydrogen atom from one of the groups in the coordination sphere of ruthenium. As demonstrated in the case of related reactions of some iridium systems [2c,4b], it is possible that the hydrogen derives from a Cp\* methyl group to give "a tucked-in" intermediate.

Another interesting aspect of these reactions is the origin of phosphine oxide. It could be tempting to attribute its formation to the adventitious presence of dioxygen, but we disregard this hypothesis since we have never observed the presence of phosphine oxides in reactions of these systems with other reagents. A second hypothesis is that the dissociated phosphine reacts with NO as already observed in the literature [14]:



A third hypothesis implies an electron transfer from the phosphine to NO<sup>+</sup> to generate a phosphine radical cation which in addition to dimerise may be intercepted by solvent impurities such as ethanol or water acting as nucleophiles to give the corresponding phosphine oxide [15].

Finally we turned our attention to the reaction of the corresponding chloro compounds of formula  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{L})_2]$  in order to investigate if also for this series the  $\text{NO}^+/\text{Ru}$  ratio influenced the reaction pattern. In the only cases described in the literature,  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PPh}_3)_2]$  [9e] and the related  $[\text{Ru}(\text{Cl})\text{Cp}(\text{PR}_3)_2]$  ( $\text{R} = \text{PMe}_3, \text{PPh}_3$ ) [13], which are reported to give only the corresponding dicationic compound by substitution of the chloride ligand with  $\text{NO}^+$  [9e,13], no mention of such dependence is done.

Indeed it was sorted out that the  $\text{NO}^+/\text{Ru}$  ratio does influence the nature of the products in the case of the chloro compounds series also. By using one equivalent of  $\text{NO}^+$ ,  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$  (**1a**) gives both the chloride (**5a**) and phosphine (**6a**) substitution products (Scheme 1), while **1b** and **1d** yield exclusively the monocations **6b** and **6d**, respectively. Instead when two equivalents of  $\text{NO}^+$  were used, **1b** gives both  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PMe}_2\text{Ph})]^+$  (**6b**) and  $[\text{RuCp}^*(\text{NO})(\text{PMe}_2\text{Ph})_2]^{2+}$  (**5b**). Surprisingly we have not been able (even by using an excess of  $\text{NO}^+$ ) to prepare the dicationic nitrosyl compound  $[\text{RuCp}^*(\text{NO})(\text{PPh}_3)_2]^{2+}$  which, as already mentioned, is reported [9e] to have been prepared just by reacting  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PPh}_3)_2]$  (**1d**) with a slight excess of  $\text{NO}^+$  ( $\text{NO}^+/\text{Ru}$  molar ratio = 1.35). We have used a  $\text{NO}^+/\text{Ru}$  ratio = 1.35 and 2.0, obtaining in both cases a light-red solid, which was identified as  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PPh}_3)]\text{BF}_4$  (**6d**) by  $^1\text{H-NMR}$  and IR spectroscopy as well as by mass spectrometry (ion spray) and elemental analysis. The  $^1\text{H-NMR}$  spectrum in  $\text{CD}_3\text{COCD}_3$  shows the  $\text{C}_5\text{Me}_5$  resonance as a doublet at  $\delta = 1.84$  ( $J_{\text{HP}} = 2.2$  Hz) and the aromatic protons of the  $\text{PPh}_3$  ligand as a multiplet at  $\delta = 7.5\text{--}7.8$ , whose integrated areas are in the 1:1 ratio. The  $\text{C}_5\text{Me}_5$  signal occurs at the same chemical shift reported in the literature for the dication, but the multiplicity is described as a triplet ( $J_{\text{HP}} \sim 2$  Hz) [9e]. The IR spectrum of **6d** in nujol shows a strong band at  $1806\text{ cm}^{-1}$  for the NO stretching, which is almost identical to the reported value ( $1805\text{ cm}^{-1}$ ) for the dicationic compound [9e]. Finally the mass spectrum in methanol, although we were unable to detect the mother ion, is consistent with that of **6d**. In fact it presents a peak at  $m/e$  566 (the cluster of peaks has the intensity expected from the contribution of the ruthenium and chlorine isotopes), corresponding to  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{MeOH})(\text{PPh}_3)]^+$ , which can be rationalised as deriving from **6d** by NO displacement by methanol.

Even by reacting **1d** in the presence of an excess of triphenylphosphine ( $\text{PPh}_3/\text{Ru} = 3$ ) with the aim to inhibit the displacement of the phosphine, we have obtained **6d** as the only product.

Then, at least in our hands, the loss of the phosphine is the preferential reactivity pattern of **1d**, as confirmed also by the reaction with CO in methanol in the presence of  $\text{NH}_4\text{PF}_6$ , which is reported to give instead the

cationic carbonyl derivative  $[\text{RuCp}^*(\text{CO})(\text{PPh}_3)_2]^+$  [9e] via loss of the chloride. In fact, when the reaction was monitored by  $^1\text{H-NMR}$  spectroscopy in  $\text{CD}_3\text{OD}$ , we observed a doublet ( $\delta = 1.54$ ,  $J_{\text{HP}} = 1.8$  Hz) for the  $\text{C}_5\text{Me}_5$  protons and multiplets in the aromatic region ( $\delta = 7.35\text{--}7.65$ ), whose integrated areas are in the 1:1 ratio. The product is only partially soluble in methanol, and well soluble in benzene. The  $^1\text{H-NMR}$  spectrum in  $\text{C}_6\text{D}_6$  showing a doublet at  $\delta = 1.38$  ( $J_{\text{HP}} = 1.8$  Hz) and multiplets at  $\delta = 7.0\text{--}7.8$ , is identical to that reported for  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{CO})(\text{PPh}_3)]$ , prepared by a different route [9e].

In all the reactions of the chloro compounds with  $\text{NOBF}_4$ , as well as for the alkyl series, the phosphine displacement results in the formation of the corresponding oxide.

Apparently the formation of the dicationic compounds depends on the properties of the phosphine ligands: in the series **1a**, **1b** and **1d** the dicationic product becomes less favoured as the ligand ability to donate electrons to the metal decreases [16]; a similar trend was found for the methyl derivatives **2a** and **2b**, where the yields of the dication are 30 and 15%, respectively (Scheme 1).

Finally, as for the two compounds of the Cp series, i.e.  $[\text{Ru}(\text{X})\text{Cp}(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Me}$ ), the reaction with  $\text{NO}^+$  appears to be insensitive to the  $\text{NO}^+/\text{Ru}$  ratio, although they give different products: in fact it has been reported that the chloro derivative gives  $[\text{RuCp}(\text{NO})(\text{PPh}_3)_2]^{2+}$  [13], while from the methyl derivative we have obtained  $[\text{Ru}(\text{Me})\text{Cp}(\text{NO})(\text{PPh}_3)]^+$  as the only product.

The mechanism of the above substitution reactions is apparently a complex one since, as already noted, formation of gas (NO) and phosphine oxide is observed in addition to the organometallic products. In general only a few mechanistic studies [17,18] are reported in the literature, and nothing has been said in the reports dealing with the reaction of the ruthenium chloro complexes  $[\text{Ru}(\text{Cl})\text{Cp}(\text{PR}_3)_2]$  ( $\text{R} = \text{Me}, \text{Ph}$ ) [13] and  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PPh}_3)_2]$  [9e] with  $\text{NO}^+$ . In particular it has not been established whether a direct ligand substitution by  $\text{NO}^+$  occurs or whether one-electron oxidation of the starting chloro compound takes place and is then followed by reaction of the oxidised product with NO generated in the redox process.

In an effort to acquire some mechanistic insight the reaction was monitored by EPR spectroscopy which showed that odd-electron species are involved. Actually, when **1a** and  $\text{NOBF}_4$  were mixed in  $\text{CH}_2\text{Cl}_2$  in an EPR tube, a signal arose after a few minutes at 203 K in fluid solution, consisting of three lines due to the hyperfine interaction of the unpaired electron with the  $^{14}\text{N}$  nucleus of the nitrosyl ligand ( $g_{\text{iso}} = 1.974$ ,  $A(\text{N})_{\text{iso}} = 18.78$  G) (Fig. 4a). The EPR spectrum of the frozen solution is rhombic and is shown in Fig. 4b

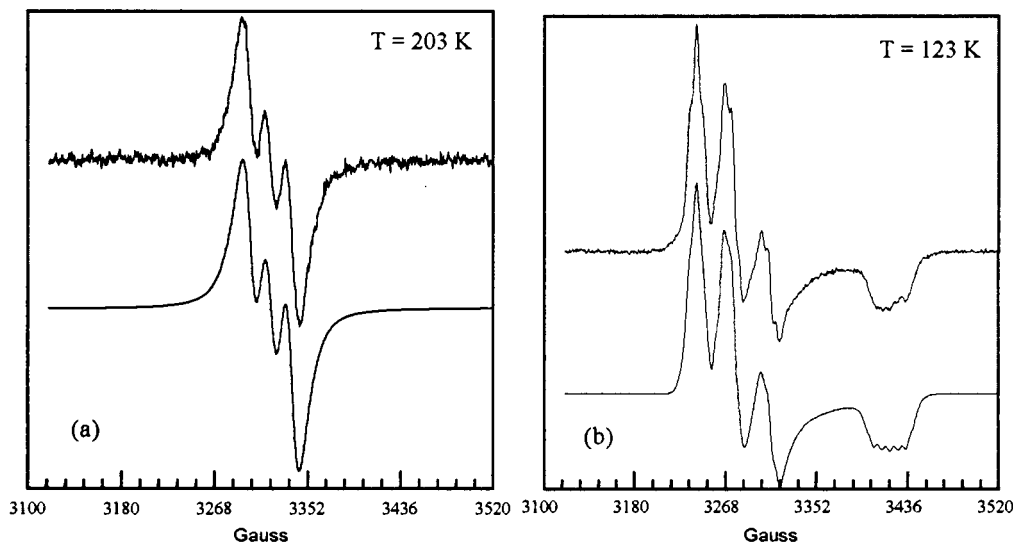


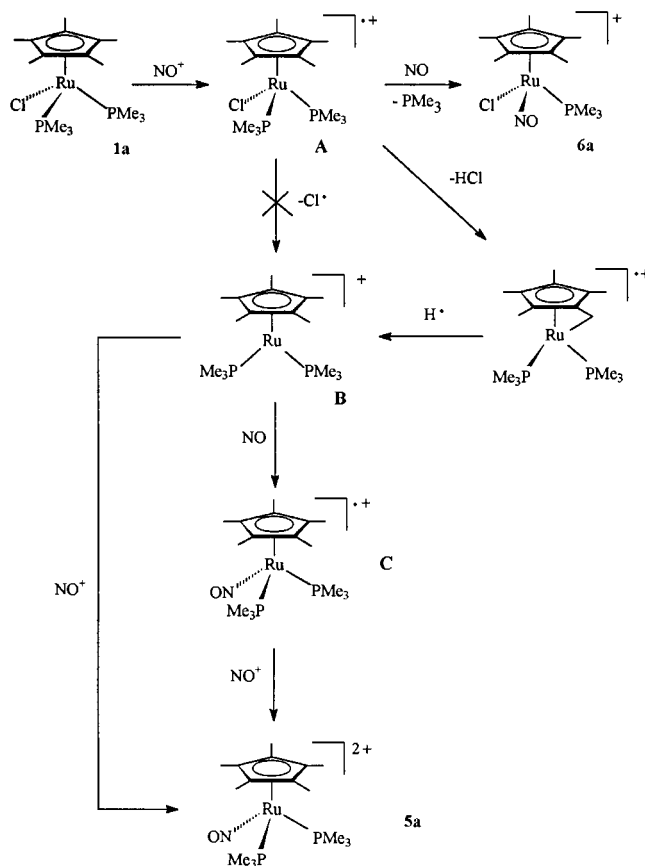
Fig. 4. EPR experimental (upper) and simulated (lower) spectra of the species generated by reaction of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_3)_2]$  (**1a**) with  $\text{NOBF}_4$  in  $\text{CH}_2\text{Cl}_2$ : (a) fluid solution; and (b) frozen solution.

together with the computer simulated spectrum [19]. The parameters are the following:  $g_x = 2.00520$ ,  $g_y = 1.99919$ ,  $g_z = 1.91541$ ;  $A(\text{N})_x = 11.77$  G,  $A(\text{N})_y = 33.34$  G,  $A(\text{N})_z = 13.60$  G,  $A(2\text{P})_x = 7.04$ ,  $A(2\text{P})_y = 6.97$  G,  $A(2\text{P})_z = 7.68$  G.

These parameters are consistent with the structure  $[\text{RuCp}^*(\text{NO})(\text{PMe}_3)_2]^{\bullet+}$ , and are identical to those obtained for the one-electron reduction product of **5a** with cobaltocene [20]. Finally on raising the temperature the intensity of the signal decreased, disappearing at room temperature. The detection of  $[\text{RuCp}^*(\text{NO})(\text{PMe}_3)_2]^{\bullet+}$  is probably of some mechanistic significance since it is possible that the formation of **5a** and/or **6a** occurs by an electron-transfer mechanism as illustrated in Scheme 2. Here it is proposed that the starting chloro compound undergoes a one-electron oxidation to **A**, as already demonstrated for reactions of related iridium compounds with  $\text{NO}^+$  [4b]. **A** can be trapped by  $\text{NO}$  to give **6a** or alternatively can eliminate  $\text{HCl}$  by extracting a hydrogen from a  $\text{Cp}^*$  methyl group giving a “tucked-in” intermediate from which, after extraction of a hydrogen from the solvent to restore the hapticity of the  $\text{Cp}^*$  ligand **B** is obtained. In principle **B** could form also by direct loss of  $\text{Cl}^\bullet$ , but we tend to disregard this possibility in order to explain the behaviour of  $[\text{Ru}(\text{Cl})\text{Cp}(\text{PPh}_3)_2]^{\bullet+}$  for which a different intermediate has been intercepted (see below). Then **B** could react directly with a second equivalent of  $\text{NO}^+$  to give the dicationic compound **5a**, or alternatively could be intercepted by  $\text{NO}$  to give the spectroscopically observed intermediate **C**, which after oxidation by  $\text{NO}^+$  [17b] generates the final product **5a**.

Then **B** might be the crucial intermediate for the formation of **5a**, and the mechanism depicted in Scheme 2 may obviously account for the general neces-

sity of an excess of  $\text{NO}^+$  (a part from the case of **1a**) in order that the dicationic product forms. We have not been able to observe a signal attributable to the other crucial odd-electron species such as  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_3)_2]^{\bullet+}$ , but there may be strong reasons for this



Scheme 2.

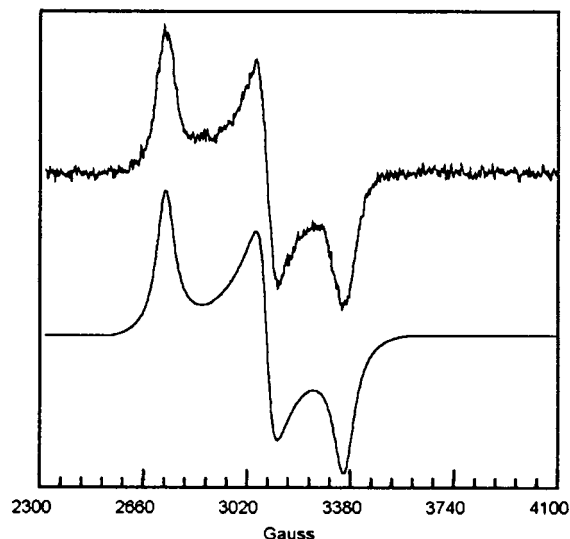


Fig. 5. EPR experimental (upper) and simulated (lower) spectrum of the species generated by reaction of  $[\text{RuClCp}(\text{PPh}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  with  $\text{NOBF}_4$  (frozen solution).

lack of observation: for instance the life time could be quite short for the EPR acquisition times.

Furthermore, although we are not in possession of spectroscopic evidences for the reactions of the corresponding alkyl derivatives with  $\text{NO}^+$ , we propose that a similar mechanistic pattern can hold good. In fact since the alkyl ruthenium derivatives respect to the chloro compounds are more easily oxidised, the odd-electron mechanism should be even more important.

A different intermediate was observed in the case of the reaction of  $[\text{RuClCp}(\text{PPh}_3)_2]$  with  $\text{NOBF}_4$ : a signal arose in the fluid solution at  $g = 2.13$ , but no hyperfine coupling with  $^{14}\text{N}$  was observed. The frozen solution spectrum (Fig. 5) has rhombic parameters:  $g_x = 2.39573$ ,  $g_y = 2.12136$ ,  $g_z = 1.95085$ .

On the basis of computer simulation [19] we assign this spectrum to the one-electron oxidation product of the starting chloro compound  $[\text{RuClCp}(\text{PPh}_3)_2]^{\cdot+}$ . The signal disappeared rapidly before reaching  $0^\circ\text{C}$ . On this basis, and by considering that no cation radical equivalent to the intermediate **C** of Scheme 2 was detected, we propose the simplest mechanism for the formation of the final dication from this radical species as shown in Scheme 3.

The reason why reactions of these chloro compounds with  $\text{NO}^+$  involve different species is not clear: a plausible hypothesis is that  $[\text{RuClCp}(\text{PPh}_3)_2]^{\cdot+}$  cannot

eliminate  $\text{Cl}^\bullet$  because the route via the “tucked-in” intermediate is unavailable, and then undergoes substitution of  $\text{Cl}^-$  with  $\text{NO}^\bullet$ . This could explain well the formation of the dicationic product even when equimolar amounts of  $\text{NO}^+$  are used. Alternatively it is possible that the classical even-electron substitution takes place in addition to the odd-electron pathway. Finally the above picture could explain also why  $[\text{Ru}(\text{Me})\text{Cp}(\text{PPh}_3)_2]$  gives only the phosphine substitution product: in fact formation of methane would be prohibited.

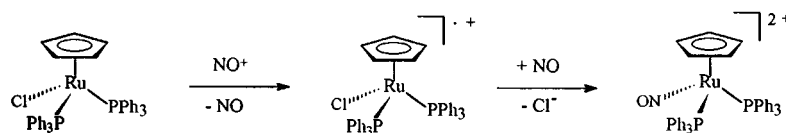
Although further work is necessary in order to validate these ideas, all the above results already show that the mechanistic pathways of these substitution reactions are less obvious than one could suspect, being finely tuned by the nature of the ligands.

### 3. Conclusions

The chemical and electrochemical oxidation of the ruthenium alkyl derivatives described here is reminiscent of what has been found for the iridium complexes  $[\text{Ir}(\text{Me})_2\text{Cp}^*(\text{phosphine})]$  [2], apart from the inability of these ruthenium systems to give ETC-catalysed C–H bond activation. In particular the reaction with  $\text{NO}^+$  produces new cationic nitrosyl compounds that formally derive from alkyl or phosphine substitution by  $\text{NO}^+$ . The corresponding chloro derivatives  $[\text{RuClCp}^*(\text{phosphine})_2]$  undergo the formally analogous chloro or phosphine substitution by  $\text{NO}^+$ . In all these reactions the nature of the products depends essentially on the  $\text{NO}^+/\text{Ru}$  ratio employed. The mechanism of the reaction is intriguing, but EPR studies show that odd-electron species are partially or fully involved even in the seemingly simple case of chloride substitution by  $\text{NO}^+$ .

### 4. Experimental

The reactions and manipulation of organometallics were carried out under dinitrogen or argon using standard techniques. The solvents were dried and distilled prior to use. The compounds  $[\text{RuClCp}^*(\text{L})_2]$  ( $\text{L} = \text{PMe}_3$  (**1a**),  $\text{PMe}_2\text{Ph}$  (**1b**)) were prepared from  $[\text{RuCl}_2\text{Cp}^*]_2$  by reaction with an excess of phosphine, according to the procedure described by Tilley [6b] for the trimethylphosphino derivative (**1a**). Some problems



Scheme 3.



with this method arise in the separation of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$  from the secondary product  $\text{trans}-[\text{Ru}(\text{Cl})_2(\text{PMe}_2\text{Ph})_4]$ : in fact when the phosphine contains aromatic groups the formation of  $\text{trans}-[\text{RuCl}_2\text{L}_4]$  becomes competitive (50–60%) and, since the solubilities of the two products are not so different to allow an easy separation by simple extraction, several crystallisations are required. Then  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$  (**1b**) was obtained in lower yield (27%) than  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_3)_2]$  (**1a**) (53%). As for  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PPh}_3)_2]$  (**1d**) several routes have been reported [6c,9b,d–i]. We have followed three different literature procedures [9d,f,g,i] preparing a product having the following NMR data:  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.13 (t, 15H,  $J_{\text{HP}} = 1.5$  Hz,  $\text{C}_5\text{Me}_5$ ), 6.90–7.80 (m, 30H,  $\text{PPh}_3$ );  $^1\text{H-NMR}$  ( $\text{THF-d}_8$ ):  $\delta$  1.05 (t, 15H,  $\text{C}_5\text{Me}_5$ ), 7.03–7.43 (bm, 30H,  $\text{PPh}_3$ ). Contradictory spectroscopic data are found in the literature: the  $\text{C}_5\text{Me}_5$  resonance is reported either as a singlet at  $\delta = 1.33$  [9b] or as a triplet ( $J_{\text{HP}} = 1$  Hz) at  $\delta = 1.02$  [9e] in  $\text{CDCl}_3$ , and as a singlet at  $\delta = 1.03$  in  $\text{THF-d}_8$  [9i]. We have found that the product is quite unstable in solution: fortuitous or deliberate introduction of air causes a gradual darkening starting from the liquid surface in contact with the atmosphere and a growing of several  $\text{Cp}^*$  signals. In particular the chlorocompound decomposes almost completely in  $\text{CDCl}_3$  solution soon after its solubilisation, even in the absence of air. Then the literature discrepancies for the  $^1\text{H-NMR}$  data in this solvent must be attributed to this behaviour.  $[\text{Ru}(\text{Cl})\text{Cp}(\text{PPh}_3)_2]$  (**2d**) was prepared by direct synthesis from  $\text{RuCl}_3$ , triphenylphosphine and cyclopentadiene in refluxing ethanol according to the published procedure [3a].  $[\text{Ru}(\text{Me})\text{Cp}(\text{PPh}_3)_2]$  was prepared according to the literature [5c,d].  $\text{AgBF}_4$  and  $[\text{FeCp}_2]\text{PF}_6$  were Aldrich products.  $\text{NOBF}_4$  (Aldrich product) was treated under vacuum before use.  $^1\text{H}$ -,  $^{31}\text{P}$ -,  $^2\text{H-NMR}$  spectra were recorded on Varian Gemini 200 and VXR 300 instruments. Mass spectroscopy was performed on a Perkin–Elmer Sciex API III plus instrument. Mass values are given for the  $^{102}\text{Ru}$  isotope. EPR spectra for the chemical oxidation reactions were obtained by using EPR Varian E 112 instrument equipped with a Varian E 257 for temperature control. The spectrometer was interfaced to an AST Premium 486/25 by means of a data acquisition system capable of acquiring up to 500 000 12-bit samples  $\text{s}^{-1}$ , including 32-bit add to memory, thus giving on-line signal averaging and a software package specially designed for EPR experiments [21]. Material and apparatus used for electrochemistry and coupled EPR measurements have been described elsewhere [22]. All the potential values are referred to the saturated calomel electrode (SCE): under the present experimental conditions the one-electron oxidation of ferrocene occurs at +0.44 V ( $\text{CH}_2\text{Cl}_2$ ). Elemental analyses were performed by the Laboratorio di Mi-

croanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, University of Pisa.

#### 4.1. Preparation of $[\text{Ru}(\text{Me})\text{Cp}^*(\text{PMe}_3)_2]$ **2a**

$[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_3)_2]$  (**1a**) (0.21 g, 0.496 mmol) was treated under stirring with  $\text{MeMgI}$  (2.8 ml of a 0.91 M solution in diethyl ether, 2.48 mmol). The mixture was stirred for 24 h at room temperature (r.t.), then evaporated to dryness. The residue was extracted with pentane and treated with 1,4-dioxane (1 ml). After removal of the magnesium salts the resulting solution was evaporated to dryness. The residue was extracted with pentane and hydrolysed with water. The organic extracts were dried over anhydrous sodium sulfate and the solvent was removed in vacuo to give (0.14 g, 70%) of  $[\text{Ru}(\text{Me})\text{Cp}^*(\text{PMe}_3)_2]$  (**2a**) as a pale-yellow oil [6c]. Anal. Found: C, 49.7; H, 9.3. Calc. for  $\text{C}_{17}\text{H}_{36}\text{P}_2\text{Ru}$ : C, 50.6; H, 8.9%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  –0.29 (t, 3H,  $J_{\text{HP}} = 6.9$  Hz,  $\text{RuMe}$ ), 1.1 (vt, 18H,  $^2J_{\text{HP}} + ^4J_{\text{HP}} = 10.6$  Hz,  $\text{PMe}_3$ ), 1.7 (t, 15H,  $J_{\text{HP}} = 1.2$  Hz,  $\text{C}_5\text{Me}_5$ );  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  –0.75 (t, 3H,  $\text{RuMe}$ ), 1.19 (vt, 18H,  $\text{PMe}_3$ ), 1.67 (t, 15H,  $\text{C}_5\text{Me}_5$ ).

#### 4.2. Preparation of $[\text{Ru}(\text{Me})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$ **2b**

$[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$  (**1b**) (0.241 g, 0.44 mmol) was treated under stirring with  $\text{MgMeI}$  (2.9 ml of a 0.91 M solution in diethyl ether, 2.64 mmol). After 72 h at r.t. the reaction mixture was worked out as above. A pale-yellow oil (0.159 g, 68%) was obtained having the same properties as  $[\text{Ru}(\text{Me})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$  (**2b**) [6c].  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.05 (t, 3H,  $J_{\text{HP}} = 6.0$  Hz,  $\text{RuMe}$ ), 1.15 (vt, 6H,  $^2J_{\text{HP}} + ^4J_{\text{HP}} = 7.2$  Hz,  $\text{PMe}$ ), 1.35 (vt, 6H,  $^2J_{\text{HP}} + ^4J_{\text{HP}} = 7.4$  Hz,  $\text{PMe}$ ), 1.5 (t, 15H,  $J_{\text{HP}} = 1.4$  Hz,  $\text{C}_5\text{Me}_5$ ), 7.05 (bm, 6H, Ph), 7.45 (bm, 4H, Ph);  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta$  –0.07 (t, 3H,  $\text{RuMe}$ ), 1.14 (vt, 6H,  $\text{PMe}$ ), 1.32 (vt, 6H,  $\text{PMe}$ ), 1.46 (t, 15H,  $\text{C}_5\text{Me}_5$ ), 7.0–7.5 (bm, 10H, Ph).

#### 4.3. Preparation of $[\text{Ru}(\text{CH}_2\text{CMe}_3)\text{Cp}^*(\text{PMe}_3)_2]$ **3a**

Compound **1a** (0.30 g, 0.708 mmol) was reacted with  $(\text{Me}_3\text{CCH}_2)\text{MeCl}$  (6.94 ml of a 0.51 M solution in diethyl ether, 3.54 mmol) following the same procedure described for **2a** to give 0.234 g (72%) of a yellow oil having the same properties as  $[\text{Ru}(\text{CH}_2\text{CMe}_3)\text{Cp}^*(\text{PMe}_3)_2]$  (**2a**) prepared as reported in the literature [6c]. Anal. Found: C, 55.4; H, 8.9. Calc. for  $\text{C}_{21}\text{H}_{44}\text{P}_2\text{Ru}$ : C, 54.9; H, 9.6%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.01 (t, 2H,  $J_{\text{HP}} = 5.8$  Hz,  $\text{RuCH}_2$ ), 1.15 (vt, 18H,  $^2J_{\text{HP}} + ^4J_{\text{HP}} = 7.2$  Hz,  $\text{PMe}_3$ ), 1.30 (s, 9H,  $\text{CMe}_3$ ), 1.67 (t, 15H,  $J_{\text{HP}} = 1.4$  Hz,  $\text{C}_5\text{Me}_5$ );  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.74 (t, 2H,  $\text{RuCH}_2$ ), 0.91 (s, 9H,  $\text{CMe}_3$ ), 1.28 (vt, 18H,  $\text{PMe}_3$ ), 1.68 (t, 15H,  $\text{C}_5\text{Me}_5$ ).

**4.4. General procedure for the reaction of [RuRCp\*L<sub>2</sub>] (R = Me, L = PMe<sub>3</sub> **2a**, PMe<sub>2</sub>Ph **2b**; R = CH<sub>2</sub>CMe<sub>3</sub>, L = PMe<sub>3</sub> **4a** and [RuMeCp(PPh<sub>3</sub>)<sub>2</sub>] **4d** with AgPF<sub>6</sub> or [FeCp<sub>2</sub>]PF<sub>6</sub>**

In an NMR tube the appropriate amount of [FeCp<sub>2</sub>]PF<sub>6</sub> or AgBF<sub>4</sub> was added to 0.030 g of the ruthenium complex dissolved in C<sub>6</sub>D<sub>6</sub> or CD<sub>3</sub>CN (1 ml), and the reaction was followed by <sup>1</sup>H-NMR spectroscopy.

**4.5. Reaction of [Ru(Me)Cp\*(PMe<sub>3</sub>)<sub>2</sub>] (**2a**) with equimolar amounts of NOBF<sub>4</sub>: formation of [Ru(Me)Cp\*(NO)(PMe<sub>3</sub>)]BF<sub>4</sub> **7a****

NOBF<sub>4</sub> (0.044 g, 0.376 mmol) was added under stirring to a solution of **2a** (0.15 g, 0.372 mmol) in 10 ml of dichloromethane. After the mixing of the reactants NOBF<sub>4</sub> gradually dissolved to give a ruby solution and a moderate formation of gas. After an hour at r.t., the solution was evaporated under vacuum to give a residue which was washed repeatedly with pentane and dried. A deep-red oil (0.125 g, 76%) was obtained which was identified as [Ru(Me)Cp\*(NO)(PMe<sub>3</sub>)]BF<sub>4</sub> (**7a**). Anal. Found: C, 37.0; H, 5.9; N, 3.0. Calc. for C<sub>14</sub>H<sub>27</sub>BF<sub>4</sub>NOPRu: C, 37.8; H, 6.1; N, 3.2%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.93 (d, 15H, J<sub>HP</sub> = 1.7 Hz, C<sub>5</sub>Me<sub>5</sub>), 1.64 (d, 9H, J<sub>HP</sub> = 10.9 Hz, PMe<sub>3</sub>), 0.86 (d, 3H, J<sub>HP</sub> = 6.1 Hz, RuMe); <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.94 (d, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.64 (d, 9H, PMe<sub>3</sub>), 0.9 (d, 3H, RuMe); FT-IR (Nujol) (cm<sup>-1</sup>): ν<sub>s</sub>(NO) 1800; ν<sub>s</sub>(BF) 1059; IS-MS (CH<sub>3</sub>OH): m/e 358 [M]<sup>+</sup>; 342 [M - CH<sub>4</sub>]<sup>+</sup>; 87 [BF<sub>4</sub>]<sup>-</sup>.

**4.6. Reaction of [Ru(Me)Cp\*(PMe<sub>3</sub>)<sub>2</sub>] **2a** with an excess di-NOBF<sub>4</sub>: formation of [RuCp\*(NO)(PMe<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> **5a** and [Ru(Me)Cp\*(NO)(PMe<sub>3</sub>)]BF<sub>4</sub> **7a****

NOBF<sub>4</sub> (0.191 g, 1.64 mmol) was added under stirring to a solution of **2a** (0.33 g, 0.819 mmol) in 15 ml of dichloromethane. Soon after mixing of the reagents methane was evolved (δ = 0.20, CD<sub>2</sub>Cl<sub>2</sub>), while a ruby-red solution formed with a dark-orange precipitate. The mixture was stirred at r.t. for 1 h, then the solid was separated from the solution, and washed with dichloromethane, benzene, pentane, and finally dried under vacuum. The residue was purified by adding dropwise a concentrated solution in acetone (1 ml) to a large excess of diethyl ether (10 ml). Pale-yellow crystals (0.14 g, 30%) of [RuCp\*(NO)(PMe<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**5a**) were obtained. The above solution was evaporated under vacuum and the residue was washed with pentane and dried under reduced pressure. The resulting oil was purified by adding a concentrated solution in dichloromethane to a large excess of diethyl ether to give a deep-red oil (0.18 g, 50%) which was identified as **7a**.

Compound **5a**: Anal. Found: C, 31.8; H, 5.9; N, 2.1. Calc. for C<sub>16</sub>H<sub>33</sub>B<sub>2</sub>F<sub>8</sub>NOP<sub>2</sub>Ru: C, 32.5; H, 5.6; N 2.4%. <sup>1</sup>H-NMR (CD<sub>3</sub>NO<sub>2</sub>): δ 2.23 (t, 15H, J<sub>HP</sub> = 2.0 Hz, C<sub>5</sub>Me<sub>5</sub>), 2.00 (vt, 18H, <sup>2</sup>J<sub>HP</sub> + <sup>4</sup>J<sub>HP</sub> = 11.2 Hz, PMe<sub>3</sub>); <sup>1</sup>H-NMR (CD<sub>3</sub>OD): δ 2.23 (t, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.00 (vt, 18H, PMe<sub>3</sub>); <sup>1</sup>H-NMR (D<sub>2</sub>O): δ 1.98 (t, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.76 (vt, 18H, PMe<sub>3</sub>); <sup>1</sup>H-NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 2.3 (t, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.11 (vt, 18H, PMe<sub>3</sub>); <sup>1</sup>H-NMR (CD<sub>3</sub>CN): δ 2.06 (t, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.84 (vt, 18H, PMe<sub>3</sub>); <sup>31</sup>P-NMR (CD<sub>3</sub>OD): δ -1.97; <sup>13</sup>C-NMR (CD<sub>3</sub>OD): δ 10.86 (C<sub>5</sub>Me<sub>5</sub>), 18 (vt, <sup>1</sup>J<sub>CP</sub> + <sup>3</sup>J<sub>CP</sub> = 36.0 Hz, PMe<sub>3</sub>), 115.09 (C<sub>5</sub>Me<sub>5</sub>); FT-IR (Nujol) (cm<sup>-1</sup>): ν<sub>s</sub>(NO) 1845; ν<sub>s</sub>(BF) 1060; IS-MS (CH<sub>3</sub>OH): m/e 209.5 [M]<sup>++</sup>; 87 [BF<sub>4</sub>]<sup>-</sup>.

**4.7. Preparation of [Ru(Me)Cp\*(NO)(PMe<sub>2</sub>Ph)]BF<sub>4</sub> **7b** by reaction of [Ru(Me)Cp\*(PMe<sub>2</sub>Ph)<sub>2</sub>] **2b** with equimolar amounts of NOBF<sub>4</sub>**

The preparation is analogous to that of **7a**: 0.102 g (0.19 mmol) of **2b** in 6 ml CH<sub>2</sub>Cl<sub>2</sub> were treated with 0.023 g (0.19 mmol) of NOBF<sub>4</sub> to give after 2 h at r.t. a maroon oil (70%), identified as [Ru(Me)Cp\*(NO)(PMe<sub>2</sub>Ph)]BF<sub>4</sub> (**7b**). Anal. Found: C, 44.8; H, 6.1; N, 2.1. Calc. for C<sub>19</sub>H<sub>29</sub>BF<sub>4</sub>NOPRu: C, 45.1; H, 5.8; N, 2.8%. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.03 (d, 3H, J<sub>HP</sub> = 6.1 Hz, RuMe), 1.84 (d, 3H, J<sub>HP</sub> = 10.7 Hz, PMe), 1.86 (d, 3H, J<sub>HP</sub> = 10.3 Hz, PMe), 1.73 (d, 15H, J<sub>HP</sub> = 1.8 Hz, C<sub>5</sub>Me<sub>5</sub>), 7.2–7.6 (bm, 5H, Ph); <sup>1</sup>H-NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 1.84 (d, 3H, RuMe), 2.01 (d, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.43 (d, 6H, PMe), 2.47 (d, 6H, PMe), 7.5–7.9 (bm, 5H, Ph); FT-IR (Nujol) (cm<sup>-1</sup>): ν<sub>s</sub>(NO) 1834; ν<sub>s</sub>(BF) 1060.

**4.8. Reaction of [Ru(Me)Cp\*(PMe<sub>2</sub>Ph)<sub>2</sub>] **2b** with an excess of NOBF<sub>4</sub>: Preparation of [RuCp\*(NO)(PMe<sub>2</sub>Ph)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> **5b** and [Ru(Me)Cp\*(NO)(PMe<sub>2</sub>Ph)]BF<sub>4</sub> **7b****

The reaction is analogous to that of **2a**. 0.1 g (0.19 mmol) of **2b** in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> were reacted with 0.044 g (0.38 mmol) of NOBF<sub>4</sub> to give after 2 h [RuCp\*(NO)(PMe<sub>2</sub>Ph)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**5b**) as a light-orange solid (0.02 g, 15%) and [Ru(Me)Cp\*(NO)(PMe<sub>2</sub>Ph)]BF<sub>4</sub> (**7b**) as a dark-red oil (0.05 g, 50%). **5b** Anal. Found: C, 43.1; H, 5.8; N, 2.0. Calc. for C<sub>26</sub>H<sub>37</sub>B<sub>2</sub>F<sub>8</sub>NOP<sub>2</sub>Ru: C, 43.6; H, 5.2; N, 1.96%. <sup>1</sup>H-NMR (CD<sub>3</sub>)<sub>2</sub>CO): δ 1.95 (t, 15H, J<sub>HP</sub> = 2.0 Hz, C<sub>5</sub>Me<sub>5</sub>), 2.10 (vt, 6H, <sup>2</sup>J<sub>HP</sub> + <sup>4</sup>J<sub>HP</sub> = 10.8 Hz, PMe), 2.35 (vt, 6H, <sup>2</sup>J<sub>HP</sub> + <sup>4</sup>J<sub>HP</sub> = 11.0 Hz, PMe), 7.6–8.1 (bm, 10H, Ph); FT-IR (Nujol) (cm<sup>-1</sup>): ν<sub>s</sub>(NO) 1800; ν<sub>s</sub>(BF) 1055.

**4.9. Reaction of [Ru(CH<sub>2</sub>CMe<sub>3</sub>)Cp\*(PMe<sub>3</sub>)<sub>2</sub>] **3a** with an excess of NOBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>: formation of [RuCp\*(NO)(PMe<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> **5a** and [Ru(CH<sub>2</sub>CMe<sub>3</sub>)Cp\*(NO)(PMe<sub>3</sub>)]BF<sub>4</sub>**

To **3a** (0.22 g, 0.48 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15

ml)  $\text{NOBF}_4$  (0.112 g, 0.96 mmol) was added. The mixing of the reagents is followed by a gas effervescence and by the formation of an orange solid. The colour of the solution changed from yellow-green to deep-red. The reaction mixture was maintained under stirring for 1 h. The solid precipitated was washed with dichloromethane, benzene and pentane, dried and purified by dropping an acetone solution to a large excess of diethyl ether (11:1). 0.081 g (29%) of **5a** were obtained. The solution was evaporated at reduced pressure and the residue was purified by dropping a dichloromethane solution to an excess of diethyl ether (20:1). 0.1 g (40%) of a deep-red solid, identified as  $[\text{Ru}(\text{CH}_2\text{CMe}_3)\text{Cp}^*(\text{NO})(\text{PMe}_3)]\text{BF}_4$ , were obtained. Anal. Found: C, 42.9; H, 6.8; N, 2.5. Calc. for  $\text{C}_{18}\text{H}_{35}\text{BF}_4\text{NOPRu}$ : C, 43.2; H, 7.0; N, 2.8%.  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.59 (d, 2H,  $J_{\text{HP}} = 7.8$  Hz,  $\text{CH}_2$ ), 0.86 (s, 9H,  $\text{CMe}_3$ ), 1.83 (d, 9H,  $J_{\text{HP}} = 11.9$  Hz,  $\text{PMe}_3$ ), 1.97 (d, 15H,  $J_{\text{HP}} = 2.1$  Hz,  $\text{C}_5\text{Me}_5$ ); FT-IR (Nujol) ( $\text{cm}^{-1}$ ):  $\nu_s$  (NO) 1806;  $\nu_s$  (BF) 1062.

**4.10. Reaction of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_3)_2]$  **1a** with  $\text{NOBF}_4$ : formation of  $[\text{RuCp}^*(\text{NO})(\text{PMe}_3)_2](\text{BF}_4)_2$  **5a** and  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PMe}_3)]\text{BF}_4$  **6a****

The reaction proceeds without variations by using a molar ratio  $\text{NO}^+/\text{Ru}$  of 1 or 2. As an example we report the reaction carried out by using equimolar amounts of reactants.  $\text{NOBF}_4$  (0.0065 g, 0.055 mmol) was added under stirring to a solution of **1a** (0.023 g, 0.055 mmol) in 1 ml of  $\text{CH}_2\text{Cl}_2$ . A gas evolved, the solution underwent a rapid colour change from orange to deep-red and a precipitate formed. After stirring 2 h at r.t., the precipitate was separated from the solution, washed with benzene and pentane, then dried. A beige solid (0.008 g, 26%) was obtained identified as  $[\text{RuCp}^*(\text{NO})(\text{PMe}_3)_2](\text{BF}_4)_2$  (**5a**). Removal of the solvent from the decanted  $\text{CH}_2\text{Cl}_2$  solution, followed by washing with pentane, gave  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PMe}_3)]\text{BF}_4$  (**6a**) (0.013 g, 50%) as a deep-red oil. **6a**  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.48 (d, 9H,  $J_{\text{HP}} = 12.9$  Hz,  $\text{PMe}_3$ ), 1.97 (d, 15H,  $J_{\text{HP}} = 1.9$  Hz,  $\text{C}_5\text{Me}_5$ ); IS-MS ( $\text{CH}_3\text{OH}$ ):  $m/e$  372  $[\text{M}]^+$ ; 87  $[\text{BF}_4]^-$ ; FT-IR (Nujol) ( $\text{cm}^{-1}$ ):  $\nu_s$  (NO) 1806;  $\nu_s$  (BF) 1059.

**4.11. Reaction of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$  **1b** with equimolar amounts of  $\text{NOBF}_4$ : formation of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PMe}_2\text{Ph})]\text{BF}_4$  **6b****

$\text{NOBF}_4$  (0.004 g, 0.034 mmol) was added in an NMR tube to a solution of **1b** (0.019 g, 0.034 mmol) in  $\text{CD}_2\text{Cl}_2$ . A gas evolved and the colour changed from orange to deep-red. After 3 h at r.t. a product formed which was identified as  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PMe}_2\text{Ph})]\text{BF}_4$  (**6b**) (92%) from the  $^1\text{H-NMR}$  spectrum. The yield was evaluated by comparison of the  $\text{C}_5\text{Me}_5$  integrated area

respect to the residual protons of the deuteriated solvent.  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.74 (d, 15H,  $J_{\text{HP}} = 2.2$  Hz,  $\text{C}_5\text{Me}_5$ ), 2.07 (d, 3H,  $J_{\text{HP}} = 11.9$  Hz,  $\text{PMe}$ ), 2.17 (d, 3H,  $J_{\text{HP}} = 11.6$  Hz,  $\text{PMe}$ ), 7.5–7.9 (bm, 5H,  $\text{PPh}$ ); IS-MS ( $\text{CH}_3\text{OH}$ ):  $m/e$  440  $[\text{M}]^+$ ; 87  $[\text{BF}_4]^-$ ; FT-IR (Nujol) ( $\text{cm}^{-1}$ ):  $\nu_s$  (NO) 1809;  $\nu_s$  (BF) 1059.

**4.12. Reaction of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PMe}_2\text{Ph})_2]$  **1b** with an excess of  $\text{NOBF}_4$ : formation of  $[\text{RuCp}^*(\text{NO})(\text{PMe}_2\text{Ph})_2](\text{BF}_4)_2$  **5b** and  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PMe}_2\text{Ph})]\text{BF}_4$  **6b****

$\text{NOBF}_4$  (0.025 g, 0.21 mmol) was added to **1b** (0.12 g, 0.22 mmol) dissolved in 20 ml of  $\text{CD}_2\text{Cl}_2$ . Soon after the mixing of the reagents the colour changed from orange to deep-red and an orange solid precipitated. After 2 h of stirring at r.t., the solid was separated and washed repeatedly with dichloromethane, benzene and pentane and dried to give  $[\text{RuCp}^*(\text{NO})(\text{PMe}_2\text{Ph})_2](\text{BF}_4)_2$  (**5b**) (0.016 g, 10%) as a light-orange solid. The solution, previously decanted, was evaporated under vacuum and the residue was washed with pentane and dried under vacuum to give  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PMe}_2\text{Ph})]\text{BF}_4$  (**6b**) (0.08 g, 70%) as a dark-red oil. **5b**  $^1\text{H-NMR}$  ( $\text{CD}_3)_2\text{CO}$ ):  $\delta$  1.95 (t, 15H,  $J_{\text{HP}} = 2.0$  Hz,  $\text{C}_5\text{Me}_5$ ), 2.10 (vt, 6H,  $^2J_{\text{HP}} + ^4J_{\text{HP}} = 10.8$  Hz,  $\text{PMe}$ ), 2.35 (vt, 6H,  $^2J_{\text{HP}} + ^4J_{\text{HP}} = 11.0$  Hz,  $\text{PMe}$ ), 7.6–8.1 (bm, 10H,  $\text{Ph}$ ); FT-IR (Nujol) ( $\text{cm}^{-1}$ ):  $\nu_s$  (NO) 1800;  $\nu_s$  (BF) 1055.

**4.13. Reaction of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{PPh}_3)_2]$  **1d** with  $\text{NOBF}_4$  in  $\text{CH}_2\text{Cl}_2$ : formation of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PPh}_3)]\text{BF}_4$  **6d****

The reaction proceeds without substantial differences utilizing a molar ratio  $\text{NO}^+/\text{Ru} = 1$  or 2. As described for **6a**, 0.180 g (0.23 mmol) of **1d** were treated with 0.053 g (0.46 mmol) of  $\text{NOBF}_4$  in 11 ml of  $\text{CH}_2\text{Cl}_2$  to give light-red crystals of  $[\text{Ru}(\text{Cl})\text{Cp}^*(\text{NO})(\text{PPh}_3)]\text{BF}_4$  (**6d**) (0.117 g, 80%). Anal. Found: C, 52.26; H, 4.80; N, 2.05. Calc. for  $\text{C}_{28}\text{H}_{30}\text{BClF}_4\text{NOPRu}$ : C, 51.6; H, 4.6; N, 2.15%.  $^1\text{H-NMR}$  ( $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  1.84 (d, 15H,  $J_{\text{HP}} = 2.3$  Hz,  $\text{C}_5\text{Me}_5$ ), 7.5–7.8 (bm, 18H,  $\text{PPh}_3$ ); IS-MS ( $\text{CH}_3\text{OH}$ ):  $m/e$  566  $[\text{M} - \text{NO} + \text{MeOH}]^+$ ; 87  $[\text{BF}_4]^-$ ; FT-IR (Nujol) ( $\text{cm}^{-1}$ ):  $\nu_s$  (NO) 1805,  $\nu_s$  (BF) 1059.

**4.14. Reaction of  $[\text{Ru}(\text{Me})\text{Cp}(\text{PPh}_3)_2]$  (**4d**) with  $\text{NOBF}_4$ : formation of  $[\text{Ru}(\text{Me})\text{Cp}(\text{NO})(\text{PPh}_3)]\text{BF}_4$**

Reactions carried out using a  $\text{NO}^+/\text{Ru}$  molar ratio of 1 or 2 afford identical results. As an example we describe the following procedure. **4d** (0.012 g, 0.017 mmol) dissolved in  $\text{CD}_2\text{Cl}_2$  (0.75 ml) was treated with  $\text{NOBF}_4$  (0.004 g, 0.034 mmol). A gas evolved and a variation of colour from yellow to red was observed. After 6 h at r.t., the  $^1\text{H-NMR}$  spectrum showed the

quantitative formation of  $[\text{Ru}(\text{Me})\text{Cp}(\text{NO})(\text{PPh}_3)]\text{BF}_4$ . The solution was evaporated under vacuum and the residue was purified by addition of a solution in  $\text{CH}_2\text{Cl}_2$  to a large excess of diethyl ether to give pale-yellow crystals (67%) of  $[\text{Ru}(\text{Me})\text{Cp}(\text{NO})(\text{PPh}_3)]\text{BF}_4$ .  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.42 (d, 3H,  $J_{\text{HP}} = 5$  Hz, RuMe), 5.7 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.3–7.7 (bm, 15H,  $\text{PPh}_3$ ); FT-IR (Nujol) ( $\text{cm}^{-1}$ ):  $\nu_s$  (NO) 1811;  $\nu_s$  (BF) 1066; IS-MS ( $\text{CH}_3\text{OH}$ ):  $m/e$  474  $[\text{M}]^+$ ; 458  $[\text{M} - \text{CH}_4]^+$ ; 429  $[\text{M} - \text{MeNO}]^+$ ; 87  $[\text{BF}_4]^-$ .

#### 4.15. EPR spectral studies of the reactions of the chloro and methyl derivatives with $\text{NOBF}_4$

A weighed amount of metal complex (typically, 5 mg) and  $\text{NOBF}_4$  (1–2 mg) was placed into a quartz tube (o.d. 3 mm; i.d. 2 mm) fitted with a quartz-Pyrex joint and a Corning Rotaflon Teflon tap (DISA, Milan, Italy). The tube was attached to a vacuum line and degassed by standard vacuum/argon techniques; then it was immersed in a dry ice-cooled acetone bath and charged with dichloromethane. The quartz tube was then introduced into the spectrometer cavity, pre-cooled to the desired temperature, and the reagents were allowed to mix gradually. The hyperfine coupling constants and linewidths were obtained by computer simulation of the EPR spectra.

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#### References

- [1] D. Astruc, *Electron Transfer and Radical Processes in Transition Metal Chemistry*, VCH Publishers, New York, 1995 (and references cited therein).
- [2] (a) P. Diversi, S. Iacononi, G. Ingrosso, F. Laschi, A. Lucherini, P. Zanello, *J. Chem. Soc. Dalton Commun.* (1993) 351. (b) P. Diversi, S. Iacononi, G. Ingrosso, F. Laschi, A. Lucherini, C. Pinzino, G. Uccello-Barretta, P. Zanello, *Organometallics* 14 (1995) 3275. (c) F. de Biani Fabrizi, P. Diversi, A. Ferrarini, G. Ingrosso, F. Laschi, A. Lucherini, C. Pinzino, G. Uccello-Barretta, P. Zanello, *Gazz. Chim. It.* 126 (1996) 391.
- [3] A. Pedersen, M. Tilset, *J. Am. Chem. Soc.* 116 (1994) 4887.
- [4] (a) P. Diversi, V. Ermini, G. Ingrosso, A. Lucherini, C. Pinzino, F. Simoncini, *J. Organomet. Chem.* 555 (1998) 135. (b) P. Diversi, F. Fabrizi de Biani, G. Ingrosso, F. Laschi, A. Lucherini, C. Pinzino, P. Zanello, *J. Organomet. Chem.* 584 (1999) 73.
- [5] A. Ceccanti, P. Diversi, G. Ingrosso, F. Laschi, A. Lucherini, S. Magagna, P. Zanello, *J. Organomet. Chem.* 526 (1996) 251.
- [6] (a) T. Blackmore, M.I. Bruce, F.G.A. Stone, *J. Chem. Soc. A* (1971) 2376. (b) T.D. Tilley, R.H. Grubbs, J.E. Bercaw, *Organometallics* 3 (1984) 274. (c) H. Lehmkuhl, M. Bellenbaum, J. Grundke, H. Mauermann, C. Krüger, *Chem. Ber.* 121 (1988) 1719 (and references cited therein).
- [7] M.F. Joseph, J.A. Page, M.C. Baird, *Organometallics* 3 (1984) 1749.
- [8] T. Aase, M. Tilset, V.D. Parker, *J. Am. Chem. Soc.* 112 (1990) 4974.
- [9] (a) M. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, *Inorg. Synth.* 28 (1991) 270. (b) P.M. Treichel, D.A. Komar, P.J. Vincenti, *Synth. React. Inorg. Met.-Org. Chem.* 14 (1984) 383. (c) N. Oshima, H. Suzuki, Y. Moro-oka, *Chem. Lett.* (1984) 1161. (d) T. Arliguie, B. Chaudret, *J. Chem. Soc. Chem. Commun.* (1986) 985. (e) F.M. Conroy-Lewis, S.J. Simpson, *J. Organomet. Chem.* 322 (1987) 221. (f) T. Arliguie, C. Border, B. Chaudret, J. Devillers, R. Poiblan, *Organometallics* 8 (1989) 1308. (g) M.S. Chinn, D.M. Heinekey, *J. Am. Chem. Soc.* 112 (1990) 5166. (h) P.J. Fagan, W.S. Mahoney, J.C. Calabrese, I.D. Williams, *Organometallics* 9 (1990) 1843. (i) L. Luo, S.P. Nolan, P.J. Fagan, *Organometallics* 12 (1993) 4305. (j) R.T. Lubián, M.A. Paz-Sandoval, *J. Organomet. Chem.* 532 (1997) 17. (k) D.C. Smith, Jr., C.M. Haar, L. Luo, C. Li, M.E. Cucullu, C.H. Mahler, S.P. Nolan, *Organometallics* 18 (1999) 2357.
- [10] E.R. Brown, J.R. Sandifer, in: B.W. Rossiter, J.F. Hamilton (Eds.), *Physical Methods of Chemistry: Electrochemical Methods*, vol. Vol. 2, Wiley, New York, 1986 (Chap. 4).
- [11] F.E. Mabbs, D. Collison, *Electron Paramagnetic Resonance of d Transition Metal Compounds*. In: *Studies in Inorganic Chemistry*, vol. Vol. 16, Elsevier, New York, 1992.
- [12] J.P. Lozos, B.M. Hoffman, C.G. Franz, *QCPE* 243 (1973) 11.
- [13] M.I. Bruce, I.B. Tomkins, F.S. Wong, B.W. Skelton, A.H. White, *J. Chem. Soc. Dalton Trans.* (1982) 687.
- [14] (a) M. Halmann, L. Kugel, *J. Chem. Soc.* (1962) 3273. (b) A.R. Middleton, G. Wilkinson, *J. Chem. Soc.* (1981) 1898.
- [15] (a) S. Yasui, K. Shioji, M. Tsujimoto, A. Ohno, *J. Chem. Soc. Perkin Trans. 2* (1999) 855. (b) S. Yasui, M. Fujii, C. Kawano, Y. Nishimura, A. Ohno, *Tetrahedron Lett.* 32 (1991) 5601.
- [16] (a) C.A. Tolman, *Chem. Rev.* 77 (1977) 313. (b) R. Longhi, R.O. Ragsdale, R.S. Drago, *Inorg. Chem.* 1 (1962) 768. (c) M.M. Rahman, H.Y. Liu, K. Eriks, A. Prock, W.P. Giering, *Organometallics* 6 (1987) 650.
- [17] N.G. Connelly, J.D. Davies, *J. Organomet. Chem.* 38 (1972) 385.
- [18] (a) K.G. Caulton, *Coord. Chem. Rev.* 14 (1975) 317. (b) N.G. Connelly, W.E. Geiger, *Chem. Rev.* 96 (1996) 877.
- [19] (a) The software was provided by the Illinois EPR Research Center, NIH Division of research, Resonances Grant. RR01811. (b) K.J. Mattson, R.B. Clarkson, R.L. Belford, in 11th International EPR Symposium, 30th Rocky Mountains Conference, Denver, CO, August 1988.
- [20] P. Diversi, M. Fuligni, C. Pinzino, unpublished results.
- [21] R. Ambrosetti, D. Ricci, *Rev. Sci. Instrum.* 62 (1991) 2281; EPR-ENDOR, ICQEM-CNR, 1992.
- [22] D. Osella, M. Ravera, C. Nervi, C.E. Housecroft, P.R. Raithby, P. Zanello, F. Laschi, *Organometallics* 10 (1991) 3253.