Synthesis, Characterization and Crystal Structures of Zwitterionic Triazoloto Complexes by Reaction of a Ruthenium Azido Complex with Excess Ethyl Propiolate

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Abstract

The synthesis and structures of two novel zwitterionic ruthenium triazoloto complexes are reported. The treatment of the ruthenium azido complex [Ru]-N₃ (1, [Ru] = (η^5 -C₅H₅)(dppe)Ru, dppe = Ph₂PCH₂CH₂PPh₂) with an excess of ethyl propiolate in CHCl₃ or CH₂Cl₂ under ambient conditions for 15 days results in the formation of a mixture of the *Z*- and *E*-forms of N(1)-bound ruthenium 3-ethylacryl-4-carboxylate-3*H*-1,2,3-triazoloto complexes [Ru]N₃(CH=CHCO₂Et)C₂H(CO₂) (**Z-3**) and (**E-3**) in a ratio of *ca.* 5:2. The structures of **E-3** and **Z-3** were confirmed by single-crystal X-ray diffraction analysis and fully characterized by ¹H, ³¹P, ¹³C NMR and IR spectroscopy, mass spectrometry, and elemental analysis. The negatively charged carboxylate moieties of the zwitterionic ruthenium triazoloto complexes **Z-3** and **E-3** are highly nucleophilic and reactive toward a variety of electrophiles, making **Z-3** and **E-3** potential starting materials for the development of biologically active 1,2,3-triazole derivatives.

Keywords

Ethyl Propiolate, Ruthenium Azide, Ruthenium Triazoloto, 1,3-Dipolar Cycloaddition

1. Introduction

Metal azido complexes are active starting materials in organometallic and material chemistry [1] because of their remarkable reactivity with various sub-

strates. Coordinated azide undergoes cycloadditions with unsaturated organic substrates such as alkynes, alkenes, nitriles and heteroallenes, giving rise to multi-functional metal-bound five-membered heterocycles [2], have attracted intensive research activities. Over the past decade, many new examples for the metal-mediated cycloaddition to alkynes have emerged and many of them have been shown to give metal-coordinated 1,2,3-triazolato complexes [2]. The triazole ring, a bioisostere of the amide group exhibiting diverse biological activities and showing excellent hydrogen donating and accepting ability, has found widespread applications in medicinal and pharmaceutical chemistry [3] [4] [5] [6] [7]. Ethyl propiolate, an active α,β -unsaturated ester, is capable of participating in a variety of cyclization reactions [8] [9] [10], as well as Diels-Alder cycloaddition [11] [12] and conjugate addition reactions [13] [14] [15] [16]. In our previous study, we reported on reactions of a ruthenium azido complex with a variety of unsaturated organics to form ruthenium triazolato complexes [17] [18] [19] [20] [21]. Among the unsaturated alkynes that we had ever used, methyl propiolate and ethyl propiolate were found to be extraordinarily reactive and afforded several novel ruthenium triazolato products [17] [20] [21]. In our previous study [21], the treatment of $[\text{Ru}]-\text{N}_3$ (**1**, $[\text{Ru}] = (\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}$, $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) with an excess of methyl propiolate afforded novel zwitterionic *Z*- and *E*-form triazolato complexes in a ratio of *ca.* 4:1. As we mentioned above, the 1,3-dipolar cycloaddition of azido metal complexes with alkynes has attracted the interest of various research groups in recent years and hundreds of metal azides have been shown to give 1,2,3-triazolato complexes [1], but to the best of our knowledge, our previous work [21] represented the first and unique example of the further addition of methyl propiolate to the thus formed triazolato ring. Recently we treated the ruthenium azido compound **1** with excess ethyl propiolate in chloroform, the thus formed ruthenium triazolato complexes slowly transferred to some new complexes which were similar to the zwitterionic triazolato products we afforded before. To investigate the details of such interesting reactions, herein we report on the reaction of a ruthenium azide with an excess of ethyl propiolate, affording novel zwitterionic triazolato complexes. The structures of thus formed triazolato complexes were confirmed by single-crystal X-ray diffraction analysis.

2. Experimental

2.1. General Procedures

All solvents and reagents were of reagent grade and were used without further purification. Elemental analyses were performed on a PerkinElmer 2400 CHN elemental analyzer. HR & LR-FAB mass spectra were recorded on a JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) with a resolution of 8000 (3000) (5% valley definition). IR spectra were collected on a PerkinElmer Paragon 1000 FT-IR spectrometer in the range of 4000 - 400 cm^{-1} using KBr pellets. NMR spectra were recorded on Bruker AVA-300 (300 NMR) spectrometers

at room temperature and are reported in units of δ with residual protons in the solvents as an initial standard (CDCl_3 , δ 7.24; C_6D_6 , δ 7.26). Complexes $[\text{Ru}]-\text{N}_3$ (**1**, $[\text{Ru}] = (\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}$, $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) and $[\text{Ru}]\text{N}_3\text{C}_2\text{HCO}_2\text{Et}$ (**2**) were prepared following methods reported in the literature [17]. Elemental analyses and X-ray diffraction studies were carried out at the Instrumentation Center located at the NTU.

2.2. Synthesis of $[\text{Ru}]\text{N}_3(\text{CH}=\text{CHCO}_2\text{Et})\text{CHC}(\text{CO}_2)$ (**3**)

To a Schlenk flask charged with $[\text{Ru}]-\text{N}_3$ (**1**, 500.1 mg, 0.825 mmol), ethyl propiolate (810 mg, 837 μL , 8.25 mmol) and CHCl_3 (50 mL) were added. The mixture was allowed to stand at room temperature for 15 days then the volume of solvent was reduced to 5 mL under a rotary evaporator. The residue was added drop-wise to 20 mL of vigorously stirred *n*-pentane to give yellow precipitate. After isolating the precipitate on a filter, it was washed with 2×5 mL of *n*-pentane and dried under a vacuum to give a mixture of *Z*- and *E*-form $[\text{Ru}]\text{N}_3(\text{CH}=\text{CHCO}_2\text{Et})\text{CHC}(\text{CO}_2)$ (**3**) (523.8 mg, 0.677 mmol, 82% yield, **Z-3:E-3** = 5:2). Spectroscopic data for **Z-3** are as follows: ^1H NMR (CDCl_3): δ 7.55 (d, 1H, $J_{\text{H-H}} = 10.0$ Hz, $\text{CH} = \text{CHCO}_2$), 7.45 - 7.17 (m, 21H, Ph and CH), 5.51 (d, 1H, $J_{\text{H-H}} = 10.0$ Hz, $\text{CH} = \text{CHCO}_2$), 4.63 (Cp), 3.99 (q, 2H, $J_{\text{H-H}} = 7.2$ Hz, OCH_2), 3.00, 2.66 (2m, $\text{PCH}_2\text{CH}_2\text{P}$), 1.22 (t, 3H, $J_{\text{H-H}} = 7.2$ Hz, CH_3). ^{31}P NMR (CDCl_3): δ 85.2. ^{13}C NMR (CDCl_3): δ 163.1, 158.2 (CO_2), 143.1 (CH), 140.3-128.2 (Ph, CCO_2 and $\text{CH} = \text{CHCO}_2$), 112.8 ($\text{CH} = \text{CHCO}_2$), 82.3 (Cp), 60.3 (OCH_2), 28.6 (t, $\text{PCH}_2\text{CH}_2\text{P}$, $J_{\text{C-P}} = 21.2$ Hz), 14.0 (CH_3). IR (KBr, cm^{-1}): $\nu(\text{CO})$ 1716 (s), 1652 (s), 1483 (w), $\nu(\text{N} = \text{N})$ 1435 (s), 1354 (m), $\nu(\text{C-O})$ 1229 (m), 1200 (m), 1099 (s), $\nu(\text{COO}^-)$ 700 (vs), 529 (vs). Spectroscopic data for **E-3** are as follows: ^1H NMR (CDCl_3): δ 8.62 (d, 1H, $J_{\text{H-H}} = 14.0$ Hz, $\text{CH} = \text{CHCO}_2$), 7.89 (s, 1H, CH), 7.45 - 7.17 (m, 20H, Ph), 4.95 (d, 1H, $J_{\text{H-H}} = 14.0$ Hz, $\text{CH} = \text{CHCO}_2$), 4.66 (Cp), 4.14 (q, 2H, $J_{\text{H-H}} = 7.2$ Hz, OCH_2), 3.00, 2.66 (2m, $\text{PCH}_2\text{CH}_2\text{P}$), 1.28 (t, 3H, $J_{\text{H-H}} = 7.2$ Hz, CH_3). ^{31}P NMR (CDCl_3): δ 85.0. ^{13}C NMR (CDCl_3): δ 164.8, 158.0 (CO_2), 144.5 (CH), 139.4 - 124.7 (Ph, CCO_2 and $\text{CH} = \text{CHCO}_2$), 111.2 ($\text{CH} = \text{CHCO}_2$), 82.1 (Cp), 60.7 (OCH_2), 28.8 (t, PCH_2 , $J_{\text{C-P}} = 23.1$ Hz), 14.0 (CH_3). MS (m/z , Ru^{102}): 776.2 ($\text{M}^+ + 1$), 732.2 ($\text{M}^+ - \text{CO}_2$), 565.1 (M^+ -triazole ring). Anal. Calcd. for $\text{C}_{39}\text{H}_{37}\text{N}_3\text{O}_4\text{P}_2\text{Ru}$: C, 60.46; H, 4.81; N, 5.42. Found: C, 60.61; H, 4.92; N, 5.37.

2.3. Structure Analysis and Refinement

Single crystals of **Z-3** suitable for X-ray diffraction study were afforded by slow evaporation of the $\text{CH}_2\text{Cl}_2/n$ -hexane solution of **3** under ambient conditions for 7 days and single crystals of **E-3** were afforded by the diffusion of *n*-pentane into CHCl_3 solution of **3** at -15°C for 10 days. The chosen single crystal was glued to glass fiber and mounted on a Bruker SMART APEX diffractometer equipped with graphite monochromatic Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection was executed using the SMART program; cell refinement and data reduction were performed with the SAINT program. The structure was determined by the SHELXTL/PC [22] program and refined by the full-matrix least-squares methods

on F^2 . Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. Crystallographic data of **E-3** and **Z-3** are summarized in **Table 1**.

3. Results and Discussion

3.1. Synthesis of Zwitterionic Triazolato Complexes **Z-3** and **E-3**

The treatment of $[\text{Ru}]-\text{N}_3$ (**1**) with 1.1-fold excess of ethyl propiolate in CHCl_3 at room temperature for 24 hours afforded the [3+2] cycloaddition product, the N(2)-bound ruthenium 4-ethoxycarbonyl-1,2,3-triazolato complex $[\text{Ru}]\text{N}_3\text{C}_2\text{HCO}_2\text{Et}$ (**2**), in 83 % isolated yield. The structure of **2** was clearly established as the N(2)-bound isomer [17]. When **1** was treated with 10-fold excess of ethyl propiolate in CHCl_3 at room temperature for 15 days, a mixture of *Z*- and *E*-form zwitterionic N(1)-bound ruthenium 3-ethylacryl-4-carboxylate-3*H*-1,2,3-triazolato complexes $[\text{Ru}]\text{N}_3(\text{CH}=\text{CHCO}_2\text{Et})\text{C}_2\text{H}(\text{CO}_2)$ (**Z-3**) and (**E-3**) in a ratio of *ca.* 5:2 was afforded in 82% isolated yield (**Scheme 1**). Because there was no obvious color change during the reaction, the reaction was monitored by ^{31}P NMR spectroscopy. When **1** was treated with a 10-fold excess of ethyl propiolate in a CDCl_3 solution for 8 h, a major singlet resonance at δ 87.5 attributed to the N(2)-bound triazole $[\text{Ru}]\text{N}_3\text{CHCO}_2\text{Et}$ (**2**) was observed and several small singlet resonances appeared at the range of δ 83.6 - 85.2 at the same time. When the mixture was allowed to stand under ambient conditions, the ^{31}P NMR spectroscopy changed slowly and complicatedly during the process and the singlet resonances at δ 87.5 of **2** disappeared in 7 days. Finally, when the reaction reached completion, the signals at δ 85.2 and 85.0 attributed to **Z-3** and **E-3**, the end products, had a ratio of *ca.* 5:2 (calculated from the integration of the residual signals in the ^{31}P NMR spectra after isolation). In the ^1H NMR, two characteristic AX pattern resonances appearing at δ 7.42, 5.42 (d, $J_{\text{H-H}} = 10.2$ Hz) and 8.52, 4.89 (d, $J_{\text{H-H}} = 14.3$ Hz) in a ratio of *ca.* 5:2 are assigned to the two vinyl protons of **Z-3** and **E-3**, respectively. Complex **3** is possibly formed by a regioselective addition of ethyl propiolate to the N(3) nitrogen of **2** and transformed to a less steric hindered N(1)-bound structure at the same time, then a hydration and losing of an ethanol molecule. The FAB mass spectrum displayed a parent peaks at m/z 776.2 (M^++1), which was consistent with the formula weight of **3**. The [3+2] cycloaddition of an electron-deficient alkyne with an azide derivative is a common route for the production of triazoles but the further addition of an unsaturated molecule to the triazole ring is rare. A few examples of reactions of ethyl propiolate with azides, have been reported [23] [24] [25]. In our previous study [21], the treatment of $[\text{Ru}]-\text{N}_3$ (**1**) with an excess of methyl propiolate afforded novel zwitterionic *Z*- and *E*-form triazolato complexes in a ratio of *ca.* 4:1. To the best of our knowledge, it represented the first example of the further addition of methyl propiolate to the thus formed triazolato ring. In this report, we duplicated the process with ethyl propiolate and **1** and afforded the similar triazolato complexes **Z-3** and **E-3** in a ratio of *ca.* 5:2. Both of the complexes **Z-3**

Scheme 1. Synthesis of zwitterionic triazolato complexes **Z-3** and **E-3**.

Table 1. Crystal and intensity collection data for complexes **E-3** and **Z-3**.

	E-3 ·CHCl ₃ ^c	Z-3 ·CH ₂ Cl ₂ ·3H ₂ O ^c
Chemical formula	C ₄₀ H ₃₈ Cl ₃ N ₃ O ₄ P ₂ Ru	C ₄₀ H ₄₅ Cl ₂ N ₃ O ₇ P ₂ Ru
Formula weight	894.09	913.70
<i>T</i> (K)	150(2)	150(2)
Cryst syst	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> (Å)	10.0598(4)	10.6381(3)
<i>b</i> (Å)	11.1706(5)	13.4634(5)
<i>c</i> (Å)	18.1664(8)	14.9736(5)
<i>α</i> (°)	94.4290(10)	82.3056(12)
<i>β</i> (°)	100.8570(10)	76.1364(11)
<i>γ</i> (°)	95.5070(10)	77.9221(11)
<i>V</i> (Å ³)	1986.13(15)	2028.09(12)
<i>Z</i>	2	2
<i>D</i> _{calc} (Mg m ⁻³)	1.495	1.496
<i>μ</i> (mm ⁻¹)	0.722	0.650
Θ range for data collection (°)	1.147 to 27.500	2.184 to 27.500
	−13 ≤ <i>h</i> ≤ 13	−13 ≤ <i>h</i> ≤ 13
Limiting indices	−14 ≤ <i>k</i> ≤ 142	−17 ≤ <i>k</i> ≤ 17
	−23 ≤ <i>l</i> ≤ 23	−19 ≤ <i>l</i> ≤ 19
Unique reflections	24,865	18,537
Reflections used [<i>I</i> > 2σ(<i>I</i>)]	9114	9315
<i>R</i> _{int}	0.0522	0.0165
Max. and min. transmission	0.765, 0.640	0.7456, 0.6934
GOF ^a on <i>F</i> ²	1.026	1.055
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	^b <i>R</i> 1 = 0.0495, w <i>R</i> 2 = 0.1147	<i>R</i> 1 = 0.0452, w <i>R</i> 2 = 0.1213
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0645 w <i>R</i> 2 = 0.1228	<i>R</i> 1 = 0.0498 w <i>R</i> 2 = 0.1262

^a GOF = $\left[\sum \left[w(F_o^2 - F_c^2)^2 \right] / (n - p) \right]^{1/2}$; *n* = number of reflections, *p* = number of parameters refined. ^b *R*1 = $(\sum \|F_o\| - \sum \|F_c\|) / \sum \|F_o\|$, w*R*2 = $\left[\sum \left[w(F_o^2 - F_c^2)^2 \right] / \sum [wF_o^4] \right]^{1/2}$.

^cThe solvents were found to incorporate with the crystals.

and *E*-**3** are stable in air and in solutions, with excellent solubility in various solvents. They are soluble in CH₂Cl₂, CHCl₃, diethyl ether, acetone, methanol, ethanol, benzene and *n*-hexane, but sparingly soluble in *n*-pentane. The good solubility could be due to the zwitterionic structure and the excellent hydrogen donating and accepting ability of **3**.

3.2. Single Crystal X-Ray Diffraction Analysis

Yellow crystals of *Z*-**3** were afforded by slow evaporation of the CH₂Cl₂/*n*-hexane solution of **3** under ambient conditions for 7 days. Yellow crystals of *E*-**3** were afforded by the diffusion of *n*-pentane into CHCl₃ solution of **3** at −15°C for 10 days, a few yellow crystals of *E*-**3** grew on the wall of the tube and were collected by hand. Structures of *Z*-**3** and *E*-**3** were determined by a single crystal X-ray diffraction analysis. ORTEP drawings are shown in **Figure 1** and **Figure 2**, respectively. Selected bond distances and bond angles are given in **Table 2**.

Table 2. Selected bond distances (Å) and angles (deg) for *Z*-**3** and *E*-**3**.

	<i>Z</i> - 3	<i>E</i> - 3
Ru–P1	2.2736(7)	2.2841(9)
Ru–P2	2.2911(7)	2.2875(9)
Ru–N1	2.110(2)	2.085(3)
N1–N2	1.323(3)	1.318(4)
N2–N3	1.346(3)	1.341(4)
N3–C2	1.365(4)	1.364(4)
N1–C1	1.356(4)	1.363(4)
C1–C2	1.364(4)	1.361(4)
C2–C3	1.513(5)	1.515(5)
O1–C3	1.239(5)	1.238(4)
O2–C3	1.256(5)	1.249(4)
P1–Ru–P2	83.90(3)	84.99(3)
N1–Ru–P1	93.93(7)	88.00(8)
N1–Ru–P2	89.34(7)	87.86(7)
Ru–N1–N2	118.15(19)	119.8(2)
Ru–N1–C1	131.7(2)	131.0(2)
N1–N2–N3	106.3(2)	106.3(2)
N2–N3–C2	111.4(2)	111.7(3)
C1–N1–N2	109.4(2)	109.2(3)
N1–C1–C2	109.0(3)	109.0(3)
N3–C2–C1	104.0(3)	103.8(3)
C1–C2–C3	128.9(3)	131.7(3)
O1–C3–C2	118.2(3)	115.2(3)
O1–C3–O2	127.9(4)	128.3(3)
O2–C3–C2	113.8(3)	116.5(3)

Figure 1. ORTEP drawing of *Z*-3 with 50% probability thermal ellipsoids. All hydrogen atoms and solvated CH_2Cl_2 and H_2O are omitted for clarity.

Figure 2. ORTEP drawing of *E*-3 with 50% probability thermal ellipsoids. All hydrogen atoms and solvated CHCl_3 are omitted for clarity.

In *Z*-3, the coordination with ruthenium is a distorted piano-stool geometry, with three facial sites being occupied by the C_5H_5 ligand ($\text{Ru}-\text{C} = 2.110(2) - 2.232(3)\text{\AA}$; average $2.2174\text{\AA}$); the other three positions are occupied by two phosphine ligands ($\text{Ru}-\text{P1} = 2.2736(7)\text{\AA}$; $\text{Ru}-\text{P2} = 2.2911(7)\text{\AA}$) and the triazolate group ($\text{Ru}-\text{N1} = 2.110(2)\text{\AA}$), which are comparable to those in other ruthenium triazolato complexes [17] [18] [19] [20] [21]. The inter-atomic distances within the five-membered triazole ring ($\text{N1}-\text{N2}$ ($1.323(3)\text{\AA}$), $\text{N2}-\text{N3}$ ($1.346(3)\text{\AA}$), $\text{N1}-\text{C1}$ ($1.356(4)\text{\AA}$), $\text{N3}-\text{C2}$ ($1.365(4)\text{\AA}$) and $\text{C1}-\text{C2}$ ($1.364(4)\text{\AA}$)), are typical and consistent with the delocalization of the electrons within the heterocycle. The bond angles of $\text{N1}-\text{N2}-\text{N3}$ ($106.3(2)^\circ$), $\text{N2}-\text{N3}-\text{C2}$ ($111.4(2)^\circ$), $\text{C1}-\text{C2}-\text{N3}$ ($104.0(3)^\circ$),

N1–C1–C2 (109.0(3)°) and N2–N1–C1 (109.4(2)°) are all in the range of C(sp²) and N(sp²) hybridization of a five-membered heterocycle ring. In the carboxylate structure of **Z-3**, the C2–C3 bond distance of 1.513(5) Å, is typical of a C–C single bond. The O1–C3 and O2–C3 bond distances of 1.239(5) and 1.256(5) Å, respectively, are both between a C–O double bond and a single bond, indicating that the carboxylate group is delocalized between the two oxygen atoms in a resonance structure. In the *Z*-form of the ethyl acryl structure, the C4–C5–C6 angles of 129.5(3)° and the C5–C4–N3 of 125.1(3)° are slightly larger than that of a typical C(sp²) hybridization.

In **E-3**, the coordination with ruthenium is a distorted piano-stool geometry, with three facial sites being occupied by the C₅H₅ ligand (Ru–C = 2.198(3) – 2.220(3) Å; average 2.2092 Å); the other three positions are occupied by two phosphine ligands (Ru–P1 = 2.2841(9) Å; Ru–P2 = 2.2875(9) Å) and the triazolate group (Ru–N1 = 2.085(3) Å). The inter-atomic distances within the five-membered triazole ring (N1–N2 (1.318(4) Å), N2–N3 (1.341(4) Å), N1–C1 (1.363(4) Å), N3–C2 (1.364(4) Å) and C1–C2 (1.361(4) Å)), are typical, consistent with the delocalization of the electrons within the heterocycle. The bond angles of N1–N2–N3 (106.3(2)°), N2–N3–C2 (111.7(3)°), C1–C2–N3 (103.8(3)°), N1–C1–C2 (109.0(3)°) and N2–N1–C1 (109.2(3)°) are all in the range of C(sp²) and N(sp²) hybridization of a five-membered heterocycle ring. In the carboxylate structure, the C2–C3 bond distance of 1.515(5) Å, is typical of a C–C single bond. The O1–C3 and O2–C3 bond distances of 1.238(5) and 1.249(4) Å, respectively, are both between a C–O double bond and a single bond, indicating that the carboxylate group is delocalized between the two oxygen atoms in a resonance structure. In the *E*-form of the acryl structure, the C5–C4–N3 and C4–C5–C6 angles of 124.1(3)° and 121.0(3)°, respectively, are quite close to that of a typical C(sp²) hybridization. The inter-atomic distances within both of the five-membered triazole rings of **Z-3** and **E-3** are typical, consistent with the delocalization of the electrons within the heterocycle. Both of the five-membered triazole rings of **Z-3** and **E-3** exhibit an irregular pentagonal structure and are essentially planar. The negatively charged carboxylate moiety of **Z-3** and **E-3** is highly nucleophilic and reactive toward a variety of electrophiles, making **Z-3** and **E-3** potential starting materials for the development of biologically active triazole derivatives. For example, the treatment of **3** with organic halides could give cationic N(1)-bound N(3)-ethylacryl-4-alkoxycarbonyl triazolato complexes and the subsequent cleavage of the Ru–N bond could give a variety of functionalized 1,5-disubstituted 1*H*-1,2,3-triazole derivatives. Studies of the reactivity and application of these zwitterionic 1,2,3-triazolato complexes are currently under investigation.

4. Conclusion

We successfully synthesized the zwitterionic 1,2,3-triazolato complexes **Z-3** and **E-3** in good yield by reaction of the ruthenium azido complex [Ru]–N₃ (**1**, [Ru] = (η⁵-C₅H₅)(dppe)Ru, dppe = Ph₂PCH₂CH₂PPh₂) with an excess of ethyl propi-

olate. Results obtained from the elemental, spectral and X-ray crystallography had confirmed the proposed structures of the synthesized triazolates. Hopefully, these findings will enable a more complete understanding of such triazolato complexes that can be produced and the development of synthetic procedures that can be used to prepare novel metal-coordinated triazolato complexes. We are currently in the process of further exploring the reactivity of these zwitterionic 1,2,3-triazolato complexes. Studies of related reactions and applications of these complexes are currently underway.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix A. Supplementary Material

CCDC 1907166 and 1867975 contains the supplementary crystallographic data for *Z*-**3** and *E*-**3**. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.