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Preliminary communication

RING-OPENING REACTIONS OF SPIRO[2.4]HEPTA-4,6-DIENE AND SPIRO[4.4]NONA-1,3-DIENE INDUCED BY TUNGSTEN(0) CARBONYLS

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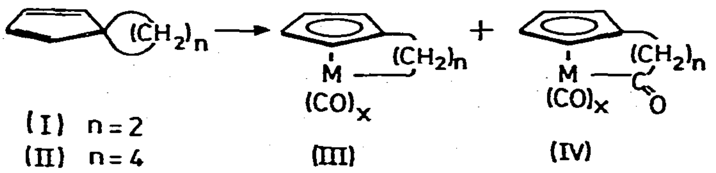
Summary

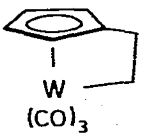
Tungsten(0) carbonyls react with the strained spiro[2.4]hepta-4,6-diene and the less strained spiro[4.4]nona-1,3-diene with C—C bond cleavage and formation of stable alkylene bridged π-cyclopentadienyl-σ-alkyl complexes. The product containing a two carbon bridge has the same unusual spectroscopic properties as the analogous molybdenum complex.

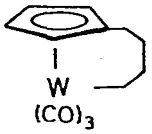
Spiro[2.4]hepta-4,6-diene (I) and spiro[4.4]nona-1,3-diene (II) both react with molybdenum carbonyls with C—C bond cleavage to form bridged π-cyclopentadienyl-σ-alkyl complexes of type III [1]. Compound I reacts with $Ni(CO)_4$ to give an acyl complex of type IV [2], whereas under similar reaction conditions II gives no organometallic products [2,3].

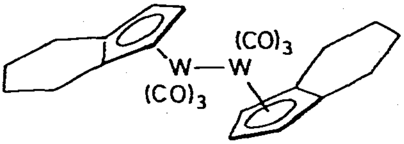


Iron(0) carbonyls and I yield mainly an acyl complex of type IV [1] while II gives a diene complex [4] and only small amounts of a bridged alkyl complex III [1]. We describe below our investigations of other Group VI metal carbonyl reactions with spirocyclopentadienes I and II.

Whereas from $Cr(CO)_6$ and $Cr(CO)_3(CH_3CN)_3$ [5] no complexes of type III and IV could be isolated [6], $W(CO)_6$ and $W(CO)_3(CH_3CN)_3$ [5] react with I and II in the same way as the molybdenum carbonyls [1] yielded 5% of complex V*. With the more reactive $W(CO)_3(CH_3CN)_3$ a 38% yield was obtained after 6 h refluxing in the same solvent. (Isolation was by column chromatography on alumina, orange needles (from hexane), m.p. 115°C; IR (CCl_4) 2010, 1935, 1915 cm^{-1}; λ_{max}(hexane) 257s, 305s, 415 nm; mass spectrum: *m/e* 360 (M^+, ^{184}W, rel.int. 28%), 332 (32%), 304 (46%), 276 (98%), 274 (100%); ^1H NMR, 60 MHz (C_6D_6), δ −0.35 (~t, 2 H, W—CH_2—), 2.36 (~t, 2 H, Cp—CH_2—), 4.49 (~t, 2.0 Hz, 2 H, Cp) and 4.60 ppm (~t, 2.0 Hz, 2 H, Cp)).


(V)


(VI)


(VII)

With the less strained hydrocarbon II none of the expected complex VI was detected from reaction with $W(CO)_6$ in boiling ligroin after 96 h. $W(CO)_3(CH_3CN)_3$ and II, however, formed 50% of VI after 24 h refluxing in ligroin. (Isolation was by column chromatography on alumina, yellow needles (from hexane), m.p. 70°C; IR (CCl_4) 2005, 1915 cm^{-1}; λ_{max}261s, 312, 356s nm (hexane); mass spectrum *m/e* 388 (M^+, ^{184}W, 17%), 360 (19%), 332 (19%), 330 (64%), 304 (76%), 302 (99%), 300 (100%); ^1H NMR, 60 MHz (C_6D_6) δ 1.2 (m, 2 H), 1.8 (m, 6 H), 4.5 ppm (m, 4 H)).

A second red band upon chromatography of the latter reaction product yielded 2% of the dinuclear complex VII (purple needles (from hexane) m.p. 184°C (dec.); IR (KBr) 1935, 1900, 1865 cm^{-1}; mass spectrum (EI)** *m/e* 718 (M^+ − 2CO, ^{184}W, 1%), (FI) *m/e* 774 (M^+, ^{184}W); ^1H NMR, 100 MHz (C_6D_6) δ 5.02 (t, 3.0 Hz, 2 H), 4.94 (d, 3.0 Hz, 4 H), 2.6 (m, 4 H), 2.3 (m, 4 H), 1.4 ppm (m, 8 H)). This compound is contaminated with small amounts of a hydrogenated product ($C_{24}H_{24}W_2O_6$), probably a complex containing the η^5-butylcyclopentadienyl ligand instead of tetrahydroindenyl. VII is evidently formed from VI under the conditions used.

These results show that molybdenum and tungsten carbonyls have similar reactivities towards both I and II. In spite of the larger size of the tungsten atom relative to VI complex V shows the unusual high field shift of the metal bound methylene protons in its NMR spectrum and bathochromic shift of the first band in the electron spectrum exhibited by the analogous molybdenum complex. This effect is due to internal strain produced by the short two carbon-alkyl bridge [7].

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