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Preliminary communication

THE RELATIVE AFFINITIES OF DINITROGEN AND OF PENTENE FOR THE $RuH_2(PPh_3)_3$ MOIETY

FILIPPO PENNELLA

Phillips Petroleum Company, Research and Development Department, Bartlesville, Oklahoma 74004 (U.S.A.)

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Summary

IR and NMR evidence indicates that N_2 has a much greater affinity than 2-pentene for $RuH_2(PPh_3)_3$.

Little attention has been given to the possible poisoning effects of N_2 on reactions of olefins catalyzed by transition metal complexes, despite the fact that these reactions are often carried out under N_2. This is due in part to the meagerness of information available about the relative affinities of N_2 and of olefins for transition metal species. We report here spectroscopic evidence that indicates that N_2 has a much greater affinity than 2-pentene for the $RuH_2(PPh_3)_3$ moiety.

The high-field ^1H NMR spectrum of $RuH_2(N_2)(PPh_3)_3$ (I) in C_6D_6 at 30°C contained a complex pattern of broad overlapping peaks from 7 to 11 ppm above TMS and a single broad peak at 12.8 ppm above TMS. The IR spectrum is characterized by a strong band at 2146 cm^{-1} ($\nu(N{\equiv}N)$) [1]. Addition of an excess of 2-pentene to a C_6D_6 solution of (I) saturated with N_2 at 1 atm had no pronounced effect on the IR and high-field ^1H NMR spectra of (I); even after four hours there was no significant decrease in the intensity of the band at 2146 cm^{-1}. When the solution was swept with argon this band disappeared. In the high-field ^1H NMR spectrum the peaks assigned to the hydridic hydrogens of (I) also disappeared and a broad quartet appeared at 10 ppm above TMS (J = 37 Hz), suggesting that a fluxional tris(triphenylphosphine) hydride (II) was formed. On readmission of N_2 (I) was regenerated, as indicated by the reappearance of both its high-field NMR spectrum and of the band at 2146 cm^{-1} in the IR spectrum.

(II) was obtained also by the reaction in C_6D_6 of 2-pentene with $RuH_4(PPh_3)_3$ (III), but not in control experiments when C_6D_6 solutions of (I) or (III) were swept with argon.

The reaction of 2-pentene with (III) in the absence of solvent yielded a yellow solid whose ^1H NMR spectrum in C_6D_6 contained peaks assignable to pentene downfield from TMS and the quartet at 10 ppm upfield from TMS. On addition of N_2 (I) was formed in good yields, as indicated by the intensity of the band at 2146 cm^{-1}. Although the limited solubility of the solid precluded intensity measurements of the NMR spectrum, these data strongly suggest that (II) is a pentene-coordinated hydrido-complex, possibly $RuH_2(C_5H_{10})(PPh_3)_3$.

It is noteworthy that, although (I) in the absence of H_2 hydrogenates 2-pentene very slowly, it does readily hydrogenate α-olefins stoichiometrically [2] yielding olefin-coordinated zerovalent complexes, $Ru(olefin)(PPh_3)_3$ [3].

The formation of (II) from (I) was inhibited by N_2, so the substitution of N_2 by the olefin must proceed by a dissociative mechanism. Since the process occurred only when N_2 was removed from the solution, it is clear that (I) is thermodynamically more stable than the olefin-coordinated complex. This is confirmed by the rapid formation of (I) when N_2 was readmitted into the solution in the presence of an excess of the olefin. These findings are in accord with the retarding influence of N_2 on the double bond isomerization and on the hydrogenation of pentenes catalyzed by (I) or (III) [2].

References

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