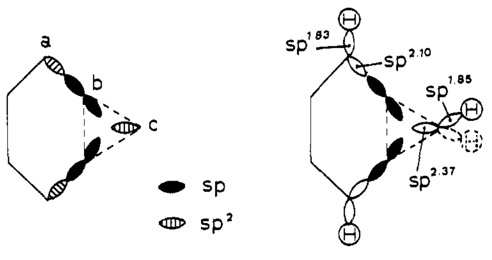
Table I. One-Bond $^{13}C-^{13}C$ Spin–Spin Coupling Constants (Hz)[a] for Compounds 1–5[b] and for Toluene[c,d]

	1	2	3	4	5	Toluene
J(a,b)	87.1	59.8	59.8	58.6	57.3	57.3
J(b,c)	20.8	35.4	41.5	41.5	43.9	44.2

[a] Maximum error ±1.22 Hz as determined by the experimental conditions; neat samples were measured with a Bruker HX-90 spectrometer operating at 22.63 MHz with simultaneous broad band ^1H decoupling at 90 MHz. [b] This work. [c] Reference 5. [d] For the chemical shift data of 1–5 see reference 9.



6 **7**

Figure 1. Hybridization models for the σ-bonds of benzocyclopropene.

Walsh model **6** for **1** can be tested with $K = 550$, a value that has been found reliable to ±50 Hz[4,7] for similar compounds. J(a,b) = 91.7 and J(b,c) = 22.9 Hz is obtained, in good agreement with the experimental results (Table I). An even better agreement with experiment is possible for J(b,c) if one considers the $^{13}C-^1H$ coupling constant of 170 Hz found at the methylene position of **1**.[9] Using eq 2[10]

$$^1J(^{13}C-^1H) = 500s(i) \qquad (2)$$

one finds 3.6% more s character in the CH_2 bonds of **1** than in those of cyclopropane ($^1J(^{13}C-^1H)$ = 161 Hz[10]). Consequently, each CC single bond in the three-membered ring of **1** has 1.8% less s character and a corrected coupling constant J(b,c) of 20.4 Hz results. A similar argument applies to J(a,b), since the $^{13}C-^1H$ coupling constant at C(a) of **1** again is larger than the corresponding value for the model compound, this time benzene (168.5 vs. 158.3 Hz[9,11]). The difference in s character amounts to 2.0% for the CH bonds at C(a) in both compounds and this in turn leads to a calculated J(a,b) of 88.9 Hz. Thus, the simple hybridization model **7** is in excellent agreement with the experimental $^{13}C-^1H$ and $^{13}C-^{13}C$ coupling constants. sp-Hybridization at C(1) and C(2) of **1** also explains the deformation of the benzene ring found for this compound[12] and the cyclopropene character at these carbons and the C(1)–C(2) bond established by X-ray analysis for 3,6-diphenyl-7,7-dicarbomethoxy-**1**.[13,14]

For **2** J(b,c) has increased but is still smaller than for indane (**3**) and tetraline (**4**). The value of 35.4 Hz agrees well with that found for the corresponding coupling constant in methylenecyclobutane (34.2 Hz[4]), indicating that the bonds of the four-membered ring of **2** still have enhanced p character. The $^{13}C-^1H$ coupling constant of 138 Hz for the CH_2 bonds[9,15] supports this interpretation. J(a,b) signals "normal" behavior for the benzene ring of **2**. The $^{13}C-^1H$ coupling constant at C(a), however, is again larger than in benzene (162 Hz[9]). A hybridization trend similar to that derived for **1** but less pronounced seems, therefore, indicated. Thus, the picture obtained for **1** and **2** lends experimental support to the Finnegan–Streitwieser model[16,17] for the enhanced acidity of protons α to strained ring systems.[18]

The data for toluene show that the methyl group in **5** does not exert any substituent effect on J(b,c). This is also true for J(a,b) in toluene, since the same value is found for $^1J(^{13}C-^{13}C)$ in benzene,[7] and other observations point in the same direction.[3]

Acknowledgments. We are indepted to the Deutsche Forschungsgemeinschaft for generous support of this research.

References and Notes

(1) Applications of ^{13}C NMR Spectroscopy, Part XXI; for Part XX see H. Günther and J. Prestien, *Org. Mag. Reson.*, in press.
(2) J. L. Marshall, D. E. Miiller, S. A. Conn, R. Seiwell, and A. M. Ihrig, *Acc. Chem. Res.*, 7, 333 (1974).
(3) K. D. Summerhays and G. E. Maciel, *J. Am. Chem. Soc.*, **94**, 8348 (1972).
(4) H. Günther and W. Herrig, *Chem. Ber.*, **106**, 3938 (1973).
(5) J. L. Marshall, A. M. Ihrig, and D. E. Miiller, *J. Mol. Spectrosc.*, **43**, 323 (1972).
(6) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).
(7) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 6021 (1972); R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *Ibid.*, **94**, 997 (1972).
(8) M. D. Newton, J. M. Schulman, and M. M. Manus, *J. Am. Chem. Soc.*, **96**, 17 (1974).
(9) H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, *Angew. Chem.*, **85**, 826 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 762 (1973).
(10) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).
(11) J. M. Read, R. E. Mayo, and J. H. Goldstein, *J. Mol. Spectrosc.*, **22**, 419 (1967).
(12) J. B. Pawliczek and H. Günther, *J. Am. Chem. Soc.*, **93**, 2050 (1971).
(13) E. Carstensen-Oeser, B. Müller, and H. Dürr, *Angew. Chem.*, **84**, 434 (1971).
(14) We must emphasize, however, that our treatment assumes two equivalent bonds at C(a) and C(b), respectively, and pure sp hybridization at C(b). The fact that the experimental value for J(a,b) is still smaller by 1.8 Hz than the calculated one seems to indicate that this is not strictly valid. The quantitative results are, therefore, afflicted with some degree of uncertainty which does, however, not affect the general picture.
(15) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964).
(16) R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965).
(17) A. Streitwieser, Jr., G. Ziegler, P. Mowery, A. Lewis, and R. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).
(18) For other experimental evidence see R. D. Rieke, S. E. Bales, C. F. Meares, L. I. Rieke, and C. M. Milliren, *J. Org. Chem.*, **39**, 2276 (1974), and earlier papers cited therein.

Harald Günther,* Wolfgang Herrig
Institut für Organische Chemie, Universität Köln
5 Cologne, Germany
Received May 12, 1975

Synthesis, Characterization, and X-Ray Structure of a Tetrahydrofuran Adduct of μ-Iodo-bis[tris(2-diphenylarsinoethyl)amine]nickel(I) Tetraphenylborate

Sir:

The tripod ligand tris(2-diphenylarsinoethyl)amine, $N[CH_2CH_2As(C_6H_5)_2]_3$, nas$_3$, reacts with nickel(II) halides to give five-coordinate complexes of nickel(II) having the general formula $[NiX(nas_3)]B(C_6H_5)_4$ (I), X = Br, I.[1] In the presence of sodium tetrahydroborate, nickel(I) complexes with the formula $[NiX(nas_3)]$ (X = Cl, Br, I)[2] are obtained. If the complexes (I) are treated with $NaBH_4$ in ethyl alcohol in less than stoichiometric amounts, however, dimeric compounds of nickel(I) having the general formula $[Ni_2X(nas_3)_2]B(C_6H_5)_4$ (X = Br, I) are obtained. This reduction can be ascribed only partly to $NaBH_4$, as the $NaBH_4$:Ni(I) ratio is 1:2; the tetraphenylborate ion, which has previously been found to reduce nickel(II),[3] is thought to be responsible for completing the reduction.

The molecular structure of the compound $[Ni_2I(nas_3)_2]B(C_6H_5)_4 \cdot 3THF$ has been determined by a three-dimensional X-ray analysis. The crystals are monoclinic, space group $C2/c$, with lattice constants a = 15.476 (2) Å, b = 25.820 (3) Å, c = 27.209 (3) Å, β = 96.42 (2)°, V = 10804.0 Å^3, d_{measd} = 1.45 g cm^{-3}, d_{calcd} = 1.444 g cm^{-3},

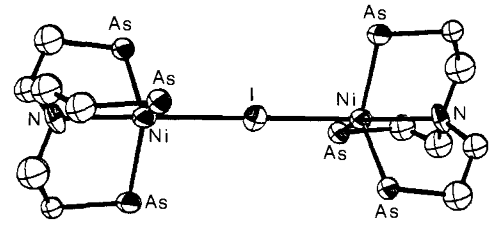


Figure 1. A schematic view of the skeleton of the $[Ni_2I(nas_3)_2]^+$ cation. The values of distances (Å) and angles (deg) are: Ni–I, 2.994 (3); Ni–N, 2.31 (2); Ni–As, 2.349 (5) (av); I–Ni–N, 178.0 (5); I–Ni–As, 95.2 (1) (av); As–Ni–As, 119.0 (2) (av).

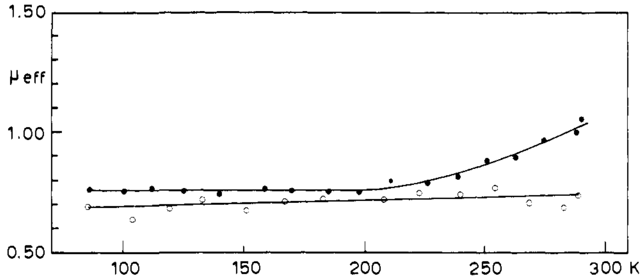


Figure 2. Variation with temperature of the magnetic moment μ_{eff} for Ni(I) in $[Ni_2Br(nas_3)_2]B(C_6H_5)_4$ (●) and in $[Ni_2I(nas_3)_2]B(C_6H_5)_4$ (○).

and $Z = 4$. The intensity data were collected on a Philips automatic diffractometer, with Mo Kα radiation, using the limitation $6° \leq 2\theta \leq 20°$. The 1588 reflections having $I \geq 3\sigma(I)$ were considered observed and were used in the solution and refinement of the structure. The structure was solved by a Patterson synthesis followed by Fourier syntheses. The structure consists of dimeric $[Ni_2I(nas_3)_2]^+$ cations and $B(C_6H_5)_4^-$ anions with interposed tetrahydrofuran solvent molecules. Each nickel atom is bonded to the four donor atoms of the nas_3 ligand and to the shared bridging iodine atom. The iodine atom lies on a center of symmetry, while the boron atom of the $B(C_6H_5)_4^-$ ion is situated on a binary axis. The chromophore can be considered to be formed by two trigonal-bipyramids sharing a vertex. A schematic view of the $[Ni_2I(nas_3)_2]^+$ cation with the most significant bonds and angles is shown in Figure 1. The long axial distances Ni-I, 2.994 (4) Å, and Ni-N, 2.31 (2) Å, are noteworthy.

This complex is one of the few binuclear metal complexes having a linear metal-iodine-metal bridge.[4]

The magnetic behavior of these compounds has been studied over the range 84-290 K; in neither case is the susceptibility found to be field dependent. Diamagnetic corrections were calculated using Pascal's constants.[5] The μ_{eff} for each nickel atom vs. T is reported in Figure 2. The iodo derivative has a μ_{eff} of ca. 0.7 BM in the temperature range of the measurements. The μ_{eff} of the bromo derivative has a constant value, 0.75 BM, from 84 to ca. 200 K; beyond this temperature the moment increases slowly up to the value of 1 BM at 288 K. The two complexes can therefore be considered essentially diamagnetic at low temperature, the residual value of μ_{eff} being attributable to paramagnetic impurities. In fact the magnetic susceptibility varies slightly from sample to sample but the plots obtained in each case are essentially the same as those in Figure 2 which shows the lowest μ_{eff} obtained.

This magnetic behavior suggests that an antiferromagnetic exchange takes place between the two nickel atoms involving the halide bridge. In terms of the Kramers-Anderson approach,[6] the antiferromagnetic coupling between the d^9 nickel cations can arise from the intermixing of a d_{z^2} orbital on each nickel atom with a P_z orbital on the bridging halide ion via the P_σ-a_1' pathway.

The best pair of values of g and J for the bromo derivative, obtained fitting the Bleaney-Bowers equation to the experimental data by the use of a direct method to minimize the error-square sum over the observed susceptibilities,[7] is 2.00 and -232 cm^{-1}, respectively.

The increasing μ_{eff} value with temperature above 200 K for the bromo derivative is interpreted as due to the population of a thermally accessible triplet level. The fact that a different behavior is observed for the iodo derivative up to 290 K suggests that the exchange coupling between nickel atoms bridged by the iodine ion is greater than that in the bromide. This is in agreement with the general finding that the transfer integral and hence the exchange coupling constant $|J|$ becomes larger as the electronegativity of the anion decreases.

The diffuse reflectance spectrum of the bromo derivative shows a band at 1×10^4 cm^{-1} and a shoulder at 1.31×10^4 cm^{-1}, while that of the iodo derivative has a band at 1.31×10^4 cm^{-1}. Both dimers show also intense bands above 1.8×10^4 cm^{-1} attributable to charge transfer transitions. The shape and position of the first electronic absorption band are similar to those of typical five-coordinate nickel(I) complexes such as $[NiX(nas_3)]^2$ and also $[NiI(np_3)]$, which has been found, by X-ray analysis,[8] to have trigonal bipyramidal geometry. The similarity of the low energy bands is reasonable because the relatively weak spin-spin coupling in the dimers is expected to be small compared to the energies of the d-d transitions (ca. 1.1×10^4 cm^{-1}).

References and Notes

(1) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **7**, 1417 (1968).
(2) L. Sacconi, P. Dapporto, and P. Stoppioni, unpublished results.
(3) L. Sacconi, C. Mealli, and D. Gatteschi, *Inorg. Chem.*, **13**, 1985 (1974).
(4) D. Baumann, H. Endres, H. J. Keller, and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 853 (1973).
(5) B. N. Figgis and J. Lewis, *Mod. Coord. Chem.*, 400 (1960).
(6) R. L. Martin in "New Pathways in Inorganic Chemistry", E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N.Y., 1968, p 175, Chapter 9, and references therein.
(7) C. Mealli, S. Midollini, and L. Sacconi, *Inorg. Chem.*, in press.
(8) L. Sacconi, C. A. Ghilardi, C. Mealli, and F. Zanobini, *Inorg. Chem.*, **14**, 1380 (1975).

L. Sacconi,* P. Dapporto, P. Stoppioni
Instituto di Chimica Generale ed Inorganica
dell'Università di Firenze and Laboratorio CNR
Florence, Italy

Received May 15, 1975

Photochemistry of β,γ-Unsaturated Ketones. Specific Reactivity of S_2, S_1, and T_1 in 2,2,7,7-Tetramethyl-3,5-cycloheptadienone and Correlations with INDO Calculations[1]

Sir:

Direct irradiation at >300 nm of 3,5-cycloheptadienone (**1a**)[2-4] and the 2-methyl analog **1b**[2] gave only the hexatrienes **2** by decarbonylation of the lowest singlet excited state, while triplet sensitization of **1a** led only to the cyclobutene **3**,[3] i.e. $\Phi_{ST} = 0$.

The bridged ketone **4**, where the diene moiety is planar or near planar, gave decarbonylation and cyclobutene formation when irradiated at >300 nm, while triplet sensitization gave the [1,2]-sigmatropic acyl shift[5] (1,2-SAS) product **5**; again $\Phi_{ST} = 0$.[6] Similar reactions were reported for the trienone **6**[7] and the tropone-cyclopentadiene adduct **7**.[8,9]