Journal of Organometallic Chemistry, 192 (1980) C6—C8
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Preliminary communication

REDUCTIVE DIMERISATION OF BUT-2-YNE ON NIOBIUM: SOME CHEMISTRY OF MONO-η-CYCLOPENTADIENYL COMPOUNDS

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(Received March 21st, 1980)

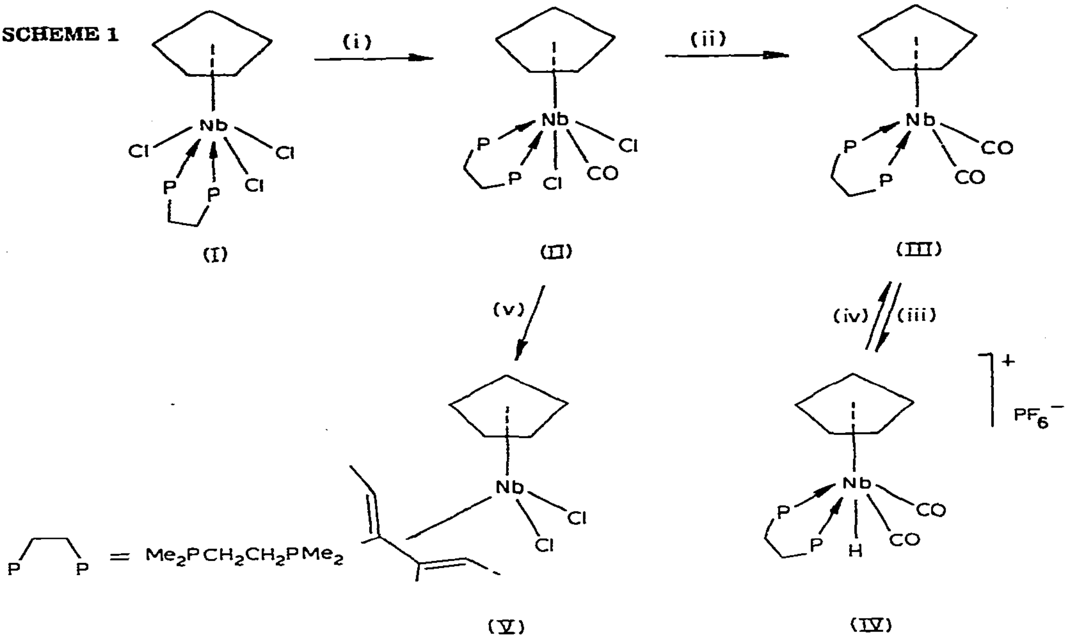
Summary

The new compounds $Nb(\eta\text{-}C_5H_5)(dmpe)Cl_3$, $Nb(\eta\text{-}C_5H_5)(dmpe)COCl_2$, $Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2$ and $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2H]PF_6$ are described. Reduction of the last in the presence of but-2-yne yields the hexa-2,4-diene derivative $Nb(\eta\text{-}C_5H_5)(\eta\text{-}MeHCCMeCMeCHMe)Cl_2$, the crystal structure of which has been determined.

Treatment of a suspension of $Nb(\eta\text{-}C_5H_5)Cl_4$ in toluene [1] with 1,2-bis-(dimethylphosphino)ethane (dmpe) and ethylaluminium dichloride gives a paramagnetic, tetravalent, deep-purple compound $Nb(\eta\text{-}C_5H_5)(dmpe)Cl_3$, I. We presume this compound has a similar structure to the related compound $Nb(\eta\text{-}C_5H_5)(dppe)Cl_3$ [2]. Reduction, using magnesium amalgam, of tetrahydrofuran solutions of I under an atmosphere of carbon monoxide (Scheme 1) gives the trivalent deep-green crystalline compound $Nb(\eta\text{-}C_5H_5)(dmpe)COCl_2$, II. Further reduction of II using $NaAlH_2[OCH_2CH_2OMe]_2$ in the presence of carbon monoxide yields monovalent $Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2$, III. This dicarbonyl is readily and reversibly protonated giving the yellow hydride cation as the hexafluorophosphate $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2H]PF_6$, IV.

Treatment of II in tetrahydrofuran with sodium amalgam in the presence of excess of but-2-yne followed by the addition of aqueous hydrochloric acid gives orange-brown crystals of the 16-electron compound $Nb(\eta\text{-}MeHCCMeCMeCHMe)Cl_2$, V, the crystal structure of which has been determined. $C_{13}H_{19}Cl_2Nb$, monoclinic a 6.531(1), b 16.113(2), c 13.756(2) Å, β 102.72(2)°. Space group $P2_1/c$, $D_c = 1.59$ g cm^{-3} for $Z = 4$, Mo-K_α radiation $\mu = 11.6$ cm^{-1}. The structure was determined by Patterson heavy atom methods from 1783 independent reflexions ($I > 3\sigma(I)$) measured with a CAD4F diffractometer and refined to $R_w = 0.047$. The structure shown in Figure 1 confirms the chemical nature of V. The general

SCHEME 1



(i) Mg/Hg in toluene under 1 atm carbon monoxide, 90%.
(ii) $Na[H_2Al(OCH_2CH_2OMe)_2]$ in toluene under carbon monoxide, 56%.
(iii) Dilute aqueous hydrochloric acid, then PF_6^- >76%.
(iv) NaOH aq ~90%.
(v) Na/Hg in THF and but-2-yne, then HCl gas, 34%.

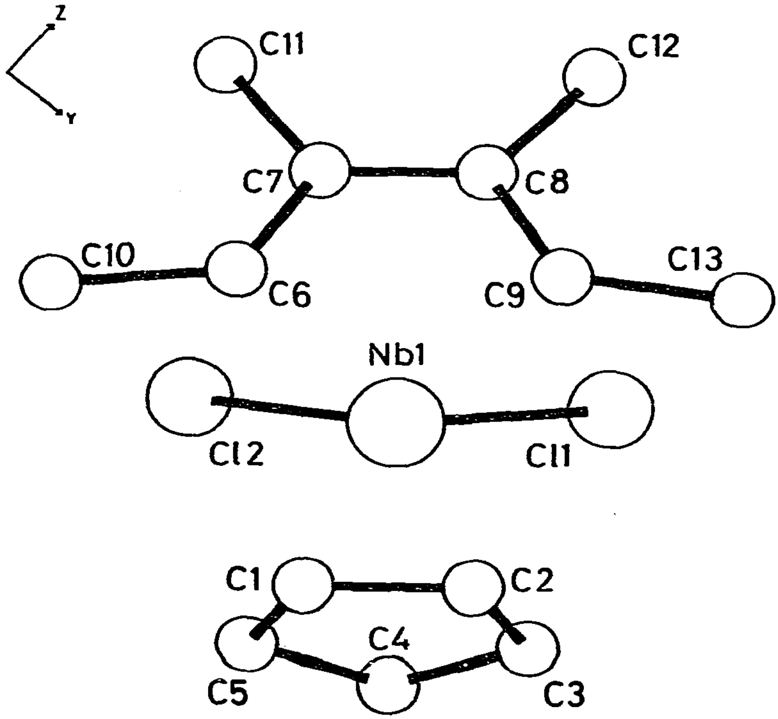


Fig. 1. The molecular structure of Nb(η-C_5H_5)(η-MeHCCMeCMeCHMe)Cl_2 projected down *a*.

form of the molecule closely resembles the iso-electronic (η-C_5H_5)$_2$$ZrCl_2$ [3]. The dimensions of the butadiene and cyclopentadienyl ligands are not significantly different from those found in other complexes [3,4]. The Cl—Nb—Cl angle 91.46(6)°, though significantly less than the Cl—M—Cl angle in 16-electron bent metallocenes [3], still follows the general pattern of angular variation in these compounds [5].

We thank the S.R.C. for support (to C.C. and M.J.B.).

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