

Preliminary communication

Bis(η^5 -cyclopentadienyl)tungsten chemistry: hydridation reactions of functional alkyl hydrides and olefin complexes

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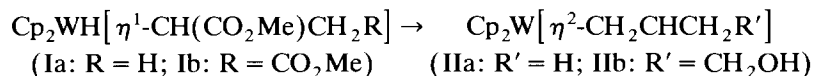
(Received October 3, 1991)

Abstract

Functional tungstenocene alkyl hydrides with ester or nitrile groups attached to the α -position of the alkyl group (e.g. $\text{Cp}_2\text{WH}(\text{CHMeCO}_2\text{Me})$) react with LiAlH_4 to give olefin complexes (e.g. $\text{Cp}_2\text{W}(\text{CH}_2\text{CHMe})$). Similarly, functional olefin complexes are reduced to give alkyl compounds. Thus, the acrylic ester complex $\text{Cp}_2\text{W}(\text{CH}_2\text{CHCO}_2\text{Me})$ affords the tungstenacyclobutane $\text{Cp}_2\text{W}(\text{CH}_2)_3$ and the fumaric ester complex $\text{Cp}_2\text{W}[\eta^2\text{-CH}(\text{CO}_2\text{Me})\text{CHCO}_2\text{Me}]$ the new tungstenacyclopentane $\text{Cp}_2\text{W}(\text{CH}_2)_4$.

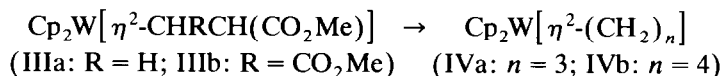
We recently described functional alkyl hydrides and olefin complexes of tungstenocene [1]. We now report that treatment of these complexes with LiAlH_4 in ether or tetrahydrofuran can take a surprising course, and often results in complete removal of the heteroatoms of the functional groups (CO_2Me , CN).

Hydridation of functional alkyl hydrido complexes such as the propionic ester complex Ia [1] reduces the ester group in the α -position of the alkyl ligand completely, thereby forming the known propene complex IIa [2]. The corresponding propionitrile derivative $\text{Cp}_2\text{WH}(\text{CHMeCN})$ is also reduced to complex IIa. The succinic ester derivative Ib [1] undergoes hydridation to afford the 3-butenol complex IIb; thus the α ester group in the vicinity of the tungsten centre is again reduced completely while the ester group in the β -position shows the normal behaviour and is transformed into a hydroxyalkyl function.

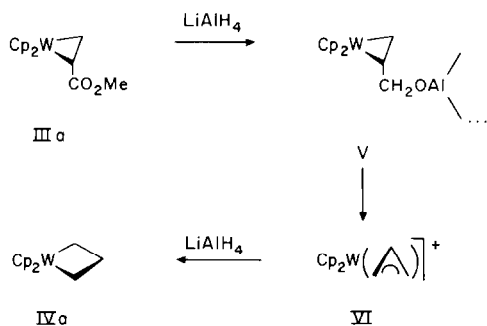


Hydridation of the functional olefin complex IIIa [1] with an acrylic ester ligand affords the known tungstenacyclobutane IVa [3]. (Complex IVa was made previously by hydride addition to the cationic allyl complex $[\text{Cp}_2\text{W}(\text{C}_3\text{H}_5)]^+$ [3].) In the

same type of reaction the fumaric ester complex IIIb [4] is transformed into the tungstenacyclopentane IVb. An earlier attempt to make this compound from Cp_2Wl_2 and 1,4-dithiobutane met with little success [5] whereas the corresponding molybdenum complex was made by this method [5]. We note that IVb is fluxional with respect to its ring conformation, showing effective C_{2v} symmetry in the ambient temperature NMR spectra, whereas the molybdenum complex has a helical tetramethylene chain with C_2 symmetry in the crystalline state [5].

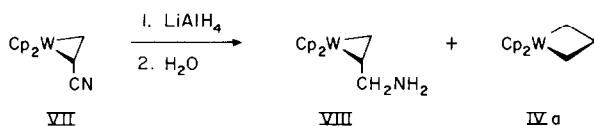


It is obvious that neighbouring group participation by the metallocene moiety plays a central role in these hydridation reactions. For instance, in the reduction of the acrylic ester complex IIIa an allyl alcohol complex V would be expected to be formed. We must assume that V can spontaneously undergo heterolytic cleavage of the allylic C–O bond to give the allylic cation VI, which is known to give the observed product IVa by nucleophilic addition of hydride ion [3].



Scheme 1

This suggestion is supported by the observation that the reduction of the acrylonitrile complex VII [1] yields, after hydrolysis of the reaction mixture, the allylamine complex VIII and minor amounts of the tungstenacyclobutane complex IVa; the amount of IVa is increased if longer reaction times and higher temperatures are used.



Scheme 2

Experimental

Experiments were carried out under dinitrogen by conventional Schlenk techniques. Ether and THF were distilled from sodium/benzophenone and pentane and toluene from Na/K alloy. Oxygen was removed by repeated distillation under dinitrogen.

Bis(η^5 -cyclopentadienyl)(η^2 -propene)tungsten (IIa). LiAlH_4 (0.50 g, 13 mmol) was added to Ia (0.60 g, 1.5 mmol) in 35 ml of Et_2O . The mixture was stirred at ambient temperature for 15 min then kept at the reflux temperature for 3 h. After removal of the volatiles toluene was added and then water. The red organic layer was separated, dried (Na_2SO_4), filtered, concentrated to about 10 ml, and cooled to -50°C . The red powder so obtained was recrystallized from Et_2O at -50°C to give 0.36 g (68%) IIa as purple red crystals; m.p. 125°C (dec. $\approx 170^\circ\text{C}$).

Bis(η^5 -cyclopentadienyl)(η^2 -3-butenol)tungsten (IIb). As described for Ia, the ester Ib (0.75 g, 1.63 mmol) in 150 ml of Et_2O was treated with LiAlH_4 (0.29 g, 7.6 mmol). Work-up as above, ending in crystallization of the product from 60 ml of Et_2O at -20°C , and drying in vacuo, gave IIb (0.35 g, 56%) as orange-yellow needles; m.p. 156°C (dec.), very air-sensitive and very soluble in toluene. Anal. Found: C, 42.80; H, 4.64. $\text{C}_{14}\text{H}_{18}\text{OW}$ calc.: C, 43.55; H, 4.70%.

MS (70 eV, 120°C) m/z ($I_{\text{rel.}}$) 386 (50; M^+), 331 (25; Cp_2WOH^+), 314 (100; WCp_2^+). ^1H NMR ($\delta(^1\text{H})$ (ppm), 80 MHz, int.TMS, C_6D_6): 4.02 (s, Cp), 3.85 (s, Cp), 3.50 (m, OH), 2.4–2.09 (m, CH_2OH), 1.66–0.6 (m, CH_2CHCH_2). ^{13}C NMR ($\delta(^{13}\text{C})$ (ppm), 67.88 MHz, int.TMS, C_6D_6): 71.94 (dqin, $^1J = 172.1$, $^{2,3}J(\text{CH})$ 6.5 Hz, Cp), 71.73 (dqin, 1J 178.9, $^{2,3}J$ 6.5 Hz, Cp), 60.36 (t, 1J 140.7 Hz, C-1), 34.46 (t, 1J 124.4 Hz, C-2), 6.63 (d, 1J 140.7 Hz, C-3), -4.54 (t, 1J 148.5 Hz, C-4).

Bis(η^5 -cyclopentadienyl)(η^2 -1,3-propanediyl)tungsten (IVa). As described for Ia the olefin complex IIIa (0.39 g, 0.97 mmol) in 120 ml of Et_2O was treated with LiAlH_4 (0.10 g, 2.6 mmol). Work-up afforded 0.150 (43%) IVa as orange powder.

Bis(η^5 -cyclopentadienyl)(η^2 -1,4-butanediyl)tungsten (IVb). LiAlH_4 (0.24 g, 6.3 mmol) was added to 0.60 g (1.31 mmol) of the ester IIIb in 50 ml of THF. The mixture was stirred at 50°C for 2 h. Work-up and crystallization from 20 ml pentane at -50°C afforded 0.30 g (62%) IVb as brownish red crystals; m.p. 95 – 96°C (no dec. observed below 220°C). Anal. Found: C, 45.34; H, 4.91. $\text{C}_{14}\text{H}_{18}\text{W}$ calc.: C, 45.43; H, 4.90%.

MS (70 eV, 70°C) m/z ($I_{\text{rel.}}$) 370 (75; M^+), 314 (100; WCp_2^+), 288 (69; WC_8H_8^+). ^1H NMR ($\delta(^1\text{H})$ (ppm), 80 MHz, int.TMS, CD_2Cl_2): 4.48 (s, 2 Cp), 1.53 (m, CH_2), 1.27 (m, CH_2). ^{13}C NMR ($\delta(^{13}\text{C})$ (ppm), 67.88 MHz, int. TMS, C_6D_6): 84.48 (dqin, 1J 179.7 Hz, $^{2,3}J$ 6.5 Hz, 2 Cp), 37.50 (t, 1J 123.9 Hz, C-2/-3), -0.17 (t, 1J 125.4 Hz, C-1/-4).

Hydridation of bis(η^5 -cyclopentadienyl)(η^2 -acrylonitrile)tungsten (VII). LiAlH_4 (0.13 g, 3.4 mmol) was added to 0.42 g (1.14 mmol) of the nitrile V in 100 ml of Et_2O . The mixture was stirred at ambient temperature for 60 h. Work-up as usual afforded impure VIII as a red powder (VIII/VII/IVa = 84/10/6). This was very sensitive and attempted chromatography on alumina resulted in decomposition.

MS (70 eV, 80°C) m/z ($I_{\text{rel.}}$) 371 (20; M^+), 314 (100; WCp_2^+), 288 (50; WC_8H_8^+). ^1H NMR ($\delta(^1\text{H})$ (ppm), 80 MHz, int. TMS, C_6D_6): 3.97 (s, Cp), 3.88 (s, Cp); CH_2N : 2.94 (dd, J 12.2, J 7.4 Hz), 2.38 (dd, J 12.1, J 7.0 Hz); 1.7–0.5 (m, $\text{W}(\text{CH}_2\text{CH}) + \text{NH}_2$).

Acknowledgements. This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

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