Russian Journal of Coordination Chemistry, Vol. 29, No. 7, 2003, pp. 501–504. From Koordinatsionnaya Khimiya, Vol. 29, No. 7, 2003, pp. 537–540.

Synthesis and Spectroscopic Studies of New Substituted Dinuclear η^5-4,5,6,7-Tetrahydroindenyl Ruthenium Complexes*

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Received July 2, 2002

Abstract—New complexes of bis(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)diruthenium tetracarbonyl and bis(3-methyl-1-phenyl-4,5,6,7-tetrahydroindenyl)diruthenium tetracarbonyl were prepared from the corresponding substituted tetrahydroindene and ruthenium carbonyl. The ligand systems were obtained by the reactions of methyl magnesium iodide and phenyl magnesium bromide with 3-methyl-2,3,4,5,6,7-hexahydroind-8(9)en-1-one.

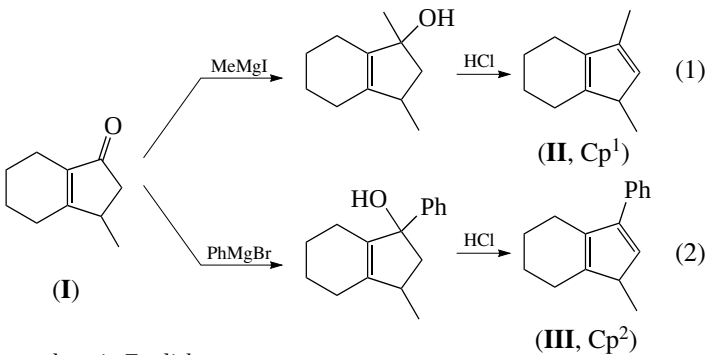
INTRODUCTION

Peralkylcyclopentadienyl ligands have proved to be extremely valuable ligands in organometallic chemistry because of their general robustness and their influence on the chemistry at the metal center [1]. Several years ago we reported the syntheses of ethyltetramethylcyclopentadienyl ruthenium complexes $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2X$ (X = Cl, Br, I) [2, 3] and a kinetic study of their carbonyl substitution reactions [4]. We have also reported the detailed chemistry of the title compounds [5].

The synthesis of cyclopentenones by the Nazarov cyclization reaction and subsequent alkylation is a route to 4,5,6,7-tetrahydroindenes that is significantly more facile and versatile than hydrogenation of metalated indenyl ligands [6]. The tetrahydroindene ligand and its derivatives with proper substituents have been considerably employed as π-ligands of metallocenes. The complexes of 4,5,6,7-tetrahydroindenes have been the focus of great interest owing to the catalytic activity of their zirconium compounds [7]. We report herein the synthesis of a symmetrical 1,3-dimethyl-4,5,6,7-tetrahydroindene and more sterically demanding 3-methyl-1-phenyl-4,5,6,7-tetrahydroindene from the same ketone precursor utilized by Nile [6]. Ruthenium carbonyl complexes of these ligands are also described.

RESULTS AND DISCUSSION

Nazarov cationic π-cyclization was employed in the synthesis of 3-methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one (**I**) reported originally by Dev [7] and later by Nile and co-workers [6]. We have improved the yield by efficiently mixing the crotonic acid and polyphosphoric acid by mechanical stirring at 60°C for 30 min before adding the cyclohexene. Addition of the cyclohexene was carried out over 30 min and the mixture was then stirred at 60°C for 3 h. This appears to prevent the occurrence of an exothermic initiation of the cyclization reported by Nile. The second alteration was the use of 10% NaOH solution in water to facilitate the decomposition of the polyphosphoric acid rather than solid ammonium sulfate. The combination of these two changes increased the yield to 30%. Structure of this α, β unsaturated ketone was established by spectroscopic methods (IR, ^{1}H NMR and mass-spectrometry). Nucleophilic addition of methyl (from methyl magnesium iodide (1)) or phenyl (from phenyl magnesium bromide (2)) anions gave allylic alcohols, which were dehydrated by using hydrochloric acid as a catalyst.



*This article was submitted by the authors in English.

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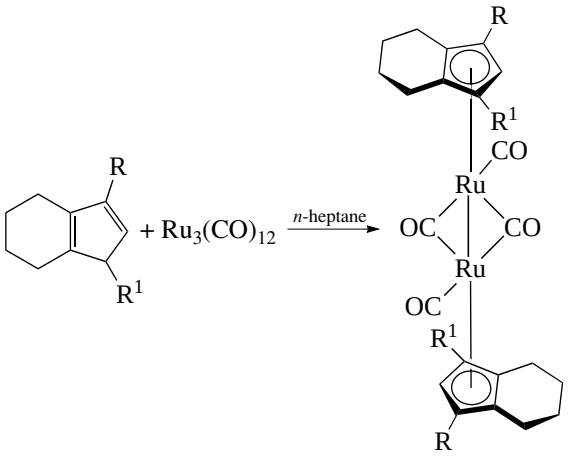
This addition-dehydration process yielded 1,3-dimethyl-4,5,6,7-tetrahydroindene (**II**) and bulky chiral ligand, 3-methyl-1-phenyl-4,5,6,7-tetrahydroindene (**III**). The products were purified by column chromatography. These substituted tetrahydroindenes appeared to be quite unstable and polymerized on standing in air. The infrared spectra of the freshly prepared ligands had olefinic bands at 1600–1640 cm^{-1} region. The gas chromatography (GC) analysis for **II** and **III** indicated the presence of several double bond isomers.

The position of double bonds in the products has not been determined with certainity, it is possible that some of these isomers do not have acidic hydrogen atoms, which may explain the low yields of transition metal complexes derived from their treatments with metal carbonyls. The reactivity of cyclopentadienyl ligand **II**, derived by deprotonation of the tetrahydroindenyl ligand with metal halide salts has been previously established [8]. In the research undertaken, we decided to investigate the reactivity of the free dienes **II** and **III** towards metallation reactions. Complexes containing more than single metal center offer an added chemical dimension over those containing a single metal. These complexes also act in a cooperative manner leading chemistry that differes appreciably from that displayed by the single metal counterparts [9]. As known, there is a general tendency for slower addition and elimination reactions when proceeding down a group in the periodic table. A unique feature in the organometallic chemistry of ruthenium is the formation of coordinatively unsaturated complexes stabilized by π-donor ligands. These complexes in many instances combine the advantage of higher stability compared to iron with increased mobility compared to osmium [10].

Therefore, at the outset we decided to try and make a symmetrical dinuclear η^5-tetrahydroindenyl carbonyl ruthenium complex according to Eq. (3):



(3)

IV: $R = R^1 = CH_3$;
V: $R = Ph$, $R^1 = CH_3$.

Prolonged reflux of **II** with $Ru_3(CO)_{12}$ in *n*-heptane gave a dark brown solution, from which a dark brown powder was precipitated by partial removal of the solvent under reduced pressure. Purification on alumina and recrystallization from 1 : 1 ratio of *n*-heptane–dichloromethane gave purple crystals of bis(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)diruthenium tetracarbonyl (**IV**) as a major isomer. The infrared spectrum of **IV** revealed the presence of a band at 1925 cm^{-1} assigned to terminal CO and a single band at 1740 cm^{-1} assigned to bridging CO stretch. This pattern of peaks, with a weak band at 1895 cm^{-1} and a shoulder at 1720 cm^{-1}, is well documented to be characteristic of *cis-trans* isomers of symmetrical $[Cp^1Ru(CO)]_2(\mu\text{-}CO)_2$ dimer. Approximately, total exclusion of the *cis* form in **IV** was assumed to be due to steric repulsions between the methyl groups in *cis* isomer. In the ^{13}C NMR spectrum, tetrahydroindenyl ligand resonances are well assigned and downfield shifts are seen for non-bridged (terminal) carbonyls.

Due to understandable effect of alkyl substituents on the ^{13}CO chemical shifts, electron donating methyl groups (with no π-acceptor capacity) on ligand system causes strong ruthenium carbonyl *d*–π* back-bonding increases the π-mobile bond order and electron density around the terminal carbonyl groups.

The main function of the chiral substituent is to direct metallation to one enantioface of a non-symmetrically substituted cyclopentadiene, therefore we synthesized more heavily substituted ligand **III** and examined its complexation to $Ru_3(CO)_{12}$. Many attempts to coordinate chiral ligand **III** to ruthenium carbonyl in toluene and heavy petroleum ether gave no trace of the expected complex bis(3-methyl-1-phenyl-4,5,6,7-tetrahydroindenyl)diruthenium tetracarbonyl (**V**) under all conditions used. Since complexation of several substituted cyclopentadienes has been published in the literatures, we concluded that the failure in this reaction was due to the solvent. Finally, the reaction in *n*-heptane with careful control of temperature and monitoring the reaction by IR, gave the complex **V**. Repeated crys-

tallization from a mixture of dichloromethane–*n*–heptane (ratio 1 : 1) furnished a pure sample of the desired complex in 22% yield. Infrared spectrum of **V** showed the presence of bands at 1965 and 1920 cm^{-1} assigned to terminal CO stretch and a single band at 1759 cm^{-1} assigned to bridging CO stretch. Similar to **IV**, this pattern of peaks together with weak shoulders at 1795 and 1895 cm^{-1} is well documented to be characteristic of *cis-trans* isomers of $[Cp^2Ru(CO)]_2(\mu\text{-}CO)_2$ dimer **V**. It has been difficult to obtain high quality ^1H NMR spectra for **V**, since even samples prepared from freshly crystallized material gave rise to a broad C–H resonances in the ^1H NMR spectrum.

Very careful sample preparation was necessary to prepare a sample from which we were able to obtain a ^1H NMR spectrum in which the 1-phenyl-3-methyl-tetrahydroindenyl ligand resonances could be assigned, although, carbonyl resonances were not observed in the ^{13}C NMR spectra. These NMR characteristics may be due to oxidation or some other decomposition processes in solution giving rise to the traces of paramagnetic impurities or from an equilibrium in solution between the ruthenium dimer $[(Cp^2)Ru(CO)]_2(\mu\text{-}CO)_2$ **V** and either a paramagnetic 17-electron monomer $[(Cp^2)Ru(CO)_2]$ or the 32-electron molecule $[(Cp^2)Ru]_2(\mu\text{-}CO)_3$ and CO. Similar dimer–monomer equilibria are well documented in group VI chemistry for $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo, W) and related complexes containing bulky cyclopentadienyl ligands [11].

EXPERIMENTAL

All starting materials were obtained from commercial suppliers and used without further purification. All reactions involving air or moisture sensitive compounds were performed under argon or nitrogen atmospheres. IR spectra were recorded on a Shimadzu 470 spectrometer. ^1H NMR spectra were measured on a Bruker 80 MHz-FT or Varian-500 MHz (DRX-Avance) spectrometer, chemical shifts are given in ppm (δ) relative to Me_4Si as internal standard. Capillary GC analyses were performed using a Buck Scientific 910 (capillary column MKhT-5, column length: 15 m) and mass spectra by Mass-QP 1100 EX Shimadzu.

Column chromatography was carried out by using silica gel 60 GF_{254} Merck (art No.: 7730, 7733). The solvents were dried according to the standard methods prior to use.

Synthesis of 3-methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one (I). Cyclohexene (27.3 g, 322 mmol) was added dropwise to a mechanically stirred mixture of crotonic acid (28.7 g, 333 mmol) and polyphosphoric acid (200 g) at 60°C. The mixture was stirred at 60°C for 2 h. A solution of 10% NaOH (100 ml) was added and the slurry stirred for 16 h to facilitate decomposition of the polyphosphoric acid. The mixture was extracted with 40–60°C petroleum ether (3 × 100 ml) and the combined organic extracts were washed with 5% ammonia solution in water (50 ml), followed by saturated sodium chloride solution (2 × 50 ml). The solution was dried over magnesium sulfate and concentrated. Distillation under reduced pressure afforded **I** as a colorless oil, (15 g, 100 mmol), 30%. IR spectrum (neat, ν, cm^{-1}): 2850–2930 s, 1700 s, 1640 s, 1180 m; ^1H NMR ($CDCl_3$, δ, ppm): 0.85 (d., 3H), 1.3–2.6 (m, 11 H). Mass (*m*/*e* (%)):150 (83), 135 (75), 107 (59), 79 (75).

Synthesis of 1,3-dimethyl-4,5,6,7-tetrahydroindene (II). Methyl magnesium iodide was prepared from methyl iodide (2 g, 15 mmol) and magnesium turnings (0.3 g, 12.5 mmol) in anhydrous diethyl ether. The reaction began in a few minutes, as was shown by gentle refluxing of the solvent. The flask was heated for another 5 min in a water bath (35°C) to complete the preparation of methyl magnesium iodide. At this point, the reaction mixture was cooled by the application of crashed ice and compound **I** (2 g, 13 mmol) was slowly added with stirring. During the addition, a green color developed. After the ketone addition completed, the mixture was allowed to warm to room temperature and stirred for 15 h. The unreacted magnesium was filtered and the solution was quenched with water. The aqueous layer was extracted with diethyl ether and the combined organic extracts were dried over magnesium sulfate and filtered. Aqueous 12 M HCl (0.5 ml) was added to the ethereal solution and stirred for 2 h. The organic phase was separated, washed with water and dried over magnesium sulfate. Ethereal solution was filtered, evaporated in vacuo and purified (SiO_2, ethyl acetate/petroleum ether 1 : 14) to yield a clear green oil (0.97 g, 6.5 mmol) in 45% yield. GC analysis indicated the presence of several isomers. IR spectrum (CCl_4, ν, cm^{-1}): 2850–2950 s, 1560–1590 w, 1375 w, 1450 w. ^1H NMR ($CDCl_3$, δ, ppm): 0.8–2.7 (m, 15 H), 5.2 (m, 1H).

Synthesis of 3-methyl-1-phenyl-4,5,6,7-tetrahydroindene (III). This ligand was prepared by using unsaturated ketone **I** and phenyl magnesium bromide in a manner analogous to **II**. The Grignard reagent was prepared from bromobenzene (0.650 g, 4.14 mmol) and magnesium turnings (0.399 g, 16.6 mmol) in a similar way as in **II**. The reaction was much slower than the methyl magnesium bromide. The reaction mixture was kept for an additional 15 min to completion of preparation, then, via syringe, unsaturated ketone **I** (2 g, 13 mmol) was added with stirring. The solution was stirred for 15 h. As in the case of **II**, work-up and dehydration with aqueous 12 M HCl (0.5 ml) yielded **III** (1.34 g) as a red oil in 48% yield. IR spectrum (neat, ν, cm^{-1}): 3000–3050 w, 2800–2900 s, 1590–1600 w, 695–730 s. ^1H NMR ($CDCl_3$, δ, ppm): 0.89–1.00 (m, 3H), 1.23–2.2 (m, 8H), 5.32 (s, 1H), 7.2–7.6 (m, 5H).

Synthesis of bis(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)diruthenium tetracarbonyl (IV). To prepare $[Cp^1Ru(CO)]_2(\mu\text{-}CO)_2$ (**IV**), tetrahydroinden ligand **II** (0.1 g, 0.6 mmol) and $Ru_3(CO)_{12}$ (0.35 g, 0.5 mmol) were refluxed in *n*-heptane (20 ml) for 24 h, without exclusion of the air. The solvent was removed

under vacuum and the dark brown precipitate was purified by chromatography on alumina (dichloromethane/petroleum ether 1 : 1). The purple band on the column was collected and the solvent removed under vacuum. Final recrystallization from petroleum ether was needed to yield the pure product of **IV** (0.15 g, 0.25 mmol) in 40% yield. IR spectrum (KBr, ν, cm^{-1}): 1925 s, 1740 s, 1895 w, 1720 h. ^1H NMR ($CDCl_3$, δ, ppm): 1.85–1.87 (m, 20H, 4$\underline{CH_3}$ and 2($\underline{CH_2}$–$\underline{CH_2}$)), 2.4 (m, 4H, 2$\underline{CH_2}$ benzylic), 2.7(m, 4H, 2$\underline{CH_2}$ benzylic), 4.36(s, 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 9.9, 32.3, 37.4, 101, 104, 109, 189.4, 199.4. Mass (*m*/*e* (%)): 608 (20), 580 (15), 552 (5), 524 (30), 495 (50), 304 (25), 157 (20).

Synthesis of bis(3-methyl-1-phenyl-4,5,6,7-tetrahydroindenyl)diruthenium tetracarbonyl (V). By refluxing freshly prepared chiral tetrahydroindene ligand **III** (0.14 g, 0.66 mmol) in 25 ml of *n*-heptane solution and $Ru_3(CO)_{12}$ (0.402 g, 0.63 mmol) for 20 h, dark brown powder precipitated. The reaction mixture was cooled at room temperature and then filtered. Further purification on alumina and final recrystallization from 1 : 1 ratio of CH_2Cl_2, *n*-heptane, provided pure product of **V** (0.1 g, 0.14 mmol) in 22% yield.

IR spectrum (KBr, ν, cm^{-1}): 1920 s, 1965 s, 1795 sh, 1759 s, 1895 sh. ^1H NMR ($CDCl_3$, δ, ppm): 1.8 s, 6H, $\underline{CH_3}$), 2.4 (m, 4H, H^5, H^5 or H^6, H^6), 2.6 (m, 4H, H^6, H^6 or H^5, H^5) 2.7 (m, 4H, H^4, H^4 or H^7, H^7), 3.1 (m, 4H, H^7, H^7 or H^4, H^4), 4.3 (s, 2H), 7.3 (m, 10H). ^{13}C NMR ($CDCl_3$, δ, ppm): 10.8, 22.7, 23.4, 23.5, 23.6, 127.7, 128.6, 128.7, 128.8, 128.9, 129, 129.1, 129.2, 132.7. Mass (*m*/*e*, %): 640 (10), 612 (10), 584 (10), 528 (15), 496 (30), 305 (15), 43 (83).

ACKNOWLEDGMENTS

Partial support of this work by Guilan University Research Council is gratefully acknowledged. We thank also Dr. Colin White, University of Sheffield in England, for his advice and dedication of ruthenium carbonyl.

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