

## Synthesis and Structure of an $\eta^2$ -Cycloallene Complex: Carbonyl( $\eta^2$ -cyclohepta-1,2-diene)( $\eta^5$ -cyclopentadienyl)triphenylphosphineiron(III) Hexafluorophosphate

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The stable  $\eta^2$ -cycloallene complex, carbonyl( $\eta^2$ -cyclohepta-1,2-diene)( $\eta^5$ -cyclopentadienyl)triphenylphosphineiron(III) hexafluorophosphate, was synthesized, permitting the first single crystal X-ray study of the distortions in a cyclic allene transition metal complex.

The effect of ring strain on the structure and bonding of allenes incorporated into relatively small rings is of continuing interest.<sup>1-3</sup> The application of this kind of stress to a normally linear perpendicular moiety should lead to a deformation of both the central bond angle and dihedral angle described by the allene's four substituents. Recent MNDO calculations predicted bond angles, heats of formation, and preferred ground-states of various cyclic allenes.<sup>1,3</sup> These calculations predicted that cyclohepta-1,2-diene would have a central bond angle compressed to 153.4° and a dihedral angle of 55.2°.<sup>1,3</sup>

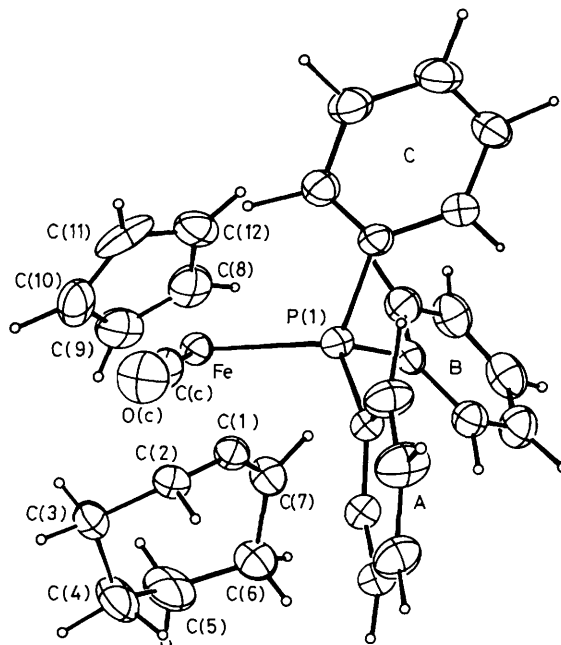
No comparable theoretical studies on transition metal complexes of cyclic allenes have been reported. However, X-ray studies of acyclic allenes have revealed bent structures with central bond angles ranging between 134° and 159° but

with little significant distortion of the allene dihedral angle.<sup>4</sup> Consequently, complexing a cyclic allene to a transition metal should reduce the strain on the central bond angle and may also reduce the twisting stress. The preparation of platinum complexes of cyclohepta-1,2-diene<sup>5</sup> and cyclohepta-1,2,4,6-tetraene<sup>6</sup> have been reported. In the former case an X-ray study was not reported and in the latter attempts to grow crystals suitable for such a study were unsuccessful.

We recently succeeded in preparing the trifluoromethanesulphonate and tetrafluoroborate salts of dicarbonyl(cyclohepta-1,2-diene)( $\eta^5$ -cyclopentadienyl)iron(II).<sup>7</sup> However, we were unable to grow crystals suitable for X-ray studies. Consequently, we synthesized carbonyl( $\eta^2$ -cyclohepta-1,2-diene)( $\eta^5$ -cyclopentadienyl)triphenylphosphineiron(II)

hexafluorophosphate<sup>†</sup> which provided crystals of suitable quality and stability to permit an X-ray structural study.<sup>‡</sup>

The cation shown in Figure 1 is the first cyclic allene transition metal complex characterized by an X-ray study. The cycloheptadiene ring is in a chair conformation with C(4) at the head. A notable feature is the small C(2)–C(1)–C(7) angle of 138.1(3)°; only octahedral ReCl(η<sup>2</sup>-H<sub>2</sub>CCCHPh) (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> has a smaller angle of 134.5(6)°.<sup>8</sup> The C–C angle in other monomeric noncyclic allenes ranges from 140.8 to 159.4°, with an average of 147(9)°.<sup>4</sup> The angle found in our structure is significantly smaller than that predicted by the MNDO calculations for the uncomplexed allene. However, the interaction of the iron atom with the C(2)–C(1) double bond will cause the C(2) hybridization to move toward sp<sup>3</sup> and C(1) toward sp<sup>2</sup>, relieving ring strain and causing the angle to become smaller. The angle between the C(3)–C(2)–C(1)–H(21) and the C(6)–C(7)–C(1)–H(71) planes of 70.7° is larger than that predicted by the MNDO calculations. However, H(21) is 0.67 Å from the C(3)–C(2)–C(1) plane which may be a consequence of the rehybridization on C(2) or a steric interaction with the CO group. The somewhat crowded nature of the cation may be appreciated from the fact that the iron atom is 0.595 Å from the plane of the allene group, one of the largest displacements observed to date. The C(2)–C(1)–C(7) plane makes an angle of 67.5° with the P(1)–Fe–CO plane. An angle close to 90° has been reported in other cases. Finally, the C(1)–C(2) and C(1)–C(7) distances indicate that the iron atom interacts almost exclusively with only one double bond. This observation together



**Figure 1.** An illustration of the [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)(PPh<sub>3</sub>)(C<sub>7</sub>H<sub>10</sub>)]<sup>+</sup> ion. Selected bond lengths: Fe–C(1), 2.007(4); Fe–C(2), 2.168(3); C(1)–C(2), 1.385(6); C(1)–C(7), 1.303(7); Fe–C(c), 1.777(5); C(c)–O(c), 1.137(6); Fe–P(1), 2.250(1); P(1)–C(1A), 1.828(4); P(1)–C(1B), 1.825(4); P(1)–C(1C), 1.831(3); Fe–C, average for C<sub>5</sub>H<sub>5</sub> ring 2.097(5) Å. Selected bond angles: P(1)–Fe–C(c), 89.5(1); P(1)–Fe–C(1), 82.9(1); C(c)–Fe–C(1), 111.3(2); Fe–C(1)–C(2), 77.0(2); Fe–C(1)–C(7), 141.9(3); C(2)–C(1)–C(7), 138.1(3); Fe–C(c)–O(c), 177.8(3); Fe–P(1)–C(1A), 110.8(1); Fe–P(1)–C(1B), 117.3(1); Fe–P(1)–C(1C), 115.1(1)°.

<sup>†</sup> A benzene–pentane (5 : 8 v/v) solution of (dicarbonyl)(η<sup>5</sup>-cyclopentadienyl)(7-methoxycycloheptene)iron(II) (1.10 g; 3.6 mmol) and triphenylphosphine (1.0 g; 3.8 mmol) was photolysed with a low pressure Hg lamp (Hanovia, 450 W) in a quartz photolysis well for 20 min. A stream of N<sub>2</sub> was passed through the solution to remove CO. The solvent was removed and the red oil was eluted down a 3" × 1" alumina column (grade II, neutral), first with hexane, then with benzene. A red band which eluted with benzene was collected to yield 0.94 g (48%) of the carbonyl(η<sup>5</sup>-cyclopentadienyl)(7-methoxycycloheptene)(triphenylphosphine)iron(II), (1).

To a benzene–pentane (1 : 1 v/v) solution of (1) (0.15 g; 0.28 mmol) at 0°C was added trimethylsilyl trifluoromethanesulphonate (0.10 ml; 0.4 mmol). The solvent was removed *in vacuo* after 10 min and ethyl acetate was added to crystallize carbonyl(η<sup>5</sup>-cyclopentadienyl)(triphenylphosphine)(η<sup>2</sup>-cyclohepta-1,2-diene)iron(II) trifluoromethanesulphonate (2) as a yellow solid (0.10 g; 56% yield).

Water was added to a methanol solution of (2) in an excess of ammonium hexafluorophosphate. The hexafluorophosphate salt of (2) precipitated as a yellow solid in quantitative yields. The crystal for X-ray study was grown from a methylene chloride–n-heptane solution at –35°C.

<sup>‡</sup> *Crystal data:* [C<sub>31</sub>H<sub>30</sub>OPFe]<sup>+</sup>PF<sub>6</sub><sup>–</sup>, *M* = 650.4, triclinic, space group *P* $\bar{1}$ , *a* = 9.998(3), *b* = 10.801(3), *c* = 14.675(4) Å, α = 91.40(2), β = 107.32(2), γ = 101.24(2)°, *U* = 1478.1(6) Å<sup>3</sup>, *D*<sub>c</sub> = 1.46 g cm<sup>–3</sup>, *F*(000) = 668, μ(Mo–Kα) = 7.0 cm<sup>–1</sup>. Nicolet R3m diffractometer, 4406 reflections [1.5 ≤ 2θ ≤ 47.0°], 3743 observed with *F*<sub>o</sub> > 3σ(*F*<sub>o</sub>). The structure was solved by direct methods (SOLV included in SHELXTL system) and refined using the 'blocked cascade' least-squares method. 380 Parameters refined: co-ordinates and anisotropic thermal parameters of non-H atoms, and isotropic thermal factors of H-atoms in 7-membered ring, and a scale factor. The final *R* and *R*<sub>w</sub> (*w* = 1/σ<sup>2</sup>) values are 0.052 and 0.042, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

with an electron count suggests that allenes co-ordinate to a metal like a simple alkene.

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