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Preliminary communication

REACTIONS OF 1-VINYLSPIRO[2.4]HEPTA-4,6-DIENE WITH NICKEL(0) AND MOLYBDENUM(0) CARBONYLS

PETER EILBRACHT

Institut für Organische Chemie der Technischen Hochschule Darmstadt, D-6100 Darmstadt (Germany)

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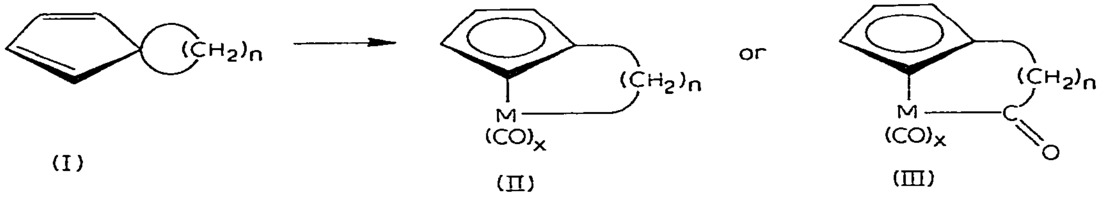
Summary

1-Vinylspiro[2.4]hepta-4,6-diene reacts both with nickel(0) and molybdenum(0) carbonyls via C—C bond cleavage and CO insertion, forming bridged π-cyclopentadienyl-σ-alkyl and acyl complexes.

The reaction of zerovalent transition-metal carbonyls of molybdenum [1], iron [1,2] and nickel [3] with spirocyclopentadienes I involves C—C bond cleavage and CO insertion to form either the alkylene-bridged η^5-cyclopentadienyl-σ-alkyl complexes II or the corresponding acyl complexes III. To obtain further information about the mechanistic and stereochemical aspects of this type of reaction, the behaviour of suitably substituted spiro [*n*,4] alkadienes has been investigated. Described below is the transformation and complexation of 1-vinylspiro[2.4]hepta-4,6-diene (IV) with $Ni(CO)_4$ and $Mo(CO)_3(THF)_3$, which represent the first cases in which both the alkyl and the acyl complexes II and III of the same metal are isolated.



Reaction of IV with $Ni(CO)_4$ in hexane at 60°C and chromatography on alumina yields the nickel carbonyl complex V* (dark red oil, IR (film) 2010 cm^{-1}, ^1H 60MHz NMR (C_6D_6) δ 5.92 (m, 1H), 5.68 (m, 1H), 5.02 (m, 4H), 2.44 (m, 2H), 2.24 ppm (m, 2H)) and the acyl complex VI (orange needles,

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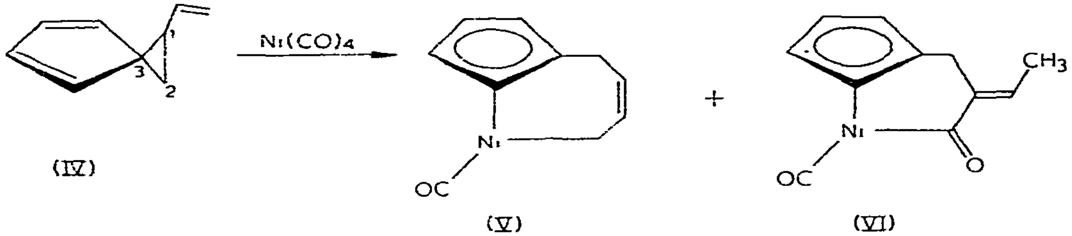
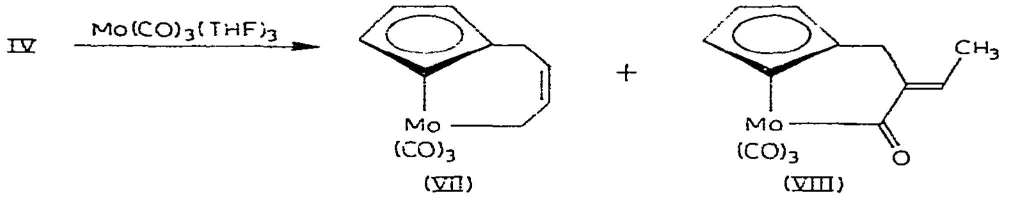
*All new compounds give satisfactory analytical results. NMR, IR and mass spectra are consistent with the assigned structures.

m.p. 41°C, IR (KBr) 2040, 1675 and 1603 cm^{-1}, ^1H 60 MHz NMR (C_6D_6) δ 5.7 (m, 1H), 5.48 (~t, 2.25 Hz, 2H), 4.84 (~t, 2.5 Hz, 2H), 2.30 (m, 2H),

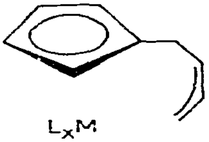


1.18 ppm (dt, 7.5 Hz and 1.5.Hz, 3H)). The position and orientation of the ethylidene group in VI were deduced from $Eu(fod)_3$ experiments.

Similar results were obtained with $Mo(CO)_3(THF)_3$ under comparable reaction conditions.



Complex VII is obtained as bright yellow needles (m.p. 91°C, IR (KBr) 2005, 1910 cm^{-1}, ^1H 60MHz NMR ($CDCl_3$) δ 6.4 (m, 2H), 5.54 (~t, 2.2 Hz, 2H), 5.03 (~t, 2.2 Hz, 2H), 2.74 (d, 5.0 Hz, 2H) and 2.32 ppm (d, 7.5 Hz, 2H)) and VIII as yellow crystals (m.p. 104°C, IR (KBr) 2015, 1915 and 1645 cm^{-1}, ^1H 60MHz NMR ($CDCl_3$) δ 5.85 (~t, 2.0 Hz, 2H), 5.78 (m, 1H), 5.12 (~t, 2.0 Hz, 2H), 3.04 (m, 2H), 1.68 ppm (dt, 1.5 and 8.0 Hz, 3H)).



(IX)

Isolation of V and VI or VII and VIII, respectively, as main products from the reactions of IV with $Ni(CO)_4$ and $Mo(CO)_3(THF)_3$ suggests the preferred cleavage of the C(1)—C(3) bond in IV leading to a complexed cyclopentadienyl—allyl system IX. No products descending from C(2)—C(3) bond cleavage could be isolated. The results provide evidence for a strong substituent effect on the metal-induced transformation of spirocyclopentadienes, but no further conclusions can be made concerning the geometry of intermediates or the sequential order of C—C bond cleavage, hydrogen shift and CO insertion.

References

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