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σ-CYCLOPENTADIENYL-π-CYCLOPENTADIENYL-π-(2,2,4-TRIMETHYL-3-HYDROXY-3-PENTENOIC ACID LACTONE)NICKEL

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SUMMARY

The lactone complex (I), σ-cyclopentadienyl-π-cyclopentadienyl-π-(2,2,4-trimethyl-3-hydroxy-3-pentenoic acid lactone)nickel has been prepared, and constitutes the first example of coordination of a four-membered lactone ring to a metal atom via π-electrons. The complex is obtained by treating dimethylketene with di-π-cyclopentadienylnickel, and in this reaction one of the π-cyclopentadienyl ligands in di-π-cyclopentadienylnickel rearranges from π- to σ-bonding. The structure of the new complex was elucidated by means of IR and NMR spectrum. The nature of another product formed in the reaction is discussed.

INTRODUCTION

The reactions between ketenes and transition-metal complexes have been little studied[1,2]. Hagihara *et al.*[1] prepared the ketene complexes by treating diphenylketene with di-π-cyclopentadienylvanadium and di-π-cyclopentadienyltitanium dicarbonyl. We have investigated the reaction of dimethylketene with di-π-cyclopentadienylnickel and obtained a new four-membered lactone complex (I), σ-cyclopentadienyl-π-cyclopentadienyl-π-(2,2,4-trimethyl-3-hydroxy-3-pentenoic acid lactone)-nickel; Heck[3] has previously prepared five-membered lactone complex (II) by treating acetylcobalt tetracarbonyl with 3-hexyne. We describe here the preparation and the properties of the complex (I).

EXPERIMENTAL

Di-π-cyclopentadienylnickel was prepared by the conventional method[4]. Toluene, benzene, diethyl ether and n-hexane were stored over and distilled from sodium wire under nitrogen. Triethylamine was dried by distillation from sodium hydroxide and isobutyryl chloride was prepared by the procedure of Brown[5]. Dimethylketene[6], formed by the reaction between 8.1 g (76 mmoles) of isobutyryl chloride and 8.0 g (79 mmoles) of triethylamine in 60 ml of diethyl ether, was distilled together with ether under nitrogen atmosphere into the reaction vessel and its yield (about 40%) was determined by Smith's method[7]. All reactions were carried out under oxygen-free dry nitrogen.

Reaction of dimethylketene with di-π-cyclopentadienylnickel

Into an ice-cooled solution of 2.0 g (10 mmoles) of di-π-cyclopentadienylnickel in 80 ml of toluene, about 2.1 g (30 mmoles) of dimethylketene, freshly distilled as a diethyl ether solution, was added. After the mixture had been stirred at room temperature for two days, the colour of the reaction mixture turned to red brown from green. The solvent was evaporated under reduced pressure to leave a red brown residue which was extracted with 20 ml of benzene. The benzene solution was concentrated under vacuum and 20 ml of n-hexane was added. Standing overnight in a refrigerator gave a precipitate which was filtered and recrystallized several times from benzene/n-hexane to give 0.5 g of orange red crystals (I) [16% yield based on $(\pi\text{-}C_5H_5)_2Ni$], m.p. 173.5–174.0° (decompn.). (Found: C, 65.92; H, 6.70; Ni, 17.40; mol.wt. cryoscopic in benzene, 329.6. $C_{18}H_{22}NiO_2$ calcd.: C, 65.71; H, 6.69; Ni, 17.86%; mol.wt., 328.7.)

To the n-hexane filtrate, which showed a terminal metal carbonyl stretching vibration at 2020 cm^{-1}, were added 4.2 g (16 mmoles) of triphenylphosphine, 20 ml of diethyl ether and 20 ml of toluene. After stirring at room temperature for two days, the colour of the reaction mixture turned to yellowish red from red. The solvent was evaporated under reduced pressure, 15 ml of n-hexane was added and the mixture was stored in a refrigerator overnight. Recrystallization of the precipitate from benzene gave 1.6 g of pale cream crystals (III), bis(triphenylphosphine)nickel dicarbonyl, [25% yield based on $(\pi\text{-}C_5H_5)_2Ni$], m.p. 205–210° (decompn.). (Found: C, 71.06; H, 4.65. $C_{38}H_{30}NiO_2P_2$ calcd.: C, 71.36; H, 4.69%.) The stretching vibrations of metal carbonyl in complex (III) appear at 2010 and 1955 cm^{-1} in cyclohexane solution. The melting point and IR spectrum of product (III) were identical to those in the literature[8].

RESULT AND DISCUSSION

The reaction of dimethylketene with di-π-cyclopentadienylnickel gives an air stable orange red complex (I), which is very soluble in diethyl ether, benzene and toluene and less soluble in n-hexane. The elemental analyses and the molecular weight indicate clearly that the molecular formula is $C_{18}H_{22}NiO_2$, corresponding with a 1 to 2 ratio of di-π-cyclopentadienylnickel to dimethylketene.

$$(\pi\text{-}C_5H_5)_2Ni + (CH_3)_2C{=}C{=}O \rightarrow \text{complex (I)} + \text{nickel carbonyl complex}$$

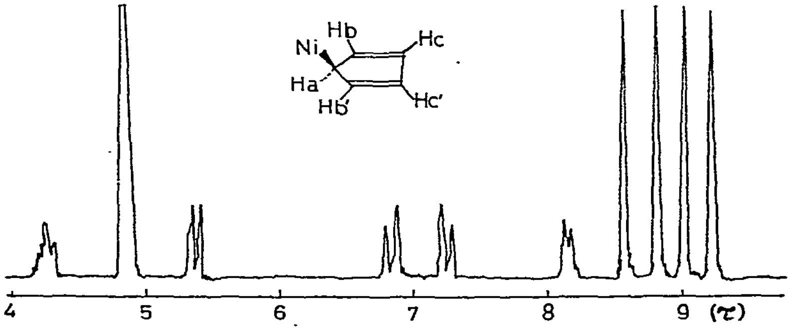

Fig. 1. The proton NMR spectrum of the complex (I), taken on a JEOL-JNM-4H-100 NMR spectrometer in CS_2 with tetramethylsilane as internal standard at τ10.

The proton NMR spectrum of the complex (I), shown in Fig. 1, showed four sharp singlets in the methyl proton region at τ 9.23, 9.02, 8.81 and 8.57 ppm (with each area 3), one sharp singlet in the π-cyclopentadienyl region at τ 4.86 ppm (with area 5) and four doublets at τ 8.14 (J_{ab} or $J_{ab'}$ 3.9 Hz), 7.23 ($J_{cc'}$ 6.8 Hz), 6.82 ($J_{cc'}$ 6.8 Hz), and 5.37 ppm (J_{ab} or $J_{ab'}$ 4.7 Hz) and a complex quartet at τ 4.24 ppm due to non-equivalent σ-cyclopentadienyl protons[9] with each area 1). This observation confirms that one of the two cyclopentadienyl rings is σ-bonded and the other π-bonded to the nickel atom. The reason why H_a appears at unusually low field is explained well by the paramagnetic anisotropy effect of the nickel atom[10]. No temperature dependence of the σ-cyclopentadienyl signals was observed in the range of 20 to 80°. This existence of all five separated signals for σ-cyclopentadienyl protons indicates that metallotropic rearrangement and free rotation of σ-cyclopentadienyl ring around the metal–carbon bond is prohibited, the environment of the nickel being considerably crowded with σ- and π-cyclopentadienyl and π-lactone ligands.

The IR spectrum of complex (I) showed three absorption bands at 1771 s, 1680 s and 1645 w cm^{-1} in the region between 1600 and 1800 cm^{-1}. The possibility that complex (I) might be a dimethylketene complex is eliminated by the fact that the stretching bands of carbonyls in diphenylketene complexes arise between 1550 and 1620 cm^{-1} and that no band appear between 1620 and 2800 cm^{-1} [11]. The carbonyl stretching bands of dione dimer of dimethylketene[6] appear at 1750 s and 1720 m cm^{-1}, and could shift to lower frequency when coordinated. Furthermore, the IR spectrum of the complex (I) has absorption characteristics similar to those of the lactone dimer of dimethylketene, having absorptions at 1873 s, 1822 w and 1741 s cm^{-1} in the region between 1700 and 1900 cm^{-1}, although the bands in the former appear at considerably lower frequencies than those in the latter. These observations confirm that the complex (I) (Fig. 2) is σ-cyclopentadienyl-π-cyclopentadienyl-π-(2,2,4-trimethyl-3-hydroxy-3-pentenoic acid lactone)nickel. It seems that the lactone group in the lactone complex interacts with the nickel atom via the π-electrons of the lactone carbonyl and the carbon–carbon double bond, in view of the large shifts in the absorptions of these bonds. On the other hand, in complex (II) prepared by Heck[3], the stretching band of lactone carbonyl in the complex appeared at 1764 cm^{-1}, only 6 cm^{-1} displaced, towards low frequency, from that in the unsymmetrical lactone dimer. The formation of a σ-cyclopentadienyl-π-cyclopentadienyl complex of nickel is the first example of rearrangement of one of the two π-cyclopentadienyl ligands in di-π-cyclopentadienylmetals from π- to σ-bonding during reaction.

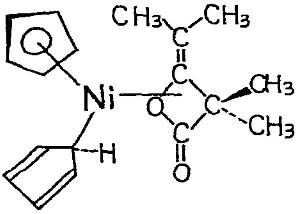

Fig. 2. σ-Cyclopentadienyl-π-cyclopentadienyl-π-(2,2,4-trimethyl-3-hydroxy-3-pentenoic acid lactone)-nickel.

The red brown pentane solution obtained after filtering off the complex (I) showed a metal terminal carbonyl band at 2020 cm^{-1} and other carbonyl bands at

1891, 1843 and 1773 cm^{-1}. Isolation of the oily compound as the triphenylphosphine derivative was more convenient than isolation of the compound itself; addition of triphenylphosphine to the solution gave the pale cream crystalline solid, bis(triphenylphosphine)nickel dicarbonyl (III), in which the carbonyl groups must have come from the dimethylketene. Decarbonylation reactions of ketenes by cobalt and rhodium complexes are known[2], but this is the first example of decarbonylation reaction by a nickel complex at room temperature.

We are investigating further the precursor of the bis(triphenylphosphine)nickel dicarbonyl and also other products of the reaction.

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