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Journal of Organometallic Chemistry 528 (1997) 191–194

Journal of Organometallic Chemistry

Preliminary communication

Facile synthesis of amino-functionalised cyclopentadienyl sodium compounds and subsequent formation of rhodium complexes: proton–deuterium exchange for the sodium salts [1]

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Received 4 April 1996; revised 6 July 1996

Abstract

Synthesis, isolation and characterisation of sodium salts of amino-substituted cyclopentadienyl compounds was carried out for the first time: these can be made on a large scale and stored easily, thus facilitating easy manipulation and applications. Rhodium derivatives, including $Rh(\eta^5\text{-}C_5H_4)CH(CH_2CH_2)_2NMe(coe)_2$ (coe = cyclo-octene), were synthesised, of which the crystal structure is reported.

Keywords: Exchange; Sodium salts; Substituted cyclopentadienyls; Rhodium

1. Introduction

The synthesis of amino-substituted cyclopentadienyl ligands has led to the preparation of a range of main group [1] and transition metal complexes [2]. Most of these complexes have been prepared using the dimethylamino cyclopentadienyl and dimethylamino tetramethyl-cyclopentadienyl lithium and potassium salts [1]. Problems associated with these salts are that the lithium salts are highly soluble in THF, suggesting an oligomeric structure in solution, and thus are not isolable as solids. Also, the potassium salts are insoluble in common solvents and extremely air sensitive.

Thus, there have been problems with their isolation, and consequently a lack of characterisation of these alkali metal salts. Owing to the problem of isolation, the salts of these ligands have generally been reacted in situ in order to synthesise new main group and organometallic compounds.

This paper concerns the synthesis, isolation, characterisation and reactivity of the sodium salts of amino-substituted cyclopentadiene ligands; this represents the first time that alkali metal salts of these types of ligand have been isolated and characterised. Also, we report the clean isolation of organometallic compounds containing the amino-substituted cyclopentadienyl ligand and their reactivity.

2. Results and discussion

We have found that the previously described method for the synthesis of the substituted cyclopentadiene **1** [3], was easily extended to the syntheses of the substituted derivatives **2–4**. In particular, this represents an improved method for the preparation of **3** [4]. We found it prudent to use the organic oils immediately after distillation, since this minimised on the decomposition of the ligands. Thus, the substituted cyclopentadienes **1–4** were reacted in THF with sodium hydride generating the corresponding sodium-substituted salts as white powders in high yield (greater than 95%) on a multigram-scale. (In a typical experiment (for preparation of **5**), one equivalent of **1** (8.0 g, 0.058 mol) was added to a solution of ice-cooled NaH (1.4 g, 0.058 mol) in THF (50 ml). A white solid immediately formed. After several hours the THF was removed under vacuum, the salt washed twice with pentane (40 ml) and then dried under vacuum. Yield 7.5 g, 81%.) These air- and water-sensitive sodium salts are thermally stable and can be stored indefinitely under an inert atmosphere.

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[1] Dedicated to Professor Malcolm L.H. Green on the occasion of his 60th birthday.

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0022-328X/97/$17.00 Published by Elsevier Science S.A.
PII S0022-328X(96)06574-6

Compounds **2** and **4–8**, were characterised by ^{1}H, ^{2}H and ^{13}C NMR spectroscopy (see Section 2.1). In isolating these salts and carrying out their characterisation using nuclear magnetic resonance, an exchange was observed between the solvent (CD_3CN) deuterons and the protons of the cyclopentadienyl ring. This occurred over a period of approximately 2 h, as evidenced by the disappearance of signals due to the cyclopentadienyl protons in the ^{1}H NMR spectrum. The ^{2}H NMR spectra showed a signal at 5.5 ppm for the deuterons of the cyclopentadienyl ring for the compounds **5–7**. We studied in detail the case of **7**; not only was the signal for the cyclopentadienyl deuterons observed in the ^{2}H NMR spectrum, but also a signal for ND_2, occurring at $\delta =$ 0.99 ppm. Further evidence that this exchange was taking place was the fact that in the $^{13}C\{^{1}H\}$ NMR spectra the singlets due to the ring carbons (non-quaternary) were observed to diminish over the same period of time to be replaced by two triplets, where $J(^{13}C-^{2}H) =$ 24 Hz for the case of **6**.

Transition metal organometallic derivatives of these cyclopentadienyl ligands were synthesised in the form of rhodium compounds. These compounds were characterised by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, microanalysis and, in one case, X-ray crystallography. Reaction of **5** and **6** with $[RhCl(cod)]_2$ in THF gives **9** and **10** as oils on extraction with diethyl ether (Scheme 1). These compounds can be subsequently protonated using one equivalent of HBF_4 in diethyl ether to give the salts **12** and **13**. Interestingly, the chloride counterion salts **14** and **15** can be prepared directly by reaction of the ligands **1** and **2** respectively with the dimeric $[RhCl(cod)]_2$. Thus, there is a transfer of a proton from the cyclopentadiene moiety to the nitrogen atom.

The synthesis of $Rh(\eta^5\text{-}C_5H_4)CH(CH_2CH_2)_2NMe(coe)_2$ **11** was carried out in a similar manner by reaction of $[RhCl(coe)_2]_2$ with **8** in THF (see equation below). The product **11** is a yellow crystalline solid, unlike the oils of **9** and **10**, and it was recrystallised using diethyl ether. Single crystals of **11** were subsequently obtained from cooling a diethyl ether solution to $-25\,^{\circ}C$.

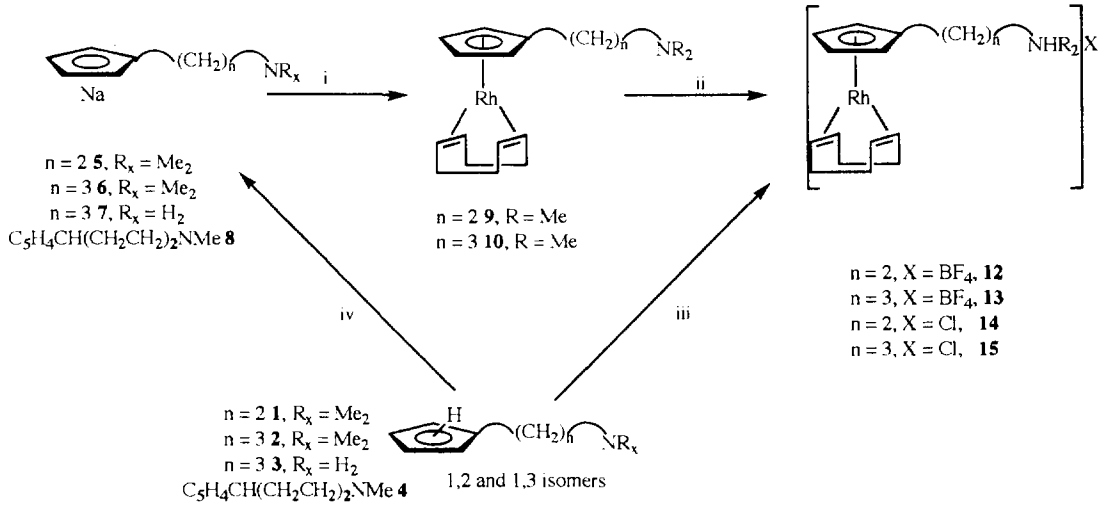
$$[Rh(coe)_2Cl]_2 + 2NaC_5H_4CH(CH_2CH_2)_2NMe \rightarrow 2RhC_5H_4CH(CH_2CH_2)_2NMe(coe)_2 + 2NaCl$$

An X-ray crystallographic determination was carried out for **11** (see Section 2.2) and the molecular structure can be seen in Fig. 1. This is the first structure amongst those of Rh and Ir complexes containing amino-substituted cyclopentadienyl groups to show an uncoordinated nitrogen atom. The chair formation of the pendant piperidine moiety can be clearly seen. In contrast, structures containing chelated nitrogen structures to have been done include $M(C_5Me_4)(CH_2)_2NMe_2I_2$ (M = Rh, Ir) where the metal centre is in a 3+ oxidation state, thus making an interaction with the nitrogen atom more favourable [5]. The Rh(III) di-iodo derivative $Rh(\eta^5\text{-}C_5H_4)(CH_2)_2NMe_2I_2$ **16** was also prepared in this study by reaction of **9** with I_2 in diethyl ether. This was characterised by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis.

In conclusion, we have isolated and characterised the sodium salts of the amino-substituted cyclopentadienide complexes for the first time. These salts can be isolated on a multigram-scale, thus furnishing the opportunity to carry out several organometallic reactions.

2.1. Selected NMR data

Spectra recorded at ambient probe temperature at 200.1 MHz, 250.1 MHz and 400.1 MHz (^{1}H), or at 50.3, 62.9, and 100.6 MHz (^{13}C), or at 61.4 MHz (^{2}H). J refers to a coupling constant in hertz.



Scheme 1. Reagents and conditions: (i) $[RhCl(cod)]_2$, THF, 70–75%; (ii) Et_2O, HBF_4, 86–90%; (iii) $[RhCl(cod)]_2$, THF, 85%; (iv) THF, NaH.

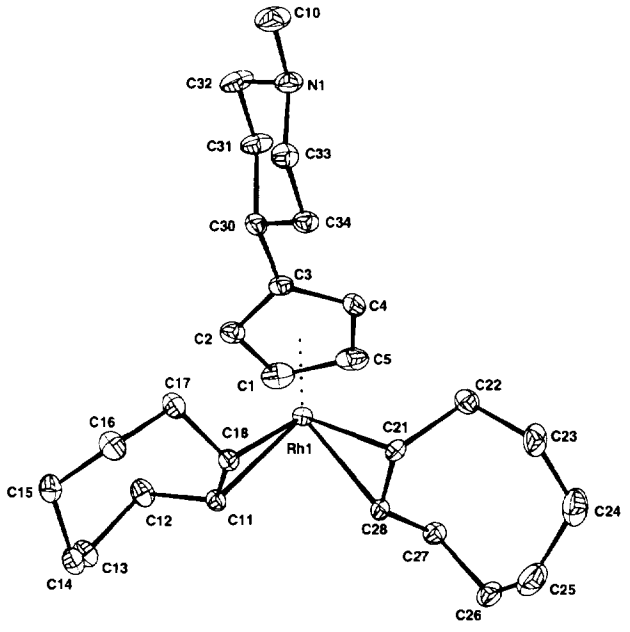


Fig. 1. Molecular structure of **11** (thermal ellipsoids at the 20% probability level), without hydrogen atoms. Selected bond lengths (Å) and angles (deg): Rh(1)–C(11) 2.129(4), Rh(1)–C(18) 2.139(5), Rh(1)–C(21) 2.155(5), Rh(1)–C(28) 2.128(5), C(21)–C(28) 1.403(7), C(11)–C(18) 1.415(7), N(1)–C(10) 1.458(9), C(3)–C(30) 1.502(8), C(3)–C(30)–C(31) 111.7(5), C(3)–C(30)–C(34) 112.3(5), Rh(1)–Cp(centroid) 1.919.

2. ^{1}H: (2 isomers — [^{2}H]chloroform) δ 6.4–5.9 (m, 6H, CH of $C_5H_5CH_2CH_2CH_2NMe_2$), 2.9–2.8 (m, 4H, CH_2 of $C_5H_5CH_2CH_2CH_2NMe_2$), 2.4–2.2 (m, 20H, $CH_2CH_2CH_2NMe_2$), 1.7–1.6 (m, 4H, $CH_2CH_2CH_2NMe_2$); ^{13}C{^{1}H}: ([^{2}H]chloroform) δ 149.3, 146.6 (s, $C(CH_2)_3NMe_2$), 134.5, 133.5, 132.2, 130.3, 126.1, 125.7 (6 × s, CH of $C_5H_5(CH_2)_3NMe_2$), 59.4 (s, overlapping $CH_2CH_2CH_2NMe_2$), 45.4 (s, overlapping $C_5H_5(CH_2)_3NMe_2$), 43.0, 41.0 (2 × s, CH_2 of $C_5H_5(CH_2)_3NMe_2$), 28.3, 27.6, 27.5, 26.7 (4 × s, $CH_2CH_2CH_2NMe_2$).

4. ^{1}H: (2 isomers — [^{2}H]chloroform) 6.5–5.9 (m, 6H, CH of $C_5H_5CH(CH_2CH_2)_2NMe$), 2.9–2.8 (m, 4H, CH_2 of $C_5H_5CH(CH_2CH_2)_2NMe$), 2.4–1.5 (m, 30H, $CH(CH_2CH_2)_2NMe$); ^{13}C{^{1}H}: ([^{2}H]chloroform) 153.6, 151.1 (2 × s, $C_5H_5CCH(CH_2CH_2)_2NMe$), 133.6, 133.2, 132.2, 130.4, 124.9, 124.3 (6 × s, CH of $C_5H_5CCH(CH_2CH_2)_2NMe$), 56.0 (2 × s, overlapping $C_5H_5CCH(CH_2CH_2)_2NMe$), 46.4, 46.0 (2 × s, $CH(CH_2CH_2)_2NMe$), 41.3, 41.0 (2 × s, CH_2 of $C_5H_5CCH(CH_2CH_2)_2NMe$), 36.9, 36.1 (2 × s, $CH(CH_2CH_2)_2NMe$), 32.7, 31.7 (2 × s, $CH(CH_2CH_2)_2NMe$).

6. ^{1}H: (in [^{2}H$_3$]acetonitrile) δ 5.50, 5.48 (2 × br s, 4H, $C_5H_4CH_2CH_2CH_2NMe_2$), 2.51–2.44 (m, 2H, $CH_2CH_2CH_2NMe_2$), 2.34–2.19 (m, 2H, $CH_2CH_2CH_2NMe_2$), 2.19 (s, 6H, $CH_2CH_2CH_2NMe_2$), 1.72–1.69 (m, 2H, $CH_2CH_2CH_2NMe_2$); ^{13}C{^{1}H} initial: (in [^{2}H$_3$]acetonitrile) δ 120.2 (s, $C(CH_2)_3NMe_2$), 102.8, 102.3 (2 × s, CH of $C_5H_4(CH_2)_3NMe_2$), 61.6 (s, $CH_2CH_2CH_2NMe_2$), 45.9 (s, $C_5H_4(CH_2)_3NMe_2$), 32.0 (s, $CH_2CH_2CH_2NMe_2$), 29.8 (s, $CH_2CH_2CH_2NMe_2$); ^{13}C{^{1}H} (after 2 h in [^{2}H$_3$]acetonitrile) δ CH of $C_5H_4(CH_2)_3NMe_2$ become 102.6, 102.0 (2 × t, $^1J(^{13}C-^2H)$ 24.0, CD of $C_5D_4(CH_2)_3NMe_2$); ^{2}H: (in [^{2}H$_3$]acetonitrile) 5.5 (2 × br s, $C_5D_4CH_2CH_2NMe_2$).

9. ^{1}H: (in [^{2}H$_6$]benzene) δ 5.02, 4.85, (2 × t, 4H, $C_5H_4CH_2CH_2NMe_2$), 3.85 (br s, 4H, CH of COD), 2.45 (m, 2H, $CH_2CH_2NMe_2$), 2.30 (m, 6H, $CH_2CH_2NMe_2$ and CH_2 of COD), 2.11 (s, 6H, $CH_2CH_2NMe_2$), 2.02 (m, 4H, CH_2 of COD); ^{13}C{^{1}H}: (in [^{2}H$_6$]benzene) δ 105.5 (s, $C(CH_2)_2NMe_2$), 87.6, 85.8 (2 × s, CH of $C_5H_4(CH_2)_2NMe_2$), 64.4 (d, $J(^{103}Rh-^{13}C)$ 13.8, CH of COD), 61.8 (s, CH_2NMe_2), 46.0 (s, $C_5H_4(CH_2)_2NMe_2$), 33.4 (s, CH_2 of COD), 26.9 (s, $CH_2CH_2NMe_2$).

12. ^{1}H: (in [^{2}H$_2$]dichloromethane) δ 7.80 (br s, NH of $C_5H_4CH_2CH_2NMe_2H^+$), 5.06 (br s, 4H, $C_5H_4CH_2CH_2NMe_2H^+$), 3.81 (br s, 4H, CH of COD), 3.35 (m, 2H, $CH_2CH_2NMe_2H^+$), 2.97 (s, 6H, $CH_2CH_2NMe_2H^+$), 2.67 (m, 2H, $CH_2CH_2NMe_2H^+$), 2.18 (m, 4H, CH_2 of COD), 1.91 (m, 4H, CH_2 of COD); ^{13}C{^{1}H}: (in [^{2}H$_2$]dichloromethane) δ 99.2 (s, $C(CH_2)_2NMe_2H^+$), 86.8, 86.7 (2 × s, CH of $C_5H_4(CH_2)_2NMe_2H^+$), 64.2 (d, $^1J(^{103}Rh-^{13}C)$ 14.1, CH of COD), 60.2 (s, $CH_2NMe_2H^+$), 44.3 (s, $C_5H_4(CH_2)_2NMe_2H^+$), 32.5 (s, CH_2 of COD), 23.3 (s, $CH_2CH_2NMe_2H^+$).

16. ^{1}H: ([^{2}H$_6$]dimethylsulphoxide) δ 6.25, 6.15 (2 × s, 4H, $C_5H_4(CH_2)_2NMe_2$), 3.50 (m, 2H, $CH_2CH_2NMe_2$), 2.99 (m, 8H, $CH_2CH_2NMe_2$ and $CH_2CH_2NMe_2$); ^{13}C{^{1}H}: ([^{2}H$_6$]dimethylsulphoxide) δ 105.2 (s, $C(CH_2)_2NMe_2$), 92.3, 89.5 (2 × d, $^1J(^{103}Rh-^{13}C)$ 5.8, CH of $C_5H_4(CH_2)_2NMe_2$), 56.8 (s, CH_2NMe_2), 44.2 (s, $C_5H_4(CH_2)_2NMe_2$), 24.3 (s, $CH_2CH_2NMe_2$).

2.2. Crystal data for 11

$C_{27}H_{44}RhN$, $M = 485.53$, monoclinic, space group $P2_1/c$, cell parameters: $a = 7.0976(8)$ Å, $b = 35.715(9)$ Å, $c = 10.162(2)$ Å, $\beta = 109.09(1)°$, $V = 2434(1)$ Å^3, $Z = 4$, $D_c = 1.325$ g cm^{-3}, $\mu = 7.02$ cm^{-1}. Crystal size: 0.17 × 0.17 × 0.50 mm^3, data range: $3 < 2\theta < 52°$, 5270 reflections collected, 4777 unique reflections ($R_{int} = 0.02$), $R = 0.0506$ and $R_w = 0.0458$ from 2676 reflections used with a criterion ($I > 3\sigma(I)$). A crystal of **11** was sealed in a glove box under an inert atmosphere in a Lindemann capillary, which was subsequently transferred to the goniometer head. Data collection was performed at room temperature ($T = 293$ K) on an Enraf–Nonius CAD4 diffractometer using a

graphite-monochromated Mo K α radiation, (ω–2θ scan mode was used). Unit cell dimensions with estimated standard deviations were obtained from a least squares refinement of the setting angles of the 25 well-centred reflections in the region $13 < 2\theta < 14°$. Three standards reflections were checked periodically and they showed no significant decrease in intensities. Corrections were made for Lorentz and polarisation effects; empirical absorption corrections were applied using DIFABS [6]. The structure was solved by direct methods SHELXS 86 [7]. Hydrogen atoms were included in refinement in constrained idealised positions (C–H = 0.96 Å) with fixed isotropic thermal of $1.2U_{eq}$ of the attached carbon atom. A Chebyshev [8] weighting scheme was applied as follows:

$$W = {}^{*}W'\left[1 - (F)/6(F_o)^2\right]^2 \text{ with}$$

$${}^{*}W' = 1/(r = 1,3)\, ArTr(X)$$

where Ar are the coefficients for the Chebyshev polynomial $Tr(X)$ with $X = F_c/F_{c(max)}$. Crystallographic calculations were carried out using the CRYSTALS [9] program adapted on a PC. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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