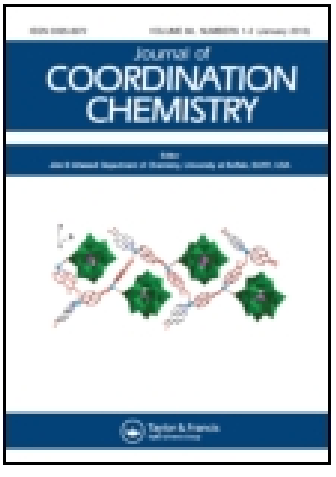


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Iridium (III) and rhodium (III) triazoles by 1,3-dipolar cycloadditons to a coordinated azide in iridium (III) and rhodium (III) compounds

Keisham S. Singh[a] & Werner Kaminsky[b]
[a] Bioorganic Chemistry Laboratory, CSIR-National Institute of Oceanography, Goa, India
[b] Department of Chemistry, University of Washington, Seattle, WA, USA

Accepted author version posted online: 02 Sep 2014.Published online: 29 Sep 2014.

To cite this article: Keisham S. Singh & Werner Kaminsky (2014) Iridium (III) and rhodium (III) triazoles by 1,3-dipolar cycloadditons to a coordinated azide in iridium (III) and rhodium (III) compounds, Journal of Coordination Chemistry, 67:19, 3252-3269, DOI: 10.1080/00958972.2014.960408

To link to this article: http://dx.doi.org/10.1080/00958972.2014.960408

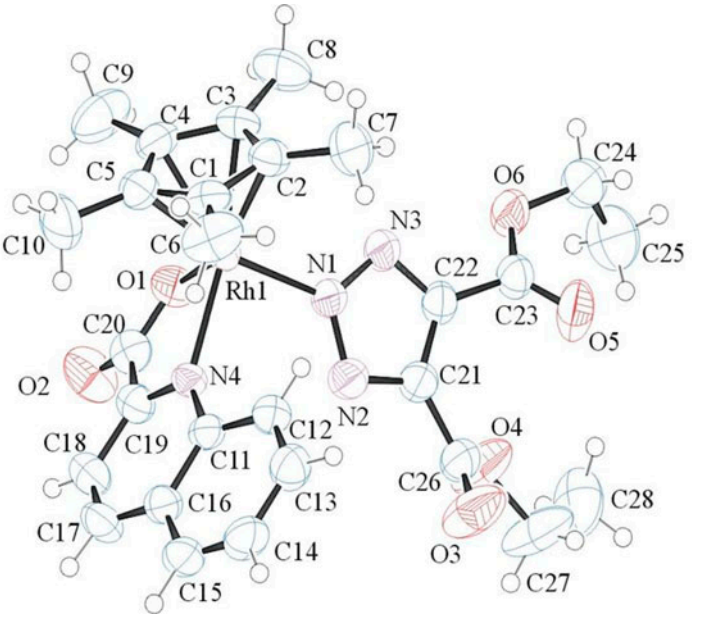
Journal of Coordination Chemistry, 2014
Vol. 67, No. 19, 3252–3269, http://dx.doi.org/10.1080/00958972.2014.960408

Iridium (III) and rhodium (III) triazoles by 1,3-dipolar cycloadditons to a coordinated azide in iridium (III) and rhodium (III) compounds

KEISHAM S. SINGH*† and WERNER KAMINSKY‡

†Bioorganic Chemistry Laboratory, CSIR-National Institute of Oceanography, Goa, India
‡Department of Chemistry, University of Washington, Seattle, WA, USA

(*Received 3 July 2014; accepted 26 August 2014*)



Azido complexes of general formula $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)N_3]$ have been prepared by the reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)(X)]_2$ (M = Ir or Rh and X = Cl or N_3) with the corresponding ligands or by the direct reaction of $[\{(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl\}]$ with NaN_3 ($L^{\cap}L$ = $N^{\cap}O$ or $O^{\cap}O$ chelate ligands). The azido complexes $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)N_3]$ undergo 1,3-dipolar cycloaddition reaction with substituted alkynes in CH_2Cl_2 and ethanol at room temperature giving iridium (III) or rhodium (III) triazoles $[(\eta^5\text{-}C_5Me_5)M\ (L^{\cap}L)\{N_3C_2(CO_2R)_2\}]$.

The reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu Cl)Cl]_2$ with the ligand ($L^{\cap}L$) in the presence of sodium methoxide yielded compounds of general formula $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl]$ (**1–10**) (where M = Ir or Rh and $L^{\cap}L$ = $N^{\cap}O$ or $O^{\cap}O$ chelate ligands). Azido complexes of formulation $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)N_3]$

*Corresponding author. Email: keisham@nio.org

(**11–20**) have been prepared by the reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)(X)]_2$ (X = Cl or N_3) with the corresponding ligands or by the direct reaction of $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl]$ with NaN_3. These azido complexes $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)N_3]$ undergo 1,3-dipolar cycloaddition reaction with substituted alkynes in CH_2Cl_2 and for the first time in ethanol at room temperature to yield iridium (III) and rhodium (III) triazoles (**21–28**). The compounds were characterized on the basis of spectroscopic data, and the molecular structures of **2** and **26** have been established by single crystal X-ray diffraction.

Keywords: Cycloaddition; Triazoles; Rhodium; Iridium; Kojic acid; Azide

1. Introduction

Half-sandwich iridium (III) and rhodium (III) complexes have received attention in the past few decades owing to their catalytic activities [1–6] and biological properties [7, 8]. Optically active half-sandwich metallocene complexes of rhodium (III) and iridium (III) have shown ability to act as active stereospecific catalysts [9]. Other Cp*M compounds, such as the cationic iridium complex, $[(\eta^5\text{-}C_5Me_5)IrMe(PMe_3)(ClCH_2Cl)]^+[BAr_4]^-$ (Ar = aryl), exhibit interesting reactivity in C–H activation reactions of various functionalized substrates at ambient temperature [10]. The Cp*M complexes were extensively explored in various catalytic reactions *namely,* hydrogenation [3], asymmetric catalysis [4], and more recently in the reactions involving C–H activation [5, 6]. In biology, both the Cp* iridium (III) and rhodium (III) complexes bearing polypyridyl ligands have shown DNA intercalating properties [11–13], while iridium (III) [7] and rhodium (III) [8] complexes with N,N chelate ligands have exhibited anticancer properties. Because of their increasing applications in biology and catalysis, synthesis of new iridium (III) or rhodium (III) complexes is highly desirable.

Triazole compounds have found wide application in medicinal chemistry [14]. Ready access to these triazoles and derivatives follows the 1,3-dipolar cycloaddition between an azide and alkynes [15–17]. Cycloaddition reaction between a coordinated azide in metal complexes and nitriles [18, 19] or isonitrile [20, 21] produced tetrazoles. Similar reactions with alkynes produced triazolate complexes; alkenes, however, reacted very slowly and resulted in a mixture of products [22]. Cycloaddition of (η^6-arene) ruthenium (II) azido complexes with alkynes is well documented [23–25]. In our previous studies, we found that such reactions are favorable with neutral complexes of the type $[(\eta^6\text{-arene})Ru(L^{\cap}L)N_3]$ (where $L^{\cap}L$ = $O^{\cap}O$ or $N^{\cap}O$ chelate ligands), but proved unfavorable with unchelated complexes, for example, $[(\eta^6\text{-arene})Ru(PTA)N_3Cl]$ (where η^6-arene = *p*-cymene or C_6Me_6 and PTA = 1,3,5-triazo-7-phosphaadamantane) [23]. Therefore, synthesis of terminal azido complexes of the type $[(L^3)M(L^{\cap}L)N_3]$ (L^3 = η^6-arene or η^5-Cp* and $L^{\cap}L$ = $O^{\cap}O$ or $N^{\cap}O$, $S^{\cap}N$ chelate ligands, etc.) is desirable for the study of cycloaddition reactions between coordinated azide and alkynes in half-sandwich systems. Keeping this in mind, we became interested in the synthesis of iridium and rhodium complexes of the type $[(\eta^5\text{-Cp*})M(L^{\cap}L)N_3]$ and their cycloaddition reactions with alkynes. To the best of our knowledge, only one report has been given for the synthesis of Cp* iridium azido complex of the above-mentioned type, for example, $[(\eta^5\text{-}C_5Me_5)Ir(S^{\cap}N)(N_3)]$ by Suzuki and coworkers (where $S^{\cap}N$ = 2-quinolene thiolate) [26].

Although dipolar addition of coordinated metal azide and alkynes has been extensively studied in (η^6-arene) ruthenium (II) azido complexes [23–25], similar reactions for Cp* iridium (III) and rhodium (III) azido complex are relatively unexplored. Rigby *et al.* [19] reported the 1,3-dipolar cycloaddition of nitriles with the *in situ* generated dimeric azido compound $[(\eta^5\text{-}C_5Me_5)Rh(\mu N_3)(N_3)]_2$. However, to date, no report appeared for the

cycloaddition of metal-coordinated azide and alkynes in Cp* iridium (III) and rhodium (III) scaffolds containing $N^{\cap}O$ or $O^{\cap}O$ chelate ligands. Further, most of the cycloaddition reactions of coordinated metal azides and alkynes were conducted in dichloromethane [23–25, 27–29]; by contrast, such reactions performed in ethanol, a less-toxic solvent, are not known. In this article, we wish to report the synthesis of a series of water-soluble complexes of general formula $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)(N_3)]$ (where $L^{\cap}L = N^{\cap}O$ or $O^{\cap}O$ chelate ligand) and their cycloaddition reaction with alkynes in dichloromethane and ethanol. The compounds were spectroscopically characterized, and the molecular structures of **2** and **26** were determined by single crystal X-ray diffraction.

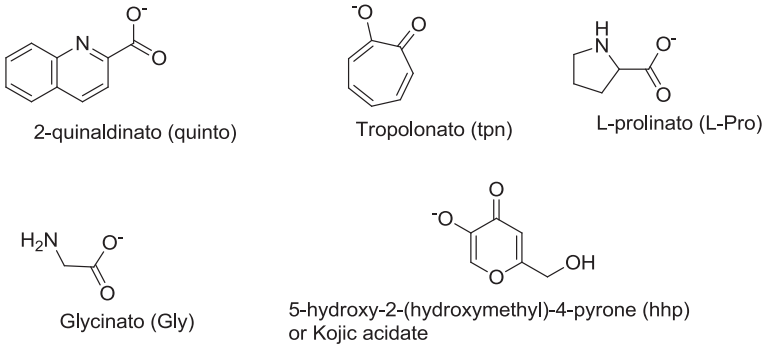
2. Experimental

2.1. *General remarks*

All solvents were of analytical grade and used as received. $IrCl_3 \cdot 3H_2O$ and $RhCl_3 \cdot 3H_2O$ were purchased from Arrora Matthey Ltd, India. 5-Hydroxy-2-(hydroxymethyl)-4-pyrone (kojic acid), tropolone, quinaldic acid, L-proline, and sodium salt of glycine were obtained from Sigma Aldrich Pvt Ltd and used as received. FTIR spectra were recorded in a diffuse reflection spectroscopy assembly (DRS) on a Shimazdzu PC-1380 spectrometer with samples prepared in KBr. NMR spectra were recorded on a Bruker 300 MHz spectrometer at 300.13 (^{1}H), 75.47 MHz (^{13}C) with $SiMe_4$ as internal reference, and coupling constants are given in hertz. The precursor compounds $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$ [30, 31], $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)Cl]_2$, and $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)(N_3)]_2$ (M = Ir, Rh) [19, 26] were prepared by following a published method. The ligands used in this study are shown in scheme 1.

2.2. *Synthesis of complexes*

2.2.1. Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(L^{\cap}L)Cl]$ {$L^{\cap}L$ = qunito (1), tpn (2), L-pro (3), Gly (4), hhp (5)}. All these complexes were prepared by a general procedure as delineated here. A mixture of ligand (0.276 mM) and NaOMe (0.015 g, 0.276 mM) was stirred in MeOH (5 mL) at room temperature for a few minutes. To this solution, $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$



Scheme 1. Chemical structures of ligands used in the study.

(0.1 g, 0.125 mM) and 30 mL methanol were added and then the mixture was stirred for 5 h (in the case of **4,** sodium salt of glycine and acetone were used). The orange solution turned bright yellow. The solvent was removed under reduced pressure. The yellow solid was extracted with dichloromethane and filtered to remove the insoluble materials. The filtrate on subsequent concentration to *ca.* 3 mL and addition of hexane afforded a bright yellow solid.

Yield and spectroscopic data are as follows:

Complex **1**

Yield: 0.096 g (72%).

FTIR (KBr, cm^{-1}): 1658 (C=O), 1456, and 1332.

^1H ($CDCl_3$, δ): 8.46 (d, 1H, $J = 8.7$), 8.40 (d, 1H, $J = 8.4$), 8.22 (d, 1H, $J = 8.4$), 7.98 (d, 1H, $J = 8.1$), 7.90 (t, 1H, $J = 6.9$), 7.78 (t, 1H, $J = 7.2$), and 1.66 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 172.91, 152.47, 144.53, 139.79, 131.30, 130.07, 130.01, 129.31, 128.68, 123.19, 86.76 (ring carbons, Cp*), and 9.12 (CH_3, Cp*).

Complex **2**

Yield: 0.098 g (81%).

FTIR (KBr, cm^{-1}): 1647, 1591, and 1433.

^{1}HNMR ($CDCl_3$, δ): 7.35 (m, 4H), 6.80 (m, 1H), and 1.74 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 184.83, 137.10, 127.21, 126.49, 82.92 (ring carbons, Cp*), and 9.12 (CH_3, Cp*).

Complex **3**: The complex was prepared by following a procedure described for **1** using L-proline.

Alternative method: The complex was also prepared following a published method [1]. To a round-bottom flask, $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (0.1 g, 0.125 mM), L-proline (0.029 g, 0.25 mM), and K_2CO_3 were suspended in acetonitrile. The mixture was stirred overnight, and then, the crude product was concentrated under vacuum and suspended in CH_2Cl_2. The solution was filtered, and n-pentane was added giving the complex as a yellow orange solid.

Yield: 0.086 g (72%).

^{1}HNMR ($CDCl_3$, δ): 4.39 (m, 1H), 3.87 (m, 1H), 3.6 (br s, 1H), 2.87 (m, 1H), 1.98 (br s, 4H), and 1.69 (s, 15H, Cp*).

Complex **4**: The complex was prepared following procedure described for **3** using glycine or sodium salt of glycine instead of L-proline.

Yield: 0.073 g (66%).

IR (KBr, cm^{-1}): 1583 and 1382.

^{1}HNMR ($CDCl_3$, δ): 4.75 (br s, 2H) and 1.72 (s, 15H, Cp*).

Complex **5**

Yield: 0.11 g, (87%); ^{1}H NMR ($CDCl_3$, δ): 7.71 (s, 1H, hhp), 6.67 (s, 1H, hhp), 4.46 (s, 2H, hhp), and 1.71 (s, 15H, Cp*).

2.2.2. Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(L^{\cap}L)Cl]$ {$L^{\cap}L$ = qunito (6), tpn (7), L-pro (8), Gly (9), hhp (10)}. A mixture of ligand (0.340 mM) and NaOMe (0.021 g, 0.340 mM) was stirred in MeOH (30 mL) at room temperature for a few minutes. To this solution,

$[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ (0.1 g, 0.162 mM) was added and then the mixture was stirred for additional 4 h (in the case of **9**, sodium salt of glycine was used). During the course of the reaction, the orange solution turned bright yellow. The solvent was removed under reduced pressure, and then the yellow solid was extracted with dichloromethane and filtered to remove the insoluble materials. The filtrate on subsequent concentration to *ca.* 3 mL and addition of hexane afforded a bright yellow solid.

Yield and spectroscopic data are as follows:

Complex **6**
Yield: 0.11 g (76%).
IR (KBr, cm^{-1}): 1649, 1332, and 1178.
^1H NMR ($CDCl_3$, δ): 8.47 (d, 1H, $J = 8.7$), 8.41 (d, 1H, $J = 8.4$), 8.26 (d, 1H, $J = 8.4$), 7.98 (d, 1H, $J = 8.1$), 7.91 (t, 1H, $J = 8.4$), 7.75 (t, 1H, $J = 7.2$), and 1.68 (t, 15H, $J = 10.8$, Cp*).

Complex **7**
Yield: 0.11 g (87%).
IR (KBr, cm^{-1}): 1589, 1506, 1433, and 1357.
^1H NMR ($CDCl_3$, δ): 7.20 (m, 4H), 6.74 (m, 1H), and 1.75 (s, 15H, Cp*).

Complex **8**
This complex was prepared by following a similar procedure described for **3** in two routes.
Yield: 0.079 g (63%).
IR(KBr, cm^{-1}): 1610.
^1H NMR ($CDCl_3$, δ): 4.22 (br s, 1H), 3.88 (m, 1H), 3.60 (m, 1H), 2.87 (m, 1H), 2.06 (m, 4H), and 1.70 (s, 15H, Cp*).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 181.67, 93.04 (ring carbons, Cp*), 63.81, 52.18, 28.66, 26.56, and 9.13 (CH_3, Cp*).

Complex **9**
Yield: 0.072 g (64%).
^1H NMR ($CDCl_3$, δ): 4.95 (br s, 2H), 3.39 (m, 2H), and 1.74 (s, 15H, Cp*).

Complex **10**
Yield: 0.11 g (82%).
^1H NMR ($CDCl_3$, δ): 7.65 (s, 1H, hhp), 6.57 (1H, hhp), 4.45 (m, 2H), and 1.73 (s, 15H, Cp*). ^{13}C $\{^1H\}$ ($CDCl_3$, δ): 185.23, 159.45, 141.18, 108.14, 91.59, 60.79, and 9.38.

2.2.3. Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(L^{\cap}L)N_3]$ $\{L^{\cap}L$ = qunito (11), tpn (12), L-pro (13), Gly (14), hhp (15)$\}$. These complexes were prepared by following two routes:

Route (*a*): To a stirring solution of ligand (0.132 mM) and NaOMe (mM) in MeOH (30 mL) was added $[Cp^*Ir(\mu N_3)Cl]_2$ (0.05 g, 0.06 mM), and the mixture was stirred at room temperature for 4 h. During the course of reaction, the color of the solution changed from red to yellow, after which the solution was rotary evaporated and the residue was dissolved in CH_2Cl_2 and then filtered to remove insoluble salts. The filtrate was concentrated to *ca.* 5 ml, and then, excess diethyl ether was added whereby the complexes precipitated

as a yellow orange solid. Yield: **11** (0.052 g, 78%), **12** (0.046 g, 75%), **13** (0.042 g, 71%), **14** (0.037 g, 68%), and **15** (0.04 g, 63%).

Route (*b*): The complex $[(\eta^5\text{-}C_5Me_5)Ir(L^{\cap}L)Cl]$ (0.1 mM) and NaN_3 (0.2 mM) in EtOH (20 mL) were stirred for 4 h. The solution was rotary evaporated, and then, the residue was extracted with dichloromethane. The solution was filtered to remove insoluble materials. To this filtrate, excess hexane was added and left at room temperature whereby compound precipitated. The solid formed was filtered and washed with hexane.

Yield: **11** (0.042 g, 78%), **12** (0.041 g, 84%), **13** (0.035 g, 72%), **14** (0.031 g, 70%), and **15** (0.035 g, 69%).

Spectroscopic data:

Complex **11**

IR (KBr, cm^{-1}): 2029 (νN_3).

^1H NMR ($CDCl_3$, δ): 8.43 (d, 1H, $J = 8.4$), 8.37 (d, 1H, $J = 8.7$), 8.23 (d, 1H, $J = 8.4$), 7.97 (m, 2H), 7.81 (t, 1H, $J = 6.9$), and 1.68 (m, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 173.20 (C=O), 152.50, 144.38, 140.38, 131.74, 131.02, 129.57, 129.29, 128.89, 123.38, 85.64 (ring carbons, Cp*), and 8.83 (CH_3, Cp*).

Complex **12**

IR (KBr, cm^{-1}): 2031 (νN_3).

^1H NMR ($CDCl_3$, δ): 7.32 (m, 4H), 6.81 (m, 1H), and 1.74 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 184.54 (C=O), 137.25, 127.17, 126.69, 82.74 (ring carbons, Cp*), and 8.67(CH_3, Cp*).

Complex **13**

IR (KBr, cm^{-1}): 2031 (νN_3).

^1H NMR ($CDCl_3$, δ): 4.71 (br s, 1H), 3.89 (br, 1H), 3.54 (m, 1H), 2.90 (m, 1H), and 2.19–1.94 (m, 4H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 184.74 (C=O), 83.97 (ring carbons, Cp*), 62.39, 54.45, 28.99, 26.92, and 8.68 (CH_3, Cp*).

Complex **14**

IR (KBr, cm^{-1}): 2036 (νN_3).

^1H NMR ($CDCl_3$, δ): 3.32 (br s, 2H) and 1.59 (15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 186.46, 84.98 (ring carbons, Cp*), 44.30 (CH_2, Gly), and 7.68 (CH_3, Cp*).

Complex **15**

IR (KBr, cm^{-1}): 2036 (νN_3).

^1H NMR ($CDCl_3$, δ): 7.71 (s, 1H), 6.66 (s, 1H), 4.45 (s, 2H), and 1.73 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 184.23, 59.22, 142.41, 108.78, 82.23 (ring carbons, Cp*), 61.23, and 8.81(CH_3, Cp*).

2.2.4. Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(L^{\cap}L)N_3]$ {$L^{\cap}L$ = qunito (16), tpn (17), L-pro (18), Gly (19), hhp (20)}. The complexes were prepared by following two routes (a) using $[Cp^*Rh(\mu N_3)Cl]_2$ (0.05 g, 0.079 mM) instead of $[Cp^*Ir(\mu N_3)Cl]_2$ and (b) using $[(\eta^5\text{-}C_5Me_5)Rh(L^{\cap}L)Cl]$ (0.1 mM) instead of $[(\eta^5\text{-}C_5Me_5)Ir(L^{\cap}L)Cl]$ as described for **10–15**. Yield: *Route* (*a*): **16** (0.051 g, 72%), **17** (0.052 g, 81%), **18** (0.048 g, 77%), **19**

(0.036 g, 64%), and **20** (0.045 g, 68%). *Route* (*b*): **16** (0.032 g, 71%), **17** (0.35 g, 88%), **18** (0.031, 79%), **19** (0.025 g, 71%), and **20** (0.032 g, 77%).

Spectroscopic data:

Complex **16**

IR (KBr, cm^{-1}): 2023 (νN_3).

^1H NMR ($CDCl_3$, δ): 8.44 (d, 1H, $J = 8.1$), 8.30 (t, 2H, $J = 8.4$), 8.02–7.93 (m, 2H), 7.80 (t, $J = 7.2$), and 1.72 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 170.52 (C=O), 154.34, 144.82, 139.96, 131.52, 130.85, 129.15, 129.00, 128.37, 123.24, 94.01(ring carbons, Cp*), and 8.75 (CH_3, Cp*).

Complex **17**

IR (KBr, cm^{-1}): 2017 (νN_3).

^1H NMR ($CDCl_3$, δ): 7.21 (d, 4H, $J = 5.1$), 6.76 (sept, 1H, $J = 5.1$), and 1.74 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 184.24 (C=O), 137.12, 126.17, 126.26, 82.72 (ring carbons, Cp*), and 8.26 (CH_3, Cp*).

Complex **18**

IR (KBr, cm^{-1}): 2027 (νN_3).

^1H NMR ($CDCl_3$, δ): 4.46 (s, 1H), 3.70 (m, 2H), 2.80 (m, 1H), 2.05–1.98 (m, 4H), and 1.71 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 181.62 (C=O), 92.69 (ring carbons, Cp*), 63.19, 52.19, 28.81, 26.55, and 8.52 (CH_3, Cp*).

Complex **19**

IR (KBr, cm^{-1}): 2029 (νN_3).

^1H NMR ($CDCl_3$, δ): 3.26 (s, 2H) and 1.62 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 183.75, 93.80 (ring carbons, Cp*), 44.98, and 8.14 (CH_3, Cp*).

Complex **20**

IR (KBr, cm^{-1}): 2023 (νN_3).

^1H NMR ($CDCl_3$, δ): 7.66 (s, 1H), 6.57 (s, 1H), 4.44 (s, 2H), and 1.71 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 185.28, 141.23, 108.21, 91.57 (ring carbons, Cp*), 60.93, and 8.92 (CH_3, Cp*).

2.2.5. Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(L^{\cap}L)\{N_3C_2(CO_2R)_2\}]$ {M = Ir, $L^{\cap}L$ = quinto, R = Me (21), Et (22), $L^{\cap}L$ = tpn, R = Me (23), Et (24)}. The complexes were prepared by following a general procedure.

(a) To a round-bottom flask charged with **11** or **12** (0.06 mM), dimethyl acetylenedicarboxylate (DMD) or diethylacetylene dicarboxylate (DED) (fourfold excess) and CH_2Cl_2 (20 mL) were added and then the reaction mixture was stirred at room temperature for 15 h. The solution was reduced to *ca.* 3 mL in a rotary evaporator, and to this solution was added 30 mL of hexane, whereby the compound precipitated as a yellow solid. The yellow solid was filtered and washed with hexanes (2 × 10 mL) and dried under vacuum.

Yield: **21** (0.032 g, 80%), **22** (0.036 g, 86%), **23** (0.03 g, 79%); and **24** (0.30 g, 76%).

(b) Alternatively, **21–26** were prepared by the reaction of azido complexes and alkynes in ethanol (20 mL) at room temperature. In this case, the solution was rotary evaporated, the residue was dissolved in a minimum amount of CH_2Cl_2, and then excess hexane was added to induce precipitation as yellow solid. The yellow solid was filtered and washed with hexanes (2 × 10 mL) and dried under vacuum.

Yield: **21** (0.033 g, 82%), **22** (0.035 g, 83%); **23** (0.03 g, 79%), and **24** (0.032 g, 81%).
Spectroscopic data of the complexes are as follows:

Complex **21**
IR (KBr, cm^{-1}): 1726 ($\nu_{C=O}$) and 1668.
^1H NMR ($CDCl_3$, δ): 8.37 (d, 1H, J = 8.4), 8.23 (d, 2H, J = 7.8), 7.90 (d, 1H, J = 7.8), 7.79 (t, 1H, J = 7.4), 7.68 (t, 1H, J = 7.2), 3.75 (s, 6H), and 1.67 (s, 15H, Cp*).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 174.11, 162.81, 152.46, 144.31, 140.14, 139.76, 131.49, 131.39, 129.46, 129.31, 128.64, 123.47, 87.46 (ring carbons, Cp*), 51.71 (OCH_3), and 9.01 (CH_3, Cp*).

Complex **22**
IR (KBr, cm^{-1}): 1724 ($\nu_{C=O}$) and 1664.
^1H NMR ($CDCl_3$, δ): 8.33 (d, 1H, J = 8.4), 8.26 (d, 1H, J = 8.7), 8.18 (d, 1H, J = 8.1), 7.87 (d, 1H, J = 8.1), 7.79 (t, 1H, J = 8.1), 7.64 (t, 1H, J = 8.4), 4.21 (qt, 4H, J = *7.2*), 1.66 (s, 15H, Cp*), and 1.24 (t, 6H, J = *7.2*).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 174.03, 162.55, 152.93, 144.22, 140.07, 139.98, 131.43, 130.91, 129.53, 129.33, 128.38, 123.40, 87.44 (ring carbons, Cp*), 60.59, 14.08, and 9.03 (CH_3, Cp*).

Complex **23**
IR (KBr, cm^{-1}): 1726 ($\nu_{C=O}$) and 1589.
^1H NMR ($CDCl_3$, δ): 7.31–7.29 (m, 4H), 6.83 (m, 1H, 3.81 (s, 6H), and 1.70 (s, 15H, Cp*).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 185.04, 162.91, 140.14, 137.19, 126.92, 84.51 (ring carbons, Cp*), 51.68, and 8.91 (CH_3, Cp*).

Complex **24**
IR (KBr, cm^{-1}): 1724 ($\nu_{C=O}$) and 1589.
^1H NMR ($CDCl_3$, δ): 7.34–7.29 (m, 4H, 6.84 (m, 1H), 4.28 (qt, 4H, J = 6.9), 1.73 (s, 15H, Cp*) and 1.27 (m, 6H).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 185.21, 162.62, 137.14, 127.21, 126.85, 126.72, 84.50 (ring carbons, Cp*), 60.41 (–CH_2–, OEt), 14.13 (CH_3, OEt), and 8.89 (CH_3, Cp*).

2.2.6. Preparation of [(η^5-C_5Me_5)Rh($L^{\cap}L$){$N_3C_2(CO_2R)_2$}]{ $L^{\cap}L$ = quinto, R = Me (25), Et (26); $L^{\cap}L$ = tpn, R = Me (27), Et (28)}. These complexes were prepared by following a similar procedure as described for **21–24** using **16** or **17** and alkynes (4 fold excess) in (a) CH_2Cl_2 or (b) EtOH.

Route (*a*): Yield: **25** (0.03 g, 84%), **26** (0.029 g, 78%), **27** (0.027 g, 83%), and **28** (0.027 g, 79%).

Route (*b*): Yield: **25** (0.029 g, 81%), **26** (0.028 g, 76%), **27** (0.026 g 80%), and **28** (0.026 g 76%).

Spectroscopic data are as follows:

Complex **25**

IR (KBr, cm^{-1}): 1724 ($\nu_{C=O}$) and 1658.

^1H NMR ($CDCl_3$, δ): 8.95 (d, 1H, $J = 8.4$), 8.35 (d, 1H, $J = 9.3$), 8.31 (m, 1H), 7.92 (d, 1H, $J = 6.3$), 7.80 (m, 1H), 7.65 (m, 1H), 3.75 (s, 6H), and 1.62 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 171.03, 162.95, 153.92, 144.28, 140.14, 139.89, 131.40, 129.75, 129.26, 129.03, 128.47, 123.16, 95.90 (ring carbons, Cp*), 51.75, and 8.84 (CH_3, Cp*).

Complex **26**

IR (KBr, cm^{-1}): 1726 ($\nu_{C=O}$) and 1658.

^1H NMR ($CDCl_3$, δ): 9.01 (d, 1H, $J = 9.0$), 8.33 (m, 2H), 7.95 (m, 1H), 7.86 (d, 1H, $J = 8.7$), 7.69 (m, 1H), 4.23 (qt, 4H, $J = 6.9$), 1.60 (s, 15H, Cp*), and 1.29 (t, 6H, $J = 7.2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 170.67, 162.76, 154.09, 145.08, 140.09, 139.94 131.38, 129.93, 129.24, 128.41, 123.46, 122.93, 95.86 (ring carbons, Cp*), 60.54, 14.11, and 8.86 (CH_3, Cp*).

Complex **27**

IR (KBr, cm^{-1}): 1726 ($\nu_{C=O}$) and 1584.

^1H NMR ($CDCl_3$, δ): 7.21–7.18 (m, 4H), 6.74 (m, 1H), 3.82 (s, 6H), and 1.68 (s, 15H, Cp*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 184.48, 163.07, 140.33, 137.32, 126.37, 126.22, 125.58, 93.22 (ring carbons, Cp*), 51.68, and 8.66 (CH_3, Cp*).

Complex **28**

IR (KBr, cm^{-1}): 1726 ($\nu_{C=O}$) and 1592.

^1H NMR ($CDCl_3$, δ): 7.22–7.19 (m, 4H), 6.75 (m, 1H), 4.28 (qt, 4H, $J = 6.6$), 1.69 (s, 15H, Cp*), and 1.29 (t, 6H, $J = 6.3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 184.46, 162.78, 140.35, 137.35, 126.95, 125.60, 93.23 (ring carbons, Cp*), 60.52, 14.15, and 8.65(CH_3, Cp*).

3. Structure analysis and refinement

X-ray quality crystals of **2** and **26** were grown by slow diffusion of hexane into an acetone solution of **2** or dichloromethane solution of **26**. The X-ray diffraction data were collected at 296 K on a Nonius Kappa CCD FR590 single-crystal X-ray diffractometer, using Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal-to-detector distance was 30 mm, and exposure time was 20 seconds per degree. Data collection was 99.2% for **2** and 99.5% for **26** complete to 25° in θ. The data were integrated and scaled using hkl-SCALEPACK [32]. The structure was solved by the direct methods (SHELXS, SIR97) [33] and refined by full-matrix least squares on F^2 using (SHELXL 97) [34]. The weighting scheme used was $W = 1/[\sigma^2(F_o^2) + 0.0407P^2]$ for **2** and $W = 1/[\sigma^2(F_o^2) + 0.0490P^2]$ for **26**, where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined anisotropically, while hydrogens were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances of 0.95–1.0 Å. Refinement converged at a final $R = 0.0377$ and 0.0324 for **2** and **26**, respectively (for observed data F), and $wR_2 = 0.0887$ and 0.0726 (for unique data F^2). Selected bond lengths and angles and data collection parameters for **2** and **26** are presented in tables 1–3.

Table 1. Selected bond lengths (Å) and angles (°) for **2**.

Bond lengths (Å)			
Ir–C1	2.141(6)	Ir–C2	2.128(7)
Ir–C3	2.129(6)	Ir–C4	2.133(6)
Ir–C5	2.129(7)	Ir–Cl	2.4017(15)
Ir–O1	2.083(4)	Ir–O2	2.101(4)
C11–O1	1.296(6)	C17–O2	1.291(7)
Bond angles (°)			
O1–Ir–O2	76.40(16)	O1–C11–C17	115.1(5)
Ir–O1–C11	116.2(4)	Ir–O2–C17	114.5(4)
O1–Ir–Cl	86.56(12)	O2–Ir–Cl	86.12(12)

Table 2. Selected bond lengths (Å) and angles (°) for **26**.

Bond lengths (Å)			
Rh–C1	2.176(4)	Rh–C2	2.168(3)
Rh–C3	2.130(3)	Rh–C4	2.148(3)
Rh–C5	2.149(3)	Rh–O1	2.094(2)
Rh–N1	2.096(3)	Rh–N4	2.145(3)
C20–O1	1.287(4)	C20–O2	1.215(5)
N1–N2	1.340(4)	N1–N3	1.321(4)
N2–C21	1.335(5)	N3–C22	1.347(4)
C21–C22	1.371(5)	C23–O5	1.205(5)
Bond angles (°)			
O1–Rh–N4	77.26(9)	N4–Rh–N1	88.10(10)
N2–N1–N3	113.7(2)	Rh–O1–C20	115.4(2)
Rh–N4–C19	111.1(2)	Rh–N4–C11	129.5(2)
C22–C23–O5	122.5(3)	C21–C26–O3	125.7(4)
C22–C23–O6	113.9(3)	C21–C26–O4	110.5(4)

4. Results and discussion

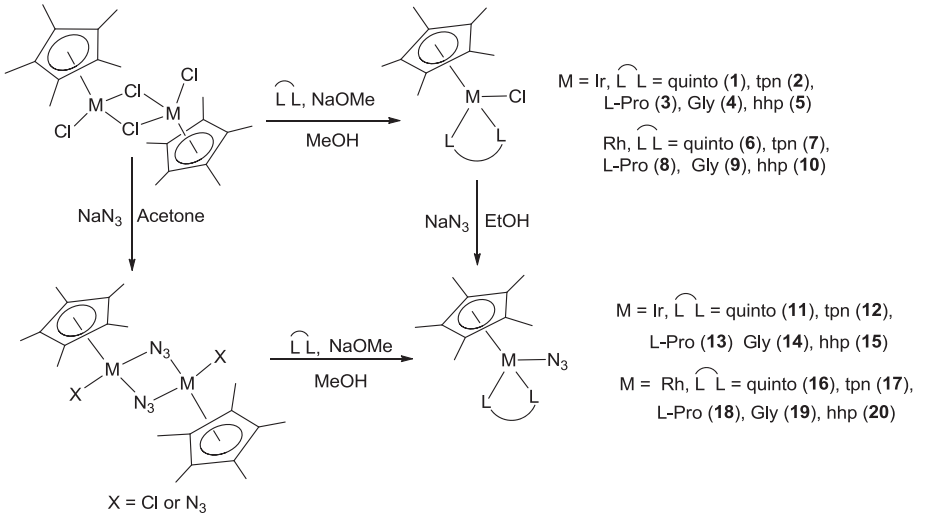
Iridium (III) and rhodium (III) complexes bearing a C_5Me_5 fragment of general formula $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl]$ (**1–10**) have been prepared by the reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu Cl)Cl]_2$ with the corresponding ligand in the presence of NaOMe (scheme 2). The complexes were obtained as a yellow solid in fairly good yield. The complexes were soluble in water and characterized on the basis of NMR spectroscopic data. The NMR spectrum of **1** shows four distinct doublets and two triplets in the aromatic region corresponding to the protons of the quinaldinato ring, while the protons of the Cp* methyl group appeared at δ 1.68. Spectroscopic data of **1–10** are well matched with their formulation and the solid-state structure of **2** established by single-crystal X-ray analysis. Previously, **3** and **4** were prepared by the reaction of $[(\eta^5\text{-}C_5Me_5)Ir(\mu Cl)Cl]_2$ with the corresponding ligand in the presence of K_2CO_3, which requires 15–20 h of reaction time [1]. We have prepared **3** using sodium methoxide and in the case of **4** utilizing the sodium salt of glycine in a comparatively shorter reaction time.

The azido complexes (**11–20**) were then prepared by the reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)Cl]_2$ with the corresponding ligand in the presence of NaOMe. The formation of these complexes was readily followed from their infrared spectra. The infrared spectra showed disappearance of starting compounds azide peaks at 2046 and 2057 cm^{-1} for rhodium and iridium azide complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu N_3)Cl\}_2]$ (M = Rh or Ir), and new peaks appeared at 2019 and 2034 cm^{-1} corresponding to the terminal azide stretching frequencies

Table 3. Summary of crystal structure determination and refinement parameters for **2** and **26**.

	Complex **2**	Complex **26**
Empirical formula	$C_{17}H_{20}ClIrO_2$	$C_{28}H_{31}N_4O_6Rh$
Formula weight	483.98	622.48
Temperature (K)	295(2)	292(2)
Wavelength (Å)	0.71073	
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
Unit cell dimensions		
a (Å)	8.0086(2)	23.6980(10)
b (Å)	12.0853(4)	8.8920(2)
c (Å)	18.0108(7)	13.0910(4)
α (°)	90	90
β (°)	101.8252(12)	90
γ (°)	90	90
Volume (Å^3)	1706.20(10)	2758.57(11)
Density (Mg m^{-3})	1.884	1.499
Reflections collected/unique	29,807/3996	60,154/6371
Theta range for data collection	2.04–28.30	2.45–28.28
Index range	$0 \le h \le 10$	$-31 \le h \le 31$
	$0 \le k \le 15$	$-11 \le k \le 11$
	$-23 \le l \le 20$	$-17 \le l \le 17$
[$R_{(int)} = 0.0500$]	0.0500	0.0355
Completeness to θ	25–99.2%	25–99.8
Refinement method	Full-matrix least squares on F^2	
GOF	1.040	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.\ 0377$	$R_1 = 0.0324$
	$wR_2 = 0.\ 0887$	$wR_2 = 0.0726$
R indices (all data)	$R_1 = 0.0649$	$R_1 = 0.0494$
	$wR_2 = 0.0964$	$wR_2 = 0.0799$
Largest difference between peak and hole (e Å^{-3})	0.828 and −1.418	0.366 and −0.369

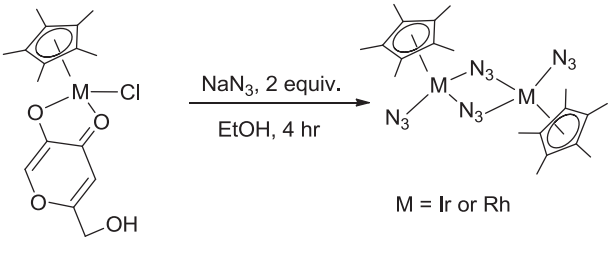
for rhodium and iridium complexes, respectively. The NMR spectroscopic data (^{1}H and ^{13}C) are well matched with the formulation of these complexes. The proton NMR spectrum of **11** showed three doublets, one multiplet, and one triplet in the aromatic regions



Scheme 2. Reaction pathways for the preparation of starting azido complexes.

corresponding to protons of coordinated quinaldinato ligand. The ^{13}C NMR spectra of the C=O group appeared at δ 173.20, while the carbons of the aromatic ring and methyl group of Cp* ligand appeared at δ 85.64 and 8.83, respectively. With the exception of **15** and **20**, the rest of the complexes can also be prepared by the reaction of tetrakis azido compound $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)(N_3)]_2$ with the corresponding ligand, but the reaction requires a longer time (scheme 2). However, a similar reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)(N_3)]_2$ (M = Ir or Rh) with kojic acid did not give the terminal azido complexes **15** and **20**; instead, unreacted starting azido complex was recovered as evident from the infrared spectral data. This indicates that the kojic acid has less affinity to undergo azide cleavage reaction with $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)(N_3)]_2$. The reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)Cl]_2$ with tropolone or quinaldic acid readily gave the terminal azide complexes $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)(N_3)]$ in 4 h. In contrast, kojic acid required 20 h and a higher ligand stoichiometric ratio. A truncated reaction time and lower ligand stoichiometric ratio resulted in low yields, and unreacted azide dimer complexes were recovered. These results further suggest that kojic acid has only a weak affinity to undergo azide cleavage as compared to the rest of the tested ligands.

We also attempted preparation of **11–20** by the direct reaction of $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl]$ with NaN_3. For **11–14** or **16–19**, the complexes were obtained in good yield by the reaction of their chloro complexes $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl]$ with twofold excess of NaN_3 in ethanol for 4 h. By contrast, a similar reaction of $[(\eta^5\text{-}C_5Me_5)M(hhp)Cl]$ with twofold excess of NaN_3 in ethanol resulted in tetrakis azido complexes $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)N_3]_2$ (scheme 3). The formation of these complexes was readily confirmed from their IR spectra, which showed two strong absorptions at 2019 and 2046 cm^{-1} for rhodium complexes corresponding to the presence of both terminal and bridging azide ligands, which appeared in the case of iridium complexes at 2032 and 2056 cm^{-1}. Further, the proton NMR spectrum of the complexes did not show peaks corresponding to the coordinated kojic acidate ligand. These complexes could have been formed due to the displacement of kojic acidate by the azide ligand. Previously, it has been observed that a similar reaction of [(*p*-cymene)Ru(hhp)Cl] (hh*p* = 5-hydroxy-4-methylpyrone or kojic acid) with NaN_3 gave a tetrakis azido complex $[(p\text{-cymene})(\mu N_3)N_3]_2$ [28], suggesting that the complex $[(\eta^5\text{-}C_5Me_5)M(hhp)Cl]$ showed a similarity to that of [(*p*-cymene)Ru(hhp)Cl] toward the reaction with NaN_3. We further studied the direct reaction of **5** and **10** with NaN_3 by using low stoichiometric amounts of NaN_3 and performing the reaction for only 1 h which resulted in the formation of the terminal azido complexes **15** and **20**. Thus, we were able to prepare the terminal azido complexes $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)N_3]$ in two routes, namely (i) by the azide cleavage reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)X]_2$ (X = Cl or N_3) with the ligands and (ii) by the direct reaction of $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl]$ with NaN_3. Although both pathways can be used for the



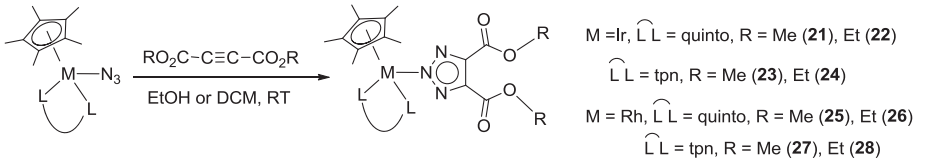
Scheme 3. Reaction of complex **5** or **10** with NaN_3.

preparation of terminal azide, the pathway (i) is particularly convenient for the preparation of terminal azido complexes containing labile ligand such as kojic acidate of the type $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)N_3]$ ($L^{\cap}L$ = kojic acid) for which the direct reactions with NaN_3 could result in the degradation of the coordinated ligand, giving tetrakis azido complexes (scheme 3). All these azido complexes have been characterized by the spectroscopic data (FTIR, ^1H and ^{13}C NMR). It should be noted that azido complexes of half-sandwich systems can be readily characterized by the infrared spectroscopic data. Thus, one can established terminal or bridging azide by simple inspection of their infrared spectral data. In our previous communication, we established solid-state structures for the analogous ruthenium (II) azido complexes, $[(\eta^6\text{-arene})Ru(L^{\cap}L)N_3]$ [25] (η^6-arene = C_6Me_6; $L^{\cap}L$ = tropolonate) and $[(\eta^6\text{-arene})Ru(N_3)N_3]_2$ [35] ((η^6-arene = *p*-cymene) by X-ray analysis. Hence, in this study, no attempts have been made for single-crystal analysis of these azido complexes.

We were interested in the study of 1,3-dipolar cycloadditon reaction of terminal azido complexes with alkynes. With several azido complexes (**11–20**) in hand, cycloadditon reaction were studied for representative complexes (one each of N^O and O^O chelate ligands of Ir and Rh), namely the iridium (III) quinaldinato and tropolonate complexes (**11** and **12**) and the analogous rhodium (III) complexes **16** and **17**. The reaction of these azido complexes and substituted alkynes such as DMD or DED at room temperature gave triazolato complexes (**21–28**) (scheme 4). The triazolato complexes were air stable and obtained as a yellow solid in 76–86% yield. The reaction was first carried out in CH_2Cl_2, the solvent of choice for such reactions, and then conducted using ethanol (a less-toxic solvent) obtaining comparable yields (scheme 4).

The reaction conducted in ethanol is very promising as it requires only a simple workup for isolation of product, and more importantly, the reactions proceed at room temperature. Our results indicate that dichloromethane could indeed be replaced by less-toxic ethanol for cycloaddtion reactions between alkynes and coordinated azide in metal complexes. Complexes (**21–28**) were characterized by FTIR, ^1H, and ^{13}C NMR spectroscopic data. The formation of these triazole complexes was followed from the complete disappearance of the starting azide peak and appearance of a peak at 1726 cm^{-1}, corresponding to the $\nu_{C=O}$ of $-CO_2R$. The infrared spectrum of starting azido complex **12** showed a strong peak for azide group at 2031 cm^{-1}, while the spectrum of triazolato complex **24** displayed disappearance of the azide peak and a strong peak appeared at 1724 cm^{-1}, corresponding to a C=O group (figure 1).

The ^1H and ^{13}C NMR spectroscopic data of the triazole complexes were well matched with the formulations of the complexes (**21–28**), which indicates that the complexes formed are *N*(*2*)-bound isomers. The proton NMR spectrum of complex **21** showed a singlet at δ 3.75 corresponding to the methoxycarbonyl group (CO_2Me), while the aromatic protons of the coordinated quinaldinato ligand appeared at δ 8.39–7.66. In the case of **22**, a quartet and a triplet were observed in the proton NMR spectrum, which are assignable to the $-CH_2-$ and $-CH_3$ protons of the $-CO_2Et$ group (figure 2). These spectra suggest the



Scheme 4. Reaction pathways for the preparation of triazoles.

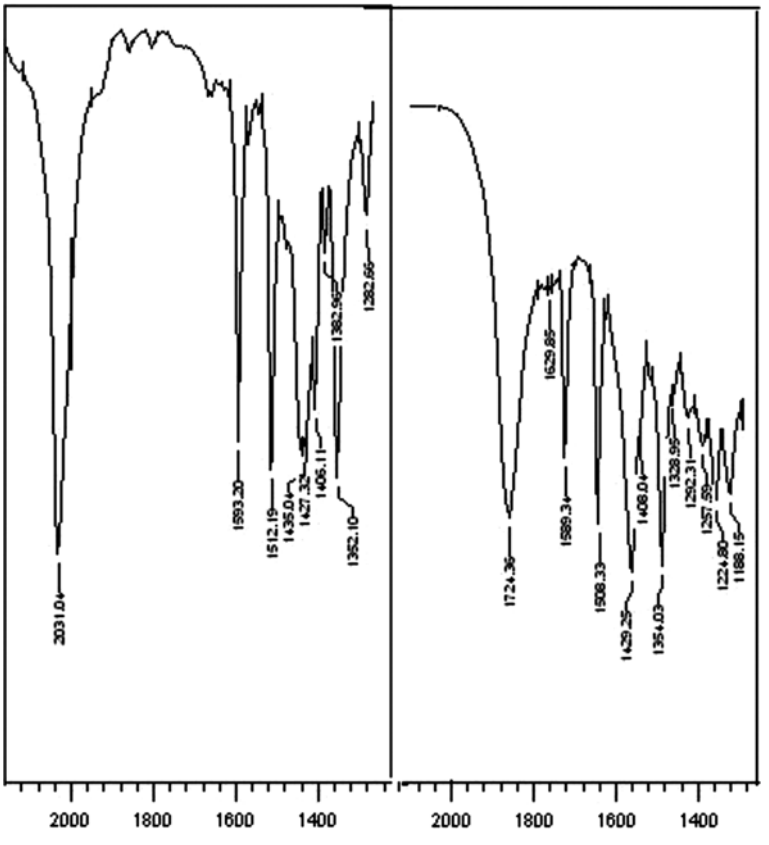


Figure 1. IR spectrum of complex **12** (left) and complex **24** (right).

triazolato complexes formed are *N*(*2*)-bound isomers. One would expect that the *N*(*1*)-bound isomer would exhibit two resonances for its anisochronous methoxy or ethoxycarbonyl group [36]. Evidence available to date indicates that the *N*(*2*)-bound isomers formed either exclusively or together with the *N*(*1*)-bound isomers [21, 37]. Triazolato complexes may have initially formed *N*(*1*)-bonded complexes which then isomerized to the *N*(*2*)-bonded complex, which is sterically more favorable. The formation of *N*(*2*)-bonded triazolato complexes was supported by spectroscopic data, and the structure was unambiguously confirmed by single-crystal X-ray analysis of **26.**

5. Crystal structures

Molecular structure of **2** and **26** were established by X-ray crystallography. Figures 3 and 4 show ORTEP diagrams [38] of **2** and **26**. Complex **2** crystallizes in space group $P2_1/c$ and **26** in $Pna2_1$. The average Ir–C and Rh–C bond distance in **2** and **26** are 2.132 and 2.154 Å, respectively. These values are comparable to related iridium [11] and rhodium complexes [39]. For both complexes, the C–C bond distances in the cyclopentadienyl ring are

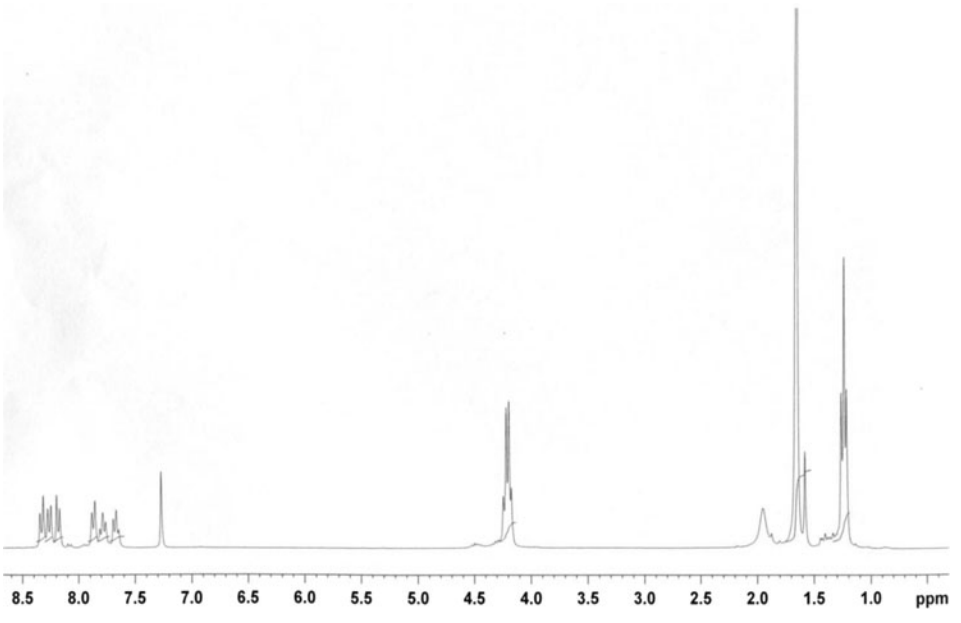


Figure 2. ^{1}HNMR spectrum of **22**.

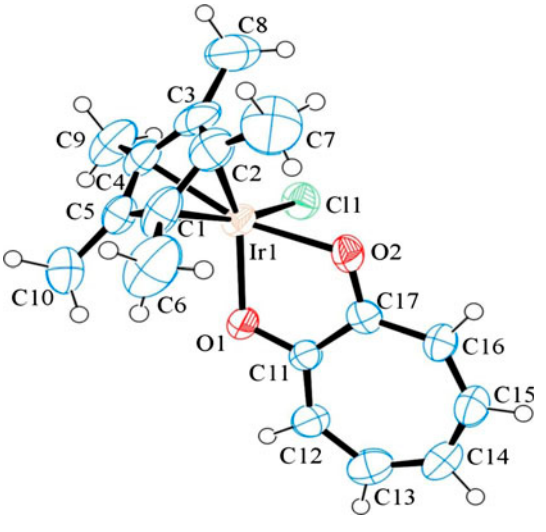


Figure 3. ORTEP diagram of [(η^5-C_5Me_5)Ir(tpn)Cl] (**2**) with thermal ellipsoids at the 50% probability level.

comparable, suggesting significant delocalization of pi electrons in the ring. The complexes adopt a typical piano stool structure in which the C_5Me_5 moiety occupied three coordination sites, while the remaining three sites were occupied by the coordinating ligands.

The triazole group in **26** is bonded to rhodium with a Rh–N distance of 2.096(3) Å, which is similar to that of the related Rh–N bond distances [19]. There is significant

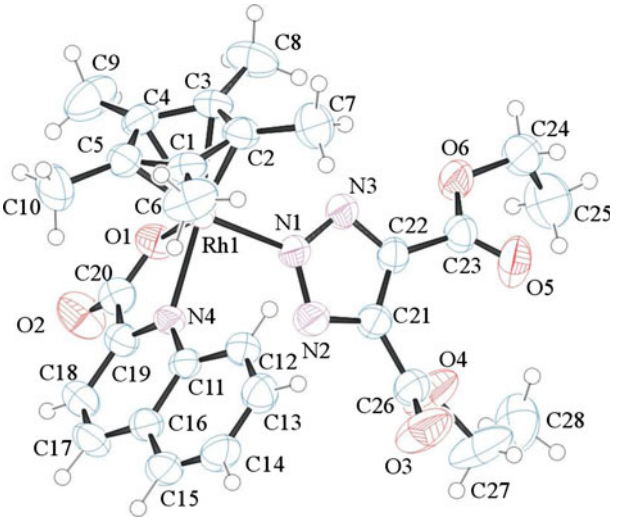


Figure 4. ORTEP diagram of $[(\eta^5\text{-}C_5Me_5)Rh(quinto)\{N_3C_2(CO_2Et)_2\}]$ (**26**) with thermal ellipsoids at the 50% probability level.

delocalization of electrons in the triazole ring as indicated by comparable bond distances of ring atoms in the triazole ring. The bite angle of N4–Rh–O1 (77.26(9)°) is close to that of the related triazole complex [23]. The C–O bond lengths of the quinaldinato ring, C20–O1 and C20–O2 are 1.287(4) and 1.215(5) Å, respectively, which is in the range of reported values [23, 40]. The heterocyclic ring of the quinaldinato group is coordinated to rhodium in such a way that the ring is pointing away from the triazole group in contrast to the analogous *p*-cymene ruthenium (II) triazolato complex, where the ring is coordinated adjacent to the triazole ring [23].

6. Conclusion

This article describes the synthesis of a series of azido complexes of Cp*M containing O,O or N,O chelate ligands. We presented two routes for the preparation azido complexes of general formula $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)N_3]$ by the azide cleavage reaction of either (i) $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)X]_2$ (X = Cl or N_3) with the corresponding ligands in the presence of NaOMe and (ii) by the direct reaction of $[(\eta^5\text{-}C_5Me_5)M(L^{\cap}L)Cl]$ (**1–10**) with NaN_3. In the case of **5** and **10**, the direct reaction with twofold excess of NaN_3 resulted in the formation of tetrakis azido compounds $[(\eta^5\text{-}C_5Me_5)M(\mu N_3)(N_3)]_2$. Further, we discussed 1,3-dipolar cycloaddition reaction of selected azido complexes **11**, **12**, **16**, and **17** with substituted alkynes in CH_2Cl_2 and for the first time in less-toxic ethanol at room temperature to generate iridium (III) and rhodium (III) triazoles (**21–28**). The reactions in ethanol are very promising as the product was obtained in good yield, requiring a simple workup, and more importantly, the reaction proceeded at room temperature. Thus, we found that the reaction of alkynes and coordinated azides in metal compounds could be explored in ethanol instead of CH_2Cl_2, which has been so far the solvent of choice to study such reactions.

Supplementary material

CCDC Nos. 764692 and 984101 contain the supplementary crystallography data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallography Data Center, 12 Union Road, Cambridge CB21 E2, UK. Fax: (+44) 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

KSS thanks the Director, CSIR-National Institute of Oceanography for providing necessary facilities. Financial support received from the Department of Science and Technology (SR/FT/CS-001/2010) and the Council of Scientific and Industrial Research (*OCEAN FINDER*), India, as well as from the EU through *MAREX* program is gratefully acknowledged.

References

[1] A. Wetzel, S. Wöckel, M. Schelwies, M.K. Brinks, F. Rominger, P. Hofmann, M. Limbach. *Org. Lett.*, **15**, 266 (2013).
[2] S.H. Park, Y. Park, S. Chang. *Org. Synth.*, **91**, 52 (2014).
[3] M. Erlandsson, V.R. Landaeta, L. Gonsalvi, M. Peruzzini, A.D. Phillips, P.J. Dyson, G. Laurenczy. *Eur. J. Inorg. Chem.*, 620 (2008).
[4] D. Carmona, M.P. Lamata, F. Viguri, R. Rodrıguez, F.J. Lahoz, I.T. Dobrinovitch, L.A. Oro. *Dalton Trans.*, 1911 (2007).
[5] M.V. Pham, B. Ye, N. Cramer. *Angew. Chem. Int. Ed.*, **51**, 10610 (2012).
[6] Y. Yang, W. Hou, L. Qin, J. Du, H. Feng, B. Zhou, Y. Li. *Chem. Eur. J.*, **20**, 416 (2014).
[7] S.J. Lucas, R.M. Lord, R.L. Wilson, R.M. Phillips, V. Sridharan, P.C. McGowan. *Dalton Trans.*, **41**, 13800 (2012).
[8] M.A. Scharwitz, I. Ott, Y. Geldmacher, R. Gust, W.S. Sheldrick. *J. Organomet. Chem.*, **693**, 2299 (2008).
[9] T. Hamada, T. Torii, K. Izawa, R. Noyori, T. Ikariya. *Org. Lett.*, **4**, 4373 (2002).
[10] B.A. Arndtsen, R.G. Bergman. *Science*, **270**, 1970 (1995).
[11] D. Herebian, W.S. Sheldrick. *J. Chem. Soc., Dalton Trans.*, 966 (2002).
[12] S. Gençaslan, W.S. Sheldrick. *Eur. J. Inorg. Chem.*, 3840 (2005).
[13] R.H. Fish. *Coord. Chem. Rev.*, **185**, 569 (1999).
[14] H.A. Bay, B. Quaddouri, A. Guaadaoui, R. Touzani, N.-E. Benchat, A. Hamal, M. Taleb, M. Bellaoui, S.E. Kadiri. *Lett. Drug. Des. Discov.*, **7**, 41 (2010).
[15] S. Patai. *The Chemistry of Azide Groups*, p. 331, Interscience, New York (1971).
[16] G. L'abbe. *Chem. Rev.*, **69**, 345 (1969).
[17] A. Padwa. *Angew Chem. Int. Ed. Engl.*, **15**, 123 (1976).
[18] P. Paul, K. Nag. *Inorg. Chem.*, **26**, 2969 (1987).
[19] W. Rigby, P.M. Bailey, J.A. McCleverty, P.M. Maitlis. *J. Chem. Soc., Dalton Trans.*, 371 (1979).
[20] P.M. Treichel, W.J. Knebel, R.W. Hess. *J. Am. Chem. Soc.*, **93**, 5424 (1971).
[21] W.P. Fehlhammer, L.F. Dahl. *J. Am. Chem. Soc.*, **94**, 3370 (1972).
[22] T. Kemmerich, J.H. Nelson, N.E. Takach, H. Boebme, B. Jablonski, W. Beck. *Inorg. Chem.*, **21**, 1226 (1982).
[23] K.S. Singh, W. Kaminsky. *Polyhedron*, **68**, 279 (2014).
[24] K.S. Singh, K.A. Kreisel, G.P.A. Yap, M.R. Kollipara. *J. Organomet. Chem.*, **691**, 3509 (2006).
[25] K.S. Singh, V. Svitlyk, Y. Mozharivskyj. *Dalton Trans.*, **40**, 1020 (2011).
[26] M. Kotera, Y. Sekioka, T. Suzuki. *Inorg. Chim. Acta*, **361**, 1479 (2008).
[27] K.S. Singh, C. Thöne, M.R. Kollipara. *J. Organomet Chem.*, **690**, 4222 (2005).
[28] K. Pachhunga, B. Therrien, M.R. Kollipara. *Inorg. Chim. Acta*, **361**, 3294 (2008).
[29] C.-W. Chang, G.-H. Lee. *Organometallics*, **22**, 3107 (2003).
[30] C. White, A. Yates, P.M. Maitlis. *Inorg. Synth.*, **29**, 228 (1992).
[31] R.G. Ball, W.A.G. Graham, D.M. Heinekey, J.K. Hoyano, A.D. McMaster, B.M. Mattson, S.T. Michel. *Inorg. Chem.*, **29**, 2023 (1990).
[32] Z. Otwinowsky, W. Minor. In *Methods in Enzymology*, C.W. Carter Jr., R.M. Sweet (Eds), Vol. 276, p. 307–326, Academic Press, New York (1997).

[33] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.*, **32**, 115 (1999) (SIR97).
[34] G.M. Sheldrick. *SHELXL97, Program for the Refinement of Crystal Structures*, University of Gottingen, Germany (1997).
[35] K.S. Singh, V. Svitlyk, P. Devi, Y. Mozharivskyj. *Inorg. Chim Acta.*, **362**, 5252 (2009).
[36] K.S. Singh, K.A. Kreisel, G.P.A. Yap, M.R. Kollipara. *J. Coord. Chem.*, **60**, 505 (2007).
[37] P.H. Kreutzer, J.C. Weis, H. Bock, J. Erbe, W. Beck. *Chem. Ber.*, **116**, 2691 (1983).
[38] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
[39] H. Aneetha, P.S. Zacharias, B. Srinivas, G.H. Lee, Y. Wang. *Polyhedron*, **18**, 299 (1998).
[40] O. Dayan, N. Özdemir, Z. Şerbetci, M. Dinçer, B. Çetinkaya, O. Büyükgüngör. *Inorg. Chim. Acta*, **392**, 246 (2012).