

Preliminary communication**A new hydrogenation catalyst formed from tris(triphenylphosphine)dinitrogen cobalt hydride and sodium naphthalene**

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SUMMARY

Tris(triphenylphosphine)dinitrogen cobalt hydride (I) reacts with sodium naphthalidene (NaNp) to give a paramagnetic binuclear cobalt complex which is a catalyst for olefin hydrogenation; for example, the system (I)/NaNp 1/1 converts 20 moles of styrene into ethylbenzene under conditions where (I) alone gives only 0.5 mole of ethylbenzene.

Tris(triphenylphosphine)dinitrogen cobalt hydride $(PPh_3)_3CoN_2H$ (I) reacts with styrene to give a paramagnetic binuclear cobalt complex¹. One pathway to this product undoubtedly involves homolysis of the cobalt–hydrogen bond followed by hydrogenation of styrene and it was of interest to establish whether or not hydridic hydrogen from (I) is transferred to the aromatic radical anion and whether this process would yield a paramagnetic cobalt complex.

If a solution of sodium naphthalene (NaNp) in THF is added to a benzene solution of (I) in a 1/1 molar ratio, a 15-line ESR signal appears instantly (Fig. 1). When NaNp is used in 2/1 excess the spectrum of the radical anion is superimposed upon the spectrum of the product which observation suggests that one mole of NaNp reacts with one mole of (I). Hydrolysis of the reaction mixture, however, does not give hydronaphthalenes as it should if there is hydrogen transfer from (I) to naphthalene, indeed naphthalene is recovered almost quantitatively. Similarly, reaction with allyl chloride gives neither chloro- nor allyl-substituted naphthalenes but naphthalene, $(PPh_3)_2CoCl_2$, together with a mixture of hexenes arising from coupling and hydrogenation of allyl radicals. A mixture of (I) + NaNp reacts with styrene to give ethylbenzene; when styrene is in a 5 molar excess, the amount of ethylbenzene obtained corresponds to the total consumption of hydridic ligand introduced in (I).

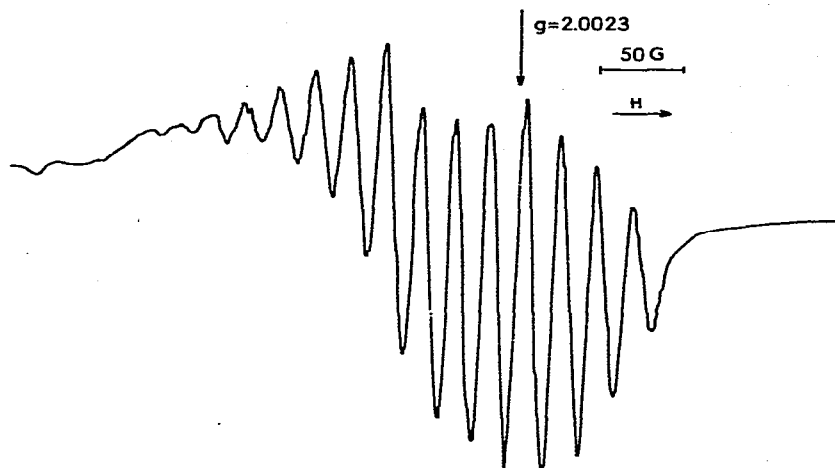
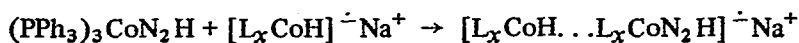
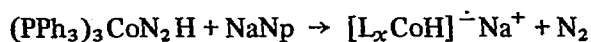


Fig. 1. ESR spectrum of the reaction mixture (I) + sodium naphthalene 1/1; $c(\text{Co})$ 0.015 M ; temperature $\sim 25^\circ$; cavity temperature, 20° ; solvents, benzene/THF 1/0.01.

During the reaction of (I) with NaNp in a 1/1 molar ratio, approximately 50% of the nitrogen present in (I) is evolved. The ESR signal then disappears when allyl chloride is added in the ratio (I)/allyl chloride 1/0.8. The IR spectrum exhibits a strong absorption at 2100 cm^{-1} which is assigned to the $\text{N}\equiv\text{N}$ stretching vibration.

All these observations suggest that (I) reacts with NaNp according to the scheme:



(II)

The first step is an electron-transfer and the second step a dimerization. In this situation the central cobalt atoms should have enhanced electron density and it follows that strongly basic cobalt should activate molecular hydrogen.

In practice, the system (I)/NaNp 1/1 is an effective hydrogenation catalyst for olefins as illustrated in Fig. 2. With the cobalt complex itself, under comparable conditions, but without sodium naphthalene, there is no uptake of hydrogen. Under these conditions styrene is hydrogenated by the hydridic hydrogen in tris(triphenylphosphine)dinitrogen cobalt hydride to yield ~ 0.5 mole of ethylbenzene per mole of cobalt complex. Aliphatic olefins are not hydrogenated. It is probable, that the binuclear, paramagnetic cobalt complex is a real catalyst. Tris(triphenylphosphine)cobalt trihydride was claimed to be a hydrogenation catalyst². The system, (I)/NaNp, is not deactivated by the carbonyl groups in non-conjugated ketones and can therefore be used as a selective catalyst to hydrogenate isolated double bonds in the presence of the CO group.

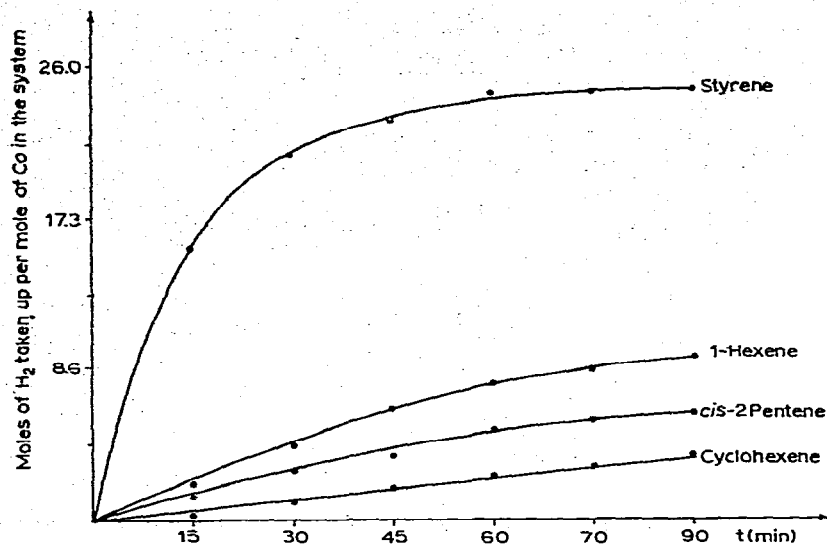


Fig. 2. Catalytic hydrogenation of olefins by the catalyst formed from tris(triphenylphosphine)-dinitrogen cobalt hydride and sodium naphthalene in the molar ratio 1/1.1; benzene/THF solution; $c(\text{Co})$ 0.02 M; molar ratio, Co/olefin 1/20; temperature 19–22°; atmospheric pressure.

Olefins containing conjugated $\text{C}=\text{C}-\text{C}=\text{O}$ units, as in acrolein, crotonaldehyde, methylacrylate as well as vinyl acetate and vinyl ethers react but the catalytic activity of the system is destroyed in the process.

REFERENCES

- 1 S. Tyrlik, K. Falkowski and K. Leibler, *Inorg. Chim. Acta*, 6 (1972) 291.
- 2 M. Hidai, T. Kuse, T. Hikita, Y. Uchida and A. Misono, *Tetrahedron Letters*, 20 (1970) 1715.