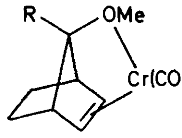
Tetracarbonylchromium(0) Complexes of *syn*-7-Alkoxynorborn-2-enes

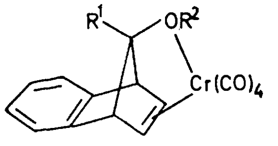
By D. Wege* and S. P. Wilkinson

(*Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia* 6009)

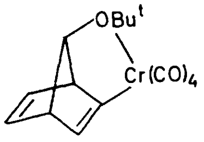
Summary *syn*-7-Alkoxynorborn-2-enes react with $Cr(CO)_6$ to yield complexes of the type (alkoxynorbornene)-$Cr(CO)_4$.



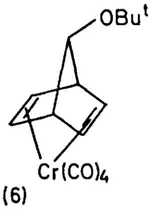
(1) R = H
(2) R = OMe



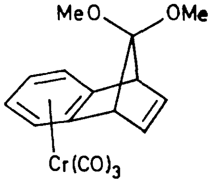
(3) R^1 = H, R^2 = Bu^t
(4) R^1 = OMe, R^2 = Me



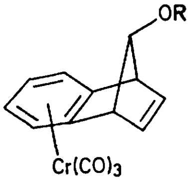
(5)



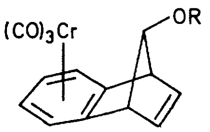
(6)



(7)



(8) R = Ac
(9) R = H



(10) R = Ac
(11) R = H

We have found that norbornenes, norbornadienes, and benzonorbornadienes having an alkoxy-group *syn* to the olefinic bond can act as bidentate ligands towards chromium-(0) through the alkoxy and alkene groups. Thus the orange, crystalline, air-stable complexes (**1**)—(**5**) were obtained in 10—50% yield by heating the appropriate substituted alkene with $Cr(CO)_6$ in di-n-butyl ether-cyclohexane at 140°. The structures of these complexes follow from analytical and spectroscopic data. Particularly revealing are their ^1H n.m.r. spectra, which show vinyl signals shifted upfield by *ca.* 1·5—2·0 p.p.m. relative to the uncomplexed alkenes, indicating that the olefinic π-bond is linked to the metal. For example, (**4**) shows δ (60 MHz; $CDCl_3$; Me_4Si internal standard) 7·40—7.00 (4H, m, ArH), 4·90 (2H, 't', '*J*' 1 Hz, vinyl), 3·70 (2H, 't', *J* 1 Hz, bridgehead), and 3·00 and 2·87 (each 3H, s, OMe) while 7,7-dimethoxybenzonorbornadiene shows δ 7·23—6·83 (4H, m, ArH), 6·62 (2H, 't', '*J*' 2·5 Hz, vinyl), 3·97 (2H, 't', '*J*' 2·5 Hz, bridgehead), and 3·20 and 3·02 (each 3H, s, OMe).

For *anti*-7-alkoxybenzonorbornadienes† bonding *via* the ether and alkene linkage occurs in preference to the normal[1] tricarbonylarene complex formation. Thus *anti*-7-t-butoxybenzonorbornadiene gave only complex (**3**), m.p. 118—120° (48%), and 7,7-dimethoxybenzonorbornadiene gave the tetracarbonyl complex (**4**), m.p. 140—145° (decomp.) (20%) and the tricarbonylarene complex (**7**) m.p. 185—187° (decomp.) (1%). The ^1H n.m.r. spectrum of (**7**) shows the usual upfield shift of the aromatic protons characteristic of the tricarbonylarene fragment, while the chemical shift of the vinyl protons is essentially the same as in the free ligand. 7-t-Butoxynorbornadiene reacted to give complex (**5**) m.p. 73—75° (13%) together with the expected[2] diene complex (**6**), m.p. 115—116° (53%).

Complexing through the ether oxygen atom and double bond can be completely suppressed by making the oxygen atom less nucleophilic. Thus *anti*-7-acetoxybenzonorbornadiene gave the normal arene complexes (**8**), m.p. 160—162° (decomp.), and (**10**) m.p. 177—178° in a 2:1 ratio. In the *endo*-complex (**8**) the 7-H acetoxy-methine signal occurs at the same chemical shift as the corresponding signal in the uncomplexed acetate (δ 4·64 p.p.m.). In the *exo*-complex (**10**) 7-H resonates at δ 5·25 p.p.m., indicating that there is considerable deshielding due to the proximity of the $Cr(CO)_3$ group.‡

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† Alkoxy group *anti* to the arene ring, and therefore *syn* to the alkene linkage.

‡ Oxidation of the complexed alcohols (**9**) and (**11**) with silver carbonate–Celite gave mainly tricarbonyl-(1-naphthaldehyde)chromium, together with minor amounts of tricarbonyl(naphthalene)chromium. The formation of the latter product suggests that complexing the arene π-system of benzonorbornadienone is not sufficient to stabilize that system (*cf.* J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, 1971, **93**, 972).

[1] R. S. Bly and R. C. Strickland, *J. Amer. Chem. Soc.*, 1970, **92**, 7459; D. K. Wells and W. S. Trahanovsky, *ibid.*, 1970, **92**, 7461.

[2] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2037.