METAL COMPLEXES WITH 2,2,1-BICYCLOHEPTADIENE

Sir:

A recent re-investigation of the interesting metal-organic compounds obtained following reaction of butadiene and its derivatives with iron pentacarbonyl led Hallam and Pauson[1] to conclude that conjugation of the double bonds was an essential feature for the metal-organic bonding. The bonding was considered to be closely related to that involved in ferrocene and other such sandwich complexes rather than that in the various platinous-non-conjugated diene complexes.[2]

We now wish to report the formation of compounds related to the butadiene complexes following reaction of iron pentacarbonyl and molybdenum hexacarbonyl with 2,2,1-bicycloheptadiene. In bicycloheptadiene the two double bonds are not in conjugation but still have a suitable spatial arrangement for possible interaction with the metal atomic orbitals.

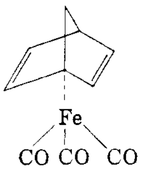
The refluxing of $Fe(CO)_5$ with excess 2,2,1-bicycloheptadiene for 15 hours and then fractional distillation led to the isolation of bicycloheptadiene iron-tricarbonyl (1) in a 30% yield (b.p. 60.5° at 0.2 mm.; found: C, 52.1; H, 3.7; mol. wt., 221). Considerable amounts of a higher boiling ketone were also obtained. The ketone was obtained as white needles from alcohol (m.p. 82°; found: C, 85.1; H, 7.3). The 2,4-dinitrophenylhydrazone formed orange needles from alcohol (m.p. 186–7°; Found C, 64.3; H, 5.3, N, 13.9).

The iron compound I is an orange red liquid at room temperature which solidifies to a yellow crystalline mass below 10°. It is stable when stored under nitrogen but is oxidized slowly in air with the deposition of iron oxide. Compound I readily dissolves in cold concentrated sulfuric acid, from which solutions it can be recovered unchanged on dilution. The solutions in concentrated sulfuric acid liberate sulfur dioxide when heated. Oxidation of I with ferric chloride liberates bicycloheptadiene, thus proving that prior rearrangement to cycloheptatriene followed by complex formation, similar to that in cycloheptatriene molybdenum tricarbonyl,[3] had not occurred.

Irradiation of $Fe(CO)_5$ in bicycloheptadiene with sunlight for 5 hours gave, in addition to I and the unidentified ketone, a solid hydrocarbon, m.p. 67–68°, which, from analysis and molecular weight determination, appears to be a dimer of bicycloheptadiene. Similar irradiation of bicycloheptadiene in the absence of $Fe(CO)_5$ did not yield this compound.

A molybdenum derivative analogous to I was obtained after reaction of $Mo(CO)_6$ with excess bicycloheptadiene. Bicycloheptadienemolybdenum-tetracarbonyl (II) formed pale yellow plates from petroleum ether which were stable in air (m.p. 76–77°; found: C, 43.6; H, 2.6; Mo, 33.0). The infrared spectrum of this compound showed three strong carbonyl peaks at 4.93, 5.05–5.2, and 5.35 μ in contrast to the one sharp peak at 5.1 μ shown by $Mo(CO)_6$. Both compounds I and II showed medium absorption peaks in the 7.0, 7.75 and 8.5 μ regions.

The butadiene-iron tricarbonyl complexes and the present compounds I and II appear to be chemically analogous as far as metal-organic bonding is concerned. It would seem therefore that it is not the conjugation of the two olefinic bonds, but a suitable spatial arrangement necessary for effective overlap with the metal atomic orbitals which is the essential factor leading to bond formation. As mono-olefinic complexes of comparative stability are not known, then the π orbitals of the diene may not be acting independently. Therefore, as with other sandwich type complexes, the formula given affords a satisfactory representation of the compound I; a similar structure is proposed for compound II.



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(1) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(2) J. Chatt, L. M. Valarino and L. M. Venanzi and references therein, *ibid.*, 2496 (1957).

(3) E. W. Abel, M. A. Bennett and G. Wilkinson, *Proc. Chem. Soc.*, 152 (1958).