Synthesis, Characterisation, Reactivity, and *X*-Ray Structure of *cis*-Carbonylchlorobis[1-methyl-3-(pyridin-2-yl)-1,2,4-triazole-N^4N']ruthenium Hexafluorophosphate†

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The compound $[Ru(L{-}L')_2(CO)Cl]PF_6$ [L–L′ = 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole] has been obtained in high yield from ruthenium trichloride and the pyridyltriazole ligand in dimethylformamide, as a mixture of co-ordination isomers. One of these isomers was obtained using crystallisation techniques and crystallises in the monoclinic space group $P2_1/n$ with unit-cell parameters a = 11.085(1), b = 13.120(2), c = 16.108(2) Å, β = 97.17(1)°, and Z = 4. The metal cation has a *cis* geometry for CO and Cl, and the triazole ring is bound to the ruthenium centre *via* its N^4 nitrogen atom. The CO and Cl groups are *trans* to the triazole rings of the pyridyltriazole ligand. The average ruthenium nitrogen distance is 2.09 Å. From this compound the species $[Ru(L{-}L')(CO)L]^+$ have been obtained, where L = NCS^- or H^-. All the compounds have been characterised by spectroscopic, electrochemical, and high-performance liquid chromatographic methods. The results, and in particular the high yield in which the title compound is obtained, strongly suggest that the pyridyltriazole ligand is a weaker π acceptor than 2,2′-bipyridyl.

There is at present much interest in the chemistry of ruthenium polypyridyl compounds because of their possible application as photochemical or electrochemical catalysts.[1–3] Recently a series of ruthenium polypyridyl carbonyl compounds have been reported[4–7] with the overall formula of $[Ru(bipy)_2(CO)L]^{n+}$ (n = 1 or 2, bipy = 2,2′-bipyridyl, L = a series of monodentate ligands including CO), showing some very unusual and interesting properties. The electronic properties of these compounds are quite different from those normally expected for ruthenium polypyridyl complexes, also photochemical lability of the carbonyl ligand has been observed. The use of the compound $[Ru(bipy)_2(CO)Cl]^+$ as a catalyst in the water-gas shift reaction has been reported.[8,9] This compound and also the osmium carbonyl hydride compound have been proposed as catalysts for the electrochemical reduction of CO_2.[10] Detailed investigations, including hydride-transfer studies, have also been carried out on $[Ru(bipy)_2(CO)H]PF_6$,[11,12] a possible intermediate in the earlier mentioned ruthenium-catalysed water-gas shift reaction.

We have started a systematic investigation[13] of the physical properties of ruthenium compounds with asymmetric ligands of the type L–L′, where L–L′ is a series of pyridyl-1,2,4-triazoles. In this contribution we report the synthesis, characterisation, and reactivity of the compound $[Ru(L{-}L')_2(CO)Cl]PF_6$, where the ligand L–L′ is 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole and the molecular structure of one of its isomers. It was anticipated that with this study information would be obtained about the electronic properties of the ligand. The properties of the compounds obtained are compared with those observed for the corresponding 2,2′-bipyridyl carbonyl compounds.

Results and Discussion

Preparation of $[Ru(L{-}L')_2(CO)Cl]PF_6$.—The compound is obtained by reaction of ruthenium trichloride trihydrate with 2 equivalents of the ligand in refluxing dimethylformamide (dmf) [reaction (1)]. The formation of such carbonyl compounds, is

$$RuCl_3 + 2L{-}L' \xrightarrow{dmf} [Ru(L{-}L')_2(CO)Cl]^+ \qquad (1)$$

most likely the result of a decarbonylation of the solvent, dmf.[4–7] The ligand was added in small portions, so as to avoid the formation of $[Ru(L{-}L')_3]^{2+}$. The corresponding bipy compound has been prepared in the same manner.[4] However, in that case the yield obtained is only about 40%, while with our pyridyltriazole ligand a yield of close to 100% is obtained. N.m.r. spectra of the products obtained (see below) clearly show the presence of different co-ordination isomers. The first fraction to crystallise out was used for the *X*-ray analysis. As this fraction contained however only about 15% of the overall yield there is no guarantee that only one isomer is obtained. For the bipy compound the main product is $[Ru(bipy)_2Cl_2]$, however no evidence for the formation of such a compound was obtained with the pyridyltriazole ligand. This suggests that

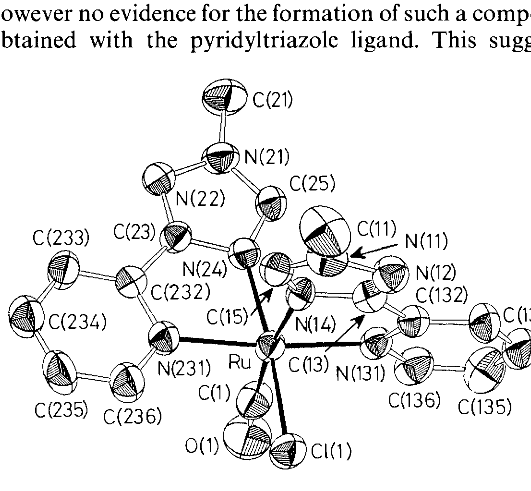

Figure 1. ORTEP drawing of *cis*-$[Ru(L{-}L')_2(CO)Cl]PF_6$, showing the atom labelling system

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Fractional atomic co-ordinates (× 10^5 for Ru; × 10^4 for C, Cl, F, O, N, and P) of $[Ru(L–L')_2(CO)Cl]PF_6$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru	23 480(4)	4 705(4)	14 941(2)	N(22)	5 049(4)	2 395(4)	878(3)
Cl	783(1)	−776(1)	1 242(1)	C(23)	4 188(5)	1 696(4)	835(3)
C(1)	3 380(5)	−567(5)	1 887(4)	N(24)	3 669(4)	1 597(3)	1 551(3)
O	3 936(5)	−1 240(4)	2 137(3)	C(25)	4 238(5)	2 265(5)	2 066(3)
N(11)	−578(5)	2 475(4)	716(3)	N(231)	2 863(4)	416(4)	281(3)
C(11)	−1 480(8)	3 062(6)	201(5)	C(232)	3 743(5)	1 067(4)	115(3)
N(12)	−694(4)	2 278(4)	1 552(3)	C(233)	4 151(5)	1 116(5)	−648(4)
C(13)	280(5)	1 729(4)	1 779(3)	C(234)	3 638(6)	486(6)	−1 282(4)
N(14)	995(4)	1 573(4)	1 162(3)	C(235)	2 753(6)	−144(6)	−1 122(4)
C(15)	431(5)	2 050(4)	507(4)	C(236)	2 386(6)	−178(5)	−350(4)
N(131)	1 697(4)	723(3)	2 634(3)	P	6 529(2)	1 026(2)	3 789(1)
C(132)	669(5)	1 295(4)	2 596(3)	F(1)	6 201(4)	738(4)	4 680(3)
C(133)	58(6)	1 440(5)	3 268(4)	F(2)	5 628(5)	1 934(4)	3 769(3)
C(134)	499(7)	977(6)	4 020(4)	F(3)	6 854(5)	1 331(4)	2 915(3)
C(135)	1 520(6)	420(6)	4 063(4)	F(4)	7 482(5)	174(4)	3 836(3)
C(136)	2 103(6)	312(5)	3 379(4)	F(5)	7 510(5)	1 733(5)	4 225(4)
N(21)	5 073(4)	2 748(4)	1 678(3)	F(6)	5 556(6)	355(6)	3 352(4)
C(21)	5 974(6)	3 497(5)	2 019(4)				

Table 2. Selected bond lengths (Å) and angles (°) of $[Ru(L–L')_2(CO)Cl]PF_6$ with estimated standard deviations (e.s.d.s) in parentheses

Ru–N(14)	2.104(5)	C(13)–N(14)	1.362(6)	C(135)–C(136)	1.352(9)	N(21)–N(22)	1.367(6)
Ru–N(131)	2.082(4)	N(14)–C(15)	1.317(6)	C(233)–C(234)	1.380(8)	N(22)–C(23)	1.318(6)
Ru–N(24)	2.074(4)	C(15)–N(11)	1.329(7)	C(234)–C(235)	1.333(9)	C(23)–N(24)	1.357(6)
Ru–N(231)	2.104(4)	C(13)–C(132)	1.450(7)	C(235)–C(236)	1.357(8)	N(24)–C(25)	1.313(6)
Ru–C(1)	1.839(7)	N(131)–C(132)	1.359(7)	N(231)–C(236)	1.336(7)	C(25)–N(21)	1.338(7)
Ru–Cl	2.382(2)	C(132)–C(133)	1.360(7)	C(1)–O	1.123(7)	C(23)–C(232)	1.458(7)
C(11)–N(11)	1.440(8)	C(133)–C(134)	1.388(9)	C(136)–N(131)	1.342(7)	N(231)–C(232)	1.348(7)
N(11)–N(12)	1.394(6)	C(134)–C(135)	1.341(9)	C(21)–N(21)	1.458(7)	C(232)–C(233)	1.363(7)
N(12)–C(13)	1.312(7)						
Cl–Ru–N(14)	87.0(1)	Ru–N(14)–C(15)	141.5(4)	N(131)–C(132)–C(133)	122.7(5)	N(24)–C(23)–C(232)	118.9(5)
Cl–Ru–N(131)	86.2(1)	Ru–N(14)–C(13)	112.3(4)	C(13)–C(132)–C(133)	123.1(6)	N(22)–C(23)–C(232)	127.3(5)
Cl–Ru–N(24)	172.6(1)	C(15)–N(14)–C(13)	104.6(5)	C(132)–C(133)–C(134)	118.5(6)	N(24)–C(25)–N(21)	109.1(5)
Cl–Ru–N(231)	95.4(1)	C(15)–N(11)–N(12)	110.5(5)	C(135)–C(134)–C(133)	119.1(6)	Ru–N(231)–C(232)	116.7(4)
Cl–Ru–C(1)	87.6(2)	C(15)–N(11)–C(11)	128.6(6)	C(136)–C(135)–C(134)	120.1(6)	Ru–N(231)–C(236)	126.7(4)
N(14)–Ru–N(131)	78.5(2)	N(12)–N(11)–C(11)	120.9(6)	N(131)–C(136)–C(135)	123.0(6)	C(232)–N(231)–C(236)	116.5(5)
N(14)–Ru–N(24)	89.9(2)	N(11)–N(12)–C(13)	101.5(5)	Ru–N(24)–C(25)	141.7(4)	N(231)–C(232)–C(23)	112.5(5)
N(14)–Ru–N(231)	93.1(2)	N(14)–C(13)–N(12)	114.4(5)	Ru–N(24)–C(23)	113.8(4)	N(231)–C(232)–C(233)	122.5(5)
N(14)–Ru–C(1)	171.7(2)	N(14)–C(15)–N(11)	109.1(5)	C(25)–N(24)–C(23)	104.5(5)	C(23)–C(232)–C(233)	125.0(5)
N(131)–Ru–N(24)	99.7(2)	N(14)–C(13)–C(132)	118.0(5)	C(25)–N(21)–N(22)	110.2(5)	C(232)–C(233)–C(234)	119.1(6)
N(131)–Ru–N(231)	171.3(2)	N(12)–C(13)–C(132)	127.6(5)	C(25)–N(21)–C(21)	128.6(5)	C(233)–C(234)–C(235)	118.3(6)
N(131)–Ru–C(1)	94.8(2)	Ru–N(131)–C(132)	115.4(3)	N(22)–N(21)–C(21)	121.0(5)	C(234)–C(235)–C(236)	120.6(6)
N(24)–Ru–N(231)	78.1(2)	Ru–N(131)–C(136)	127.6(4)	N(21)–N(22)–C(23)	102.3(4)	N(231)–C(236)–C(235)	122.9(6)
N(24)–Ru–C(1)	96.2(2)	C(132)–N(131)–C(136)	116.6(5)	N(24)–C(23)–N(22)	113.8(5)	Ru–C(1)–O	174.9(6)
N(231)–Ru–C(1)	93.7(2)	N(131)–C(132)–C(13)	114.2(5)				

the pyridyltriazole ligands are less strong π acceptors, as weak π acceptors are expected to stabilise the chlorocarbonyl compound with respect to the dichloride because of a decreased competition for electron density with the carbonyl ligand.[4]

The compound $[Ru(L–L')(CO)_2Cl_2]$ was obtained as reported before for the corresponding bipy compound in high yield, by treating L–L′ with a CO-containing methanol–water solution of $RuCl_3$.[4b]

X-Ray Structure of cis-$[Ru(L–L')_2(CO)Cl]PF_6$.—Fractional co-ordinates are given in Table 1, relevant bond distances and angles in Table 2. An ORTEP projection of the $[Ru(L–L')_2(CO)Cl]^+$ cation is shown in Figure 1 together with the atom labelling system used. The unit-cell packing of the $[Ru(L–L')_2(CO)Cl]PF_6$ ion pairs is shown in Figure 2

The co-ordination geometry around the central metal ion is slightly distorted octahedral, with the L–L′ ligands co-ordinated in a *cis* fashion in such a way that the triazole groups are mutually *cis* and the pyridines mutually *trans*. The largest distortion is the small value of the angle between the ruthenium ion and two co-ordinating nitrogen atoms [*e.g.* N(14)–Ru–N(131) 78.5, N(24)–Ru–N(231) 78.1°]. These angles, which are significantly smaller than 90°, appear to be imposed on the

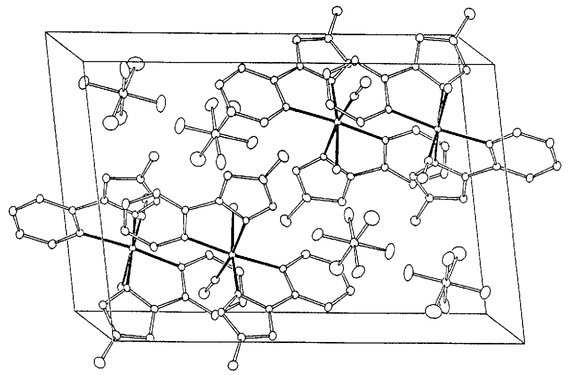

Figure 2. Unit-cell packing of $[Ru(L–L')_2(CO)Cl]PF_6$. The hydrogen atoms are omitted for clarity

structure by the rigidity of the pyridyltriazole ligands. The small bite angle has been observed before in compounds containing ligands with comparable geometries[14] and is similar to that found for bipy.[15,16] The ligands are bound to the metal ion *via* the pyridine nitrogen and the N^4 atom of the triazole ring. Co-ordination through this nitrogen atom of the triazole ring leads to less steric hindrance than that through the N^2 atom. The pyridine groups are *trans* to each other with the carbonyl and chloride ligands *trans* to triazole ring, probably because in this manner the possibilities for metal-to-ligand back bonding are optimised. The Ru–N distances of between 2.104 and 2.074 Å are as expected for divalent ruthenium compounds. The *trans* effect observed for the CO and Cl ligands is, however, much smaller than that observed in $[Ru(bipy)_2(CO)Cl]^+$, where a difference of 0.11 Å for the Ru–N distances *trans* to these ligands was observed (2.06 *vs.* 2.17 Å).[4a] This is possibly related to the fact that the triazole ring is not expected to be involved in the π-back bonding system. The Ru–C bond is 1.84 Å with the C–O distance of 1.12 Å and a Ru–C–O angle of 175°. These values and also the other metal–ligand distances are very similar to those in the corresponding bipy compound.[4a]

Reactivity.—Attempts were made to prepare a series of compounds with the general formula $[Ru(L\text{–}L')_2(CO)L]^{n+}$ by refluxing $[Ru(L\text{–}L')_2(CO)Cl]^+$ in the presence of an excess of ligand [reaction (2)]. As attempts to isolate the different isomers of the chloro carbonyl compound failed, the reactivity studies were carried out with samples containing a mixture of co-ordination isomers. Reaction (2) was found to be efficient for the

$$[Ru(L\text{–}L')_2(CO)Cl]^+ + L \longrightarrow [Ru(L\text{–}L')_2(CO)L]^{n+} + Cl \quad (2)$$

preparation of the bipy analogues and a range of compounds with L = pyridine, acetonitrile, NCS^-, *etc.* has been reported.[4d] For the chlorocarbonyl compound reported here reaction (2) was extremely slow and it appeared to be very difficult to replace the chloride ligand with neutral ligands. The chloride ligand is not exchanged at all upon refluxing in organic solvents for up to 3 d. The addition of water to the reaction mixture does lead to a slow release of the anion. Numerous attempts were made to prepare $[Ru(L\text{–}L')_2(CO)(H_2O)]^{2+}$, from refluxing acetone–water mixtures, also in the presence of acids, base, or $AgNO_3$. However, no pure products were obtained in this manner. The best results were obtained by the acid decomposition of the hydride compound. The results given below for the aqua and CH_3CN compounds are obtained from samples prepared in this manner.

As the variations in electronic spectra, obtained as a result of the ligand-exchange process, are very small u.v.–visible spectroscopy could not be used to monitor these reactions. The reactions were therefore followed by high-performance liquid chromatography (h.p.l.c.). In experiments where we tried to prepare compounds with a 2+ charge, compounds with ligands such as H_2O and CH_3CN, recombination of the displaced chloride ligand with the 2+ species formed occurred upon injection of a sample of the reaction mixture into the, mainly organic, mobile phase.

The exchange of the chloride ion with other anions is more efficient. The NCS^- compound could be prepared, but this is also not very stable. The compound $[Ru(L\text{–}L')_2(CO)H]ClO_4$ was prepared at room temperature [reaction (3)].[4c] It is

$$[Ru(L\text{–}L')_2(CO)Cl]^+ + NaBH_4 \xrightarrow{CH_3OH} [Ru(L\text{–}L')_2(CO)H]^+ \quad (3)$$

however, not very stable. Addition of NH_4PF_6 and also excess of the borohydride decomposed the compound, but the hydride could be isolated as the perchlorate salt using $NaClO_4$. A similar behaviour was observed before for $Ru(bipy)_2$ hydrides containing phosphine ligands and can be attributed to the acidity of the NH_4^+ group.[4e] The stability of the chlorocarbonyl compound is further emphasised by the experiments carried out with $[Ru(L\text{–}L')(CO)_2Cl_2]$. When we attempted to prepare $[Ru(L\text{–}L')_2(CO)_2]^{2+}$ by treating $[Ru(L\text{–}L')(CO)_2Cl_2]$ with 1 equivalent of the chelating ligand the major product obtained was the chlorocarbonyl compound, with only a relatively small amount of a dicarbonyl species identified by i.r. spectroscopy and h.p.l.c.

As expected the carbonyl ligands are photochemically labile.[4d] The chlorocarbonyl compound was photolysed in acetonitrile using u.v. irradiation. Both h.p.l.c. and u.v.–visible spectroscopy show the formation of one product, with a $\lambda_{max.}$ in the visible of 420 nm for short irradiation times. Upon prolonged irradiation a small amount of a second product is formed with an absorption maximum at about 385 nm. The products obtained were not isolated, but from spectroscopic and h.p.l.c. data it is concluded that the initial product is most likely $[Ru(L\text{–}L')_2(CH_3CN)Cl]^+$. A similar product was obtained for the corresponding bipy compound.[4d] while the second product most likely is $[Ru(L\text{–}L')_2(CH_3CN)_2]^{2+}$.

Purification of the compounds prepared by column chromatography using neutral alumina was not possible as they did adhere to the top of the column. The purity of the compounds was therefore checked by h.p.l.c. using a method described in the Experimental section. The retention times observed are given in Table 3. It proved very difficult to obtain samples having satisfactory elemental analyses. Satisfactory spectroscopic and electrochemical data could be obtained for the compounds with L = H_2O, CH_3CN, Cl^-, NCS^-, or H^-. The purity of these compounds was better than 95% as judged by h.p.l.c. Satisfactory elemental analyses could only be obtained for the Cl^-, NCS^-, and H^- compounds. Most likely slow decomposition of the compounds is taking place.

N.M.R. Spectroscopy.—N.m.r. spectroscopy was used to establish the co-ordination sphere around the ruthenium ion. This technique is particularly suited to identify isomers, especially because of the presence of a methyl group in the pyridyltriazole ligand.[13] All compounds prepared show a series of resonances in the δ 7.5—10.0 range which can be attributed to the pyridyltriazole ligands. Around δ 4.0, signals due to the methyl groups in the complex are observed. The proton spectrum of the sample used for the *X*-ray analysis is given in Figure 3. Assignments were made by comparison with spectra obtained for the free ligand and for similar compounds reported in the literature.[13] For this compound, two further signals, attributed to methyl resonances, are observed at δ 4.01 and 3.97. The presence of these two methyl resonances and also the presence of two resonances for the triazole H^5 proton are in agreement with the crystal structure obtained. The n.m.r. spectrum shows clearly that both pyridyltriazole ligands are inequivalent. This is confirmed by the ^{13}C n.m.r. spectrum of this sample (see Experimental section).

An ^1H n.m.r. spectrum of other samples of the chlorocarbonyl compound appeared to be far more complicated. Depending on the particular sample, between 6 and 10 signals were obtained in the δ 4—5 region that can be attributed to the triazole methyl group. This strongly suggests the presence of more than one isomer. Because of the asymmetry of the ligand six geometrical isomers can be obtained for the *cis* compound. On the basis of molecular models all isomers are expected to be of the *cis* configuration. As a result of the complexity of the situation no analysis of the spectra obtained was carried out to identify these isomers. There are however two distinctly different sets of

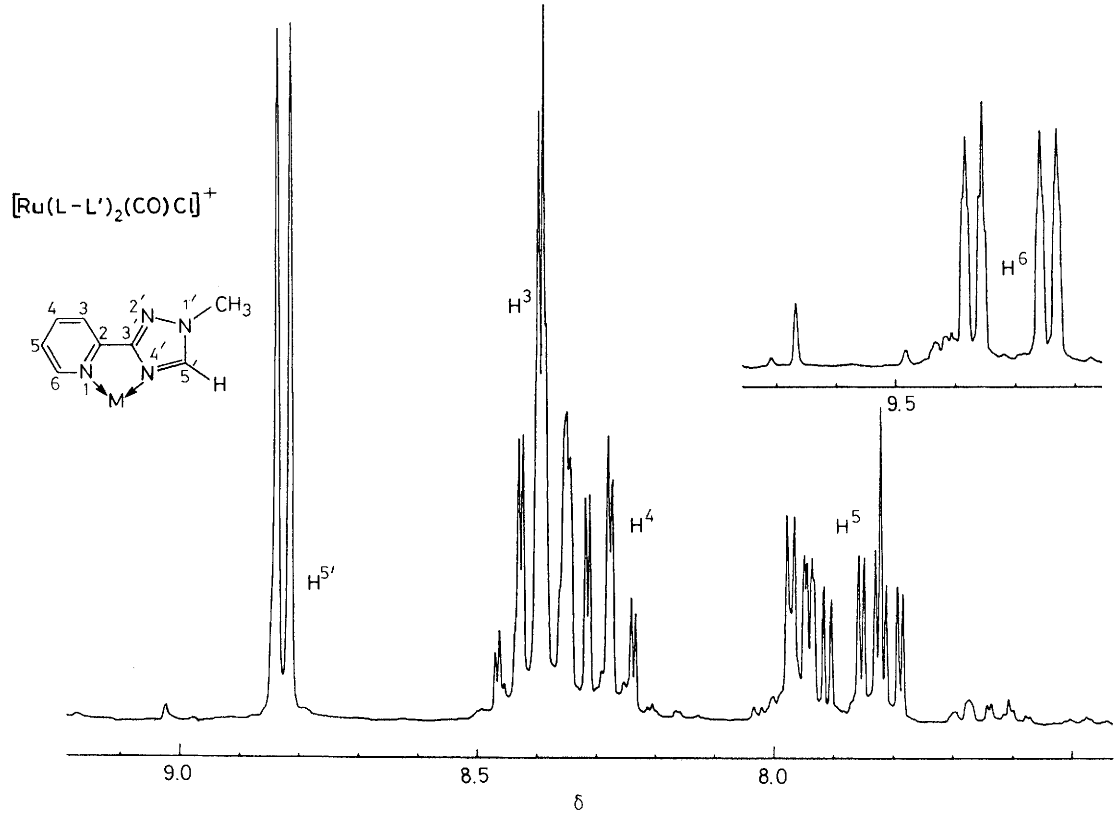

Figure 3. 200-MHz Proton n.m.r. spectrum of the *X*-ray sample of $[Ru(L-L')_2(CO)Cl]PF_6$, together with the assignment of the different resonances. Solvent $(CD_3)_2SO-(CD_3)_2CO$ (4:1)

Table 3. Spectroscopic, electrochemical, and h.p.l.c. data for $[Ru(L-L')_2(CO)L]^{n+}$ and some related compounds

Compound	ν(CO)/ cm^{-1}	Ru$^{2+/3+}$ ligand-based reductions/ V *vs.* s.c.e.		H.p.l.c. retention time/min
$[Ru(L-L')_2(CO)Cl]^+$	1 967	1.58	−1.56*	2.67
$[Ru(L-L')_2(CO)(NCS)]^+$	1 983	1.47*	−1.57*	2.30
$[Ru(L-L')_2(CO)H]^+$	1 916	1.15*	−1.83*	2.04
$[Ru(L-L')_2(CO)(H_2O)]^{2+}$	1 981		−1.56*	8.20
$[Ru(L-L')_2(CO)(CH_3CN)]^{2+}$	2 008		−1.47*	8.12
$[Ru(L-L')(CO)_2Cl_2]$	2 067, 1 988			2.00
$[Ru(bipy)_2(CO)Cl]^+$	1 970	1.50	−1.34 −1.56	
$[Ru(bipy)_2(CO)(NCS)]^+$	1 982	1.47*	−1.25 −1.46	
$[Ru(bipy)_2(CO)H]^+$	1 912	1.03*	−1.55 −1.75	
$[Ru(bipy)_2(CO)(H_2O)]^{2+}$	1 995			
$[Ru(bipy)_2(CO)(CH_3CN)]^{2+}$	2 015		−1.18 −1.38	
$[Ru(bipy)(CO)_2Cl_2]$	1 997, 2 055			

Data on bipy compounds from ref. 4*d*.
* Irreversible redox process.

methyl resonances, one set at about δ 4.0 and another at about 4.3 with a ratio of about 1:1. The presence of a set of resonances at about δ 4.3 suggests strongly that the triazole N^2 atom is also able to co-ordinate to the central metal ion.[13] This is contrary to the results obtained for compounds of the type $[Ru(bipy)_2(L-L')]^{2+}$, where for the ligand reported here only co-ordination *via* N^4 was observed.[13b] The different behaviour found here is possibly explained by the extra space present round the metal ion because of the absence of the bipy ligands.

The spectrum obtained for the hydride compound contains resonances at δ −12.51, −12.66, −13.46, and −13.57 that can be attributed to the hydride ion,[4e] also suggesting the presence of several isomers in this compound. Carbon-13 n.m.r. spectra were obtained for $[Ru(L-L')_2(CO)Cl]PF_6$ and $[Ru(L-L')(CO)_2Cl_2]$ (see Experimental section). For the first compound, using the *X*-ray analysis fraction, two sets of resonances were observed indicating the presence of two different pyridyltriazole ligands. The ^{13}C n.m.r. spectrum obtained for $[Ru(L-L')(CO)_2Cl_2]$ shows one set of resonances, indicating the presence of only one isomer. This is further confirmed by the proton n.m.r. spectrum of this compound (see Experimental section). For the dicarbonyl compound two resonances are obtained for the CO ligands at δ 206.5 and 196.2 p.p.m. For the chlorocarbonyl compound one signal is found at 206.8 p.p.m.

Infrared Spectroscopy.—The carbonyl stretching frequencies of the compounds together with those observed for a number of analogous bipy compounds are given in Table 3. The i.r. spectra did not give any indication for the presence of more than one isomer. Within the series of pyridyltriazole compounds the frequency of the carbonyl vibration varies with the nature of the sixth ligand as expected.[4] The small differences observed between the series and those found for the corresponding bipy compounds is surprising in view of the differences in π-acceptor properties of the pyridyltriazole and bipy ligands. The presence of the chloride ligand in $[Ru(L-L')_2(CO)Cl]PF_6$ is confirmed by a M–Cl stretching vibration at 330 cm^{-1}, absent for all other monocarbonyl compounds obtained. For $[Ru(L-L')(CO)_2Cl_2]$ a single M–Cl stretching vibration is found at 330 cm^{-1}. For the hydride no metal–hydrogen stretching vibration could be observed. This band is however expected to be hidden under the strong CO stretching vibration.[4] The presence of the NCS$^-$

group was confirmed by medium-strong bands at 2 110 and 2 057 cm^{-1}. The presence of the two bands is again indicative of the fact that more than one isomer is formed.

Electronic Spectra.—The u.v.–visible absorption spectra are dominated by the strong $\pi \longrightarrow \pi^*$ L–L′ based transitions at about 240 and 270 nm. As for the analogous bipy compounds, $d_\pi \longrightarrow \pi^*$ transitions are expected in the u.v. region and are hidden by the strong ligand-based transitions. The high energy of these transitions is explained by the strong back donation to the carbonyl ligand.[4] Only the hydride compound shows a well defined transition in the visible region (400 nm), in agreement with the strong donor properties of the hydride ion.[4c,7]

Electrochemistry.—The data obtained are given in Table 3. No reversible ligand-based reductions were found. Of the ruthenium-based oxidations only the chlorocarbonyl compound shows a reversible $Ru^{2+/3+}$ redox couple. For the compounds with a 2+ charge no metal-based oxidation was observed; as for the bipy compounds such an oxidation is expected at potentials around 2 V *vs.* saturated calomel electrode (s.c.e.), outside the range of the solvent used. The $Ru^{2+/3+}$ redox potentials obtained for the L–L′ compounds are very similar to those obtained for their bipy analogues and show the expected variation.[4d]

Conclusions

The fact that in the reaction between $RuCl_3$ and 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole the chlorocarbonyl complex is obtained as the only product can be considered to be strong evidence for the reduced π-acceptor properties of this ligand with respect to bipy. Also the reduced stability of the hydride points to reduced π-acceptor properties for the pyridyl triazole ligand. It is therefore somewhat surprising that the physical properties of the compounds, such as metal-to-ligand distances, ν(CO) frequencies, and redox potentials, are so similar to those obtained for the corresponding bipy compounds. An exception has to be made however for the reactivity. Whereas the synthesis of compounds of the type $[Ru(bipy)_2(CO)L]^{n+}$ from the parent compound $[Ru(bipy)_2(CO)Cl]^+$ is easy, the synthesis of the corresponding L–L′ compounds is much more difficult especially when the sixth ligand is neutral. As the NCS^- and H^- compounds are formed more easily, the stability of the parent chloro compound is probably based on kinetic rather than thermodynamic reasons.

Another point worth mentioning is the presence of many co-ordination isomers. Although this would be expected on the basis of the asymmetry of the pyridyltriazole ligands, the n.m.r. evidence that the N^2 atom is able to bind to the ruthenium ion is somewhat unexpected considering the presence of the methyl group on the neighbouring nitrogen atom. Certainly this co-ordination mode is not found in the $Ru(bipy)_2$ complex of 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole.[13b]

Experimental

X-Ray Crystallography.—A yellow bar-shaped crystal with approximate dimensions of 0.4 × 0.2 × 0.3 mm was used. The density of the crystals was determined using the flotation method.

Crystal data. $C_{17}H_{16}ClF_6N_8OPRu$, $M = 629.86$, monoclinic, space group $P2_1/n$, $a = 11.085(1)$, $b = 13.120(2)$, $c = 16.108(2)$ Å, $\beta = 97.17(1)°$, $U = 2\,324.2(2)$ Å^3, $D_m = 1.81(1)$ Mg m^{-3}, $Z = 4$, $D_c = 1.80$ Mg m^{-3}, $F(000) = 1\,243.56$, μ(Mo-K_α) = 9.2 cm^{-1}, λ(Mo-K_α) = 0.710 730 Å.

Data collection and processing. An Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation was employed. Intensities of 5 304 independent reflections were measured at room temperature ($2.0 < \theta < 27.0$). Lattice parameters were determined by measuring 25 reflections with θ from 9.5 to 14.0°. No absorption correction was applied. The range of *h*, *k*, and *l* used was $-14 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 16$, and $0 \leqslant l \leqslant 20$. The intensity standards used were the reflections (6 1 1), (1 6 0), and (−1 0 11). The intensity variation throughout the experiment was 5%.

Solution and refinement of the structure. Atomic scattering factors for neutral atoms with corrections for anomalous dispersion were taken from ref. 17. Patterson techniques and the program AUTOFOUR[18] were used to find the positions of the heavy atoms. All subsequent least-square refinements and Fourier synthesis were based on the 2 501 significant reflections $[I > 2\sigma(I)]$ only. All but one of the hydrogen atoms were located in successive difference Fourier maps. The position of the last hydrogen atom, H(236), was calculated geometrically before least-squares refinement. In this refinement all hydrogen atoms were given the thermal parameter of the carbon atom to which they are bound and were kept at a given distance from this carbon atom.

In the final difference Fourier synthesis, having a minimum value of −0.32 e Å^{-3} and a maximum value of + 0.82 e Å^{-3}, there were still three small but significant peaks. These were located near the ruthenium atom. Disorder of the fluorine atoms can be deduced from the high anisotropy in the thermal parameters. A model was applied consistently of two $[PF_6]^-$ units with identical phosphorus positions and different positions for the fluorine atoms.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

The conventional final residual was $R = \Sigma|\Delta F|/\Sigma F_o = 0.037$ for the 2 501 reflections used in the refinement, $R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}} = 0.044$.

Physical Measurements.—High performance liquid chromatography was carried out using a Waters 990 photodiode array h.p.l.c. system in conjunction with a NEC APC III computer, a Waters pump model 6000 A, a 20-μl injector loop, and a μ Partisil SCX radial PAK cartridge; the detection wavelength was 280 nm. The chromatography was carried out using acetonitrile–water (80:20) containing 0.08 mol dm^{-3} $LiClO_4$ as a mobile phase. The flow rate was 3.0 cm^3 min^{-1}.

U.v.–visible spectra were recorded on a Shimadzu UV 240 spectrophotometer, i.r. spectra on a Perkin-Elmer 599 spectrophotometer as KBr disks. Proton n.m.r. spectra were obtained on a JEOL JNX-FX 200 spectrometer, ^{13}C n.m.r. spectra on a JEOL 50.1-MHz spectrometer, using $SiMe_4$ as an internal standard. Electrochemical measurements were carried out using an E.G. and G. PAR model 174A polarographic analyser, a PAR 175 universal programmer and a platinum working electrode. The samples were measured in spectroscopic grade MeCN dried over molecular sieves using 0.1 mol dm^{-3} NEt_4ClO_4 as supporting electrolyte. The scan rate used was 100 mV s^{-1}. A KCl-saturated electrode was used as the reference electrode.

Materials.—The ligand 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole was prepared as described before.[13,19] The compound $RuCl_3{\cdot}3H_2O$ was obtained from Johnson Matthey. All other materials used for the syntheses were of reagent grade used without further purification.

Preparation of Compounds.—$[Ru(L\text{–}L')_2(CO)Cl]PF_6$. The salt $RuCl_3{\cdot}3H_2O$ (2.10 g, 8 mmol) was refluxed in dmf (60 cm^3) for 1 h. Then 2 equivalents of L–L′ were added in five portions at

5-min interval. The resulting mixture was heated at reflux for another 6 h. The product was precipitated by the addition of an excess of aqueous NH_4PF_6, recrystallised from an acetone–toluene mixture, and dried *in vacuo* at room temperature. Yield 2.1 g (85%) (Found: C, 32.1; H, 2.5; Cl, 6.0; N, 17.9. $C_{17}H_{16}ClF_6N_8OPRu$ requires C, 32.4; H, 2.6; Cl, 5.6; N, 17.8%). ^{13}C N.m.r. [$(CD_3)_2SO$]: δ 38.0, 37.7 (Me), 122.5, 122.6 (C^3), 127.2, 127.6 (C^5), 139.3, 140.4 (C^4), 145.7, 147.6, 148.7 ($C^{5'}$, C^2), 153.2, 156.7 (C^6), 160.0, 161.2 ($C^{3'}$), and 206.8 p.p.m. (CO).

[Ru(L–L′)$_2$(CO)(NCS)]PF_6·0.5H_2O. This compound was prepared as the analogous bipy complex.[4d] Yield 75% (Found: C, 32.2; H, 2.4; N, 19.3. $C_{18}H_{17}F_6N_9O_{3.5}PRuS$ requires C, 32.6; H, 2.6; N, 19.0%).

[Ru(L–L′)$_2$(CO)H]ClO_4·H_2O. This compound was prepared as the corresponding bipy complex.[4c] It was precipitated however by addition of $NaClO_4$ as the perchlorate compound as addition of NH_4PF_6 resulted in decomposition of the hydride. Yield 90% (Found: C, 35.6; H, 2.8; N, 19.5. $C_{17}H_{19}ClN_8O_4Ru$ requires C, 35.9; H, 3.3; N, 19.7%).

[Ru(L–L′)(CO)$_2$Cl$_2$]. This was prepared like the corresponding ruthenium bipy analogue.[4b] Yield 86% (Found: C, 31.0; H, 1.9; Cl, 18.6; N, 14.8. $C_{10}H_8Cl_2N_4O_2Ru$ requires C, 31.0; H, 2.1; Cl, 18.3; N, 14.4%). N.m.r. [$(CD_3)_2SO$]: ^1H, δ 9.81 (1 H, s, $H^{5'}$), 9.16 (1 H, q, H^6), 8.32 (2 H, m, H^3, H^4), 7.85 (1 H, m, H^5), and 4.16 (3 H, s, Me); ^{13}C δ 37.9 (Me), 122.5 (C^3), 128.0 (C^5), 141.0 (C^4), 146.1 (C^2), 147.2 ($C^{5'}$), 153.3 (C^6), 160.4 ($C^{3'}$), 196.2 (CO), and 206.5 p.p.m. (CO).

Attempted Preparations.—[Ru(L–L′)$_2$(CO)(H_2O)][PF_6]$_2$ *by acid hydrolysis of the hydride.* The hydride compound (0.16 g) was dissolved in acetone (20 cm^3) and then water (30 cm^3) was added. Concentrated H_2SO_4 (0.5 cm^3) was added but subsequent addition of NH_4PF_6 did yield pure material (h.p.l.c.).

[Ru(L–L′)$_2$(CO)(CH_3CN)][PF_6]$_2$. For this compound the same approach was used. Acetonitrile was however used to dissolve the hydride compound. The product obtained was h.p.l.c. pure but, as for the aquo compound, did not yield a satisfactory elemental analysis.

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