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Preliminary communication

THE CHEMISTRY OF CYCLOPENTADIENYL-RUTHENACYCLOPENTATRIENES: NOVEL CARBON MONOXIDE AND ISOCYANIDE INSERTION REACTIONS IN $[(\eta^5\text{-}C_5H_5)Ru(C_4Ph_2H_2)Br]$; CRYSTAL STRUCTURE OF $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_5Ph_2H_2NBu^t)Br]$

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Summary

Reaction of the novel ruthenacyclopentatriene $[(\eta^5\text{-}C_5H_5)Ru(C_4Ph_2H_2)Br]$ (**1**) with isocyanides gives the imino-2,5-diphenylcyclopentadiene complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_5Ph_2H_2NR)Br]$ (**2**, R = Me, Et, Cy, t-Bu, 2,6-$Me_2C_6H_3$); a novel fluxional process involving phenyl substituent rotation and imino nitrogen inversion has been identified for **2** (R = t-Bu, 2,6-$Me_2C_6H_3$), the interpretation of which is supported by the X-ray crystal structure determination of **2** (R = t-Bu).

The cyclodimerization of two molecules of alkyne at a range of transition metal centres gives metallacyclopentadiene complexes [1], species central to the catalyzed cyclotrimerization of alkynes to aromatics [2], and the catalyzed reactions of alkynes with nitriles [3] and isonitriles [4]. We recently reported [5] the novel cyclodimerization of phenylacetylene at the ruthenium(II) centre in $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Br]$ (C_8H_{12} = cycloocta-1,5-diene) a reaction which does not give a metallacyclopentadiene but rather the first example of a metallacyclopentatriene. Herein we wish to report on novel carbon monoxide and isocyanide insertion reactions in $[(\eta^5\text{-}C_5H_5)Ru(C_4Ph_2H_2)Br]$, results which pertain to the mode of formation of organic nitrogen compounds in the transition metal catalyzed reactions of alkynes with isocyanides [4].

Reaction of the ruthenacyclopentatriene $[(\eta^5\text{-}C_5H_5)Ru(C_4Ph_2H_2)Br]$ (**1**) [5] with a stoichiometric amount of isocyanide RNC (R = Me, Et, Cy, t-Bu, 2,6-$Me_2C_6H_3$) occurs rapidly at room temperature (Scheme 1) giving high yields of purple crystalline solids having the composition $[(\eta^5\text{-}C_5H_5)Ru(C_4Ph_2H_2)(CNR)Br]$ (**2**) [6]. The IR spectra of these compounds typically display ν(C=N) bands (1650–1600 cm^{-1}) strongly suggesting that isocyanide insertion has occurred giving imino-2,5-diphenylcyclopentadiene complexes [7,8]. The ^1H NMR spectrum of **2** (303 K,

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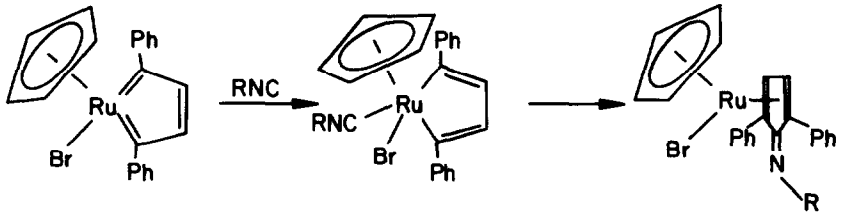
R = t-Bu) shows the expected singlets at δ 4.98 (5H) and 0.92 (9H) ppm for the cyclopentadienyl ring and the isocyanide methyl groups respectively, and two broad resonances for the phenyl protons at δ 7.87 (4H) and 7.20 (6H) ppm. No signals attributable to the metallacycle ring protons are evident. A similarly broadened spectrum is observed for **2** (R = 2,6-$Me_2C_6H_3$), but for the remaining alkyl isocyanide products **2** (R = Me, Et, Cy), the expected two doublets for the ring protons are observed between δ 6.55 and 6.85 ppm. These data, together with the fact that similarly well resolved ^{1}H NMR spectra may be obtained for **2** (R = t-Bu, 2,6-$Me_2C_6H_3$) on cooling to 243 K, suggests that a fluxional process involving inversion at the nitrogen centre [9] occurs when bulky isocyanide substituents are involved. The explanation for these observations was not immediately apparent from the available information and for this reason the X-ray crystal structure of **2** (R = t-Bu) has been determined [10].

The structure of **2** (R = t-Bu) is given in Fig. 1. The most striking feature is the rotation away from co-planarity with the cyclopentadiene ring (inter-plane angle: 86(1)°) of one phenyl ring due to non-bonded repulsions from the t-butylimino substituent. This orientation clearly removes potential resonance stabilization which would accrue to the ligand system from a co-planar phenyl moiety, thereby raising the ground state energy of the molecule. This effectively lowers the activation energy of the *N*-inversion process [9], introducing a pathway for novel fluxionality involving phenyl substituent rotation and imino nitrogen inversion (Scheme 2). By analogy, the inherent resonance stabilization arising from conjugation of the aromatic ring of the 2,6-dimethylphenyl group in **2** (R = 2,6-$Me_2C_6H_3$) is clearly reason for this group to be planar with the iminocyclopentadiene ring. Thus, in exerting its maximum cone angle effect [11], the imino substituent once again forces from co-planarity one of the pentadiene-phenyl substituents and introduces a fluxional phenyl ring rotation-nitrogen inversion process observable by NMR spectroscopy. Clearly for the remaining compounds **2** (R = Me, Et, Cy) such considerations are not pertinent, and as in the only other comparable systems [7,8], this mitigates against fluxionality being observed for these compounds [12].

An investigation of the kinetics of the conversion **1** → **2** (R = t-Bu) in acetone and in the presence of excess isocyanide by stopped-flow spectrophotometry showed a pseudo first-order rate law: $-d[\mathbf{1}]/dt = k_{obsd}[\mathbf{1}]$ where $k_{obsd} = k$[t-BuNC]. The specific rate constant and associated activation parameters are: $k = 13.7\ s^{-1}\ M^{-1}$ (25°C), $\Delta H^{\ddagger} = 9.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -24.2$ cal mol^{-1} K^{-1}. The kinetic results therefore favour a rate-determining associative mode of activation which most likely



(1) (3) (2)

SCHEME 1

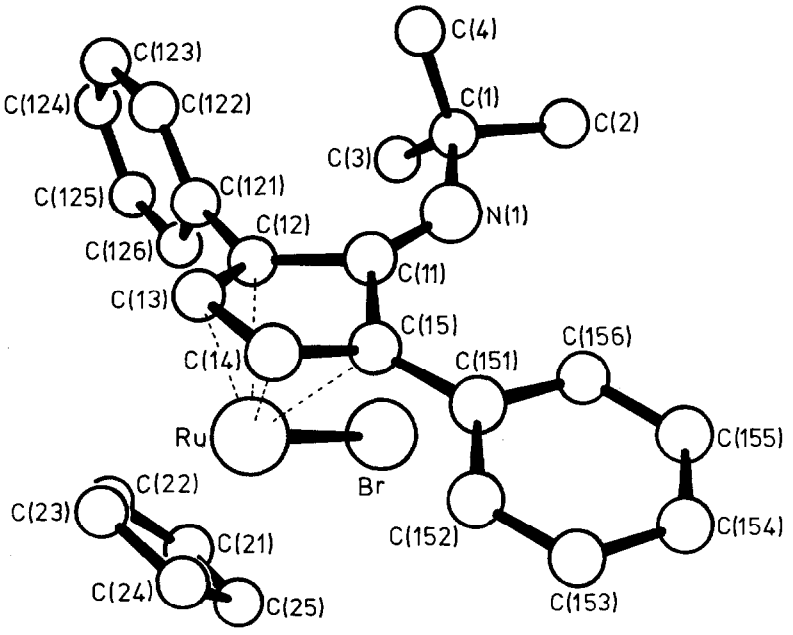
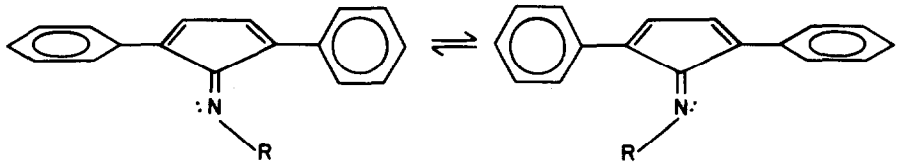


Fig. 1. A perspective view of **2** (R = t-Bu) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru–Br 2.568(1), Ru–C(12) 2.24(1), Ru–C(13) 2.14(1), Ru–C(14) 2.14(2), Ru–C(15) 2.28(1), C(11)–C(12) 1.53(2), C(12)–C(13) 1.40(2), C(13)–C(14) 1.41(2), C(14)–C(15) 1.39(2), C(15)–C(11) 1.52(2), C(11)–N(1) 1.27(2), N(1)–C(1) 1.46(2), Ru–C(cp) (mean) 2.20(2), C(15)–C(11)–C(12) 100.2(10), C(11)–C(12)–C(13) 106.3(12), C(12)–C(13)–C(14) 109.0(11), C(13)–C(14)–C(15) 109.5(12), C(14)–C(15)–C(11) 107.2(12).

involves nucleophilic attack at the metal centre [5] by isocyanide to produce the intermediate $[(\eta^5\text{-}C_5H_5)Ru(C_4Ph_2H_2)(CNR)Br]$ (**3**) (Scheme 1). The conversion **3** → **2**, which would include "insertion" and subsequent rearrangement [7], must be a facile process and non rate determining since the persistence of well defined isobestic points (520, 590 nm) during the entire course of the overall reaction rules out any significant build-up of **3**. The possibility of isocyanide attack on a coordinated carbene atom directly [13] followed by a rapid rearrangement to **2** can be discounted in this system on the basis of the very similar activation parameters obtained for the reaction of $P(OMe)_3$ [5] and t-BuNC with **1**. Significantly different $\Delta H^{\ddagger}$ values would be expected if these two nucleophiles were to respectively, attack the metal and carbene carbon centres, each of significantly different electrophilic character.



SCHEME 2

The reaction of either **1** or **2** with excess isocyanide proceeds rapidly at room temperature via facile imino-2,5-diphenylcyclopentadiene displacement and the quantitative formation of $[(\eta^5\text{-}C_5H_5)Ru(CNR)_2Br]$; the isolation of the organic product can be effected by column chromatography. This reaction thus represents the first recorded displacement of this ring system from a metal ion [7,8], and consequently, the first example of the metal mediated stoichiometric preparation of this molecule which shows synthetic potential in organic chemistry. Under a carbon monoxide atmosphere **1** reacts rapidly at room temprature to give the η^4-cyclopentadienone complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_5Ph_2H_2O)Br]$, a 2,5-diphenyl substituted analogue of the recently reported $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_5H_4O)Br]$ [14]. Kinetically this transformation appears to follow the same pattern as observed for the isocyanide reactions.

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