tomatic indexing procedures gave cell dimensions in agreement with the photographic work. Least-squares refinement of the cell dimensions with higher angle reflections yielded the values given in Table I.

Data were collected in one quadrant of reciprocal space ($+h,+k,\pm l$) by using measurement parameters given in Table I. Systematic absences consistent only with space group $P2_1/c$ occurred at $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. Corrections for absorption or decay were unnecessary. Systematically absent reflections were eliminated, and symmetry-equivalent reflections were averaged to yield the set of unique reflections. Only those data with $I > 3\sigma(I)$ were used in the least-squares refinement.

The structure was solved by normal heavy-atom methods, hindered slightly by near-special heavy-atom coordinates. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, and a p factor of 0.03 for intense reflections was used throughout refinement. The analytical forms for the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[10]

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Hydrogen atoms were not located. In the final cycle, all atomic positions and anisotropic thermal parameters were included in the full-matrix least-squares refinement. Final refinement parameters are given in Table I. All peaks in the final difference Fourier map had intensities of less than 0.31 e $Å^{-3}$, and the largest were located near fluorine atom positions or the phosphine methyl groups.

Registry No. $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, axial, 72453-45-3; $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, equatorial, 76036-79-8; $Mo_2(O_2CCF_3)_4$, 36608-07-8.

Supplementary Material Available: Figure 4 showing a stereopair packing diagram of the unit cell contents, Figure 5 giving the numbering scheme for the O_2CCF_3 ligands, Table IV giving thermal parameters, and Table V giving structure factors (27 pages). Ordering information is given on any current masthead page.

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Structures of and Bonding in η^1-Cycloheptatrienylidene Complexes of Iron

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The crystal structures of the PF_6^- salts of two η^1-cycloheptatrienylidene complexes of iron of the form $[(\eta^5-C_5H_5)(\eta^1-CHT)Fe(CO)_2]PF_6$, in which CHT = C_7H_6 (**1**) or $C_{11}H_8$ (**7**), have been determined by single-crystal X-ray diffraction techniques with three-dimensional data gathered at -35 °C by counter methods. Yellow-orange crystals of **1** form as irregular blocks in triclinic space group $P\bar{1}$ with unit cell constants (at -35 °C) $a = 7.981$ (4) Å, $b = 14.378$ (3) Å, $c = 7.133$ (1) Å, $\alpha = 98.52$ (1)°, $\beta = 100.75$ (1)°, and $\gamma = 93.33$ (1)°. The calculated density of 1.728 g cm^{-3}, with the assumption of two formula weights of **1** per unit cell, agrees with the measured value of 1.70 g cm^{-3}. Dark red crystals of **7** form as irregular hexagonal prisms in space group $P\bar{1}$ with unit cell constants (at -35 °C) $a = 8.2086$ (6) Å, $b = 15.238$ (2) Å, $c = 7.4361$ (8) Å, $\alpha = 90.509$ (7)°, $\beta = 104.396$ (5)°, and $\gamma = 94.676$ (6)°. The calculated density of 1.691 g cm^{-3}, with the assumption of two formula weights of **7** per unit cell, agrees with the measured value of 1.68 g cm^{-3}. Full-matrix least-squares refinements of the structures have converged with conventional R indices (on $|F|$) of 0.057 and 0.041 for **1** and **7**, respectively, with use of (in the same order) the 4042 and 4414 symmetry-independent reflections with $I_o/\sigma(I_o) > 2.0$. Aside from the difference in the η^1-CHT rings, the molecular geometries of **1** and **7** are virtually identical, although the shorter Fe—C_{carb} bond (by 0.017 Å) in **1** suggests stronger Fe—carbene back-bonding in **1** than in **7**. In addition, from carbonyl stretching frequencies and ^1H and ^{13}C NMR data, it is concluded that, despite the existence of these CHT ligands in the carbene form, metal back-bonding with these η^1 ligands is less important than in similar nonheteroatom-stabilized carbene complexes such as $[(\eta^5-C_5H_5)(\eta^1-CH(Ph))Fe(CO)_2](CF_3SO_3)$. It is noteworthy that the orientation of the CHT rings is ~ 90° from that observed in one Fe=CH_2- and two Ta=CHR-containing complexes.

Introduction

Transition-metal–carbene complexes, or more specifically methylene complexes, have long been considered as intermediates in olefin metathesis,[1–4] cyclopropanation,[4–7] polymerization, and other reactions.[6,8] Though their existence, however transitory, had thus often been inferred,[4–9] the first species to be isolated were the prototypical heteroatom-stabilized complexes $MeC(OMe)W(CO)_5$, $PhC(OMe)W(CO)_5$, and $MeC(OMe)Cr(CO)_5$, which were prepared by Fischer[10] and characterized structurally by Mills.[11] Since singlet carbene carbon atoms (C_{carb}) possess an unshared pair of electrons and an empty p orbital (i.e., sp^2 hybridization), the bonding between metal and ligand is potentially similar to that between a transition metal and a CO ligand (i.e., synergistic).[12]

However, since the electrophilic C_{carb} atoms in Fischer-type complexes are bonded directly to a heteroatom which possesses
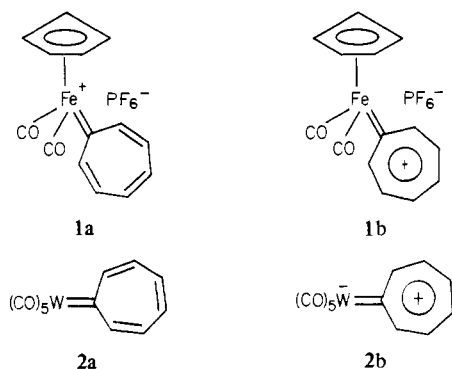
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unshared pairs of electrons, the complex gains additional stability at the expense of back-donation from the metal and ease of reactivity (in comparison to many of the nonheteroatom-stabilized species cited below) from the donation of π-electron density by the heteroatom. This is reflected in the shortening of the heteroatom to C_{carb} bond[11,13] (from a nominal single-bond length) and in an increase in the rotational barrier about this bond.[14]
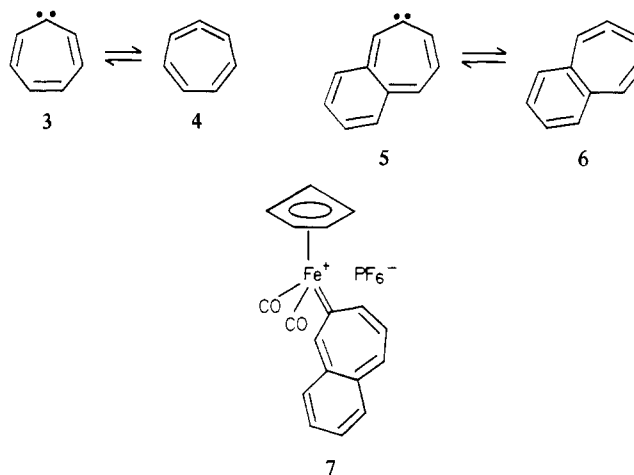
The early publications of Fischer stimulated a great deal of work in this area, which led not only to extensions and modifications of these heteroatom–carbene systems but eventually to the preparation of a variety of interesting and synthetically useful carbene complexes, including (2,3-diphenylcyclopropenylidene)pentacarbonylchromium,[15] (2,3-cyclopropenylidene)dichloropalladium,[16] $Ph_2C=W(CO)_5$,[1] $[Cp(Bzcb)Fe(CO)_2]^+$(Bzcb = benzocyclobutenylidene),[17] $Cp(CO)_2Mn=C(Ph)C(O)Ph$,[18] $Cp_2MeTa=CH_2$ (the only isolated methylene complex),[19] $[Cp(CO)_2Fe=CHPh]^+$,[20] and $[Cp(Ph_2PCH_2CH_2PPh_2)Fe=CH_2]^+$,[21] none of which depend upon electron donation from a heteroatom to the carbene carbon atom for stability. The stability of many of these complexes is doubtless related to the proximity of electron-rich phenyl substituents or to the aromaticity of the ring containing the carbene carbon atom itself.

Since the cycloheptatrienyl cation ring possesses an empty p orbital and is stabilized by an aromatic six-π-electron system, it was suspected that it would coordinate with a transition-metal atom in a carbene-like manner much like the 1,2-diphenylpropenylidene ligand. Thus, following the successful hydride abstraction route used in the synthesis of $[Cp(Bzcb)Fe(CO)_2]^+$,[17] the cycloheptatrienylidene complexes 1 and 2 were prepared in one of our laboratories as previously reported.[22]

In addition, it has long been assumed that the seven-membered-ring intermediate on the C_7H_6 energy surface could be represented by planar carbene **3**.[23] Recently, however, evidence has accumulated which supports the existence of an isomeric twisted allene form **4** that may be of lower energy.[24,25]

Furthermore, INDO calculations[26] predict that benzannelation as in **5** should favor allene form **6** over carbene isomer **5** by ca. 45 kcal/mol.[27] So that it could be determined if benzannelation would also cause the allene form to be favored when complexed to a transition metal, the synthesis of the iron complex of **7** with a carbene ligand benzannelated as in **5** was carried out, as communicated earlier.[28]

In this paper, we present a full account of the syntheses of 1 and 7 as well as a detailed description of their structures, as determined by X-ray crystallography. We also present an assessment of the metal to cycloheptatrienylidene (CHT) bonding, based upon these crystallographic results and upon the spectroscopic data obtained by infrared and ^1H and ^{13}C NMR methods. Included in this presentation is an interpretation, based upon spectroscopic data, of the Fe to CHT bonding in the 4,5-benzannelated isomer of **7**. The synthesis and spectral characterization of this isomer (**8**) appear elsewhere.[28]

Experimental Section

General Procedures and Techniques. Reactions were performed under oxygen-free nitrogen with use of standard Schlenk techniques. Tetrahydrofuran was purified by distillation from sodium potassium alloy–benzophenone under nitrogen. Reagent grade methylene chloride was distilled from P_2O_5 under nitrogen and used immediately. Unless otherwise noted, all other solvents were reagent grade and used without further purification. The alumina used was Fisher certified neutral alumina, Brockman Activity 1, to which 3% w/w water was added. It was further purged several times with nitrogen and allowed to stand for 2 or more days. The silica gel was purchased from Baker (60–300 mesh).

1-, 2-, and 3-Lithiocycloheptatrienes. To a cold (dry ice and isopropyl alcohol) addition funnel was added dropwise 16.5 mL (26.4 mmol, 1.6 M solution in hexane) of butyllithium with a syringe to a stirred solution of 4.52 g (26.4 mmol) of 1-, 2-, and 3-bromocycloheptatrienes in 30 mL of tetrahydrofuran. The dark green solution was allowed to stir for 30 min and was used immediately.

1-, 2-, and 3-Cycloheptatrienylcyclopentadienyldicarbonyliron. A cold solution of 26.4 mmol of 1-, 2-, and 3-lithiocycloheptatrienes in tetrahydrofuran was added to a rapidly stirred solution of 8.2 g (26.9 mmol) of cyclopentadienyliron dicarbonyl iodide in 20 mL of tetrahydrofuran cooled by a dry ice–isopropyl alcohol bath. The reaction mixture was stirred for 45 min. It was then warmed to room tem-

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perature and stirred an additional 20 min. A small amount of alumina was added to the reaction mixture, and the tetrahydrofuran was removed in vacuo. The reaction products coated on the alumina were chromatographed on alumina with pentane as the eluent. Two simultaneously eluted bright yellow bands were collected. Removal of the solvent in vacuo (rotary evaporator) gave 2.02 g (29%) of a yellow, air-sensitive oil.

The spectral data were as follows: ^{1}H NMR (CDCl$_3$) δ 2.15, 2.25, 2.62 (2 H, t, t, d, saturated CH), 4.65, 4.79, 4.84 (5 H, s, s, s, Cp), 4.98–5.50, 5.78–6.83 (5 H, br m, br m, vinyl); IR (neat) 3020, 2020, 1950, 1495, 1430, 1015, 830, 725 cm^{-1}; MS m/e 268.018 41 (calcd 268.018 60).

(η^1-Cycloheptatrienylidene)(η^5-cyclopentadienyl)dicarbonyliron Hexafluorophosphate (1). A solution of 2.02 g (7.55 mmol) of 1-, 2-, and 3-cycloheptatrienylcyclopentadienyldicarbonyliron in 10 mL of methylene chloride was cooled in a dry ice and isopropyl alcohol bath. To the stirred solution was added with a syringe 2.93 g (7.55 mmol) of triphenylcarbenium hexafluorophosphate in 30 mL of methylene chloride. The reaction mixture was stirred for 30 min and then was allowed to warm to room temperature. Immediately after 30 min of additional stirring, ca. 20 mL of methylene chloride was rapidly removed in vacuo and ca. 60 mL of ethyl ether (freshly opened can) was rapidly added via syringe to precipitate the complex. The solid was immediately collected on a medium-grade glass frit and was washed with several 15-mL portions of ethyl ether. The remaining solvent was removed in vacuo. This yielded 2.8 g (90%) of a yellow-orange, air-stable solid. Recrystallization from methylene chloride gave orange-yellow plates, mp 180.0–180.5 °C dec.

The spectral data were as follows: ^{1}H NMR (0 °C, acetone-d_6), δ 10.01 (2 H, d, J = 10.0 Hz, H(2), H(7)), 8.48–8.74 (2 H, m, H(4), H(5)), 7.94–8.30 (2 H, m, H(3), H(6)), 5.50 (5 H, s, Cp); decoupled-^{13}C NMR (0 °C, acetone-d_6) δ 242.3 (C(1)), 212.8 (CO), 170.0, 148.3, 138.2 (C(2), C(3), C(4)), 88.3 (Cp); IR (CH$_2$Cl$_2$) 2045, 1996 cm^{-1} (KBr) 3130, 2040, 1980, 1460, 1005, 830, 730, 590, 555 cm^{-1}; UV–VIS (acetonitrile) [λ_{max} (log ϵ)] 205 (4.41), 220 (sh), 340 (sh), 405 (3.60).

Anal. Calcd for C$_{14}$H$_{11}$F$_6$FeO$_2$P: C, 40.81; H, 2.69. Found: C, 40.55; H, 2.71.

1-Bromo-1,2,3,4-tetrahydronaphthalene.[29] A solution of 404 g (3.06 mol) of tetralin and 500 mL of carbon tetrachloride were heated to reflux. With an addition funnel, 443 g (2.77 mol) of bromine was added over a 3.5-h period. The mixture was allowed to stand at room temperature overnight. The solvent was removed in vacuo (rotary evaporator). The untreated residue, 636.1 g, was used in the next step.

1,2-Dihydronaphthalene.[29] An aqueous sodium hydroxide solution (160 g of NaOH in 500 mL of H$_2$O) was brought to reflux. The above bromide was added over a 2-h period. After an additional 0.5 h of reflux, the mixture was allowed to stand at room temperature overnight.

The mixture was twice extracted with 200-mL portions of petroleum ether. The organic extracts were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo (rotary evaporator). The residue was vacuum distilled. This distillate was a mixture of dihydronaphthalene, tetralin, and naphthalene. The amount of dihydronaphthalene (0.610 mol) was determined by NMR integration.

1,2-Benzo-4-bromo- and 1,2-Benzo-6-bromocycloheptatrienes. A mixture of naphthalene, tetrahydronaphthalene, dihydronaphthalene (0.610 mol in a 218-g mixture), benzyltriethylammonium chloride (0.8 g), and bromoform (459.4 g, 1.8 mol) was mechanically stirred and cooled with a water bath. To this mixture was added dropwise 500 g of 50% w/w aqueous sodium hydroxide. After 24 h of stirring, 500 mL of H$_2$O was added and the organic layer was washed twice with 250-mL portions of water. After drying with anhydrous magnesium sulfate, the organic layer was filtered through Celite. The bromoform was removed by vacuum distillation (10 torr, 32 °C to 3.5 torr, 60 °C). The residue was taken up in 500 mL of pentane and filtered to remove the brown polymer. The organic products were concentrated in vacuo (rotary evaporator).

Distillation of this residue (1.5 torr, 60 °C) removed the tetrahydronaphthalene. Three distillations (3 torr, 140 °C; 2.75 torr, 92–118 °C; finally with a Nester Faust spinning band column at 0.25 torr, 90–100 °C) resulted in loss hydrogen bromide and gave a mixture

of the two bromides (51.9 g, 38%) that was suitable for further use.

The spectral data were as follows: ^{1}H NMR (CDCl$_3$) δ 3.08, 3.52 (2 H, d, J = 7 Hz, s, saturated CH), 5.45–6.5 (2 H, m, vinyl), 6.9–7.55 (4.5 H, m, vinyl and aromatic); IR (neat) 3000, 1601, 1480, 1440, 1420, 1340, 1190, 1110, 1030, 980, 860, 780, 755 cm^{-1}; MS m/e 219.989 53 (calcd 219.988 50).

1,2-Benzo-4-lithio- and 1,2-Benzo-6-lithiocycloheptatrienes. To an addition funnel cooled with a dry ice–isopropyl alcohol mixture and containing a stirred solution of 5.22 g (23.6 mmol) of 1,2-benzo-4-bromo- and 1,2-benzo-6-bromocycloheptatrienes in 32 mL of tetrahydrofuran was added 14.5 mL (2.32 mmol, 1.6 M solution in hexane) of butyllithium dropwise with a syringe. The green solution was stirred for 30 min and then used immediately.

1,2-Benzo-4- and 1,2-Benzo-6-cycloheptatrienylcyclopentadienyldicarbonyliron. A cold solution of (2.32 mmol) 1,2-benzo-4-lithio- and 1,2-benzo-6-lithiocycloheptatrienes in 32 mL of tetrahydrofuran was added rapidly to a stirred solution of 7.2 g (2.4 mmol) of cyclopentadienyldicarbonyliron iodide in 20 mL of tetrahydrofuran cooled with dry ice–isopropyl alcohol. The cold reaction mixture was stirred for 45 min and then warmed to room temperature. At this time, 40 mL of alumina was added to the reaction mixture and the tetrahydrofuran was removed in vacuo. The reaction products coated on the alumina were chromatographed on alumina with pentane and then a benzene–pentane mixture (gradually increasing the benzene content to 15% v/v benzene–pentane). The yellow band was collected. Removal of the solvent in vacuo (rotary evaporator) gave 2.74 g (37%) of a yellow, air-sensitive oil.

The spectral data were as follows: ^{1}H NMR (CDCl$_3$) δ 2.9, 3.45 (2 H, d, s, saturated CH), 4.9 (5 H, s, Cp), 5.35, 6.2, 6.7, 7.2 (8 H, complex multiplets, vinyl and aromatics); IR (neat) 3020, 2010, 1950, 1775, 1525, 1480, 1430, 1020, 910, 830, 730 cm^{-1}; MS m/e 318.033 02 (calcd 318.034 10).

(η^1-3,4-Benzocycloheptatrienylidene)(η^5-cyclopentadienyl)dicarbonyliron Hexafluorophosphate (7). A solution of 2.74 g (8.60 mmol) of 1,2-benzo-4- and 1,2-benzo-6-cycloheptatrienylcyclopentadienyldicarbonyliron in 15 mL of methylene chloride was cooled in a dry ice–isopropyl alcohol bath. To the stirred solution was added dropwise with a syringe 3.34 g (8.60 mmol) of triphenylcarbenium hexafluorophosphate in ca. 30 mL of methylene chloride. The reaction mixture was stirred for 1 h and then warmed to room temperature. Partial rapid removal of the methylene chloride (ca. 30 mL) in vacuo followed by rapid addition of ethyl ether (ca. 60 mL) aided the precipitation of the complex. The solid was immediately collected on a medium-grade glass frit and was washed with several 10-mL portions of ethyl ether. The residual solvent was removed in vacuo. This yielded 3.5 g (88%) of a brick red solid. Recrystallization from methylene chloride gave violet needles, mp 176–177 °C dec.
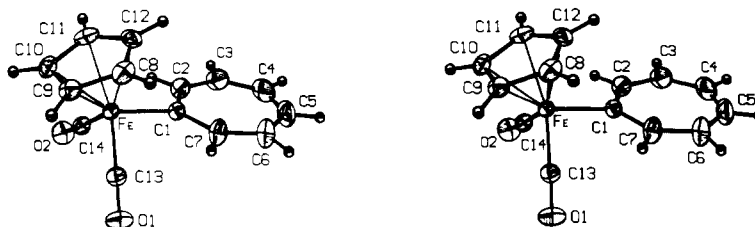
The spectral data were as follows: ^{1}H NMR (8 °C, nitromethane-d_3), δ 10.4 (1 H, d, J = 2 Hz), 9.92 (1 H, d, J = 10.6 Hz), 9.23 (1 H, d of m, J = 10.6, 0.5 Hz), 8.50, 8.16 (5 H, m, t, J = 10.6 Hz); decoupled ^{13}C NMR (0 °C, nitromethane-d_3), δ 215 (CO), 201 (C-1), 176, 174, 155, 145, 139, 138, 138, 137, 136, 133 (C-2 through C-11), 89 (Cp); IR (CH$_2$Cl$_2$) 2037, 1992 cm^{-1}, (KBr) 3140, 2025, 1975, 1420, 840, 595, 560 cm^{-1}; UV–VIS (CH$_2$Cl$_2$) [λ_{max} (log ϵ)] = 380 (3.52), 313 (sh), 280 (4.36), 232 (4.28).

Anal. Calcd for C$_{18}$H$_{13}$F$_6$FeO$_2$P: C, 46.79; H, 2.84. Found: C, 46.68; H, 2.86.

Crystallographic Studies. Single crystals of **1** and **7** were grown by evaporation at ca. −15 °C (to retard decomposition) of solutions of freshly distilled CH$_2$Cl$_2$. Whereas **7** crystallized as dark red prisms with dimensions acceptable for single-crystal X-ray diffraction work, **1** formed as large yellow-orange blocks which had to be cut to proper size. Suitable specimens of **1** and **7** so obtained were glued to glass fibers which then, in turn, were fixed to a goniometer head. Weissenberg photographs and preliminary experiments with a Syntex P2$_1$ autodiffractometer indicated symmetry no higher than that of the triclinic system (space groups $P1$ and $P\bar{1}$) for crystals of both compounds. The data crystals were maintained in a stream of cold (−35 °C), dry nitrogen during the course of all experiments with the diffractometer. Crystal data and details of data collection for **1** and **7** are summarized in Table I. The measured X-ray intensities were reduced and assigned standard deviations (with p = 0.02) as described elsewhere.[30]

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(30) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 381.

Figure 1. Stereoscopic view of the $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_7H_6)Fe(CO)_2]^+$ ion illustrating the atom numbering scheme used herein. Nonhydrogen atoms are shown as ellipsoids of 30% probability, and hydrogen atoms are shown as spheres of radius 0.1 Å.

Solution and Refinement of the Structures. Both structures were solved by standard heavy-atom procedures and refined by full-matrix least-squares methods.[31] The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Fe, P, F, O, C,[32] and H[33] were used in these calculations, and the real $(\Delta f')$ and imaginary $(\Delta f'')$ corrections[32] for anomalous scattering of Mo Kα radiation were applied to the Fe and P scattering curves.

$[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_7H_6)Fe(CO)_2]PF_6$ (1). Full-matrix least-squares refinement was conducted in centrosymmetric space group $P\bar{1}$, with use of only those 4042 data with $I_o/\sigma(I_o) > 2.0$, for a model in which all nonhydrogen atoms were treated anisotropically and hydrogen atoms isotropically. Since satisfactory refinement was attained in this space group and since the positions of all hydrogen atoms were located from a difference electron density map, refinement in noncentrosymmetric space group $P1$ was unnecessary. At least-squares convergence, $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.057$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.071$, and a standard deviation of an observation of unit weight = $[\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 3.84$ for $m = 4042$ observations and $s = 261$ variables. Inspection of the data revealed no indication of secondary extinction. A structure factor calculation with all 4627 data measured during data collection gave R and R_w values of 0.065 and 0.071, respectively.

In the final cycle of refinement, all shifts in nonhydrogen atom parameters were less than 0.7 of a corresponding estimated standard deviation (esd) (the larger shifts were generally associated with PF_6^-), while no shift of a hydrogen atom parameter exceeded 2.2 times an appropriate esd. The largest peaks in a final difference electron density map were 0.2–0.4 e Å^{-3}.

$[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_{11}H_8)Fe(CO)_2]PF_6$ (7). As in the case of the structure of 1, because least-squares refinement and location of all hydrogen atoms from a difference electron density map were successful in space group $P\bar{1}$, structure refinement in space group $P1$ was not conducted. Convergence was reached with a model equivalent to that used for 1 (nonhydrogen atoms refined anisotropically and hydrogen atoms isotropically) with R, R_w, and a standard deviation of an observation of unit weight of 0.040, 0.044, and 2.20, respectively, for $m = 4414$ observations (with $I_o/\sigma(I_o) > 2.0$) and $s = 305$ variables. Calculation of structure factors using all 5290 reflections measured during data collection yielded R and R_w indices of 0.051 and 0.045, respectively. In the last cycle of refinement the largest shifts in nonhydrogen and hydrogen parameters were less than 0.7 and 1.0 times a corresponding esd. There was no evidence for secondary extinction in the data set. The largest peaks in a final difference electron density map were ~0.1 e Å^{-3}.

Table II presents atomic positions with corresponding esd's as derived from the least-squares inverse matrix for the structure of 1; the equivalent information for the structure of 7 is given in Table III. Tabulations of observed and calculated structure factor amplitudes and of anisotropic thermal parameters for both crystal structures are available.[34]

Results and Discussion

Crystal Structures of 1 and 7. The crystal structures of 1 and 7 are composed of discrete cations and anions with no

(31) A listing of principal computer programs used in these studies is provided in ref 30.
(32) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(33) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(34) Supplementary material.

Table I. Crystallographic Summary

	$[(\eta^5\text{-}C_5H_5)$-$(\eta^1\text{-}C_7H_6)$-$Fe(CO)_2]PF_6$	$[(\eta^5\text{-}C_5H_5)$-$(\eta^1\text{-}C_{11}H_8)$-$Fe(CO)_2]PF_6$
Crystal Data at -35 °C[a]		
a, Å	7.981 (4)	8.2986 (6)
b, Å	14.378 (3)	15.238 (2)
c, Å	7.133 (1)	7.4361 (8)
α, deg	98.52 (1)	90.509 (7)
β, deg	100.75 (1)	104.396 (5)
γ, deg	93.33 (1)	94.676 (6)
V, Å^3	792.1 (9)	907.3 (5)
d_{measd}, g cm^{-3} (19 °C)[b]	1.70	1.68
d_{calcd}, g cm^{-3} (-35 °C)	1.728	1.691
empirical formula	$C_{14}H_{11}F_6FeO_2P$	$C_{18}H_{13}F_6FeO_2P$
fw	412.05	462.11
crystal system	triclinic	
space group	$P1$ (no. 1) or $P\bar{1}$ (no. 2)[c]	
Z	2	2
$F(000)$, electrons	412	464
Data Collection at -35 °C[d]		
radiation (Mo Kα)	0.710 69	
mode	ω scan, recentered automatically after each batch of 1000 reflections	
scan range	symmetrically over 1.0° about Kα$_{1,2}$ max	
bkgd	offset 1.0 and -1.0° in ω from Kα$_{1,2}$ max	
scan rate, deg min^{-1}	variable, 2.0–5.0	
check reflctns	4 remeasured after every 96 reflections; analyses[e] of these data indicated overall decreases in intensity of 6 and 2%, respectively, during the 92 and 91 h of data collection for which the appropriate corrections were applied	
2θ range, deg	4.0–60.0	
total reflctns measd	4627	5290
data crystal dimens, mm	0.21 × 0.52 × 0.59	0.17 × 0.31 × 0.40
data crystal volume, mm^3	0.031	0.027
data crystal faces	(020), (0$\bar{2}$0), and 7 other "faces" formed by cutting	(100), ($\bar{1}$00), (020), (0$\bar{2}$0), (1$\bar{1}$0), ($\bar{1}$10), (101), (10$\bar{1}$)
abs coeff, μ(Mo Kα), cm^{-1}	11.5	10.2
transmission factor range	0.66–0.82	0.73–0.88

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections with $28 < 2\theta < 33°$ for 1 and 55 reflections with $26 < 2\theta < 30°$ for 7. [b] Flotation in a mixture of carbon tetrachloride and bromoform. [c] Shown by successful refinement to be $P\bar{1}$ for both structures (see text). [d] Syntex P2$_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert-gas low-temperature delivery system. [e] Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1511.

unusually close interionic contacts. Figures 1 and 2 provide stereoscopic views of the cations of 1 and 7 and indicate the atomic numbering schemes used in this paper. A compilation of the bond lengths and angles of 1 is presented in Table IV; the same information for 7 is listed in Table V. Deviations of atoms from the mean planes of the CHT ligands are given in Supplementary Table VI.

Table II. Fractional Coordinates for Nonhydrogen Atoms of $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_7H_6)Fe(CO)_2]PF_6{}^a$

atom	x	y	z
Fe	0.29692 (5)	0.86933 (3)	0.25044 (6)
P	−0.1911 (1)	0.6956 (1)	0.5556 (2)
F(1)	−0.0153 (5)	0.7589 (3)	0.6145 (4)
F(2)	−0.1681 (5)	0.6888 (3)	0.3371 (5)
F(3)	−0.2714 (7)	0.7899 (3)	0.5297 (9)
F(4)	−0.2119 (8)	0.7048 (4)	0.7636 (5)
F(5)	−0.1037 (8)	0.6021 (3)	0.5587 (10)
F(6)	−0.3616 (5)	0.6327 (3)	0.4934 (6)
O(1)	0.6376 (4)	0.9158 (2)	0.1859 (5)
O(2)	0.4068 (4)	0.8526 (2)	0.6551 (4)
C(1)	0.3205 (4)	0.7334 (2)	0.1534 (5)
C(2)	0.2310 (5)	0.6677 (3)	0.2492 (6)
C(3)	0.2021 (6)	0.5696 (3)	0.2048 (8)
C(4)	0.2361 (7)	0.5087 (3)	0.0451 (10)
C(5)	0.3074 (7)	0.5318 (3)	−0.1023 (9)
C(6)	0.3660 (8)	0.6210 (4)	−0.1271 (7)
C(7)	0.3621 (6)	0.7066 (3)	−0.0172 (6)
C(8)	0.1524 (5)	0.9187 (3)	0.0125 (5)
C(9)	0.2113 (5)	0.9942 (3)	0.1620 (6)
C(10)	0.1465 (5)	0.9795 (3)	0.3241 (6)
C(11)	0.0441 (5)	0.8914 (3)	0.2757 (6)
C(12)	0.0463 (5)	0.8551 (3)	0.0831 (6)
C(13)	0.5041 (4)	0.8961 (2)	0.2117 (5)
C(14)	0.3661 (4)	0.8569 (2)	0.4953 (5)

^{a} See Figure 1 for identity of the atoms. Numbers in parentheses are the estimated standard deviations in the units of the least significant digits for the corresponding parameter.

Table III. Fractional Coordinates for Nonhydrogen Atoms of $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_{11}H_8)Fe(CO)_2]PF_6{}^a$

atom	x	y	z
Fe	0.70402 (4)	0.11886 (2)	0.71933 (4)
P	0.16040 (9)	0.27846 (4)	0.37769 (9)
F(1)	0.2566 (4)	0.1966 (2)	0.3722 (5)
F(2)	−0.0085 (3)	0.2171 (1)	0.3267 (3)
F(3)	0.1658 (2)	0.2679 (1)	0.5908 (2)
F(4)	0.3253 (3)	0.3412 (2)	0.4282 (3)
F(5)	0.1486 (3)	0.2938 (1)	0.1657 (3)
F(6)	0.0595 (3)	0.3623 (1)	0.3853 (3)
O(1)	0.5930 (2)	0.1373 (1)	0.3198 (2)
O(2)	0.3732 (2)	0.0865 (1)	0.7826 (3)
C(1)	0.7185 (2)	0.2481 (1)	0.7748 (3)
C(2)	0.6644 (3)	0.2780 (1)	0.9257 (3)
C(3)	0.6721 (2)	0.3616 (1)	1.0135 (3)
C(4)	0.7450 (2)	0.4436 (1)	0.9638 (3)
C(5)	0.8193 (3)	0.4550 (1)	0.8151 (3)
C(6)	0.8421 (3)	0.3946 (1)	0.6876 (3)
C(7)	0.7974 (3)	0.3047 (1)	0.6683 (3)
C(8)	0.5982 (3)	0.3631 (2)	1.1675 (3)
C(9)	0.5991 (3)	0.4385 (2)	1.2664 (3)
C(10)	0.6729 (3)	0.5181 (2)	1.2191 (4)
C(11)	0.7422 (3)	0.5206 (1)	1.0735 (4)
C(12)	0.6339 (3)	0.1316 (1)	0.4769 (3)
C(13)	0.5819 (3)	0.1609 (1)	0.7561 (3)
C(14)	0.9465 (3)	0.0904 (2)	0.7159 (4)
C(15)	0.8394 (3)	0.8115 (2)	0.6884 (4)
C(16)	0.7767 (3)	0.0892 (2)	0.8438 (4)
C(17)	0.8420 (3)	0.0717 (2)	0.9700 (4)
C(18)	0.9486 (3)	0.1262 (2)	0.8911 (4)

^{a} See Figure 2 for identity of the atoms. The information given in the footnote to Table II also applies to this table.

Table IV. Bond Lengths (Å) and Angles (Deg) for $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_7H_6)Fe(CO)_2]PF_6$ **(1)**^{a}

Fe–C(1)	1.979 (3)	C(6)–C(7)	1.363 (7)
Fe–C(8)	2.107 (4)	C(8)–C(9)	1.395 (6)
Fe–C(9)	2.099 (4)	C(9)–C(10)	1.390 (6)
Fe–C(10)	2.106 (4)	C(10)–C(11)	1.428 (6)
Fe–C(11)	2.097 (4)	C(11)–C(12)	1.399 (6)
Fe–C(12)	2.111 (4)	C(13)–O(1)	1.142 (5)
Fe–C(13)	1.757 (4)	C(14)–O(2)	1.138 (4)
Fe–C(14)	1.770 (3)	P–F(1)	1.580 (4)
C(1)–C(2)	1.393 (5)	P–F(2)	1.592 (4)
C(1)–C(7)	1.406 (5)	P–F(3)	1.555 (5)
C(2)–C(3)	1.395 (6)	P–F(4)	1.511 (4)
C(3)–C(4)	1.410 (8)	P–F(5)	1.549 (5)
C(4)–C(5)	1.358 (9)	P–F(6)	1.542 (5)
C(5)–C(6)	1.387 (7)		

Cp_c–Fe–C(1)^b	120.0 (1)	C(3)–C(4)–C(5)	128.0 (5)
Cp_c–Fe–C(13)^b	124.8 (1)	C(4)–C(5)–C(6)	127.5 (5)
Cp_c–Fe–C(14)^b	123.0 (1)	C(5)–C(6)–C(7)	129.7 (5)
C(1)–Fe–C(13)	92.5 (1)	C(6)–C(7)–C(1)	132.4 (4)
C(1)–Fe–C(14)	93.8 (1)	C(9)–C(8)–C(12)	107.3 (4)
C(13)–Fe–C(14)	94.6 (2)	C(8)–C(9)–C(10)	109.5 (4)
Fe–C(1)–C(2)	118.6 (3)	C(9)–C(10)–C(11)	107.4 (4)
Fe–C(1)–C(7)	118.9 (3)	C(10)–C(11)–C(12)	107.6 (4)
C(2)–C(1)–C(7)	122.3 (3)	C(11)–C(12)–C(8)	108.2 (4)
C(1)–C(2)–C(3)	131.2 (4)	Fe–C(13)–O(1)	178.2 (3)
C(2)–C(3)–C(4)	128.8 (5)	Fe–C(14)–O(2)	176.7 (3)

^{a} Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. C–H distances range from 0.68 (5) to 1.18 (5) Å and average 0.93 Å; C–C–H angles of the C_7 ring range from 108 (5) to 122 (5)° and those of the C_5 ring from 122 (4) to 131 (4)°. The F–P–F angles of $PF_6{}^-$ range from 84.8 (3) to 96.5 (4)°. ^{b} Cp_c represents the coordinates of the centroid of the $\eta^5\text{-}C_5H_5$ ligand.
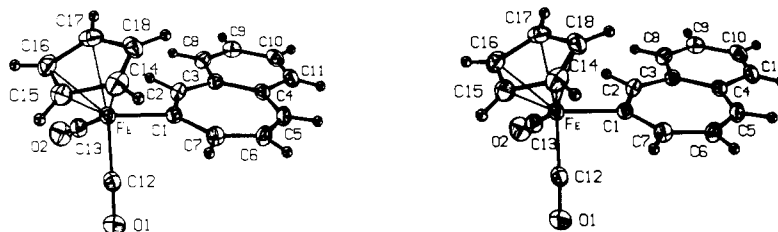
this crystallographic study to support the existence of a twisted allene structure like that of **6**.

Although there is considerable variation in the C–C distances about the rings, the mean values in **1** (1.40 ± 3 Å) and **7** (1.39 ± 2 Å) do not differ significantly and are in agreement with the average C–C distance in the phenyltropylium ion (1.39 ± 8 Å)[35] and with the distance expected for an aromatic C–C bond.[36] Moreover, no C–C bond length in the C_7 ring of either of these complexes differs substantially from this value. The mean values for the internal angles of the seven-membered rings of **1** and **7** are 129 ± 3 and 129 ± 4°, respectively, which are consistent with the idealized angle of 128.6° for a regular heptagon. The largest deviations from the idealized value occur at the bridgehead atoms of **7** (C(3) and C(4)) and at C_{carb} (or C(1)) in both complexes. In **1**, the angles about C_{carb} are 118.6, 118.9, and 122.3°, while in **7** these angles are 117.7, 119.4, and 122.6°, values which are closer to those of an idealized sp²-hybridized atom (120°) than to those of an idealized C_7 ring (116, 116, 128°) and which thereby indicate the carbene character of these CHT ligands. However, aside from these angle deviations, bonding of the CHT ligands with Fe has not had an appreciable effect upon the geometry of the rings. Thus, there is no evidence for the bond localization depicted in the drawings of **1** (i.e., **1a**) and **7** of the Introduction, and hence the aromaticity of these CHT rings has been maintained.

There is, however, structural evidence for dπ(Fe)→pπ-(CHT) back-bonding. Comparison of the Fe–C_{carb} distances of 1.979 (3) and 1.996 (2) Å in the cations of **1** and **7** with the Fe–C(sp²) distances of 2.025 (6) Å in cation {(η^5-C₅H₅)[η^1-(Ph)HC=C(PPh₃)]Fe(CO)₂}⁺ [37] and 1.996 (8) Å

As shown by the figures, both complexes are cationic Fe-carbene species with pseudotetrahedral geometries—if the position of η^5-C₅H₅ ring centroid (Cp_c) is considered as a tetrahedral vertex—which differ principally in the nature of the CHT ligand. In both complexes the C_7 rings are planar; in the benzannelated complex the eleven carbon atoms (C(1) through C(11)) which constitute the CHT ligand are virtually planar, with a dihedral angle of only 1.1° between the planes of the fused C_7 and C_6 rings. Hence, there is no evidence from

(35) Takusagawa, R. A.; Jacobson, R. A.; Trahanovsky, W. S.; Robbins, M. D. *Cryst. Struct. Commun.* **1976**, *5*, 753.
(36) "Handbook of Chemistry and Physics, College Edition", 50th ed.; The Chemical Rubber Publishing Co., Cleveland, OH, 1969.

Figure 2. Stereoscopic view of the $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_{11}H_8)Fe(CO)_2]^+$ ion illustrating the atom numbering scheme. The same conditions as noted for Figure 1 were used in the preparation of this drawing.

Table V. Bond Lengths (Å) and Angles (Deg) for
$[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_{11}H_8)Fe(CO)_2]PF_6$ (7)^a

Fe–C(1)	1.996 (2)	C(9)–C(10)	1.402 (4)
Fe–C(12)	1.769 (2)	C(10)–C(11)	1.346 (4)
Fe–C(13)	1.766 (2)	C(11)–C(4)	1.429 (3)
Fe–C(14)	2.099 (3)	C(12)–O(1)	1.140 (3)
Fe–C(15)	2.101 (2)	C(13)–O(2)	1.138 (3)
Fe–C(16)	2.103 (2)	C(14)–C(15)	1.418 (4)
Fe–C(17)	2.098 (3)	C(14)–C(18)	1.403 (4)
Fe–C(18)	2.106 (3)	C(15)–C(16)	1.387 (4)
C(1)–C(2)	1.395 (3)	C(16)–C(17)	1.412 (4)
C(1)–C(7)	1.407 (3)	C(17)–C(18)	1.402 (4)
C(2)–C(3)	1.416 (3)	P–F(1)	1.541 (3)
C(3)–C(4)	1.435 (3)	P–F(2)	1.581 (2)
C(4)–C(5)	1.400 (3)	P–F(3)	1.585 (2)
C(5)–C(6)	1.373 (3)	P–F(4)	1.567 (2)
C(6)–C(7)	1.388 (3)	P–F(5)	1.576 (2)
C(3)–C(8)	1.429 (3)	P–F(6)	1.592 (2)
C(8)–C(9)	1.358 (3)		

Cp$_c$–Fe–C(1)^b	119.0 (1)	C(4)–C(3)–C(8)	117.5 (2)
Cp$_c$–Fe–C(12)^b	123.9 (1)	C(3)–C(8)–C(9)	121.7 (2)
Cp$_c$–Fe–C(13)^b	124.5 (1)	C(8)–C(9)–C(10)	120.5 (2)
C(1)–Fe–C(12)	93.1 (1)	C(9)–C(10)–C(11)	120.1 (2)
C(1)–Fe–C(13)	93.2 (1)	C(10)–C(11)–C(4)	122.0 (2)
C(12)–Fe–C(13)	95.0 (1)	C(3)–C(4)–C(11)	118.1 (2)
Fe–C(1)–C(2)	119.4 (1)	C(5)–C(4)–C(11)	116.5 (2)
Fe–C(1)–C(7)	117.7 (2)	Fe–C(12)–O(1)	177.2 (2)
C(2)–C(1)–C(7)	122.6 (2)	Fe–C(13)–O(2)	177.5 (2)
C(1)–C(2)–C(3)	134.0 (2)	C(15)–C(14)–C(18)	107.3 (2)
C(2)–C(3)–C(4)	127.0 (2)	C(14)–C(15)–C(16)	108.1 (2)
C(3)–C(4)–C(5)	125.4 (2)	C(15)–C(16)–C(17)	108.6 (2)
C(4)–C(5)–C(6)	130.2 (2)	C(16)–C(17)–C(18)	107.3 (2)
C(5)–C(6)–C(7)	130.1 (2)	C(17)–C(18)–C(14)	108.6 (2)
C(6)–C(7)–C(1)	130.6 (2)		
C(2)–C(3)–C(8)	115.5 (2)		

^{a} Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 2 for identity of the atoms. C–H distances range from 0.90 (2) to 0.98 (3) Å and average 0.94 Å; C–C–H angles of the fused ring system range from 110 (1) to 125 (2)° and those of the C_5 ring from 122 (2) to 130 (2)°. The F–P–F angles of PF_6^- range from 86.8 (1) to 92.6 (2)°. ^{b} Cp$_c$ represents the coordinates of the centroid of the η^5-C_5H_5 ligand.

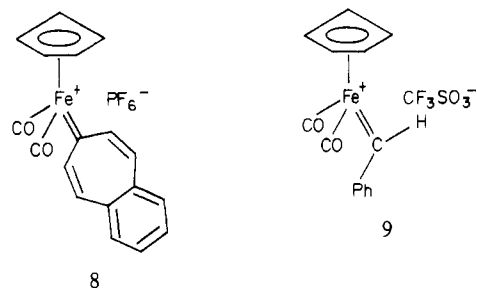in neutral $(\eta^5\text{-}C_5H_5)(H_2COS(O)(Me)C{=}C)Fe(CO)_2$[38] implies some degree of Fe–CHT multiple bonding, which is greater in parent compound **1** than benzannelated compound **7**. This is expected since **7** probably has a small LUMO coefficient (as does the uncomplexed carbocation[39]) at C_{carb}.

The dihedral angle between the plane of the CHT ligand and the plane of the C_{carb}, Fe, and Cp$_c$ positions is 87.6° in **1** and 89.5° in **7**; hence, the acceptor $p\pi$ orbital of the CHT rings lies virtually in the plane of the C_{carb}, Fe, and Cp$_c$ positions, suitably oriented to back-bond with the donor 1a′ d-hybrid orbital, although not with the more favorable a″ orbital.[40] Overlap with the latter is believed to cause CH_2

in $[Cp(Ph_2PCH_2CH_2PPh_2)Fe{=}CH_2]^+$[21] to prefer an orientation that is essentially 90° from that observed for the CHT ligands. However, in the case of CHT, the energy gained by back-donation with the higher energy a′ orbital is apparently not sufficient to offset steric repulsion between the CHT and the Cp ligands and the net result is the sterically favorable conformation.

Unfortunately, efforts to examine the interaction (i.e., the disposition) of the phenyl ring—an aromatic ring without an empty p orbital at the carbene carbon atom—with the iron atom in $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_6H_5)Fe(CO)_2$ have been thwarted by the inability to grow useful single crystals.

Spectral Data. Let us now consider the NMR (^{1}H and ^{13}C) and infrared data obtained for the three Fe–CHT cations of **1**, **7**, and **8**—the latter being the PF_6^- salt of the symmetrically substituted 4,5-benzo CHT complex[41]—in an attempt to appraise the $d\pi{\to}p\pi$ back-bonding in these complexes from a spectroscopic viewpoint. (Efforts to obtain satisfactory single crystals of **8** have so far been unsuccessful.) From simple
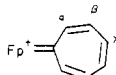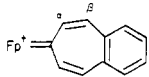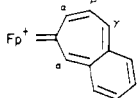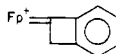

theoretical considerations it is predicted that the stability of transition-metal complexes of aromatic carbenes should be less dependent upon metal to C_{carb} back-bonding than complexes of simpler carbenes. In molecular orbital terms, the aromaticity of the CHT rings raises the energy of the LUMO, while in resonance terms, contributors including M=C forms as in **1a** and **2a** destroy the aromaticity of the complexed rings and hence are less important than in structures such as **9**,[20] for example. This is expected to be particularly prominent in **7**, which probably has a small LUMO coefficient at C_{carb} as noted above,[39] and is consistent with the longer Fe–C_{carb} distance in **7**.

Since metal–carbene back-bonding should reduce the positive charge of the CHT rings, the ^{1}H NMR resonances of the remote ring hydrogen atoms would be expected to shift the higher fields upon complexation. This should be most pronounced in **8**, and indeed as shown in Table VI, the resonances

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Table VI. Spectroscopic Data for Some Iron–Carbene Complexes

complex[a]	ν_{str}(CO), cm^{-1}	^{13}C NMR, ppm C_{carb}[b]	H_α	H_β	H_γ	ref
Fp⁺ cycloheptatrienylidene	2045, 1996	242.3	10.0	8.1	8.48	21
Fp⁺ benzocycloheptatrienylidene	2045, 2000	265.9	9.58	8.26		this work, 27
Fp⁺ structure	2037, 1992	201.0	9.92, 10.4	8.5	9.23	this work, 27
Fp⁺=CH(C₆H₅)Cp(dppe)Fe⁺=CH₂[c] (9)		342.4 / 317.5				20 / 21
Fp⁺ structure	2065, 2020					17
Fp⁺ structure (with O)	2073, 2029					40
Fp–Cl	2050, 2002					41
Fp– structure		145.4				42
tropylium structure		160.6	9.55	9.55		43, 44
benzotropylium structure			9.1	9.95		45

[a] Fp represents the $(C_5H_5)Fe(CO)_2$ moiety. [b] C_{carb} represents the carbon atom bonded directly to Fe. [c] dppe represents the $Ph_2PCH_2CH_2PPh_2$ ligand.

Table VII. Structural Parameters for Some Cationic Iron Carbonyl Complexes[a]

complex	Fe–CO, Å	C–O, Å	ν(CO), cm^{-1}	ref
$[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$	1.816 ± 13	1.112 ± 14	2120, 2068	53, 54
$[(\eta^5\text{-}C_5H_5)(PPh_3)Fe(CO)_2]^+$	1.771 ± 4	1.139 ± 1	2070, 2025	54, 55
$[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_{11}H_8)Fe(CO)_2]^+$ (7)	1.767 ± 2	1.139 ± 1	2037, 1992	this work, 28
$[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_7H_6)Fe(CO)_2]^+$ (1)	1.764 ± 6	1.140 ± 2	2045, 1996	this work, 22
$[(\eta^5\text{-}C_5H_5)(dppe)Fe(CO)]^+$	1.744 (5)	1.139 (7)	1980	55, 56

[a] Mean bond lengths are given for the first four complexes. Numbers in parentheses are the standard errors associated with the least significant digit. Numbers indicated as "±" represent the range of observed values in that determination.

of the H_β atoms appear upfield from those of the benzotropylium ion by 1.69 ppm. Because back-bonding may be less important in 1, it is reasonable that the upfield chemical shifts of its H_β and H_γ atoms, compared to those of the uncomplexed tropylium ion, are smaller (by 1.44 and 1.07 ppm, respectively) than those of 8. Furthermore, the absorptions of the H_β and H_γ atoms of 7, which appear only 0.6 and 0.72 ppm upfield from those of the corresponding H atoms of the benzotropylium ion, indicate little π back-bonding in this complex, which is also consistent with its longer Fe–C_{carb} bond.

An interesting property of carbene complexes that is believed to be related to, among other things, the dπ–pπ bonding between the metal and the carbene[48] is the downfield shift in the ^{13}C NMR spectra. For example, these resonances are observed at 342.4, 350.9, and 358.3 ppm for the electrophilic C_{carb} atoms of 9,[20] PhC(OMe)Cr(CO)₅,[49] and (Ph)₂CW(CO)₅,[1] respec-

tively, and 236–299 ppm for the nucleophilic C_{carb} atoms of a series of Ta=CHR complexes.[50] The resonances of 1, 7, and 8 appear in this same region (201–266 ppm). Although these shifts are substantially upfield from the resonances of the strongly electrophilic species (the value of 201.0 ppm for 7 is apparently a high-field extreme), the carbene carbon, at least of 1, is significantly influenced by the metal as evidenced by a downfield shift of 80 ppm from that of the tropylium ion and approximately 100 ppm downfield from its (i.e., 1) remote carbon atoms.[22] The ^{13}C NMR spectrum of the benzotropylium ion which corresponds to the carbene ligands of 7 and 8 is not available for comparisons.[51] It is noteworthy that the resonances of the remote carbon atoms of 1 are 12 and 22 ppm upfield from those of the tropylium ion. Hence, it appears that, as indicated by resonance structure 1a, some positive charge does reside on Fe, and that the positive charge

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of the C_7H_6 ring (as in **1b**) has been reduced by electron donation from Fe.

It is well-established that the values of the carbonyl IR stretching frequencies for related complexes are a reliable measure of changes in metal–carbonyl back-bonding. The absorptions of **1**, **7**, and **8** occur at slightly lower values than those of other reported carbonyl-containing carbene complexes[52] (see Table VI), implying that in these aromatic carbene species more π-electron density is available at Fe for back-bonding to the CO ligands; i.e., CHT ligands are poorer acceptors of electron density than other carbene ligands. Table VII lists selected bond lengths and CO stretching frequencies for cationic complexes of the type $[(\eta^5\text{-}C_5H_5)(L)_nFe(CO)_{3-n}]^+$, in which n = 0–2. Comparison of the Fe–C(carbonyl) bond lengths and the CO absorptions suggests that the CHT ligand(s) is a better σ donor (similar to PPh_3?) than π acceptor. However, as shown by the IR data of Table VI, the virtual equivalence of the CO stretching frequencies of **1**, **7**, and **8** precludes an ordering of the relative back-bonding capabilities of these CHT complexes from these IR data alone.

It appears, therefore, that CHT carbene ligands are principally donor ligands, which upon complexation with a transition-metal atom depend not upon the back-donation of

electron density from the metal for stability but rather primarily upon the aromaticity of the CHT ring. Nonetheless, from both crystallographic and spectroscopic data, there is sufficient evidence to indicate that $d\pi\rightarrow p\pi$ back-bonding is not altogether absent and, in fact, may be significant in **1** and perhaps in **8** but is far less so in **7**. Finally, comparison of the chemical and thermal reactivity of $(C_7H_6)W(CO)_5$ (**2**) with the closely related complexes (2,3-diphenylpropenylidene)-pentacarbonyltungsten and (2,3-di-*tert*-butylcyclopropenylidene)pentacarbonyltungsten[57] has shown that **2** is more reactive. Since spectral data suggest more W→CHT back-bonding in **2** than in the other two $W(CO)_5$ complexes, this greater reactivity may be a consequence of easier loss of CO from **2** in reactions in which CO loss is important.

Registry No. 1, 67758-08-1; **7**, 73601-68-0; **8**, 73601-71-5.

Supplementary Material Available: Tabulations of observed and calculated structure amplitudes, anisotropic thermal parameters, and hydrogen positional and isotropic thermal parameters (54 pages). Ordering information is given on any current masthead page.

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Structural Characterization of 6:4′,5′-[1-(η-C₅H₅)Co-2,3-(CH₃)₂C₂B₄H₃][2′,3′-(CH₃)₂C₂B₄H₅]: A Coupled-Cage Cobaltacarborane Complex Containing a Three-Center Boron Linkage

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The molecular structure of 6:4′,5′-[1-(η-C₅H₅)Co-2,3-(CH₃)₂C₂B₄H₃][2′,3′-(CH₃)₂C₂B₄H₅] has been determined from single-crystal X-ray diffraction data. The compound was shown to be a coupled-cage cobaltacarborane consisting of a [(CH₃)₂C₂B₄H₃]Co(η-C₅H₅) sandwich complex linked to a (CH₃)₂C₂B₄H₅ carborane fragment by means of a three-center boron–boron–boron bond. Crystal data: space group $P2_1/n$, Z = 4, a = 14.092 (4) Å, b = 13.270 (1) Å, c = 9.988 (2) Å, β = 103.06 (2)°, V = 1819 (2) Å³. The structure was refined by full-matrix least-squares methods to a final R of 0.042 and R_w of 0.048 for the 2282 reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We have previously reported[2] that the mercury-sensitized photolysis of various small boranes and carboranes leads in certain cases to the corresponding coupled-cage borane or carborane in high yields. Furthermore, we also demonstrated[3] the insertion of metals into these multicage systems to produce a range of novel linked-cage metal complexes. In particular, the reaction of [2,3-(CH₃)₂C₂B₄H₅]₂ with sodium hydride followed by reaction with sodium cyclopentadienide and cobaltous chloride was found to yield a variety of such complexes, including compounds that contain metals in either or both of the cages. The spectroscopic data obtained for the major products of this reaction suggested that the two cages in each

compound were linked by a single boron–boron bond. We report here, however, that a structural investigation of one of these compounds[4] has revealed that it does not contain such a simple boron–boron cage linkage, but instead the two cages are joined by a single boron–boron–boron three-center bond. Full details of this structural determination are reported.

Experimental Section

Several crystals of the compound were grown over an 18-h period by evaporation of a dilute heptane solution. A very thin rectangular-shaped crystal, 0.19 × 0.58 × 0.029 mm, was selected for data collection, mounted on a glass fiber, and then transferred to the diffractometer. The Enraf-Nonius program SEARCH was used to obtain 25 reflections, which were then used in the program INDEX to obtain an orientation matrix for data collection. This orientation matrix was improved by the substitution of new reflections, and refined cell dimensions and their standard deviations were obtained from the

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