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Preliminary communication

TRIS(ACETONITRILE)TRICARBONYLCHROMIUM(0) CATALYZED 1,4-ADDITION OF HYDROGEN TO 1,3-DIENES

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Summary

The $Cr(CO)_3(CH_3CN)_3$ complex is found to catalyze the 1,4-addition of hydrogen to 1,3-dienes such as 2-methyl-1,3-butadiene, *trans*-1,3-pentadiene, and *trans,trans*-2,4-hexadiene at low temperature (40°) and low H_2 pressure (20 psi). For *trans,trans*-2,4-hexadiene the only product obtained when D_2 is used is 2,5-dideuterio-*cis*-3-hexene. The catalytic 1,4-hydrogenation can be carried out in neat dienes, and turnover numbers for the catalyst of greater than 3000 have been observed.

The observations that $Cr(CO)_6$ photocatalyzes 1,4-addition of hydrogen to 1,3-dienes at 1 atm H_2 and room temperature [1] and (arene)$Cr(CO)_3$ thermally catalyzes [2] the same reaction at high pressures (700 psi) and high temperatures (150-175°) have led us to suspect similar catalytically active species in both catalyst systems. The fact that 1,4-addition of hydrogen proceeds in the dark at 25° and 1 atm H_2 pressure after photolysis [1] coupled with the postulate [3] of intermediates of stoichiometry $Cr(CO)_3\,H_2$(diene) in (arene)$Cr(CO)_3$ thermal catalysis suggests that $Cr(CO)_3L_3$ complexes could serve as catalysts for the 1,4-addition of hydrogen at very low temperatures and pressures provided that the Cr—L bond is thermally substitution labile. Such a complex is $Cr(CO)_3(CH_3CN)_3$ which is known [4] to thermally react at low temperatures in the presence of arene to give (arene)$Cr(CO)_3$ complexes. We now describe the preliminary results of our investigation of the catalytic activity of this species. The dramatic moderation of reaction conditions that we find has practical advantages compared to either of the other two chromium carbonyl catalyst systems [1, 2] in that neither light nor high temperature and pressures are required.

Addition of an acetonitrile solution of $Cr(CO)_3(CH_3CN)_3$ (synthesized by

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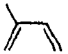
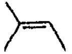
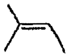
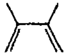
TABLE 1

$(CH_3CN)_3Cr(CO)_3$ CATALYZED 1,4-ADDITION OF H_2 TO 1,3-DIENES[a]

Exp. number	Starting diene (moles)		Time reacted (h)	Initial moles $(CH_3CN)_3Cr(CO)_3$	Product (moles)	
1		(8.0×10^{-2})	5	3.6×10^{-6}		(1.14×10^{-2})
2		(7.0×10^{-2})	7	1.4×10^{-4}		(1.19×10^{-2})
3a		(1.0×10^{-2})	1.5	4.5×10^{-6}		(1.2×10^{-2})
3b		(1.0×10^{-2})	1.5	4.5×10^{-6}		(trace)
4a		(8.8×10^{-3})	1.5	1.8×10^{-6}		(3.8×10^{-5})
4b		(8.8×10^{-3})	1.5	1.8×10^{-6}	—	No reaction
5		(6.0×10^{-2})	6	*b*		(4.8×10^{-2})
6		(2.0×10^{-2})	8	*b*		(1.8×10^{-2})
7		(8.8×10^{-3})	13	*b*		(6.2×10^{-3})

[a] The dienes were run as neat liquids and the $(CH_3CN)_3Cr(CO)_3$ was introduced in CH_3CN solution (exp. 1-4) with final CH_3CN concentration less than 1.0 *M*. For exp. 5-7 the catalyst was introduced as a pure solid but it is only sparingly soluble in the dienes. Solutions were deoxygenated by purging with H_2 prior to catalyst addition or by three freeze-pump-thaw cycles. Solutions were stirred continuously during the reaction, exposed to 20 psi H_2, and thermostatted at 40°. Products were identified by a combination of NMR and gas chromatography by comparison with authentic samples. Products are 99% pure.

[b] Saturated solutions of pure catalyst in the diene.

the published procedures [5] and characterized by spectroscopic data [6] given in the literature) to a neat 1,3-diene exposed to H_2 (20 psi) and heated to 40° leads to 1,4-addition of hydrogen to the diene. Typical results and reaction conditions are set out in Table 1. Experiments 1-4 were designed to determine the catalyst specificity and the products as well as to gain some feel for turnover numbers. Experiments 5-7 are included to demonstrate that the 1,3-dienes can be hydrogenated in synthetic quantities in reasonable reaction times. Preliminary results also reveal that $W(CO)_3(CH_3CN)_3$ operates as a diene hydrogenation catalyst under these mild conditions. As shown in Table 1 the number of moles of alkene formed far exceeds the number of moles of $Cr(CO)_3(CH_3CN)_3$ initially present. Hydrogenation of the 1,3-dienes yields *cis*-alkenes. Neither hydrogenation nor isomerization of the alkene product is found, and when *trans,trans*-2,4-hexadiene is deuterated (20 psi D_2) only 2,5-dideuterio-*cis*-3-hexene is obtained as a product*. The data suggest that dienes having alkyl substituents in the 1 and/or 4 positions of the diene undergo hydrogenation less readily, but a definitive conclusion here must await the results of competition experiments in progress.

In experiments 3 the small conversions reflect relative rates and allow us to conclude that *trans*-1,3-pentadiene undergoes reaction at a much faster rate than *cis*-1,3-pentadiene, and likewise in experiment 4 the rate of hydrogenation of *trans,trans*-2,4-hexadiene occurs at a faster rate than that of the *cis,cis* isomer. As in the $Cr(CO)_6$ photocatalyzed reaction [1], the dienes capable of achieving the *s-cis* conformation (*trans*-1,3-pentadiene and *trans,trans*-2,4-hexadiene) are much more reactive than the corresponding geometrical isomers (*cis*-1,3-pentadiene and *cis,cis*-2,4-hexadiene) which are sterically prevented from adopting the *s-cis* conformation.

The catalytic action of $Cr(CO)_3(CH_3CN)_3$ parallels the $Cr(CO)_6$ photocatalysis action and the (arene)$Cr(CO)_3$ high temperature catalysis. These results are consistent with a catalytic chromium tricarbonyl species which reacts with diene and H_2 to complete its coordination sphere. Presumably the role of light in the $Cr(CO)_6$ photocatalyzed reaction [1] is to generate this catalyst and to accelerate certain steps in the subsequent catalytic cycles. The moderate reaction conditions realized here with $Cr(CO)_3(CH_3CN)_3$ may be improved further by utilization of an even more labile $Cr(CO)_3L_3$ complex, but at some point it is possible that other steps in the catalytic cycle will require larger thermal activation than that involved in converting $Cr(CO)_3L_3$ to the actual catalyst. The results obtained here are consistent with earlier findings where more labile (arene)$Cr(CO)_3$ complexes are effective 1,4-hydrogenation catalysts at lower temperatures [2], and the reaction conditions used here are modest enough to be of preparative utility.

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*2,5-Dideuterio-*cis*-3-hexene was unambiguously identified and levels of purity established by its deuterium decoupled 100MHz PMR spectrum and gas chromatography under conditions where all hexene isomers are separated (a 25 ft × 1/2 in. 35% $\beta\beta$-ODPN column operated at 25°).

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