

Synthesis and crystal structure of the six-coordinate ruthenium nitrosyl complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$

Fiona M. Conroy-Lewis, Alan D. Redhouse * and Stephen J. Simpson *

Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT (UK)

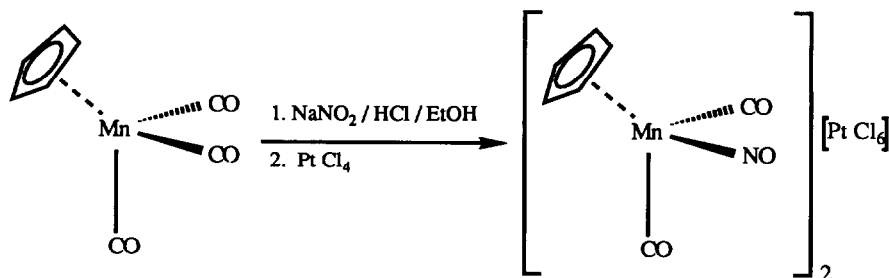
(Received June 8th, 1990)

Abstract

Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ (1) with sodium nitrite in hot acidified ethanol followed by anion exchange gave the red crystalline solid $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$ (2) in good yield. Compound 2 has been crystallographically characterised and shows a large interligand angle at ruthenium between the chloride and nitrosyl ligands. The dication $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{NO})][\text{BF}_4]_2\}$ (4) has been prepared from $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{Cl})]$ (3) and nitrosonium tetrafluoroborate.

Introduction

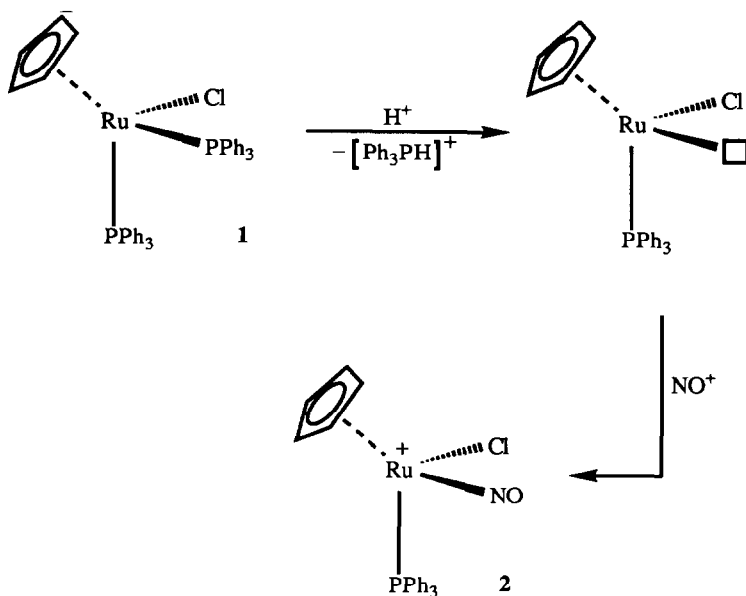
Nitrosyl complexes are known for most of the transition metal block and have been prepared mainly from nitric oxide or nitrosonium salts. The oxidation of ammine salts by nitrates [1] or perchloric acid [2] has also been reported. Piper, Cotton, and Wilkinson described some very vigorous approaches in early papers involving the addition of concentrated nitric acid to hot ethanol solutions or the milder alternative of generating nitrous acid in hot ethanol [3]. An interesting historical feature of this work was the use of platinum tetrachloride in hydrochloric acid to allow isolation of cationic products as the hexachloroplatinate salt, for example:



The dicationic nitrosyls $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NO})][\text{PF}_6]_2\}$ and $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2(\text{NO})][\text{PF}_6]_2\}$ have been prepared from the reaction of the chlorides **1** and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2(\text{Cl})]$ respectively with nitrosonium hexafluorophosphate [4]. The trimethylphosphine complex is indefinitely stable, while the former is unstable over extended periods. Ruthenium has the greatest affinity for the nitrosyl ligand of all transition block metals [5] and this combined with the robustness of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2]$ moiety puzzled us. Since nitrosonium salts are very prone to decomposition to yield some very reactive by-products it was possible that these had affected the stability of the isolated product. We decided to effect the preparation of $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NO})][\text{PF}_6]_2\}$ using the simple approach of Wilkinson et al. [3] in order to attempt to confirm our belief in the stability of this complex even under strongly acidic reducing conditions. The partial success of this aim is reported in this paper.

Results and discussion

Dropwise addition of aqueous sodium nitrite to a refluxing ethanol solution containing **1** and concentrated hydrochloric acid causes an immediate reaction to occur, brown nitrous fumes are produced and the solution colour changes from orange to bright red. Addition of aqueous ammonium hexafluorophosphate and cooling gave red microcrystals which were crystallised from dichloromethane–diethyl ether as red platelets or needles of **2**. The infrared spectrum of **2** contained a strong band at 1849 cm^{-1} indicative of a linear nitrosyl group while the ^1H NMR



spectrum in deuterioacetone contained a multiplet centred at δ 7.68 due to a single triphenylphosphine ligand and the cyclopentadienyl group appeared as a singlet at δ 6.43; the latter chemical shift is characteristic of a good π -acceptor ligand attached to a monocyclopentadienylruthenium moiety. Treatment of **2** with hot concentrated nitric acid gave a solution which contained chloride ion as shown by a silver nitrate test. Microanalysis and mass spectroscopy confirmed that the correct formulation of **2** was the unusual six coordinate ruthenium nitrosyl $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$.

The loss of one triphenylphosphine ligand from **1** is not entirely surprising since we reported earlier that the use of sulphur [6] or acids [7] traps dissociated triphenylphosphine in the presence of carbon monoxide. A possible mechanism is shown above which incorporates the fact that nitrous acid is a source of nitrosonium ion under conditions of low concentration, high acidity and low water activity [8].

Reaction of **1** with nitrosonium tetrafluoroborate in dichloromethane gave results identical to those described by Bruce [4] in that a colour change from yellow to red was seen and addition of diethyl ether gave a buff precipitate which slowly darkened over two hours at room temperature. The infrared spectrum of the fresh solid contained a band at 1850 cm^{-1} assignable to the nitrosyl group. The decomposition product of the buff solid did not contain any sign of compound **2**. Treatment of **1** with nitrosonium tetrafluoroborate in acetone gave an initial red solution which rapidly darkened, producing a black oily product on the addition of diethyl ether which did not contain either **2** or $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NO})][\text{PF}_6]_2\}$. However, the use of nitrosonium chloride in dichloromethane with **1** gave compound **2** in moderate yield after a work up including anion exchange. Reaction of **1** with nitrosonium chloride in a mixture of dichloromethane and methanol (1 : 2) has been reported to lead to loss of the cyclopentadienyl group [9] with the production of orange-brown crystals of $[\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{Cl}_3]$.

Treatment of $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{Cl})]\}$ (**3**) with nitrosonium tetrafluoroborate in acetone gave yellow crystalline $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{NO})][\text{BF}_4]_2\}$ (**4**) in high yield. Compound **4** exhibits bands at 2250 and 1898 cm^{-1} in the infrared which are assignable to $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{N}\equiv\text{O})$ respectively. The cyclopentadienyl protons resonated at δ 6.73 in the ^1H NMR spectrum of **4** in deuterioacetone, consistent with the dicationic character of **4**. When acetone was replaced by dichloromethane or methanol in the above reaction, the results were irreproducible and brown solids or brown oils were obtained after a variety of colour changes in the reaction mixture.

We are unable to rationalise this solvent dependence as acetone appears at first sight to be a poor choice of solvent for a reactive reagent such as the nitrosonium ion. It is possible that acetone is acting to remove adventitious acid present in the nitrosonium tetrafluoroborate, but since this solvent does not lead to tractable products for the reaction with **1** it seems likely that the explanation is less simple than this. The nitrosonium ion is able to function as a powerful oxidant and redox processes involving both solvent and ruthenium species may be operative. Solvent dependent reactions of nitrosonium salts have been reported by others [10].

An iron analogue of **2**, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{P}\{\text{OPh}\}_3)(\text{NO})(\text{I})]\text{PF}_6$ [11] prepared from the reaction of nitrosonium hexafluorophosphate and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{P}\{\text{OPh}\}_3)(\text{CO})(\text{I})]$, and a neutral iron analogue, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{NO})(\text{I})]$ [12] have been reported but very little spectroscopic data was provided.

X-Ray structure of 2

Dark red needles were obtained by crystallisation from a dichloromethane–diethyl ether solution. A suitable crystal was obtained by cutting a needle and was mounted

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for compound **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ru	−5086(1)	4312(1)	6881(1)	39(1)
P(1)	−3862(2)	2414(1)	7118(1)	33(1)
C(1)	−6844(10)	4276(6)	8458(5)	53(4)
C(2)	−7751	4435	7744	75(5)
C(3)	−7303	5530	7232	103(6)
C(4)	−6118	6048	7629	91(6)
C(5)	−5835	5274	8387	76(5)
C(6)	−6154(20)	4807(16)	8518(8)	81(8)
C(7)	−7454	4273	8240	101(9)
C(8)	−7817	4980	7466	129(13)
C(9)	−6742	5950	7265	67(7)
C(10)	−5713	5843	7916	80(8)
C(11)	−3259(7)	2294(5)	8275(4)	38(2)
C(12)	−2626(8)	3258(5)	8578(4)	47(2)
C(13)	−1902(9)	3138(6)	9392(5)	57(2)
C(14)	−2025(10)	2094(7)	9910(5)	65(3)
C(15)	−2726(10)	1139(7)	9610(5)	69(3)
C(16)	−3366(8)	1221(5)	8804(4)	50(2)
C(21)	−5186(7)	1178(4)	7124(4)	35(2)
C(22)	−4753(7)	317(5)	6382(4)	45(2)
C(23)	−5781(9)	−622(6)	6407(5)	59(3)
C(24)	−7261(9)	−676(6)	7164(6)	61(3)
C(25)	−7713(9)	167(6)	7904(5)	57(2)
C(26)	−6671(7)	1109(5)	7895(4)	48(2)
C(31)	−1923(7)	2106(5)	6110(4)	39(2)
C(32)	−1775(8)	2429(6)	5123(4)	52(2)
C(33)	−289(8)	2240(6)	4365(5)	57(2)
C(34)	1072(9)	1722(6)	4593(5)	64(3)
C(35)	958(9)	1383(7)	5560(6)	69(3)
C(36)	−516(8)	1573(6)	6320(5)	53(2)
Cl	−5845(2)	3389(2)	5551(1)	57(1)
N	−3101(7)	4844(4)	6230(4)	47(2)
O	−1877(7)	5285(5)	5896(4)	80(2)
P(2)	1961(2)	2847(2)	1220(1)	59(1)
F(1)	505(13)	2077(9)	1805(7)	101(3)
F(2)	1551(10)	3823(7)	2127(5)	78(2)
F(3)	3141(12)	2086(8)	1663(7)	109(3)
F(4)	2303(12)	2001(8)	293(7)	90(3)
F(5)	802(13)	3740(9)	741(7)	90(3)
F(6)	3381(10)	3741(7)	639(6)	79(2)
F(11)	−17(15)	2583(11)	1787(9)	55(3)
F(12)	2211(20)	3391(14)	2227(11)	80(4)
F(13)	1273(60)	3971(43)	842(34)	248(21)
F(14)	1662(23)	2255(15)	231(12)	85(5)
F(15)	1948(42)	1629(26)	1859(21)	173(9)
F(16)	3763(20)	3224(15)	571(11)	78(4)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

on a glass fibre with epoxy resin. Oscillation photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite monochromatized Mo- K_α X-rays.

Crystal data. $C_{23}H_{15}NOF_6P_2ClRu$, $M = 638.9$, triclinic, space group $P\bar{1}$, $a = 8.408(3)$, $b = 11.179(3)$, $c = 13.820(4)$ Å, $\alpha = 89.52(2)$, $\beta = 72.80(2)$, $\gamma = 87.14(3)^\circ$, $U = 1239.3(6)$ Å³, $D_c = 1.698$ g cm⁻³ for $Z = 2$. $F(000) = 626$, $\mu(\text{Mo-}K_\alpha) = 9.17$ cm⁻¹, $T = 23^\circ\text{C}$, crystal size $0.40 \times 0.16 \times 0.23$ mm. Cell dimensions were obtained from centred reflections with 2θ values from 22 to 38° . Intensity data in the range $3 < 2\theta < 50^\circ$ were collected using a θ - 2θ scan technique. The data were corrected for a 16% decay in intensity which was indicated by the measurement of three reflections periodically over the data collection time. A total of 4631 reflections were collected of which 4303 were independent, and 3398 for which $I > 3\sigma(I)$ were used in the refinement. The structure was solved by standard heavy atom routines and refined by blocked-matrix least-squares methods.

All non-hydrogen atoms except fluorine were given anisotropic thermal parameters. The hydrogen atoms associated with the phenyl groups were placed in their calculated positions and allowed to ride on their respective carbon atoms with fixed isotropic thermal parameters. There was evidence for considerable disorder both in the cyclopentadienyl ring and the PF_6^- group. An attempt was made to model the disorder by;

(a) assigning a 60:40% occupancy to two rings (C1–C5; C6–C10). Hydrogen atoms were not added to these carbon atoms and the rings were refined in separate blocks.

(b) assigning a 67:33% occupancy to two PF_6^- octahedra with a common phosphorus atom.

The highest peaks in the final difference map were less than $1 \text{ e}\text{\AA}^{-3}$ and associated with the PF_5^- group. At convergence $R = 4.74\%$ and $R_w = 6.66\%$, $w = [\sigma^2(F) + 0.00094 F^2]^{-1}$, $S = 1.66$ for 265 parameters, $\Delta/\sigma < 0.6$ (associated with fluorine atoms). For all data $R = 6.41\%$ and $R_w = 9.21\%$.

Calculations were performed using SHELXTL-PLUS on a MicroVAX II. The final positional parameters are given in Table 1, and selected bond lengths and angles are given in Table 2.

Discussion of the solid-state structures of 2

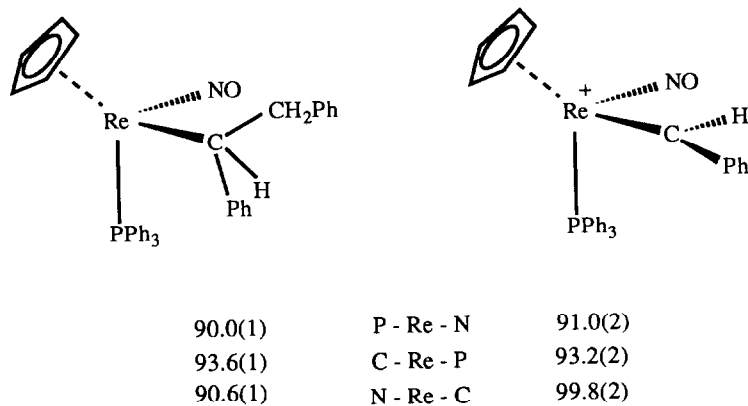
Figure 1 shows the structure of the cation present in 2. The coordination geometry at the ruthenium atom is a distortion from the usual pseudo-octahedral geometry found for compounds of general formula $[(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{L})_3]$ where the

Table 2

Selected bond lengths (Å) and bond angles ($^\circ$) for 2

Ru–C(1)	2.245(6)	Ru–C(2)	2.203(7)
Ru–C(3)	2.187(7)	Ru–C(4)	2.219(7)
Ru–C(5)	2.254(7)	Ru–N	1.775(5)
Ru–P(1)	2.375(2)	Ru–Cl	2.375(2)
N–O	1.132(7)		
N–Ru–P(1)	91.1(2)	N–Ru–Cl	102.0(2)
P(1)–Ru–Cl	86.4(1)	Ru–N–O	172.2(5)

cyclopentadienyl group occupies three facial sites. The nitrosyl group is effectively linear with the angle at nitrogen being $172.2(5)^\circ$ while the ruthenium to nitrogen bond length of $1.775(5) \text{ \AA}$ is at the extreme end of the range for linear nitrosyls of ruthenium [mean 1.743 \AA , σ 0.027 \AA] cited by Orpen et al. [13]. The nitrogen to oxygen bond at $1.132(7) \text{ \AA}$ is much shorter in comparison [mean 1.176 \AA , σ 0.030 \AA] but these citation data are for predominantly neutral molecules. X-Ray crystal structures of cationic ruthenium nitrosyl complexes are rare and of relatively low precision, e.g. in $[\text{Ru}(\text{NO})_2\text{Cl}(\text{PPh}_3)_2]^+$ the linear nitrosyl has Ru–N at $1.743(2) \text{ \AA}$, N–O at $1.158(19) \text{ \AA}$, and an angle of $178(2)^\circ$ for Ru–N–O [14]. The determined structure of **2** has lower standard deviations for these parameters mainly due to the absence of disorder in the nitrosyl group. The most striking feature of the solid-state structure of **2** is the value of the angle Cl–Ru–NO at $102.0(2)^\circ$; generally the interligand angles in the pseudo-octahedral complexes $[(\eta^5\text{-C}_5\text{R}_5)\text{Ru}(\text{L})_3]$ are $90 \pm 5^\circ$ [15]. The opening up of interligand angles at metal centres when a nitrosyl group is involved has been well documented for four [16] and five [17] coordination. Qualitatively it has been observed that the trend is P–M–P < P–M–(CO) < P–M–(NO) < (CO)–M–(CO) < (CO)–M–(NO) < (NO)–M–(NO) for ‘tetrahedral’ complexes. The effect is even more pronounced on going from a neutral nitrosyl complex to an isoelectronic cationic complex, e.g. $[\text{Fe}(\text{NO})_2(\text{PPh}_3)_2]$ and $[\text{Co}(\text{NO})_2(\text{PPh}_3)_2]^+$ have values for (NO)–M–(NO) of 123.8 and 136.7° respectively. It has been concluded that the non-bonded radius of a π -acid ligand is a function of the degree of population of its acceptor orbitals and will be susceptible to competition from other π -acceptors in the coordination sphere and thus the nitrosyl ligand will exhibit a larger effect than a carbonyl ligand. Six coordinate nitrosyl compounds have not been systematically studied for these effects since the steric effects of other ligands is more pronounced and will tend to mask the repulsions due to the nitrosyl ligands. Gladysz [18–20] has provided a large number of structures of two series of isoelectronic rhenium complexes, neutral $[(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{PAR}_3)(\text{NO})(\text{X})]$ and the cations $[(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{PAR}_3)(\text{NO})(\text{L})]^+$. When unambiguously six coordinate compounds are compared the interligand angles are seen to be significantly increased in the cationic compounds, e.g. $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{PPh}_3)(\text{NO})(\text{CHO})]$ (N–Re–C $92.7(4)^\circ$) [18] and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{PPh}_3)(\text{NO})(=\text{CH}_2)]\text{PF}_6$ (N–Re–C $101.6(8)^\circ$) [19]. The following pair of molecules represent the best structural comparison [20]:



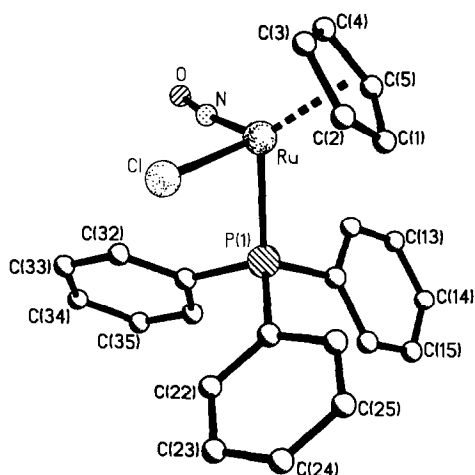


Fig. 1. Proposed molecular structure of the cation in $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$ (**2**).

First row metal complexes illustrate the repulsive effect of the nitrosyl ligand in neutral six coordination, e.g. the manganese compounds $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CS})(\text{NO})(\text{I})]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})(\text{NO})(\text{C}\{\text{O}\}\text{C}\{\text{O}\}\text{-}p\text{-C}_6\text{H}_4\text{Me})]$ where the interligand angles involving nitrosyl are $96.4(3)$, $94.6(2)$ and $96.2(2)$, $98.0(2)^\circ$ respectively [21,22].

The neutral carbonyl compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CO})(\text{Cl})]$ which is the carbonyl analogue of **2** has been crystallographically characterised [23] and exhibits 'normal' interligand angles of $89.5(6)$, $90.7(4)$, and $93.4(6)$ which emphasise that the non-bonded radius of the linear NO^+ is larger than that of the isoelectronic CO in six coordination. It would be of considerable interest to obtain crystallographic data for $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{P}(\text{OPh})_3)(\text{NO})(\text{I})]\text{PF}_6$ [11] and particularly $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{NO})(\text{I})]$ [12] to confirm these observations.

The ruthenium to chlorine bond length in **2** is $2.375(2)$ Å which is shorter than that of $2.396(6)$ Å found for $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CO})(\text{Cl})]$ [23] and the value of $2.453(2)$ Å found for **1** [24], reflecting the net positive charge in **2**. We have been unable to remove chloride ion from **2** with silver or thallium ion and accordingly its reactivity is lower than that of its neutral carbonyl analogue [6,23] as expected from this bondlength.

Experimental

All reactions and preparations were carried out under nitrogen by standard Schlenk-tube techniques. Diethyl ether and light petroleum ether (b.p. $40\text{--}60^\circ\text{C}$) were dried over sodium wire and distilled. Dichloromethane was dried over phosphorus pentoxide and distilled. Analar grade acetone and methanol were used as supplied. Infrared spectra were recorded on a Perkin-Elmer 1710 FT-IR instrument. Nuclear magnetic resonance spectra were recorded on Perkin-Elmer R32 (90 MHz, ^1H) and Bruker AC300 (300.13 MHz, ^1H ; 121.49 MHz, ^{31}P ; 75.47 MHz, ^{13}C) spectrometers. Elemental analyses were by Butterworth Laboratories, London. Fast Atom Bombardment (FAB) mass spectra were obtained on a Kratos Concept S1

spectrometer. The compounds **1** and **3** were prepared as described previously [24]. Nitrosonium chloride was prepared and purified by a published procedure [25] and stored and used as a dichloromethane solution (ca. 2 M). Nitrosonium tetrafluoroborate was obtained from Lancaster Synthesis and was washed rapidly with ice cold dichloromethane under nitrogen prior to immediate use.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$ (**3**)

A suspension of **1** (0.5 g, 0.69 mmol.) in ethanol (100 cm³) containing hydrochloric acid (conc., 2 cm³) was heated under reflux. Sodium nitrite solution (1.0 g, 14.5 mmol) in water (10 cm³) was added dropwise over two minutes with the immediate formation of a deep red homogeneous solution. The hot solution was filtered and an aqueous solution of ammonium hexafluorophosphate (6.0 g in 10 cm³, excess) was added immediately with stirring. Red crystals formed immediately and the reaction mixture was allowed to stand before being filtered while still warm. The product was washed with ethanol (2 × 5 cm³) and petroleum ether (30 cm³). The crude product was recrystallised from dichloromethane–diethyl ether as deep red platelets, yield 0.30 g (66%). (Found: C, 43.23; H, 3.21; N, 2.33. C₂₃H₂₀ClF₆NO₂Ru calcd.: C, 43.19; H, 3.15; N, 2.15%). IR (nujol): ν_{max} 1849 s cm⁻¹ (NO); ¹H NMR ([CD₃]₂CO): δ 7.75–7.58 (m, 15H, Ph), 6.43 (s, 5H, C₅H₅) ppm.; ¹³C{¹H} NMR ([CD₃]₂CO): δ 134.5 (d, *J*(PC) 10.6 Hz, C_{ortho}), 133.7 (s, C_{para}), 13.5 (d, *J*(PC) 11.6 Hz, C_{meta}), 129.3 (d, *J*(PC) 57.5 Hz, C_{ipso}), 103.4 (s, C₅H₅) ppm.; ³¹P{¹H} NMR ([CD₃]₂CO): δ 37.1 ppm; M.S. [FAB]: *m/z* 639 {M⁺}.

Preparation of 3 from 1 and nitrosonium chloride

Nitrosonium chloride solution (5 cm³, ca. 2 M in dichloromethane) was added dropwise to a stirred solution of **1** (0.5 g, 0.69 mmol) in dichloromethane (20 cm²). The red solution was stirred for 30 min after which diethyl ether (10 cm³) was added to precipitate an oily red solid which was isolated by filtration and dried under reduced pressure. The solid was dissolved in acetone (30 cm³) and ammonium hexafluorophosphate (0.5 g, 3.1 mmol) was added. The suspension was stirred for 30 min prior to removal of the solvent under reduced pressure. The solid remaining was extracted with dichloromethane (2 × 25 cm³) to yield a red solution which was concentrated under reduced pressure (ca. 10 cm³). Addition of diethyl ether to the stirred solution gave red crystals of **3**, yield 0.15 g (34%).

$\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{NO})][\text{BF}_4]_2\}$ (**4**)

Nitrosonium tetrafluoroborate (0.1 g, 0.85 mmol) was added to a solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{Cl})]$ (**3**) (0.2 g 0.37 mmol) in acetone (20 cm³). The initial orange solution turned red immediately. After stirring at room temperature for 15 min the colour returned to orange and the volume was reduced to ca. 8 cm³ under reduced pressure. Addition of diethyl ether to the stirred concentrate gave yellow crystals. The crude product was recrystallised from dichloromethane–diethyl ether as bright yellow crystals, yield 0.21 g (80%), (Found: C, 46.92; H, 4.07; N, 3.91. C₂₈H₂₉B₂F₈N₂OPRu calcd.: C, 47.02; H, 4.09; N, 3.93%). IR (nujol): ν_{max} 2250 s (CN) and 1898 s cm⁻¹ (NO); ¹H NMR ([CD₃]₂CO): δ 7.50–7.43 (m, 15H, Ph), 6.73 (s, 5H, C₅H₅), 1.39 (s, 9H, CMe₃) ppm; ³¹P{¹H} NMR ([CD₃]₂CO): δ 34.5 ppm.

Acknowledgements

We thank the S.E.R.C. for a studentship [F.M.C.-L], Johnson Matthey Chemicals Ltd. for a generous loan for RuCl_3 , and the University of Salford Research Committee Fund for support.

References

- 1 M.L.H. Green, T.R. Sanders, and R.N. Whitely, *Z. Naturforsch. B*, 23 (1968) 106.
- 2 J.A. Broomhead and H. Taube, *J. Am. Chem. Soc.*, 91 (1969) 1261.
- 3 T.S. Piper, F.A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1 (1955) 165.
- 4 P.M. Treichel and D.A. Komar, *Synth. React. Inorg Met.-Org. Chem.*, 10 (1980) 205; M.I. Bruce, I.B. Tomkins, F.S. Wong, B.W. Skelton, and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1982) 687.
- 5 W.P. Griffith, *The Chemistry of the Rarer Platinum Metals (Os, Ru, Ir, and Rh)*, Wiley-Interscience, London, 1976; E.A. Seddon and K.R. Seddon, *Topics in Inorganic and General Chemistry*, Vol. 19: *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984.
- 6 S.G. Davies and S.J. Simpson, *J. Chem. Soc., Dalton Trans.*, (1984) 993.
- 7 F.M. Conroy-Lewis and S.J. Simpson, *J. Organomet. Chem.*, 322 (1987) 221.
- 8 T.A. Turney and G.A. Wright, *Chem. Rev.*, 59 (1959) 497.
- 9 R.F.N. Ashok, M. Gupta, K.S. Arulsamy, and U.C. Agarwala, *Inorg. Chim. Acta.*, 98 (1985) 169.
- 10 N.G. Connelly and J.D. Davies, *J. Organomet. Chem.*, 38 (1972) 385; P.K. Ashford, P.K. Baker, N.G. Connelly, R.L. Kelly, and V.A. Woodley, *J. Chem. Soc., Dalton Trans.*, (1982) 477; M.R. Snow and F.L. Wimmer, *Aust. J. Chem.*, 29 (1976) 2349 and references therein.
- 11 P.M. Treichel, K.P. Wagner, and H.J. Mueh, *J. Organomet. Chem.*, 86 (1975) C13.
- 12 V.N. Pandey, *Transition Met. Chem.*, 2 (1977) 48.
- 13 A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S1.
- 14 C.G. Pierpoint and R. Eisenberg, *Inorg. Chem.*, 11 (1972) 1088.
- 15 J.I. Seeman and S.G. Davies, *J. Am. Chem. Soc.*, 107 (1985) 6522; typical crystal structures are exemplified by E. Cesarotti, A. Chiesa, G.F. Ciani, A. Sironi, R. Vefghi, and C. White, *J. Chem. Soc., Dalton Trans.*, (1984) 653; M.I. Bruce, D.N. Duffy, M.G. Humphrey, and A.G. Swincer, *J. Organomet. Chem.*, 282 (1985) 383; E. Cesarotti, M. Angoletta, N.P.C. Walker, M.B. Hursthouse, R. Vefghi, P.A. Schofield and C. White, *ibid.*, 286 (1985) 343; J.M. Wisner, T.J. Bartczak, and J.A. Ibers, *Inorg. Chim. Acta.*, 100 (1985) 115; G.O. Nelson and C.E. Summer, *Organometallics*, 5 (1986) 1983.
- 16 V.G. Albano, A. Araneo, P.L. Bellon, G. Ciani, and M. Manassero, *J. Organomet. Chem.*, 67 (1974) 413 and references therein.
- 17 J.-L. Roustan, N. Ansari, J.-P. Charland, and Y. Le Page, *Can. J. Chem.*, 67 (1989) 2016; M. Laing, R.H. Reinmann, and E. Singleton, *Inorg. Chem.*, 18 (1979) 2666 and references therein.
- 18 G.S. Bodner, A.T. Patton, D.E. Smith, S. Georgiou, W. Tam, W.-K. Wong, C.E. Strouse, and J.A. Gladysz, *Organometallics*, 6 (1987) 1954.
- 19 A.T. Patton, C.E. Strouse, C.B. Knobler, and J.A. Gladysz, *J. Am. Chem. Soc.*, 105 (1985) 5804.
- 20 W.A. Kiel, G.-Y. Lin, A.G. Constable, F.B. McCormick, C.E. Strouse, O. Eisenstein, and J.A. Gladysz, *J. Am. Chem. Soc.*, 104 (1982) 4865.
- 21 J.A. Potenza, R. Johnson, S. Rudich, and E. Efraty, *Acta Cryst B*, 36 (1980) 1933.
- 22 J.B. Sheridan, G.L. Geoffroy, and A.L. Rheingold, *J. Am. Chem. Soc.*, 109 (1987) 1584.
- 23 T. Wilczewski and Z. Dauter, *J. Organomet. Chem.*, 312 (1986) 349.
- 24 M.I. Bruce, F.S. Wong, B.W. Skelton, and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1981) 1398.
- 25 J.R. Morton and H.W. Wilcox, *Inorg. Synth.*, 4 (1953) 48.