DALTON

Formation of *N*-imidoylimidatoruthenium(II) complexes *via* ruthenium-promoted hydration of nitriles

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The hydridoruthenium(II) complex $[RuCl(H)(CO)(PPh_3)_3]$ **1** reacted with aromatic nitriles at 120 °C in the presence of water to give novel *N*-imidoylimidatoruthenium(II) complexes $[RuCl(NH{=}CRN{=}CRO)(CO)(PPh_3)_2]$ ($R = C_6H_4Me$-*p* **2**, Ph **3**, or C_6H_4Me-*m* **4**). In contrast, reaction of *o*-toluonitrile with **1** gave a small amount of the corresponding *N*-imidoylimidato complex and a considerable amount of *o*-toluamide. When **1** was heated at 120 °C in a 1 : 1 mixture of an amide R^1CONH_2 and a nitrile R^2CN a cross-linked *N*-imidoylimidato complex $[RuCl(NH{=}CR^2N{=}CR^1O)(CO)(PPh_3)_2]$ **6** (R^1 = Ph, $R^2 = C_6H_4Me$-*p*) or **7** ($R^1 = C_6H_4Me$-*p*, R^2 = Ph) was obtained. Single-crystal structure analyses of **2** and **6** have been performed.

In a wide variety of known nitrile-containing complexes the nitriles are usually considered to be neutral and substitution labile.[1,2] Therefore such complexes have been used as convenient precursors in the synthesis of more stable complexes. In contrast, the activation and catalytic conversion of nitriles by transition-metal complexes are rarely reported, *e.g.*, platinum complex-catalysed hydration of nitriles[3,4] and reduction of nitriles catalysed by triiron and triosmium clusters.[5,6] However, nitriles tend to act only as a ligand not as a reactant in most cases.

Recently, hydration of nitriles catalysed by lower-valent ruthenium complexes has been reported by some groups.[7,8] The ruthenium-catalysed hydration has been exceptionally successful in activating various types of nitriles and provides advantageous methods to yield amides from nitriles. It is also a key step in the catalytic transformation of nitriles to the corresponding esters[9] and *N*-substituted amides.[10] The catalytic hydration of nitriles is perhaps so attractive that many chemists have been interested in improving the yield of amides. However, complexes that remained in the reaction mixture have not been characterized in most of these systems. Only a few reports have mentioned the formation of *N*-acylamidoplatinum complexes along with the catalytic hydration of nitriles.[3]

Independently of the catalytic hydration, reactions of trifluoroacetonitrile with some transition-metal complexes have been investigated since the 1960s as rare examples of the activation of this nitrile. Two types of ligands derived by bond formation between two CF_3CN molecules have been reported. First a head-to-tail dimerization affords the five-membered metallacyclic complex $[ML\{C(CF_3){=}NC(CF_3){=}NH\}]$ [$ML = Fe(\eta\text{-}C_5H_5)(CO)$ or $Ir(CO)(PPh_3)_2$].[11] Secondly, a combination of two CF_3CN molecules and an extra nitrogen atom gives a six-membered triazametallacyclic complex incorporating an unusual degradation of CF_3CN by traces of water.[12–14]

In the field of activation of organic substrates, we have been working on insertion of some unsaturated compounds into the Ru–H bond of $[RuCl(H)(CO)(PPh_3)_3]$ **1**.[15] In the course of our study, one of the authors attempted the insertion of acrylonitrile into the Ru–H bond and reported the formation of some new (1-cyanoethyl)ruthenium(II) complexes.[16] Unfortunately, the insertion of acrylonitrile never occurs at a nitrile function but at an olefinic one. We describe here a real activation and an unusual coupling of aromatic nitriles promoted by **1** to give novel *N*-imidoylimidato chelate ligands $[NH{=}CR^2N{=}CR^1O]^-$. The molecular structures of the two of the novel complexes were determined by single-crystal X-ray diffraction.

Results and Discussion

Synthesis and spectroscopic characterization of imidoylimidato complexes

The starting complex $[RuCl(H)(CO)(PPh_3)_3]$ reacts with *p*-toluonitrile in the presence of water to give a novel *N*-imidoylimidatoruthenium(II) complex $[RuCl\{NH{=}CRN{=}CRO\}(CO)(PPh_3)_2]$ **2** ($R = C_6H_4Me$-*p*). The *N*-imidoylimidate ligand is constructed of two nitrile molecules combined head-to-tail and an additional oxygen atom derived from water, as confirmed by X-ray structure analysis (see below). The following reaction conditions for *p*-toluonitrile are typical: a mixture of the hydrido complex **1** and about 10 times as much water in *p*-toluonitrile was sealed under vacuum and heated at 120 °C for several hours. After the reaction is over, addition of hexane to the mixture precipitates the *N*-imidoylimidato complex **2** in 92% yield. In the IR spectrum of **2** the characteristic ν(Ru–H) absorption at 2010 cm^{-1} of **1** was absent as was the C≡N stretch of *p*-toluonitrile. One very strong absorption at 1925 cm^{-1} indicates the presence of one carbonyl ligand. New bands at 1585 and 1538 cm^{-1} are found in the region for conjugated C=O and C=N.

The ^1H, $^{31}P\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ NMR data for complex **2** are summarized in Tables 1 and 2, respectively. The NMR data suggest some structural features, especially the novel *N*-imidoylimidate ligand. Two sets of the signals for the methyl and 4-substituted phenyl groups are observed in the ^1H NMR spectrum, suggesting the presence of two inequivalent *p*-tolyl moieties. In the ^{13}C NMR spectrum two singlets at δ 163.9 and 170.0 arising from nitrile carbon are found in the sp^2 region in addition to the signals of the two *p*-tolyl groups. The singlet (δ 27.76) in the ^{31}P NMR spectrum indicates that the two triphenylphosphine ligands are equivalent. The *o*-protons of the phenyl groups are split by means of virtual coupling to the two phosphorus atoms situated mutually *trans*. These results are consistent with a structure in which the six coordination sites are occupied by the CO, the *N*-imidoylimidato chelate, two *trans*-PPh_3 ligands, and Cl.

Table 1 Proton and $^{31}P-\{^1H\}$ NMR data for the *N*-imidoylimidatoruthenium(II) complexes in $CDCl_3$ [a]

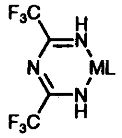
Complex	^1H (δ) Me	NH	Aromatic region [b]		$^{31}P-\{^1H\}$ (δ)
2	2.32	5.75 (br)	6.78 (d, 2 H, 8.1)	6.90 (d, 2 H, 8.1)	27.76
	2.37		7.06 (d, 2 H, 8.1)	7.96 (d, 2 H, 8.1)	
3		5.88 (br)	6.90 (d, 2 H, 7.7)	7.25 (t, 4 H, 7.7)	27.91
			7.36 (t, 2 H, 7.3)	8.06 (d, 2 H, 7.3)	
4 [c]	2.25	5.85 (br)	6.60 (s, 1 H)	6.71 (d, 1 H, 7.7)	28.03
	2.37		7.00 (t, 1 H, 7.7)	7.05 (d, 1 H, 7.7)	
			7.82 (s, 1 H)	7.84 (d, 1 H, 7.3)	
6	2.32	5.80 (br)	6.80 (d, 2 H, 8.2)	6.90 (d, 2 H, 8.2)	28.00
			7.25 (t, 2 H, 8.2)	7.35 (t, 1 H, 8.2)	
			8.05 (d, 2 H, 8.4)		
7	2.37	5.83 (br)	6.89 (d, 2 H, 7.7)	7.06 (d, 2 H, 7.7)	27.67
			7.10 (t, 2 H, 7.7)	7.24 (t, 1 H, 7.7)	
			7.97 (d, 2 H, 7.7)		

[a] Chemical shift values are given in ppm downfield from $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P). Resonances due to triphenylphosphine are not included. Multiplicity, signal intensity and coupling constants (*J*/Hz) are given in parentheses. [b] Phenyl and phenylene protons of the *N*-imidoylimidato chelate. [c] Some resonances due to the *N*-imidoylimidato chelate are obscured by those of the triphenylphosphines.

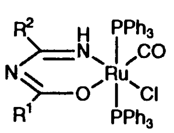
Table 2 The $^{13}C-\{^1H\}$ NMR data for the *N*-imidoylimidatoruthenium(II) complexes in $CDCl_3$ [a]

Complex	Me	C=N	RuCO	Aromatic region [b]	PPh_3
2	21.3	163.9	204.4 (t, 15.6 [c])	126.2, 127.7, 127.9, 129.7, 135.5, 139.7, 140.5	128.1
	21.6	170.0			129.6
					131.7 (t, 21.5 [d])
					134.3
3		164.1	204.4 (t, 13.7 [c])	126.1, 127.0, 127.3, 130.5, 138.0	128.1
		170.0			129.6
					131.6 (t, 21.6 [d])
					134.3
4	21.3	164.4	204.5 (t, 13.7 [c])	123.4, 126.7, 126.9, 127.3, 130.1, 130.3, 131.2, 136.3, 136.8, 138.0, 138.3	128.1
	21.5	170.8			129.6
					131.7 (t, 21.6 [d])
					134.3
6	21.3	164.0	204.4 (t, 13.7 [c])	126.1, 127.0, 128.0, 130.3, 135.4, 138.1, 139.8	128.1
		169.9			129.6
					131.7 (t, 21.6 [d])
					134.3
7	21.6	163.9	204.4 (t, 15.7 [c])	126.1, 127.2, 127.8, 129.7, 135.4, 138.1, 140.7	128.1
		170.1			129.6
					131.7 (t, 21.5 [d])
					134.3

[a] Chemical shift values are given in ppm downfield from $SiMe_4$. All signals are singlets unless stated in parentheses. Multiplicity and coupling constants (*J*/Hz) are given in parentheses. [b] Phenyl or phenylene groups of the *N*-imidoylimidato chelate. [c] $|^2J(CP)|$. [d] $|^1J(CP) + {}^3J(CP)|$ Value of the virtual triplet.



ML = Fe(η-C_5H_5)(CO) or Ir(CO)(PPh_3)$_2$



	R^1	R^2
2	C_6H_4Me-*p*	C_6H_4Me-*p*
3	Ph	Ph
4	C_6H_4Me-*m*	C_6H_4Me-*m*
5	C_6H_4Me-*o*	C_6H_4Me-*o*
6	Ph	C_6H_4Me-*p*
7	C_6H_4Me-*p*	Ph

Benzonitrile and *m*-toluonitrile react similarly with **1** to afford the corresponding *N*-imidoylimidato complexes [RuCl(NH=CRN=CRO)(CO)(PPh_3)$_2$] **3**: (R = Ph, yield 55%) and **4** (R = C_6H_4Me-*m* 40%), respectively. They show satisfactory elemental analysis and spectroscopic data (Tables 1 and 2) consistent with a similar molecular structure to that of the *p*-tolyl complex **2**. One ^{31}P singlet, virtually coupled *o*-protons of PPh_3, and a ^{13}C triplet for the co-ordinated CO all indicate that the two phosphines occupy the apical sites situated mutually *trans*. The ^1H and ^{13}C NMR spectra of each complex contain the signals of two inequivalent aryl groups. The IR spectra indicate the presence of π-delocalized C=N or C=O bonds and the disappearance of the C≡N bond of the nitriles.

In contrast, when *o*-toluonitrile reacted with complex **1** in the presence of water a very small amount of the expected *N*-imidoylimidato complex [RuCl{NH=CRN=CRO}(CO)(PPh_3)$_2$] **5** (R = C_6H_4Me-*o*) was formed. Its presence was confirmed only spectroscopically and a few by-products were also recognized in the ^{31}P NMR spectrum of the reaction mixture. All attempts to isolate **5** resulted in failure. Additionally, a considerable amount of *o*-toluamide (approximately nine times as much as the amount of **1**) was obtained. The amide is apparently a catalytic hydration product of *o*-toluonitrile. However, only trace amounts of amides were detected in the reaction mixtures of the other nitriles. It is noteworthy that the reaction of *o*-toluonitrile with **1** and water differs considerably from those of the other nitriles; in other words, **1** shows catalytic activity for hydration of nitrile when the formation of the *N*-imidoylimidato complex is prevented. In the case of *o*-toluonitrile the formation of the chelate ligand is suppressed considerably owing to steric repulsion of the two *o*-tolyl groups by the two comparatively bulky PPh_3 ligands.

Crystal structure of complex 2

A single crystal of complex **2** suitable for the structure analysis was obtained by recrystallization from $CHCl_3$–diethyl ether solution. The asymmetric unit consists of one molecule of **2** and one of $CHCl_3$. The structure is depicted in Fig. 1. Selected bond lengths and angles are summarized in Table 3; atomic coordinates including those of the $CHCl_3$ moiety are listed in Table 4.

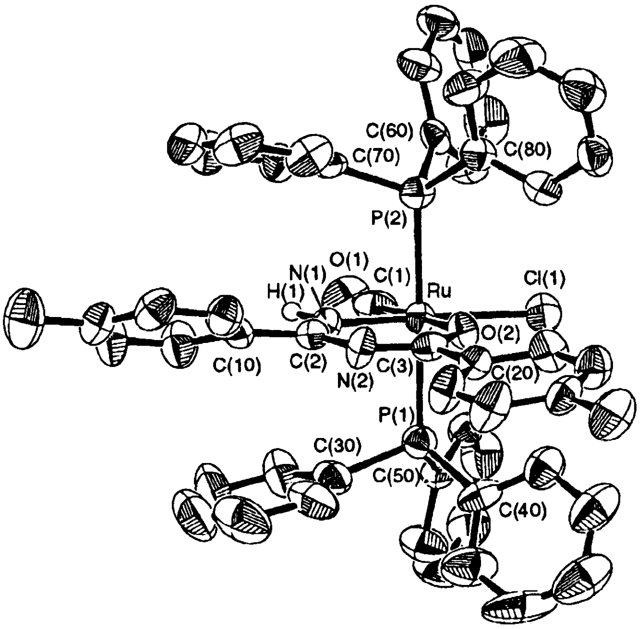
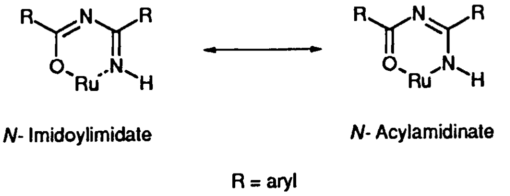


Fig. 1 Perspective view and atom numbering scheme for complex **2**, excluding all the hydrogen atoms except for H(1) for clarity



The molecule has a slightly distorted octahedral co-ordination around the ruthenium centre. The two triphenylphosphine ligands are mutually *trans* [P(1)–Ru–P(2) 178.4(1)°], and the Ru–P bond lengths [2.399(3) and 2.401(3) Å] fall within the range of those reported.[17] The Ru–Cl [2.435(2) Å] and the Ru–CO [1.847(10) Å] lengths are also similar to reported values for complexes having the $RuCl(CO)(PPh_3)_2$ moiety.[18]

The six atoms of the *N*-imidoylimidato chelate ring are located on a plane within 0.06 Å. The dihedral angles between each *p*-tolyl substituent and the chelate ring are 23.4 and 14.8°. Thus, the two *p*-tolyl substituents are not coplanar with the chelate ring. Steric repulsion between the N(1)-bonded proton and *o*-C(11)-bonded one causes the larger distortion of the C(2)-bonded *p*-tolyl substituent than of the C(3)-bonded one. Hence, the π electrons of the ligand are actually localized on each aromatic ring and the six-membered chelate. Owing to this the C_{ipso}–$C_{chelate}$ bonds are normal single C–C bonds.[19]

As for bond lengths in the chelate ring, three C–N bonds are longer than a normal C=N double bond and shorter than a normal C–N single bond.[19] The N(2)–C(2) length [1.370(9) Å] is significantly longer than those of N(1)–C(2) and N(2)–C(3) [1.300(10) and 1.319(9) Å, respectively]. The last two are comparable with the reported C–N bond lengths [1.308(7) and 1.315(7),[20a] and 1.300(14) and 1.328(14) Å[20b]] of the formamidinato complexes $[RuX(RNCHNR')(CO)(PPh_3)_2]$ [X = H, R = R′ = C_6H_4Me-*p* and X = Cl, R = $CHMe_2$, R′ = $CMe(=CH_2)$, respectively]. The O(2)–C(3) distance [1.284(8) Å] also falls between normal C–O and C=O bonds,[19] and is almost the same within error as the C–O distances [1.264(10) and 1.258(11) Å] of the acetato ligand in $[RuCl(O_2CMe)(CO)(PPh_3)_2]$.[21] These C–N and C–O distances of the *N*-imidoylimidate ligand are typical of a delocalized C_{sp^2}–heteroatom bond.[19] In addition, an sp^2-like nature of N(1) is indicated by its trigonal-planar geometry where H(1) is located coplanar to N(1), Ru and C(2) in the final electron-density map. Hence two limiting structures such as *N*-imidoylimidate and *N*-acylamidinate contribute to the bond lengths in the chelate ligand.

Noticeably, the Ru–N distance [2.031(7) Å] is apparently shorter than not only the Ru–O [2.092(5) Å], but also Ru–N in $[Ru(\eta\text{-}C_5H_5)\{NH=C(CF_3)N=C(CF_3)NH\}\{P(OMe)_3\}]$ [2.070(5)–2.089(5) Å][14] and $[Ru\{NH=C(CF_3)N=C(CF_3)NH\}$-

Table 3 Selected bond lengths (Å) and angles (°) for complexes **2** and **6**

	2	**6**		**2**	**6**
Ru–Cl(1)	2.435(2)	2.442(1)	O(2)–C(3)	1.284(8)	1.267(4)
Ru–P(1)	2.399(3)	2.398(1)	N(1)–H(1)	0.90(6)	0.82(4)
Ru–P(2)	2.401(3)	2.407(1)	N(1)–C(2)	1.300(10)	1.294(5)
Ru–O(2)	2.092(5)	2.094(3)	N(2)–C(2)	1.370(9)	1.361(5)
Ru–N(1)	2.031(7)	2.035(3)	N(2)–C(3)	1.319(9)	1.323(5)
Ru–C(1)	1.847(10)	1.847(5)	C(2)–C(10)	1.48(1)	1.496(5)
O(1)–C(1)	1.119(9)	1.115(4)	C(3)–C(20)	1.495(10)	1.496(5)
Cl(1)–Ru–P(1)	89.99(8)	91.61(4)	N(1)–Ru–C(1)	91.1(3)	91.9(2)
Cl(1)–Ru–P(2)	91.19(8)	90.90(4)	Ru–O(2)–C(3)	126.9(5)	126.5(3)
Cl(1)–Ru–O(2)	86.0(2)	86.05(7)	Ru–N(1)–H(1)	109(4)	115(2)
Cl(1)–Ru–N(1)	170.8(2)	170.7(1)	Ru–N(1)–C(2)	130.1(6)	129.4(3)
Cl(1)–Ru–C(1)	98.1(3)	97.4(1)	C(2)–N(1)–H(1)	120(4)	114(2)
P(1)–Ru–P(2)	178.4(1)	177.31(4)	C(2)–N(2)–C(3)	124.7(7)	123.0(3)
P(1)–Ru–O(2)	90.4(2)	89.70(7)	Ru–C(1)–O(1)	176.1(9)	175.7(4)
P(1)–Ru–N(1)	90.2(2)	89.38(9)	N(1)–C(2)–N(2)	124.8(8)	126.2(4)
P(1)–Ru–C(1)	90.0(3)	89.8(1)	N(1)–C(2)–C(10)	120.2(8)	119.5(4)
P(2)–Ru–O(2)	90.7(2)	91.42(7)	N(2)–C(2)–C(10)	115.0(8)	114.3(4)
P(2)–Ru–N(1)	88.8(2)	88.29(9)	O(2)–C(3)–N(2)	127.9(8)	129.6(4)
P(2)–Ru–C(1)	88.9(3)	89.0(1)	O(2)–C(3)–C(20)	115.3(7)	114.8(4)
O(2)–Ru–N(1)	84.8(2)	84.7(1)	N(2)–C(3)–C(20)	116.7(7)	115.6(4)
O(2)–Ru–C(1)	175.9(3)	176.5(1)			
Dihedral angles*	23.36	25.05		14.84	11.14

* Between the aromatic rings and the chelate ring.

Table 4 Atomic coordinates of complex **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.198 85(6)	0.202 06(5)	0.224 71(7)	C(42)	−0.157 9(8)	0.178 1(10)	0.252(1)
Cl(1)	0.366 4(2)	0.166 6(2)	0.333 0(2)	C(43)	−0.199 1(9)	0.263(1)	0.269(1)
P(1)	0.139 2(2)	0.220 0(2)	0.388 4(2)	C(44)	−0.143(1)	0.339 5(9)	0.325(1)
P(2)	0.254 4(2)	0.182 0(2)	0.057 5(2)	C(45)	−0.038 5(8)	0.327 6(8)	0.367 0(9)
O(1)	0.119 8(5)	0.013 8(4)	0.117 5(2)	C(50)	0.188 4(7)	0.312 4(6)	0.521 2(7)
O(2)	0.241 7(4)	0.339 2(4)	0.290 5(4)	C(51)	0.283 6(7)	0.343 9(6)	0.546 9(8)
N(1)	0.066 2(5)	0.253 0(5)	0.144 5(6)	C(52)	0.325 6(9)	0.409 0(8)	0.649 3(10)
N(2)	0.092 1(5)	0.413 3(5)	0.218 0(6)	C(53)	0.275(1)	0.442 4(8)	0.731 3(10)
C(1)	0.152 4(7)	0.083 7(6)	0.160 3(8)	C(54)	0.182(1)	0.411 9(8)	0.708(1)
C(2)	0.036 9(6)	0.337 5(6)	0.149 5(7)	C(55)	0.138 9(9)	0.348 7(7)	0.604 4(9)
C(3)	0.185 3(6)	0.410 5(5)	0.282 0(7)	C(60)	0.311 6(6)	0.070 0(5)	−0.003 7(7)
C(10)	−0.062 2(6)	0.357 4(6)	0.076 5(7)	C(61)	0.324 6(7)	0.046 3(6)	−0.113 3(8)
C(11)	−0.141 8(7)	0.298 0(7)	0.032 9(8)	C(62)	0.374 8(8)	−0.035 4(8)	−0.155 8(9)
C(12)	−0.231 4(7)	0.319 6(7)	−0.037 3(9)	C(63)	0.408 9(7)	−0.093 2(7)	−0.089(1)
C(13)	−0.246 9(7)	0.400 0(7)	−0.067 1(8)	C(64)	0.395 0(7)	−0.073 9(6)	0.016 6(10)
C(14)	−0.167 3(7)	0.457 5(6)	−0.026 6(8)	C(65)	0.345 5(7)	0.008 8(6)	0.060 3(8)
C(15)	−0.077 6(7)	0.438 4(6)	0.046 1(7)	C(70)	0.347 7(6)	0.260 8(5)	0.070 0(7)
C(16)	−0.343 3(8)	0.424 3(7)	−0.142 2(9)	C(71)	0.360 5(8)	0.276 4(7)	−0.027 2(8)
C(20)	0.232 5(6)	0.500 9(5)	0.352 0(7)	C(72)	0.439 3(9)	0.327 2(8)	−0.016 5(10)
C(21)	0.176 6(7)	0.580 4(7)	0.364 5(8)	C(73)	0.505 8(8)	0.363 9(7)	0.090(1)
C(22)	0.221 5(8)	0.663 2(6)	0.433 7(8)	C(74)	0.493 2(6)	0.350 6(6)	0.185 8(8)
C(23)	0.322 2(7)	0.667 9(6)	0.487 2(7)	C(75)	0.414 0(6)	0.299 3(6)	0.175 9(7)
C(24)	0.378 4(7)	0.587 1(6)	0.472 8(8)	C(80)	0.147 7(6)	0.192 2(6)	−0.062 5(6)
C(25)	0.334 2(6)	0.504 5(5)	0.406 3(8)	C(81)	0.084 0(6)	0.119 1(6)	−0.119 2(7)
C(26)	0.369 7(8)	0.757 0(6)	0.562 7(8)	C(82)	−0.005 2(7)	0.127 1(7)	−0.199 2(8)
C(30)	0.155 3(6)	0.119 8(6)	0.441 2(7)	C(83)	−0.032 9(7)	0.208 1(8)	−0.224 8(8)
C(31)	0.217 3(6)	0.046 7(6)	0.407 5(7)	C(84)	0.029 7(8)	0.280 4(7)	−0.171 7(9)
C(32)	0.231 6(7)	−0.027 1(6)	0.451 0(9)	C(85)	0.119 4(7)	0.274 1(6)	−0.089 9(8)
C(33)	0.181 9(8)	−0.028 1(7)	0.529 2(9)	H(1)	0.028(5)	0.206(5)	0.092(6)
C(34)	0.119 3(8)	0.043 8(8)	0.562 3(9)	Cl(2)	0.367 0(3)	0.171 2(2)	0.689 5(3)
C(35)	0.104 5(7)	0.117 5(6)	0.518 7(8)	Cl(3)	0.552 3(3)	0.212 3(3)	0.672 7(4)
C(40)	0.003 3(7)	0.240 1(7)	0.351 4(8)	Cl(4)	0.513 8(3)	0.028 3(2)	0.649 1(3)
C(41)	−0.058 5(7)	0.165 0(7)	0.292 5(9)	C(90)	0.462 1(8)	0.131 2(7)	0.624 3(8)

$H(CO)(PPh_3)_2]$ [2.101(7) and 2.119(6) Å].[22] The difference in these bond distances is due to the strong *trans* effect of the CO, C_5H_5, or H ligand situated *trans* to the latter bonds. Furthermore, the Ru–N and Ru–O distances in complex **2** are shorter than the Ru–N [2.183(5) and 2.248(5) Å] of the formamidinato complex[20a] and the Ru–O [2.152(6) and 2.144(6) Å] of the acetato complex.[21] This is interpreted as a result of the less strain in the six-membered chelate ring than in the four-membered one.

Our *N*-imidoylimidato complex, which contains an oxygen atom in the chelate ring, has not been reported so far. As indicated above, however, the *N*-imidoylimidate ligand closely resembles the previously reported triazachelate ligand $[NH{=}C(CF_3)N{=}C(CF_3)NH]^-$. This type of ligand, exemplified by the complexes $[ML\{NH{=}C(CF_3)N{=}C(CF_3)NH\}]$ [ML = $Ir(CO)(PPh_3)_2$ or $Ru(\eta\text{-}C_5H_5)(PPh_3)$],[13,14] is derived from CF_3CN with the aid of the metal. Another way to form this monoanionic triazachelate ligand has recently been reported in the reaction of some complexes of Ru^{II}, Os^{II}, and Ir^{III} and trifluoroacetamidine, $NH{=}C(CF_3)NH_2$.[22] Both the *N*-imidoylimidate and the triazachelate ligands are practically planar with evident π-electron delocalization on the chelate rings. The corresponding internal bond distances and angles of these chelate rings are very similar. In spite of the differences between the O and NH moieties, the $[Ru\{NH{=}CRN{=}CRO\}]$ metallacycle ($R = C_6H_4Me\text{-}p$) is very similar to $[Ru\{NHC(CF_3){=}NC(CF_3){=}NH\}]$.*

Role of water; cross-linked complexes derived from nitrile and amide

The formation of the triazachelate was reported to proceed more easily in non-dried solvents because a trace amount of water was required for the degradation of CF_3CN.[12] Water is also essential to the formation of the *N*-imidoylimidate ligand. When *p*-toluonitrile is used as purchased, the *N*-imidoylimidato complex **2** is obtained in 43% yield because of the presence of water as contaminant. In contrast, when the reaction is carried out in freshly distilled *p*-toluonitrile without water no *N*-imidoylimidato complex is formed. Although the ^{31}P NMR spectra of the reaction mixture indicated that the starting complex **1** disappears within 3 h, no signals of the *N*-imidoylimidate ligand, especially the two characteristic resonances of the *p*-methyl groups, occurred in the ^1H NMR spectra.

In order to clarify the role of water in the formation of the *N*-imidoylimidate ligand, complex **1** was heated at 120 °C in benzamide–*p*-toluonitrile (1:1). Under these conditions the absence of water must prevent the hydration of *p*-toluonitrile giving *p*-toluamide. After the reaction, the only product is an *N*-(*p*-toluimidoyl)benzimidatoruthenium(II) complex $[RuCl\{NH{=}C(C_6H_4Me\text{-}p)N{=}CPhO\}(CO)(PPh_3)_2]$ **6**, in which one benzamide molecule and one *p*-toluonitrile molecule are joined together. When a mixture of *p*-toluamide and benzonitrile is employed another cross-linked complex, $[RuCl\{NH{=}CPhN{=}C(C_6H_4Me\text{-}p)O\}(CO)(PPh_3)_2]$ **7** is obtained. Therefore, the combination of the amide and nitrile

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* Since the structure of the *N*-imidoylimidato chelate ring is quite similar to those of previously reported triazachelate ligands, we wondered whether we had mistaken the *N*-imidoylimidato chelate for a triazachelate. However, the N(1)–C(2)–N(2)–C(3)–O(2) framework of the *N*-imidoylimidato chelate is confirmed by the X-ray diffraction analysis in the following way. When an N(3)H moiety was employed instead of O(2) in the structure refinement of complex **2** the geometry around the introduced N(3) atom became improperly distorted, *e.g.* Ru–N(3)–H 3°. Moreover, the isotropic thermal parameters of N(3) converged to very small values compared to those of the other atoms in the chelate ring. These chemically meaningless results indicate that the chelate ligand of **2** does not have a triaza structure but is indeed the *N*-imidoylimidate.

requires no water to form the *N*-imidoylimidate ligand. This result suggests that the water reacts to produce an amide from the nitrile before the combination of the amide and the nitrile.

Elemental analysis data for complexes **6** and **7** are almost the same but their NMR spectroscopic data are rather different. The ^1H NMR spectrum of **6** contains a singlet at δ 2.32 (Me) and two doublets at δ 6.80 and 6.90 with AB-pattern splitting, which are due to a *p*-tolyl group. This set of resonances due to the *p*-tolyl group is quite similar to one of the two sets for **2** (a singlet at δ 2.32 and doublets at δ 6.78 and 6.90). The *p*-tolyl group of **6** is attached to the NH=CN moiety (the *N*-imidoyl group) of the chelate ligand. In a similar manner, the ^1H NMR spectrum of **7** contains the resonances of the N=C(C_6H_4Me-*p*)O moiety (the *p*-toluimidato group) at δ 2.37 (s), 7.10 (d) and 7.97 (d). The chemical shifts of these resonances vary by only 0.03 ppm compared to those of the corresponding *p*-toluimidato group of **2**. The NMR spectroscopic similarity between the NH=C(C_6H_4Me-*p*)N groups of **6** and **2**, or between the N=C(C_6H_4Me-*p*)O groups of **7** and **2**, implies structural similarity among these complexes.

A single crystal suitable for X-ray diffraction analysis was obtained from a dichloromethane–methanol solution of complex **6**. The crystal contains a disordered dichloromethane molecule in the asymmetric unit which was roughly approximated by Cl(2)–Cl(8) in the refinement. The molecular structure of **6** is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3, atomic coordinates in Table 5. The oxygen of the benzimidato moiety is located *trans* to the CO ligand and the NH of the *N*-*p*-toluimidoyl moiety *trans* to the Cl. Two triphenylphosphines co-ordinate at the apical sites. All the bond distances and angles and torsional angles are similar to those of **2** except for the absence of one CH_3 group as expected from the spectroscopic data.

The Mechanism

On the basis of these results the mechanism of the formation of the *N*-imidoylimidato complexes is depicted in Scheme 1. The formation of *o*-toluamide from *o*-toluonitrile indicates that the catalytic hydration of nitriles to the corresponding amides takes place first in the reaction mixture. The ruthenium complex-catalysed hydration of nitriles has been reported by Murahashi *et al.*[8] They stated that the [$RuH_2(PPh_3)_4$]-catalysed hydration of nitriles required a reaction temperature higher than 100 °C.

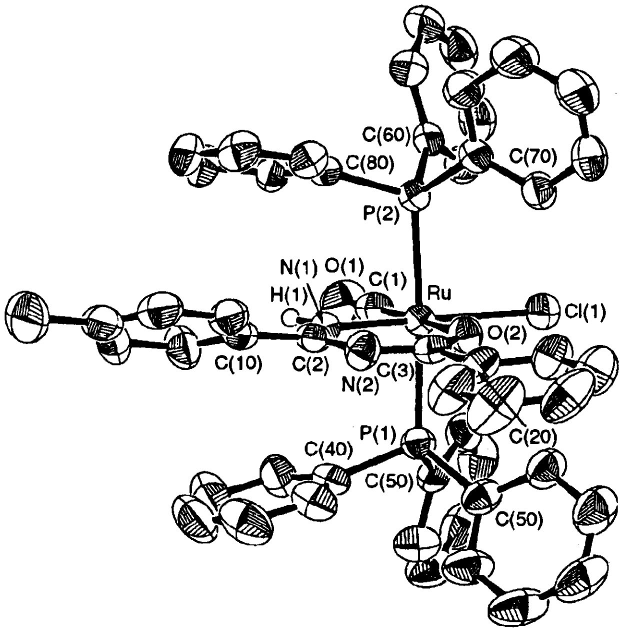
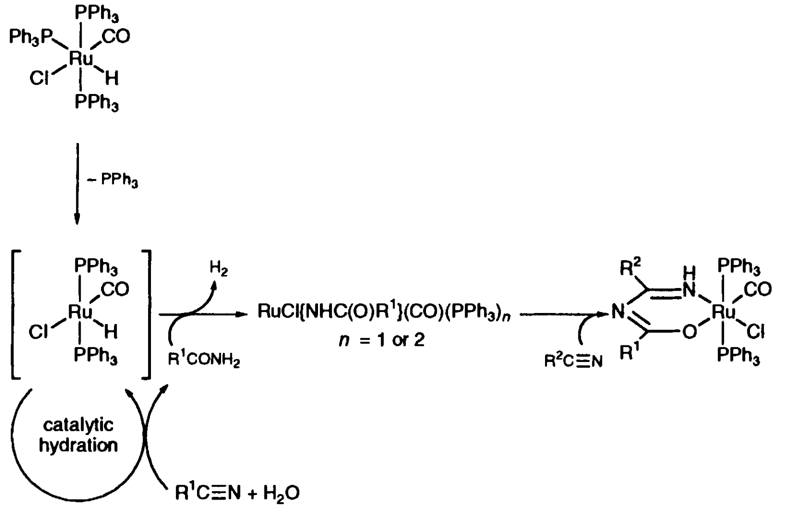


Fig. 2 Perspective view and atom numbering scheme for complex **6**, excluding all the hydrogen atoms except for H(1) for clarity

Table 5 Atomic coordinates of complex **6** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.709 86(2)	0.697 29(2)	0.711 59(3)	C(44)	0.839 1(4)	0.911 2(4)	1.155 0(5)
Cl(1)	0.880 65(8)	0.663 57(8)	0.811 20(9)	C(45)	0.797 8(4)	0.842 7(3)	1.045 3(4)
P(1)	0.651 26(8)	0.716 23(7)	0.882 13(9)	C(50)	0.667 8(3)	0.614 4(3)	0.932 4(3)
P(2)	0.760 71(7)	0.676 97(7)	0.534 81(9)	C(51)	0.733 9(3)	0.541 1(3)	0.896 3(4)
O(1)	0.634 5(2)	0.501 5(2)	0.599 3(3)	C(52)	0.748 4(4)	0.465 6(3)	0.937 9(4)
O(2)	0.750 2(2)	0.839 9(2)	0.785 6(2)	C(53)	0.695 9(4)	0.463 7(4)	1.015 3(4)
N(1)	0.575 0(2)	0.747 4(2)	0.637 7(3)	C(54)	0.629 5(4)	0.535 2(4)	1.050 8(4)
N(2)	0.599 3(3)	0.913 2(2)	0.717 1(3)	C(55)	0.615 4(4)	0.610 5(3)	1.010 4(4)
C(1)	0.666 4(3)	0.573 9(3)	0.643 2(4)	C(60)	0.815 4(3)	0.562 1(3)	0.462 5(3)
C(2)	0.545 9(3)	0.833 8(3)	0.647 0(3)	C(61)	0.823 2(3)	0.536 6(3)	0.345 3(4)
C(3)	0.693 0(3)	0.910 7(3)	0.779 8(3)	C(62)	0.871 6(3)	0.453 8(4)	0.293 7(4)
C(10)	0.445 2(3)	0.852 1(3)	0.574 4(3)	C(63)	0.911 9(3)	0.393 3(3)	0.354 7(5)
C(11)	0.429 7(3)	0.933 2(3)	0.544 8(4)	C(64)	0.903 0(3)	0.415 6(3)	0.468 1(4)
C(12)	0.338 9(4)	0.950 5(4)	0.472 5(4)	C(65)	0.855 6(3)	0.500 2(3)	0.523 3(4)
C(13)	0.261 9(4)	0.888 5(5)	0.431 0(4)	C(70)	0.651 1(3)	0.687 7(3)	0.419 1(3)
C(14)	0.276 1(3)	0.808 3(4)	0.460 9(5)	C(71)	0.624 5(3)	0.770 4(3)	0.393 6(4)
C(15)	0.367 8(3)	0.789 8(4)	0.531 9(4)	C(72)	0.532 8(4)	0.778 9(3)	0.316 6(4)
C(16)	0.162 8(4)	0.909 0(5)	0.353 8(5)	C(73)	0.467 2(3)	0.705 7(4)	0.265 7(4)
C(20)	0.739 3(3)	1.005 0(3)	0.853 5(3)	C(74)	0.492 0(3)	0.623 9(3)	0.290 0(4)
C(21)	0.839 9(4)	1.011 3(3)	0.910 5(4)	C(75)	0.583 6(3)	0.614 0(3)	0.365 8(3)
C(22)	0.883 7(4)	1.097 7(4)	0.978 1(5)	C(80)	0.851 8(3)	0.758 8(3)	0.544 1(4)
C(23)	0.827 2(6)	1.179 4(4)	0.991 8(5)	C(81)	0.916 4(3)	0.804 9(3)	0.653 5(4)
C(24)	0.727 1(5)	1.174 7(4)	0.937 2(5)	C(82)	0.993 2(3)	0.858 6(3)	0.660 6(4)
C(25)	0.682 9(4)	1.088 1(3)	0.867 2(4)	C(83)	1.005 3(4)	0.867 7(4)	0.560 2(5)
C(30)	0.516 4(3)	0.738 2(3)	0.851 2(4)	C(84)	0.940 7(4)	0.824 3(4)	0.451 0(5)
C(31)	0.475 1(4)	0.829 0(3)	0.872 4(4)	C(85)	0.864 3(3)	0.770 2(3)	0.443 3(4)
C(32)	0.371 3(5)	0.842 4(4)	0.836 5(6)	H(1)	0.536(3)	0.707(3)	0.588(3)
C(33)	0.310 8(4)	0.764 9(5)	0.777 7(6)	Cl(2)	0.955 9(5)	0.270 1(5)	0.844 5(6)
C(34)	0.350 7(4)	0.675 6(4)	0.754 7(5)	Cl(3)	1.002 8(5)	0.421 7(5)	0.811 9(6)
C(35)	0.452 8(3)	0.662 0(3)	0.790 9(4)	Cl(4)	0.956 9(7)	0.282 9(6)	0.896 4(8)
C(40)	0.702 5(3)	0.811 6(3)	1.021 8(4)	Cl(5)	0.993 9(8)	0.457 9(8)	0.851(1)
C(41)	0.649 3(4)	0.850 4(3)	1.108 3(4)	Cl(6)	1.022 9(7)	0.362 4(7)	0.912 3(8)
C(42)	0.691 6(5)	0.918 4(4)	1.215 4(5)	Cl(7)	0.898(1)	0.374(1)	0.738(1)
C(43)	0.786 4(5)	0.947 0(4)	1.237 6(4)	Cl(8)	1.079(1)	0.344(1)	0.849(1)



Scheme 1 Formation of an *N*-imidoylimidato chelate from a nitrile and amide

Although no comment was made as to whether complex **1** is catalytically effective for the hydration of nitriles or not, our reaction conditions are suitable for this. The catalytically active ruthenium species has to be a five-co-ordinate hydrido complex where one of the triphenylphosphines is liberated to give a vacant co-ordination site. The phosphine situated *trans* to the hydride is known to be very substitution labile because of the strong *trans* effect of the latter.[15e,23]

When an appropriate amount of the amide is formed in the reaction mixture the next step between it and the hydrido complex takes place. Recently, Hursthouse *et al.*[24] reported that [RuCl(H)(PPh$_3$)$_3$] reacted with benzamide in refluxing toluene to give a unique quadruply bridged dinuclear complex [Ru$_2$(μ-Cl)(μ-H){μ-NHC(O)Ph}$_2$(PPh$_3$)$_4$], evolving dihydrogen. Moreover, treatment of the benzamidato derivative with carbon monoxide afforded a carbonylation product [Ru$_2$(μ-Cl)(μ-H){μ-NHC(O)Ph}$_2$(CO)$_2$(PPh$_3$)$_2$]. We therefore attempted the reaction of **1** with an excess of *p*-toluamide in refluxing benzene for 92 h. The ^{31}P-{^{1}H} NMR spectrum of the resulting red solution exhibited nine singlets in the range δ 26.4–49.5, which were ascribable to some carbonyl(*p*-toluamidato)(triphenylphosphine)ruthenium species, although their precise characterization was difficult. A large excess of benzonitrile was added to the red solution, and the mixture was refluxed additionally for 20 h. The ^{31}P-{^{1}H} NMR spectrum of the final reaction mixture showed a strong singlet at δ 27.67 due to **7**, whereas four among the nine singlets disappeared completely and the others remained unchanged. Accordingly, the former four singlets corresponded to intermediates in the conversion of **1** to **7**, and might be assignable such formulations as RuCl{NHC(O)C$_6$H$_4$Me-*p*}(CO)(PPh$_3$)$_n$ (n = 1 or 2), similar to [Ru$_2$(μ-Cl)(μ-H){μ-NHC(O)Ph}$_2$(CO)$_2$(PPh$_3$)$_2$][24] or [Ru{NHC(O)CF$_3$}$_2$(CO)(H$_2$O)(PPh$_3$)$_2$].[25] We suppose that dihydrogen is evolved in the reaction between the hydrido complex and the amide in a similar fashion to that between [RuCl(H)(PPh$_3$)$_3$] and benzamide.[24] The intermediary amidatoruthenium(II) species reacts with another nitrile molecule, forming a new bond between the amidato N and the nitrile C accompanied by a 1,3-hydrogen shift to give the *N*-imidoylimidate ligand.

As stated above, only a trace amount of the amide was found in the reaction mixture among complex **1**, water, and benzonitrile or *p*- or *m*-toluonitrile. Moreover, when the reaction is carried out in a mixture of equimolar amounts of *p*-toluonitrile and benzamide only the cross-linked complex **6** is obtained; there was no *p*-toluonitrile-linked complex **2** in the reaction mixture regardless of the presence of water. The predominant formation of **6** is due to a rapid combination of the amide with the nitrile to give the *N*-imidoylimidate ligand. The hydration of *p*-toluonitrile into *p*-toluamide is depressed by the competitive formation of **6**. These facts indicate that the formation of the *N*-imidoylimidato chelate proceeds in competition with the catalytic hydration of the nitrile, and is relatively faster than the hydration. Furthermore, once the *N*-imidoylimidato complex is produced it does not catalyse the hydration of the nitrile.

Experimental

All experiments were performed in standard Schlenk tubes under a dry nitrogen atmosphere or in sealed tubes under vacuum. Infrared spectra were recorded on a JASCO A-100 spectrometer using KBr tablets, NMR spectra on a JEOL GX-400 spectrometer operating at 400 MHz for ^{1}H, 101 MHz for ^{13}C referenced to SiMe$_4$, and at 162 MHz for ^{31}P referenced to 85% H$_3$PO$_4$. The GLC analyses were performed on a Hitachi model 263–30 instrument equipped with a 3 m × 3 mm stainless-steel column (2% silicone OV-17 on 60–80 mesh Uniport HP) and a flame ionization detector. Elemental analyses were made on a Yanagimoto MT-3 CHN Corder and FAB mass spectra recorded on a JEOL JMS-DX303 spectrometer at the Center for Instrumental Analysis, Nagasaki University.

All nitriles were dried and distilled over P$_2$O$_5$ under nitrogen before use unless otherwise stated. Amides were used as purchased. Solvents for the silica-gel column chromatography were deoxygenized by bubbling nitrogen gas prior to use. The compound [RuCl(H)(CO)(PPh$_3$)$_3$] was prepared according to the literature.[26] All other reagents and chemicals were used without further purification.

Synthesis of complexes

[RuCl{NH=C(C$_6$H$_4$Me-*p*)N=C(C$_6$H$_4$Me-*p*)O}(CO)(PPh$_3$)$_2$] 2. A mixture of [RuCl(H)(CO)(PPh$_3$)$_3$] **1** (105 mg, 0.11 mmol) and water (0.05 cm^3, 2.7 mmol) in *p*-toluonitrile (3 cm^3) was heated at 120 °C overnight in a sealed tube *in vacuo*. After the reaction, hexane was added to the reaction mixture until a yellow powder precipitated. This was filtered off, washed with hexane, and dried *in vacuo* to give spectroscopically pure complex **2**. Yield: 96 mg (92%). Recrystallization from a CH$_2$Cl$_2$–hexane solution gave yellow microcrystals which contained CH$_2$Cl$_2$ as crystallization solvent (Found: C, 63.80; H, 4.90; N, 2.60. Calc. for C$_{54}$H$_{47}$Cl$_3$N$_2$O$_2$P$_2$Ru: C, 63.25; H, 4.60; N, 2.75%). IR (KBr tablet): ν(N–H) 3370m, ν(C≡O) 1925vs, ν(C–O) and ν(C=N) 1585s, 1538s cm^{-1}.

Table 6 Crystal data and details of measurements for complexes **2** and **6***

	2	**6**
Formula	$C_{53}H_{45}ClN_2O_2P_2Ru{\cdot}CHCl_3$	$C_{52}H_{43}ClN_2O_2P_2Ru{\cdot}CH_2Cl_2$
M	1059.80	997.30
Crystal size/mm	0.15 × 0.10 × 0.25	0.30 × 0.25 × 0.60
a/Å	14.042(4)	13.910(1)
b/Å	15.367(4)	15.158(2)
c/Å	12.737(3)	12.487(1)
α/°	108.84(2)	111.488(8)
β/°	107.66(2)	106.276(7)
γ/°	82.86(2)	82.939(8)
U/Å^3	2477(1)	2351.1(4)
D_c/g cm^{-3}	1.421	1.409
F(000)	1084.00	1020.00
μ(Mo-Kα)/cm^{-1}	6.40	6.14
Scan width/°	$1.10 + 0.30 \tan \theta$	$1.31 + 0.30 \tan \theta$
No. reflections	11 842	6479
No. unique reflections	11 379	6177
No. observations [$I \geqslant 3\sigma(I)$]	3953	4854
No. variables	589	573
R,R'	0.052, 0.038	0.033, 0.036

* Details in common: yellow, prismatic; triclinic, space group $P\bar{1}$ (no. 2); $Z = 2$; 2θ range 4–55°; $w = 1/\sigma^2(F_o^{\,2})$.

[RuCl(NH=CPhN=CPhO)(CO)(PPh$_3$)$_2$] 3. A mixture of complex **1** (161 mg, 0.17 mmol) and water (0.05 cm^3, 2.7 mmol) in benzonitrile (1.5 cm^3) was heated at 120 °C for 24 h in a sealed tube *in vacuo*. The reaction mixture was applied to a silica-gel column (eluent: toluene). The first eluted yellow band was collected and concentrated *in vacuo* to give a yellow powder of pure **3**. Yield: 85 mg (55%) (Found: C, 67.45; H, 4.90; N, 2.85. Calc. for $C_{51}H_{41}ClN_2O_2P_2Ru$: C, 67.15; H, 4.55; N, 3.05%). IR (KBr tablet): ν(N–H) 3370m, ν(C≡O) 1938vs, ν(C–O) and ν(C=N) 1590s, 1540s cm^{-1}.

[RuCl{NH=C(C$_6$H$_4$Me-*m*)N=C(C$_6$H$_4$Me-*m*)O}(CO)(PPh$_3$)$_2$] 4. A mixture of complex **1** (142 mg, 0.15 mmol) and water (0.05 cm^3, 2.7 mmol) in *m*-toluonitrile (4 cm^3) was heated at 120 °C for 20 h in a sealed tube *in vacuo*. The reaction mixture was applied to a silica gel column (eluent: benzene). The yellow band eluted first was collected and concentrated *in vacuo* to give a yellow powder of **4**. Yield: 56 mg (36%) (Found: C, 68.60; H, 5.10; N, 2.95. Calc. for $C_{53}H_{45}ClN_2O_2P_2Ru$: C, 67.70; H, 4.80; N, 3.00%). IR (KBr tablet): ν(N–H) 3360m, ν(C≡O) 1936vs, ν(C–O) and ν(C=N) 1589m, 1545s cm^{-1}.

[RuCl{NH=C(C$_6$H$_4$Me-*o*)N=C(C$_6$H$_4$Me-*o*)O}(CO)(PPh$_3$)$_2$] 5. A mixture of complex **1** (151 mg, 0.16 mmol) and water (0.05 cm^3, 2.7 mmol) in *o*-toluonitrile (1.5 cm^3) was heated at 120 °C for 20 h in a sealed tube *in vacuo*. The ^{31}P NMR spectrum of the crude reaction mixture contained a small singlet due to **5** at δ 27.70 as well as signals due to by-products. The presence of **5** was confirmed by the FAB mass spectrum: the M^+ peaks exhibited the appropriate distribution centred at m/z 940 according to the isotopes of Ru and Cl, whereas the $[M - \mathrm{Cl}]^+$ peaks were observed near m/z 905 with a distribution corresponding to the ruthenium isotopes.

[RuCl{NH=C(C$_6$H$_4$Me-*p*)N=CPhO}(CO)(PPh$_3$)$_2$] 6. A mixture of complex **1** (149 mg, 0.16 mmol) and benzamide (2.024 g, 16.75 mmol) in *p*-toluonitrile (2 cm^3) was heated at 120 °C for 18 h in a sealed tube *in vacuo*. The reaction mixture was applied to a silica gel column (eluent: benzene). The yellow band eluted first was collected and concentrated *in vacuo* to give a yellow powder of **6**. Yield: 52 mg (36%). Further recrystallization from CH_2Cl_2–hexane gave pure **6** including CH_2Cl_2 as solvent of crystallization (Found: C, 63.05; H, 4.65; N, 2.75. Calc. for $C_{53}H_{45}Cl_3N_2O_2P_2Ru$: C, 62.95; H, 4.50; N, 2.75%). IR (KBr tablet): ν(N–H) 3360m, ν(C≡O) 1936vs, ν(C–O) and ν(C=N) 1588s, 1539s cm^{-1}

[RuCl{NH=CPhN=C(C$_6$H$_4$Me-*p*)O}(CO)(PPh$_3$)$_2$] 7. A mixture of complex **1** (157 mg, 0.15 mmol) and *p*-toluamide (410 mg, 3.03 mmol) in benzonitrile (1.5 cm^3) was heated at 120 °C for 18 h in a sealed tube *in vacuo*. The reaction mixture was applied to a silica gel column (eluent: benzene). The yellow band eluted first was collected and concentrated *in vacuo* to give a yellow powder of **7**. Yield: 34 mg (36%) (Found: C, 67.90; H, 5.05; N, 2.85. Calc. for $C_{52}H_{43}ClN_2O_2P_2Ru$: C, 67.40; H, 4.70; N, 3.00%). IR (KBr tablet): ν(N–H) 3360m, ν(C≡O) 1941vs, ν(C–O) and ν(C=N) 1590s, 1540s cm^{-1}.

Stepwise reactions of complex 1 with *p*-toluamide and benzonitrile

A mixture of complex **1** (195 mg, 0.20 mmol) and *p*-toluamide (105 mg, 0.76 mmol) in benzene (20 cm^3) was refluxed for 92 h. About 2 cm^3 of the sample were removed from the resulting red solution and the ^{31}P-{^{1}H} NMR spectrum showed nine singlets: a comparatively strong singlet at δ 37.8, singlets with intermediate intensities at δ 32.0, 33.4, and 33.8, and five weak singlets. There was no triplet at δ 12.1 or doublet at 37.8 due to **1**. A large excess amount of benzonitrile (1.50 g, 14.5 mmol) was added to the red solution, and the mixture refluxed for 20 h. The ^{31}P-{^{1}H} NMR spectrum of the final reaction mixture exhibited a strong singlet at δ 27.67 due to **7**, whereas the two singlets at δ 32.0 and 37.8 and two of the weak singlets disappeared.

X-ray crystallography

Details of the crystal data, data collection, and refinement are summarized in Table 6. All the measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å) at 20 °C. The crystals were glued on a glass fibre (**2**) or sealed in a glass capillary of 0.5 mm diameter (**6**). Cell constants were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20 < 2\theta < 25°$ for **2** and 25 reflections in the range $37.5 < 2\theta < 40°$ for **6**. During the data collection the intensities of three representative reflections were measured after every 150; no variation was observed for **2** and an absorption correction was applied for **6** (transmission range 0.86–1.00). The observed data were corrected for Lorentz and polarization effects. All the calculations were performed using the TEXSAN software package.[27]

The crystal of complex **2** was obtained from a $CHCl_3$–diethyl ether solution. It includes a $CHCl_3$ molecule as solvent. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. One hydrogen atom [H(1)] was located from Fourier-difference maps and refined isotropically. The other hydrogen atoms were included in fixed positions.

The crystal of complex **6** contains a CH_2Cl_2 molecule as solvent. The structure was solved as for **2**. Owing to the poor quality of the crystal the disordered CH_2Cl_2 molecule could only be approximated by seven atoms Cl(2)–Cl(8). These were refined isotropically with the occupancy factors 0.3 [Cl(2)], 0.4 [Cl(3)], 0.2 [Cl(4)], 0.2 [Cl(5)], 0.4 [Cl(6)], 0.2 [Cl(7)] and 0.3 [Cl(8)], respectively.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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