Table I. SCF Total Energies in Hartrees for the C-Bridged 2-Norbornyl Cation and Relative Energies in Hartrees (kcal mol^{-1}) for the Classical and H-Bridged Structures[a]

basis	total energy C bridged	relative energy	
		classical	H bridged
DZ	−271.107 15	−0.001 57 (−1.0)	+0.026 74 (+16.8)
DZD	−271.231 80	−0.000 19 (−0.1)	+0.018 76 (+11.8)
DZDP	−271.252 80	−0.000 09 (−0.05)	+0.016 12 (+10.1)
TZ	−271.130 59	−0.000 78 (−0.5)	+0.023 90 (+15.0)
TZD	−271.251 26	+0.000 59 (+0.4)	+0.019 80 (+12.4)
TZDD	−271.256 58	+0.000 69 (+0.4)	
TZDP	−271.273 97	+0.000 78 (+0.5)	+0.018 06 (+11.3)

[a] All calculations were performed at the optimized 4-21G SCF geometries.

a 4-31G basis.[6] The 4-31G structures are in good agreement with the 4-21G structures. Both bases give partially bridged classical structures; the difference between the 4-31G classical and C-bridged structures is even less than was observed for the corresponding 4-21G structures.[1] On the 4-31G potential surface, the classical structure is a minimum, while the C- and H-bridged structures are saddle points with single imaginary frequencies of 136 and 798 cm^{-1}, respectively. Structure optimization using 6-31G* SCF wave functions yielded bridged structures in good agreement with the corresponding 4-31G structures. However, 6-31G* calculations starting from the 4-31G classical structure converged to the C-bridged structure. An extensive search using SCF wave functions and STO-3G, 4-31G, and 6-31G* basis sets revealed no additional minima on the potential surface.

Table I documents a systematic approach to the HF-limit energy differences between the 4-21G-optimized 2-norbornyl cation structures. Every improvement of the basis beyond double ζ[7] (DZ) stabilizes the bridged structures relative to the classical. The improvements include: extension to triple ζ (TZ),[8] addition of one set of six Cartesian *d* functions with exponent 0.75 on each carbon (DZD, TZD), addition of two sets of *d* functions with exponents 1.4 and 0.6 on each carbon (TZDD), and addition of one set of *p* functions with exponent 0.9 on each hydrogen (DZDP, TZDP). For the TZD, TZDD, and TZDP bases, the C-bridged structure is more stable than the classical. Therefore, in the HF limit, the 4-21G C-bridged structure should be lower in energy than the 4-21G classical structure. Additional TZD and TZDD SCF calculations along an approximate reaction path between the 4-21G classical and C-bridged structures indicated a potential curve with a single minimum at the C-bridged structure. Thus, the true HF potential surface most probably has a C-bridged minimum near the corresponding 4-21G structure and no other stationary points near the 4-21G classical structure. The 4-21G classical ion then must be an artifact of the limited basis set. The results described in this and the preceding paragraphs strongly suggest that the true HF potential surface has no minimum corresponding to a classical structure.

Our CI calculations used a DZD′ basis, obtained from DZD by deleting (1) the 3*s* component of each set of Cartesian *d* functions and (2) all *d* functions on carbon 4, the only one unconnected by a σ bond to any one of the three bridged carbons in the C-bridged structure. These calculations used the ALCHEMY II symbolic matrix direct CI program[9] and included all single and double excitations from the SCF configuration, excluding seven core and seven core-complement orbitals, giving 1 432 278, 717 346, and 718 006 configurations for the classical, C-, and H-bridged structures, respectively. The CI energies in Table II show that electron correlation stabilizes the bridged structures relative to the classical. Our best calculations give stabilization energies of 2.1 and 5.4 kcal mol^{-1} for the C- and H-bridged structures, respectively. These values are probably lower bounds to the true stabilization energies, because DZD SDQ calculations generally underestimate correlation effects. Our CI results are in qualitative agreement with the MP2 calculation by Krishnan et al.[10]

Table II. SCF and CI Total Energies in Hartrees for the C-Bridged 2-Norbornyl Cation and Relative Energies in Hartrees (kcal mol^{-1}) for the Classical and H-Bridged Structures[a]

calculation	total energy C bridged	relative energy	
		classical	H bridged
SCF(DZ)	−271.107 15	−0.001 57 (−1.0)	+0.026 74 (+16.8)
SDCI(DZ)	−271.638 56	−0.000 16 (−0.1)	+0.026 12 (+16.4)
SDQ(DZ)	−271.727 26	+0.000 86 (+0.5)	+0.026 40 (+16.6)
SCF(DZD′)	−271.212 27	−0.000 20 (−0.1)	+0.018 76 (+11.8)
SDCI(DZD′)	−271.927 65	+0.001 34 (+0.8)	+0.015 17 (+9.5)
SDQ(DZD′)	−272.055 97	+0.003 26 (+2.0)	+0.013 51 (+8.5)

[a] All calculations were performed at the optimized 4-21G SCF geometries.

Some conclusions about the shape of the true potential surface of the 2-norbornyl cation follow from our results. Since correlation favors a C-bridged structure that is a minimum on the HF surface, it should also be a minimum on the true surface. Our failure to find a minimum near the 4-21G classical structure on the 6-31G* and TZD SCF surfaces, our failure to find additional classical SCF structures, and the relative magnitudes of the correlation energy contributions all point to a true potential surface with no minimum–energy structure corresponding to the classical ion.

Acknowledgment. We thank Prof. H. C. Brown for inspiring this study and Dr. G. Castro for support and encouragement.

Registry No. 2-Norbornyl cation, 24321-81-1.

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Stabilization of an α-Diazo Thioketone (a New Class of Compound) by a Unique Linear Triiron Cluster[1a]

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Whereas α-diazo ketones are well-established compounds with some synthetic utility,[2] the corresponding α-diazo thio(seleno)ketones are unknown. Isomeric 1,2,3-thia(selena)diazoles do exist and also have a synthetic utility as intermediates in the synthesis of acetylenes and heterocyclic compounds.[3,4] Oxadiazoles are not known, while 1,2,3-triazoles and their isomeric α-diazo imines exist in thermal equilibrium.[5,6]

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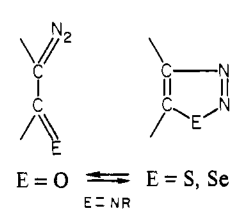


During studies on the interactions of π-heterocycles with transition-metal complexes, we have observed a wide range of reactivity for thia(selena)diazoles. Thus, from reactions with $Fe_2(CO)_9$ we have been able to isolate thio(seleno)ketocarbene,[7-9] selenoketoketene,[10,11] thioketoimine,[12] and thiolatohydrazonato[13] complexes of diiron hexacarbonyl. This pattern of chemistry is reminiscent of that reported by Mills,[14] Herrmann,[15-17] and Curtis[18] from reactions of metal complexes with an assortment of diazo compounds, including α-diazo ketones. Thus, it seems reasonable to postulate that the various thia and selena complexes we have observed result from a ring opening of the diazoles to form an α-diazo thio(seleno)ketone, as illustrated in Scheme I. Such ring opening could occur subsequent to binding of the intact ligand to the metal center via the S(Se) or N atoms.

Intact diazole complexes of the group 6 metal carbonyls have been reported;[10,19,20] however, in none of the reactions leading to the complexes noted above have we observed any evidence for the presence of α-diazo thio(seleno)ketone complexes.

To remedy this problem we have used a diazole modified by substitution that incorporates the carbon atoms into an aromatic ring. This offers the possibility of stabilizing the thio(seleno)ketone by retarding the loss of N_2 since formation of the corresponding carbene upon an aromatic ring is not favored. Thus, we have studied the reactions of 1,2,3-benzothiadiazole[21] with various metal complexes and now report the results of such a study with $Fe_2(CO)_9$.

In a typical reaction, 1.0 g of 1,2,3-benzothiadiazole was stirred with 6.0 g of $Fe_2(CO)_9$ in 100 mL of dry oxygen-free hexane at room temperature. After 24 h the reaction was stopped and the solvent removed under vacuum. The resulting material was placed upon an alumina column and eluted with a hexane/methylene chloride mixture (1:1). A dark green band was collected and the product recrystallized from the same solvent mixture, $C_{19}H_8Fe_3N_4O_7S_2$: M_r 635.97; found, 636 by FD–MS; %C 35.88, %H 1.27, %N 8.81; found, 35.76, 1.17, 8.76; IR (CO) 2074, 2054, 2009 cm^{-1} (analysis and FD–MS provided by H. Wandinger and K. K. Mayer of the University Regensburg, Bavaria, Germany).

The structure of the resulting complex was determined by a single-crystal X-ray analysis and is illustrated in Figure 1. The important features of the structure are as follows: (1) Ring opening of the diazole has been effected without loss or gain of any atoms, cleavage occurring between the S and N atoms. (2) The ring-opened fragment results in both the S and N atoms being available for complexation. Each heteroatom bridges two Fe atoms, but not the same pair. The molecule possesses a C_2 symmetry, with two molecules of the α-diazo thioketone doubly bridging the three Fe atoms. (3) The three Fe atoms form a linear cluster with equal Fe–Fe bond lengths. The two equivalent outer atoms are tricarbonyl units, complexed by a sulfur and nitrogen atom. The central Fe atom is a monocarbonyl unit complexed by two S and two N atoms.

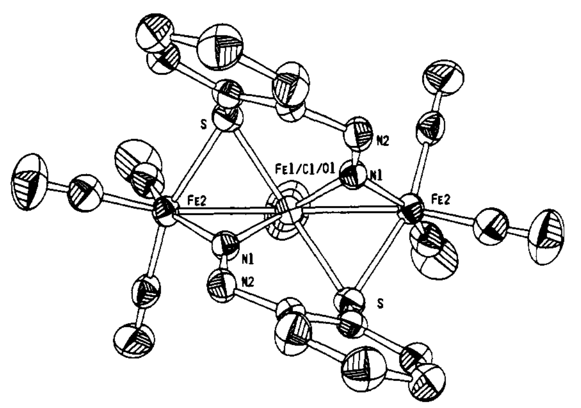
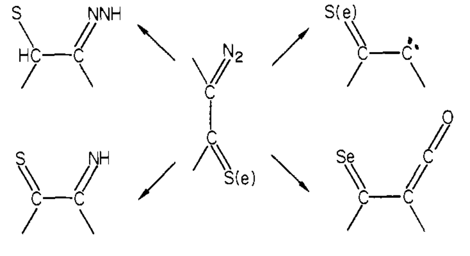


Figure 1. Crystal structure of $C_{19}H_8Fe_3N_4O_7S_2$. Space group $C2/c$ with a = 14.676 (2) Å, b = 10.253 (2) Å, c = 15.954 (3) Å, and Z = 4. Data were collected on a Syntex $P2_1$ diffractometer using θ–2θ scans. Refinement using SHELX-76 gave a final R = 0.029. Selected bond lengths (Å): Fe(1)–Fe(2) = 2.494 (0); C–N = 1.438 (3); N–N = 1.238 (3); Fe(1)–N = 1.879 (1); Fe(2)–N = 1.847 (2); Fe(1)–S = 2.301 (1); Fe(2)–S = 2.258 (1). Selected bond angles (deg): Fe(2)Fe(1)Fe(2) = 178.7 (1); CNN = 118.8 (2).

Scheme I



The complex thus represents the first example of a stabilized α-diazo thioketone *and* the first example of a linear triiron cluster.

The bond lengths and angles of the CN_2/M portion of the structure are similar to other diazo complexes as typified by the structure of diphenyldiazomethane complex of molybdenum, $Cp_2Mo_2(CO)_4(N_2CPh_2)$.[22] Thus, the C–N–N angle of 118.8° compares to the published value of 122.4, and the C–N and N–N bond lengths of 1.438 and 1.238 Å, respectively, compare to 1.279 and 1.352 Å. From these comparisons the shorter bond of the N–N unit of the α-diazo thioketone suggests a greater degree of multiple bonding, closer to that reported for a quinone diazide structure.[23] The coordinating N atom is somewhat asymmetrically bound to the two Fe atoms, a situation identical with that in the molybdenum complex. The sulfur-bridging part of the structure is very similar to the many examples of S-bridging diiron hexacarbonyl structures.[24]

The geometry around the three iron atoms is striking. The outer $Fe(CO)_3$ iron atoms have strongly distorted octahedral geometry while the central atom is heptacoordinate, a distorted capped trigonal prism. The Fe–Fe–Fe bond angle is 178.7° and the Fe–Fe

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bond lengths are equal at 2.494 Å. Since this is the first linear triiron complex no comparisons are possible; however, it is of interest that a predicted bond length of 2.708 Å has been published for a linear triiron cluster, albeit without bridging ligands.[24] The two almost planar α-diazo thioketone units complex on the same side of the linear triiron backbone, with a dihedral angle of 80°, forming a delightful butterfly configuration.

We are currently investigating the synthetic utility of the complexes discussed above, in particular the chemical properties of the various organic fragments liberated via decomplexation reactions.

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Supplementary Material Available: Observed and calculated structure factors for the iron carbonyl sulfur complex (8 pages). Ordering information is given on any current masthead page.

Methyl Effects on the Basicities of Cyclopentadienide and Indenide Ions and on the Chemistry of Their Transition-Metal Complexes

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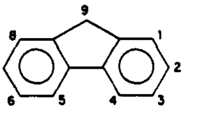
The replacement of cyclopentadiene ligands in transition-metal complexes by pentamethylcyclopentadiene ligands often leads to striking changes in their chemistry. In this paper we show that this is associated with a large increase in basicity of the pentamethylcyclopentadienide ion.

1,3-Cyclopentadiene (C_5H_5H) is the most acidic of the monocyclic hydrocarbons. Its conjugate base, cyclopentadienide ion ($C_5H_5^-$), is aromatic and forms strong multicentered bonds with most transition metals.[1] The cyclopentadienyl moieties in fluorene (**1**) and indene (**2**) exhibit similar properties, but fusion of benzene rings onto the cyclopentadiene C=C bonds causes a progressive decrease in acidity and modifies the ability of the conjugate bases to act as ligands.[2] Replacement of C_5H_5 ligands by $C_5(CH_3)_5$ ligands in metal complexes has been shown to give rise to compounds with significantly different chemistry.[1,3] The changes in properties of these complexes are believed to be due to increased electron density and donor strength of the permethylated ligand ring[4] and perhaps, in certain instances, to steric protection of the metal by the methyl groups.[1,3,5,6] For example, the shifts to lower frequencies of the carbonyl stretches of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ from 2051 and 1987 cm^{-1} to 2020 and 1965 cm^{-1} for $Rh[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ indicate that Rh is more electron rich in the pentamethylcyclopentadienyl compound due to the increased electron-donor strength of the permethylated ligand.[6] A larger steric effect for the $C_5(CH_3)_5$ ligand is suggested by examples such as the formation of $U[\eta^5\text{-}C_5(CH_3)_5][N(C_2H_5)_2]_3$ from the reaction of $C_5(CH_3)_5H$ (**3**) with $U[N(C_2H_5)_4]$ under conditions where $U(\eta^5\text{-}C_5H_5)_2[N(C_2H_5)_2]_2$ was formed from C_5H_5H and $U[N(C_2H_5)_4]$.[5] We now wish to report results of a study of the acidities of some methyl-substituted cyclopentadienes, indenes, and fluorenes, which provide new insights into methyl effects in these hydrocarbons and their conjugate bases (Table I).



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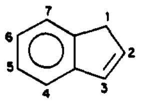

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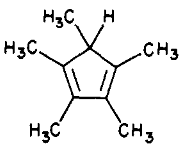

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Table I. Comparison of the Effect of Methyl Substitution on the Equilibrium Acidities of Cyclopentadiene, Indene, and Fluorene in Me_2SO Solution at 25 °C

hydrocarbon	pK_a[a]	ΔpK_a[g]
1,3-cyclopentadiene (C_5H_5H)	18.0[b]	(0.0)
1,2,3,4,5-pentamethylcyclopentadiene ($C_5(CH_3)_5H$)	26.1	7.8
indene	20.1[c]	(0.0)
2-methylindene	21.8	1.7[h]
3-methylindene	22.5	2.4[h]
1,2,3,4,5,6,7-heptamethylindene ($C_9(CH_3)_7H$)	27.4	7.0
fluorene	22.6[d]	(0.0)
9-methylfluorene	22.3[d]	−0.6
2-methylfluorene	23.1[e]	0.5
3-methylfluorene	23.4[f]	0.8

[a] pK_a values were determined by the method previously described.[7] [b] Reference 8. [c] Reference 9. [d] Reference 7. [e] Reference 10. [f] Branca, J. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1977. [g] Statistically corrected for the number of protons at the acidic site. [h] Measurements in Me_2SO/H_2O give ΔpK_a values for 2- and 3-methylindenes of 1.0 and 1.3, respectively.[11]

Rapid perusal of Table I shows that methyl substitution at the 9-position of fluorene (**1**) is uniquely acid strengthening. This effect is believed to be caused by hyperconjugative stabilization in the delocalized anion accompanying the change in hybridization at the acidic site from sp^3 to sp^2 upon deprotonation.[10] A similar acid-strengthening hyperconjugative effect is expected in the indenide and cyclopentadienide ions if a methyl substituent is present at the acidic site in their conjugate acids. Further examination of Table I shows that 2-methyl- and 3-methylindene are 1.7 and 2.4 pK_a units less acidic than indene, respectively, and that 2-methyl- and 3-methylfluorene are 0.5 and 0.8 pK_a units less acidic than fluorene, respectively. These acid-weakening effects, which result from methyl substitution for hydrogen at an sp^2 carbon atom, are believed to be due in part to a greater hyperconjugative methyl stabilizing effect in the undissociated acid than in its conjugate base and in part to steric inhibition of solvation in the ion.[10] Variable Electronegativity SCF calculations predict a larger concentration of charge at the 3- than at the 2-position in both the indenide and fluorenide ions.[12] Therefore, the change in solvation due to the steric effect of methyl should be of greater magnitude and result in a greater acid-weakening effect when methyl is substituted for hydrogen at the 3-position of fluorene (**1**) and indene (**2**), rather than at the 2 position, as observed.

The acid-weakening effect of the five methyl groups in 1,2,3,4,5-pentamethylcyclopentadiene is 7.8 pK_a units (Table I). For each of the four methyl groups attached to the C=C bonds in the diene, the effect amounts to about 2 pK_a units per methyl group. (The methyl group attached to the acidic site is expected to have an *acid-strengthening* effect of about 0.6 pK_a unit by analogy with that found in 9-methylfluorene.) The seven methyl

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