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PREPARATION AND STUDY OF FUNCTIONALIZED 1,2,4-TRIAZINE DERIVATIVES OF THE (η^6-ARENE)Ru^{II} (ARENE = BENZENE OR *p*-CYMENE) AND (η^5-C_5Me_5)Rh^{III} MOIETIES

GABRIEL GARCIA, ISABEL SOLANO, GREGORIO SANCHEZ and GREGORIO LOPEZ*

Departmento de Química Inorgánica, Universidad de Murcia, 30071-Murcia, Spain

and

JAUME CASABO

Departamento de Química, Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain

and

ELIES MOLINS and CARLES MIRAVITLLES

Institut de Ciència de Materials, CSIC, Campus Universitari de Bellaterra, 08193-Cerdanyola, Spain

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Abstract—In dichloromethane the complexes [{(η^6-arene)RuCl(μ – Cl)}$_2$] (arene = benzene or *p*-cymene) and [{(η^5-C_5Me_5)RhCl(μ-Cl)}$_2$] react with the triazines 4-amino-6-methyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine (3-S-ATAZ), 4-amino-6-methyl-5-oxo-3-phenylamino-4,5-dihydro-1,2,4-triazine (3-PhNH-ATAZ) and 4-amino-6-methyl-5-oxo-3-amino-4,5-dihydro-1,2,4-triazine (3-NH_2-ATAZ) to form the corresponding complexes [(η^6-arene)RuCl(triazine)]Cl and [(η^5-C_5Me_5)RhCl(triazine)]Cl. The new compounds have been characterized by conductance measurements and spectroscopic (IR, ^{1}H, ^{13}C) methods. In every case the triazine acts as a chelating bidentate ligand, which has been confirmed by a single-crystal diffraction study carried out with [(η^5-C_5Me_5)RhCl(3-PhNH-ATAZ)]$PF_6 \cdot H_2O$.

The (η^6-arene)Ru^{II} and (η^5-C_5Me_5)Rh^{III} fragments are isoelectric and both form the chloride-bridged binuclear complexes [{(η^6-arene)RuCl(μ-Cl)}$_2$] and [{(η^5-C_5Me_5)RhCl(μ-Cl)}$_2$]. Both complexes undergo cleavage of the chloride bridges with the various monodentate ligands (L) to give the monomeric compounds [(η^6-arene)$RuCl_2$L][1–10] and [(η^5-C_5Me_5)$RhCl_2$L],[11–15] respectively. Further halide substitution may afford the cationic derivatives [(η^6-arene)RuClL_2]$^+$ [7,16–22] and [(η^5-C_5Me_5)RhClL_2]$^+$ [11–14,23–26] with monodentate (L) or bidentate (L_2) donors.

Following our study[27,28] on the reactivity of [{(η^6-arene)$RuCl_2$(μ-Cl)}$_2$] and [{(η^5-C_5Me_5)$RhCl_2$(μ-Cl)}$_2$] to neutral mono- and bidentate ligands, we have now investigated the reactions of these complexes with some functionalized 1,2,4-triazines. 4-Amino-5-oxo-1,2,4-triazines are biologically active

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* Author to whom correspondence should be addressed.

compounds.[29] For example, it has been shown that 4-amino-5-oxo-3-phenylamino-1,2,4-triazine has a powerful inhibiting effect on the cell wall lignification catalysed by peroxidases, and alters the integrity of chloroplast.[30,31] Complexes of Ni^{II} and Co^{II} with 4-amino-6-methyl-5-oxo-3-phenylamino-4,5-dihydro-1,2,4-triazine[32] (3-PhNH-ATAZ) and 4-amino-6-methyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine[33,34] (3-S-ATAZ), and of Ni^{II},[35] Pd^{II},[36] Ru^{II}[28] and Rh^{III}[27] with 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine have been reported previously.

In this paper we present the results obtained from the reaction between both $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ and $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ and three 4-amino-triazines: 4-amino-6-methyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine (3-S-ATAZ), 4-amino-6-methyl-5-oxo-3-phenylamino-4,5-dihydro-1,2,4-triazine (3-PhNH-ATAZ) and 4-amino-6-methyl-5-oxo-3-amino-4,5-dihydro-1,2,4-triazine ($3\text{-}NH_2$-ATAZ). The cationic complexes $[(\eta^6\text{-arene})RuCl(LL)]^+$ and $[(\eta^5\text{-}C_5Me_5)RhCl(LL)]^+$ are obtained, where the triazine (LL) acts as a chelating bidentate ligand.

EXPERIMENTAL

All the manipulations were carried out under nitrogen. The solvents were dried by conventional methods. $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene or *p*-cymene)[37,38] and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$[12] were prepared by published procedures. 4-Amino-6-methyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine (3-S-ATAZ),[39] 4-amino-6-methyl-5-oxo-3-phenyl-amino-4,5-dihydro-1,2,4-triazine (3-PhNH-ATAZ)[40] and 3,4-diamino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazine ($3\text{-}NH_2$-ATAZ)[39] were synthesized as described elsewhere and were recrystallized from ethanol. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200E instrument. IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer as Nujol mulls. The C, H and N analyses were performed with a Perkin–Elmer 240C microanalyser. Thermal decomposition studies were carried out on a Mettler TG-50 thermobalance. Conductivities were measured with a Crison 525 conductimeter.

Preparation of the complexes

Complexes **1** *and* **3**. These were prepared according to the following procedure. To a dichloromethane (8 cm^3) suspension of $[(\eta^6\text{-benzene})RuCl_2]_2$ (0.20 mmol) was added the appropriate triazine (0.50 mmol). The resulting suspension was stirred for 1 h and the precipitate was separated by filtration. The solid was repeatedly washed with acetone (complex **1**) or dichloromethane–diethyl ether (complex **2**).

Complexes **2** *and* **4**. The triazine (3-S-ATAZ or 3-PhNH-ATAZ respectively; 0.40 mmol) was added to a solution of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.16 mmol) in dichloromethane (5 cm^3). After stirring the solution for 1 h, it was vacuum-concentrated and subsequent addition of diethyl ether afforded a precipitate which was repeatedly washed with diethyl ether and acetone.

Complexes **5** *and* **6**. To an ethanol (10 cm^3) solution of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene or *p*-cymene; 0.20 mmol) was added the triazine ($3\text{-}NH_2$-ATAZ; 0.40 mmol). The resulting suspension was boiled under reflux for 2 h, then cooled to room temperature. After partial evaporation of solvent, the solid was filtered off and washed with diethyl ether.

Complex **7**. To a dichloromethane (8 cm^3) solution of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (100 mg; 0.16 mmol) was added 3-S-ATAZ (51.69 mg; 0.32 mmol). The resulting red suspension turned orange on stirring for 1 h. The yellow–orange precipitate was separated by filtration under vacuum, then washed several times with diethyl ether.

Complexes **8** *and* **9**. To a dichloromethane (8 cm^3) solution of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (100 mg; 0.16 mmol) was added 3-PhNH-ATAZ (70.20 mg; 0.32 mmol) or $3\text{-}NH_2$-ATAZ (45.65 mg; 0.32 mmol) respectively. The resulting red solution was stirred for *ca* 1 h. After partial evaporation of solvent under vacuum, diethyl ether was added to precipitate an orange (complex **8**) or yellow (complex **9**) solid which was washed with diethyl ether.

$[(\eta^5\text{-}C_5Me_5)RhCl(3\text{-PhNH-ATAZ})]PF_6 \cdot H_2O$. To an ethanol (8 cm^3) solution of complex **8** (100 mg; 0.19 mmol) was added KPF_6 (34.99 mg; 0.19 mmol) and a few drops of water. The resulting suspension was stirred for 1 h. After partial evaporation of the solvent, diethyl ether was added to yield a yellow precipitate. Crystals (decomposition temperature 207°C) of the title compound were obtained by recrystallization from acetone–diethyl ether. Satisfactory analytical data were obtained (Found: C, 37.0; H, 4.6; N, 10.7. Calc.: C, 36.7; H, 4.3; N, 10.7%) and the IR spectrum showed a broad, strong band at *ca* 840 cm^{-1} owing to the PF_6^--anion. The NMR data are discussed in the next section.

X-ray structure determination of $[(\eta^5\text{-}C_5Me_5)RhCl(3\text{-PhNH-ATAZ})]PF_6 \cdot H_2O$. Details of crystal analysis, data collection and structure refinement are given in Table 1. Final fractional atomic coordinates and anisotropic thermal par-

Table 1. Crystal data for [(η^5-C$_5$Me$_5$)RhCl(3-PhNH-ATAZ)]PF$_6\cdot$H$_2$O

Chemical formula	$C_{20}H_{26}N_5OClRh \cdot PF_6$
Formula weight	653.8
Formula weight	653.8
Colour	Orange
Crystal habit	Needle
Crystal size (mm)	$0.66 \times 0.07 \times 0.01$
Symmetry	Monoclinic, $C2/c$
Unit cell dimensions	
a, b, c (Å)	17.071(3), 27.818(8), 13.792(2)
β (°)	114.63(1)
V (Å^3)	5954(2)
Z	8
D_c (g cm^{-3})	1.454
Monochromated Mo-K_α radiation	
λ (Å)	0.71069
μ (mm^{-1})	0.68
No. of reflections for lattice parameters	25
θ range for lattice parameters (°)	8–16
Temperature (K)	294(1)
Diffractometer	Enraf-Nonius CAD4
Absorption correction type	empirical, DIFABS[41]
No. of reflections measured	4903
No. of independent reflections	4400
Criterion for observed	$I > 2\sigma(I)$
$h_{min}, k_{min}, l_{min}$	$-19, 0, 0$
$h_{max}, k_{max}, l_{max}$	19, 31, 15
Collection method	ω–2θ
Absorption correction, min–max	0.802–1.215
θ_{max} (°)	47
No. of standard reflections	3, measured each hour
Variation of standards	-1.01% (92 h)
R	0.066
R	0.071
$(\Delta/\sigma)_{max}$	0.67
No. of reflections used in refinement	2100
Weighting scheme	$w = 1/\sigma^2(F) + 0.005812(F^2)$
$(\Delta\rho)_{min}$, $(\Delta\rho)_{max}$ (e Å^{-3})	$-0.51, 0.85$

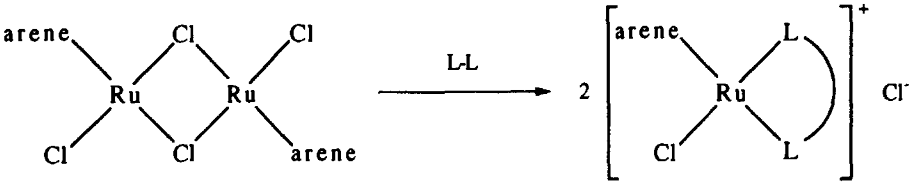
ameters, full listing of bond lengths and angles and observed and calculated structure factors have been deposited and are available from the Editor or the authors. The structure was solved by using the OMEGA program[42] and refined with the SHELX-76 program.[43]

RESULTS AND DISCUSSION

In dichloromethane the complexes [{(η^6-arene)RuCl(μ-Cl)}$_2$] (arene = benzene or p-cymene) react with the triazines 3-S-ATAZ, 3-PhNH-ATAZ and 3-NH$_2$-ATAZ to form the corresponding complexes [(η^6-arene)RuCl(triazine)]Cl (**1**–**6**) shown in Scheme 1. Every triazine molecule is acting as a chelating bidentate ligand to the ruthenium atom in the cationic complex formed. Yields, partial elemental analyses and decomposition temperatures are listed in Table 2. Complex **2** is orange but all the other ruthenium complexes are yellow. The molar conductivity data in dimethyl sulphoxide (Table 2) are consistent with the behaviour as 1 : 1 electrolytes.[44]

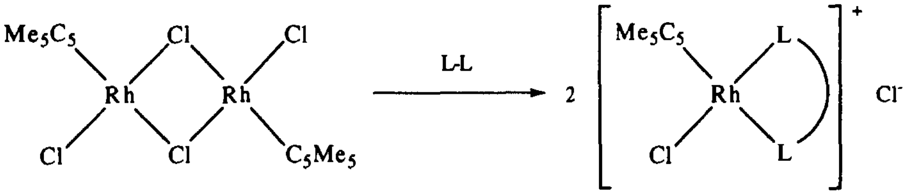
The IR spectra of complexes **1**–**6** (Table 3) show the band attributed to the C=O stretching vibration of the 5-oxo group shifted to higher wavenumber than in the free triazines, indicating that the carbonyl group is not involved in coordination to ruthenium (the carbonyl oxygen is likely to be hydrogen bonded in the uncoordinated triazine). In contrast, the bands arising from ν(N—H) are observed below 3300 cm^{-1}, so there is coordination of the triazine through the 4-amino substituent (for the three triazines) as well as the 3-phenylamino or 3-amino groups of 3-PhNH-ATAZ and 3-NH$_2$-ATAZ respectively. 3-S-ATAZ is a heterocyclic thione for which prototropic tautomerism may occur, i.e. it may exist in thione or thiol forms[45] and can coordinate as a neutral (thione) or monoanionic (thiolate) ligand. In the IR spectrum of the free triazine two partially overlapped bands are observed at 1400–1380 cm^{-1}, attributed to the thiomide II band.[46–48] The presence of a band at 1330–1340 cm^{-1} in the spectra of complexes **3** and **4** is attributed to coordination of 3-S-ATAZ through the sulphur atom of the 3-thiocarbonyl group, so this triazine acts as a neutral bidentate N,S-donor. The Ru—Cl stretching vibration is observed at 275–290 cm^{-1}.

The Ru^{II} derivatives **1**, **3** and **5** all show a singlet resonance at σ *ca* 5.5–6.0 in the ^{1}H NMR spectra (Table 3), owing to the η^6-benzene fragment. Complex **2** gives two doublets (aromatic ring, AB system), a singlet (Me) and a septet and a doublet (Pr^i), respectively, for the η^6-bonded p-cymene. However, complexes **4** and **6** exhibit double aromatic and isopropyl methyl proton resonances (two AB systems and two doublets respectively), because the three donor atoms forming the three legs of the piano-stool arrangement around the ruthenium atom are different.[49,50] The same effect is observed in the ^{13}C NMR spectra and six different resonances are provided by the six carbon atoms of the aromatic ring, even for complex **2**. The ^{1}H NMR spectra also show that the hydrogen atoms of each amino group are diastereotopic because chelation of the triazine prevents rotation about the Ru—N bond.

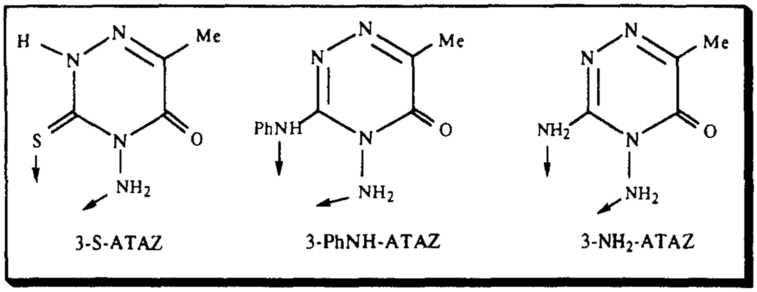


arene = η^6– C_6H_6; L-L = 3-S-ATAZ (**1**), 3-PhNH-ATAZ (**3**), 3-NH_2-ATAZ (**5**)

η^6 – *p* - cymene; L-L = 3-S-ATAZ (**2**), 3-PhNH-ATAZ (**4**), 3-NH_2-ATAZ (**6**)



L-L = 3-S-ATAZ (**7**), 3-PhNH-ATAZ (**8**), 3-NH_2-ATAZ (**9**)



Scheme 1.

Table 2. Analytical data and physical properties for the Ru and Rh complexes

Complex	Colour	Yield (%)	M.p.[a] (°C)	Analysis [Found (Calc.) %] C	H	N	S	Λ_M[b]
1	Yellow	90	144	29.1	3.2	13.7	7.6	37
				(29.4)	(3.0)	(13.7)	(7.9)	
2	Orange	95	151	36.5	4.4	12.0	7.1	33
				(36.2)	(4.3)	(12.1)	(6.9)	
3	Yellow	95	172	39.9	3.7	14.7		26
				(41.1)	(3.7)	(15.0)		
4	Yellow orange	70	169	45.7	4.8	13.3		32
				(45.9)	(4.8)	(13.4)		
5	Yellow	75	193	30.4	3.5	17.6		29
				(30.7)	(3.4)	(17.9)		
6	Yellow	85	184	37.4	5.1	15.3		28
				(37.6)	(4.7)	(15.7)		
7	Yellow	40	151	35.7	4.9	11.6		18
				(36.0)	(4.5)	(12.0)		
8	Yellow	75	211	45.3	5.3	13.0		28
				(45.6)	(5.0)	(13.3)		
9	Yellow	80	207	37.3	5.3	15.5		26
				(37.4)	(4.9)	(15.6)		

[a] With decomposition.

[b] Ohm^{-1} cm^2 mol^{-1} (in dimethyl sulphoxide).

The Rh^{III} complexes **7**–**9** are obtained when $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ is reacted with the appropriate triazine in dichloromethane. The analytical data (Table 2) and IR data (Table 3) are consistent with the proposed formulae (Scheme 1), with the triazine as a chelating bidentate ligand. However, the conductance measurements of the solutions of **7**–**9** in dimethyl sulphoxide (Table 2) suggested that a dissociation process took place, since the values of the molar conductivities are low for 1 : 1 electrolytes. The ^1H NMR spectra of **7**–**9** (in dimethyl sulphoxide-d_6) showed that there was displacement of neutral ligands (triazine) by solvent according to eq. (1).

$$2[(\eta^5\text{-}C_5Me_5)RhCl(\text{triazine})]^+Cl^- + \text{dmso} \rightleftharpoons [(\eta^5\text{-}C_5Me_5)RhCl_2(\text{dmso})] + \text{triazine} \quad (1)$$

Each spectrum consisted of the signals from the rhodium–triazine complex (**7**, **8** or **9**; data in Table 3), those from the neutral rhodium–dmso complex (a singlet at δ1.60) and free triazine [3-S-ATAZ, δ13.0(s, NH), 6.43 (s, NH_2), 2.15 (s, 6-Me); 3PhNH-ATAZ, δ9.06 (s, NH), 7.78 (d, 2H, Ph), 7.33 (d, 2H, Ph), 7.06 (s, 1 H, Ph), 5.78 (s, NH_2), 2.26 (s, 6-Me); 3-NH_2-ATAZ, δ7.02 (s, NH_2), 5.57 (s, NH_2), 2.16 (s, 6-Me)]. The relative intensities showed that the dmso solutions contained 75% of **7**, 60% of **8** and 55% of **9**, respectively. Complex **8** was converted into the hexafluorophosphate salt by the exchange reaction with KPF_6 in ethanol (see Experimental). The new compound $[(\eta^5\text{-}C_5Me_5)RhCl(3\text{-PhNH-ATAZ})]PF_6 \cdot H_2O$ is soluble in acetone and its molar conductivity (138 ohm^{-1} cm^2 mol^{-1}; $c = 5 \times 10^{-4}$ mol dm^{-3}) is consistent with that of a 1 : 1 electrolyte. In $(CD_3)_2CO$ the following data were obtained: ^1H, δ11.42 (br s, NH), 8.18 (br s, 1H, NH_2), 7.91 (br s, 1H, NH_2), 7.48 (m, 5H, Ph), 2.15 (s, 3H, 6-Me), 1.54 (s, 15H, C_5Me_5); ^{13}C, δ154.50 (s, CO), 148.94 (s, C-NHPh), 143.98 (s, C-CH_3 of triazine), 142.85 (s, C-NH of Ph), 130.79 (CH of Ph), 128.12 (s, CH of Ph), 126.38 (s, CH of Ph), 96.54 (d, C_5Me_5, $J_{RhC} = 8.7$ Hz), 15.86 (s, 6-Me of triazine), 8.48 (s, C_5Me_5).

Figure 1 gives a view of the structure of the cation in $[(\eta^5\text{-}C_5Me_5)RhCl(3\text{-PhNH-ATAZ})]PF_6$. Selected bond parameters are collected in Table 4. The rhodium atom displays a characteristic three-legged "piano-stool" arrangement, with opening angles N1—Rh1—Cl1 (87.5(4)°), Cl1—Rh1—N8 [86.9(4)°) and N8—Rh1—N1 (76.3(4)°] comparable with those found in $[(\eta^5\text{-}C_5Me_5)RhCl(1,10\text{-phenantroline})]^+$,[51] $[(\eta^5\text{-}C_5Me_5)IrCl(2,2'\text{-biimidazole})]^+$[24] and $[(\eta^5\text{-}C_5Me_5)IrCl(2,2'\text{-bipyridine})]^+$.[51] The metal is bound to one η^5-C_5Me_5 group and a *fac*-Cl, N, N set involving the 4-amino

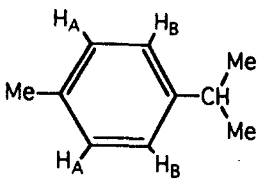
Table 3. IR (Nujol; cm^{-1}) and NMR data (J in Hz) for the Ru complexes

Complex	Relevant IR bands	^{1}H (δ, SiMe$_4$)	^{13}C (δ, SiMe$_4$)
1	3260 m ν(N—H)	10.64 (d, 1H, NH$_2$, J 8.6)	172.8 (C=S)
	3150 m ν(N—H)	9.09 (d, 1H, NH$_2$, J 8.6)	152.2 (C=O)
	1720 vs ν(C=O)	5.91 (s, 6H, C$_6$H$_6$)	150.3 (*C*—Me)
	1330 s ν(C=S)	2.22 (s, 3H, 6-Me)	85.0 (C$_6$H$_6$)
	280 m ν(Ru—Cl)		16.2 (6-Me)
2	3150 m ν (N—H)	10.58 (s, br, 1H, NH$_2$)	172.81 (C=S)
	1710 vs ν(C=O)	9.01 (s, br, 1H, NH$_2$)	152.22 (C=O)
	1330 s ν(C=S)	5.91 (d, 2H, H$_{A/B}$, J 16)	150.12 (*C*—CH$_3$)
	285 m ν(Ru—Cl)	5.63 (d, 2H, H$_{B/A}$, J 24)	106.26 (C—^{i}Pr)
		2.77 (spt, 1H, C*H* Me$_2$)	99.67 (C—Me)
		2.22 (s, 3H, 6-Me)	83.84 (C$_{B/A}$)
		2.17 (s, 3H, Me)	83.35 (C$_{A/B}$)
		1.21 (d, 6H, CHMe$_2$, J 6.6)	82.04 (C$_{B/A}$
			80.77 (C$_{A/B}$)
			30.51 (*C*HMe$_2$)
			22.25 (CHMe$_2$)
			21.86 (CHMe$_2$)
			18.07 (Me)
			16.10 (6-Me)
3	3120 m ν(N—H)	12.36 (s, br, 1H, NH)	153.52 (C=O)
	1695 vs ν(C—O)	10.67 (d, 1H, NH$_2$, J 8.7)	147.95 (ATAZ ring)
	280 m ν(Ru—Cl)	8.72 (d, 1H, NH$_2$, J 8.7)	146.04 (ATAZ ring)
		7.44 (m, 5H, Ph)	142.83 (Ph)
		5.54 (s, 6H, C$_6$H$_6$)	130.09 (Ph)
		2.11 (s, 3H, 6-Me)	127.21 (Ph)
			125.13 (Ph)
			84.05 (C$_6$H$_6$)
			15.75 (6-Me)
4	3220 m, br ν(N—H)	12.33 (d, 1H, NH)	153.55 (C=O)
	3180 m, br ν(N—H)	10.26 (d, 1H, NH$_2$, J 9.5)	148.07 (ATAZ ring)
	1720 vs, ν(C=O)	8.75 (d, 1H, NH$_2$, J 9.5)	145.57 (ATAZ ring)
	270 m, ν(Ru—Cl)	6.76 (m, 5H, Ph)	142.80 (Ph)
		5.59 (d, 1H, H$_{A/B}$, J 5.9)	129.86 (Ph)
		5.51 (d, 1H, H$_{A/B}$, J 5.9)	127.08 (Ph)
		5.18 (d, 1 ; H, H$_{B/A}$, J 5.9)	125.50 (Ph)
		5.07 (d, 1H, H$_{B/A}$, J 5.8)	104.77 (C—^{i}Pr)
		2.43 (spt, 1H, CH)	96.77 (C—Me)
		2.13 (s, 3H, 6-Me)	83.70 (C$_{B/A}$)
		2.05 (s, 3H, CH$_3$)	82.35 (C$_{A/B}$)
		1.11 (q, 6H, CHMe$_2$, J 3.0)	81.95 (C$_{B/A}$)
			80.74 (C$_{A/B}$)
			29.80 (C*H*Me$_2$)
			22.12 (CHMe$_2$)
			21.86 (CHMe$_2$)
			17.71 (Me)
			15.75 (6-Me)

Table 3. *Continued.*

Complex	Relevant IR bands	^{1}H (δ, SiMe$_4$)	^{13}C (δ, SiMe$_4$)
5	3130 m ν(N—H)	13.16 (s, 1H, NH)	153.79 (C=O)
	3210 m ν(N—H)	10.14 (d, 1H, NH$_2$, J 9.3)	150.85 (ATAZ ring)
	3080 m ν(N—H)	8.37 (d, 1H, NH$_2$, J 9.3)	141.90 (ATAZ ring)
	1715 vs ν(C=O)	8.23 (s, 1H, NH)	83.35 (C$_6$H$_6$)
	285 s ν(Ru—Cl)	5.79 (s, 6H, C$_6$H$_6$)	15.68 (6-Me)
		2.10 (s, 3H, 6-Me)	
6	3160 m ν(N—H)	13.23 (s, 1H, NH)	153.73 (C=O)
	1710 vs ν(C=O)	10.02 (d, 1H, NH$_2$ J 9.2)	151.13 (ATAZ ring)
	285 m ν(Ru—Cl)	8.26 (d, 1H, NH$_2$, J 9.3)	141.78 (ATAZ ring)
		8.13 (s, 1H, NH)	103.46 (*C*—^{i}Pr)
		5.65 (m, 4H, H$_A$+H$_B$)	97.62 (*C*—Me)
		2.81 (spt, 1H, CH, J 6.7)	81.88 (C$_{B/A}$)
		2.12 (s, 3H, 6-Me)	81.50 (C$_{A/B}$)
		2.08 (s, 3H, Me)	80.76 (C$_{B/A}$)
		1.19 (dd, 6H, CHMe$_2$, J 7.3)	80.67 (C$_{A/B}$)
			30.25 (*CHMe*$_2$)
			22.41 (CH*Me*$_2$)
			21.95 (CH*Me*$_2$)
			18.12 (Me)
			15.70 (6-Me)
7	3240 m ν(N—H)	13.80 (s, 1H, NH)	172.11 (C=S)
	1716 vs ν(C=O)	9.57 (d, 1H, NH$_2$)	152.26 (C=O)
	240 m ν(Rh—Cl)	9.09 (d, 1H, NH$_2$, J 8.5)	150.61 (*C*—Me)
		2.22 (s, 3H, 6-Me)	96.88 (d, C$_5$Me$_5$, J_{RhC} 8.2)
		1.74 (s, 15H, C$_5$Me$_5$)	16.42 (6-Me, TAZ)
			9.07 (me-C$_5$Me$_5$)
8	3390 m, br ν(N—H)	12.23 (s, 1H, NH)	153.64 (C=O)
	3120 m ν(N—H)	9.17 (d, 1H, NH$_2$)	149.75 (ATAZ ring)
	1710 vs ν(C=O)	8.82 (d, 1H, NH$_2$, J, 8.3)	142.79 (ATAZ ring)
	270 m ν(Rh—Cl)	7.32 (m, 5H, Ph)	142.51 (Ph)
		2.04 (s, 3H, 6-Me)	129.93 (Ph)
		1.39 (s, 15H, C$_5$Me$_5$)	126.96 (Ph)
			125.52 (Ph)
			94.99 (d, *C*$_5$Me$_5$, J_{RhC} 8.8)
			15.92 (6-Me)
			8.18 (C$_5$*Me*$_5$)
9	3370 vs ν(N=H)	8.87 (s, br, 1H, NH$_2$)	153.79 (C=O)
	3282 vs ν(N—H)	8.20 (s, br, 1H, HN$_2$)	151.61 (ATAZ ring)
	1722 vs ν(C=O)	7.52 (s, br, 1H, NH$_2$)	141.86 (ATAZ ring)
	256 vs ν(Rh—Cl)	5.62 (s, br, 1H, NH$_2$)	94.78 (d, *C*$_5$Me$_5$, J_{RhC} 8.8)
		2.06 (s, 3H, 6-Me)	15.97 (6-Me)
		1.68 (s, 15H, C$_5$Me$_5$)	9.02 (C$_5$*Me*$_5$)

Labelling of the *p*-cymene protons:



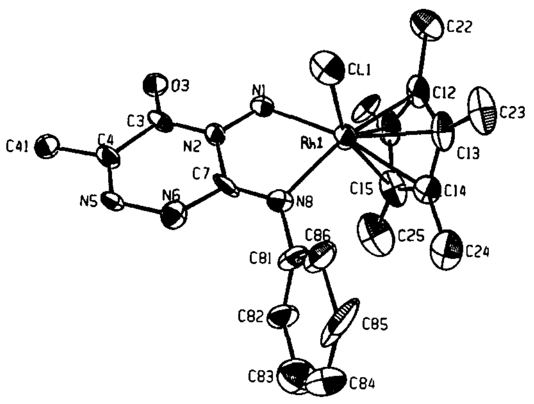


Fig. 1. Perspective view of the $[(\eta^5\text{-}C_5Me_5)RhCl(3\text{-}PhNH\text{-}ATAZ)]^+$ ion in the hexafluorophosphate compound, with atom numbering.

Table 4. Selected bond lengths (Å) and angles (°) with their e.s.d.s

(a) Bond lengths			
Rh1—Cl1	2.412(4)	Rh1—C12	2.095(15)
Rh1—N1	2.151(12)	Rh1—C13	2.148(15)
Rh1—N8	2.135(12)	Rh1—C14	2.161(15)
Rh1—C11	2.114(18)	Rh1—C15	2.171(15)
(b) Bond angles			
N1—Rh1—Cl1	87.5(4)	N1—N2—C7	116.8 (11)
N8—Rh1—Cl1	86.9(4)	N2—C7—N8	119.9(13)
N8—Rh1—N1	76.3(4)	C7—N8—Rh1	114.7(10)
N2—N1—Rh1	110.8(8)		

[Rh1—N1 = 2.151(12) Å] and 3-phenylamino [Rh1—N8 = 2.135(12) Å] substituents on the triazine ring and a chloride [Rh1—Cl1 = 2.412(4) Å].

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