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Preliminary communication

THE PROTONATION OF $Co(C_5Me_4Et)(C_2H_4)_2$

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Summary

Reversible protonation of the bis-ethylene complex, $Co(C_5Me_4Et)(C_2H_4)_2$ yields $[Co(C_5Me_4Et)(C_2H_4)_2H][BF_4]$, which readily exchanges its hydridic and olefinic protons stereospecifically at low temperatures; subsequent protonation at room temperature yields cobalt(III) complexes, C_2H_4 and C_2H_6.

The successive protonation and reduction of olefins to alkanes catalysed by metal complexes offers an interesting alternative to conventional hydrogenation in that the energy of reaction may in some circumstances be released as electricity rather than heat when the process is carried out in a fuel cell. In this context, the protonation of olefin metal complexes forms part of a catalytic cycle for an electrochemical hydrogenation process.

When $Co(C_5Me_4Et)(C_2H_4)_2$ (I) [1] in CH_2Cl_2/Et_2O at 20°C is treated with HBF_4/Et_2O, a blue material results together with roughly equal quantities of ethene and ethane (by GC). Traces of 1-butene are also formed. The blue species may be converted to recognisable organometallic species by treatment with suitable ligands in the presence of NH_4PF_6. Thus acetonitrile gives $[Co(C_5Me_4Et)(MeCN)_3][PF_2]_2$ (II), (ν(CN) 2330, 2305 cm^{-1}) and toluene gives $[Co(C_5Me_4Et)(toluene)][PF_6]_2$. Both of these complexes were identified by ^{1}H NMR and IR spectra, which corresponded to previously reported data [1].

When I is treated with CF_3CO_2D under similar conditions to the above HBF_4/Et_2O reaction, ethane and ethene are again the major gaseous products, but GC/MS shows a random distribution of deuterium in both alkane and alkene. This result leads one to expect to isolate an intermediate in the protonation reaction and indeed, when the reaction of I with 2 mol HBF_4/Et_2O is carried out at −78°C in CH_2Cl_2/Et_2O, a red temperature sensitive compound (III) crystallises out (ca. 80% yield). Back-titration of excess acid in the

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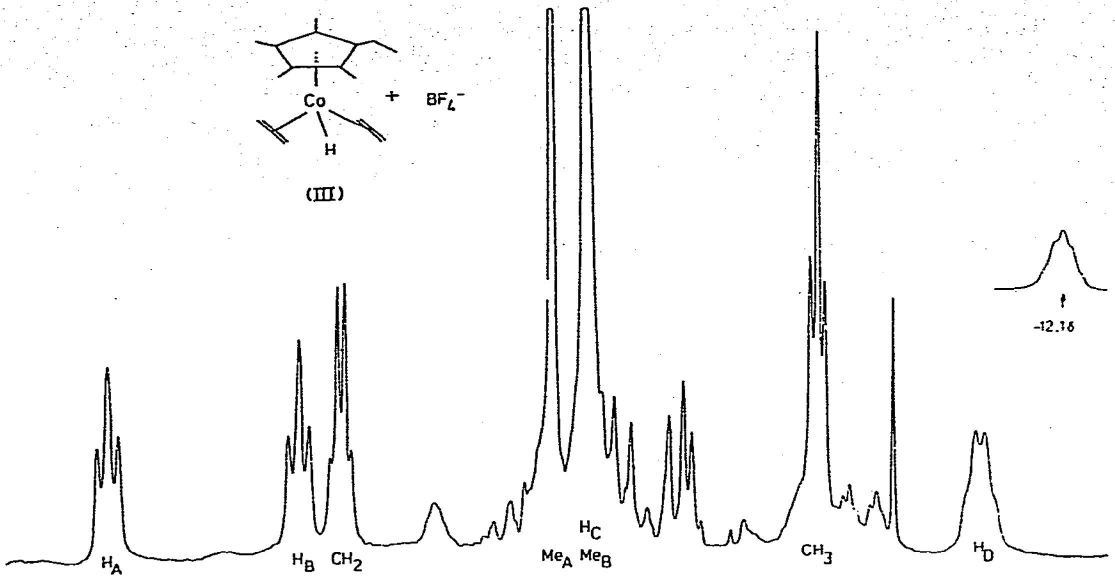
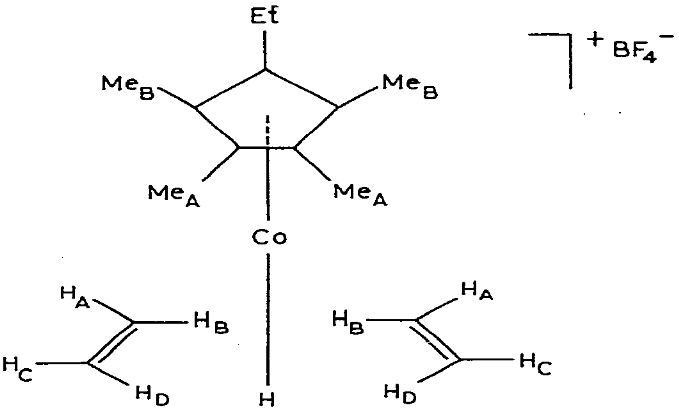


Fig. 1. 400 MHz ^1H NMR spectrum of III in CD_2Cl_2 at −85°C.

supernatant shows that one mole of H^+ has reacted per mole of Co (by atomic absorption on the red product). Treatment of III with bases such as proton sponge, pyridine and water gives back I as the only organometallic species observed by ^1H NMR. No gases are evolved.

Reaction of III with aqueous HBF_4 similarly gives ethene, ethane and $Co^{III}(C_5Me_4Et)$ complexes with small amounts of 1-butene. This shows that the ether present in the earlier reactions is not the source of the hydrocarbons.

The 400 MHz ^1H NMR spectrum of III in CD_2Cl_2 at −85°C is shown in Fig. 1 [2]. There are four olefinic resonances (2.74, t, $J_{cis} + J_{trans} = 21.7$, (2), H_A; 2.22, t, $J_{cis} + J_{trans} = 21.7$, (2), H_B; 1.48, m, H_C; 0.46, m, (2), H_D), a hydride (−12.1, quintet, $J = 9.3$), (1)) and the ring resonances (2.11, q, $J = 7.4$, (2), CH_2 of Et; 1.57, s, (6), Me_A; 1.48, s, Me_B; 0.88, t, $J = 7.4$, (3), CH_3 of Et). The spectrum and preceding data are consistent with a structure for III of:



Decoupling experiments eliminate alternative assignments for the olefinic protons. Thus, irradiation at H_A does not alter H_B, but irradiation at either H_C or H_D decouples both H_A and H_B. Also, irradiation at the hydride narrows the H_C and H_D resonances and vice-versa. Only if the hydride is situated on the vertical mirror plane of symmetry but to one side of the main molecular

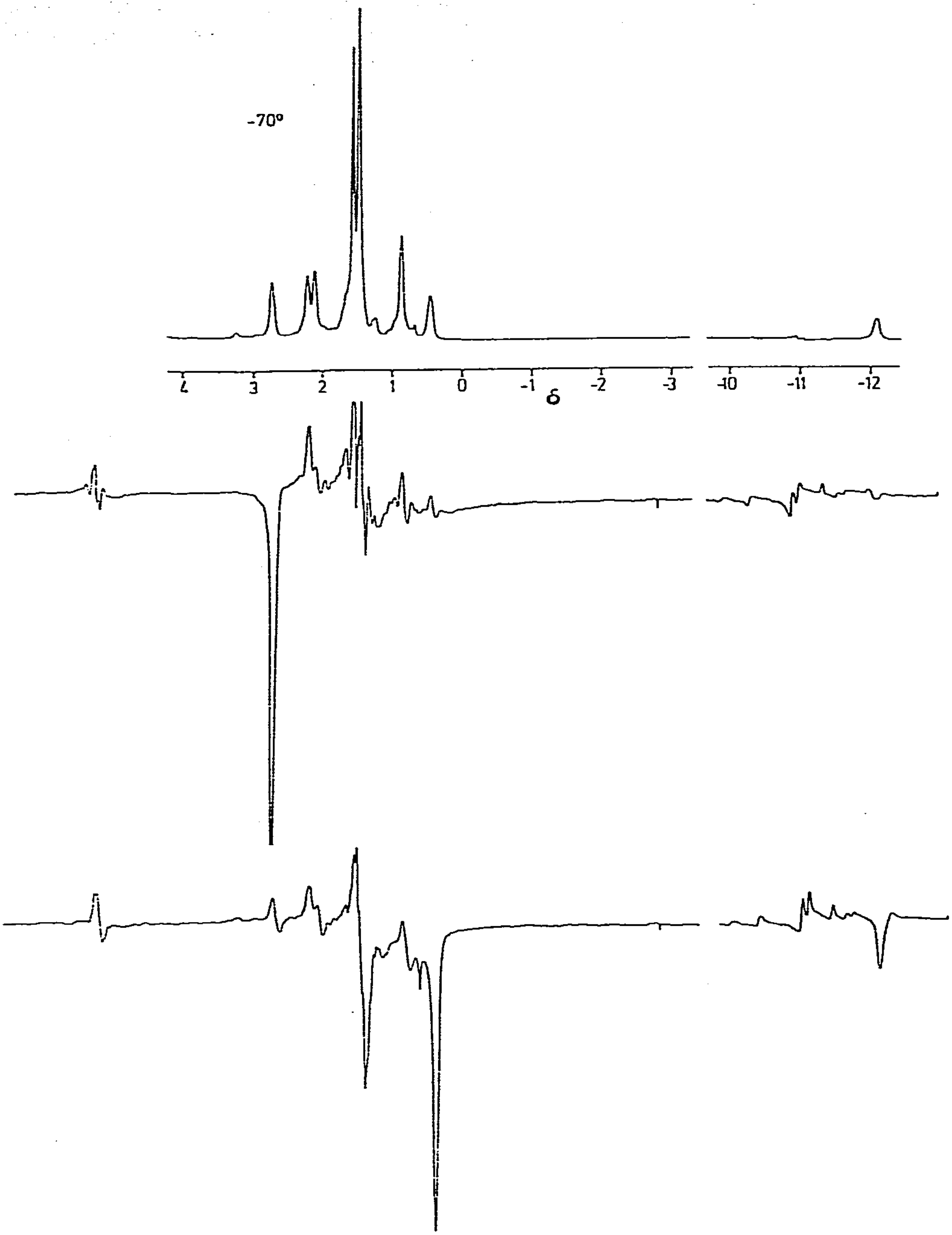


Fig. 2. Saturation transfer experiments on (III) at 400 MHz.

axis can the olefinic protons be unique and yet equivalent to their opposite numbers on the adjacent olefin.

When the ^{1}H NMR spectrum of III is recorded at higher temperatures the hydridic, H_C and H_D resonances broaden and disappear. At still higher temperatures, H_A and H_B also broaden until at −20°C only traces of the H_A and H_B peaks remain, together with the peralkylcyclopentadienyl peaks, which remain well defined. Cooling reverses these observations. Further heating results in decomposition to a complex mixture of products dependent on solvent.

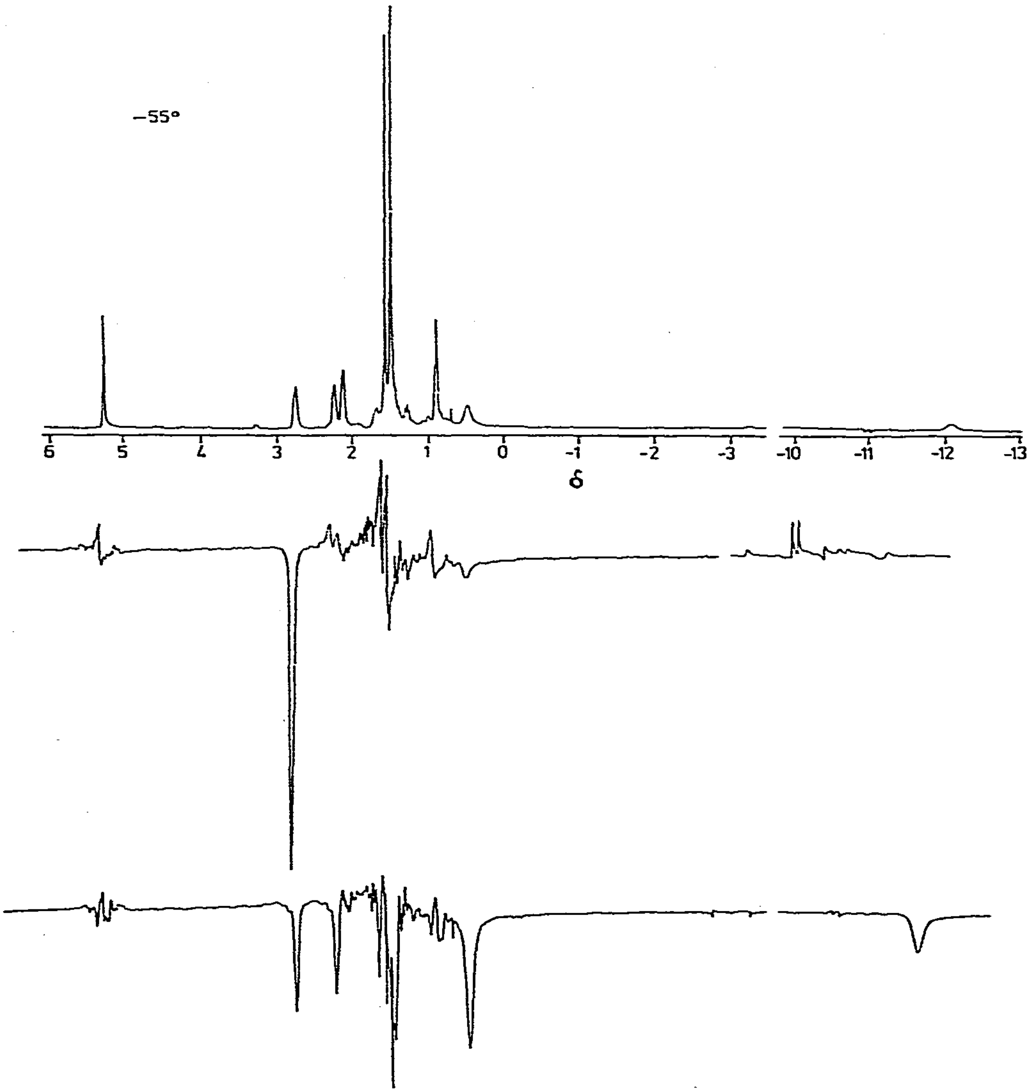


Fig. 2 (continued).

Figure 2 shows the results of saturation-transfer experiments on III as a function of temperature. The normal spectrum is shown at the top for −70, −55 and −40°C. Beneath each are traces multiplied by 16, of the difference between the normal spectrum and one recorded by irradiating at a specific

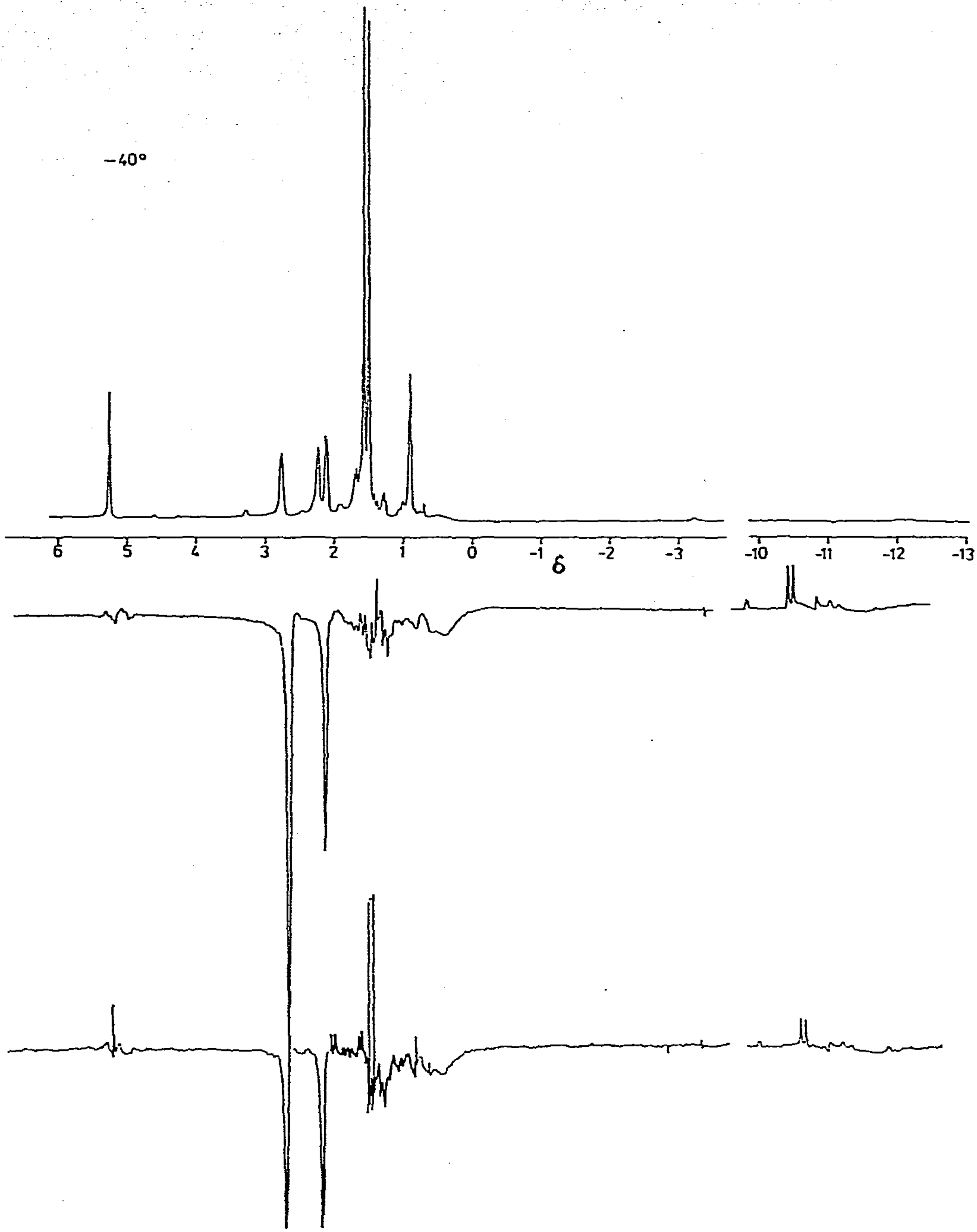


Fig. 2 (continued).

line in the spectrum. The upper trace shows the result of irradiating at H_A, the lower trace, at H_D. The programs used are discussed elsewhere [3].

As may be seen, at −70° transfer of magnetisation is observed only between H_C, H_D and the hydride, while at −55 and −40°, magnetisation is transferred evenly between all the olefinic protons and the hydride.

These experiments demonstrate how deuterium exchange mentioned above occurs with the olefin ligands in I. The following conclusions may be drawn. (1) The 'hydride proton' in III exchanges specifically with H_C and H_D, E_a = 30 kJ mol^{-1} and with H_A and H_B, E_a = 40 kJ mol^{-1} (line width analysis).

(2) Attack of the hydride does not appear to occur perpendicular to the olefinic plane, and coupling between the hydride and H_C and H_D suggests orbital overlap in the starting material between the hydride and one end of the olefins. (If the coupling were via the metal, H_A and H_B would also be expected to couple). Similar geometrical questions arise in a recently reported olefin insertion reaction [4].

(3) There is little change in chemical shift of H_A and H_B (ca. δ 0.05 ppm from −85 to −20°C) during rapid exchange of H_C, H_D and the hydride. Although correlation of hydridisation with chemical shift is very dubious in these systems, such a correlation would indicate that the geometry of the olefin is unchanged as attack by the hydride occurs. It would then follow that the attack is by hydride migration and not olefin insertion.

(4) The system is similar in behaviour to $Mo(dppe)_2(C_2H_4)_2$ [5].

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2 ^{1}H NMR data given as chemical shift, δ (ppm), multiplicity, coupling constant, Hz, integrated intensity, assignment. H_C and Me_B signals overlap, the combined intensity is consistent with the assignment.

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