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Synthesis of 1,4,5-trisubstituted triazoles by [3+2] cycloaddition of a ruthenium azido complex with ynoate esters

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ABSTRACT

The [3 + 2] cycloaddition reactions of a series of ynoate esters with a ruthenium azido complex [Ru]−N_3 (**1**, [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = $Ph_2PCH_2CH_2PPh_2$) were investigated. The reaction products, metal-bound heterocyclic complexes such as the triazolato complexes [Ru]$N_3C_2(CO_2Et)_2$ (**2**), [Ru]$N_3C_2(CO_2Et)(CF_3)$ (**3**), [Ru]$N_3C_2(CO_2Me)(Ph)$ (**4**) and [Ru]$N_3C_2(CO_2Et)(CH_3)$ (**5**) were produced from diethyl acetylene dicarboxylate, ethyl 4,4,4-trifluoro-2-butynoate, methyl phenylpropiolate and ethyl 2-butynoate, respectively. The complexes were all structurally characterized as being N(2)-bound. The alkylation of **2** with organic halides resulted in the cleavage of the Ru−N bond and the formation of a series of 1-alkylated-4,5-bis(ethoxycarbonyl)-1,2,3-triazoles $N_3(CH_2R)C_2(CO_2Et)_2$ (**6a**, R = H; **6b**, R = C_6F_5; **6c**, R = Ph; **6d**, R = 4-CH_2Br-C_6H_4; **6e**, R = 4-CN-C_6H_4). The high regioselective alkylation of **4** with organic halides gave a 1-alkylated-4-phenyl-5-methoxycarbonyl-1,2,3-triazoles $N_3(CH_2C_6F_5)C_2(Ph)(CO_2Me)$ (**N^3-7a**). The structures of complexes **2**, **3**, **4**, **5** and **N^3-7a** were confirmed by single-crystal X-ray diffraction analysis.

1. Introduction

The 1,2,3-triazole structure, a nitrogen-containing heterocycle found in biomolecules [1–3], has found widespread applications in agricultural [4–7], medicinal [8–14] and material [15–18] chemistry during the past decades. In recent years, the chemistry of triazole and derivatives thereof have been heavily studied, given the pharmacological importance of the heterocyclic nucleus and because of their diverse biological activities [19,20]. Such 1,2,3-triazole derivatives are typically prepared by the Huisgen 1,3-dipolar cycloaddition of azides and alkynes [21]. Metal catalyzed cycloaddition reactions [22–26] have also been employed in recent years and based on the so called “click chemistry” concept [27], a huge number of reports dealing with copper-catalyzed azide-alkyne cycloaddition (CuAAC) [28] and ruthenium-catalyzed azide-terminal-alkyne cycloaddition (RuAAC) [29] reactions to give 1,4-disubstituted and 1,5-disubstituted 1,2,3-triazoles have appeared. On the contrary, the application of a [3 + 2] cycloaddition strategy for the synthesis of fully substituted 1,4,5-trisubstituted 1,2,3-triazoles has not been found to be generally applicable, since the final products are frequently mixtures of regioisomers [30]. Internal alkynes are not ideal staring products, because they do not easily react with azides to give fully substituted triazoles due to their weak activity and difficulties associated with controlling the regiochemistry of the reactions. As a result, only few examples of the regiospecific synthesis of fully substituted triazoles by CuACC have been reported [31].

The [3 + 2] cycloaddition reaction between a metal-coordinated azide group and an alkyne was first reported by Fehlhammer's group for the reaction of $(Ph_3P)_2Pd(N_3)_2$ with dimethylacetylene dicarboxylate (DMAD) [32i]. Reactions of azido metal complexes with alkynes has attracted the interest of various research groups for decades, and many metal azides have been shown to give 1,2,3-triazolato complexes [32]. In most cases, the activated alkynes used as dipolarophiles are limited to highly electron-poor alkynes such as dialkylacetylene dicarboxylate, $CF_3C{\equiv}CCF_3$ and HC≡CCN [32]. The formation of an N-coordinate metal triazolato complex by the [3 + 2] cycloaddition of a metal-coordinated azide with a less electron-poor internal alkyne, such as $CH_3C{\equiv}CCO_2Et$ and $PhC{\equiv}CCO_2Me$, is rare [32a]. In a previous study, we reported on the [3 + 2] cycloaddition of a ruthenium azido complex with excess amounts of alkenes and alkynes to form a variety of ruthenium triazolato complexes [33] and successfully developed a reaction

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cycle for the synthesis of organic triazoles [34]. Our continuing interest in ruthenium triazolato complexes involves the synthesis of functionalized organic 1,2,3-triazoles and the development of reaction cycles involve regiospecific alkylation and the subsequent Ru-N bond cleavage of various ruthenium triazolato complexes. Herein we report on our recent findings regarding the reactivity of ruthenium azide toward a series of ynoate esters, α,β-unsaturated carboxylic esters with the general formula $R^1C{\equiv}C{-}CO_2R^2$ ($R^2 \neq H$) in which the ester C=O function is conjugated to a C≡C triple bond located at the α, β position. We now report on the results of detailed synthetic and structural investigations into this reaction. A preliminary account of the steric and electronic effects for the structures and the reactivity of the thus formed triazolato complexes with organic halides are reported.

2. Experimental section

2.1. General procedures

All solvents and reagents were of reagent grade and were used without further purification. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. HR & LR-FAB mass spectra were conducted on a JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) with a resolution of 8000(3000) (5% valley definition). IR spectra were measured on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. NMR spectra were recorded on Bruker AV3-400 and AVA-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; CD_3OD, δ 3.35). Complexes [Ru]-N_3 (**1,** [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = $Ph_2PCH_2CH_2PPh_2$) [33], were prepared following methods reported in the literature. Elemental analyses were carried out at the Institute of Chemistry, Academia Sinica. X-ray diffraction studies were carried out at the Instrumentation Center located at the National Taiwan University.

2.2. Synthesis of Cp(dppe)$RuN_3C_2(CO_2Et)_2$ (**2**)

To a Schlenk flask charged with **1** (300.0 mg, 0.495 mmol), diethyl acetylenedicarboxylate (252 mg, 237 μL, 1.485 mmol) and $CHCl_3$ (30 mL) were added. The mixture was stirred at room temperature for 36 h and the volume of solvent was reduced to 2 mL under a rotary evaporator. To the residue, 20 mL of *n*-pentane was added to give a yellow precipitate. After isolation the precipitate on a filter, it was washed with 2 × 5 mL of *n*-pentane and dried under a vacuum to give **2** (357.3 mg, 0.46 mmol, 93% yield). Spectroscopic data for **2** are as follows: IR (KBr, cm^{-1}): ν(C=O) 1708 (vs), ν(N=N) 1431 (s), ν(C–O) 1285 (m), 1077 (s), ν(COO^-) 693 (s), 528 (s). ^1H NMR ($CDCl_3$): δ7.46–7.13 (m, 20H, Ph), 4.65 (Cp), 4.19 (q, 4H, J_{H-H} = 7.20 Hz, OCH_2), 3.25, 2.52 (2 m, PCH_2CH_2P), 1.19 (t, 6H, J_{H-H} = 7.20 Hz, CH_3). ^{31}P NMR ($CDCl_3$): δ 87.2. ^{13}C NMR ($CDCl_3$): δ 161.8 (CO_2), 142.2 (CCO_2), 142.4–127.0 (Ph), 81.9 (Cp), 59.8 (OCH_2), 28.5 (t, PCH_2CH_2P, J_{C-P} = 23.1 Hz), 14.2 (CH_3). c 777.1 (M^+), 565.1 (M^+–triazolato ring). Anal. Calcd. for $C_{39}H_{39}N_3O_4P_2Ru$: C, 60.30; H, 5.06; N, 5.41 Found: C, 60.32; H, 5.07; N, 5.39.

2.3. Synthesis of Cp(dppe)$RuN_3C_2(CO_2Et)(CF_3)$ (**3**)

To a Schlenk flask charged with **1** (198 mg, 0.327 mmol), ethyl 4,4,4-trifluoro-2-butynoate (233.5 μL, 271 mg, 1.634 mmol) and CH_2Cl_2 (20 mL) were added. The mixture was stirred at room temperature for 24 h and the volume of solvent was then reduced to 2 mL under a rotary evaporator. To the residue, 20 mL of *n*-pentane was added to give a 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 **3** (232.1 mg, 0.301 mmol, 92% yield). Spectroscopic data for **3** are as follows: IR (KBr, cm^{-1}): ν(C=O) 1720 (vs), ν(N=N) 1435 (s), ν(C–O) 1310 (m), 1184 (vs), 1127 (vs), 1160 (vs), 1050 (vs), ν(COO^-) 695 (s), 528 (s). ^1H NMR ($CDCl_3$): 7.68–7.13 (m, 20H, Ph), 4.66 (Cp), 4.15 (q, 4H, J_{H-H} = 7.20 Hz, OCH_2), 3.20, 2.55 (2 m, PCH_2CH_2P), 1.22 (t, 6H, J_{H-H} = 7.20 Hz, CH_3). ^{31}P NMR ($CDCl_3$): 87.0. ^{13}C NMR ($CDCl_3$): 160.5 (CO_2), 137.6 (q, J_{CCF} = 37.2 Hz, CCF_3), 135.4 (CCO_2), 121.0 (q, J_{CF} = 267.6 Hz, CF_3), 142.2–127.7 (Ph), 81.9 (Cp), 59.9 (OCH_2), 28.5 (t, PCH_2CH_2P, J_{C-P} = 22.6 Hz), 14.0 (CH_3). MS (*m/z*, Ru^{102}): 773.2 (M^+), 565.1 (M^+–triazolato ring). Anal. Calcd. for $C_{37}H_{34}F_3N_3O_2P_2Ru$: C, 57.51; H, 4.44; N, 5.44 Found: C, 57.66; H, 4.43; N, 5.40.

2.4. Synthesis of N(2)-bound Cp(dppe)$RuN_3C_2(CO_2Me)(Ph)$ (**4**)

To a Schlenk flask charged with **1** (524.1 mg, 0.865 mmol), methyl phenylpropiolate (834 mg, 780 μL, 4.32 mmol) and benzene (10 mL) were added. The mixture was heated to reflux for 48 h and the volume of solvent was then reduced to 2 mL under a rotary evaporator. To the residue, 20 mL of *n*-hexane was added to give a yellow precipitate. After isolating the precipitate on a filter, it was washed with 2 × 3 mL of *n*-hexane and dried under a vacuum to give **4** (623.0 mg, 0.813 mmol, 94% yield). Spectroscopic data for **4** are as follows: IR (KBr, cm^{-1}): 2917 (m), ν(C=O) 1700 (vs), 1536 (m), 1477 (s), ν(N=N) 1433 (s), 1397 (m), ν(C–O) 1312 (m), 1295 (m), 1184 (m), 1098 (vs), ν(COO^-) 705 (vs), 526 (s). ^1H NMR ($CDCl_3$): δ 7.56–6.65 (m, 25H, Ph), 4.62 (Cp), 3.69 (s, 3H, CH_3), 3.18, 2.60 (2 m, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$): δ 86.9. ^{13}C NMR ($CDCl_3$): δ 162.8 (CO_2), 149.1 (CCO_2), 142.9–119.5 (Ph, N_3CPh), 82.0 (Cp), 51.0 (OCH_3), 28.9 (t, PCH_2CH_2P, J_{C-P} = 22.6 Hz). MS (*m/z*, Ru^{102}): 767.1 (M^+), 565.1 (M^+–triazolato ring). Anal. Calcd. for $C_{41}H_{37}N_3O_2P_2Ru$: C, 64.22; H, 4.86; N, 5.48 Found: C, 64.32; H, 4.88; N, 5.45.

2.5. Synthesis of Cp(dppe)$RuN_3C_2(CO_2Et)(CH_3)$ (**5**)

To a Schlenk flask charged with **1** (127.2 mg, 0.177 mmol), ethyl 2-butynoate (198.6 mg, 211 μL, 98% purity, 1.77 mmol) and toluene (10 mL) were added. The mixture was heated under a 120 °C silicone oil bath for 48 h and the volume of solvent was then reduced to 1 mL under a rotary evaporator. To the residue, 10 mL of *n*-pentane was added to give a yellow precipitate. After isolationg the precipitate on a filter, it was washed with 2 × 3 mL of *n*-pentane and dried under a vacuum to give the **5** (106.8 mg, 0.149 mmol, 84% yield). Spectroscopic data for **5** are as follows: IR (KBr, cm^{-1}): ν(C=O) 1700 (vs), 1529 (m), ν(N=N) 1433 (s), 1384 (s), ν(C–O) 1314 (m), 1273 (m), 1128 (m), 1071 (vs), ν(COO^-) 700 (vs), 527 (s). ^1H NMR ($CDCl_3$): δ 7.46–7.11 (m, 20H, Ph), 4.58 (Cp), 4.06 (q, 2H, J_{H-H} = 7.2 Hz, OCH_2), 3.24, 2.52 (2 m, PCH_2CH_2P), 1.20 (t, 3H, J_{H-H} = 7.2 Hz, CH_3). ^{31}P NMR ($CDCl_3$): δ 87.6. ^{13}C NMR ($CDCl_3$): δ 162.7 (CO_2), 146.2 (CCO_2), 143.1–127.4 (Ph, N_3CCH_3), 81.7 (Cp), 58.8 (OCH_3), 28.7 (t, PCH_2CH_2P, J_{C-P} = 22.6 Hz). MS (*m/z*, Ru^{102}): 719.1 (M^+), 565.1 (M^+–triazolato ring). Anal. Calcd. for $C_{37}H_{37}N_3O_2P_2Ru$: C, 61.83; H, 5.19; N, 5.85 Found: C, 61.95; H, 5.20; N, 5.82.

2.6. Synthesis of $N_3(CH_3)C_2(CO_2Et)_2$ (**6a**) and other organic triazoles

To a Schlenk flask charged with **2** (100.1 mg, 0.129 mmol) and CH_3I (82 μL, 182.9 mg, 1.288 mmol) was added $CHCl_3$ (20 mL). The resulting solution was warmed under a 50 °C silicone oil bath for 24 h and the solvent and the excess CH_3I were then removed by vacuum evaporation. To the residue was added 10 mL of cold *n*-pentane. After filtration, the orange precipitate was washed with 2 × 10 mL of *n*-pentane and dried under a vacuum to give [Ru]-I

(81.9 mg, 0.118 mmol, 92% yield). The filtrate was dried and extracted with 2 × 5 mL of cold *n*-pentane. The extract was filtered and the filtrate was dried under a vacuum to give a colorless liquid, which is the organic triazole $N_3(CH_3)C_2(CO_2Et)_2$ (**6a**, 17.6 mg, 0.077 mmol, 60%). Spectroscopic data for **6a** are as follows: ^{1}H NMR (C_6D_6): δ 4.24, 4.10 (2q, 4H, J_{H-H} = 7.2 Hz, OCH_2), 3.44 (s, 3H, NCH_3), 1.12, 1.07 (2t, 6H, J_{H-H} = 7.2 Hz, CH_3). ^{13}C NMR (C_6D_6): δ 160.9, 158.5 (CO_2), 141.6, 129.7 (CCO_2), 62.2, 61.5 (OCH_2), 22.7 (NCH_3), 14.2, 13.8 (CH_3). MS (*m/z*): 228.1 (M^++1). HRMS (*m/z*) calcd for $C_9H_{13}N_3O_4$ $[M+H]^+$ 228.0981, found 228.0983. Complexes $N_3(CH_2Ph)C_2(CO_2Et)_2$ (**6b**), $N_3(CH_2C_6F_5)C_2(CO_2Et)_2$ (**6c**), $N_3[CH_2(4\text{-}CN\text{-}C_6H_4)]C_2(CO_2Et)_2$ (**6d**) and $N_3[CH_2(4\text{-}CH_2Br\text{-}C_6H_4)]C_2(CO_2Et)_2$ (**6e**) were prepared with similar procedure as that of **6a** to give a mixture of the organic triazole and organic bromides. Spectroscopic data for **6b** (colorless liquid) are as follows: ^{1}H NMR ($CDCl_3$): δ 7.31, 7.30, 7.27 (Ph), 5.08 (s, 2H, NCH_2), 4.44 (q, 2H, J_{H-H} = 6.9 Hz, OCH_2), 4.34 (q, 2H, J_{H-H} = 7.2 Hz, OCH_2), 1.41 (t, 3H, J_{H-H} = 7.2 Hz, CH_3), 1.28 (t, 3H, J_{H-H} = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 160.0, 158.4 (CO_2), 140.4, 133.9 (CCO_2), 129.8, 129.3, 128.8, 127.9 (Ph), 62.7, 61.8 (OCH_2), 53.7 (NCH_2), 14.1, 13.7 (CH_3). MS (*m/z*): 306.1 (M^++1). Spectroscopic data for **6c** (colorless liquid) are as follows: ^{1}H NMR ($CDCl_3$): δ 7.86, 7.40, 7.25, 7.13 (m, Ph), 5.88 (s, 2H, NCH_2), 4.46 (q, 2H, J_{H-H} = 7.2 Hz, OCH_2), 4.42 (q, 2H, J_{H-H} = 7.2 Hz, OCH_2), 1.41 (t, 3H, J_{H-H} = 7.2 Hz, CH_3), 1.40 (t, 3H, J_{H-H} = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 160.5, 158.3 (CO_2), 147.2, 143.0, 140.4, 139.9, 133.9, 129.9, 107.6 (CCO_2 and Ph), 63.2, 62.0 (OCH_2), 41.1 (NCH_2), 14.1, 13.8 (CH_3). MS (*m/z*): 394.1 (M^++1). Spectroscopic data for **6d** (white solid) are as follows: ^{1}H NMR ($CDCl_3$): δ 7.87–7.08 (m, Ph), 5.84 (s, 2H, NCH_2), 4.41 (q, 2H, J_{H-H} = 7.2 Hz, OCH_2), 4.32 (q, 2H, J_{H-H} = 7.2 Hz, OCH_2), 1.38 (t, 3H, J_{H-H} = 7.2 Hz, CH_3), 1.28 (t, 3H, J_{H-H} = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 160.1, 158.2 (CO_2), 142.8, 141.1, 139.1 (CN and CCO_2), 134.0, 131.4, 128.9, 128.0 (Ph), 63.0, 62.1 (OCH_2), 53.1 (NCH_2), 14.2, 13.8 (CH_3). MS (*m/z*): 329.1 (M^++1). Spectroscopic data for **6e** (milk-white solid) are as follows: ^{1}H NMR ($CDCl_3$): δ 7.86–7.07 (m, Ph), 5.76 (s, 2H, NCH_2), 4.42 (s, 2H, CH_2Br), 4.40 (q, 2H, J_{H-H} = 7.1 Hz, OCH_2), 4.30 (q, 2H, J_{H-H} = 7.1 Hz, OCH_2), 1.37 (t, 3H, J_{H-H} = 7.1 Hz, CH_3), 1.27 (t, 3H, J_{H-H} = 7.1 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 160.0, 158.4 (CO_2), 140.5, 138.4, 134.1, 133.9131.3, 128.9, 128.4, 127.9 (CCO_2 and Ph), 62.8, 61.8 (OCH_2), 53.3 (NCH_2), 31.8 (CH_2Br), 14.1, 13.7 (CH_3). MS (*m/z*): 396.1 (M^++1). Spectroscopic data for $N_3(CH_2C_6F_5)C(CO_2Me)C(Ph)$ (**N^3-7a**) are as follows: ^{1}H NMR ($CDCl_3$): δ 7.69–7.41 (m, 2H, Ph), 7.43–7.41 (m, 3H, Ph), 6.00 (s, 2H, NCH_2), 3.87 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 159.6 (CO_2), 150.4 (CCO_2), 147.3, 143.8, 140.2, 133.9, 133.0, (5 m, C_6F_5), 129.7, 129.35, 129.2, 128.1 (C_6H_5), 108.3 (t, C_6F_5), 52.6 (OCH_3), 42.0 (NCH_2). MS (*m/z*): 384.1 (M^++1). HRMS: calc. for $C_{17}H_{10}F_5N_3O_2$: *m/z* 383.0691, found 383.0693.

2.7. X-ray analysis

Single crystals suitable for X-ray diffraction study were grown as mentioned above. The chosen single crystal was glued to a glass fiber and mounted on a Bruker SMART APEX diffractometer equipped with graphite monochromatic Mo-*Kα* radiation (λ = 0.71073 Å). Data collection was executed using the SMART program; cell refinement and data reduction were performed with the SAINT program [35]. The structure was determined by the SHELXTL/PC [36] 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. Crystal data of complex **2**, **3**, **4**, **5** and **N^3-7a** are listed in Table 1.

CCDC 1891931, 1891932, 1891933, 1891934 and 1907581 contains the supplementary crystallographic data for this paper.

3. Results and discussion

3.1. Preparation of triazolato complexes 2–5

Treatment of **1** with a 5-fold excess of diethyl acetylene dicarboxylate in $CHCl_3$ at room temperature under an atmosphere of air for 36 h afforded a [3 + 2] dipolar cycloaddition product, the N(2)-bound 4,5-bis(ethoxycarbonyl)-1,2,3-triazolato complex [Ru]$N_3C_2(CO_2Et)_2$ (**2**), in 93% isolated yield (Scheme 1). A molecular ion peak at *m/z* 777.1 (M^+) in the FAB mass spectrum of **2** was observed. The structure of **2** was clearly established as the N(2)-bound isomer based on its ^{1}H NMR spectrum, which showed a quartet signal centered at δ 4.19 (q, 2H, J_{H-H} = 7.2 Hz) and a triplet signal centered at δ 1.19 (t, 3H, J_{H-H} = 7.2 Hz), attributed to the two anisochronous ethoxycarbonyl protons of **2**. The ^{1}H spectrum of an N(1)-bound isomer would show two sets of AX pattern resonances for its two asynchronous ethoxycarbonyl groups. It should be noted that the triazole and tetrazole anion could be coordinated to the metal through either its N(1) or N(2) nitrogen atom [37], which are essentially isoenergetic, as evidenced by molecular orbital calculations [38]. The evidence obtained to date indicates that either the two N(1)- and N(2)-bonded isomers are formed simultaneously or that the N(2)-bound isomer is the exclusive product [37,38]. In our case, the time-elapsed ^{31}P NMR study of the formation of **2** did not provide any evidence for the formation of the N(1)-bound isomer during the reaction.

Treatment of **1** with a 5-fold excess of ethyl 4,4,4-trifluoro-2-butynoate in $CHCl_3$ at room temperature for 24 h afforded the N(2)-bound 4-ethoxycarbonyl-5-trifluoromethyl-1,2,3-triazolato complex [Ru]$N_3C_2(CO_2Et)(CF_3)$ (**3**), in 92% isolated yield (Scheme 1). When the reaction was monitored by ^{31}P NMR spectroscopy, only one new singlet resonance at δ 87.0 was observed. In the ^{1}H NMR spectrum, a quartet signal centered at δ 4.15 and a triplet signal centered at δ 1.22 attributed to the ethoxycarbonyl protons of **3** appeared. The FAB mass spectrum of **3** displayed a molecular ion peak at *m/z* 773.2 (M^+). Analogous [3 + 2] cycloadditions of methyl phenylpropiolate and ethyl 2-butynoate with **1** cleanly produced the triazolates [Ru]$N_3C_2(CO_2Me)(Ph)$ (**4**) [Ru]$N_3C_2(CO_2Et)(CH_3)$ (**5**) and in 94% and 84% isolated yields, respectively. Both of the reactions did not proceed at room temperature. The preparation of [Ru]$N_3C_2(CO_2Me)(Ph)$ (**4**) was accomplished by treating **1** with a 5-fold excess of methyl phenylpropiolate in refluxing benzene (b.p. 80.1 °C) for 48 h. The preparation of **5** was accomplished in a more vigorous condition. When **1** was treated with a 10-fold excess of ethyl 2-butynoate in refluxing toluene (b.p. 110.6 °C) for 12 h, the resonance of **1** at δ 81.5 in the ^{31}P NMR spectrum became smaller and a new peak at δ 87.6, attributed to **5** appeared. The reaction was completed in 48 h.

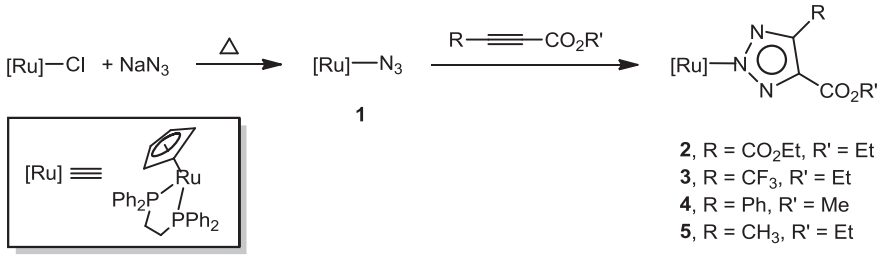
All four triazolate complexes **2**, **3**, **4** and **5** obtained by [3 + 2] cycloaddition with the internal alkynes exhibit an N(2)-coordination of the five-membered ring and time-elapsed ^{31}P NMR studies of the formation of **2-5** did not provide any evidence for the formation of the N(1)-bound isomer during the reaction. In most cases, the activated alkynes used as dipolarophiles are limited to highly electron-poor alkynes. The formation of an N-coordinate metal triazolato complex by the [3 + 2] cycloaddition of a metal-coordinated azide with a less electron-poor internal alkyne, such as $PhC{\equiv}CCO_2Me$ and $CH_3C{\equiv}CCO_2Et$, is rare [32a]. To the best of our knowledge, compound **5** prepared using 2-butynoate is the first example of the preparation of an N-coordinated metal triazolato complex.

In this study, the different reaction times and reaction temperatures indicate that the reactivity of dipolar [3 + 2] cycloaddition reactions is highly related to the nature of the alkyne being used and is highly temperature dependent. Diethyl acetylene

Table 1
Crystal and intensity collection data for complexes 2, 3, 4, 5 and N3-7a.

	2	3	4	5	N^3-7a
Empirical formula	$C_{39}H_{39}N_3O_4P_2Ru$	$C_{37}H_{34}F_3N_3O_2P_2Ru$	$C_{41}H_{37}N_3O_2P_2Ru$	$C_{37}H_{37}N_3O_2P_2Ru$	$C_{17}H_{10}F_5N_3O_2$
Formula wight	776.74	772.68	766.74	718.70	383.28
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	1.54178
Cryst syst	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	Pnma	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	9.4876(2)	22.1330(7)	11.6658(2)	9.4817(5)	14.5885(4)
b, Å	21.7420(6)	16.0430(5)	19.1128(4)	21.7681(10)	7.4116(2)
c, Å	16.7037(4)	9.4444(3)	16.8525(4)	16.0285(8)	28.8007(7)
β, deg	97.6614(7)	90	109.9796(5)	91.8215(12)	93.4111(8)
V, Å^3	3414.87(14)	3353.51(18)	3531.39(13)	3306.6(3)	3108.53(14)
Z	4	4	4	4	8
Density (calcd), Mg/m^3 1.511	1.530	1.442	1.444	1.638	
Absorption coeff., mm^{-1} 0.600	0.618	0.575	0.609	1.326	
F(000) 1600	1576	1576	1480	1552	
θ range, deg 2.360 to 27.489	2.236 to 27.481	2.489 to 29.998	2.262 to 27.443	3.319 to 74.996	
Reflections collected 23784	22759	33805	7494	20912	
Independent reflections 7831	3982	10289	7494	6397	
GOF[a] on F^2 1.050	1.294	1.057	1.064	1.052	
R (I > 2σ(I)) [b]R1 = 0.0250,	R1 = 0.0887,	R1 = 0.0305,	R1 = 0.0482,	R1 = 0.0361,	
	w*R2* = 0.0588	w*R2* = 0.2036	w*R2* = 0.0640	w*R2* = 0.1160	w*R2* = 0.0918
R (all data) R1 = 0.0302,	R1 = 0.0920,	R1 = 0.0378,	R1 = 0.0628	R1 = 0.0417,	
	w*R2* = 0.0626	w*R2* = 0.2058	w*R2* = 0.0673	w*R2* = 0.1283	w*R2* = 0.0988
Peak, hole, e Å^{-3} 0.367, −0.400	1.840, −0.943	0.463, −0.646	1.480, −0.756	0.315, −0.278	

[a] GOF = $[\Sigma[w(F^2_o\text{-}F^2_c)^2]/(n\text{-}p)]^{1/2}$; n = number of reflections, p = number of parameters refined.
[b] R1 = $(\Sigma||F_o|-|F_c||)/\Sigma|F_o|$, w*R2* = $[\Sigma[w(F^2_o\text{-}F^2_c)^2]/\Sigma[wF^4_o]^{1/2}$.



Scheme 1.

dicarboxylate and ethyl 4,4,4-trifluoro-2-butynoate, internal alkynes with two strong electron-withdrawing groups, participated smoothly in a [3 + 2] cycloaddition with [Ru]-N_3 (**1**) at room temperature and the reaction was complete in 48 and 24 h, respectively. Methyl phenylpropiolate and ethyl 2-butynoate, less electron-poor alkynes, failed to react with **1** at room temperature and more drastic, vigorous conditions were needed to complete the reaction. These results indicate that the ynoate ester with a CF_3 substituent showed best reactivity, and the trend was $CF_3 > CO_2Et >> C_6H_5 > CH_3$, which is directly proportional to their electron-withdrawing ability.

The molecular structures of the triazolato complexes **2**-**5** have been established by single crystal X-ray diffraction analysis. Diffraction-quality crystals were obtained by allowing *n*-hexane to diffuse into $CHCl_3$ solutions of **2**–**5**. ORTEP drawings are shown in Figs. 1–4, respectively. Crystallographic and refinement data for **2**-**5** are summarized in Table 1. Selected bond distances and angles are given in Table 2.

The triazolate ligands in **2**–**5** are all bonded to the Ru *via* their N(2) atom. For **2**, the coordination with ruthenium is a distorted piano-stool geometry, with three facial sites being occupied by the C_5H_5 ligand (Ru-C = 2.2878(4)-2.2034(18) Å; average 2.2088 Å); the other three positions are occupied by two phosphine ligands

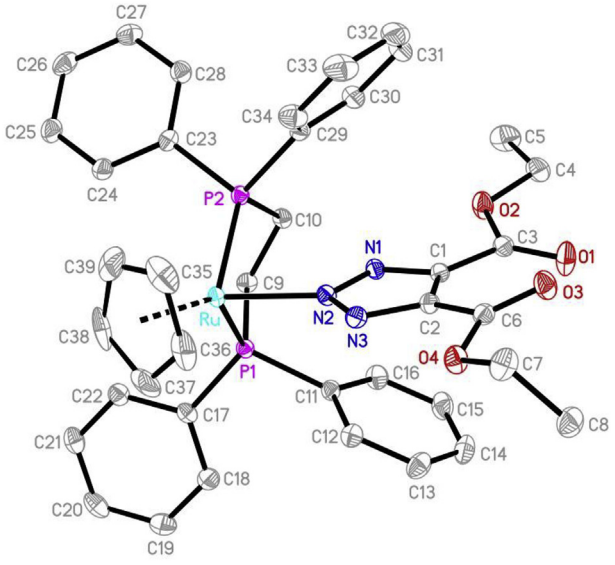


Fig. 1. ORTEP drawing of **2**; thermal ellipsoids are drawn at the 50% probability level.

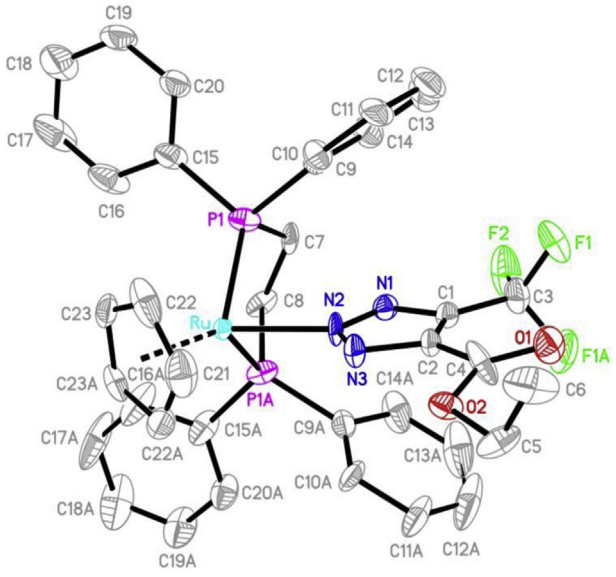


Fig. 2. ORTEP drawing of **3**; thermal ellipsoids are drawn at the 50% probability level.

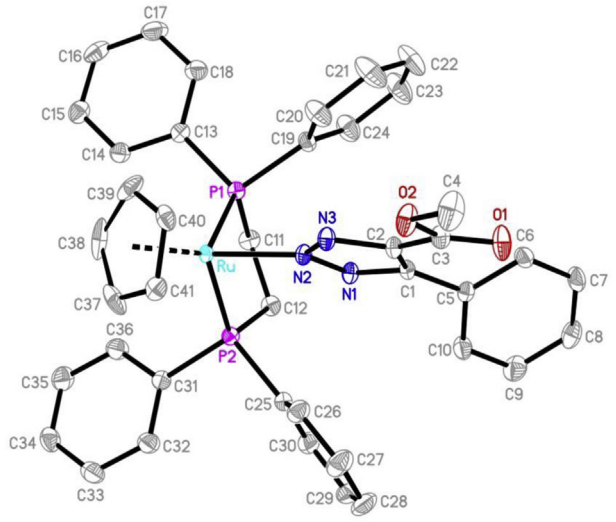


Fig. 3. ORTEP drawing of **4**; thermal ellipsoids are drawn at the 50% probability level.

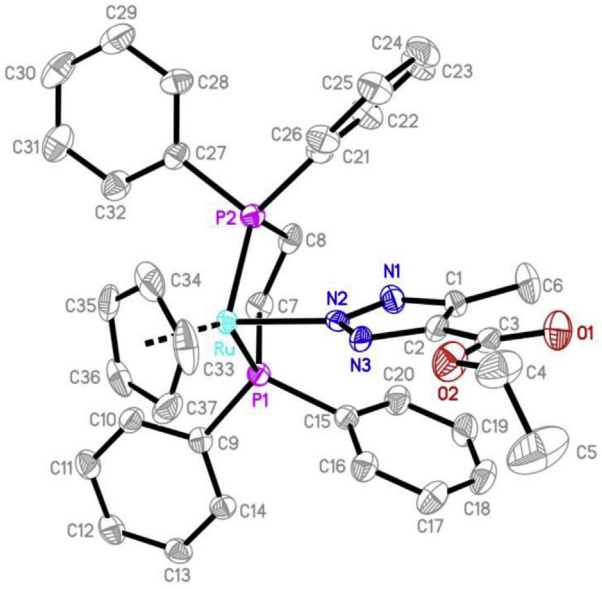


Fig. 4. ORTEP drawing of **5**; thermal ellipsoids are drawn at the 50% probability level.

Table 2
Selected bond distances (Å) and angles (deg) for 2, 3, 4 and 5.

	2	3	4	5
Ru–P1	2.2878(4)	2.2847(18)	2.2808(4)	2.2790(11)
Ru–P2	2.2940(4)	2.2847(18)	2.2712(4)	2.2823(12)
Ru–N2	2.0869(13)	2.167(7)	2.0748(13)	2.071(3)
N1–N2	1.3316(19)	1.299(12)	1.3446(19)	1.347(4)
N2–N3	1.3397(19)	1.263(12)	1.3276(19)	1.322(4)
N3–C2	1.351(2)	1.366(12)	1.362(2)	1.349(5)
C1–C2	1.396(2)	1.394(15)	1.401(2)	1.395(6)
N1–C1	1.341(2)	1.334(12)	1.343(2)	1.344(5)
P1–Ru–P2	83.386(15)	84.29(9)	85.201(16)	84.14(4)
N2–Ru–P1	89.50(4)	88.1(2)	87.90(4)	90.54(9)
N2–Ru–P2	85.69(4)	88.1(2)	87.57(4)	86.27(9)
N1–N2–Ru	122.18(10)	119.6(6)	128.31(10)	124.1(2)
N3–N2–Ru	124.91(11)	121.7(8)	124.92(10)	122.9(2)
N2–N3–C2	105.10(13)	103.3(8)	104.86(13)	105.4(3)
N1–N2–N3	112.83(13)	119.1(8)	113.13(23)	112.9(3)
N2–N1–C1	106.18(13)	102.4(8)	106.17(13)	105.8(3)
N1–C1–C2	107.66(14)	108.7(9)	107.19(14)	107.3(3)
N3–C2–C1	108.22(14)	106.4(9)	108.55(14)	108.6(3)

(Ru-P1 = 2.2878(4) Á; Ru-P2 = 2.2940(4) Á) and the triazolate group (Ru-N2 = 2.0869(13) Á), which are comparable to those in other ruthenium triazolato complexes [33,34]. The inter-atomic distances within the five-membered triazole ring (N1-N2 (1.3316(19)Å), N2-N3 (1.3397(19)Á), N1-C1 (1.341(2)Á), N3-C2 (1.351(2)Á) and C1-C2 (1.396(2)Á)), are typical, consistent with the delocalization of the electrons within the heterocycle. The bond angles of N1-N2-N3 (112.83(13)^{O}), N2-N3-C2 (105.10(13)^{O}), N3-C2-C1 (108.22(14)^{O}), N1-C1-C2 (107.66(14)^{O}) and N2-N1-C1 (106.18(13)^{O}) are all in the range of C(sp^2) and N(sp_2) hybridization of a five-membered heterocycle ring. The five-membered triazole ring exhibits an irregular pentagonal structure and is essentially planar.

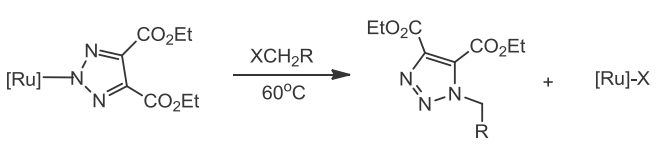
The molecular structures of complexes **3**-**5** are identical to **2**, which can be described as distorted piano-stool geometry, with the central atom being surrounded by C_5H_5, triazolate and two phosphine ligands. The bond lengths and angles of **4** and **5** are essentially identical to **2** and those of the triazole rings of **2**, **4** and **5** are with derivatives below 0.02 Å and 0.3°, respectively, indicating that the electronic and steric influences of substituents in the 4- and 5-position on the triazolate rings of **2**, **4** and **5** on the parameters are negligible. The steric effects between the CO_2Et, C_6H_5 and CH_3 groups are only slightly different and have no obvious effects on the structures of **2**, **4** and **5**. The electron withdrawing and donating ability of the three substrates on the tetrazolates seems have no obvious effects on the structures neither. It is worth noting that the bond lengths and angles of **3** are slightly different from the others. For **3**, the Ru-N2 bond distance (2.167(7) Å) is slightly longer than those in compound **2**, **4** and **5**, which can be attributed to the larger steric effects between the CF_3 group of the triazole ring ligand and the bulky dppe ligand. The N1-N2, N2-N3 and N1-C1 distances of 1.299(12), 1.263(12) and 1.334(12), respectively, are slightly shorter than those of **2**, **4** and **5**, indicating a marginally smaller structure of the triazolate ring of **3**. The inter-atomic bond angles N1-N2-N3 (119.1(8)^{O}), N2-N3-C2 (103.3(8)^{O}), N3-C2-C1 (106.4(9)^{O}), N1-C1-C2 (108.7(9)^{O}) and N2-N1-C1 (102.4(8)^{O}) of the triazolate ring of **3** are slightly deviated from those of **2**, **4** and **5**, indicating that the shape

of the five-membered triazole ring of **3** is slightly distorted in comparison with those of **2**, **4** and **5**, which could be due to the more steric-expulsive CF_3 substituent on the triazolate ligand of **3**. Apparently, the steric effects appear to be the major determinant for the N(2)-bonding mode and structures of **2**–**5** but that electronic effects appear to account for their conformation.

3.2. Reactions of **2**–**5** with electrophiles

The treatment of **2** with a 10-fold excess of CH_3I in $CHCl_3$ at room temperature for one week or at 60 °C in a silicone oil bath for 24 h resulted in the cleavage of the Ru-N bond and the formation of [Ru]-I and a colorless liquid, which is 1-methyl-4,5-bis(ethoxycarbonyl)-1,2,3-triazole $N_3(CH_3)C_2(CO_2Et)_2$ (**6a**), in 60% isolated yield (Scheme 2). The reaction was monitored by NMR spectroscopy. When **2** was treated with CH_3I in $CDCl_3$ at 60 °C for 24 h, the ^{31}P NMR spectral resonance for **2** at δ 87.9 disappeared and a peak at δ 79.0, attributed to [Ru]-I, appeared. In the ^1H NMR spectrum a singlet resonance appeared at δ 4.50, attributed to the Cp of [Ru]-I, and two quartet signals centered at δ 4.24, 4.10 (q, 2H, $J_{H\text{-}H} = 7.2$ Hz) and two triplet signals centered at δ 1.12, 1.07 (t, 3H, $J_{H\text{-}H} = 7.2$ Hz) appeared, which are attributed to the formation of the free organic triazole **6a**. The FAB mass spectrum of the crude mixture displayed molecular ion peaks at *m/z* 720.2 and 228.1, attributed to [Ru]–I and **6a**, respectively. A similar reaction of **2** with other organic bromides resulted in Ru-N bond cleavage to give a series of 1,4,5-trisubstituted-1,2,3-triazole complexes. The cleavage of the Ru-N bond of **2** was a very slow process at room temperature, requiring more than 7 days to reach completion. We accelerated the reaction by conducting the reaction at 60 °C in a silicone oil bath for 24-48 h, which afforded the 1-alkylated-4,5-bis(ethoxycarbonyl)-1,2,3-triazole $N_3(R)C_2(CO_2Et)_2$ (**6b**, R = $CH_2C_6F_5$; **6c**, R = CH_2Ph; **6d**, R = CH_2(4-CN-C_6H_4); **6e**, R = CH_2(4-CH_2Br-C_6H_4) and [Ru]-Br (Scheme 2). The structure of these free triazoles were clearly established as N(1)-alkylated based on their ^1H NMR spectra, which exhibited two sets of AB pattern proton resonances for their anisochronous ethoxycarbonyl groups. [Ru]–Br is easily isolated as an orange-yellow precipitate in a cold *n*-pentane solution with a high recycling ratio but the organic triazoles **6b-6e**, which were mixed with the excess organic bromide in *n*-pentane, were difficult to isolate in pure form. Nelson and coworkers [39] examined the alkylation of the cobalt triazolato complexes, but the isolation of the free triazole was also not successful.

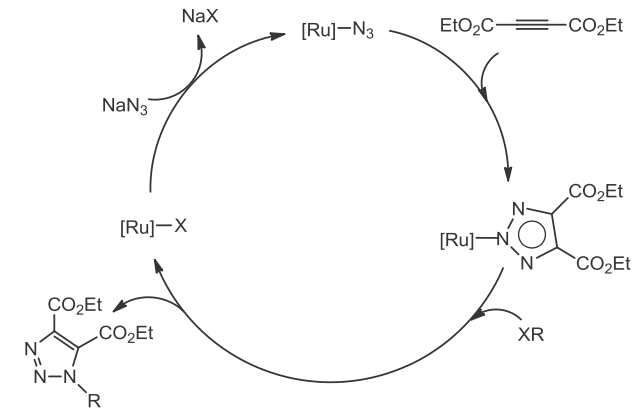
Complexes **2** and the triazoles **6a-6e** are stable in air and in solution, which permitted these reactions to be carried out under an atmosphere of air. The [Ru]-Br, which, on reacting with sodium azide, would afford [Ru]-N_3 (**1**) thus forming a reaction cycle (Scheme 3). Most of the procedures in this cycle could be carried out under an atmosphere of air, thus providing an economical and convenient approach for the synthesis of functionalized 1,4,5-trisubstituted 1,2,3-triazoles and derivatives thereof. In addition, the 1,2,3-triazole and derivatives prepared in CuAAC and RuAAC



2

6a, R = H; X = I
6b, R = C_6F_5; X = Br
6c, R = Ph; X = Br
6d, R = 4-CN-C_6H_4; X = Br
6e, R = 4-CH_2Br-C_6H_4; X = Br

Scheme 2.



Scheme 3.

reactions are largely limited to 1,4-disubstituted and 1,5-disubstituted 1,2,3-triazoles. The reaction reported here, therefore, represents a complementary method for the synthesis of fully decorated 1,4,5-trisubstituted 1,2,3-triazoles.

We recently reported [34] that the triazolato complex [Ru]$N_3C_2HCO_2Et$ reacts with a series of alkyl halides to regiospecifically alkylate the triazole ring. Since all of the triazolate complexes **3**-**5** contain an N(2)-bound triazolate, this prompted us to determine if they would react similarly to produce regiospecifically alkylated triazoles. Accordingly, complexes **3**-**5** were reacted with alkyl halides in $CDCl_3$ in a 5-mm NMR tube, and the progress of the reaction was followed by ^1H and ^{31}P NMR spectroscopy. No alkylation was observed when **3** was treated with an excess of an electrophile such as $BrCH_2C_6F_5$, $BrCH_2Ph$ and CH_3I, even under drastic, vigorous conditions.

Treatment of **4** with a 10-fold excess of $BrCH_2C_6F_5$ in C_6D_6 on an 60 °C silicon oil bath for 48 h afforded a N^3-alkylated triazole $N_3(CH_2C_6F_5)C_2(CO_2Me)(Ph)$ (**N^3-7a**) and a trace amount of N^1-alkylated regioisomer. The reaction was monitored by ^1H NMR spectroscopy. When **4** was treated with a 10-fold excess of $BrCH_2C_6F_5$ in C_6D_6 on an 60 °C silicon oil bath, in the ^1H NMR two set of singlet resonances of NCH_2 and CCH_3 appeared at δ 6.00, 3.87 and δ 5.15 and 3.82, attributed to of the N^3-alkylated triazole, the major produt, and the N^1-alkylated triazole, the minor product, respectively, in a ratio of *ca.* 8:1. The FAB mass spectrum of the crude mixture displayed parent peaks at *m/z* 646.1 and 384.1, attributed to [Ru]-Br and the 1,4,5-trisubstituted triazole $N_3(CH_2C_6F_5)C_2(CO_2Me)(Ph)$ (**7a**), respectively. Colorless crystals of **N^3-7a** were formed by slow evaporation of the solvent of the crude mixture. The structure of **N^3-7a** was determined by a single crystal X-ray diffraction analysis. Although the unit cell of **N^3-7a** contains two crystallographically different molecules, only one molecule is displayed due to the difference being insignificant. An ORTEP drawing is shown in Fig. 5 and the selected bond distances and angles are listed in Table 3. In **N^3-7a**, the 4-phenyl-5-methoxycarbonyl-triazole moiety is N(1)-alkylated by the pentafluorobenzyl group. The N1–N2, N2–N3, N1–C1, N3–C2 and C1–C2 bond lengths of 1.3348(16), 1.3133(16), 1.3625(17), 1.3621(17) and 1.3852(17) Å, respectively, all displaying partial double-bond character, are indicative of several resonance contributions and the five-membered triazole ring is essentially planar and aromatic. The N1–N2–N3, N2–N3–C2, N2–N1–C1, N1–C1–C2 and N3–C2–C1 bond angles of 107.72(11)°, 109.40(11)°, 110.76(11)°, 104.47(11)° and 107.65(12)°, respectively, are indicative of the irregular pentagonal structure of the triazole ring.

Similar reaction of **4** with $BrCH_2Ph$ and CH_3I both afforded N^3- and N^1-alkylated triazole $N_3(CH_2R)C_2(Ph)(CO_2Me)$ in a ratio of *ca.*

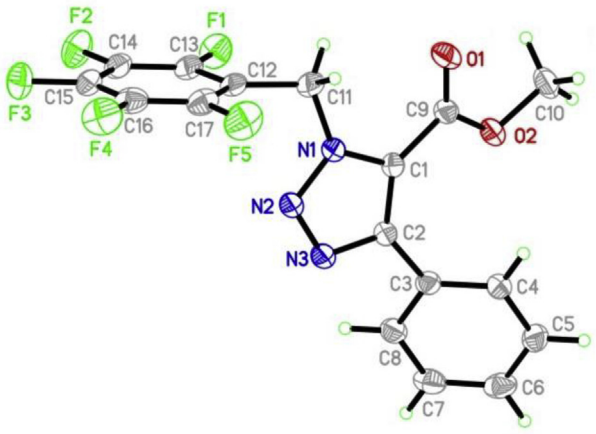


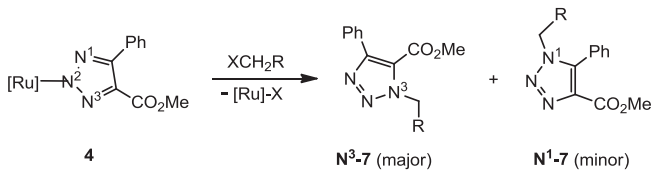
Fig. 5. ORTEP drawing of **N^3-7a**; thermal ellipsoids are drawn at the 50% probability level.

Table 3
Selected bond distances (Å) and angles (o) for N3-7a.

N1–N2	1.3348(16)	N2–N3	1.3133(16)
N1–C1	1.3625(17)	N3–C2	1.3621(17)
C1–C2	1.3852(18)	C2–C3	1.4798(18)
C1–C9	1.2059(16)	O1–C9	1.2032(17)
N1–C11	1.4785(17)	O2–C9	1.3253(18)
N1–N2–N3	107.72(11)	N2–N3–C2	109.40(11)
N2–N1–C1	110.76(11)	N3–C2–C1	107.65(12)
N1–C1–C2	104.47(11)	N3–C2–C3	117.91(11)
C1–N1–C11	130.30(11)	C1–C2–C3	134.42(12)
N2–N1–C11	118.93(11)	N1–C1–C9	120.57(12)
C2–C1–C9	134.91(13)	C1–C9–O1	123.35(13)
O1–C9–O2	125.37(13)	O2–C9–O1	111.28(11)

6:1 and 4:1 (calculated from the integration of the NCH_2 signals of the two regioisomers in the ^1H NMR spectra and assigned by comparing with the NCH_2 signals of **6a**-**6e** and **7a**), respectively. The two regioisomers could be produced by electrophilic attack of CH_2R^+ at both the N^1 and N^3 nitrogen and the subsequent liberation of the alkylated trazolates gave two triazole regioisomers (Scheme 4). The results indicate that the alkylation of **4** is not regiospecific, but highly regioselective.

When **5** was treated with a 10-fold excess of CH_3I in $CDCl_3$ at room temperature for 3 days, two sets of characteristic singlet resonances at δ 4.24, 2.50 and 3.96, 2.54, attributed to NCH_3, CCH_3 of two regioisomers of the organic 1,4,5-trisubstituted triazole, respectively, appeared at the same time in the ^1H NMR spectrum. The ratio of the two regioisomers was determined to be *ca.* 1:2. Similar alkylation reactions of **5** with $BrCH_2Ph$ and $BrCH_2C_6F_5$ at



4 **N^3-7** (major) **N^1-7** (minor)

7a, R = C_6F_5 (N^3 : N^1 = 8:1)
7b, R = Ph (N^3 : N^1 = 6:1)
7c, R = H (N^3 : N^1 = 4:1)

Scheme 4.

room temperature resulted in Ru-N bond cleavage and both afforded two regioisomers in ratios of *ca.* 1:2 and 2:3, respectively. The results of the NMR experiments indicate that the alkylation of the triazolato complex **5** is not regiospecific and regioselectivity is low.

The different alkylation reaction temperatures between complexes **2-5** indicate that the reactivity of these systems is highly related to these substituents on the triazole rings of complexes being used. The steric hindrance of a bulkier CF_3 group substituted on the triazole ring of **3** appears to disfavor the electrophilic attack of organic halides, since no reaction was observed, even at temperatures of 100 °C or above. The alkylation of **4**, which is substituted with a moderately steric bulky phenyl group, was activated at higher temperature with more regioselectivity but no regiospecificity. The least steric hindered CH_3 group substituted on the triazole ring of **5** favors an electrophilic attack even at room temperature but lacks regioselectivity. These results indicated that the steric effects of these substituents on the triazole rings of complexes **2**-**5** are the predominant factor and electronic effects are the minor factor for the reactivity and regioselectivity of the alkylation reaction.

3.3. Conclusion

We successfully synthesized a series of triazolato complexes by [3 + 2] cycloaddition reactions of ynoate esters with a ruthenium azido complex. The reaction products, metal-bound heterocyclic complexes such as the triazolato complexes $[Ru]N_3C_2(CO_2Et)_2$ (**2**), $[Ru]N_3C_2(CO_2Et)(CF_3)$ (**3**), $[Ru]N_3C_2(CO_2Me)(Ph)$ (**4**) and $[Ru]N_3C_2(CO_2Et)(CH_3)$ (**5**) were produced from diethyl acetylene dicarboxylate, ethyl 4,4,4-trifluoro-2-butynoate, methyl phenylpropiolate and ethyl 2-butynoate, respectively. The resulting triazolato complexes, which were characterized by X-ray structure analysis, confirms the N(2)-bonding type of the addition products. In the study, we demonstrated that the steric effects appear to be the major determinant for the N(2)-bonding mode and structures of **2**–**5** but that electronic effects appear to account for their conformation. The Ru-N bond-cleavage of **2** occurred in the presence of an excess amount of organic halides, affording a series of 1-alkylated-4,5-bis(ethoxycarbonyl)-1,2,3-triazoles and [Ru]-X (X = I or Br), which, on reaction with sodium azide, gave the [Ru]-N_3 (**1**) thus forming a reaction cycle. Monitoring the alkylation reactions of organic halides with **4** and **5** by NMR indicated that, both gave two regioisomers of 1,4,5-trisubstituted 1,2,3-triazoles in different ratios, indicating that the alkylation reactions of both **4** and **5** are not regiospecific. Steric effects account for the electrophilic attack of ruthenium triazolato complexes and appear to be a determining factor for the conformation of the thus formed 1,4,5-trisubstituted 1,2,3-triazoles. We are currently in the process of further exploring the synthesis and the reactivity of new ruthenium triazolato complexes and new triazole derivatives. Studies of related reactions and applications of these complexes are currently underway.

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