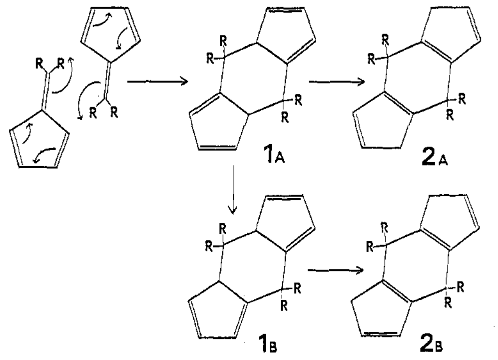
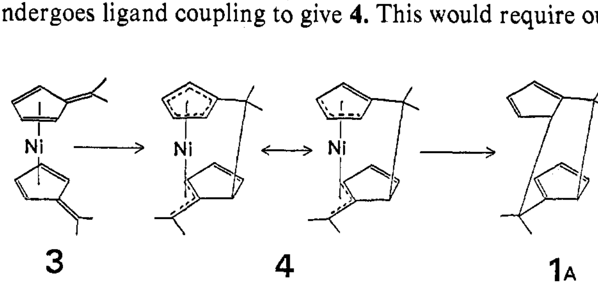
Nickel Atom Promoted Dimerization of Dimethylfulvene. A Formal [6 + 6] Cycloaddition

Sir:

The reactions of fulvenes with low-valent transition-metal complexes have produced a veritable organometallica exotica.[1] Although 6,6-dialkylfulvenes are known to polymerize,[2] simple dimers do not appear to have been isolated. In an attempt to produce an alkyl-bridged nickelocene, 6,6-dimethylfulvene and nickel vapor were codeposited at −196 °C in a conventional metal atom reactor.[3] In contrast to the analogous reaction with iron vapor which produced a [2]ferrocenophane,[4] the only product isolated upon sublimation of the residue was identified by elemental analysis and mass spectrometry as a dimer of dimethylfulvene. Typically, 250 mg of Ni vapor yields ~130 mg of dimer. This product is not formed via thermolysis or photolysis in the metal vapor reaction,[5] nor do iron, chromium, or palladium vapors bring about this dimerization. The conventional spectroscopic techniques[6] did not permit an unequivocal assignment of the structure but it was identified crystallographically[7] as a mixture[8] of 4,4,8,8-tetramethyl-1,4,5,8-tetrahydro-*s*-indacene (**2a**) and the 1,4,7,8 isomer (**2b**) (Figure 1, Table I). The molecule is formally derivable by a thermally forbidden [6 + 6] cycloaddition process followed by [1,5]-hydrogen shifts.



Nevertheless, although the photochemical [6 + 6] cycloaddition has precedent,[9] we suggest that this particular process is a stepwise dimerization on a nickel atom template. A reasonable initial product is the 18-electron tetrahedral complex **3** which, unlike bis(cyclopentadiene)nickel,[10] cannot form a stable complex simply by hydrogen transfer,[11] and so undergoes ligand coupling to give **4**. This would require out-of-plane bending of the exocyclic carbon of the fulvene toward the metal, but this phenomenon has been observed previously.[12] Subsequent coupling of two π-allyl moieties parallels the now classic work of Wilke's group;[13] the requisite hydrogen shifts are well documented in nickel vapor reactions.[14] Presumably, the tendency to form 20-electron nickelocene systems is low and the dimerization process is thermodynamically favored.



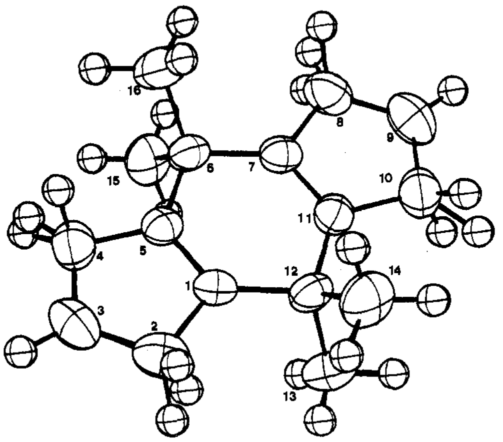


Figure 1. ORTEP view of the molecule showing the numbering scheme used in the structure determination. Temperature ellipsoids are drawn at the 50% probability level. All hydrogen atoms, including those at the disordered positions, are drawn with uniform isotropic thermal parameters.

Table I. Bond Distances (Ångstroms) and Bond Angles (Degrees) with Standard Deviations in Parentheses

bond lengths, (Å)		bond angles, deg	
C(1)-C(2)	1.469 (4)	C(2)-C(1)-C(5)	109.0 (2)
C(1)-C(5)	1.341 (3)	C(2)-C(1)-C(12)	125.8 (2)
C(1)-C(12)	1.490 (3)	C(5)-C(1)-C(12)	125.3 (2)
C(2)-C(3)	1.395 (5)	C(1)-C(2)-C(3)	107.0 (3)
C(3)-C(4)	1.403 (5)	C(2)-C(3)-C(4)	109.6 (3)
C(4)-C(5)	1.488 (5)	C(3)-C(4)-C(5)	106.2 (3)
C(5)-C(6)	1.496 (4)	C(4)-C(5)-C(1)	108.3 (3)
C(6)-C(7)	1.496 (3)	C(4)-C(5)-C(6)	125.4 (2)
C(6)-C(15)	1.539 (4)	C(1)-C(5)-C(6)	126.3 (2)
C(6)-C(16)	1.541 (4)	C(5)-C(6)-C(7)	107.9 (2)
C(7)-C(8)	1.481 (5)	C(5)-C(6)-C(15)	109.8 (2)
C(7)-C(11)	1.338 (3)	C(5)-C(6)-C(16)	109.9 (3)
C(8)-C(9)	1.394 (5)	C(7)-C(6)-C(15)	110.2 (3)
C(9)-C(10)	1.403 (5)	C(7)-C(6)-C(16)	110.2 (2)
C(10)-C(11)	1.475 (4)	C(15)-C(6)-C(16)	108.9 (3)
C(11)-C(12)	1.496 (4)	C(6)-C(7)-C(8)	125.5 (2)
C(12)-C(13)	1.544 (4)	C(6)-C(7)-C(11)	126.2 (2)
C(12)-C(14)	1.541 (4)	C(8)-C(7)-C(11)	108.3 (2)
		C(7)-C(8)-C(9)	107.0 (3)
		C(8)-C(9)-C(10)	109.2 (3)
		C(9)-C(10)-C(11)	106.7 (3)
		C(10)-C(11)-C(7)	108.9 (2)
		C(10)-C(11)-C(12)	125.8 (2)
		C(7)-C(11)-C(12)	125.3 (2)
		C(11)-C(12)-C(1)	108.9 (2)
		C(11)-C(12)-C(13)	109.4 (2)
		C(11)-C(12)-C(14)	110.3 (2)
		C(1)-C(12)-C(13)	109.6 (2)
		C(1)-C(12)-C(14)	110.4 (2)
		C(13)-C(12)-C(14)	108.2 (3)

Interestingly, the product, which is a head-to-tail dimer (in some ways analogous to the nickel promoted isoprene dimer so crucial to Billups' [15] elegant grandisol synthesis), lends support to the ideas of Ehntholt and Kerber[1] with respect to the series of molecules of the type (fulvene)$_2$Fe$_2$(CO)$_x$ prepared in the pioneering investigations of Weiss and Hubel.[16] These latter molecules are being reinvestigated in the light of the present results.

Acknowledgment. We thank the National Research Council of Canada for financial support.

References and Notes

(1) R. C. Kerber and D. J. Ehntholt, *Synthesis*, 449 (1970).

(2) P. Yates, *Adv. Alicycl. Chem.*, **2**, 59 (1968).

(3) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972); K. J. Klabunde, *Acc. Chem. Res.*, **8**, 383 (1975).

(4) T.-S. Tan, J. L. Fletcher, and M. J. McGlinchey, *J. Chem. Soc., Chem. Commun.*, 771 (1975).

(5) This possibility was eliminated by blank reactions using normal cocondensation conditions but with no metal in the crucible.

(6) IR showed strong or medium bands at 3093, 3071, 3060, 3040, 2967 (s), 2951 (s), 2890 (s), 2855, 1647, 1537 (s), 1465, and 1208 cm^{-1}. ^{1}H NMR (in CD$_2$Cl$_2$) showed a doublet (5.43 Hz) of triplets (2.50 Hz) at δ 6.51 (2 H),

0002-7863/79/1501-2203$01.00/0

a doublet (5.43 Hz) of triplets (1.45 Hz) at δ 6.32 (2 H), a doublet (2.50 Hz) of doublets (1.45 Hz) at δ 3.01 (4 H), and singlets at δ 1.32 (3 H), 1.29 (6 H), and 1.27 (3 H). ^{13}C NMR (proton coupled) showed a singlet at δ 145.1 (>C=), a doublet at δ 131.3 (–CH=), a triplet at δ 38.9 (CH_2), a singlet at 34.8 (>CMe_2), and quartets at δ 31.5, 30.1 (double intensity), and 28.7 (CH_3's). Major mass spectral peaks occurred at *m/e* 212, 197, 182, 167, 152, 141, 139, 128, 115, and 89. All of these data are now readily rationalizable in the light of the X-ray result. The Raman spectra of the product were essentially identical in CH_2Cl_2 solution and in the solid state.

(7) Clear, colorless needle shaped crystals, mp 79–80.5 °C, were obtained by vacuum sublimation and were sealed in Lindemann capillaries. Preliminary X-ray data established the space group as $P2_12_12_1$ (No. 19) with four formula units ($C_{16}H_{20}$) in a cell of dimensions $a = 11.928$ (3), $b = 6.746$ (2), and $c = 16.127$ (5) Å. Three-dimensional data were collected on a Syntex $P2_1$ diffractometer using Mo Kα radiation to a maximum 2θ of 52°. The structure was solved using the acentric direct methods routines of the program SHELX, the best *E* map revealing all of the nonhydrogen atoms. The hydrogen atoms were located in subsequent difference maps and indicated disorder at the 1, 3, 5, and 7 positions. Block-diagonal least-squares refinement using 1085 observed reflections ($I/\sigma(I) \geq 2.0$) and with the carbon atoms having anisotropic temperature factors, converged to a final $R (= \Sigma||F_o| - |F_c||/\Sigma|F_o|^2)$ of 0.045 and weighted $R (= [\Sigma\omega||F_o| - |F_c||^2/\Sigma\omega|F_o|^2]^{1/2})$ of 0.032 where the weights used were $[1/\sigma(F)]^2$. The molecule is completely planar in the crystal possessing a noncrystallographic center of symmetry and overall D_{2h} symmetry, although this arises from considering the lattice to contain an equal distribution of the dimers **2a** and **2b** with C_{2h} and C_{2v} symmetry, respectively. Bond distances and angles are close to accepted values (Table I).

(8) Attempts to separate these isomers by TLC on alumina or silica gel have, thus far, proven unsatisfactory.

(9) T. Mukai, T. Tezuka, and Y. Akasaki, *J. Am. Chem. Soc.*, **88**, 5025 (1966).

(10) P. L. Timms, *Chem. Commun.*, 1033 (1969).

(11) M. J. McGlinchey and P. S. Skell in "Cryochemistry", G. A. Ozin and M. Moskovits, Eds. Wiley, New York, 1976, p 169.

(12) V. G. Andrianov, Y. T. Struchkov, V. N. Setkina, V. I. Zdanovich, A. Z. Zhakaeva, and D. N. Kursanov, *J. Chem. Soc., Chem. Commun.*, 117 (1975); Th. A. Albright, R. Hoffmann, and P. Hofmann, *Chem. Ber.*, **111**, 1599 (1978).

(13) P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organomet. Chem.*, **8**, 29 (1970).

(14) P. S. Skell and M. J. McGlinchey, *Angew. Chem., Int. Ed. Engl.*, **14**, 195 (1975).

(15) W. E. Billups, J. H. Cross, and C. V. Smith, *J. Am. Chem. Soc.*, **95**, 3438 (1973).

(16) E. Weiss and W. Hübel, *Chem. Ber.*, **95**, 1186 (1962).

Nguyen Hao, Jeffery F. Sawyer
Brian G. Sayer, Michael J. McGlinchey*
Department of Chemistry, McMaster University
Hamilton, Ontario, L8S 4M1, Canada

Received October 5, 1978

σ and π Components of Substituent Effects in Saturated Systems. Monosubstituted Methanes

Sir:

A molecular orbital description of methane utilizes one MO derived from the C 2s orbital and three degenerate molecular orbitals derived from the C 2p orbitals. These MO's differ in energy by 10 eV and have the proper symmetry for a system in the T_d point group.[1] When a substituent is introduced, the maximum degeneracy is reduced to 2. The methyl group 2s and 2p orbital directed toward the substituent form σ-type MO's. The other two 2p orbitals lead to a pair of π-type degenerate MO's. A substituent such as fluorine will interact with the methyl group orbitals to give a pair of low energy s-σ orbitals, a pair of p-σ orbitals (one of which will be antibonding), and two sets of degenerate π-type orbitals.

This description of a monosubstituted methane suggests that there should be σ and π interactions in a fashion similar to that in benzene. A π interaction involving back-bonding by the fluorine lone pairs has been suggested,[2] but the ionization potential of methyl fluoride has been interpreted as indicating a minimal interaction of this type.[3] In order to explore the possible importance of such interactions, extended basis set calculations have been carried out for a variety of monosubstituted methanes.

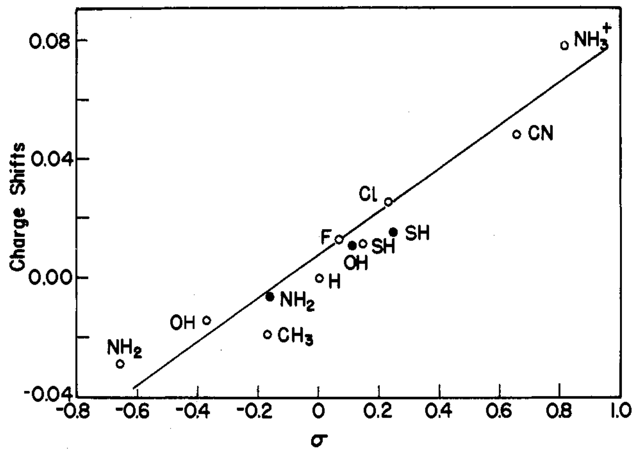


Figure 1. Relation between H charge shifts and σ for CH_3X. With X = NH_2, OH, and SH, the open circles represent hydrogens trans to lone pairs and are plotted against σ_p. The closed circles represent hydrogens trans to X–H bonds and are plotted against σ_m.

Table I. Calculated Charge Shifts at Hydrogen

X	q_H[a]	Δq_H	X	q_H	Δq_H
O^-	1.028	−0.131	NH_2	0.925[b]	−0.029
S^-	0.981	−0.084		0.902[c]	−0.005
CH_3	0.915	−0.019	OH	0.910[b]	−0.014
H	0.896	(0.000)		0.885[c]	+0.012
F	0.883	0.013	SH	0.885[b]	0.011
Cl	0.871	0.026		0.882[c]	0.015
CN	0.848	0.048			
NH_3^+	0.818	0.078			

[a] The hydrogen electron density plus one half the electron density in the C–H bond function. [b] Hydrogen trans to a lone pair. [c] Hydrogen trans to an X–H bond.

It has been found that the 4-31G basis set, when augmented by bond functions (an s orbital at the midpoint of C–H bonds and a set of s and p orbitals at the midpoint of C–X bonds), leads to a good electron density distribution for methane, methyl fluoride, and methyl chloride.[4] This basis set has been used for the present calculations. In order to be able to use a Mulliken population analysis[5] to give hydrogen charge shifts caused by substituents, a constant geometry was used, with tetrahedral angles about the methyl carbon and 1.09-Å C–H bond lengths. Most methyl compounds have geometries close to these values (±1°, ±0.005 Å).[6] The remaining geometrical parameters were taken as the experimental values.[6] The results are summarized in Table I.

The small effect of fluorine compared with chlorine and the electron-releasing effect on a hydroxy or amino group for the methyl hydrogens trans to the lone pairs provide clear evidence for a π interaction. With all substituents except methyl, the σ inductive effect will transfer electron density from the methyl group to the substituents and this will be opposed by the π interaction. The calculated effects are, in fact, very close to those observed with benzene derivatives for which σ and π effects are well established. This is clearly shown in Figure 1 in which the charge shift at hydrogen is plotted against the Hammett σ values. In the case of X = OH, NH_2, and SH, there are two charge shifts for the methyl hydrogens. The shift for the hydrogens of the C–H bonds which overlap the X lone pairs are plotted against σ_p, whereas the shift for the other hydrogens is plotted against σ_m. The σ_p values were used for the other substituents. The only substituent with a large deviation from linearity is X = O^-, and here solvent effects would be expected to be particularly important in determining the value of σ.[7]

The effect of substituents on the valence orbital energies is also of interest (Figure 2). The lowest energy MO corresponds to a C–X s-σ bond, and the energies change in accord with the electronegativity of the substituent. The energies of the other MO's change relatively little, except when a molecular charge

0002-7863/79/1501-2204$01.00/0