are ordered *along the crystallographic C* axis*.[1] These results thus represent the first direct determination by NMR spectroscopy of structural parameters in protein crystals.

The results presented in this communication open a new area for NMR of protein crystals, since the difficulties of preparing large single crystals are eliminated. Observation of "sharp" resonances in magnetically ordered samples (Figure 1B) permits rapid data acquisition due to increased signal-to-noise ratios and naturally permits resolution of signals from numerous sites which would normally all overlap. Dynamic studies of individual resolved sites may now be carried out, and results compared with those obtained from crystallography.[10] The method should also be applicable for investigating the structures of a wide variety of paramagnetic organometallic compounds.

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References and Notes

(1) T. M. Rothgeb and E. Oldfield, unpublished results.

(2) (a) W. C. Jones, Jr., T. M. Rothgeb, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **97**, 3875 (1975); (b) W. C. Jones, Jr., T. M. Rothgeb, and F. R. N. Gurd, *J. Biol. Chem.*, **251**, 7452 (1976).

(3) G. Jaeck and F. W. Benz, *Biochem. Biophys. Res. Commun.*, **86**, 885 (1979).

(4) J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic, and T. P. Higgs, *Chem. Phys. Lett.*, **42**, 390 (1976).

(5) E. Oldfield, R. Gilmore, M. Glaser, H. S. Gutowsky, J. C. Hsung, S. Y. Kang, T. E. King, M. Meadows, and D. Rice, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 4657 (1978).

(6) J. E. Bennett, J. F. Gibson, and D. J. E. Ingram, *Proc. R. Soc. London, Ser. A*, **240**, 67 (1957); J. S. Griffith, *ibid.*, **235**, 23 (1956).

(7) H. Hori, *Biochim. Biophys. Acta*, **251**, 227 (1971).

(8) J. R. Wasson, C. Trapp, C.-I. Shyr, and D. Smith, *J. Chem. Phys.*, **49**, 5197 (1968); C. Trapp, D. Smith, and J. R. Wasson, *ibid.*, **51**, 1419 (1969); D. Smith and C. Trapp, *ibid.*, **52**, 4923 (1970); M. J. Nilges and R. L. Belford, *J. Magn. Reson.*, **35**, 259 (1979).

(9) T. Takano, *J. Mol. Biol.* **110**, 537 (1977).

(10) H. Frauenfelder, G. A. Petsko, and D. Tsernoglou, *Nature* (*London*), **280**, 558 (1979); P. J. Artymiuk, C. C. F. Blake, D. E. P. Grace, S. J. Oatley, D. C. Phillips, and M. J. E. Sternberg, *ibid.*, **280**, 563 (1979).

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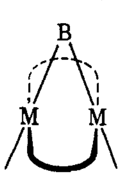
Molecular A Frames. Synthesis from Binuclear Rh(0) Precursors and Catalytic Activity in the Water Gas Shift Reaction and Alkyne Hydrogenation

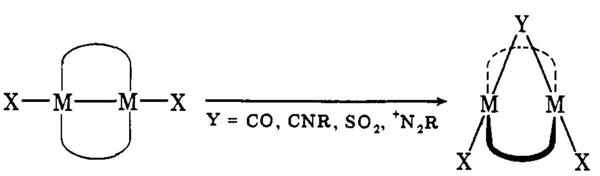
Sir:

The first binuclear complexes of the "A-frame" type geometry, I, were reported in 1977,[1,2] and, since then, other



I

complexes of this structure type have been described including several which bind a small molecule (e.g., CO) on the endo side of the A frame in the so-called "pocket".[3] One approach to the synthesis of A-frame complexes has been through the insertion of small molecules into the metal-metal bond of the bis(diphosphine)-bridged system [$M_2X_2(dpm)_2$] [M = Pd, Pt; dpm = bis(diphenylphosphino)methane] (eq 1), as evidenced in the



(1)

reports of Balch, Puddephatt, and others.[2,4–7] We report herein our ability to use this approach with the highly reactive and hitherto unknown Rh(0) system [$Rh_2(CO)_2(dpm)_2$], leading to the synthesis of new Rh A-frame systems including an acetylene species active as a hydrogenation catalyst and a bridging carbonyl hydride formed by the successive addition of H^+ and CO in either order. This latter complex is characterized by a single-crystal X-ray study as well as by spectroscopic methods, and shows itself to be a highly active water gas shift catalyst.

The purple, highly reactive Rh(0) species [$Rh_2(CO)_2(dpm)_2$], **1**, is synthesized by treatment of [$Rh_2Cl_2(CO)_2(dpm)_2$][8] with $NaBH_4$ in ethanol. Complex **1**, which precipitates from solution, shows only a single ν_{CO} at 1915 cm^{-1} and the absence of any hydride resonance in the range of 0 to −25 ppm relative to Me_4Si. No change in the IR spectrum is observed when $NaBD_4$ is used as the reducing agent. The extreme chemical reactivity of **1** has made definitive characterization more difficult, but the nature of **1** as a metal-metal bonded Rh(0) dimer is strongly supported by its reaction chemistry (vide infra) and by the preparation of an apparent isomer of **1** starting with $RhH(CO)(PPh_3)_3$ in which stoichiometric evolution of H_2 is observed.[9] There is no spectroscopic or chemical evidence to support a hydride formulation of **1**.

Complex **1** reacts with both H^+ and CO. Protonation of **1** with 1 equiv of a noncoordinating acid, HA (A^- = *p*-$CH_3C_6H_4SO_3^-$ or PF_6^-), leads to brown [$Rh_2(H)(CO)_2(dpm)_2]^+A^-$, **2**. Only a trace of H_2 is observed in the course of the reaction. The ^1H NMR and IR spectra of **2** reveals a featureless hydride resonance at −10.1 ppm and two ν_{CO} at 1962 and 1945 cm^{-1}. The reaction of **1** with CO is accompanied by a rapid solution color change to red-orange after which [$Rh_2(\mu\text{-}CO)(CO)_2(dpm)_2$], **3**, may be isolated in analytically pure form. The IR spectrum of **3** shows a bridging carbonyl stretch at 1835 cm^{-1} in addition to terminal stretches at 1920 and 1940 cm^{-1}. The controlled addition of CO to **1** shows that 1 equiv of CO is consumed; no H_2 is produced. The ^1H NMR spectrum of **3** displays no resonance attributable to a Rh hydride formulation, while the $^{31}P\{^1H\}$ NMR spectrum shows a complicated mirror symmetry pattern centered at δ 15.72 (relative to trimethyl phosphate) with two major lines separated by 144 Hz.

The identities of **1**, **2**, and **3** are further supported by reactions which lead to the formation of a μ-hydride-μ-carbonyl complex, **4**. Protonation of complex **3** with HA produces the deep purple complex [$Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+A^-$, **4**, which is also obtained by the addition of CO to **2**. These reactions are reversible. Heating **4** at 60 °C in THF under N_2 regenerates **2**, while the addition of 1 equiv of $NaHB(OMe)_3$ to **4** yields **3** and 1 equiv of H_2. **4** exhibits ν_{CO} of 1972, 1957, and 1870 cm^{-1} and a broad hydride resonance at −9.71 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **4** is complicated but symmetric. Suitable single crystals of **4** were obtained from THF solution as the *p*-toluenesulfonate salt and used in a definitive X-ray structural study of the complex.

[$Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2$]($p\text{-}CH_3C_6H_4SO_3$)·2THF crystallizes in space group $C2/m$ in a cell of dimensions a = 24.391 (11), b = 18.863 (9), c = 14.440 (6) Å; β = 107.81 (2)° (Z = 4; ρ_{calcd} = 1.44, ρ_{obsd} = 1.42 (2) g/cm^2). Intensity data

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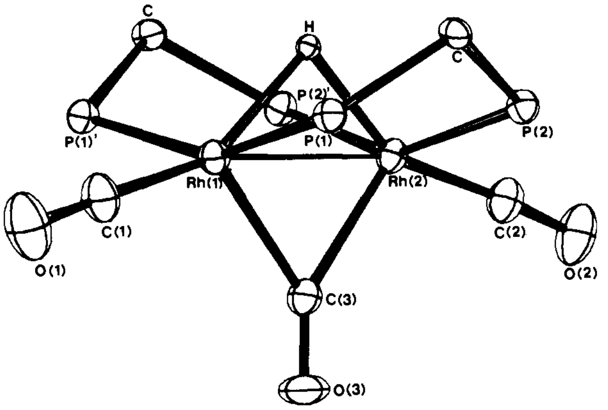


Figure 1. A view of the $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$ cation without phenyl rings. Selected bond distances and angles follow. Distances: Rh(1)-H, 1.9 (1); Rh(2)-H, 1.8 (1); Rh(1)-C(3), 2.17 (2); Rh(2)-C(3), 2.15 (2); average Rh-P, 2.309 (4) Å. Angles: P(1)-Rh(1)-P(1), 155.2 (2); P(2)-Rh(2)-P(2), 150.0 (2), Rh(1)-H-Rh(2), 93 (5); Rh(1)-C(3)-Rh(2) 78.4 (7)°.

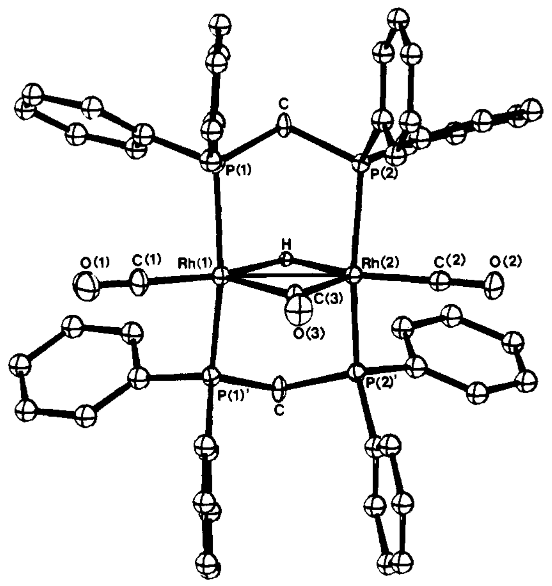
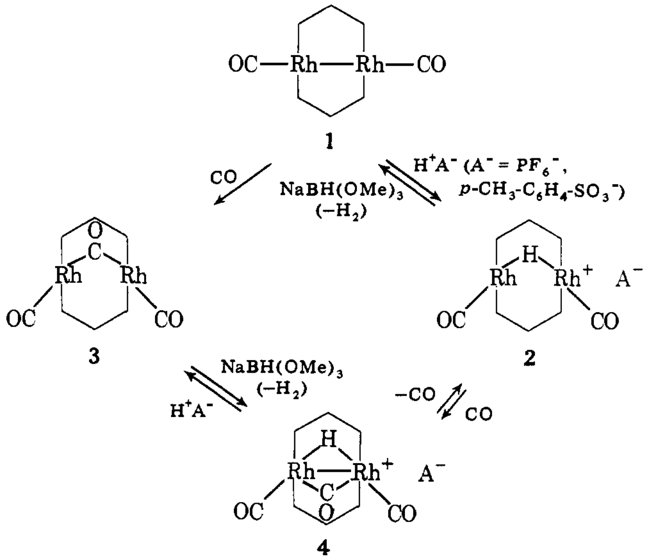


Figure 2. A perspective drawing of the $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$ cation. The two rhodium atoms, bridging hydride, and three carbon monoxides all lie on a crystallographic mirror plane which relates the two dpm ligands.

were collected using Mo Kα radiation by the θ-2θ scan technique in the range $3° < 2\theta < 40°$. The structure was solved by the usual Patterson-least-squares-Fourier methods and refined to discrepancy factors R and R' of 0.066 and 0.081, respectively, for 182 parameters and 2127 observations.[10]

The structure of **4** has crystallographic *m* symmetry and is shown in Figures 1 and 2. Owing to the mirror symmetry element, the single hydride ligand is constrained to lie on the mirror plane containing the two rhodium atoms and three carbonyls where it was successfully located. The structure of **4** is best described as a hydride A frame of Rh(I) with a carbon monoxide bound in the pocket. The two terminal carbonyls are approximately trans to the bridging hydride [H-Rh(1)-C(1) = 153 (3), H-Rh(2)-C(2) = 152 (3)°] and exhibit much smaller angles with the bridging CO [C(1)-Rh(1)-C(3) = 114.3 (9), C(2)-Rh(2)-C(3) = 111.6 (9)°]. The Rh-Rh separation of 2.732 (2) Å lies within the range reported for Rh-Rh single bonds.[3,11-14] Other distances and angles are given in Figure 1 (caption). The present structure bears a strong resemblance to the previously reported carbonyl adduct of the μ-Cl A-frame complex, $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dpm)_2](BPh_4)$,[3] in spite of the fact that the electron counts for the two complexes differ by two, bridging halide normally being acknowledged as a 3e$^-$ donor in contrast with μ-H as a 1e$^-$ donor.

Scheme I



The reversible carbonylation of **2** to **4**, together with the structural data for **4** and the spectroscopic data for both complexes, points to the identity of **2** as a hydride A frame of Rh(I)—i.e., in **2**, H$^+$ occupies the bridgehead position of I. The carbonylation-decarbonylation of **2** appears analogous to that reported by Sanger et al.[3] for the μ-Cl complex, the CO adduct of which is structurally very similar to **4**. The observation of a single bridging ν_{CO} and two terminal ν_{CO}'s for **3**, together with its facile protonation to form **4**, provides compelling evidence that **3** is a carbonyl bridged A-frame complex analogous to the Pd[2,15] and Pt[6] species reported previously, and it is therefore suggested that **3** does not have a Rh-Rh bond. Complex **4** may thus be viewed as resulting from either the introduction of CO into the pocket of the hydride A frame, **2**, or from the protonation of the neutral carbonyl A frame, **3**. The reactions interrelating **1-4** are summarized in Scheme I.

The activity of **4** as a catalyst for the water gas shift reaction, $H_2O + CO = H_2 + CO_2$, is striking. When 0.05 g of **4** is dissolved in 30 mL of *n*-PrOH with 2 molar equiv of LiCl in 1 mL of H_2O added, and the system is placed under 1 atm of CO at 90 °C, we observe water gas shift catalysis using previously established procedures and gas chromatographic analysis.[16] The rate of catalysis corresponds to 2.5 turnovers/h which is one of the most active yet found under these very mild temperature and pressure conditions.[16-21] The catalysis proceeds much more slowly in the absence of Cl$^-$, and is pH sensitive. The detailed nature of this catalysis is under continuing study.

Complex **1** adds other substrates to its Rh-Rh bond besides CO and H$^+$. For example, **1** reacts with acetylene in toluene to produce an intense emerald green solution containing $[Rh_2(C_2H_2)(CO)_2(dpm)_2]$, **5**. The corresponding blue-green phenylacetylene complex **6** is similarly prepared by the addition of 1 equiv of phenylacetylene to a solution of **1**.[22] While **2** and **3** do not react with H_2, the acetylene complexes **5** and **6** readily do so at 80 °C. Under an atmosphere of 2:1 H_2/C_2H_2, toluene solutions of **1** at 80 °C hydrogenate acetylene to ethane at a rate of (~3.3 mol of ethane/mol of **1**)/h. No cyclotrimerization is observed in this reaction, and the rate of acetylene reduction to ethane is greater than the rate of ethylene hydrogenation under similar conditions (~0.1 turnovers/h). Finally, **1** reacts with 1 equiv of isocyanide to give a μ-isocyano A-frame species (ν_{CN} 1830 cm^{-1}, R = Me). In the presence of excess RNC, the two terminal CO ligands are also replaced yielding $[Rh_2(\mu\text{-}CNR)(CNR)_2(dpm)_2]$ which is isoelectronic with the Pd dication $[Pd_2(\mu\text{-}CNR)(CNR)_2(dpm)_2]^{2+}$ reported by Balch.[2]

We have thus shown that complex I provides a useful entry into the synthesis of A-frame complexes, and that some of these resultant species exhibit significant catalytic activity in the shift reaction and acetylene hydrogenation.

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References and Notes

(1) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977,** *99*, 6129.

(2) Olmstead, M. M.; Hope, H .; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977,** *99*, 5502.

(3) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978,** *100*, 3628. Cowie, M. *Inorg. Chem.* **1979,** *18*, 286.

(4) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *Inorg. Chim. Acta* **1977,** *23*, L27.

(5) Rattray, A. D.; Sutton, D. *Inorg. Chim. Acta* **1978,** *27*, L85.

(6) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Manojlovic-Muir, Lj.; Muir, K. W.; Solomun, T.; Seddon, K. R. *Inorg. Chim Acta* **1977,** *23*, L33.

(7) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *J. Am. Chem. Soc.*, in press.

(8) Mague, J. T. *Inorg. Chem.* **1969,** *8*, 1975. Mague, J. T.; Mitchener, J. P. *Ibid.* **1969,** *8*, 119.

(9) Elemental analysis for **1** is satisfactory. Calcd for $C_{52}H_{44}P_4O_2Rh_2$: C, 60.60; H, 4.30; P, 12.02. Found: C, 60.25; H, 4.69; P, 11.57. The $^{31}P\{^1H\}$ NMR spectrum for **1** shows a symmetric multiplet centered at δ 29.51 relative to $OP(OMe)_3$ with four principal lines. This pattern which is not unambiguously interpretable differs from those found for A-frame type complexes with bridgehead ligands in which the mirror symmetric spectrum shows only two principal lines. The ^1H spectrum shows in addition to the phenyl protons only one broad resonance at δ 4.32 for the $-CH_2-$ protons of the dpm ligand. The isomer of **1** obtained by the reaction of $RhH(CO)(PPh_3)_3$ with dpm appears in solution to be $Rh_2(\mu\text{-}CO)(CO)(dpm)_2(PPh_3)$ by an IR spectrum showing terminal and briding ν_{CO} at 1915 and 1800 cm^{-1}, and by the identity of the IR and NMR spectra for this system with those obtained by adding PPh_3 to a solution of 1. Upon isolation, however, this "isomer" appears to lose PPh_3 and is consistent with analytical data for $[Rh_2(CO)_2(dpm)_2(solvent)]$. A key feature of the characterization of **1** and its isomer is that in all of their reactions identical products are obtained.

(10) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The programs and procedures are similar to those reported previously by Goldberg, S. Z.; Kubiak, C.; Meyer, C. D.; Eisenberg, R. *Inorg. Chem.* **1975,** *14*, 1650.

(11) Corey, E. R.; Dahl, L. F.; Beck, W. *J. Am. Chem. Soc.* **1963,** *85*, 1202.

(12) Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967,** *10*, 337. Mills, O. S.; Paulus, E. F. *Ibid.* **1967,** *10*, 331.

(13) Paulus, E. F.; Fisher, E. O.; Fritz, H. P.; Schuster-Woldan, H. *J. Organomet. Chem.* **1967,** *10*, P3. Paulus, E. F. *Acta Crystallogr., Sect. B* **1969,** *25*, 2206.

(14) Wei, C. H. *Inorg. Chem.* **1969,** *8,* 2384.

(15) Colton, R.; McCormick, M. J.; Pannan, C. D. *J. Chem. Soc., Chem. Commun.* **1977,** 823.

(16) Cheng, C. H.; Hendriksen, D. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1977,** *99*, 2791.

(17) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977,** *99*, 252.

(18) Cheng, C. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1978,** *100*, 5968.

(19) Ford, P. C.; Rinker, R. G.; Ungermann, C.; Laine, R. M.; Landis, V.; Moya, S.A. *J. Am. Chem. Soc.* **1978,** *100*, 4595.

(20) Kang, H. C.; Mauldon, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977,** *99*, 8323.

(21) King, R. D.; Frazier, C. C.; Hanes, R. M.; King, A. D. *J. Am. Chem. Soc.* **1978,** 100, 2925.

(22) Complex **5** in C_6H_6 solution shows ν_{CO} at 1946 (s, sh) and 1938 (vs) cm^{-1}. The ^1H NMR spectrum shows dpm $-CH_2-$ resonances at δ 3.35 and 2.91 (m), similar to that found in many A-frame complexes. The $^{31}P\{^1H\}$ spectrum shows a symmetric multiplet centered at δ 17.66 with two intense principal lines separated by 133.0 Hz. The spectrum is qualitatively similar to that for **3.** The phenylacetylene complex analyzes for a solvated species $[Rh_2(CO)_2(PhCCH)(dpm)_2]\cdot$solvent and shows ν_{CO} at 1958 (vs) and 1930 (s) cm^{-1}. The ^1H NMR spectrum shows dpm $-CH_2-$ resonances at δ 3.77 and 2.89, while the $^{31}P\{^1H\}$ spectrum lacks the symmetry of other A-frame systems as would be expected for acetylene binding in the manner recently described by Balch[23] for $CF_3C{\equiv}CCF_3$ addition to $Pd_2Cl_2(dpm)_2$.

(23) Balch, A. L.; Lee, C.-L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979,** *177*, C22–C26.

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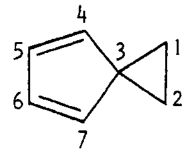
Microwave Spectrum, Dipole Moment, and Structure of Spiro[2.4]hepta-4,6-diene. Evidence for Significant Cyclopropyl Conjugation

Sir:

The question of whether the cyclopropyl ring is able to conjugate with adjacent unsaturated π systems has been one of long-standing interest. One fundamental measure of such an interaction is that of molecular structure. The matter has been discussed theoretically by Hoffmann[1] who pointed out that electron donation from the highest occupied molecular orbital (HOMO) of cyclopropane (3e′) to the lowest unoccupied molecular orbital (LUMO) of a π system should lead to predictable changes in structural parameters. One of the best documented cases is that of cyclopropyl cyanide, for which the C_1–C_2 bond is 0.028 Å longer than the C_2–C_3 bond,[2] in accord with theoretical expectations. Recent high-quality ab initio calculations[3] for this molecule are in complete agreement with the experimental findings.

Spiro[2.4]hepta-4,6-diene (**1**) is a molecule for which such π conjugation might be expected to have significant structural consequences. Conjugation (π delocalization) in molecules of this type has been discussed theoretically by Gleiter et al.[4] and by Kao and Radom.[5] Experimental PES[4] and NMR measurements[6] support the view that significant π conjugation occurs. On the other hand, electron diffraction (ED) structural results[7] showed the spiroheptadiene bond lengths to be essentially the same as in the parent cyclopropane and cyclopentadiene moieties. Because of previous difficulties[8] in the unambiguous ED determination of bond lengths in hydrocarbons containing several similar but nonidentical C–C bonds, we have undertaken a microwave spectroscopic investigation of **1**.



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The microwave spectrum was remarkably intense, and consisted of easily assignable a-type R-branch transitions characteristic of a near-prolate asymmetric rotor. A total of 52 transitions, including a few high-J Q-branch lines, were analyzed to obtain the rotational constants of the normal isotopic species given in Table I. The complete set of measured lines is available in a supplementary microfilm table. Intensity

Table I. Rotational Constants and Moments of Inertia of the Normal Isotopic Species of Spiro[2.4]hepta-4,6-diene

A	6102.149 ± 0.014[a]	I_a	82.81984[b]
B	2454.223 ± 0.001	I_b	205.9222
C	2028.890 ± 0.001	I_c	249.0914

[a] Units are MHz, uncertainties are one standard deviation. [b] Units are amu Å^2, computed using the factor 505 379.

Table II. Dipole Moment Measurements

transition	M	$(\Delta\nu/E^2) \times 10^5$ obsd[a]	$(\Delta\nu/E^2) \times 10^5$ calcd[a]
$5_{23} \rightarrow 6_{24}$	2	−0.2436	−0.2431
$5_{23} \rightarrow 6_{24}$	1	−0.0644	−0.0637
$5_{24} \rightarrow 6_{25}$	2	0.2462	0.2468
$5_{24} \rightarrow 6_{25}$	1	0.0587	0.0586
$\mu_T = \mu_a = 0.947 \pm 0.003$[b]			

[a] Units are MHz/(V/cm)^2. [b] Uncertainty represents 3σ.

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