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Half Sandwich Electron Deficient *N,N′,N″*-Triarylguanidinatoruthenium(II) Complexes: Syntheses, Reactivity Studies and Structural Aspects

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Abstract Three symmetrical *N*,*N*′,*N*″-triarylguanidinatoruthenium(II) complexes, [(η^6-*p*-cymene)RuCl{κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar)}] (Ar = 2-(CF$_3$)C$_6$H$_4$ (**1**), 4-(CF$_3$)C$_6$H$_4$ (**2**) and 3,5-(CF$_3$)$_2$C$_6$H$_3$ (**3**)) were isolated in good yields. The reaction of **3** with NaOAc, NaN$_3$ and KSCN afforded [(η^6-*p*-cymene)RuX{κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar)}] (X = OAc (**4**), N$_3$ (**5**) and an admixture of SCN (**6**) and NCS (**7**)) respectively in very good yields. On the other hand, metathesis reaction of **3** with AgSbF$_6$ in the presence of MeCN afforded [(η^6-*p*-cymene)Ru(MeCN){κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar)}][SbF$_6$] (**8**) in good yield. Complex **5** upon treatment with diethylacetylenedicarboxylate and bis(diphenylphosphino)acetylene separately afforded guanidinate(1–) complex, [(η^6-*p*-cymene)Ru(N$_3$C$_2$(C(O)OEt)$_2$){κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar)}] (**9**) and guanidinate(2–) complex, [(η^6-*p*-cymene)Ru{κ^2(*N*,*N*′)((ArN)$_2$C=NAr)}(κ^1*P*-Ph$_2$PC≡CPPh$_2$)] (**10**) in good yields. The formation **9** versus **10** is ascribed to the subtle difference in the electron richness of alkynes. The new complexes were characterized by analytical, IR and NMR spectroscopy and single crystal X-ray diffraction. Complex **3** catalyses [3+2] cycloaddition reaction involving phenylacetylene and 4-tolyl azide to afford an admixture of 1,4- and 1,5-disubstituted 1,2,3-triazoles, **23** and **24** in 99% conversion.

Introduction

Metal complexes of *N*-susbstituted guanidinates have been widely studied in the past due to their relevance in the fields of inorganic, organometallic, and materials chemistry.[1,2] Additionally, these complexes have been invoked as intermediates in metal catalyzed guanylation of amines with carbodiimides for guanidine synthesis.[3] Synthetic, structural aspects, reactivity studies and applications of guanidinate complexes of platinum group metals have been reviewed recently by Francos and Cadierno.[4] Numerous guanidinatoruthenium(II) complexes of symmetrical *N*,*N*′,*N*″-triphenylguanidine,

[$(PhNH)_2C$=NPh] have been prepared and stucturually characterized.[5] Subsequently, half sandwich guanidinatoruthenium(II)-, rhodium(III)- and iridium(III) complexes of symmetrical *N*,*N*′,*N*″-triarylguanidines, [$(ArNH)_2C$=NAr] were prepared by us and others with the objectives aimed at understanding their structures in solid state and in solution and to further understand their utility as catalysts in base free and base assisted transfer hydrogenation reactions.[6–11]

Half sandwich ruthenium(II)/osmium(II)- and bis(allyl)ruthenium(IV) complexes of unsymmetrical *N*,*N*′,*N*″-trisubstituted guanidines, [$(^{i}PrNH)_2C$=NR] (R = Variously substituted aryl rings, C(O)R′; R′ = 2-thienyl and 2-furyl) have been prepared and key complexes have been structurally characterized. Further, the utility of these complexes as catalysts in base free isomerization of allylic alcohols, dehydration of aldoximes and as anticancer agents was explored.[12–15] Diruthenium complexes of both acyclic and cyclic guanidinates and half sandwich ruthenium(II) complexes of cyclic guanidinates have been studied with the objectives aimed at understanding the structural and magnetic properties of the former complexes and the structural aspects and catalytic utility of the latter complexes in isomerization of 1-octen-3-ol into octane-3-one.[16]

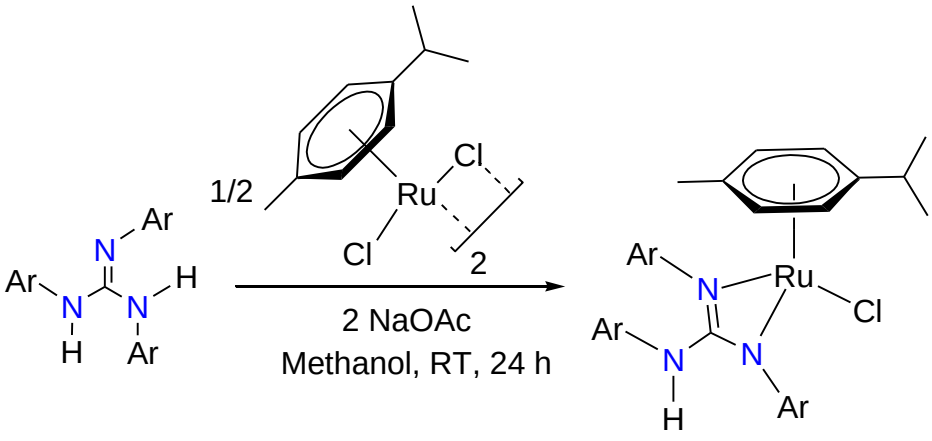
In the present investigation, we report syntheses and characterization of **1–3**. Reactivity studies of complex **3** was carried out with acetato, azido and isothiocyanato and thiocyanato nucleophiles which resulted in the formation of complexes **4–7**. A copper(I) catalyzed click reaction involving organic azides and alkynes to afford 1,4-disubstituted 1,2,3-triazoles selectively is known since the pioneering work of Fokin, Sharpless and Meldal published in 2002.[17,18] Such reactions involving metal azide/alkyne known as early as 1974, metal alkyne/organic azide, metal azide/metal alkyne, popularly known as iclick reaction, are the emerging reactions for metal triazolate complexes that could contain either a metal-nitrogen bond or a metal-carbon bond depending upon the reaction partners.[19–25] Continuing

our interests in understanding the reactions of guanidinatometal azido complexes with alkynes and factors that dictate the stereochemistry of *o*-substituted *N*,*N*′,*N*″-triarylguanidinato ligand in the resulting triazolate complexes,[8,11] we report herein the reactions of **5** with diethylacetylenedicarboxylate (DEAD) and bis(diphenylphosphino)acetylene (DPPA) which afforded two distinct products, namely **9** and **10** respectively. The utility of **3** as catalyst in click reaction involving phenyl acetylene and 4-tolyl azide was also explored.

Results and Discussion

Syntheses The reaction of [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ with symmetrical *N*,*N*′,*N*″-triarylguanidines, **L1**–**L3** in methanol in presence of NaOAc afforded **1**–**3** respectively as orange solids in ≥82% yields (see Scheme 1). The separate reactions of **3** with excess of NaOAc, NaN_3, and KSCN in methanol or ethanol at RT for 24 h afforded the corresponding acetato (**4**), azido (**5**), and isomeric mixture of thiocyanato (**6**) and isothiocyanato (**7**) complexes respectively as orange solids in ≥89% yields (see Scheme 2).

Scheme 1



	Ar	
L1	2-(CF_3)C_6H_4	**1**
L2	4-(CF_3)C_6H_4	**2**
L3	3,5-(CF_3)$_2C_6H_3$	**3**

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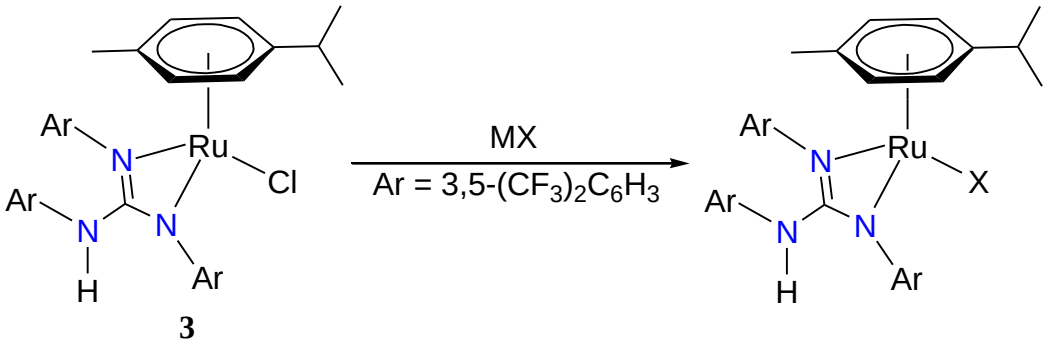
Scheme 2



3 **4–7**

	X
4	OC(O)Me
5	N_3
6	SCN[a]
7	NCS[a]

[a] Isolated as a mixture of **6** and **7**

Complex **3** upon treatment with $AgSbF_6$ in MeCN in dark for 24 h at RT afforded cationic complex **8** as yellow orange solid in 85% yield (see Scheme 3). Metal azido complexes have been used extensively as metallo-dipolarophile in azide-alkyne cycloaddition (AAC) reactions which afforded the respective triazolate complexes under mild reaction condition.[19–25] Considerable efforts have been expended in understanding the factors that promote AAC reactions involving ruthenium(II) azido-dipolarophile.[8,25] Hence, complex **5** was separately treated with DEAD and DPPA in CH_2Cl_2 at RT for 24 h which afforded **9** as anticipated and **10** as unanticipated products in the form of orange solid in 86% and 87% yields respectively (see Scheme 4).

The reaction of **5** with DPPA can possibly afford an acyclic intermediate **A** through the cleavage of Ru–N_{imine} bond of the guanidinate ligand (see Figure 1). The intermediate **A** upon amine-imine tautomerisation can give rise to another acyclic intermediate **B** which subsequently undergoes ring closure of the guanidinate ligand assisted by elimination of HN_3 to afford guanidinate(2–) complex, **10**. Thus, DPPA merely acts as a Lewis base rather than as a dipolarophile in the reaction depicted in Scheme 4 but once coordinated to the Ru(II) atom in the intermediate **B**, it reduces π-basicity of the metal thereby stabilizing the

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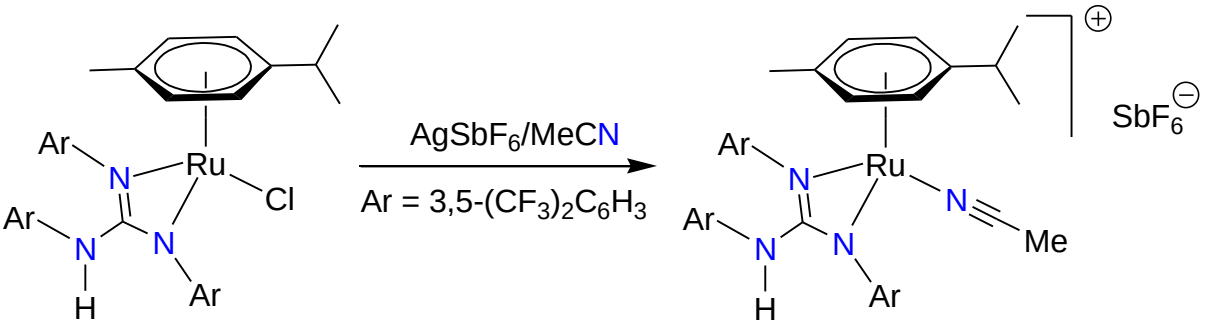
intermediate **B**. The transformation of the guanidinate(1–) to the guanidinate(2–) in the primary coordination sphere of the metal shown through the conversion of **5** to **10** appears to be partly driven by electron deficient nature of the guanidinate(1–) ligand in the former complex. Other hypothetical complexes such as **C**, which would have formed if AAC has occurred and phosphazide intermediate **D** or iminophosphorane species **E** which would have formed if Staudinger reaction has occurred have not been formed (see Figure 2).[19,26]

Scheme 3



Scheme 4

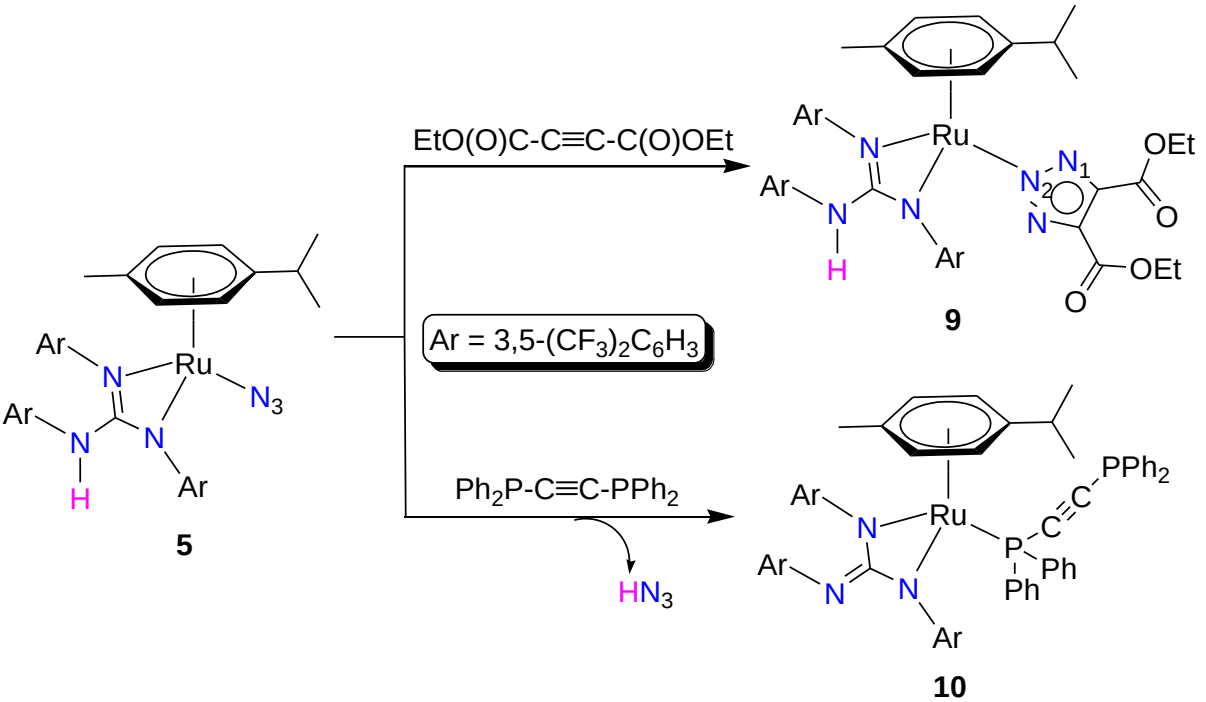


Figure 1

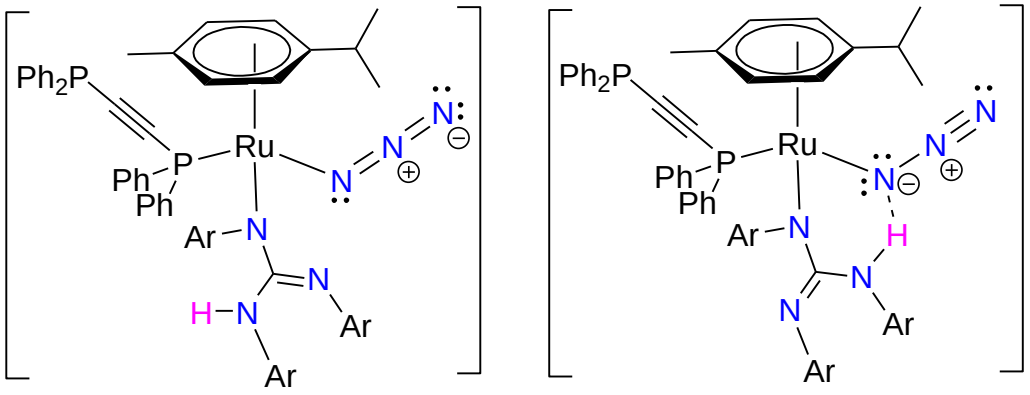
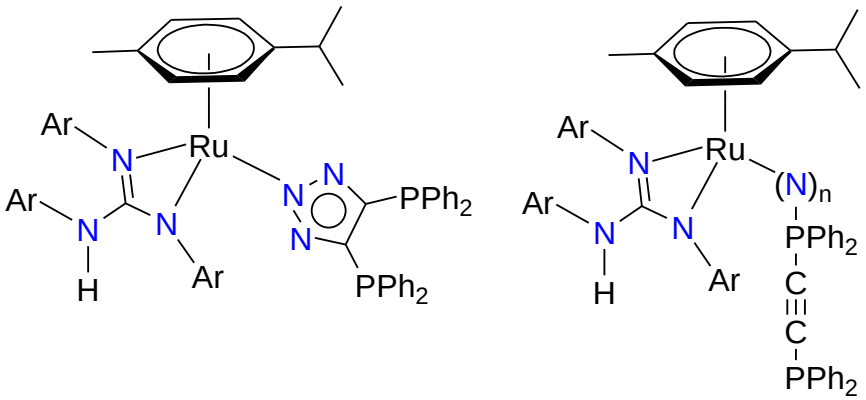


Figure 2



It is to be noted that the transformation of metal bound *N*,*N*′,*N*″-triacetylguanidinate(1–) to metal bound *N*,*N*′,*N*″-triacetylguanidinate(2–) was shown to occur only in the presence of Ag_2O as an external base.[7] Further, the transformation of metal bound *N*,*N*′,*N*″-trialkylguanidinate(1–) to metal bound *N*,*N*′,*N*″-trialkylguanidinate(2–) was reported to occur in the presence of additional reagents such as $LiNMe_2$, MeMgBr or XyN≡C.[27,28] Thus, the deprotonation of metal bound guanidinate(1–) in **5** upon reaction with DPPA in the formation of **10** shown in Scheme 4 illustrates non-innocent nature of ancillary

ligand of metal azido complexes in [3+2] cycloaddition reaction with alkynes and this observation is unprecedented in the literature.

Molecular Structures Molecular structures of **1**–**4**, **5**·MeOH, **6**, **7**·$CHCl_3$, **8**·MeOH, **9**–**10** with atom labeling Scheme are shown in Figures 3–7. The CF_3 group in some molecular structures depicted revealed large unsymmetrical ellipsoids due to thermal disorder. The coordination environment around the Ru(II) atom in **1**–**3** is identical to that observed in previously reported complexes [(η^6-*p*-cymene)RuCl{κ^2(*N*,*N*′)($(ArN)_2C$–N(H)Ar}] (Ar = Ph (**11**),[6] 2-MeC_6H_4 (**12**) and 4-MeC_6H_4 (**13**)[8]). When the guanidinate ligand contains *ortho* substituted aryl rings such as that present in **1** and related complex **12**, and [(η^5-C_5Me_5)M{κ^2(*N*,*N*′)($(ArN)_2C$–N(H)Ar}] (M = Rh, Ar = 2-$(CF_3)C_6H_4$ (**14**) and M = Ir, Ar = 2-MeC_6H_4 (**15**)), in principle, four types of conformers are possible namely *syn-syn*, *syn-anti*, *anti-syn*, and *anti-anti* as discussed in our previous publications (see also Figure S1 in the Supporting Information, SI).[8,10,11] Accordingly, the guanidinate ligand in **1** revealed *syn-syn* conformation.

The bond parameters pertinent to the guanidinate ligand in structurally characterized complexes are listed in Table 1 and these parameters in **4**, **5**·MeOH, **6**, **7**·$CHCl_3$, **8**·MeOH and **9** are comparable with the corresponding parameters found in **3**. Interestingly, one of the coordinated N atoms of the guanidinate in all three crystallographically distinct molecules of **3** deviates significantly from planarity and this feature is even more pronounced in **4** while the other coordinated N atom in both complexes is planar. The degree of pyramidality of one of the coordinated N atoms in **5**·MeOH is smaller than that in **3** probably due to greater σ-donor but poorer π-donor characters of the coordinated N atom of the guanidinate ligand in the former complex.[29] This stereochemical difference could be ascribed to a better π-donor strength of Cl^- in **3** than N_3^- in **5**·MeOH. The NH proton of guanidinate ligand in **4** is involved in intermolecular N–H···O hydrogen bond with ketonic oxygen atom of the acetate

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moiety from the adjacent molecule related by the glide plane in the crystal lattice (N3···O2 = 2.875 Å, H3···O2 = 2.052 Å, N3–H3···O2 = 160.09°; see Figure S2 in the SI).

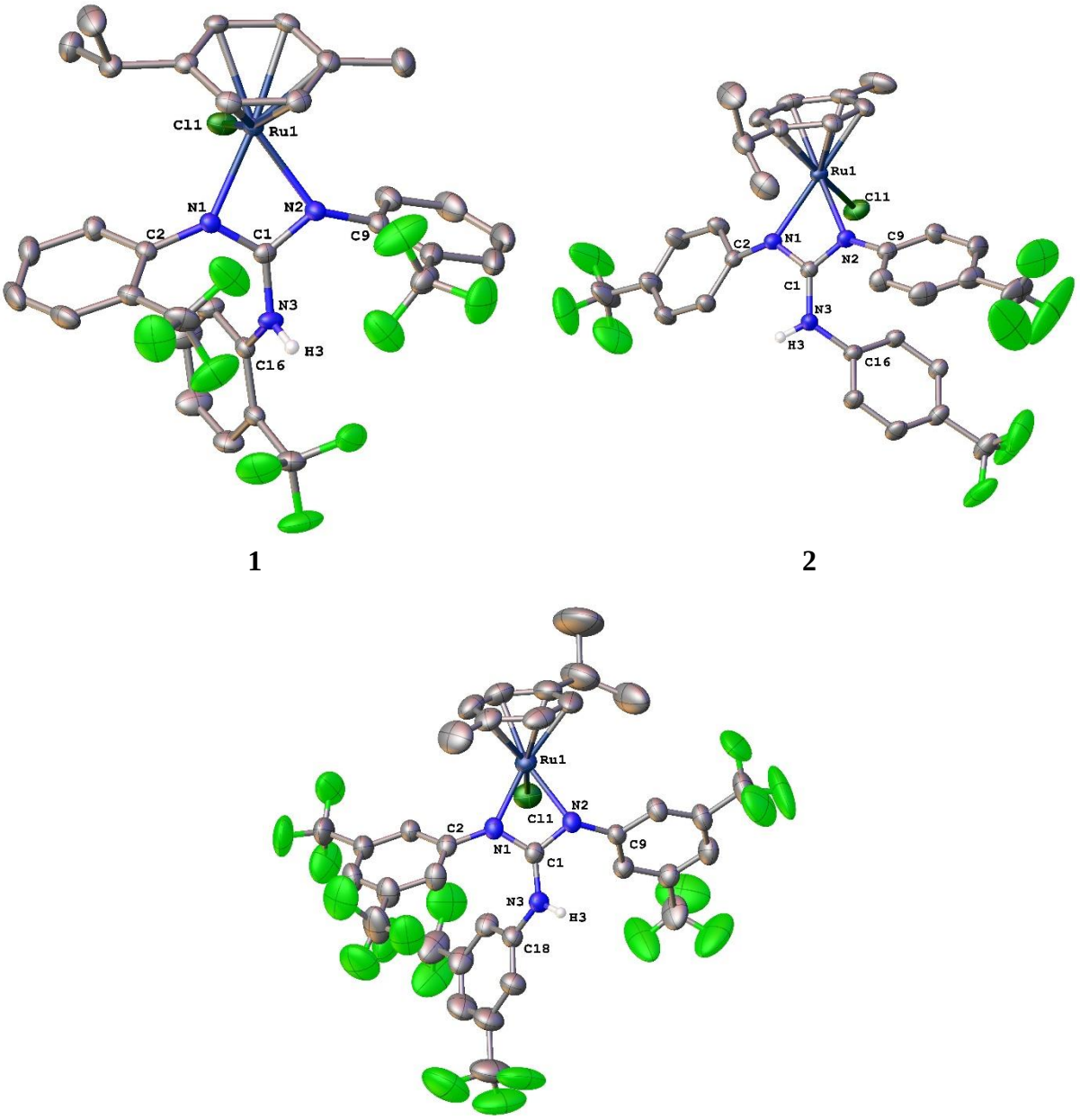

Figure 3 Molecular structures of **1**–**3** at the 30% probability level. Two and three molecules are found in the crystal lattices of **2** and **3** respectively but only one molecule is shown in each case for clarity. Only H atom of the –N(H)Ar moiety is shown for clarity.

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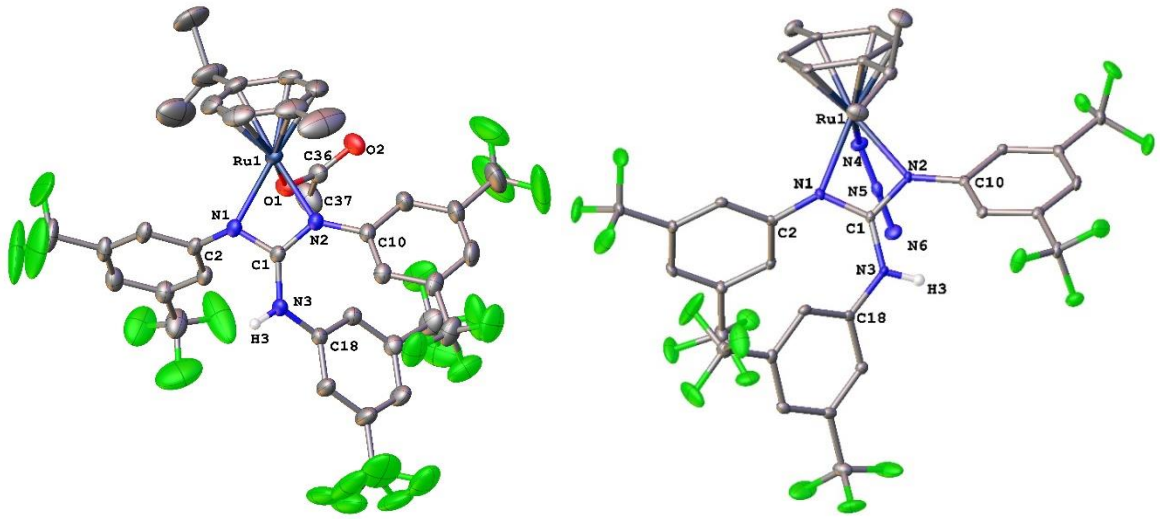
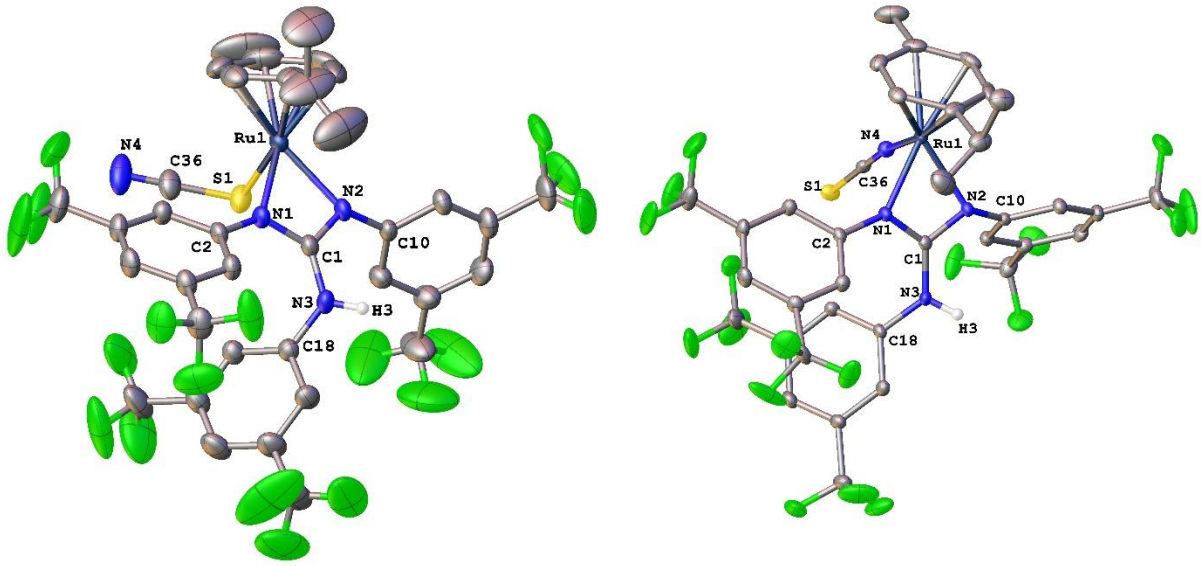


4 **5**·MeOH

Figure 4 Molecular structures of **4** and **5**·MeOH at the 30% probability level. Methanol in **5**·MeOH and H atoms other than that in –N(H)Ar moiety in both complexes are not shown for clarity.



6 **7**·$CHCl_3$

Figure 5 Molecular structures of **6** and **7**·$CHCl_3$ at the 30% probability level. $CHCl_3$ in **7**·$CHCl_3$ and H atoms other than that in –N(H)Ar moiety in both complexes are not shown for clarity.

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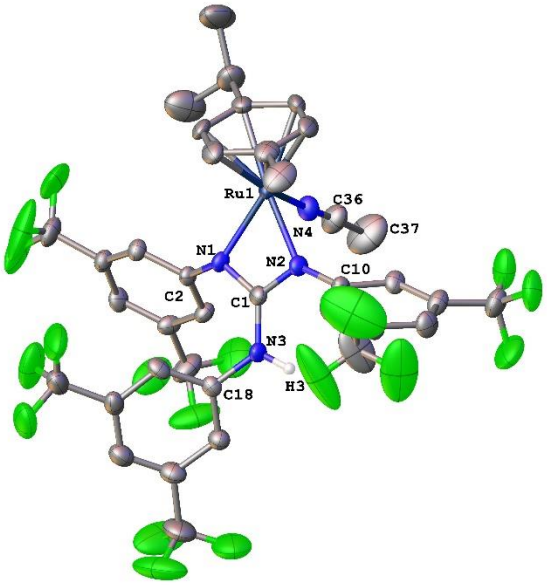
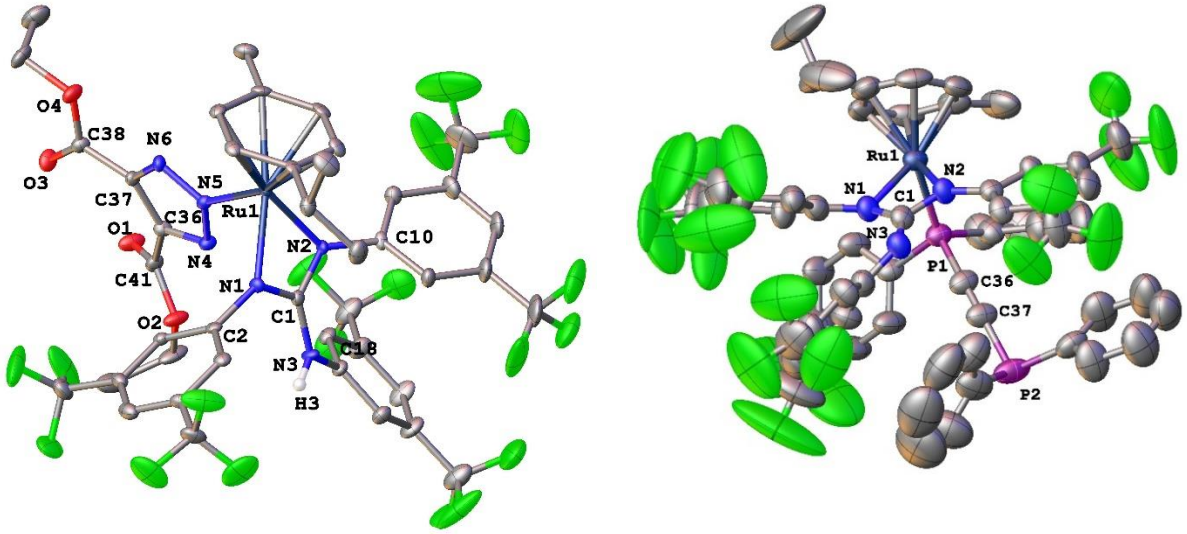


8·MeOH

Figure 6 Molecular structure of **8**·MeOH at the 30% probability level. The counteranion, SbF_6^- and solvent have been omitted and only H atom of the –N(H)Ar moiety is shown for clarity.



9 **10**

Figure 7 Molecular structures of **9** and **10** at the 30% probability level. Only H atom of the –N(H)Ar moiety in **9** is shown for clarity.

Table 1 Comparison of structural features of **1–4**, **5**·MeOH, **6**, **7**·$CHCl_3$, **8**·MeOH and **9**.

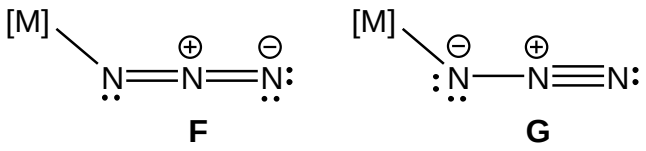
Complex	Δ_{CN} (Å)	$\Delta_{CN'}$ (Å)	ΣN(coordinated) (deg)	ΣN(noncoordinated) (deg)	φ^a (deg)
1	0.000(6)	0.081(6)	355.0, 359.7	360.0	71.9
2 (molecule 1)	0.023(6)	0.062(6)	353.7, 360.0	360.0	34.7
2 (molecule 2)	0.015(6)	0.057(6)	354.9, 360.0	357.9	50.3
3 (molecule 1)	0.023(7)	0.053(7)	344.8, 360.0	360.0	42.3
3 (molecule 2)	0.014(7)	0.066(7)	346.0, 359.9	360.0	38.3
3 (molecule 3)	0.007(7)	0.057(8)	344.2, 360.0	360.0	39.9
4	0.017(7)	0.037(7)	341.3, 359.2	360.0	39.9
5·MeOH	0.005(6)	0.033(6)	350.4, 359.4	360.0	14.3
6	0.007(6)	0.033(6)	353.4, 359.8	360.0	33.7
7·$CHCl_3$	0.008(3)	0.041(5)	345.4, 359.9	360.0	30.8
8·MeOH	0.022(13)	0.048(13)	348.3, 359.7	360.0	19.7
9	0.021(8)	0.054(8)	354.1, 354.5	359.5	18.3

[a] φ = Dihedral angle between the HNC(Ar) plane and the chelating –N-C=N- plane

The bond parameters around the azido unit in **5**·MeOH are comparable with the identical unit present in [(η^6-*p*-cymene)Ru(N_3){κ^2(*N*,*N*′)(($ArN)_2$C–N(H)Ar}] (Ar = 4-MeC_6H_4 (**16**)).[8] An intermolecular N–H···O and O–H···N hydrogen bonds are present between MeOH and (i) H atom of the amino moiety and (ii) terminal N atom of the azido moiety (N3···O1 = 2.829 Å, H3···O1 = 2.119 Å, N3–H3···O1 = 137.22°; O1···N6 = 2.964 Å, H1···N6 = 2.284 Å, O1–H1···N6 = 151.25°; see Figure S3 in the SI). The azido unit in **5**·MeOH can exist in two resonance forms namely **F** and **G** as illustrated in Figure 8.[11,25b,25e,30] The resonance form **F** was shown to be more suitable for AAC reaction while

the metal bound N atom of the azido moiety in resonance form **G** was shown to be more suitable for an attack by an electrophile such as proton (see also Figure 1).[25b,25e,30]

Figure 8



F **G**

Previously, only two pairs of *cationic* thiocyanatoruthenium(II) linkage isomers, [(η^6-*p*-cymene)Ru(2,2′-bipyridine)X]PF_6 (X = SCN (**17**) and NCS (**18**)) and [Ru(terpy)(tbbpy)X] (terpy = 2,2′:6′,2″-terpyridine, tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, X = SCN (**19**) and NCS (**20**)) have been structurally characterized.[31,32] Hence, **6** and **7**·$CHCl_3$ represent the first pair of structurally characterized *neutral* thiocyanatoruthenium(II) linkage isomers to be reported in the literature. The bond parameters around the SCN ligand in **6** are comparable with those parameters reported for the same ligand in **17** and **19** except a smaller RuEC angle found in the former complex (E = S, 100.50(17)° (**6**) and 104.35(6)° (**17**), 106.7(5)° (**19**); E = N, 165.7(2)° (**7**) and 175.9(1)° (**18**) 175.7(6)° (**20**)). This difference in RuEC angle between neutral versus cationic thiocyanatoruthenium(II) complexes mentioned above could partly be ascribed to difference in the coordination environment around the metal atom and partly be ascribed to the packing forces as shall be outlined below.

The SCN ligand in **6** is involved in intermolecular N–H···N hydrogen bond involving N end of the thiocyanate and H atom of the amino moiety of the guanidinate ligand in the neighboring molecule related by a glide plane (N···N = 2.905 Å, H···N = 2.064 Å, N–H···N = 165.8°; see Figure S4 in the SI). The NCS ligand in **7** is involved in intermolecular N–H···S hydrogen bond involving S atom of the thiocyanate and H atom of the amino moiety of the guanidinate ligand in the neighboring molecule related by a 2-fold screw axis (N···S = 3.316 Å, H···S = 2.470 Å, N–H···S = 168.22°; see Figure S5 in the SI). The N bonded isomer of

metal thiocyanate complexes was shown to be a thermodynamic product while the S bonded isomer was shown to be a kinetic product.[32,33,34] However, S-bonded isomer of metal thiocyanate complexes was frequently found in the crystal lattice as the stabilization energy obtained through intermolecular interaction is greater than the energy difference between the gas phase monomers of both the linkage isomers.[33,34]

The Lewis base, MeCN is coordinated to the Ru(II) atom in **8**·MeOH in place of Cl in its precursor **3**. Further, SbF_6^- is present outside the coordination sphere of the metal in **8**·MeOH. The triazolate ligand in **9** is coordinated to the Ru(II) atom through the central N atom (*N2*) and this coordination mode is believed to be the result of the formation of a thermodynamic product.[35,36] The structurally characterized *N1* coordinated triazolate complexes are uncommon with a few exceptions[37] while *N2* coordinated triazolate complexes are common. The bond parameters associated with the guanidinate ligand in **8**·MeOH and **9** resemble with the corresponding parameters discussed for the same ligand in **3**.

The Ru(II) atom in **10** is surrounded by a guanidinate(2–) ligand, one end of the DPPA and the η^6-*p*-cymene ring. Previously, molecular structures of [(η^6-*p*-cymene)Ru{κ^2(*N*,*N*′)((RN)$_2$C=NR)}(PPh$_3$)] (R = C(O)Me; **21**) and [(η^4-1,5-cyclooctadiene)RuCl{κ^2(*N*,*N*′)((RN)$_2$C=NR))}] (R = Ph; **22**) that contained a chelating guanidinate(2–) were reported by Henderson and Bailey and co-workers, respectively.[7,38] The poor quality of X-ray data of **21** precluded the publication of key bond parameters and moreover, key bond parameters of **22** remain unpublished. Therefore, complex **10** represents the first fully characterised guanidinatoruthenium(II) complex that contain a doubly deprotonated guanidinate(2–) ligand. As anticipated, the C–N distance, 1.304(6) Å involving non-coordinated N atom of the CN_3 unit in **10** is shorter than the C–N distances, 1.357(6) and 1.385(6) Å involving the pair of coordinated N atoms. Further, both the Ru–N distances,

2.091(3) and 2.108(3) Å of the guanidinate ligand in **10** are comparable with each other within 3σ cut off which contrasts with the unequal Ru–N bond distances observed in **3** (2.088(4)/2.143(3) Å (molecule 1), 2.084(3)/2.142(4) Å (molecule 2) and 2.104(4)/2.148(4) Å (molecule 3)**)**. The C atom and one of the coordinated N atoms of the CN_3 unit in **10** is planar while the remaining coordinated N atom deviates significantly from planarity (∑N = 349.5°). Thus, one coordinated N atom acts as a pure σ-donor and while the other predominantly acts as σ-donor contaminated with a slight amount of π-donor character.[21] The values of both Δ_{CN} 0.053(8) Å and Δ_{CN}' 0.054(8) Å found in **10** are comparable with the corresponding values observed for **3** within the 3σ cut off. The bond parameters pertinent to DPPA in **10** are comparable with those parameters published for the related complex, [(η^6-*p*-cymene)$RuCl_2$(κ^1*P*-$Ph_2PC{\equiv}CPPh_2$)].[39]

Spectroscopic Studies IR spectra of all new complexes except that of **10** revealed one band in the range 3295–3447 cm^{-1} attributable to the ν(NH) stretch. In addition, the IR spectrum of **4** revealed two bands at 1534 and 1342 cm^{-1} ascribed to ν_a(OCO) and ν_s(OCO) stretches, respectively. The $\Delta\nu$ = ν_a(OCO) – ν_s(OCO) value of 192 cm^{-1} supports the presence of a hydrogen bonded monodentate acetate coordination mode as found in the solid state (see above).[40] An intense band was also observed at 2033 cm^{-1} for **5** which is ascribed to the $\nu(N_3)$ stretch.[19a] The IR spectrum of isomeric mixture of **6** and **7**·$CHCl_3$ revealed a band at 2038 cm^{-1}. The value of ν(SC≡N) stretch of thiocyanate is greater for the S bound isomer (≥ 2100 cm^{-1}, sharp) than for the N bound isomer (≤ 2050 cm^{-1}, more intense and broad) although this rule is not universal.[32,34] The bandwidth at half height for the aforementioned band is 7 cm^{-1} and further both the S and N ends of the thiocyanate ligand in **6** and **7**·$CHCl_3$ are involved in intermolecular N–H···N and N–H···S hydrogen bonding, respectively. Thus, the magnitude of difference in ν(SC≡N) stretch between **6** and **7**·$CHCl_3$

could lie well within 7 cm^{-1}. Complex **9** revealed one band at 1731 cm^{-1} attributable to the ν(C=O) stretch of the ester moiety.

The ^{1}H NMR spectrum of **1** revealed the presence of three species in about 0.14:1.00:0.11 ratios and the presence of three species was also independently verified by ^{19}F NMR spectroscopy. The three solution species are assigned to any three isomers from *syn-syn*, *syn-anti*, *anti-syn*, and *anti-anti* isomers, most likely to the former three isomers (see Experimental section and Figure S1 in the SI). The formation of *syn-anti* and *anti-syn* isomers from *syn-syn* isomer which is observed in solid state is likely due to guanidine centered rearrangement in solution involving an acyclic intermediate as previosusly discussed by two of us.[8–11] VT ^{1}H NMR spectra of previously known complex **12** revealed the presence of three species in solution and these species were suggested to arise from the restricted N_2C–N(H)Ar single bond rotation yielding *syn-syn*, *syn-syn a* and *syn-syn b* rotamers.[8] The difference in the nature of solution species between **1** and **12** is ascribed to the difference in greater effective van der Waals radius of CF_3 groups in the former complex than that of Me groups in the latter (2.20 Å versus 1.80 Å).[41]

^{1}H, ^{19}F and ^{13}C NMR spectra of **2**–**5** revealed the presence of a single species in solution as anticipated due to the presence of a symmetrically substituted aryl rings in the guanidinate ligands. The ^{1}H NMR spectrum of isomeric mixture of **6** and **7** revealed the presence of two species in about 1.00:0.37 ratio (see Experimental section). The major species is tentatively assigned to the S bound isomer as this isomer is more soluble in $CDCl_3$ and the minor species is assigned to the N bound isomer. The ^{1}H NMR spectrum of cationic complex **8** revealed the presence of four species in about 1.00:0.10:0.45:0.39 ratios. The presence of symmetrical aryl rings in the guanidinate moiety of **8** suggests that these four species could not have originated for the reasons putforward for **1** but possibly could have

originated from any four out of six possible rotamers that arise from the *p*-cymene ring rotation about the metal center.[8]

The ^{1}H NMR spectrum of **9** revealed the presence of two species in about 1.00:0.05 ratio (see Experimental Section). These two species could arise due to either linkage isomerism caused by the triazolate ligand (N_1 versus N_2 coordination) or the *p*-cymene ring rotation about the metal as discussed previously for **8**. If the observed ^{1}H NMR spectral pattern is due to linkage isomerism, one would then anticipate three quartets for CH_2CH$_3$ protons with two of these quartets being of equal intensity and three triplets for CH$_2$CH_3 protons with two of these triplets being of equal intensity.[36] The ^{1}H NMR spectrum of **9** revealed the presence of two triplets for CH$_3$ protons and two quartets for CH$_2$ protons of the C(O)OEt moiety both in about 1.00:0.05 ratio which suggest the cause of two isomers being the *p*-cymene ring rotation about the metal centre.[8]

Multinuclear (^{1}H, ^{13}C, ^{19}F and ^{31}P) NMR spectra of **10** revealed the presence of a single species in solution. The ^{31}P{^{1}H} NMR spectrum of **10** revealed two singlets located at δ ^{31}P 18.05 and –31.34 ppm assignable to coordinated and pendant P nuclei respectively. The δ ^{31}P shift value found for coordinated P in **10** is downfield shifted while the δ ^{31}P shift value found for pendant P is somewhat comparable to the corresponding δ ^{31}P shifts reported for [(η^6-*p*-cymene)RuCl$_2$(κ^1*P*-Ph$_2$PC≡CPPh$_2$)] (δ (^{31}P) = 0.4 (s, Ru–*P*), –34.2 (d, J_{PP} = 3.6 Hz, pendant *P*)).[39]

Ruthenium catalyzed azide alkyne cycloaddition (RuAAC) The reaction of organic azide with terminal alkyne in the presence of metal salts was shown to afford 1,4- and 1,5-disubstituted triazoles under mild reaction condition. This reaction is known as metal catalyzed AAC reaction.[42,43] There is a constant demand for newer catalysts that selectively affords either 1,4- or 1,5-disubstituted triazoles from the reaction involving terminal alkynes and organic azides. Fokin and Sharpless first reported the use of [(η^5-Cp*)Ru(PPh$_3$)$_2$Cl] as a

catalyst for AAC involving alkyl azide and terminal/internal alkynes that afforded 1,5-disubstituted triazoles in > 80% yield.[44] Since then, RuAAC has been studied with alkyl azides/terminal or internal alkynes which afforded exclusively either 1,5- or 1,4-disubstituted triazoles or a mixture of these triazoles.[45,46]

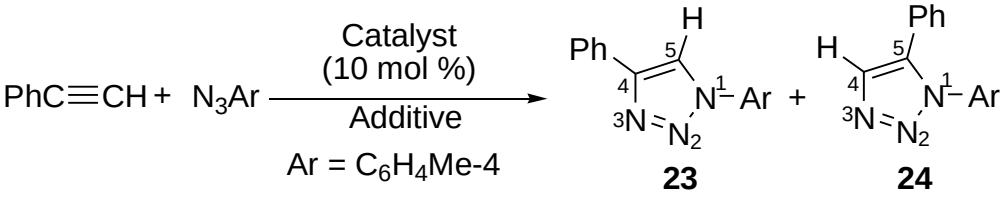
We wanted to test catalytic efficacy of **3** in RuAAC reaction involving 4-tolyl azide and phenyl acetylene as coupling partner (see Table 2). This reaction was carried out in CH_2Cl_2 at RT for 24 h in the absence of catalyst and AgOAc as additive which afforded no trace of triazole (entry 1). Further, the aforementioned reaction carried out in the presence of either AgOAc alone or a mixture of $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)Cl]_2$ and AgOAc (Ru:Ag = 1:10) in CH_2Cl_2 at RT for 24 h which afforded no trace of triazole (entries 2 and 3). RuAAC carried out in the presence of **3** and in the absence of AgOAc also did not give triazole (entry 4). Pleasingly, the combination of **3** and AgOAc (Ru:Ag = 1:10) in CH_2Cl_2 at RT for 24 h afforded a mixture of 1,4- and 1,5-disubstituted 1,2,3-triazoles (**23** and **24**) in 99% conversion with the isomer ratio being 73:27 (entry 5). The triazole **23** was isolated from the reaction mixture by column chromatography in 62% yield. The composition of **23** was confirmed by melting point measurement, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and SCXRD (see Figure S6 in the SI). The use of **11** in place of **3** in the above-mentioned click reaction gave a mixture of **23** and **24** in 98% conversion with their ratio being 55:45 (entry 6). Complexes **1** and **2** were also screened for RuAAC reaction outlined in Table 2, but neither of the triazoles were obtained in reasonable yields from these reactions. The formation of a mixture of **23** and **24** is anticipated to arise from putative intermediates **H** and **I**, respectively (see Figure 9).[45a]

Conclusions

Complexes **1**–**3** were isolated in good yields following the established method. Complex **3** was subjected to nucleophilic substitution reaction with OAc^-, N_3^-, and SCN^- which afforded **4**, **5** and an admixture of **6** and **7** in good yields. The metathesis reaction of **3** with $AgSbF_6$ in

the presence of MeCN afforded cationic complex **8** in 85% yield. The AAC reaction of **5** with DEAD gave the *N2* bound triazolate complex **9** in 86% yield while the reaction of **5** with DPPA gave a novel guanidinate(2−) complex **10** in 87% yield. The new complexes were characterized by analytical, IR and NMR (^{1}H, ^{13}C and ^{19}F) spectroscopic techniques. Further, molecular structures of eleven new compounds were determined by SCXRD. The guanidinate ligand in **1** revealed *syn-syn* conformation. The isolation of linkage isomers **6** and **7** and their structure determination through SCXRD is a noteworthy result reported in this manuscript. Further, complex **10** represents the first fully characterized guanidinatoruthenium(II) complex which contain guanidinate(2−) ligand to be reported in the literature. The presence of more than one solution species was shown to depend upon (i) steric property and substitution

Table 2 Results of RuAAC of phenylacetylene and 4-tolyl azide.

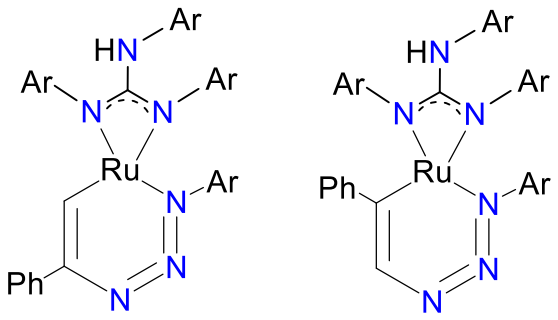


Entry	Catalyst	Additive	Conversion[a] (%)	**23**/**24** ratio[a]
1	Blank	–	0	0/0
2	–	AgOAc	0	0/0
3	[(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$	AgOAc	0	0/0
4	**3**	–	0	0/0
5	**3**	AgOAc	99	73(62[b])/27
6	**11**	AgOAc	98	55/45

[a]Conversion and ratio of **23** and **24** were estimated by ^{1}H NMR spectroscopy.

[b]Isolated yield.

pattern of the aryl rings of the guanidinate ligand in **1** and (ii) steric encumbrance around the metal which induces *p*-cymene ring rotation as found in **8** and **9**. The utility of **3** as catalyst in RuAAC reaction involving 4-tolyl azide and phenyl acetylene was briefly explored which afforded 1,4-disubstituted triazole **23** in 62% isolated yield.



H **I**

Figure 9 Plausible intermediates **H** and **I** responsible for the formation of 1,4- and 1,5-troazoles, respectively formed during the click reaction

Experimental section

[(η^6-*p*-cymene)RuCl{κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar}] (Ar = 2-(CF$_3$)C$_6$H$_4$; 1) Guanidine **L1** (80.2 mg, 0.163 mmol) was dispersed in methanol (10 mL) in a 25 mL round bottom (RB) flask and the content in the flask were stirred at RT to afford a clear solution. NaOAc (13.4 mg, 0.163 mmol) was added to the aforementioned solution and stirred. Subsequently, [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50.0 mg, 0.082 mmol) was added all at once to the aforementioned mixture and stirred at RT for 24 h. The reaction mixture was filtered and the filtrate evaporated under vacuum to afford the solid. The solid was dissolved in CH_2Cl_2 and filtered to remove NaCl as white precipitate. The filtrate was layered with *n*-hexane and the resulting solution stored at RT to afford **1** as orange needle shaped crystals. Yield: 84% (99.4 mg, 0.131 mmol). Mp: 191 °C. Anal. Calcd for $C_{32}H_{27}ClF_9N_3Ru$ (M_w: 761.08): C, 50.50; H, 3.58; N, 5.52. Found: C, 50.50; H, 3.74; N, 5.38. IR (KBr): $\bar{\nu}$ = 3447 (m, NH), 1546 (s, C=N), 1483 (s, CF_3, str, asym), 1116 (s, CF_3, str, sym), 843 (w, CF_3, def, asym) cm^{-1}. The ^{1}H NMR

spectrum of **1** revealed the presence of three species, hereafter indicated as isomers 1, 2 and 3 in about 0.14:1.00:0.11 ratios as estimated from the integrals of alkyl protons. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 0.93, 1.03 (each d, $J_{H,H}$ = 7.2 Hz, 2 × 6H, $CH(CH_3)_2$, isomers 1 and 2, respectively), 1.20 (d, $J_{H,H}$ = 6.8 Hz, 6H, $CH(CH_3)_2$, isomer 3), 1.69 (s, 2 × 3H, CH_3, isomers 1 and 3), 1.76 (s, 3H, CH_3, isomer 2), 2.51 (m, 1H, $CHMe_2$, isomer 2), 2.73 (m, 2 × 1H, $CHMe_2$, isomers 1 and 3), 4.98 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4, isomer 1), 5.14 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4, isomer 3), 5.18 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4, isomer 2), 5.24 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4, isomer 1), 5.45 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4, isomer 2), 5.49 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4, isomer 3), 5.52 (s, 2 × 1H, N*H*, isomers 1 and 3), 5.63 (s, 1H, N*H*, isomer 2), 6.67 (t, $J_{H,H}$ = 7.8 Hz, 1H, Ar*H*, isomer 2), 6.75 (t, $J_{H,H}$ = 7.6 Hz, 1H, Ar*H*, isomer 1), 6.85 (t, $J_{H,H}$ = 7.4 Hz, 1H, Ar*H*, isomer 3), 7.00 (t, $J_{H,H}$ = 7.6 Hz, 1H, Ar*H*, isomer 2), 7.05–7.18 (m, 3 × 4H, Ar*H*, isomers 1–3), 7.31 (dt, $J_{H,H}$ = 7.7 Hz, $J_{H,H}$ = 1.4 Hz, 2H, Ar*H*, isomer 2), 7.40 (d, $J_{H,H}$ = 8.0 Hz, 3 × 1H, Ar*H*, isomers 1–3), 7.44 (br, 2 × 2H, Ar*H*, isomers 1 and 3), 7.48 (dd, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 1.6 Hz, 1H, Ar*H*, isomer 2), 7.68 (d, $J_{H,H}$ = 7.2 Hz, 2 × 2H, Ar*H*, isomers 1 and 3), 7.78 (d, $J_{H,H}$ = 8.0 Hz, 2H, Ar*H*, isomer 2), 8.12 (d, $J_{H,H}$ = 8.0 Hz, 2 × 2H, Ar*H*, isomers 1 and 3) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –61.92 (s, 3F, CF_3, isomer 1), –61.52 (s, 2 × 3F, CF_3, isomers 2 and 3), –59.52 (s, 6F, CF_3, isomer 3), –59.28 (s, 6F, CF_3, isomer 2), –58.60 (s, 6F, CF_3, isomer 1) ppm. MS (ESI^+) *m/z* [ion]: 726 $[M - Cl]^+$, 492 $[\mathbf{L1}H]^+$.

[(η^6-*p*-cymene)RuCl{κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar}] (Ar = 4-(CF_3)C_6H_4; 2) Complex **2** was prepared from **L2** (80.2 mg, 0.163 mmol), NaOAc (13.4 mg, 0.163 mmol), and [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50.0 mg, 0.082 mmol) in methanol (10 mL) by following a procedure analogous to that described for complex **1**. The sample was crystallized from a mixture of CH_2Cl_2 and toluene at RT over the period of two days to afford **2** as orange needle shaped

crystals. Yield: 82% (106.8 mg, 0.1404 mmol). Mp: 221 °C (decompn). Anal. Calcd for $C_{32}H_{27}ClF_9N_3Ru$ (M_w: 761.08): C, 50.50; H, 3.58; N, 5.52. Found: C, 50.43; H, 3.45; N, 5.69. IR (KBr): $\bar{\nu}$ = 3423 (m, br, NH), 1512 (m, C=N), 1324 (vs, CF_3, str, asym), 1105 (s, CF_3, str, sym), 834 (m, CF_3, def, asym) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 1.23 (d, $J_{H,H}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.25 (s, 3H, CH_3), 2.69 (m, 1H, C*H*Me$_2$), 5.19 (d, $J_{H,H}$ = 4.8 Hz, 2H, C_6H_4), 5.40 (d, $J_{H,H}$ = 5.2 Hz, 2H, C_6H_4), 6.24 (s, 1H, N*H*), 6.83 (d, $J_{H,H}$ = 8.0 Hz, 2H, Ar*H*), 7.14 (d, $J_{H,H}$ = 7.6 Hz, 2H, Ar*H*), 7.21, 7.38 (each d, $J_{H,H}$ = 7.6 Hz, 2 × 4H, Ar*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, 298 K): δ = 19.26 (*C*H$_3$), 22.50 (CH(*C*H$_3$)$_2$), 31.62 (*C*HMe$_2$), 78.94, 80.85, 98.56, 99.78 (*p*-cymene Ar*C*H/Ar*C*), 120.01, 123.36, 123.98 (q, $J_{C,F}$ = 268.9 Hz, *C*F$_3$), 124.45 (q, $J_{C,F}$ = 271.2 Hz, *C*F$_3$), 124.86 (q, $J_{C,F}$ = 32.5 Hz, *C*CF$_3$), 125.36 (q, $J_{C,F}$ = 32.9 Hz, *C*CF$_3$), 125.96, 126.00, 126.20, 126.23, 140.38, 149.41, 152.78 (Ar*C*H/Ar*C* and *C*=N) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –62.20 (s, 3F, CF_3), –61.83 (s, 6F, CF_3) ppm. MS (ESI^+) *m/z* [ion]: 762 $[M + H]^+$, 726 $[M – Cl]^+$, 492 $[\mathbf{L2}H]^+$.

[(η^6-*p*-cymene)RuCl{κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar}] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$; 3) Complex **3** was prepared from **L3** (113.5 mg, 0.1633 mmol), NaOAc (13.4 mg, 0.163 mmol), and [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (50.0 mg, 0.082 mmol) in methanol (10 mL) by following a procedure analogous to that described for **1**. The sample was crystallized from a mixture of CH_2Cl_2 and methanol at RT over the period of several days to afford **3** as orange needle shaped crystals. Yield: 84% (127.6 mg, 0.1323 mmol). Mp: 215 °C. Anal. Calcd for $C_{35}H_{24}ClF_{18}N_3Ru$ (M_w: 965.08): C, 43.56; H, 2.51; N, 4.35. Found: C, 43.37; H, 2.34; N, 4.31. IR (KBr): $\bar{\nu}$ = 3432 (br, NH), 1542 (m, C=N), 1376 (s, CF_3, str, asym), 1278 (vs, CF_3, str, sym), 1130 (s, CF_3, def, asym), 887 (w, CF_3, str, sym) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 1.24 (d, $J_{H,H}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.23 (s, 3H, CH_3), 2.68 (m, 1H, C*H*Me$_2$), 5.27 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4), 5.42 (d, $J_{H,H}$ = 6.4 Hz, 2H, C_6H_4), 6.43 (s, 1H, N*H*), 7.23 (s, 1H, Ar*H*), 7.30 (s, 2H, Ar*H*), 7.42 (s, 2H, Ar*H*), 7.55 (s, 4H, Ar*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz,

298 K): δ = 19.2 (*C*H_3), 22.4 (CH(*C*H_3)$_2$), 31.7 (*C*HMe_2), 79.7, 80.5, 97.1, 101.3 (*p*-cymene Ar*C*H/Ar*C*), 116.7 (br), 117.7 (br), 121.4, 122.6 (q, $J_{C,F}$ = 273.1 Hz, *C*F_3), 123.1 (q, $J_{C,F}$ = 272.7 Hz, *C*F_3) 123.4, 132.4, 132.5 (each q, $J_{C,F}$ = 33.9 Hz, *C*CF_3), 137.8, 147.2, 152.5 (Ar*C* and *C*=N) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –63.55 (s, 6F, C*F*$_3$), –63.06 (s, 12F, C*F*$_3$) ppm. MS (ESI$^+$) *m/z* [ion]: 969 [M – Cl + K]$^+$, 930 [M – Cl]$^+$, 696 [**L3**H]$^+$.

[(η^6-*p*-cymene)Ru(OAc){κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar}] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$; 4) Complex **3** (100.0 mg, 0.1036 mmol) was stirred with excess of NaOAc (849.8 mg, 10.36 mmol) in methanol (10 mL) in a 25 mL RB flask fitted with a $CaCl_2$ guard tube at RT for 24 h. The volatiles were removed under vacuum to afford orange solid. The solid was dissolved in CH_2Cl_2 and filtered to remove unreacted NaOAc and NaCl. The filtrate was layered with *n*-hexane and the resulting solution stored at RT for 24 h to afford **4** as orange needle shaped crystals. Yield: 89% (91.1 mg, 0.092 mmol). Mp: 215 °C (decompn). Anal. Calcd for $C_{37}H_{27}F_{18}N_3O_2Ru$ (M_w: 988.68): C, 44.95; H, 2.75; N, 4.25. Found: C, 44.74; H, 2.43; N, 4.28. IR (KBr): $\bar{\nu}$ = 3423 (br, NH), 1597 (m, C=N), 1534 (br, OC(O), str, asym), 1380 (s, CF_3, str, asym), 1342 (s, OC(O), str, sym), 1282 (vs, (CF_3, str, sym), 1127 (vs, CF_3, def, asym), 886 (w, CF_3, str, sym) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 1.15 (d, $J_{H,H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 2.01 (s, 3H, OC(O)C*H*$_3$), 2.06 (s, 3H, C*H*$_3$), 2.55 (m, 1H, C*H*Me_2), 5.38, 5.56 (each d, $J_{H,H}$ = 6.0 Hz, 2 × 2H, C$_6$*H*$_4$), 6.29 (s, 1H, N*H*), 7.06 (s, 2H, Ar*H*), 7.25 (s, 1H, Ar*H*), 7.44 (s, 2H, Ar*H*), 7.63 (s, 4H, Ar*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ = 19.1 (*C*H_3), 22.5 (CH(*C*H_3)$_2$), 23.9 (OC(O)*C*H_3), 31.6 (*C*HMe_2), 78.3, 81.1, 96.8, 99.5 (*p*-cymene Ar*C*H/Ar*C*), 116.6 (br), 117.1 (br), 120.2, 122.6 (q, $J_{C,F}$ = 273.5 Hz, *C*F_3), 123.2 (q, $J_{C,F}$ = 273.1 Hz, *C*F_3), 124.0, 128.4, 129.2, 130.5, 132.4 (q, $J_{C,F}$ = 33.2 Hz, *C*CF_3), 132.5 (q, $J_{C,F}$ = 33.8 Hz, *C*CF_3), 138.4, 147.4, 154.3 (Ar*C* and *C*=N), 178.4 (O*C*(O)) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –63.46 (s, 6F, C*F*$_3$), –63.02 (s, 12F, C*F*$_3$) ppm. MS (ESI$^+$) *m/z* [ion]: 969 [M – OAc + K]$^+$, 930 [M – OAc]$^+$.

[(η^6-*p*-cymene)RuN$_3$\{κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar\}] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$; 5) Complex **3** (100.0 mg, 0.1036 mmol) was stirred with 2 equiv of NaN_3 (13.5 mg, 0.207 mmol) in ethanol (10 mL) in a 25 mL RB flask fitted with a $CaCl_2$ guard tube at RT for 24 h. The volatiles were removed under vacuum to afford orange solid. The solid was dissolved in CH_2Cl_2 and filtered to remove excess of NaN_3 and NaCl. Subsequently, CH_2Cl_2 extract was layered with *n*-hexane and the resulting solution stored at RT for 30 h to afford **5** as orange rhombic shaped crystals. Yield: 93% (93.6 mg, 0.096 mmol). Mp: 152 °C (decompn). Anal. Calcd for $C_{35}H_{21}F_{18}N_6Ru{\cdot}H_2O$ (M_w: 968.62 +18.02): C, 42.61; H, 2.35; N, 8.52. Found: C, 42.92; H, 2.72; N, 8.33. IR (KBr): $\bar{\nu}$ = 3422 (br, w, NH), 2033 (s, N_3), 1550 (m, C=N), 1376 (vs, CF_3, str, asym), 1279 (vs, CF_3, str, sym), 1130 (s, CF_3, def, asym), 887 (w, CF_3, str, sym) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 1.25 (d, $J_{H,H}$ = 7.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.17 (s, 3H, C*H*$_3$), 2.66 (m, 1H, C*H*Me$_2$), 5.18, 5.37 (each d, 2 × 2H, $J_{H,H}$ = 6.0 Hz, C$_6$*H*$_4$), 6.51 (s, 1H, N*H*), 7.22 (s, 2H, Ar*H*), 7.26 (s, 1H, Ar*H*), 7.46 (s, 2H, Ar*H*), 7.48 (s, 4H, Ar*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ = 18.6 (*C*H$_3$), 22.5 (CH(*C*H$_3$)$_2$), 31.4 (*C*HMe$_2$), 79.1, 81.2, 97.6, 101.4 (*p*-cymene Ar*C*H/Ar*C*), 117.0 (br), 117.3 (br), 120.6, 122.6 (q, $J_{C,F}$ = 273.1 Hz, *C*F$_3$), 123.1 (q, $J_{C,F}$ = 273.1 Hz, *C*F$_3$), 123.3, 132.5 (q, $J_{C,F}$ = 33.8 Hz, *C*CF$_3$), 132.7 (q, $J_{C,F}$ = 33.5 Hz, *C*CF$_3$), 138.1, 147.3, 153.6 (Ar*C* and *C*=N) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –63.54 (s, 6F, C*F*$_3$), –63.08 (s, 12F, C*F*$_3$) ppm. MS (ESI+) *m/z* [ion]: 969 [M – N_3 + K]$^+$, 930 [M – N_3]$^+$, 696 [**L3**H]$^+$.

[(η^6-*p*-cymene)RuX\{κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar\}] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$, X = SCN (6) and X = NCS (7)) Complex **3** (100.0 mg, 0.1036 mmol) was stirred with two equiv of KSCN (20.1 mg, 0.207 mmol) in methanol (10 mL) in a 25 mL RB flask fitted with a $CaCl_2$ guard tube at RT for 24 h. Subsequently, the volatiles were removed under vacuum to afford an orange solid. The solid was dissolved in CH_2Cl_2 and filtered to remove unreacted KSCN and KCl. The filtrate was layered with *n*-hexane and the resulting solution stored at RT for

several days to afford a mixture of S-bound isomer, **6** and N-bound isomer, **7** as rhombic orange crystals. Complexes **6** and **7** were characterized as an admixture in all cases except SCXRD. Crystals of **6** and **7** were separated by dissolving in $CDCl_3$ and during the course of this process, a small amount of the latter complex left undissolved due to its lower solubility. Yield: 92% (94.1 mg, 0.095 mmol). Mp: 158 °C (decompn). Anal. Calcd for $C_{36}H_{24}F_{18}N_4SRu$ (M_w: 987.71): C, 43.78; H, 2.45; N, 5.67; S, 3.25. Found: C, 44.11; H, 2.34; N, 6.07; S, 3.48. IR (KBr): $\bar{\nu}$ = 3422 (br, w, NH), 2038 (s, S–C≡N/N=C=S), 1562 (br, w, C=N), 1376 (s, CF_3, str, asym), 1283 (vs, CF_3, str, sym), 1128 (s, CF_3, def, asym), 881 (w, CF_3, str, sym) cm^{-1}. The ^1H NMR spectrum of the sample revealed the presence of **6** and **7** in about 1.00:0.37 ratio respectively as estimated from the integrals of aromatic protons of the *p*-cymene ring. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 1.25, 1.26 (each d, $J_{H,H}$ = 6.8 Hz, 2 × 6H, $CH(CH_3)_2$, **6** and **7** respectively), 2.18, 2.20 (each s, 2 × 3H, CH_3, **7** and **6** respectively), 2.68 (m, 2 × 1H, $CHMe_2$, **6** and **7**), 5.25, 5.29 (each d, 2 × 2H, $J_{H,H}$ = 6.0 Hz, C_6H_4, **7** and **6** respectively), 5.45 (d, 2H, $J_{H,H}$ = 6.4 Hz, C_6H_4, **7**), 5.47 (d, 2H, $J_{H,H}$ = 6.0 Hz, C_6H_4, **6**), 6.66 (s, 2 × 1H, N*H*, **6** and **7**), 7.10 (s, 2H, Ar*H*, **7**), 7.14 (s, 3H, Ar*H*, **6** (2H) and **7** (1H)), 7.16 (s, 1H, Ar*H*, **6**), 7.26 (s, 2H, Ar*H*, **6**), 7.29 (s, 2H, Ar*H*, **7**), 7.47 (s, 4H, Ar*H*, **6**), 7.50 (s, 4H, Ar*H*, **7**) ppm. The ^{19}F NMR spectrum revealed the presence of **6** and **7** in about 1.00:0.28 ratio. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –63.52 (s, 6F, CF_3, **7**), –63.43 (s, 6F, CF_3, **6**), –63.03 (s, 12F, CF_3, **7**), –62.90 (s, 12F, CF_3, **6**) ppm.

[(η^6-*p*-cymene)Ru(NCMe){κ^2(*N*,*N'*)((ArN)$_2$C–N(H)Ar}][SbF_6](Ar = 3,5-$(CF_3)_2C_6H_3$; 8)

Complex **3** (100.0 mg, 0.1036 mmol) and $AgSbF_6$ (53.40 mg, 0.1554 mmol) were dispersed in acetonitrile and the resulting heterogeneous mixture stirred at RT for 12 h in dark in a 25 mL RB flask which was protected with $CaCl_2$ guard tube. The volatiles from the reaction mixture were removed under vacuum to afford dark orange solid. The solid was extracted with CH_2Cl_2 and the unreacted $AgSbF_6$ and AgCl were filtered off. The extract was layered

with *n*-hexane and the resulting solution stored at RT for several days to afford **8** as orange needle shaped crystals suitable for SCXRD. Yield: 85% (106.2 mg, 0.0880 mmol). Mp: 205 °C (decompn). Anal. Calcd for $C_{37}H_{24}F_{24}N_4RuSb{\cdot}3H_2O$ (M_w: 1203.40 + 54.05): C, 35.34; H, 2.40; N, 4.46. Found: C, 35.37; H, 2.23; N, 4.50. IR (KBr): $\bar{\nu}$ = 3351 (w, NH), 1577 (m, C=N), 1376 (s, CF_3, str, asym), 1284 (s, CF_3, str, sym), 1174 (s, CF_3, def, asym), 896 (w, CF_3, str, sym), 664 (m, Sb–F) cm^{-1}. Note: No band was observed for MeCN in the IR spectrum of **8**. The ^{1}H NMR spectrum of **8** revealed the presence of four isomers in about 1.00:0.10:0.45:0.39 ratios as estimated from the integrals of aromatic protons of the *p*-cymene ring. ^{1}H NMR (CD_3OD, 400 MHz, 298 K): δ = 1.21, 1.28 (each d, 2 × 6H, $J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$, isomers 3 and 4, respectively), 1.30, 1.31 (d, 2 × 6H, $J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$, isomers 1 and 2), 2.04 (s, 2 × 3H, CH_3, isomers 1 and 3), 2.07, 2.11 (each s, 2 × 3H, CH_3, isomers 4 and 2 respectively), 2.16, 2.17, 2.20, 2.55 (each s, 4 × 3H, CH_3CN, isomers 2, 4, 3 and 1 respectively), 2.67 (m, 3 × 1H, $CHMe_2$, isomers 2–4), 2.78 (m, 1H, $CHMe_2$, isomer 1), 5.21, 5.42 (each d, 2 × 2H, $J_{H,H}$ = 6.0 Hz, C_6H_4, isomer 1), 5.49 (s, 1H, NH, isomer 1), 5.53 (d, 2H, $J_{H,H}$ = 4.0 Hz, C_6H_4, isomer 2), 5.66 (d, 2H, $J_{H,H}$ = 6.0 Hz, C_6H_4, isomer 3), 5.72 (d, 2H, $J_{H,H}$ = 6.4 Hz, C_6H_4, isomer 4), 5.79 (d, 2H, $J_{H,H}$ = 4.4 Hz, C_6H_4, isomer 2), 5.87 (d, 2H, $J_{H,H}$ = 6.0 Hz, C_6H_4, isomer 3), 5.99 (d, 2H, $J_{H,H}$ = 6.0 Hz, C_6H_4, isomer 4), 7.02 (s, 1H, NH, isomer 2), 7.10 (each s, 2 × 1H, NH, isomers 3 and 4), 7.27 (s, 2 × 2H, ArH, isomers 1 and 2), 7.28 (s, 2 × 1H, ArH, isomers 1 and 2), 7.36 (s, 3H, ArH, isomer 3), 7.39 (s, 3H, ArH, isomer 4), 7.61 (s, 2H, ArH, isomer 4), 7.64 (s, 2H, ArH, isomer 3), 7.65 (s, 4H, ArH, isomer 4), 7.68 (s, 2 × 2H, ArH, isomers 1 and 2), 7.78 (s, 4H, ArH, isomer 3), 7.89 (s, 2 × 4H, ArH, isomers 1 and 2) ppm. The ^{19}F NMR spectrum of **8** revealed the presence of three isomers in about 1.00:0.39:0.25 ratios in solution as estimated from the integrals of CF_3 fluorine. ^{19}F NMR (CD_3OD, 376.5 MHz, 298 K): δ = –64.83, –64.81, –64.77

(each s, 3 × 6F, CF_3, isomers 1–3 respectively), –64.54, –64.45, –64.38 (each s, 3 × 12F, CF_3, isomers 1–3 respectively) ppm. Λ_m (Ω^{-1} cm^2 mol^{-1}, MeCN): 90.6 (10^{-3} M).

[(η^6-*p*-cymene)Ru(N_3C_2(COOEt)$_2$){κ^2(*N*,*N*′)((ArN)$_2$C–N(H)Ar}] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$; 9) Complex **5** (50.0 mg, 0.051 mmol) was dissolved in CH_2Cl_2 (5 mL) in a 25 mL RB flask. To the aforementioned solution, a CH_2Cl_2 (5 mL) solution of DEAD (26.3 mg, 0.154 mmol) was slowly added, and stirred at RT for 24 h. The reaction mixture was concentrated under vacuum to about 2 mL, layered with *n*-hexane (5 mL) and the resulting solution stored at RT for 24 h to afford **9** as yellow crystals. Yield: 86% (50.5 mg, 0.044 mmol). Mp: 229 °C (decompn). Anal. Calcd for $C_{43}H_{34}F_{18}N_6O_4Ru$ (M_w: 1141.82): C, 45.23; H, 3.00; N, 7.36. Found: C, 45.12; H, 3.32; N, 7.51. IR (KBr): $\bar{\nu}$ = 3295 (m, NH), 1731 (s, C=O), 1573 (m, C=N), 1376 (s, CF_3, str, asym), 1275 (s, CF_3, str, sym), 1174 (s, CF_3, def, asym), 900 (w, CF_3, str, sym) cm^{-1}. The ^{1}H NMR spectrum of **9** revealed the presence of two isomers (major/minor) in about 1.00:0.05 ratio as estimated from the integrals of aromatic protons of the *p*-cymene ring. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 1.156 (d, $J_{H,H}$ = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$, major), 1.164 (d, $J_{H,H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$, minor), 1.243 (t, $J_{H,H}$ = 6.8 Hz, 2 × 3H, CH_2C*H*$_3$, major), 1.250 (t, $J_{H,H}$ = 7.4 Hz, 2 × 3H, CH_2C*H*$_3$, minor), 1.808, 2.128 (each s, 2 × 3H, C*H*$_3$, major and minor respectively), 2.760 (m, 2 × 1H, C*H*Me$_2$, major and minor), 4.278, 4.285 (each q, $J_{H,H}$ = 7.2 Hz, 2H, C*H*$_2$CH$_3$, major and minor respectively), 5.274 (d, $J_{H,H}$ = 6.0 Hz, 2H, C_6H_4, minor), 5.426 (d, $J_{H,H}$ = 8.8 Hz, 2H, C_6H_4, minor), 5.445 (d, $J_{H,H}$ = 6.4 Hz, 2H, C_6H_4, major), 5.619 (d, $J_{H,H}$ = 5.2 Hz, 2H, C_6H_4, major), 7.115 (br, 1H, N*H*, minor), 7.176 (s, 1H, N*H*, major), 7.207 (s, 1H, Ar*H*, major), 7.243 (s, 2H, Ar*H*, major), 7.256 (s, 1H, Ar*H*, minor), 7.268 (s, 2H, Ar*H*, minor), 7.319 (s, 4H, Ar*H*, major), 7.376 (s, 2H, Ar*H*, major), 7.426 (br, 2H, Ar*H*, minor), 7.552 (s, 4H, Ar*H*, minor) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ = 14.0 (CH_2CH_3), 19.0 (*C*H$_3$), 22.6 (CH(*C*H$_3$)$_2$), 31.3 (*C*HMe$_2$), 61.0 (*C*H$_2$CH$_3$), 81.7, 83.4, 98.5, 103.7 (*p*-cymene Ar*C*H/Ar*C*), 116.7 (br), 120.4

(br), 122.7 (q, $J_{C,F}$ = 273.1 Hz, *C*F_3), 123.0 (q, $J_{C,F}$ = 272.8 Hz, *C*F_3), 123.8, 132.2 (q, $J_{C,F}$ = 33.5 Hz, *C*CF_3), 132.3 (q, $J_{C,F}$ = 33.2 Hz, *C*CF_3), 138.3, 140.1, 147.5, 155.7 (Ar*C* and *C*=N), 162.5 (O*C*(O)) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –63.46 (s, 6F, C*F*$_3$), –63.03 (s, 12F, C*F*$_3$) ppm.

[(η^6-*p*-cymene)Ru(PPh$_2$C≡CPPh$_2$){κ^2(*N*,*N*′)((ArN)$_2$C–NAr}] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$; 10)

Complex **5** (100 mg, 0.102 mmol) was dissolved in CH_2Cl_2 (10 mL) in a 25 mL RB flask. To the aforementioned solution, a solution of DPPA (26.3 mg, 0.154 mmol) in CH_2Cl_2 (5 mL) was slowly added, and stirred at RT for 24 h. The volatiles were removed under vacuum to afford an orange solid which was dissolved in *n*-hexane and stored at RT for four days to afford **10** as orange crystals. Yield: 87% (118.6 mg, 0.089 mmol). Mp: 178 °C. Anal. Calcd for $C_{61}H_{43}F_{18}N_3P_2Ru$ (M_w: 1023.00): C, 55.38; H, 3.28; N, 3.18. Found: C, 55.70; H, 3.65; N, 3.52. IR (KBr): $\bar{\nu}$ = 1536 (m, C=N), 1373 (s, CF_3, str, asym), 1280 (s, CF_3, str, sym), 1126 (m, CF_3, def, asym), 909 (w, CF_3, str, sym) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 1.05 (d, $J_{H,H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.75 (s, 3H, C*H*$_3$), 2.34 (m, 1H, C*H*Me$_2$), 4.96 (d, $J_{H,H}$ = 5.6 Hz, 2H, C$_6$*H*$_4$), 5.31 (d, $J_{H,H}$ = 6.0 Hz, 2H, C$_6$*H*$_4$), 6.73 (s, 2H, Ar*H*), 6.82 (s, 1H, Ar*H*), 7.09 (s, 2H, Ar*H*), 7.27 (m, 3H, Ar*H*), 7.34–7.40 (m, 8H, Ar*H*), 7.53–7.65 (m, 13H, Ar*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ = 18.28 (*C*H$_3$), 22.51 (CH(*C*H$_3$)$_2$), 30.97 (*C*HMe$_2$), 86.61, 88.62, 88.66 (*p*-cymene Ar*C*H/Ar*C*), 99.68, 100.48 (each d, $J_{C,P}$ = 5.7, 4.8 Hz respectively, Ph$_2$P*CC*PPh$_2$), 102.84, 111.19 (br), 111.95 (br), 112.71, 113.04, 113.47, 113.55, 121.25, 121.69, 123.78 (q, $J_{C,F}$ = 272.7 Hz, *C*F_3), 123.83 (q, $J_{C,F}$ = 272.7 Hz, *C*F_3), 125.16 (br), 127.88 (br), 128.92, 129.03, 129.10, 129.18, 130.07, 130.68 (q, $J_{C,F}$ = 32.6 Hz, *C*CF_3), 130.70, 131.08 (q, $J_{C,F}$ = 33.6 Hz, *C*CF_3), 131.52, 131.99, 132.11, 133.06, 133.27, 133.44, 133.50, 149.2, 152.0, 161.6 (Ar*C* and *C*=N) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 298 K): δ = –63.03 (s, 6F, C*F*$_3$), –62.72 (s, 12F, C*F*$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz, 298 K): δ = 18.05 (s, 1P, uncoordinated), –31.34 (s, 1P, coordinated) ppm.

Procedure forRuAAC A mixture of phenylacetylene (102.2 mg, 1.000 mmol), 4-tolyl azide (66.6 mg, 0.500 mmol) was dissolved in CH_2Cl_2 (5.0 mL) in a 10 mL RB flask. To the aforementioned flask, 1 mol % of the catalyst was added and stirred at RT for 30 min. Subsequently, 10 mol % of AgOAc (83.2 mg, 0.05 mmol) was added to the flask and stirred at RT for 24 h under dark. The reaction mixture was kept at RT for several days to afford **23** as colorless crystals suitable for SCXRD. The % conversion and the relative ratio of **23** and **24** in the reaction mixture were estimated by ^{1}H NMR spectroscopy. The reaction mixture was subjected to column chromatography on silica gel using ethyl acetate/*n*-hexane mixture (5/95, v/v) as eluent to afford **23** for the following data. Yield: 62% (73.0 mg, 0.31 mmol).

Characterization Data of 23 Mp: 167.0 °C (Mp 165.0–167 °C[36]). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 2.43 (s, 3H, C*H*$_3$), 7.32–7.38 (m, 3H, Ar*H*), 7.46 (t, $J_{H,H}$ = 7.4 Hz, 2H, Ar*H*), 7.66 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 7.90–7.92 (m, 2H, Ar*H*), 8.16 (s, 1H, Ar*H*, triazole ring proton) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ = 21.2 (*C*H$_3$), 117.8, 120.6, 126.0, 128.5, 129.0, 130.4, 130.5, 134.9, 139.0, 148.4 (Ar*C*H/Ar*C*) ppm. ^{1}H and ^{13}C{^{1}H} NMR data reported herein closely matched with those reported in the literature.[47]

Supporting Information

General considerations, details pertinent to data collections, structure solution, and refinements of the crystallographically characterized compounds are presented in Tables S1–S3. Possible solution species of compound such as **1**, non-covalent interactions in the crystal lattice of **4**, **5**·MeOH, **6** and **7**·$CHCl_3$ and molecular structure of **23** are illustrated in Figures S2–S6 in the SI. Structural data in CIF format is available as the SI. CCDC 1896082–1896092 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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