Selective Hydrogenations of Dienes and Olefins by $[W_2(OCH_2Bu^t)_6(py)_2]$

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Hydrocarbon solutions of $[W_2(OCH_2Bu^t)_6(py)_2]$ in the presence of H_2 (3 atm, 23 °C) hydrogenate linear 1,3-dienes to 3-enes, 1,3- and 1,5-cyclooctadiene to cyclooctene, 1,3-cyclohexadiene to cyclohexene, cyclopentene to cyclopentane, and norbornene to norbornane, but do not hydrogenate α- and internal olefins to alkanes, or internal conjugated or unconjugated dienes.

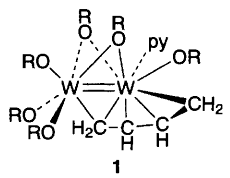
Homogeneous hydrogenation catalysts typically involve metal hydride ligands, *e.g.* as in Wilkinson's catalyst $[RhCl(PPh_3)_3] + H_2 \rightleftharpoons [RhCl(H)_2(PPh_3)_n]$, where $n = 2$ or 3, and these hydride ligands are often labile to reversible insertion reactions prior to reductive elimination of the hydrocarbon.[1] Consequently, selective hydrogenation of specific carbon–carbon double bonds is of particular interest.

A group of catalysts that effect the specific hydrogenation of conjugated dienes to olefins include $[Co(CN)_5]^{3-}$ and $[Cr(CO)_3(\eta^6\text{-methylbenzoate})]$.[2,3] The latter compound yields 1,4-addition of H_2 to the diene while the former yields a mixture of (*cis* and *trans*) but-1-ene and -2-ene in reactions with 1,3-butadiene. We describe here the hydrogenation behaviour of $[W_2(OCH_2Bu^t)_6(py)_2]$ towards various dienes and olefins.

In hydrocarbon solvents $[W_2(OCH_2Bu^t)_6(py)_2]$ reversibly dissociates pyridine, allowing the reversible uptake of both ethene and 1,3-butadiene.[4,5]

Steric factors are evidently important in controlling adduct formation since no reactions are observed with α-olefins or internal olefins. Similarly, while 1,3-butadiene and isoprene, $CH_2{=}CMeCH{=}CH_2$, show evidence of coordination in solution (blue–black colour and complex multiplets in the OCH_2Bu^t region of the ^1H NMR spectra) other conjugated and non-conjugated dienes do not. Given that the solid-state structure of $[W_2(OCH_2Bu^t)_6(\mu,\eta^1,\eta^4\text{-}C_4H_6)(py)]$ contains a labile pyridine ligand the potential for uptake of a small molecule such as H_2 appeared plausible, even though $[W_2(OCH_2Bu^t)_6(py)_2]$ and H_2 do not form detectable hydrido or dihydrogen species.

Consistent with this reasoning we find that $[W_2(OCH_2Bu^t)_6(py)_2]$ serves as a hydrogenation catalyst for conjugated 1,3-dienes giving the internal 3-monoene. The reactions were typically carried out at ambient temperatures, 23 °C, and 3 atm. H_2 pressure in a J. Young tube and monitored by NMR spectroscopy. Reactions with D_2 reveal that the addition is strictly 1,2 as in the formation of $CH_2DCHDCH{=}CH_2$ from 1,3-butadiene. With isoprene it is the sterically unencumbered C=C double bond that is hydrogenated yielding $CH_2{=}CMeCH_2CH_3$. Ethene, α-olefins and linear internal olefins and dienes are not hydrogenated. However, strained olefins as in cyclopentene and norbornene are hydrogenated. The exceptions to the rule that only 1,3-conjugated dienes are hydrogenated are seen in the conversion of 1,5-cyclooctadiene to cyclooctene and in the polymerization of norbornadiene.[6] Neither furan, nor thiophene are hydrogenated, presumably because their conjugated double bonds are contained within a pseudo-aromatic ring. However, styrene and allyl ether are. The results of the hydrogenations are summarized in Table 1.



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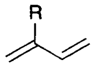
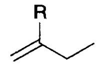
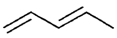
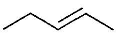
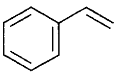
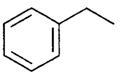
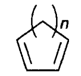
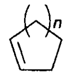
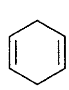
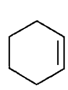
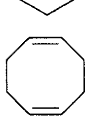
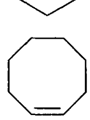
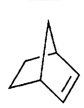
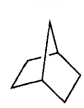
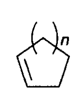
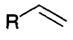
Collectively these serve as a starting point for the development of selective hydrogenation catalysts involving $(W{\equiv}W)^{6+}$ centres supported by alkoxide ligands. It seems likely that the specificity for hydrogenation of 1,3-dienes is related to the novel coordination modes of the dienes to the dimetal centre (see **1**), wherein one C=C unit is more reduced than the other. Similarly for styrene, diallylether 1,4-cyclohexadiene, and 1,5-cyclooctadiene a chelate effect may operate to facilitate the activation of the C=C double bond as indeed an olefin in a strained ring is activated toward coordination to the dinuclear centre.

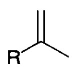
Table 1 Selective hydrogenation of polyenes catalysed by $[W_2(OCH_2Bu^t)_6(py)_2]$. The turnover numbers are in the order of 2 mol substrate/mol of catalyst per hour

Substrate	Hydrogenation Products
 R = H or Me	
	
	
 n = 1, 2, 3, 4	
	
	
	
 n = 1, 2, 3, 4	
$CH_2{=}CH{-}O{-}CH{=}CH_2$	$CH_2{=}CH{-}O{-}CH_2{-}Me$

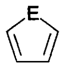
Hydrogenation was not observed for the following:



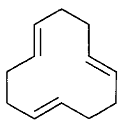
R = H, Me, Et, $CH_2CH_2CH{=}CH_2$, C(O)H, C(O)Me

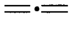


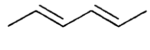
R = Me, C≡CH

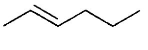


E = O or S









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References

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988, ch. 28.

2 J. Kwiatek, I. L. Mador and J. K. Seyler, in *Advances in Chemistry 70*, ACS, Washington, D.C., 1963, ch. 15.

3 L. W. Gosser, *US Pat.* 3 673 270, 1972.

4 R. H. Cayton, S. T. Chacon, M. H. Chisholm and J. C. Huffman, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 903.

5 M. H. Chisholm. J. C. Huffman, E. A. Lucas and E. B. Lubkovsky, *Organometallics,*, 1991, **10**, 3424.

6 The NMR spectra for the polymer formed was consistent with the NMR spectra for poly(norbornadiene) prepared independently by $ClAlEt_2$, a known cationic initiator. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, ch. 4.