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 $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_5Ph_2H_2NBu^t)Br]$

MICHEL O. ALBERS, DIRK J.A. DE WAAL, DAVID C. LILES, DAVID J. ROBINSON
and ERIC SINGLETON*

National Chemical Research Laboratory, Council for Scientific and Industrial Reserach, P.O. Box 395, Pretoria 0001 (Republic of South Africa)

(Received January 28th, 1987)

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, $2,6\text{-}Me_2C_6H_3$); a novel fluxional process involving phenyl substituent rotation and imino nitrogen inversion has been identified for **2** (R = t-Bu, $2,6\text{-}Me_2C_6H_3$), 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, $2,6\text{-}Me_2C_6H_3$) 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 $\nu(C=N)$ 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,
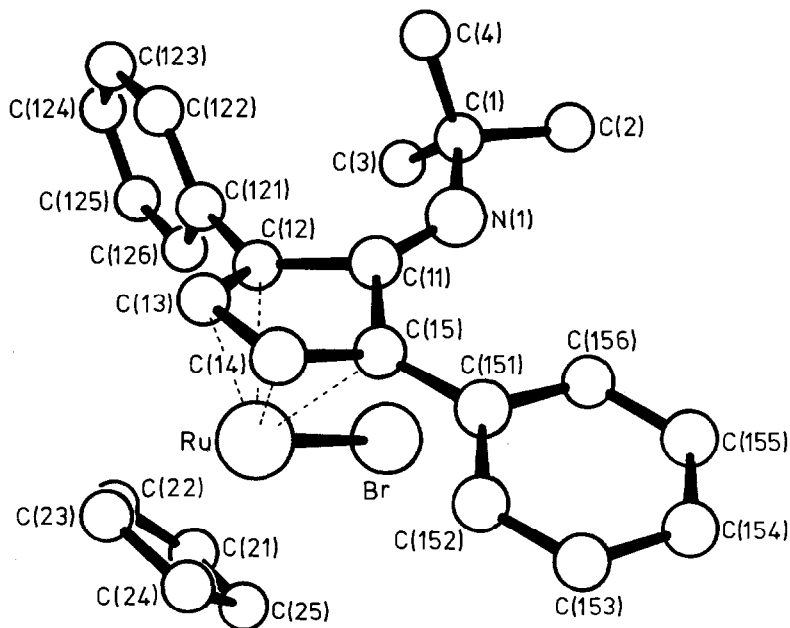
R = t-Bu) shows the expected singlets at δ 4.98 (5H) and 0.92 (9H) ppm for the cyclopentadienyl ring and the isocyanide methyl groups respectively, and two broad resonances for the phenyl protons at δ 7.87 (4H) and 7.20 (6H) ppm. No signals attributable to the metallacycle ring protons are evident. A similarly broadened spectrum is observed for 2 (R = 2,6-Me$_2$C$_6$H$_3$), 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$_2$C$_6$H$_3$) 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$_2$C$_6$H$_3$) 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: $-\mathrm{d}[1]/\mathrm{d}t = k_{obsd}[1]$ where $k_{obsd} = k[\text{t-BuNC}]$. 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 [(η^5-C$_5$H$_5$)Ru(C$_4$Ph$_2$H$_2$)(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.
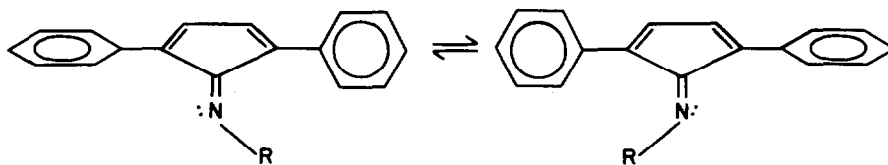
SCHEME 2

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.

References

1 (a) J.P. Collman and L.S. Hegedus: Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, California, 1980, p. 505–535 and references therein. (b) S.D. Chappell and D.J. Cole-Hamilton, Polyhedron, 1 (1982) 739.

2 K.P.C. Vollhardt, Acc. Chem. Res., 10 (1977) 1; P.M. Maitlis, ibid., 9 (1976) 93.

3 H. Bönnemann, Angew. Chem., 90 (1978) 517; Angew. Chem. Int. Ed. Engl., 17 (1978) 505.

4 See for example: S. Otsuka and A. Nakamura, Adv. Organomet. Chem., 14 (1976) 245.

5 M.O. Albers, D.J.A. de Waal, D.C. Liles, D.J. Robinson, E. Singleton and M.B. Wiege, J. Chem. Soc., Chem. Commun., (1986) 1680.

6 Representative data for **2** (R = t-Bu): ^{1}H NMR (500.13 MHz, CDCl$_3$, 243 K): δ 7.92 (4H, m, Ph), 7.21 (6H, m, Ph), 6.35 (1H, d, J 3.0, CH), 5.78 (1H, d, J 3.0, CH), 5.00 (5H, s, C$_5$H$_5$), 0.91 (9H, s, Me) ppm. ^{13}C{^{1}H} NMR (125.76 MHz, CDCl$_3$, 243 K): δ 139.3, 133.9 (CPh), 127.6, 127.4, 127.2 (Ph), 83.6 (C$_5$H$_5$), 80.7, 74.8 (CH), 53.9 (CMe$_3$), 32.5 (Me) ppm.

7 J.L. Davidson, M. Green, J.Z. Nyathi, F.G.A. Stone and A.J. Welch, J. Chem. Soc. Dalton Trans., (1977) 2246.

8 H. Yamazaki and Y. Wakatsuki, Bull. Chem. Soc. Jpn., 52 (1979) 1239.

9 J. Bellerby, M.J. Boylan, M. Ennis and A.R. Manning, J. Chem. Soc., Dalton Trans., (1978) 1185.

10 The structure of **2** (R = t-Bu) was determined using an Enraf–Nonius CAD4F diffractometer (Mo-K_α, λ 0.71069 Å, $3 \leqslant \theta \leqslant 25°$, 293 K, empirical absorption corrections); monoclinic, $P2_1/n$, a 10.094(8), b 16.249(7), c 13.993(3) Å, β 107.25(4)°, U 2191.9(3) Å^3, $Z = 4$. Solution (heavy atom methods) and refinement ($\Sigma|\Delta F|^2$ minimized) using SHELX; 2334 reflections $[|F_o| \geqslant 4\sigma(F_o)]$; non-hydrogen atoms anisotropic, hydrogen atoms calculated (D(C–H) 0.95 Å); $R = 0.0747$. A list of atomic coordinates can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

11 Y. Yamamoto, K. Aoki and H. Yamazaki, Inorg. Chem., 18 (1979) 1681.

12 Certain iminocyclopentadienecobalt complexes [8] would, however, be predicted to show similar effects.

13 For examples of nucleophilic attack on carbene species see J.A.S. Howell and P.M. Burkinshaw, Chem. Rev., 83 (1983) 557.

14 T.P. Smith, K.S. Kwan, H. Taube, A. Bino and S. Cohen, Inorg. Chem., 23 (1984) 1943.