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Journal of Organometallic Chemistry 690 (2005) 4222–4231

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Part 1: 1,3-Dipolar addition of activated alkyne towards coordinated azido group in ruthenium(II) complexes containing η^5-cyclichydrocarbons

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Received 6 May 2005; received in revised form 8 June 2005; accepted 16 June 2005

Abstract

The indenyl and pentamethylcyclopentadienyl ruthenium(II) complexes $[(\eta^5\text{-}L_3)Ru(L_2)Cl]$ ($L_3 = C_9H_7$, $L_2 =$ dppe (**1a**), $L_2 =$ dppm (**1b**); $L_3 = C_5Me_5$, $L_2 =$ dppe (**2a**); $L_2 =$ dppm (**2b**) (where, dppe $= Ph_2PCH_2CH_2PPh_2$ and dppm $= Ph_2PCH_2PPh_2$) reacts with NaN_3 to yield the azido complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)N_3]$, $L_2 =$ dppe (**3a**), dppm (**3b**) and $[(\eta^5\text{-}C_5Me_5)Ru(L_2)N_3]$, $L_2 =$ dppe (**4a**), dppm (**4b**), respectively. The azido complexes undergo [3 + 2] dipolar cycloaddition reaction with dimethylacetylenedicarboxylate to yield triazole complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)(N_3C_2(CO_2Me)_2)]$, $L_2 =$ dppe (**5a**), dppm (**5b**) and $[(\eta^5\text{-}C_5Me_5)Ru(L_2)(N_3C_2\text{-}(CO_2Me)_2)]$, $L_2 =$ dppe (**6a**), dppm (**6b**), respectively. The complexes were fully characterized on the basis of microanalyses, FT-IR and NMR spectroscopy. The crystal structures of the starting complex (**1a**) and representative complexes **5a**, **5b** and **6a** have been established by single X-ray study.

Keywords: Indenyl; Pentamethylcyclopentadienyl; Dimethylacetylenedicarboxylate; Azide; Ruthenium; Crystal structure

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1. Introduction

1,3-Dipolar cycloaddimbtion is a common process in organic chemistry. The process involves the reaction between 1,3-dipoles having allyl and dipolarophiles type. Among various 1,3-dipoles, organic azides are particularly known to be important for the synthesizing heterocyclic compounds [1–6]. By analogy, Dori and Ziolo [7a] and Fruhauf [7b] have reported that coordinated azide in metal complexes can also undergo cycloaddition reaction. Thus azido complexes have been reported to react with nitriles [8–14] and isonitriles [9,15–17] to produce metal–nitrogen and metal–carbon bonded tetrazoles, respectively. Interestingly it has been reported that tetrazole complexes can also be produce by the reaction of coordinated nitrile in metal complex with NaN_3 [18].

Literature surveys, reveals that most of the cycloaddition reactions of the azido complexes have been studied with platinum(II) [11c,16] and palladium(II) metals [14b,19] although a few have been known in compounds of other transition metals, viz., rhodium(I) iridium(I), cobalt(III) and tin(IV) [20]. However, cycloaddition reaction of coordinated azido complexes in half-sandwich systems has not been studied much except a report appeared in cyclopentadienyl ruthenium cases in recent years [21]. In contrast, to the best of our knowledge, such cycloaddition reactions of coordinated azido complexes in indenyl and pentamethylcyclopentadienyl systems have not been studied so far. It has been

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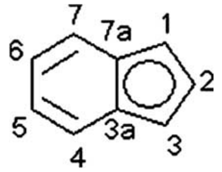
doi:10.1016/j.jorganchem.2005.06.016

reported that the chemistry of indenyl and pentamethylcyclopentadienyl ruthenium complexes are differ from the analogous cyclopentadienyl ruthenium complex in certain aspects such as higher reactivity and labile nature of the *organic moieties*. The higher reactivity of the Cp* complexes is attributed to the sterric and inductive effect whereas in the case of indenyl complexes ring slippage nature from η^5- to η^3- and back to η^5- of the indenyl ligand is the solely responsible for the high reactivity [22]. It is noteworthy that reversible slippage of the metal across the five-membered ring can form a more reactive η^3-indenyl tautomer that has both benzenoid resonance stabilization and accesible coordination site [23]. Our current study on the reactivity of the indenyl and Cp* ruthenium bis phosphine complexes, viz., [Cp*Ru(PPh$_3$)$_2$Cl] or [(ind)Ru(PPh$_3$)$_2$Cl] (where, ind = indenyl) towards N-base ligands reveals that the stability of the indenyl or Cp* ligands are largely depend on the steric nature of the incoming ligand, such that reaction of [Cp*Ru(PPh$_3$)$_2$(CH$_3$CN)]$^+$ or [(ind)Ru(PPh$_3$)$_2$(CH$_3$CN)]$^+$ with satirically demanded multidented ligand, tetra-2-pyridyl-1,4-pyrazine (tppz), displaced the *organic moiety* and isolated the complex of the type [Ru(tppz)(PPh$_3$)$_2$(CH$_3$CN)]$^+$ [24]. However, the reaction with less sterric N-base ligand, the *organic moiety* remain intact to the metal and thus forming complex of the type [η^5-L$_3$)Ru(PPh$_3$)(L$_2$)]$^+$ [25] (where L$_3$ = indenyl or Cp*). In general, sterically demanded multidentate ligand displaced them from the complexes. The part 1 of this communication, we described the syntheses of azido complexes of indenyl and pentamethylcyclopentadienyl ruthenium(II) and their reactions with dimethylacetylenedicarboxylate to generate triazole complexes (**5a**,**b** and **6a**,**b**). The spectral and structural characterization of the complexes has been discussed.

2. Experimental

All solvents were dried in appropriate drying agents and distilled prior to use [26]. RuCl$_3 \cdot 3$H$_2$O (Arora Matthey Limited) and dimethylacetylenedicarboxylate (Aldrich) were used as received. NMR spectra were recorded on an AMX-400 MHz spectrometer at 400.13 (^{1}H), 161.97 (^{31}P) or 100.61 MHz (^{13}C) with SiMe$_4$ or 85% H$_3$PO$_4$ as internal references and coupling constants are given in hertz. Infrared spectra were recorded as a KBr pellets on a Perkin–Elmer Model 983 spectrometer. Elemental analyses were carried out at the Regional Sophisticated Instrumentation centre (RSIC) Shillong, using a Perkin–Elmer 2400 CHN/S analyzer. Electronic spectra were recorded on a Hitachi-330 spectrophotometer in dichloromethane at ca. 10^{-4} M. The precursor complexes [(η^5-C$_9$H$_7$)Ru(dppe)Cl] (**1a**) and [(η^5-C$_9$H$_7$)Ru(dppm)Cl] (**1b**) were prepared following a literature method [27] while the complexes [(η^5-C$_5$Me$_5$)Ru(dppe)Cl] (**2a**) and [(η^5-C$_5$Me$_5$)Ru(dppm)Cl] (**2b**) were prepared by slight modification of the reported method [28] as described below. ^{13}C{^{1}H} NMR data for the indenyl complexes are presented in Table 1. The following atom labeling scheme is used for the ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data of indenyl complexes.



2.1. Synthesis of precursor complex [(η^5-C$_5$Me$_5$)-Ru(dppe)Cl] (2a)

A two neck round bottom flask was charged with [(η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl] (100 mg, 0.125 mmol), dppe (60 mg, 0.150 mmol) and 50 ml of toluene was added. The mixture was heated to reflux under nitrogen atmosphere for 15 h and cooled to room temperature. The solvent was removed under reduced pressure and the solid residue was purified by column chromatography over alumina. A bright yellow band was collected when eluted with dichloromethane which on concentration

Table 1
^{13}C{^{1}H} NMR data for the indenyl complexes[a,b]

Complex	η^5-C$_9$H$_7$						Others
	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3a,7a)[b]	C-4,5	C-6,7	
3a	65.08	87.71	109.33	−21.37	124.63	125.78	27.86 (m, P(CH$_2$)$_2$P), 127.66–133.73 (m, PPh$_2$)
3b	63.09	87.14	109.07	−21.63	123.20	125.65	49.40 (t, $J_{\text{C-P}} = 19.7$, (P(CH$_2$)P)), 128.32–137.69 (m, PPh$_2$)
5a	66.35	93.60	108.81	−21.89	125.13	127.51	29.42 (m, P(CH$_2$)$_2$P), 51.21 (s, (OCH$_3$)), 127.66–133.73 (m, Ph), 138.12 (C(CO$_2$ Me)), 167.8 (s, (CO$_2$))
5b	66.50	89.44	108.76	−21.94	124.98	125.18	49.66 (t, $J_{\text{C-P}} = 21.4$, (P(CH$_2$)P)), 51.11 (s, (OCH$_3$)), 127.59–134.61 (m, Ph), 138.04 (C(CO$_2$ Me)), 168.72 (s, (CO$_2$))

[a] Spectra recorded in CDCl$_3$; δ in ppm and J in Hz. Abbreviations: s, singlet; t, triplet; m, multiplet.

[b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a)(η-indenyl complex) − δ(C-3a,7a (sodium indenyl)), δ(C-3a, 7a) for sodium indenyl, 130.70 ppm.