Inorganic Chemistry
Article
pubs.acs.org/IC

1,3-Dipolar Cycloadditions of Ruthenium(II) Azido Complexes with Alkynes and Nitriles

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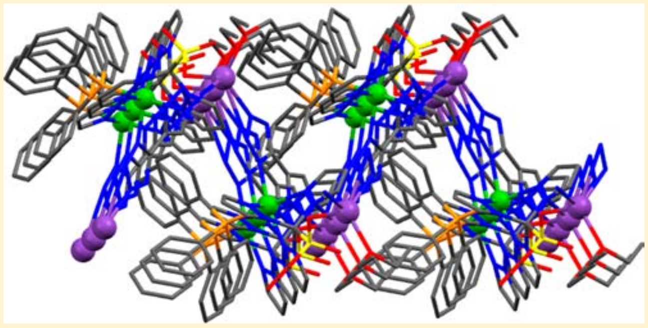
Supporting Information

ABSTRACT: The diazido complex [Na][Ru$(N_3)_2\{\kappa^3(N,N,N)$-Tpms$\}(PPh_3)$] (**1**) (Tpms = tris(pyrazolyl)methanesulfonate) has been synthesized, and its reactivity toward dipolarophiles has been investigated. Thus, the reaction of **1** with alkynes leads to complexes with one or two triazolate ligands depending on the alkyne and the reaction conditions. Complex **1** also reacts with nitriles. Thus, the reaction with RCN (R = Me, Ph) leads to the substitution products [Ru(N_3)(NCR)$\{\kappa^3(N,N,N)$-Tpms$\}(PPh_3)$]. However, when fumaronitrile is used, a complex containing a new $\kappa^2(N^1,N^3)$-5-(1,2,3-triazol-4-yl)-1,2,3,4-tetrazolate ligand is obtained as the result of two consecutive cycloaddition reactions. The mechanism for this unusual reaction has been unambiguously established through the isolation of the intermediate complex resulting from a first cycloaddition between a coordinated azide and the C═C double bond.



INTRODUCTION

1,3-Dipolar cycloaddition reactions are common processes in organic chemistry[1] which involve the reaction of 1,3-dipoles with unsaturated dipolarophiles. Among various 1,3-dipoles, organic azides are particularly important[2] as they provide an entry into the synthesis of triazoles and tetrazoles, which are interesting organic molecules. In particular, 1,2,3-triazoles have found a range of important applications in the pharmaceutical and agricultural industries,[3] and the preparation of 5R-substituted tetrazoles presents a great interest due to the use of 5R-tetrazole-containing coordination compounds of Pt(II) and Pt(IV) as cytostatic agents, resulting in a minimization of the negative effects of platinum anticancer drugs.[4]

The Huisgen 1,3-dipolar cycloaddition of azides and alkynes[5] is one of the most useful synthetic methods leading to these heterocycles. However, even though the reaction is highly exothermic (−50 to −65 kcal/mol), its high activation barrier results in exceedingly low reaction rates for unactivated reactants even at elevated temperatures. The copper-catalyzed 1,3-dipolar azide−alkyne cycloaddition (CuAAC)[6] and more recently the ruthenium catalyzed 1,3-dipolar azide−alkyne cycloaddition (RuAAC)[7] represent an important advance in the chemistry of 1,2,3-triazoles.

Metal coordinated azido ligands can also undergo 1,3-dipolar cycloaddition reactions. An excellent review[8] was published in 1997 by Frühauf. To that date, the metals involved in this chemistry most often were Pd(II), Pt(II), and Co(III) and in less extension Ni(II), Rh(I), Ir(I), Cu(I), Au(I), and Au(III). Recently, Mo(II)[9] and especially Ru(II)[10−13] examples have been reported.

In particular, ruthenium azido complexes have been reported to react with alkynes to produce triazolato complexes and the reactions with nitriles and isonitriles produce metal−nitrogen and metal−carbon bonded tetrazolates respectively.

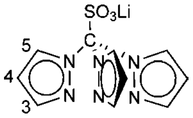
Our interest in the chemistry of ruthenium complexes lead us to explore the behavior of azido complexes in the fragment [Ru$\{\kappa^3(N,N,N)$-Tpms$\}(PPh_3)_2$] (Tpms = tris(pyrazolyl)methanesulfonate). Thus, in this paper we present 1,3-dipolar cycloadditions of a diazido ruthenium(II) complex with alkynes and nitriles to give triazolato or tetrazolato complexes respectively. A ruthenium complex with a new $\kappa^2(N^1,N^3)$-5-(1,2,3-triazol-4-yl)-1,2,3,4-tetrazolate ligand is described and its X-ray structure is reported.

EXPERIMENTAL SECTION

Materials and Instrumentation. All manipulations were performed under an atmosphere of dry nitrogen using a vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compound [RuCl$\{\kappa^3(N,N,N)$-Tpms$\}(PPh_3)_2$] was prepared by previously reported methods.[14] Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, N, and S analyses were carried out with a Perkin-Elmer 2400, LECO CHNS-932, and VTF-900 microanalyzers. Conductivities were measured at room temperature in ca. 5 × 10^{-4} mol dm^{-3} solutions, with a crison EC-Meter BASIC 30+ conductimeter. Electrospray mass spectra (ESI-MS) were recorded on a Bruker Esquire 6000 instrument, operating in the

Received: October 16, 2012
Published: March 29, 2013

positive or negative mode and using dichloromethane or methanol solutions. NMR spectra were recorded on a Bruker AV-400 instrument at 400.1 MHz (^{1}H), 162.1 (^{31}P), or 100.6 MHz (^{13}C) and a Bruker AV-300 instrument at 300.1 MHz (^{1}H), 75.5 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments were carried out for all the compounds. Coupling constants *J* are given in hertz. Resonances due to the Tpms ligand are reported by chemical shift and multiplicity only, since all $^3J_{HH}$ values for pyrazolyl rings are 2.5 Hz. Abbreviations used: br, broad signal; s, singlet; d, doublet; m, multiplet; t, triplet. The following atom labels have been used for the ^{1}H and ^{13}C{^{1}H} spectroscopic data of the tris(pyrazolyl)-methanesulfonate (Tpms) ligand:



Synthesis of [Na][Ru(N$_3$)$_2${κ^3(N,N,N)-Tpms}(PPh$_3$)] (1). NaN_3 (70 mg, 1.05 mmol) was added to a solution of complex [RuCl{κ^3(*N,N,N*)-Tpms}$(PPh_3)_2$] (100 mg, 0.105 mmol) in a 1:3 dichloromethane/methanol mixture (20 mL), and the reaction mixture was heated at 65 °C for 4 h. Solvents were removed under a vacuum, and the solid residue was extracted with cold acetone. The resulting solution was filtered through kieselguhr and concentrated under a vacuum to a volume of approximately 1 mL. Addition of hexane afforded a yellow precipitate. Solvents were decanted and the solid was washed with dichloromethane (2 × 20 mL) and hexane (3 × 30 mL) and dried under reduced pressure. Yield: 52 mg (65%). $S_{20°C}$ (H_2O): 6.4 mg/mL. Anal. Calcd. for $C_{28}H_{24}N_{12}NaO_3PRuS$: C, 44.04; H, 3.17; N, 22.01; S, 4.20. Found: C, 44.23; H, 3.34; N, 21.73; S, 4.01. MS-ESI (*m/z*): 741 ([M]$^-$, 100%). Molar conductivity in acetone: Λ_M = 89 S cm^2 mol^{-1}. IR (KBr): 2048 (ν(N=N=N)); 1281 and 1055 (ν(S−O)); 832 (ν(C−N)); 622 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 8.95 (m, 3H, H^{3,5} pz), 8.52 (d, 1H, H^{3,5} pz), 7.42 - 7.25 (m, 15H, PPh$_3$), 6.70 (d, 2H, H^{3,5} pz), 6.59 (dd, 1H, H^4 pz), 6.01 (dd, 2H, H^4 pz) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 147.1 (s, C-3,5 pz), 143.7 (s, C-3,5 pz), 136.3 (s, C-3,5 pz), 135.2 (s, C-3,5 pz), 133.9 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 129.1 (s, PPh$_3$), 127.8 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 106.3 (s, C-4 pz), 106.0 (s, C-4 pz), 90.8 (s, *C*-SO$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 52.5 (s, PPh$_3$) ppm.

*Synthesis of [Na][Ru{κ(N^2)-N$_3$C$_2$(CO$_2$R)$_2$}$_2${κ^3(N,N,N)-Tpms}(PPh$_3$)] (R = Me (**2a**), Et (**2b**)).* The corresponding alkyne (1.31 mmol) (dimethyl acetylenedicarboxylate (DMAD), 158 μL for **2a**, diethyl acetylenedicarboxylate (DEAD), 217 μL for **2b**) was added to a solution of complex [Na][Ru(N$_3$)$_2${κ^3(*N,N,N*)-Tpms}(PPh$_3$)] (**1**) (100 mg, 0.131 mmol) in acetone (20 mL). The reaction mixture was stirred at room temperature for 3 h (for **2a**) or 18 h (for **2b**). Solvents were then removed under a vacuum, the solid residue was extracted with dichloromethane, and the resultant solution was filtered through kieselguhr and concentrated under vacuum. Addition of hexane afforded an orange precipitate. Solvents were decanted and the solid was washed with hexane (3 × 30 mL) and diethyl ether (2 × 20 mL) and dried under reduced pressure. **2a.** Yield: 70 mg (51%). Anal. Calcd. for $C_{40}H_{36}N_{12}NaO_{11}PRuS$: C, 45.85; H, 3.46; N, 16.04. Found: C, 45.91; H, 3.46; N, 15.97. MS-ESI (*m/z*): 1025 ([M]$^-$, 100%); 763 ([M-PPh$_3$]$^-$, 55%). Molar conductivity in acetone: Λ_M = 92 S cm^2 mol^{-1}. IR (KBr): 2071 (ν(C=N)); 1732 (ν(C=O)); 1294 and 1092 (ν(S−O)); 833 (ν(C−N)); 622 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 9.02 (d, 2H, H^{3,5} pz), 8.91 (d, 1H, H^{3,5} pz), 8.02 (d, 1H, H^{3,5} pz), 7.31 (m, 4H, PPh$_3$), 7.22 (d, 2H, H^{3,5} pz), 7.13 (m, 5H, PPh$_3$), 6.91 (m, 6H, PPh$_3$), 6.29 (dd, 1H, H^4 pz), 6.08 (dd, 2H, H^4 pz), 3.79 (s, 12H, CH$_3$) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 163.0 (s, C=O), 149.0 (s, C-3,5 pz), 144.1 (s, C-3,5 pz), 139.3 (s, *C*CO$_2$CH$_3$), 136.1 (s, C-3,5 pz), 135.5 (s, C-3,5 pz), 134.2 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 133.8 (d, J_{CP} = 39.0 Hz, C-1 PPh$_3$), 129.0 (s, PPh$_3$), 127.5 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 106.0 (s, C-4 pz), 105.3 (s, C-4 pz), 90.8 (s, *C*-SO$_3$), 51.2 (s, CH$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 51.8 (s, PPh$_3$) ppm. **2b.** Yield: 77 mg (53%). Anal. Calcd. for $C_{44}H_{44}N_{12}NaO_{11}PRuS$: C, 47.87; H, 4.02; N, 15.22; S, 2.90. Found: C, 47.81; H, 3.93; N, 15.07; S, 3.11. MS-ESI (*m/z*): 1081 ([M]$^-$, 57%). Molar conductivity in acetone: Λ_M = 81 S cm^2 mol^{-1}. IR (KBr): 2077 (ν(C=N)); 1725 (ν(C=O)); 1296 and 1092 (ν(S−O)); 834 (ν(C−N)); 622 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 9.00 (d, 2H, H^{3,5} pz), 8.90 (d, 1H, H^{3,5} pz), 8.18 (d, 1H, H^{3,5} pz), 7.30 (m, 5H, H^{3,5} pz and PPh$_3$), 7.13 (m, 6H, PPh$_3$), 6.94 (m, 6H, PPh$_3$), 6.31 (d, 1H, H^4 pz), 6.06 (d, 2H, H^4 pz), 4.26 (c, 8H, $^3J_{HH}$ = 7.0 Hz, CH$_2$), 1.28 (t, 12H, $^3J_{HH}$ = 7.0 Hz, CH$_3$) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 162.8 (s, C=O), 149.0 (s, C-3,5 pz), 144.2 (s, C-3,5 pz), 139.5 (s, *C*CO$_2$Et), 136.0 (s, C-3,5 pz), 135.5 (s, C-3,5 pz), 134.2 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 133.9 (d, J_{CP} = 39.0 Hz, C-1 PPh$_3$), 128.9 (s, PPh$_3$), 127.4 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 105.9 (s, C-4 pz), 105.1 (s, C-4 pz), 90.6 (*C*-SO$_3$), 60.4 (s, CH$_2$), 13.6 (s, CH$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 51.9 (s, PPh$_3$) ppm.

Synthesis of [Na][Ru(N$_3$){N$_3$C$_2$HCO$_2$Me}{κ^3(N,N,N)-Tpms}(PPh$_3$)] (3). Methyl propiolate (117 μL, 1.31 mmol) was added to a solution of complex [Na][Ru(N$_3$)$_2${κ^3(*N,N,N*)-Tpms}(PPh$_3$)] (**1**) (100 mg, 0.131 mmol) in acetone (20 mL). The reaction mixture was stirred at room temperature for

Fifteen hours and a yellow precipitate was formed. Solvents were decanted, and the solid residue was washed with hexane (3 × 20 mL) and dried under reduced pressure. Yield = 44 mg (40%). Anal. Calcd. for $C_{32}H_{28}N_{12}NaO_5PRuS$: C, 45.34; H, 3.33; N, 19.83; S, 3.78. Found: C, 45.39; H, 3.45; N, 20.06; S, 3.64. MS-ESI (*m/z*): 825 ([M]$^-$, 100%); 563 ([M-PPh$_3$]$^-$, 48%). Molar conductivity in acetone: Λ_M = 89 S cm^2 mol^{-1}. IR (KBr): 2052 (ν(N=N=N)); 1708 (ν(C=O)); 1295 and 1055 (ν(S−O)); 833 (ν(C−N)); 622 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 9.01 (d, 1H, H^{3,5} pz), 8.98 (d, 1H, H^{3,5} pz), 8.89 (d, 1H, H^{3,5} pz), 7.87 (s, 1H, C*H*), 7.36 (m, 3H, PPh$_3$), 7.31 (d, 1H, H^{3,5} pz), 7.21 (m, 7H, PPh$_3$), 6.99 (d, 1H, H^{3,5} pz), 6.98 (d, 1H, H^{3,5} pz), 6.85 (m, 5H, PPh$_3$), 6.43 (d, 1H, H^4 pz), 6.21 (d, 1H, H^4 pz), 6.05 (d, 1H, H^4 pz), 3.81 (s, 3H, CH$_3$) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 163.1 (s, C=O), 149.8 (s, C-3,5 pz), 146.9 (s, C-3,5 pz), 138.9 (s, CH), 137.7 (s, *C*CO$_2$CH$_3$), 136.1 (s, C-3,5 pz), 136.0 (s, C-3,5 pz), 133.2 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 132.7 (s, PPh$_3$), 127.9 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 106.5 (s, C-4 pz), 106.1 (s, C-4 pz), 91.5 (s, *C*-SO$_3$), 52.6 (s, CH$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 52.5 (s, PPh$_3$) ppm.

Synthesis of [Na][Ru{N$_3$C$_2$HCO$_2$Me}$_2${κ^3(N,N,N)-Tpms}(PPh$_3$)] (4). Methyl propiolate (117 μL, 1.31 mmol) was added to a solution of complex [Na][Ru(N$_3$)$_2${κ^3(*N,N,N*)-Tpms}(PPh$_3$)] (**1**) (100 mg, 0.131 mmol) in acetone (30 mL). The reaction mixture was refluxed for 6 h, and a yellow precipitate was formed. Solvents were decanted and the solid residue was washed with hexane (3 × 20 mL) and dried under reduced pressure. Yield =56 mg (46%). Anal. Calcd. for $C_{36}H_{32}N_{12}NaO_7PRuS$: C, 46.40; H, 3.46; N, 18.04. Found: C, 46.33; H, 3.78; N, 17.86. MS-ESI (*m/z*): 909 ([M]$^-$, 100%). Molar conductivity in methanol: Λ_M = 109 S cm^2 mol^{-1}. IR (KBr): 2047 (ν(C=N)); 1707 (ν(C=O)); 1297 and 1055 (ν(S−O)); 748 (ν(C−N)); 623 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 9.01 (d, 2H, H^{3,5} pz), 8.95 (d, 1H, H^{3,5} pz), 7.82 (s, 2H, C*H*), 7.31 (m, 3H, PPh$_3$), 7.10 (m, 6H, PPh$_3$), 6.91 (d, 2H, H^{3,5} pz), 6.70 (m, 6H, PPh$_3$), 6.55 (d, 1H, H^{3,5} pz), 6.32 (d, 1H, H^4 pz), 6.15 (d, 2H, H^4 pz), 3.77 (s, 6H, CH$_3$) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 162.3 (s, C=O), 148.8 (s, C-3,5 pz), 143.6 (s, C-3,5 pz), 139.7 (s, CH), 137.4 (s, *C*CO$_2$CH$_3$), 136.2 (s, C-3,5 pz), 135.3 (s, C-3,5 pz), 133.3 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 132.8 (d, J_{CP} = 39.0 Hz, C-1 PPh$_3$), 129.2 (s, PPh$_3$), 127.6 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 106.9 (s, C-4 pz), 106.2 (s, C-4 pz), 91.4 (s, *C*-SO$_3$), 50.1 (s, CH$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 51.5 (s, PPh$_3$) ppm.

Synthesis of [Na][Ru(N$_3$){κ(N)-NCS}{κ^3(N,N,N)-Tpms}(PPh$_3$)] (5). CS_2 (35 μL, 0.576 mmol) was added to a solution of complex [Na][Ru(N$_3$)$_2${κ^3(*N,N,N*)-Tpms}(PPh$_3$)] (**1**) (100 mg, 0.131 mmol) in acetone (30 mL), and the mixture was refluxed for 8 h. Solvents were then removed under a vacuum, and the purple residue was washed with diethyl ether (3 × 30 mL) and dried under reduced pressure. Yield: 56 mg (55%). Anal. Calcd. for $C_{29}H_{24}N_{10}NaO_3PRuS_2$: C, 44.67; H, 3.10; N, 17.96; S, 8.22. Found: C, 44.52; H, 3.29; N, 18.05; S, 8.52. MS-ESI (*m/z*): 757 ([M]$^-$, 48%). Molar conductivity in acetone: Λ_M = 113 S cm^2 mol^{-1}. IR (KBr): 2117 (ν(NCS)); 2060 (ν(N$_3$)); 1275 and 1056 (ν(S−O)); 832 (ν(C−N)); 623 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 8.95 (m, 3H, H^{3,5} pz), 7.34–7.30

Table 1. Crystal Data and Structure Refinement for Compounds 2b·2(C_3H_6O), 7·CH_2Cl_2, and 9·$C_4H_{10}O$

	2b·2(C_3H_6O)	**7**·CH_2Cl_2	**9**·$C_4H_{10}O$
empirical formula	$C_{44}H_{44}N_{12}NaO_{11}PRuS$, 2($C_3H_6O$)	$C_{30}H_{27}N_{10}O_3PRuS$, ($CH_2Cl_2$)	$C_{31}H_{25}N_{13}NaO_3PRuS$, ($C_4H_{10}O$)
formula weight	1220.16	824.64	888.85
temperature/K	293(2)	150(2)	293(2)
wavelength/Å	1.5418	1.5418	1.5418
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	13.3422(3)	8.335(5)	10.5803(2)
b/Å	14.4554(3)	12.319(5)	29.3713(3)
c/Å	14.7576(3)	16.685(5)	12.3860(1)
α/°	97.852(2)	84.777(5)	90
β/°	94.281(2)	87.554(5)	93.596(1)
γ/°	98.419(2)	85.771(5)	90
Z	2	2	4
volume/Å^3	2776.14(10)	1700.3(13)	3841.46(9)
calculated density/g cm^{-3}	1.460	1.611	1.537
μ/mm^{-1}	3.606	6.620	4.803
F(000)	1260	836	1816
crystal size/mm	0.02 × 0.015 × 0.01	0.025 × 0.015 × 0.01	0.03 × 0.02 × 0.01
θ range/°	3.04−74.80	3.61−74.41	3.01−74.74
no. of reflns. collected	29266	11305	29270
no. of unique reflns.	10991 [R(int) = 0.0245]	6346 [R(int) = 0.0393]	7657 [R(int) = 0.0361]
completeness to θ_{max} (%)	96.3	91.2	97.1
no. of parameters/restraints	688/3	443/0	507/0
goodness-of-fit on F^2	1.0593	1.049	1.020
R_1 [$I > 2\sigma(I)$]^a	0.0422	0.0460	0.0333
wR_2 [$I > 2\sigma(I)$]^a	0.1173	0.1181	0.0810
R_1 (all data)	0.0455	0.0553	0.0416
wR_2 (all data)	0.1209	0.1247	0.0858
largest diff. peak and hole/e Å^{-3}	2.101 and −1.783	0.836 and −1.467	0.431 and −0.844

$^a R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

(m, 15H, PPh$_3$), 6.74 (d, 1H, H^{3,5} pz), 6.65 (d, 1H, H^{3,5} pz), 6.57 (d, 1H, H^{3,5} pz), 6.10 (d, 1H, H^4 pz), 6.07 (d, 1H, H^4 pz), 6.03 (d, 1H, H^4 pz) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 147.1 (s, C-3,5 pz), 146.9 (s, C-3,5 pz), 146.7 (s, C-3,5 pz), 136.4 (s, C-3,5 pz), 136.2 (s, C-3,5 pz), 135.1 (s, C-3,5 pz), 134.5 (s, NCS), 134.1 (d, $^2J_{CP}$ = 12.0 Hz, PPh$_3$), 133.4 (d, J_{CP} = 41.0 Hz, C-1 PPh$_3$), 129.2 (s, PPh$_3$), 128.0 (d, $^2J_{CP}$ = 12.0 Hz, PPh$_3$), 106.4 (s, C-4 pz), 106.2 (s, C-4 pz), 106.1 (s, C-4 pz), 91.2 (s, C-SO$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 51.5 (s, PPh$_3$) ppm.

*Synthesis of [Na][Ru{κ(N)-NCS}$_2${κ^3(N,N,N)-Tpms}(PPh$_3$)] (**6**).* CS$_2$ (790 μL, 13.1 mmol) was added to a solution of complex [Na][Ru(N$_3$)$_2${κ^3(*N,N,N*)-Tpms}(PPh$_3$)] (**1**) (100 mg, 0.131 mmol) in acetone (30 mL), and the mixture was refluxed for 3.5 h. Solvents were then removed under vacuum. Addition of diethyl ether (30 mL) afforded a brown precipitate. Solvents were decanted and the solid residue was washed with diethyl ether (3 × 10 mL) and dried under reduced pressure. Yield: 80 mg (77%). Anal. Calcd. for $C_{30}H_{24}N_8NaO_3PRuS_3$: C, 45.28; H, 3.04; N, 14.08; S, 12.09. Found: C, 44.71; H, 3.01; N, 13.67; S, 11.85. MS-ESI (*m/z*): 773 ([M]$^-$, 100%). Molar conductivity in acetone: Λ_M = 108 S cm^2 mol^{-1}. IR (KBr): 2121 (ν(NCS)); 1275 and 1058 (ν(S−O)); 833 (ν(C−N)); 622 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 8.96 (dd, 2H, H^{3,5} pz), 8.92 (m, 1H, H^{3,5} pz), 8.17 (m, 1H, H^{3,5} pz), 7.50−7.21 (m, 15H, PPh$_3$), 6.64 (m, 3H, H^{3,5} and H^4 pz), 6.10 (dd, 2H, H^4 pz) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 147.0 (s, C-3,5 pz), 144.1 (s, C-3,5 pz), 136.5 (s, C-3,5 pz), 136.0 (s, NCS), 135.2 (s, C-3,5 pz), 134.0 (d, $^2J_{CP}$ = 10.1 Hz, PPh$_3$), 133.4 (d, J_{CP} = 40.2 Hz, C-1 PPh$_3$), 129.6 (s, PPh$_3$), 128.3 (d, $^2J_{CP}$ = 9.1 Hz, PPh$_3$), 106.8 (s, C-4 pz), 106.4 (s, C-4 pz), 91.1 (s, C-SO$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 50.9 (s, PPh$_3$) ppm.

*Synthesis of [Ru(N$_3$)(NCMe){κ^3(N,N,N)-Tpms}(PPh$_3$)] (**7**).* A solution of complex [Na][Ru(N$_3$)$_2${κ^3(*N,N,N*)-Tpms}(PPh$_3$)] (**1**) (100 mg, 0.131 mmol) in acetonitrile (30 mL) was heated to reflux temperature for 6 days. After this time period, the solvents were removed under a vacuum, and the yellow residue was extracted with dichloromethane and the resultant solution was filtered through kieselguhr and concentrated under vacuum to a volume of approximately 1 mL. Addition of hexane afforded a yellow precipitate. Solvents were decanted and the solid residue was washed with hexane (3 × 30 mL) and dried under reduced pressure. Yield: 83 mg (86%). Anal. Calcd. for $C_{30}H_{27}N_{10}O_3PRuS$: C, 48.71; H, 3.68; N, 18.94; S, 4.33. Found: C, 48.50; H, 3.68; N, 19.24; S, 4.25. MS-ESI (*m/z*): 763 ([M + Na]$^+$, 100%). IR (KBr): 2131 (ν(NCMe)); 2036 (ν(N$_3$)); 1281 and 1054 (ν(S−O)); 834 (ν(C−N)); 625 (ν(C−S)) cm^{-1}. ^{1}H NMR in acetone-d_6 (δ): 9.03 (d, 1H, H^{3,5} pz), 8.99 (d, 2H, H^{3,5} pz), 8.32 (d, 1H, H^{3,5} pz), 7.54 - 7.24 (m, 15H, PPh$_3$), 7.10 (d, 1H, H^{3,5} pz), 6.95 (d, 1H, H^{3,5} pz), 6.67 (d, 1H, H^4 pz), 6.24 (d, 1H, H^4 pz), 6.17 (d, 1H, H^4 pz), 2.47 (s, 3H, CH$_3$) ppm. ^{13}C{^{1}H} NMR in acetone-d_6 (δ): 147.2 (s, C-3,5 pz), 146.9 (s, C-3,5 pz), 143.5 (s, C-3,5 pz), 137.1 (s, C-3,5 pz), 137.0 (s, C-3,5 pz), 135.9 (s, C-3,5 pz), 133.6 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 131.9 (d, J_{CP} = 41.0 Hz, C-1 PPh$_3$), 130.0 (s, PPh$_3$), 128.3 (d, $^2J_{CP}$ = 9.0 Hz, PPh$_3$), 124.0 (s, NCCH$_3$), 107.2 (s, C-4 pz), 106.9 (s, C-4 pz), 106.8 (s, C-4 pz), 90.9 (s, C-SO$_3$), 4.1 (s, NCCH$_3$) ppm. ^{31}P NMR in acetone-d_6 (δ): 49.2 (s, PPh$_3$) ppm.

*Synthesis of [Ru(N$_3$)(NCPh){κ^3(N,N,N)-Tpms}(PPh$_3$)] (**8**).* Benzonitrile (66 μL, 0.650 mmol) was added to a solution of complex [Na][Ru(N$_3$)$_2${κ^3(*N,N,N*)-Tpms}(PPh$_3$)] (**1**) (100 mg, 0.131 mmol) in toluene (15 mL), and the reaction mixture was heated at reflux temperature for 5 h. Solvents were removed under a vacuum, and the yellow residue was extracted with dichloromethane. The resulting solution was filtered through kieselguhr and concentrated under vacuum to a volume of approximately 1 mL. Addition of hexane afforded a yellow precipitate. Solvents were decanted and the solid was washed with hexane (3 × 20 mL) and dried under reduced pressure.

Yield: 92 mg (88%). Anal. Calcd. for $C_{35}H_{29}N_{10}O_3PRuS$: C, 52.43; H, 3.65; N, 17.47; S, 4.00. Found: C, 52.35; H, 4.00; N, 17.34; S, 3.60. MS-ESI (m/z): 825 ($[M + Na]^+$, 49%); 721 ($[M\text{-NCPh} + Na]^+$, 95%). IR (KBr): 2136 (ν(NCPh)); 2038 ($\nu(N_3)$); 1284 and 1054 (ν(S–O)); 802 (ν(C–N)); 621 (ν(C–S)) cm^{-1}. ^1H NMR in acetone-d_6 (δ): 9.05 (d, 1H, $H^{3,5}$ pz), 9.01 (d, 2H, $H^{3,5}$ pz), 8.40 (d, 1H, $H^{3,5}$ pz), 7.77 - 7.19 (m, 21H, PPh_3, Ph and $H^{3,5}$ pz), 7.16 (d, 1H, $H^{3,5}$ pz), 7.00 (d, 1H, H^4 pz), 6.30 (d, 1H, H^4 pz), 6.20 (d, 1H, H^4 pz) ppm. $^{13}C\{^1H\}$ NMR in acetone-d_6 (δ): 148.0 (s, C-3,5 pz), 146.6 (s, C-3,5 pz), 143.5 (s, C-3,5 pz), 137.0 (s, C-3,5 pz), 135.9 (s, C-3,5 pz), 133.7 (d, $^2J_{CP}$ = 9.0 Hz, PPh_3), 131.8 (s, Ph), 130.1 (s, PPh_3), 128.9 (s, Ph), 128.4 (d, $^2J_{CP}$ = 9.0 Hz, PPh_3), 128.1 (s, Ph), 125.2 (s, NCPh), 107.4 (s, C-4 pz), 107.1 (s, C-4 pz), 106.9 (s, C-4 pz), 90.9 (s, C-SO_3) ppm. ^{31}P NMR in acetone-d_6 (δ): 48.8 (s, PPh_3) ppm.

*Synthesis of [Na][Ru{κ^2(N^1,N^3)-$N_3C(H)C$–CN_4}{κ^3(N,N,N)-Tpms}-(PPh$_3$)] **(9)**.* Fumaronitrile (52 mg, 0.655 mmol) was added to a solution of complex $[Na][Ru(N_3)_2\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**1**) (100 mg, 0.131 mmol) in acetone (30 mL). The reaction mixture was heated at the reflux temperature for 5 h and the resulting solution was concentrated under vacuum to a volume of approximately 1 mL. Addition of hexane afforded a yellow solid which was washed with hexane (3 × 30 mL) and dried under reduced pressure. Yield: 43 mg (40%). Anal. Calcd. for $C_{31}H_{25}N_{13}NaO_3PRuS$: C, 45.70; H, 3.09; N, 22.35; S, 3.94. Found: C, 45.64; H, 3.30; N, 22.09; S, 3.81. MS-ESI (m/z): 792 ($[M]^-$, 95%). Molar conductivity in acetone: Λ_M = 95 S $cm^2\ mol^{-1}$. IR (KBr): 2055 (ν(C=N)); 1624 (ν(C=C)); 1298 and 1056 (ν(S–O)); 746 (ν(C–N)); 623 (ν(C–S)) cm^{-1}. ^1H NMR in acetone-d_6 (δ): 9.10 (d, 2H, $H^{3,5}$ pz), 9.04 (d, 1H, $H^{3,5}$ pz), 7.89 (s, 1H, CH), 7.59 (d, 1H, $H^{3,5}$ pz), 7.53 (d, 1H, $H^{3,5}$ pz), 7.34–6.59 (m, 15H, PPh_3), 6.27 (d, 1H, H^4 pz), 6.21 (d, 1H, H^4 pz), 6.16 (m, 2H, H^4 and $H^{3,5}$ pz) ppm. $^{13}C\{^1H\}$ NMR in acetone-d_6 (δ): 158.2 (s, N_4C), 149.1 (s, C-3,5 pz), 148.6 (s, C-3,5 pz), 140.5 (s, C-3,5 pz), 136.4 (s, C-3,5 pz), 136.3 (s, C-3,5 pz), 135.6 (s, CH-C), 135.3 (s, C-3,5 pz), 133.4 (d, $^2J_{CP}$ = 9.0 Hz, PPh_3), 133.1 (d, J_{CP} = 41.0 Hz, C-1 PPh_3), 129.3 (s, PPh_3), 127.8 (d, $^2J_{CP}$ = 9.0 Hz, PPh_3), 127.6 (s, CH), 106.5 (s, C-4 pz), 106.3 (s, C-4 pz), 106.1 (s, C-4 pz), 91.3 (s, C-SO_3) ppm. ^{31}P NMR in acetone-d_6 (δ): 52.2 (s, PPh_3) ppm.

*Synthesis of [Na][Ru(N$_3$){κ(N^1)-N$_3$CH(CN)CH(CN)}{κ^3(N,N,N)-Tpms}(PPh$_3$)] **(10)**.* Fumaronitrile (52 mg, 0.655 mmol) was added to a solution of complex $[Na][Ru(N_3)_2\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**1**) (100 mg, 0.131 mmol) in acetone (60 mL) and the reaction mixture was heated at the reflux temperature for 45 min. Then, the solution was cooled quickly at 0 °C and concentrated at the same temperature. The solid residue was washed with diethyl ether (3 × 30 mL) and dried under reduced pressure. Yield: 64 mg (58%). Anal. Calcd. for $C_{32}H_{26}N_{14}NaO_3PRuS$: C, 45.66; H, 3.11; N, 23.30; S, 3.81. Found: C, 45.66; H, 3.30; N, 23.62; S, 3.84. MS-ESI (m/z): 819 ($[M]^-$, 53%). IR (KBr): 2232 (ν(CN)); 2048 (ν(N=N=N) and ν(C=N)); 1277 and 1055 (ν(S–O)); 833 (ν(C–N)); 623 (ν(C–S)) cm^{-1}. ^1H NMR in acetone-d_6 (δ): 8.99 (d, 2H, $H^{3,5}$ pz), 8.79 (d, 1H, $H^{3,5}$ pz), 7.90 - 6.96 (m, 18H, $H^{3,5}$ pz and PPh_3), 6.25 (d, 2H, H^4 pz), 6.20 (d, 1H, H^4 pz), 4.82 (d, 1H, $^3J_{HH}$ = 11.0 Hz, CH(CN)), 4.02 (d, 1H, $^3J_{HH}$ = 11.0 Hz, CH(CN)) ppm. $^{13}C\{^1H\}$ NMR in acetone-d_6 at 252 K (δ): 147. Nine (s, C-3,5 pz), 147.7 (s, C-3,5 pz), 141.1 (s, C-3,5 pz), 140.6 (s, C-3,5 pz), 133.7 (d, $^2J_{CP}$ = 9.0 Hz, PPh_3), 129.2 (s, PPh_3), 128.0 (d, $^2J_{CP}$ = 9.0 Hz, PPh_3), 120.6 (s, CN), 119.8 (s, CN), 106.7 (s, C-4 pz), 106.4 (s, C-4 pz), 91.0 (s, C-SO_3), 66.1 (s, CH(CN)), 60.0 (s, CH(CN)) ppm. ^{31}P NMR in acetone-d_6 (δ): 54.3 (s, PPh_3) ppm.

X-ray Crystal Structure Determination of Complexes $2b{\cdot}2C_3H_6O$, $7{\cdot}CH_2Cl_2$, and $9{\cdot}C_4H_{10}O$. The most relevant crystal and refinement data are collected in Table 1.

In all cases, diffraction data were recorded on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu–Kα radiation (λ = 1.5418 Å). Images were collected at a 63 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (2–10), (15–55), and (6–20) s for **2b**, **7**, and **9** respectively. Data collection strategy was calculated with the program CrysAlis Pro CCD.[15] Data reduction and cell refinement were performed with the program CrysAlis Pro RED.[15] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[15]

The software package WINGX[16] was used for space group determination, structure solution, and refinement. The structure for the complexes **2b** and **7** were solved by direct methods using SIR92.[17] For **9** the structure was solved by Patterson interpretation and phase expansion using DIRDIF.[18]

Isotropic least-squares refinement on F^2 using SHELXL97[19] was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located and their coordinates were refined riding on their parent atoms. The function minimized was $([\Sigma wF_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (for **2b**, a = 0.0732, b = 2.2361, for **7** a = 0.0689, b = 1.4515 and for **9**, a = 0.0382, b = 3.0240) with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}\ (F_o^2, 0) + 2F_c^2)/3$.

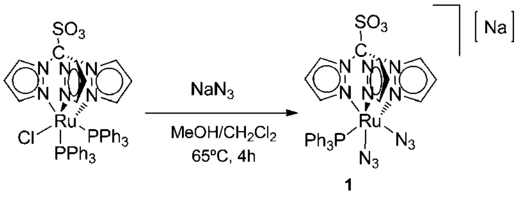
Atomic scattering factors were taken from the International Tables for X-ray Crystallography International.[20] The crystallographic plots were made with PLATON.[21]

CCDC: 905387, 905388, and 905389 contain the supplementary crystallographic data for $\mathbf{2b}{\cdot}2C_3H_6O$, $\mathbf{7}{\cdot}CH_2Cl_2$, and $\mathbf{9}{\cdot}C_4H_{10}O$ respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

*Synthesis of the Diazido Complex [Na][Ru(N$_3$)$_2${κ^3(N,N,N)-Tpms}(PPh$_3$)] **(1)**.* Reaction of complex $[RuCl\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)_2]$ with an excess of sodium azide in a mixture dichloromethane/methanol (1:3) at 65 °C leads to the anionic complex $[Na][Ru(N_3)_2\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**1**) in 65% yield (Scheme 1).

Scheme 1. Synthesis of $[Na][Ru(N_3)_2\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$



Complex **1** is isolated as a yellow powder. The molar conductivity value found for complex **1** in acetone (89 S $cm^2\ mol^{-1}$) is lower than expected for a 1:1 electrolyte (100–140 S $cm^2\ mol^{-1}$).[22] Complex **1** has been analytically and spectroscopically characterized (IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR). In particular, the IR spectrum (KBr) shows the characteristic absorptions for the ligand Tpms in a κ^3(N,N,N)-coordination mode:[23] two medium signals at 1281 and 1055 cm^{-1} due to the ν(S–O) from the sulfonate moiety, a weak band at 832 cm^{-1} due to the ν(C–N) of the pyrazole rings and the absorption at 622 cm^{-1} assigned to the stretching ν(C–S). Finally, the absorption due to the azide group appears as a strong signal at 2048 cm^{-1}.

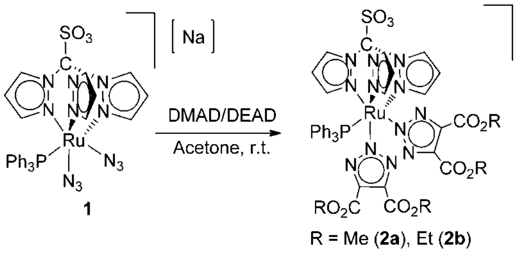
$^{31}P\{^1H\}$ spectrum exhibits a singlet at 52.5 ppm due to the PPh_3 phosphorus atom. ^1H and $^{13}C\{^1H\}$ NMR spectra agree with the proposed structure (see Experimental Section).

The presence of two azide ligands is evidenced by the electrospray mass spectrum measured in a negative mode for complex **1** that shows a peak at m/z 741 for the anion $[Ru(N_3)_2(Tpms)(PPh_3)]^-$.

Cycloaddition Reactions with the Alkynes DMAD and DEAD. *Synthesis of the Complexes [Na][Ru{κ(N^2)-*

*$N_3C_2(CO_2R)_2\}_2\{\kappa^3(N,N,N)$-Tpms}($PPh_3$)] (R = Me (**2a**), Et (**2b**)).* The reaction of complex **1** with an excess of dimethyl acetylenedicarboxylate (DMAD) or diethyl acetylenedicarboxylate (DEAD) in acetone at room temperature leads to the *N*(2)-bound 4,5-bis(alkoxycarbonyl)-1,2,3-triazolato complexes [Na][Ru{κ(N^2)-$N_3C_2(CO_2R)_2$}$_2${κ^3(*N,N,N*)-Tpms}(PPh_3)] (R = Me (**2a**), Et (**2b**)) (Scheme 2), generated by the 1,3-dipolar cycloaddition of the two azido groups with two molecules of the alkyne.

Scheme 2. Synthesis of Complexes [Na][Ru{κ(N^2)-$N_3C_2(CO_2R)_2$}$_2${κ^3(*N,N,N*)-Tpms}(PPh_3)]



The formation of these complexes was readily confirmed by the disappearance of the characteristic azide IR absorption and the appearance of the C=N stretching bands at 2071 (**2a**) and 2077 (**2b**) cm^{-1} as well as the C=O stretching bands from the carbonyl groups at 1732 (**2a**) and 1725 (**2b**) cm^{-1}.

The NMR spectroscopic data agree with the proposed stoichiometries. The more remarkable features are as follows: (i) ^1H NMR spectra show a singlet for the four methyl groups at 3.79 ppm for complex **2a** and one triplet (1.28 ppm, $^3J_{HH}$ = 7 Hz) and one cuatriplet (4.26 ppm, $^3J_{HH}$ = 7 Hz) for the four ethyl groups in complex **2b**, indicating that the two rings are bound through the N(2) atom for these complexes; (ii) the $^{31}P\{^1H\}$ spectra exhibit a singlet at 51.8 (**2a**) and 51.9 (**2b**) ppm according to the presence of the PPh_3 ligand; (iii) the signals on the $^{13}C\{^1H\}$ NMR spectra have been fully assigned through HSQC and HMBC experiments and agree with the proposed complexes. Thus, for the N(2)-bound triazolate groups, the spectra show a singlet signal for the equivalent heterocyclic carbons at 139.3 (**2a**) and 139.5 (**2b**) ppm and for the carbonyl atoms at 163.0 (**2a**) and 162.8 (**2b**) ppm.

For both complexes the electrospray mass spectra show the corresponding peak at *m*/*z* 1025 for [Ru{$N_3C_2(CO_2Me)_2$}$_2$(Tpms)(PPh_3)]$^-$ (**2a**) and at *m*/*z* 1081 for [Ru{$N_3C_2(CO_2Et)_2$}$_2$(Tpms)(PPh_3)]$^-$ (**2b**).

The molar conductivity values found for complexes **2a**,**b** in acetone (92 (**2a**) and 81 (**2b**) S cm^2 mol^{-1}) are lower than expected for a 1:1 electrolyte (100−140 S cm^2 mol^{-1}).[22] These low values can be attributed to ionic associations between the sodium cations and the anionic moieties.

Slow evaporation of a concentrated solution of complex **2b** in acetone resulted in crystals of **2b**·2 C_3H_6O suitable for X-ray diffraction studies. A thermal ellipsoid plot is shown in Figure 1, and selected bond lengths and angles are presented in the caption.

The ruthenium atom exhibits a distorted octahedral coordination geometry bonded κ^3(*N,N,N*) to the Tpms ligand, to the phosphorus atom of the PPh_3 and to the *N(2)* of the two planar five-membered triazolate rings. For the Tpms ligand, the interligand N−Ru−N angles (82.64−85.48°) and the Ru−N bond distances (2.093(2)−2.100(2) Å) are in the range of those found for other ruthenium(II) Tpms complexes.[14] The distances from the ruthenium atom to the triazolate rings Ru(1)−N(8) and Ru(1)−N(11) are 2.082(2) and 2.075(2) in accordance with those found for [Ru{$N_3C_2H(CO_2Me)$}(η^5-C_5H_5)(dppe)] (2,090(2) Å).[13]

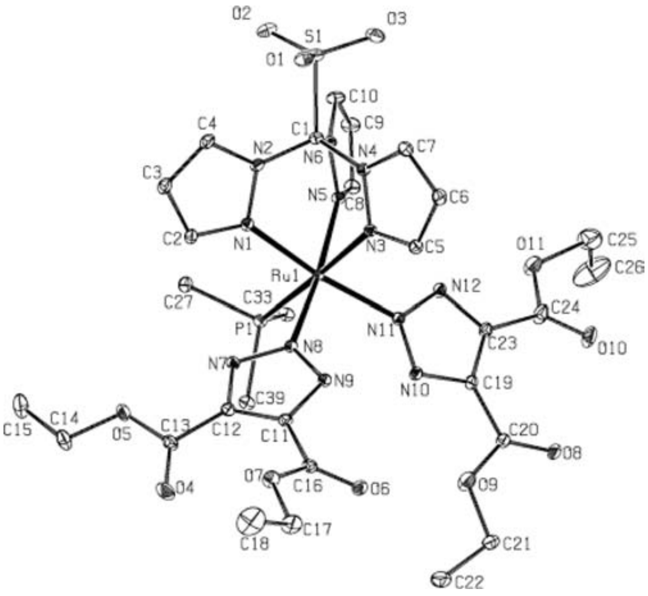


Figure 1. Perspective view of the anion of **2b**·2C_3H_6O with atom numbering scheme showing 10% probability thermal ellipsoids. Solvent molecules, hydrogen atoms, phenyl rings, and sodium atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)−N(1) = 2.093(2), Ru(1)−N(3) = 2.100(2), Ru(1)−N(5) = 2.095(2), Ru(1)−P(1) = 2.341(1), Ru(1)−N(8) = 2.082(2), Ru(1)−N(11) = 2.075(2), N(7)−N(8) = 1.331(3), N(8)−N(9) = 1.337(3), N(11)−N(12) = 1.331(3), N(10)−N(11) = 1.334(3). Selected bond angles (°): N(1)−Ru(1)−N(3) = 83.36(9), N(3)−Ru(1)−N(5) = 82.64(9), N(5)−Ru(1)−N(1) = 85.48(9), N(8)−Ru(1)−N(11) = 93.90(9), N(8)−Ru(1)−P(1) = 87.46(7), N(11)−Ru(1)−P(1) = 94.11(7).

An important feature of this crystal structure is that the complex in the solid state consists of linear chains generated by the crystal periodicity along the *a* axis. These chains are produced by electrostatic interactions between the anionic complexes and the sodium atoms which are located in the front leading to a tubular structure (Figure 2).

Thus, three ruthenium complexes surround each sodium atom leading to a heptacoordinate environment provided by two oxygen atoms from two carboxylic groups of one anionic moiety, two oxygen atoms and two nitrogen atoms from two triazolate groups of a second one and an oxygen atom from the sulfonate group of a third unit (Figure 3).

The existence of these ionic associations can explain the low values for the molar conductivity found for complexes **2a**,**b**.

For complexes **2a**−**b**, only the *N(2)*-bound triazolate ligand has been observed. However, initial formation of the complex containing the *N(1)*-bound triazolate ligand and subsequent conversion to the thermodynamically more stable *N(2)*-bound isomer cannot be excluded, in agreement with previously reported data.[10b,13]

Attempts to obtain the free organic triazoles were accomplished. The treatment of complex **2a** with benzyl bromide, in acetone, at 60 °C for 24 h, causes the cleavage of the Ru−N bond as observed by NMR spectroscopy. Thus, $^{31}P\{^1H\}$ spectrum shows the disappearance of the signal at 51.8 ppm, while a new signal at 47.8 ppm appears. Moreover, the

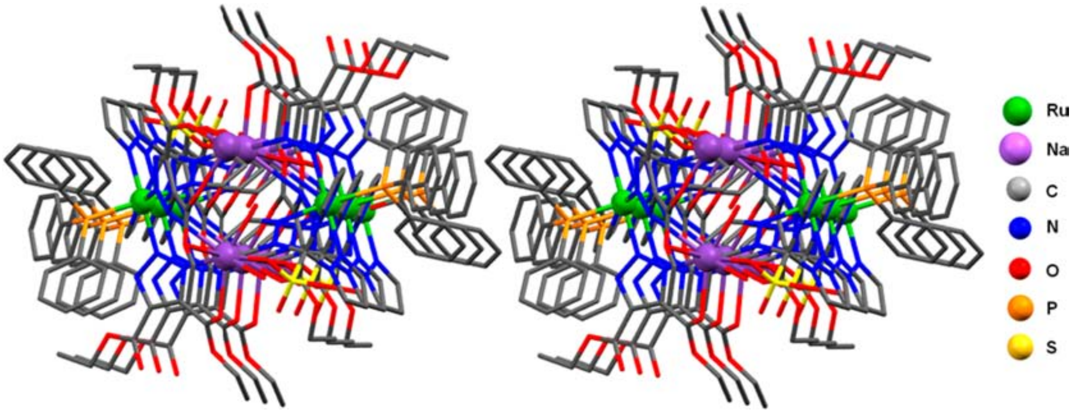


Figure 2. Tubular chain structure for complex [Na][Ru{κ(N^2)-$N_3C_2(CO_2Et)_2$}$_2${κ^3(*N,N,N*)-Tpms}(PPh_3)]·$2C_3H_6O$ (**2b**·$2C_3H_6O$).

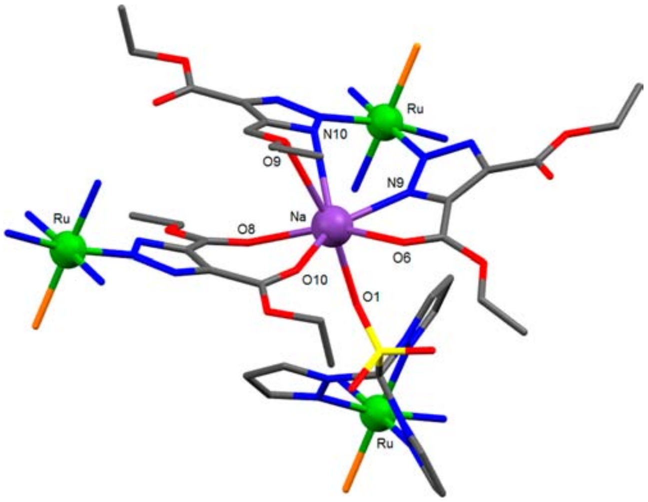


Figure 3. Sodium coordination sphere in the structure of complex [Na][Ru{κ(N^2)-$N_3C_2(CO_2Et)_2$}$_2${κ^3(*N,N,N*)-Tpms}(PPh_3)]·$2C_3H_6O$ (**2b**·$2C_3H_6O$).

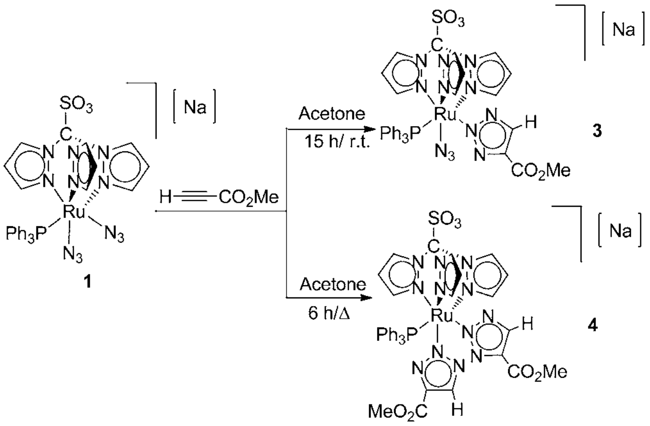
signals for the organic triazole can be identified in ^{1}H NMR spectrum of the crude product.[12] Unfortunately, all the attempts to isolate the free organic triazole were unsuccessful.

Cycloaddition Reactions with Methyl Propiolate. *Synthesis of the Complexes [Na][Ru(N_3){$N_3C_2H(CO_2Me)$}{κ^3(N,N,N)-Tpms}(PPh_3)] (**3**) and [Na][Ru{$N_3C_2H(CO_2Me)$}$_2${κ^3(N,N,N)-Tpms}(PPh_3)] (**4**).* The reaction of complex **1** with an excess of methyl propiolate in acetone at room temperature for 15 h affords the complex [Na][Ru(N_3)-{$N_3C_2H(CO_2Me)$}{κ^3(*N,N,N*)-Tpms}(PPh_3)] (**3**) resulting in the cycloaddition of one azido group with the carbon−carbon triple bond of the alkyne. When this reaction is carried out in refluxing acetone, the complex with two triazolate rings [Na][Ru{$N_3C_2H(CO_2Me)$}$_2${κ^3(*N,N,N*)-Tpms}(PPh_3)] (**4**) is obtained (Scheme 3).

Complexes **3** and **4** are stable yellow solids and have been characterized by analytical and spectroscopic methods. The IR spectra for both complexes show the corresponding absorptions for the Tpms and triazolate ligands. IR spectrum of complex **3** also shows a strong band at 2052 cm^{-1} due to the azide ligand.

The ^{31}P{^{1}H} NMR spectra exhibit singlet resonances at 52.5 and 51.5 ppm for complexes **3** and **4**, respectively. ^{1}H and ^{13}C{^{1}H} NMR spectra agree with the proposed structure (see Experimental Section). In particular, the proton for the CH and the methyl groups of triazolate rings appear at 7.87 and 3.81 ppm (**3**) and 7.82 and 3.77 ppm (**4**), respectively, in the ^{1}H NMR spectra.

Scheme 3. Synthesis of complexes [Na][Ru(N_3){$N_3C_2H(CO_2Me)$}{κ^3(*N,N,N*)-Tpms}(PPh_3)] (3) and [Na][Ru{$N_3C_2H(CO_2Me)$}$_2${κ^3(*N,N,N*)-Tpms}(PPh_3)] (4)



The electrospray mass spectrum of complex **3** shows peaks at *m/z* 825 for the anion [Ru(N_3){$N_3C_2H(CO_2Me)$}(Tpms)-(PPh_3)]$^-$ and *m/z* 563 for the anion [Ru(N_3){N_3C_2H-(CO_2Me)}(Tpms)]$^-$.

Even when the spectroscopic data do not allow one to establish the coordination mode of the triazolate ligands, the coordination through the *N(2)* is proposed in agreement with the isomer obtained for complexes **2a,b** and the structure of the previously reported complex [Ru{$N_3C_2H(CO_2Me)$}(η^5-C_5H_5)-(dppe)].[13]

Reaction with Carbon Disulfide. *Synthesis of [Na][Ru-(N_3){κ(N)-NCS}{κ^3(N,N,N)-Tpms}(PPh_3)] (**5**) and [Na][Ru{κ(N)-NCS}$_2${κ^3(N,N,N)-Tpms}(PPh_3)] (**6**).* Complex **1** also reacts with CS_2 in refluxing acetone to give the isothiocyanato complexes [Na][Ru(N_3){κ(*N*)-NCS}{κ^3(*N,N,N*)-Tpms}(PPh_3)] (**5**) and [Na][Ru{κ(*N*)-NCS}$_2${κ^3(*N,N,N*)-Tpms}(PPh_3)] (**6**) depending on the amount of excess CS_2 used. Both complexes have been characterized by analytical and spectroscopic methods. Significant spectroscopic data are given: (i) the stretching frecuency of the NCS group (2117 cm^{-1} for complex **5** and 2121 cm^{-1} for complex **6**) and the peak corresponding to the terminal azide group for complex **5** (2060 cm^{-1}) appear in the IR spectra (KBr), together with the typical absorptions for the κ^3(*N,N,N*)-Tpms ligand; (ii) the ^{31}P{^{1}H} NMR spectra show the signal for the phosphorus atom of the PPh_3 ligand at 51.5 (**5**) and 50.9 (**6**) ppm; (iii) $^{13}C\{^1H\}$ NMR spectra show the signal corresponding to the NCS group at 134.5 (**5**) and 136.0 (**6**) ppm. The rest of signals as well as the ^1H NMR spectra agree with the proposed structures (see Experimental Section).

Molar conductivity values in acetone (113 S cm^2 mol^{-1} for **5** and 108 S cm^2 mol^{-1} for **6**) are in the range expected for electrolytes 1:1 and the electrospray mass spectra show the peak at *m/z* 757 for $[Ru(N_3)(NCS)(Tpms)(PPh_3)]^-$ (**5**) and 773 for $[Ru(NCS)_2(Tpms)(PPh_3)]^-$ (**6**).

The formation of complexes **5** and **6** from complex **1** and CS_2 is a well-known transformation[24] and can be explained through a [3 + 2] cycloaddition reaction of CS_2 with azido groups yielding thiothiazolinate intermediates which are thermally unstable and decompose, in the reaction conditions, leading to the obtained isothiocyanato complexes.[25]

Reaction with Nitriles. *Synthesis of the Complexes* $[Ru(N_3)(NCR)\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ *(R = Me* (**7**)*, Ph* (**8**)*).* Heating an acetonitrile solution of complex **1** at reflux temperature leads to the substitution product $[Ru(N_3)(NCMe)\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**7**). In the same way, when complex **1** was refluxed with an excess of PhCN in toluene, the analogous $[Ru(N_3)(NCPh)\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**8**) was obtained. Both complexes have been analytically and spectroscopically characterized. Significant spectroscopic data are given: (i) the IR spectra (KBr) exhibit the absorptions corresponding to the $\nu(C\equiv N)$ at 2131 (**7**) and 2136 (**8**) cm^{-1}, and the absorptions due to the azido ligands at 2036 (**7**) and 2038 (**8**) cm^{-1}; ii) the $^{31}P\{^1H\}$ NMR spectra show singlet signals at 49.2 (**7**) and 48.8 (**8**) ppm; (iii) the $^{13}C\{^1H\}$ NMR spectra show the signal for the $C\equiv N$ carbon at 124.0 (**7**) and 125.2 (**8**) ppm; (iv) the ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **7** show singlet signals for the methyl group of the nitrile at 2.47 ppm (^1H) and 4.1 ppm (^{13}C).

The structure of complex **7** was determined by single crystal X-ray diffraction analysis. Slow evaporation of a dichloromethane solution of complex **7** enables one to obtain crystals suitable for X-ray diffraction studies of $7\cdot CH_2Cl_2$. A thermal ellipsoid plot of the complex is shown in Figure 4, and selected bond lengths and angles are presented in the caption.

The ruthenium atom exhibits a distorted octahedral coordination geometry bonded $\kappa^3(N,N,N)$ to the Tpms ligand, to the nitrogen atoms of azido and acetonitrile groups and the phosphorus atom of the PPh_3 ligand. The Ru–N bond length *trans* to the phosphane ligand is significantly longer than those *trans* to the acetonitrile and azido groups, in accordance with the higher *trans* influence for the phosphane ligands.[26]

The acetonitrile and the azido groups display a linear (Ru–N–C, 174.20°) and angular (Ru–N–N, 120.50°) arrangement respectively, in accordance with the different hybridization of the nitrogen in both ligands. The Ru–N(7) and Ru–N(10) bond distances are in agreement with the data found for other ruthenium complexes containing azido[12] and nitrile[27] groups respectively.

Reaction with Fumaronitrile. *Synthesis of* $[Na][Ru\{\kappa^2(N^1,N^3)\text{-}N_3C(H)C\text{–}CN_4\}\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**9**) *and* $[Na][Ru(N_3)\{N_4C(CH{=}CH(CN)\}\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**10**). The reaction of complex **1** with an excess of fumaronitrile in refluxing acetone affords a new complex $[Na][Ru\{\kappa^2(N^1,N^3)\text{-}N_3C(H)C\text{–}CN_4\}\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ (**9**), which contains a bidentate ligand 5-(1,2,3-triazol-4-yl)-1,2,3,4-tetrazolate[28] coordinated through the *N(1)* of the tetrazole ring and the *N(3)* of the triazole ring (Scheme 4). This complex **9** is the result of the cycloaddition reaction of the two azide groups with the $C\equiv N$ and $C{=}C$ bonds of fumaronitrile.

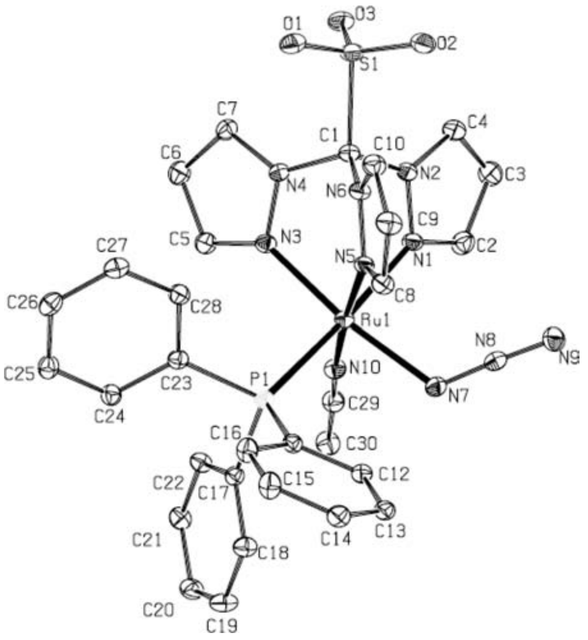
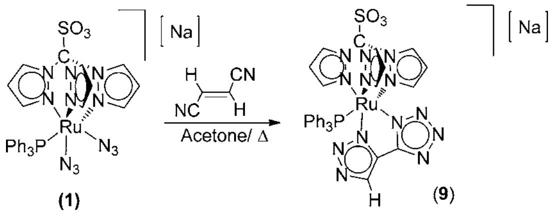


Figure 4. Molecular structure and atom-labeling scheme for the complex $[Ru(N_3)(NCMe)\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]\cdot CH_2Cl_2$. Hydrogen atoms and solvent molecules have been omitted for clarity. Non-hydrogen atoms are represented by 20% probability ellipsoids. Selected bond lengths (Å): Ru(1)–N(1) = 2.105(3), Ru(1)–N(3) = 2.069(3), Ru(1)–N(5) = 2.044(3), Ru(1)–P(1) = 2.330(1), Ru(1)–N(7) = 2.120(3), Ru(1)–N(10) = 2.018(4), N(7)–N(8) = 1.207(5), N(8)–N(9) = 1.153(5), N(10)–C(29) = 1.154(9), C(29)–C(30) = 1.448(6). Selected bond angles (°): N(1)–Ru(1)–N(3) = 82.15(13), N(3)–Ru(1)–N(5) = 87.81(13), N(5)–Ru(1)–N(1) = 84.47(13), N(7)–Ru(1)–P(1) = 93.99(10), N(10)–Ru(1)–P(1) = 92.70(11), N(10)–Ru(1)–N(7) = 86.35(15), Ru(1)–N(7)–N(8) = 120.50(3), N(7)–N(8)–N(9) = 177.10(4), Ru(1)–N(10)–C(29) = 174.20(3), N(10)–C(29)–C(30) = 177.30(5).

Scheme 4. Synthesis of Complex $[Na][Ru\{\kappa^2(N^1,N^3)\text{-}N_3C(H)C\text{–}CN_4\}\{\kappa^3(N,N,N)\text{-Tpms}\}(PPh_3)]$ **(9)**



The stoichiometry of this complex was confirmed through elemental analyses and electrospray mass spectrum which shows the peak at *m/z* 792 for the anion $[Ru\{N_3C(H)C\text{–}CN_4\}(Tpms)(PPh_3)]^-$.

Complex **9** has been also spectroscopically characterized (IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR). In particular, the IR spectrum (KBr) shows the characteristic absorptions for the ligand Tpms in a $\kappa^3(N,N,N)$-coordination mode and the absorptions due to the $C{=}N$ bonds. The reaction through the two azide groups is also confirmed by the disappearance of the terminal azide peak.

^1H and $^{13}C\{^1H\}$ NMR spectra agree with the proposed structure. Thus, for the triazolate ring the proton appears as a singlet at 7.89 ppm and the carbon atoms at 135.6 (cuaternary carbon) and 127.6 (CH) ppm and for the tetrazolate ring the carbon atom appears at 158.2 ppm.

Slow diffusion of diethyl ether into a solution of **9** in acetone resulted in crystals of $\mathbf{9}\cdot C_4H_{10}O$ suitable for a single crystal X-ray diffraction studies. A thermal ellipsoid plot of the anion of the complex is shown in Figure 5, and selected bond lengths and angles are presented in the caption.

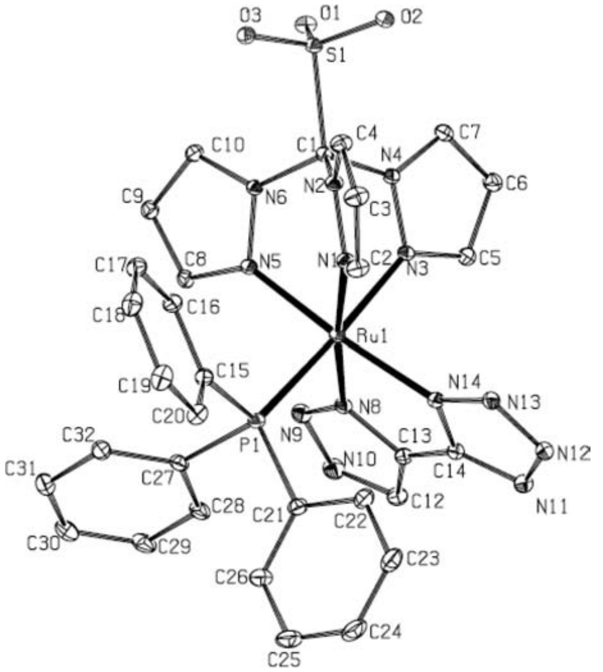


Figure 5. Perspective view of the anion of complex $\mathbf{9}\cdot C_4H_{10}O$ with atom numbering scheme showing 10% probability thermal ellipsoids. Solvent molecules, hydrogen atoms, and sodium atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)−N(1) = 2.058(2), Ru(1)−N(3) = 2.096(2), Ru(1)−N(5) = 2.054(2), Ru(1)−P(1) = 2.314(1), Ru(1)−N(8) = 2.070(2), Ru(1)−N(14) = 2.070(2), N(8)−N(9) = 1.329(3), N(8)−C(13) = 1.359(3), N(9)−N(10) = 1.333(4), N(10)−C(12) = 1.353(4), C(12)−C(13) = 1.355(4), C(13)−C(14) = 1.443(4), N(13)−N(14) = 1.327(3), N(14)−C(14) = 1.347(3), N(12)−N(13) = 1.323(3), N(12)−N(11) = 1.361(4), N(11)−C(14) = 1.336(4). Selected bond angles (°): N(1)−Ru(1)−N(3) = 84.17(9), N(3)−Ru(1)−N(5) = 82.74(9), N(5)−Ru(1)−N(1) = 87.20(8), N(8)−Ru(1)−N(14) = 77.18(9), N(8)−Ru(1)−P(1) = 92.75(7), N(14)−Ru(1)−P(1) = 94.19(7), N(8)−N(9)−N(10) = 108.0(2), N(9)−N(8)−C(13) = 108.7(2), N(10)−C(12)−C(13) = 106.8(3), C(12)−C(13)−C(14) = 138.3(3), N(8)−C(13)−C(14) = 114.3(2), C(13)−C(14)−N(14) = 115.4(2), C(14)−N(14)−N(13) = 107.4(2), N(11)−C(14)−C(13) = 134.8(3).

The ruthenium atom exhibits a distorted octahedral coordination geometry bonded κ^3(*N,N,N*) to the Tpms ligand, to the phosphorus atom of the PPh_3 and to two nitrogen atoms of the bidentate $\kappa^2(N^1,N^3)$-5-(1,2,3-triazol-4-yl)-1,2,3,4-tetrazolate ligand.

For the Tpms ligand, the interligand N−Ru−N angles (82.74−87.20°) and the Ru−N bond distances (2.054(2) − 2.096(2) Å) agree with those found for other ruthenium(II) Tpms complexes.[14] The distances from the ruthenium atom to the triazolate ring Ru(1)−N(8) (2.070(2) Å) and to the tetrazolate ring Ru(1)−N(14) (2.070(2) Å) are in the range of those described for complex **2a** (2.082(2) and 2.075(2) Å).

The torsion angle N(8)−C(13)−C(14)−N(11) (2.4(4)°) agrees with the planarity of the two rings.

In the solid state, complex **9** shows periodicity along the *a* and *c* axis leading to a layer structure (Figure 6). These layers are generated by electrostatic interactions between the anionic complexes and the sodium atoms which show a tetracoordinated environment provided by an oxygen atom of the sulfonate group of an anionic unit, two nitrogen atoms of a second and third anionic units and the oxygen atom of a diethyl ether molecule (Figure 7).

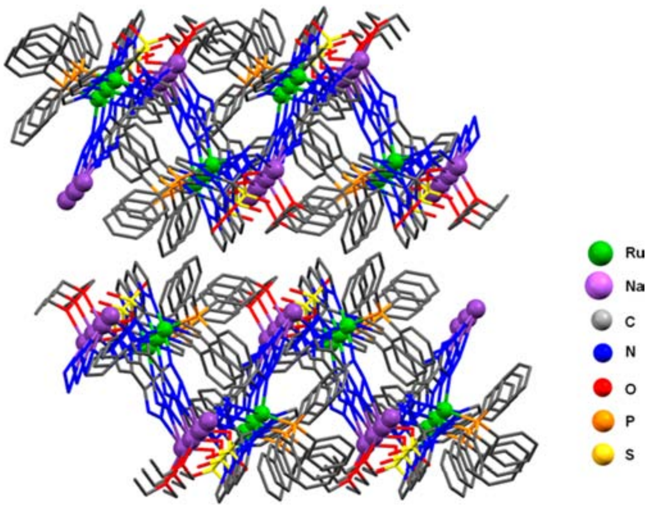


Figure 6. Layer structure in complex $[Na][Ru\{\kappa^2(N^1,N^3)\text{-}N_3C(H)C\text{–}CN_4\}\{\kappa^3(N,N,N)\text{-}Tpms\}(PPh_3)]\cdot C_4H_{10}O$ ($\mathbf{9}\cdot C_4H_{10}O$).

The cycloaddition reaction of fumaronitrile with azides can take place via either the C═C or the C≡N bond. In our case, the unprecedented formation of complex **9** can be explained as the result of two consecutive cycloaddition reactions, and therefore three different pathways can be proposed according to the literature data (Scheme 5).

In the Via 1, the process would be initiated by the cycloaddition of one azide group and one nitrile group of fumaronitrile, to give the tetrazolato intermediate I. The intramolecular [3 +2] cycloaddition between the second azide ligand and the C═C double bond following removal of a HCN molecule would form the final product. Intermediate I is proposed as the *N(1)* bound isomer, since this isomer is proposed to be the kinetically more stable isomer for tetrazolate complexes.[29] Thermodinamically stable *N(2)*-bound cyanovinyltetrazolate complexes have been described in the reaction of fumaronitrile with azido complexes of Mo,[9] In,[30] and Mn.[31]

The first step of Vias 2 and 3 would involve the [3 +2] cycloaddition of one azide ligand with the C═C double bond. For Via 2, HCN elimination occurs in this first step, leading to the 4-cyano-1,2,3-triazolato complex (intermediate II). Intramolecular cycloaddition reaction between the second azide ligand and the C≡N bond leads to the observed complex **9**. This mechanism agrees with the reported reactions of ruthenium complexes with fumaronitrile in which complexes containing a *N(2)*-bound 4-cyano-1,2,3-triazolate ligand have been isolated.[11−13]

For Via 3, the [3 +2] cycloaddition of one azide ligand with the C═C double bond leads to a triazolinato complex III. Removal of a HCN molecule and intramolecular [3 + 2] cycloaddition between the azide ligand, and the remaining CN

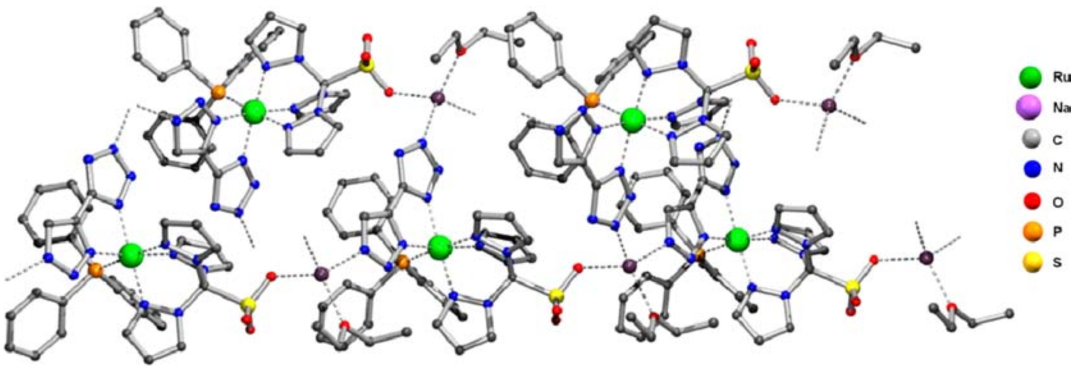
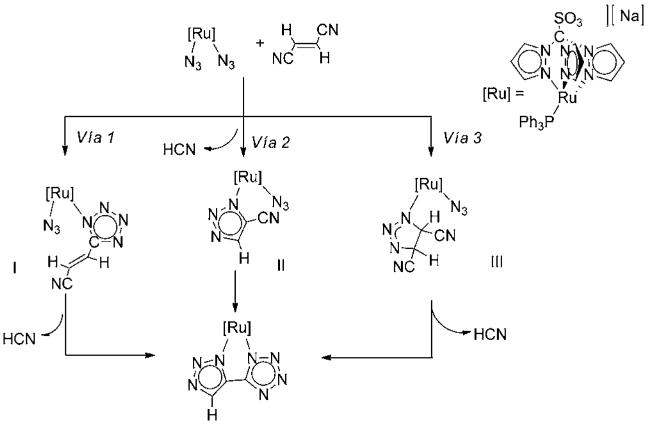


Figure 7. Sodium coordination sphere in the structure of complex $[Na][Ru\{\kappa^2(N^1,N^3)\text{-}N_3C(H)C{-}CN_4\}\{\kappa^3(N,N,N)\text{-}Tpms\}(PPh_3)]\cdot C_4H_{10}O$ ($\mathbf{9}\cdot C_4H_{10}O$).

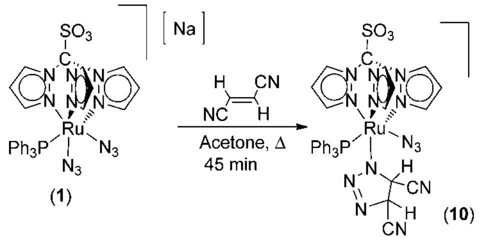
Scheme 5. Mechanistic Routes for the Formation of Complex 9



group would allow the final product. Unstable triazolinato complexes have been claimed to form in reaction of azido complexes of Pd,[25] Ni,[32] and Co[33] with olefins.

In order to get insight into the reaction mechanism for our system, the reaction of **1** with fumaronitrile was monitorized by $^{31}P\{^1H\}$ NMR. The formation of a transient species is assessed by the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, which shows, after 45 min in refluxing acetone, a singlet resonance (δ = 54.3 ppm). The reaction mixture was then drastically cooled to 0 °C, and the *N(1)*-bound 4,5-dicyano-1,2,3,-triazolinate complex $[Na][Ru(N_3)\{N_3CH(CN)CH(CN)\}\{\kappa^3(N,N,N)\text{-}Tpms\}(PPh_3)]$ (**10**), intermediate III, was isolated (Scheme 6). Complex **10** is unstable in solution at room temperature and evolves readily to complex **9**. On the basis of this finding, Via 3 can be assumed as the mechanistic route for the formation of complex **9**.

Scheme 6. Synthesis of $[Na][Ru(N_3)\{N_3CH(CN)CH(CN)\}\{\kappa^3(N,N,N)\text{-}Tpms\}(PPh_3)]$ (10)



Complex **10** is isolated as a yellow stable solid and has been analytically and spectroscopically characterized (IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR). In particular, it must be noted that (i) the IR spectrum (KBr) exhibits absorptions corresponding to the Tpms ligand coordinated $\kappa^3(N,N,N)$ as well as the absorption corresponding to the C≡N triple bond (2232 cm^{-1}). This spectrum also shows a strong band at 2048 cm^{-1} due to the azide ligand; (ii) $^{31}P\{^1H\}$ spectrum exhibits the expected singlet corresponding to the PPh_3 ligand at 54.3 ppm; (iii) the ^1H NMR spectrum shows the triazolinato ligand bound through the *N(1)*. Thus, the CH(CN) protons are unequivalent and appear as two doublets ($^3J_{HH}$ = 11.0 Hz.) at 4.82 and 4.02 ppm indicating, unambiguously, that the heterocycle is *N(1)*-bound; (iv) $^{13}C\{^1H\}$ NMR spectrum was measured at 252 K and agrees with the proposed structure. Thus, the two CH(CN) carbon atoms appear at 66.1 and 60.0 ppm and the CN carbon atoms at 119.8 and 120.6 ppm.

For complex **10**, the electrospray mass spectrum shows the corresponding peak at *m*/*z* 819 for $[Ru(N_3)\{N_3CH(CN)CH(CN)\}(Tpms)(PPh_3)]^-$.

Triazolinate complexes are thermally unstable and to our knowledge, complex **10** is the first triazolinate ruthenium complex isolated and fully spectroscopically characterized.

■ CONCLUSIONS

The diazido complex $[Na][Ru(N_3)_2\{\kappa^3(N,N,N)\text{-}Tpms\}(PPh_3)]$ (**1**) reacts with dipolarophiles such alkynes or nitriles in 1,3-dipolar cycloaddition reactions. Depending on the alkyne and the reaction conditions, the cycloaddition reactions can occur through one or the two azido groups leading to ruthenium with triazolate ligands coordinated through the *N(2)*. The reaction of complex **1** with nitriles such as NCMe or PhCN leads to complexes $[Ru(N_3)(NCR)\{\kappa^3(N,N,N)\text{-}Tpms\}(PPh_3)]$ in which one azide group has been substituted by the nitrile. However, when fumaronitrile is used, a complex containing a new bidentate ligand 5-(1,2,3-triazol-4-yl)-1,2,3,4-tetrazole coordinated through the *N(1)* of the tetrazole ring and the *N(3)* of the triazole ring is isolated. The formation of this new ligand is the result of two consecutive 1,3-dipolar cycloaddition reactions, and the mechanism for this transformation has been unambiguously established through the isolation of the intermediate complex $[Na][Ru(N_3)\{N_3CH(CN)CH(CN)\}\{\kappa^3(N,N,N)\text{-}Tpms\}(PPh_3)]$ resulting from a first cycloaddition between a coordinated azide and the olefine group of fumaronitrile.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data of **2b**$\cdot 2C_3H_6O$, **7**$\cdot CH_2Cl_2$, and **9**$\cdot C_4H_{10}O$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Spanish Ministerio de Educación y Ciencia (CTQ-2010-17005 and CTQ-2011-26481) and Consolider Ingenio 2010 (CSD2007-00006). S. Martínez de Salinas thanks the Spanish Ministerio de Educación, Cultura y Deporte for a scholarship.

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