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Preliminary communication

IRON AND MOLYBDENUM CARBONYLS OF 5,6,7,8-TETRAMETHYLENEBICYCLO[2.2.2]-OCT-2-ENE

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SUMMARY

The reaction of the title ligand with iron carbonyls under various conditions gives (tetrahapto)5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene-exotricarbonyliron (I) and the bis(tetrahapto)endoexo-(II) and diexohexacarbonyl diiron (III) complexes as main products. The monoexo complex reacts with $Mo(CO)_3(CH_3CN)_3$ giving a (tetrahapto)iron(hexahapto)molybdenum complex (IV).

Iron and molybdenum tricarbonyl entities tend to coordinate readily two or three carbon-carbon double bonds giving tetra- or hexahapto complexes respectively. This allows a partial blocking of the π system of polyolefins prior to reactions with dienophiles or electrophiles, for example. We have therefore examined the interaction of 5,6,7,8-tetramethylenebicyclo[2.2.2]-oct-2-ene, a new pentaolefin [1], with iron and molybdenum carbonyls under various experimental conditions (Scheme).

Irradiation of the ligand (0.7 g)(high pressure Hg lamp, pyrex vessel) at -80° in pentane in the presence of $Fe(CO)_5$ in excess, followed by chromatography on Florisil (n-hexane as eluent) gives (tetrahapto)5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene-exotricarbonyliron (I) in a low yield (7%) because of polymerization of the ligand. The reaction of the title

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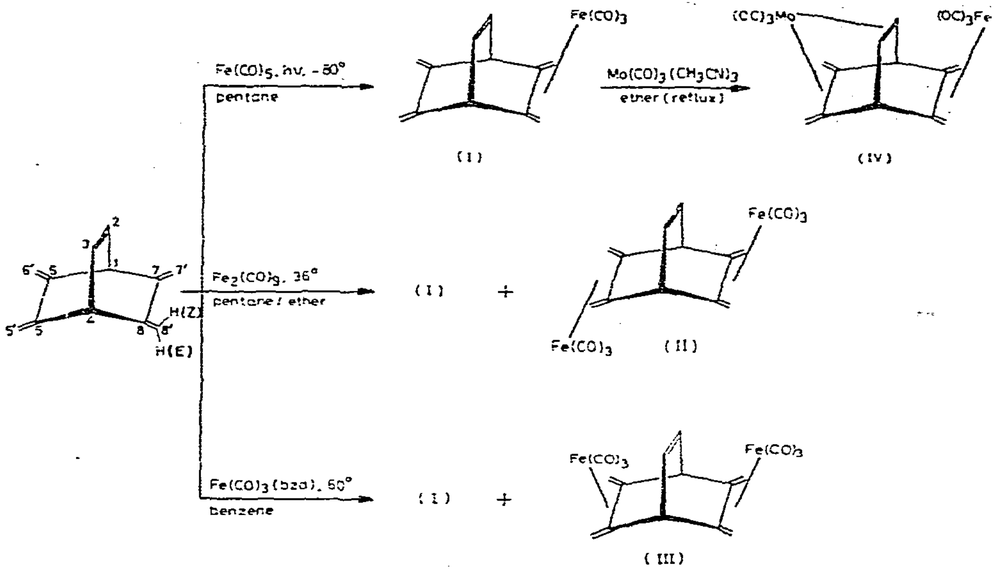

ligand (0.3 g) with excess $Fe_2(CO)_9$ in refluxing pentane/ether for 2 days, followed by chromatography on silica gel (eluent: n-hexane/2v% ether) yields I (40%) and bis(tetrahapto)5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene-endoexohexacarbonyldiiron (II)(20%), together with traces of the monoendo-tricarbonyliron and the diexohexacarbonyldiiron complexes. On treatment with $Fe(CO)_3$(benzalacetone) (1 g) [2] in benzene at 60° for 3 days (chromatography on Florisil with n-hexane as eluent), the ligand (0.4 g) gives I (40%) and bis(tetrahapto)5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene-diexohexacarbonyldiiron (III) (5%). I reacts smoothly with excess $Mo(CO)_3(CH_3CN)_3$ (prepared by refluxing 1 g $Mo(CO)_6$ in acetonitrile [3]) under reflux in ether for 36 hours and yields after chromatography on Florisil (eluent: n-hexane/25v% ether) (tetrahapto,hexahapto)5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene-exotricarbonylirontricarbonylmolybdenum (IV) (60%).

The structures of I, II, III and IV follow from their physical, analytical and spectroscopic properties*, and from comparison with data reported for related simpler complexes [4].

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* All compounds gave satisfactory microanalyses.

I : pale yellow, m.p. 109-110^{o}:, MS (70 eV) m/e^{+}: 296 (M^{+}), 268, 240, 212 (loss of 3 CO); IR (n-hexane): ν(CO) 2063, 1984, 1973 cm^{-1}; ^{1}HNMR (CD$_2$Cl$_2$, δ(TMS) 0 ppm): 6.5 (dd; H-2,H-3), 5.4 (s; H5'(Z),H6'(Z)), 5.2 (s; H5'(E), H6'(E)), 4.0(dd; H-1,H-4), 2.1 (d; H7'(E),H8'(E)), 1.1 (d; H7'(Z),H8'(Z)), , ^{3}J(H-2,H-1)app 4.6 Hz, ^{4}J(H-2,H-4)app 3.3 Hz, ^{2}J(H7'(Z),H7'(E)) 2.6 Hz.

II: yellow, m.p. 142^{o}; MS (70 eV) m/e^{+}: 436 (M^{+}), 408, 380, 352, 324w, 296, 268 (loss of 6 CO); IR (n-hexane): ν(CO) 2059, 1986, 1973 cm^{-1}; ^{1}HNMR (CD$_2$Cl$_2$, TMS): 7.0 (dd; H-2,H-3), 4.3 (dd; H-1,H-4), 2.2 (d; H-5'(E),H-6'(E),H-7'(E), H-8'(E)), 0.7 (d; H-5'(Z),H-6'(Z)), 0.6 (d; H-7'(Z),H-8'(Z)); , ^{3}J(H-2,H-1)app 4.3 Hz, ^{4}J(H-2,H-4)app 3.0 Hz, ^{2}J(H-7'(Z),H-7'(E)) 3.3 Hz, ^{2}J(H-5'(Z),H-5'(E)) 2.9 Hz.

III: orange, m.p. 166^{o}; MS (70 eV) m/e^{+}: same as II; IR (n-hexane): ν(CO) 2058, 1985, 1972 cm^{-1}:, ^{1}HNMR (CD$_2$Cl$_2$,TMS): 6.8 (dd; H-2,H-3), 4.3(dd; H-1,H-4), 2.3 (d; H-5'(E),H-6'(E),H7'(E),H-8'(E)), 0.6 (d; H-5'(Z),H-6'(Z),H-7'(Z), H-8'(Z)); ^{3}J + ^{4}J(H-1)app 7.8 Hz, ^{3}J(H-2,H-1)app 4.5 Hz, ^{4}J(H-2,H-4)app 3.4 Hz, ^{2}J(H-5'(Z),H-5'(E)) 2,7 Hz.

IV: deep orange, m.p. 140-142; MS (70 eV) m/e^{+}: 476 (M^{+} with ^{96}Mo), 448, 420, 392, 364, 336, 308 (loss of 6 CO); IR (n-hexane): ν(CO) 2062, 1990, 1978 (Fe-CO), 1999, 1942, 1912 (Mo-CO), tentative assignement following the literature [5]; ^{1}HNMR (CD$_2$Cl$_2$,TMS): 3.8 (dd; H-2,H-3), 3.6 (d; H-5'(E),H-6'(E)), 3.4 (dd; H-1,H-4), 2.2 (d; H-7'(E),H-8'(E)), 1.8 (d; H-5'(Z),H-6'(Z)), 0.7 (d; H-7'(Z),H-8'(Z)); , ^{3}J(H-2,H-1)app 4.4 Hz, ^{4}J(H-2,H-4)app 2.7 Hz, ^{2}J(H-5'(Z),H-5'(E)) 1.6 Hz, ^{2}J(H-7'(Z),H-7'(E)) 2.7 Hz*.

A crystal structure determination of II is in progress, as well as the study of the reactivity of I and the molybdenum and tungsten analogs.

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