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Arene ruthenium(II) azido complexes incorporating N∩O chelate ligands: Synthesis, spectral studies and 1,3-dipolar-cycloaddition to a coordinated azide in ruthenium(II) compounds

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ABSTRACT

The arene ruthenium(II) azido compounds [{(*p*-cymene)Ru(N∩O)N_3}] have been prepared by the reaction of [{(*p*-cymene)Ru(μN_3)Cl}$_2$] with the corresponding ligands. The ruthenium azido compounds [{(*p*-cymene)Ru(N∩O)N_3}] undergo 1,3-dipolar additions with substituted alkynes at room temperature to give the (η^6-arene) ruthenium triazolato compounds [(*p*-cymene)Ru(N∩O){$N_3C_2(CO_2R)_2$}]. The compounds were characterized on the basis of FTIR, NMR (^{1}H and ^{13}C) and the molecular structure of a representative compound has been established with the help of single crystal X-ray diffraction.

1. Introduction

Synthesis of (η^6-arene) ruthenium(II) complexes has attracted considerable attention owing to their anti-cancer [1–3], antiviral [4] and catalytic properties [5–7]. The catalytic activities of these complexes range from hydrogen transfer to ring closing metathesis via a variety of C–C bond formation reactions [8,9]. Water soluble (η^6-arene) ruthenium compounds bearing carboxylate or pyronate groups show promising catalytic performance in water [10,11]. Notably, water soluble (η^6-arene) ruthenium compounds have been prepared by functionalization of the (η^6-arene) moiety with ethoxyhydroxyl [12] or coordination of water soluble ligand such as kojic acid to the ruthenium centre [13].

Triazole and its derivatives have shown wide application in medicinal chemistry [14]. The most efficient route for synthesizing 1,2,3-triazole compounds is the cycloaddition reactions of an alkyl or aryl azide with alkynes [15,16]. Although such reactions have been studied extensively for synthesizing heterocycles [15–18], dipolar cycloaddition reactions of azide coordinated metal complexes are relatively unexplored. Dori, Ziolo and Fruhauf have reported pioneering work on the 1,3-dipolar cycloaddition of coordinated azide and alkynes [19,20]. Later, several other groups have studied the cycloaddition reactions of alkynes or nitriles with various azide coordinated metal complexes [21–25].

Previously, we have described the synthesis of various half sandwich ruthenium(II) triazolato complexes bearing (η^6-arene) [26,27], (η^5-indenyl) and (η^5-C_5Me_5) moieties [28,29] by the cycloaddition reactions of alkynes or nitriles with the corresponding metal azido complexes. In our previous work, we have studied cycloaddition reactions using ruthenium(II) azido complexes bearing either oxygen or phosphine chelate ligands [26–29]. However, to the best of our knowledge, these reactions have not been explored with (η^6-arene) ruthenium(II) azido complexes bearing N∩O chelate ligands. In a continuation of our study, herein we report the synthesis of a series of (η^6-arene) ruthenium azido complexes bearing N,O-chelate ligands and the cycloadditon reaction of a coordinated azide with alkynes. The complexes were characterized with the help of IR and NMR spectroscopic data and a representative molecular structure was established by single X-ray diffraction.

2. Experimental

2.1. General remarks

Solvents were dried according to standard procedures. $RuCl_3.3H_2O$ (Arrora Matthey), L-proline, glycine, dimethylacetylene dicarboxylate (DMD), diethylacetylene dicarboxylate (DED) and

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sodium azide (Sigma Aldrich), were used as received. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300.13 (^{1}H) and 75.47 MHz (^{13}C) with $SiMe_4$ as an internal reference and coupling constants are given in Hertz. Infra red spectra were recorded in a diffused reflection spectroscopy (DRS) assembly on a Shimadzu-8201PC spectrometer with the sample prepared in KBr. The precursor complexes [{(η^6-*p*-cymene)$RuCl_2$}$_2$] [30,31], [{(η^6-*p*-cymene)Ru(μN_3)Cl}$_2$] [32][1] and [{(η^6-*p*-cymene)Ru(quinto)Cl}] [33] were prepared according to literature procedures.

2.2. Preparation of (η^6-arene) ruthenium azido complexes

2.2.1. Preparation of [{(*p*-cymene)Ru(quinto)N_3}] (**1**)

Two routes were used to prepare this complex.

Route (a): A mixture of quinaldic acid (0.042 g, 0.24 mmol) and NaOMe (0.013 g, 0.24 mmol) in dry MeOH (40 ml) was stirred for 5 min, after which the complex [(*p*-cymene)Ru(μN_3)Cl]$_2$ (0.07 g, 0.11 mmol) was added to the mixture and stirring was continued for an additional 5 h. The solution was rotary evaporated to dryness and the residue was taken in dichloromethane to precipitate out NaCl. The solution was filtered and concentrated to *ca.* 3 ml, then excess hexane was added which induces precipitation of a yellow solid. The yellow solid was collected and washed with hexane (2 × 10 ml) and dried under vacuum.

Yield: 0.072 g (72%).

Route (b): A mixture of [{(*p*-cymene)Ru(quinto)Cl}] (0.07 g, 0.168 mmol) and NaN_3 (0.01 g, 0.168 mmol) in methanol (20 ml) was stirred for 4 h at room temperature, after which the solution was rotary evaporated and then the residue was dissolved in dichloromethane. To this filtrate, excess hexane was added and the solution was kept for 3 h. The yellow precipitate that formed was filtered and dried under vacuum.

Yield: 0.045 g (63%).

FTIR (KBr, cm^{-1}): 2030, 1651, 1330.

^{1}H NMR ($CDCl_3$, δ): 8.59 (d, 1H, J = 8.7), 8.43 (d, 1H, J = 8.4), 8.22 (d, 1H, J = 8.4), 7.99 (q, 2H, J = 8.1), 7.80 (t, 1H, J = 7.8), 5.73 (d, 1H, J = 6.3), 5.54 (t, 2H, J = 4.8), 5.41 (d, 1H, J = 5.7), 2.63–2.61 (sept., 1H, J = 6.6), 2.27 (s, 3H), 1.11 (d, 3H, J = 6.9), 1.00 (d, 3H, J = 6.9).

^{13}C{^{1}H} NMR ($CDCl_3$, δ): 171.35, 152.63, 147.31, 140.18, 131.93, 130.62, 129.18, 128.33, 122.69, 103.51, 100.82, 85.63, 81.62, 80.28, 79.95, 30.93, 22.68, 22.05, 18.08.

2.2.2. Preparation of [{(*p*-cymene)Ru(thiqc)N_3}] (**2**)

This complex was prepared following a similar method as described for **1** (route *a*) using [(*p*-cymene)Ru(μN_3)Cl]$_2$ (0.1 g, 0.159 mmol), ligand (0.06 g, 0.34 mmol), NaOMe (0.18 g, 0.34 mmol) and MeOH (40 ml).

Yield: 0.077 g (44%).

FTIR (KBr, cm^{-1}): 2037, 1631, 1629.

^{1}H NMR ($CDCl_3$, δ): 6.93–6.66 (m, 4H), 5.73 (d, 1H, J = 5.4), 5.61 (m, 2H), 5.54 (d, 1H, J = 5.4), 4.17 (d, 1H, J = 15), 3.90 (t, 1H, J = 11), 2.91 (m, 1H), 2.57 (m, 1H), 2.28 (m, 1H), 2.24 (s, 3H), 2.03 (m, 1H), 1.36 (s, 6H).

^{13}C{^{1}H} NMR ($CDCl_3$, δ): 180.61, 133.63, 133.37, 129.07, 126.41, 125.80, 125.64, 101.90, 93.95, 83.19, 81.74, 80.99, 79.20, 58.18, 54.39, 30.80, 22.78, 22.26, 17.67.

2.2.3. Preparation of [{(*p*-cymene)Ru(pico)N_3}] (**3**)

This complex was prepared following a similar method as described for **1** (route *a*) using [(*p*-cymene)Ru(μN_3)Cl]$_2$ (0.09 g, 0.143 mmol), ligand (0.041 g, 0.31 mmol), NaOMe (0.017 g, 0.31 mmol) and MeOH (40 ml).

Yield: 0.07 g (61%).

FTIR (KBr, cm^{-1}): 2029, 1660, 1324.

^{1}H NMR ($CDCl_3$, δ): 8.97 (s, 1H), 8.06 (d, 1H, J = 7.2), 7.98 (d, 1H, J = 6.9), 7.61 (s, 1H), 5.59 (s, 2H), 5.43 (d, 2H, J = 12.3), 2.80 (m, 1H), 2.25 (s, 3H), 1.21 (d, 6H, J = 6.3).

^{13}C{^{1}H} NMR ($CDCl_3$, δ): 171.16, 152.13, 150.95, 139.51, 128.14, 127.05, 102.53, 99.20, 83.31, 83.09, 81.09, 80.28, 30.94, 22.61, 22.30, 18.11.

FTIR (KBr, cm^{-1}): 2036, 1629.

2.2.4. Preparation of [{(*p*-cymene)Ru(hquinto)N_3}] (**4**)

This complex was prepared following a similar procedure as described for **1** (route *a*) using [(*p*-cymene)Ru(μN_3)Cl]$_2$ (0.1 g, 0.159 mmol), 8-hydroxyquinoline (0.048 g, 0.335 mmol), NaOMe (0.018 g, 0.335 mmol) and MeOH (40 ml).

Yield: 0.069 g (51%).

FTIR (KBr, cm^{-1}): 2036, 1573.

^{1}H NMR ($CDCl_3$, δ): 8.88 (d, 1H, J = 4.8), 8.11 (t, 1H, J = 5.4), 7.39–7.34 (m, 2H), 6.87 (d, 1H, J = 11), 6.86 (t, 1H, J = 7.8), 5.59 (d, 1H, J = 5.4), 5.50 (d, 1H, J = 5.7), 5.39 (d, 1H, J = 5.7), 5.28 (d, 1H, J = 5.7), 2.75 (m, 1H), 2.30 (s, 3H), 1.16 (d, 6H, J = 6.6).

^{13}C{^{1}H} NMR ($CDCl_3$, δ): 168.26, 147.86, 144.19, 137.84, 130.38, 121.83, 115.03, 110.75, 101.29, 99.22, 83.06, 82.06, 80.60, 80.09, 30.93, 30.26, 22.57, 22.41, 18.07.

2.2.5. Preparation of [{(*p*-cymene)Ru(pyrole-2-carboxylate)N_3}] (**5**)

This complex was prepared following a similar method as described for **1** (route *a*) using [(*p*-cymene)Ru(μN_3)Cl]$_2$ (0.05 g, 0.0799 mmol), pyrole-2-carboxylic acid (0.018 g, 0.167 mmol), NaOMe (0.009 g, 0.167 mmol) and MeOH (40 ml).

Yield: 0.042 g (68%).

FTIR (KBr, cm^{-1}): 2032, 1631.

^{1}H NMR ($CDCl_3$, δ): 6.98 (s, 1H), 6.25 (s, 1H), 5.48–5.20 (m, 4H), 3.40 (br, 1H), 2.88 (m, 1H), 2.27 (s, 3H), 1.26 (m, 6H).

2.2.6. Preparation of [{(*p*-cymene)Ru(L-Pro)N_3}] (**6**)

This complex was prepared following the procedure described for **1** (route *a*) using [(*p*-cymene)Ru(μN_3)Cl]$_2$ (0.05 g, 0.079 mmol), L-proline (0.019 g, 0.165 mmol), NaOMe (0.01 g, 0.18 mmol) and MeOH (40 ml).

Yield: 0.035 g (57%).

Alternative method: A mixture of complex [{(*p*-cymene)Ru(μN_3)Cl}$_2$] (0.07 g, 0.11 mmol), L-proline (0.026 g, 0.23 mmol) and K_2CO_3 (0.034 g, 0.25 mmol) were stirred in acetonitrile (30 ml) for 18 h. The reaction mixture was rotary evaporated and the residue was extracted with CH_2Cl_2. The solution was filtered through celite and the cake was washed with several times with CH_2Cl_2. The filtrate was concentrated to *ca.* 5 ml and excess pentane was added. The solution was kept for 2 h at room temperature and the yellow solid that formed was collected and dried under vacuum.

Yield: 0.045 g (52%).

FTIR (KBr, cm^{-1}): 2036, 1651, 1624.

^{1}H NMR ($CDCl_3$, δ): 5.43 (m, 2H), 5.34 (d, 1H, J = 5.7), 5.20 (d, 1H, J = 6), 4.09 (bs, NH, 1H), 3.81 (m, 1H), 3.45 (m, 1H), 3.05 (m, 1H), 2.91 (m, 1H, cym), 2.26 (s, 3H), 2.21 (m, 2H), 1.97–1.95 (m, 2H), 1.33 (m, 6H, cym).

2.2.7. Preparation of [{(*p*-cymene)Ru(Gly)N_3)}] (**7**)

This complex was prepared following a similar procedure as described for **1** (route *a*) using [(*p*-cymene)Ru(μN_3)Cl]$_2$ (0.1 g, 0.159 mmol) and the sodium salt of glycine (0.034 g, 0.351 mmol) in methanol.

Yield: 0.076 g (68%).

Alternative method: This complex was prepared using an alternative method as described for complex **6** using [(*p*-cymene)Ru(μN_3)Cl]$_2$

[1] The (*p*-cymene) ruthenium(II) azide dimer was synthesised using sodium azide instead of trimethylsilyl azide.