Observation of a π- to σ-Rearrangement upon Proton Addition to Bicyclo[6,1,0]nonatrienetricarbonylmolybdenum

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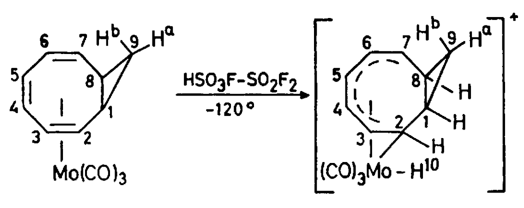
Summary Proton addition to bicyclo[6,1,0]nonatrienetricarbonylmolybdenum (I) gives complex (II) in which a π- to σ-rearrangement has taken place with σ-bonding between Mo and C(2) and π-bonding between Mo and the pentadienyl C(3)—C(7).

Transition metals in low oxidation states can serve as Lewis bases and a wide variety of Lewis acid–base adducts has been synthesized, many from proton addition to transition-metal complexes.[1] Frequently, adduct formation leads to large structural reorganizations of the complex due to the low stereochemical activity of the lone pairs in the transition-metal base.[1] Here, we report an unusual structural change in which proton addition to molybdenum in a trienemolybdenum tricarbonyl complex results in a π to σ change in the nature of the bonding of the triene to the metal.



(I) (II)

Protonation of bicyclo[6,1,0]nonatrienetricarbonylmolybdenum (I)[2] in degassed $HSO_3F–SO_2F_2$ at −120° yields compound (II) in which the entering proton is bound to molybdenum and molybdenum is σ-bonded to C(2) and π-bound to the pentadienyl unit C(3)—C(7); τ (in $HSO_3F–SO_2F_2$ against $CHDCl_2$) 18·75 [H(10), $J_{2,10}$ 19, $J_{1,10}$ 8 $J_{3,10}$ 3], 9·75 [H(9b), $J_{(9b,8)}$ $J_{(9b,1)}$ 4, $J_{(9b,9a)}$ 4], 9·18 [H(9a), H(8)], 8·74 [H(1)], 6·24 [H(2), $J_{2,3}$ 7], 4·30 [H(6), $J_{5,6}$ 8], 3·90 [H(7) $J_{6,7}$ 10], 3·66 [H(3), H(4)], and 3·10 [H(5), $J_{4,5}$ 8].

The postulated C(2)–Mo σ-bond is supported by the strong coupling between the metal-bound proton, H(10), and H(2) and the upfield shift of H(2) in (II) relative to (I) (τ 5·5).[2]

Although the bonding of the metal to the C(3)—C(7) pentadienyl system must obviously be unsymmetrical, the chemical shifts and coupling constants of H(3)—H(7) are in reasonable accord with the postulated π-bound pentadienyl structure based on other model pentadienyl systems.[3]

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