kaloid had not been readily isolated but chemically correlated from the natural quebrachamine (17) in a low yield on mild oxidation.[27] For establishment of the structure of the product 15, it was reduced (LiAlH₄, THF, room temperature) and then acetylated to give (±)-1-acetylaspidospermidine (16) in 64% yield, which was identified with the authentic specimen synthesized by us through the other route.[23e] The reaction mechanism of this unexpected cyclization could be explained by presuming that the hydroxy group in the amino alcohol 22 generated by reduction of the lactam 21b might be blocked by the nine-membered ring and thereby resistant to further reduction under mild conditions and would by treatment with acid give the iminium salt,[27] which may be readily cyclized to 15. Therefore, 21b was reduced under forcing conditions [LiAlH₄ (excess), dioxane, reflux, 4 h] and then treated with acid to furnish (±)-quebrachamine (17)[22,21a,28] in 45% yield. Thus, by controlling the reduction condition at the final stages, a variety of *Aspidosperma* alkaloids were produced through the regioselective formation of the iminium salt, thus answering problem 4. Studies along this approach are further in progress.

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Synthesis and Reactions of a Dimetallacyclohexene. Thermal Conversion to an *o*-Xylylene Complex and Phosphine-Induced Conversion to Free *o*-Xylylene and a New Reactive Dinuclear Cobalt Complex

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Saturated metallacycles containing two metals in the ring are proving to have a chemistry at least as rich and varied as that of their mononuclear predecessors. Several kinetically stable three-membered dimetallacycles have now been found and studied,[1] and results in at least one five-membered system suggest that in the cobalt series this ring size confers a similar degree of stability on a molecule.[2] However, saturated dinuclear metallacycles containing four[3] or six[4] atoms in the ring are exceedingly rare.

(1) See, for example: (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 800-812. (b) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, K.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* 1981, *103*, 63-75. (c) Hursthouse, M. B.; Jones, R. A.; Abdul Malik, A. M.; Wilkinson, G. *Ibid.* 1979, *101*, 4128-4150. (d) Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* 1980, 1771-1778. (e) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1980, 237. (f) Halbert, R. T.; Leonowicz, M. E.; Maydonovitch, D. J. *J. Am. Chem. Soc.* 1980, *102*, 5101-5102. (g) Levisalles, J.; Rudler, H.; Dahan, F.; Jeanning, Y. *J. Organomet. Chem.* 1980, *187*, 233-242. (h) Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* 1980, *102*, 1752-1754. (i) Theopold, K. H.; Bergman, R. G. *Ibid.* 1981, *103*, 2489-2491.

(2) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1980, *102*, 5694-5695.

Scheme I
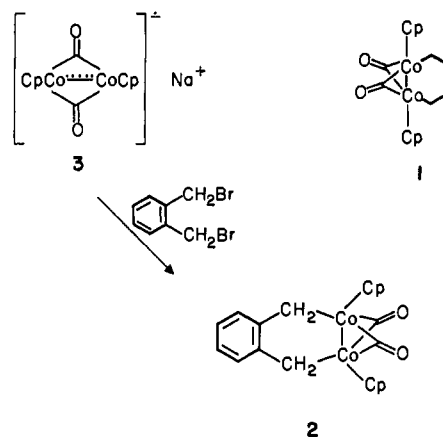
Scheme II
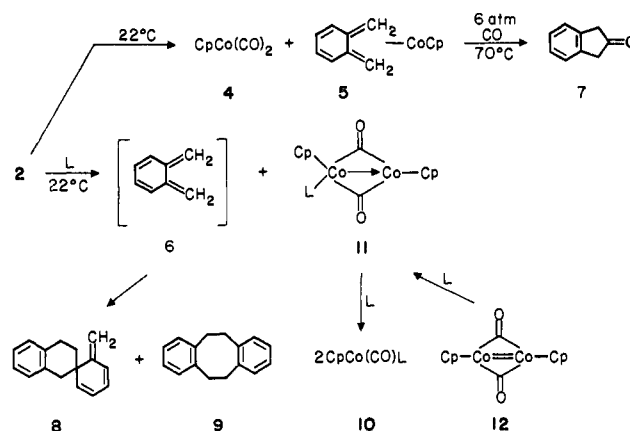
The larger metallacycles are of particular interest as models for possible dinuclear intermediates in reactions such as alkene and diene oligomerization; in addition, insertion of small unsaturated fragments (i.e., CO, C₂H₄) followed by reductive elimination could lead to new organic annulation procedures. Our attempts to prepare the six-membered cobalt system 1 (Cp = η₅-cyclopentadienyl) have been frustrated, apparently by facile β-elimination processes which can occur in such complexes.[5] In order to preclude this decomposition pathway, we sought to prepare the benzannulated analogue 2. We now report (1) the successful synthesis of this complex, which is, to our knowledge, the first dimetallacyclohexene, (2) its thermal and ligand-induced decompositions, (3) cyclic ketone formation from a decomposition product of 2, and (4) the detection and independent synthesis of an unstable dinuclear reaction intermediate which contains a dative metal–metal bond.

Synthesis of 2 was accomplished by analogy to the established procedure,[2] by addition of THF to a 1.5:1 mixture of α,α'-dibromo-*o*-xylene and radical anion 3 (Scheme I). After stirring for 5 min the solvent was removed and the residue chromatographed quickly on alumina II under air-free conditions, eluting

(3) There are a few examples of unsaturated four-membered dimetallacycles. See, e.g.: (a) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Rehani, S. K. *J. Organomet. Chem.* 1976, *113*, C42-C44. (b) Smart, L. E.; Browning, J.; Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 1777-1785. (c) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* 1977, *99*, 7870-7876. (d) Dickson, R. S.; Mok, C.; Pain, G. *J. Organomet. Chem.* 1979, *166*, 385-402. (e) Boag, N. M.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1980, 1281-1282.

(4) Known unsaturated six-membered dimetallacycles are mostly of the type formed by oligomerization of alkynes. See, for example, ref 3b and the following: (a) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. J. *Chem. Soc., Chem. Commun.* 1978, 221-223. (b) Slater, S.; Muetterties, E. L. *Inorg. Chem.* 1980, *20*, 946-947.
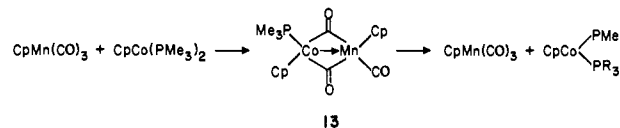
(5) Theopold, K. H.; Hersh, W. H.; Bergman, R. G. *Israel J. Chem.*, in press.

with benzene. After removal of the frozen solvent by sublimation, 2 was obtained as an air-stable green powder in 40% yield.[6,7] The spectral data—particularly the aromatic resonances that are typical of *o*-dialkylbenzenes and the upfield shift of the methylene carbons in the ^{13}C NMR—support the metallacyclic structure shown. However, close examination of the proton signal at δ 1.57 reveals that it is significantly broader, at 22 °C, than is the cyclopentadienyl signal at δ 5.10. In fact, cooling the sample to -80 °C results in the disappearance of the signal at δ 1.57 with formation of two new methylene doublets (J = 6 Hz).[8] This result is consistent with a fluxional process, having $\Delta G^\ddagger$ (-40 °C) = 10 ± 1 kcal/mol, involving interconversion of two (presumably boat) conformations of the metallacycle. Strong bending of the cyclohexene ring of 2 could, in the extreme, result in its being more accurately described as a π complex in which *o*-xylylene is bound to two cobalt atoms.[9a] However, evidence that this is not the case is provided by the similar methylene α-C–H coupling constants of 2 (J_{CH} = 139 Hz)[6] and the fully saturated five-membered ring dicobalt complex Cp(μ-CO)Co-CH(CH₃)(CH₂)₂-Co(μ-CO)Cp (J_{CH} = 135 Hz)[9b] which cannot adopt a π structure.

Some chemistry of 2 is summarized in Scheme II. Although 2 is relatively stable in comparison to 1, it does undergo clean first-order decomposition in solution (k = 4 × 10⁻⁵ s⁻¹, THF-d_8, 22 °C), giving CpCo(CO)₂ (4) and the previously unknown mononuclear *o*-xylylene complex 5.[10] While other metal complexes of *o*-xylylene (6) are known,[11] only those in the iron group[11a,e] may be considered (by virtue of the effective atomic number rule) to be π complexes of 6. In accord with this judgement, their ^{1}H NMR spectra are very similar to that of 5. Further evidence of the diene nature of the organic ligand in 5 is provided by the large (relative to 2) methylene C–H coupling constant of 156 Hz.[10] This value is the same as that observed in the corresponding 1,3-butadiene complex.[12]

A clean CO double insertion occurred when 5 was heated in the presence of carbon monoxide to give 2-indanone (7) in quantitative yield, a reaction which represents, to our knowledge, the first example of purely thermal CO insertion in an isolable diene complex.[13–15] In contrast, carbonylation of 2 gave rise to

(6) Data for 2: mp 109 °C dec; MS (field desorption), *m/e* 408 (M⁺); IR (benzene) 1855 (w), 1811 (s) cm⁻¹; ^{1}H NMR (THF-d_8, 22 °C) δ 6.81, 6.71 (AA′BB′, 4 H), 5.10 (s, 10 H), 1.57 (s, 4 H); ^{13}C NMR (CDCl₃, 0 °C) δ 147.8, 126.2 (d, J = 155 Hz), 124.2 (d, J = 160 H) (aromatic); 92.3 (d, J = 178 Hz, cyclopentadienyl); 6.7 (t, J = 139 Hz, methylene). Anal. Calcd for C₂₀H₁₈O₂Co₂: C, 58.84; H, 4.44; Co, 28.87. Found: C, 58.68; H, 4.55; Co, 28.6.

(7) Crystallization from toluene/pentane gave analytically pure fine black-green needles, but reproducible crystallizations in preparative quantities (to afford spectroscopically pure material) could only be accomplished from methylene chloride/pentane, giving crystalline material with mp 106 °C dec.

(8) ^{1}H NMR (THF-d_8, -80 °C) δ 6.83, 6.69 (2 br s, 4 H), 5.21 (s, 10 H), 2.71 (d, J = 6 Hz, 2 H), 0.22 (d, J = 6 Hz, 2 H).

(9) (a) Following submission of this paper, a complex was reported having the composition Rh₂(μ-CO)(π-cyclohexadiene)(η⁵-indenyl)₂; its X-ray structure shows the diene ligand is bound in π, rather than σ, fashion. It seems likely, on the basis of this observation and the effective atomic number rule, that the mode of bonding correlates with the number of carbonyl ligands attached to the metal centers. We are attempting to remove a single CO from 2 to determine whether this generates a monocarbonyl having a structure analogous to the dirhodium complex. Cf. Al-Obaidi, Y. N.; Green, M.; White, N. D.; Bassett, J.-M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1981, 494–496. (b) Yang, G. K.; Bergman, R. G. unpublished results.

(10) Data for 5: mp 63–64 °C; MS, *m/e* 228 (M⁺); ^{1}H NMR (THF-d_8) δ 7.4, 7.2 (AA′BB′, 4 H), 4.49 (s, 5 H), 2.65 (d, J = 2 Hz, 2 H), -0.78 (d, J = 2 Hz, 2 H); ^{13}C NMR (CDCl₃, undecoupled) δ 135.0 (d, J = 158 Hz), 127.3 (d, J = 161 Hz) ("aromatic"); 92.1 (s, quaternary); 79.7 (d, J = 176 Hz, cyclopentadienyl); 26.1 (t, J = 156 Hz, methylene). Anal. Calcd for C₁₃H₁₈Co: C, 68.43; H, 5.74; Co, 25.83. Found: C, 68.31; H, 5.68; Co, 25.7.

(11) (a) Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* 1967, 2053–2058. (b) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* 1980, 238–239. (c) Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *Ibid.* 1980, 476–477. (d) Lappert, M. F.; Martin, T. R.; Milne, C. R. C.; Atwood, J. L.; Hunter, W. E.; Pentilla, R. E. *J. Organomet. Chem.* 1980, *192*, C35–C38. (e) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* 1981, 319–320.

(12) ^{13}C NMR spectrum of CpCo(butadiene) (CDCl₃, undecoupled) δ 79.5 (d, J = 175 Hz, cyclopentadienyl), 78.3 (d, J = 167 Hz, methine), 30.9 (t, J = 157 Hz, methylene).

(13) For an insertion which requires the aid of a catalyst, see: Johnson, B. F. G.; Lewis, J.; Thompson, D. J. *Tetrahedron Lett.* 1974, 3789–3790.

Scheme III

13

a fast reaction at room temperature, but instead of CO insertion,[2] the only organic products observed were dimers 8 and 9 of *o*-xylylene (6). Phosphines induce a similar reaction,[16] leading to 8, 9, and phosphinecarbonyl complex 10 as final products.

Infrared monitoring of the reaction of 2 with triphenylphosphine revealed the presence of an unstable intermediate having a single carbonyl absorption at 1758 cm⁻¹ (benzene). Reactions of 2 with PPh₂Me, PPhMe₂, or PEt₃ were more striking: rapid disappearance of the carbonyl band of 2 was accompanied by formation of a single carbonyl band at about 1750 cm⁻¹ in each case. This band then slowly disappeared with concomitant formation of the band due to 10 as the final product. Examination of the reaction of 2 with PEt₃ by ^{1}H NMR spectroscopy showed rapid consumption of 2 with formation of 8 and 9 and a new organometallic product exhibiting two cyclopentadienyl resonances (δ 4.82, 4.65, toluene-d_8) of equal intensity and signals due to one bound phosphine. Similar NMR results were obtained with PMe₃,[17] PPhMe₂, and PPh₂Me. In the PPh₃ reaction only a single broad cyclopentadienyl peak was observed at room temperature, but cooling the sample to -30 °C gave rise to the two peaks[18] of the intermediate. A fluxional process[19] involving PPh₃ hopping between two cyclpentadienylcobalt moieties can account for this result.

The spectral properties of the intermediate are consistent with the dinuclear structure 11 shown in Scheme II. Two pieces of evidence provide additional support for this structure. First, addition of phosphines to the neutral metal–metal double-bonded dimer 12 gave an instantaneous color change from the blue-green color of 12 to dark green and then more slowly to the orange color of 10. Infrared and ^{1}H NMR spectra showed the same characteristic absorptions as were observed in the reactions of 2; the dark green color in the reaction of 12 is presumably due to 11. Support for this conclusion was obtained by NMR observation of the reaction between 12 and PPhMe₂; the NMR signals due to the transient green species were identical with those attributed to 11 formed from 2. This result also demonstrates that stepwise addition of a dative ligand to metal–metal multiple-bonded systems can occur.[20] Second, an isoelectronic manganese–cobalt complex (13, Scheme III) is known,[21] and it, like 11, exhibits an unusually low IR carbonyl absorption at 1757 cm⁻¹ (as well as a terminal CO band at 1902 cm⁻¹).

Experiments are now under way aimed at elucidating the mechanisms of these processes. Preliminary results on the kinetics

(14) The [Rh(CO)₂Cl]₂-catalyzed carbonylation of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0²,⁶]hexane to give 4,5,6,7-tetramethylindan-2-one may proceed via a transient *o*-xylylene complex: Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* 1976, *98*, 6040–6042.

(15) Reaction of carbon monoxide with CpCo(1,3-butadiene) resulted only in formation of free butadiene and CpCo(CO)₂.

(16) The organic products were easily separated, by chromatography on alumina, from the organometallic products when 1,2-bis(diphenylphosphino)ethane was the reactant, giving a 95:5 mixture of 8:9. 8: ^{1}H NMR (CCl₄) δ 7.00 (s, 4 H), 6.08 (d, J = 9 Hz, 1 H), 5.78 (m, 3 H), 4.98 (d, J = 12.5 Hz, 2 H), 2.85 (approximate AB q, J = 15 Hz, 4 H), 1.91, 1.76 (m, 2 H). 9: ^{1}H NMR (CCl₄) δ 6.88 (s, 8 H), 3.02 (s, 8 H). These spectra have been very briefly described: Errede, L. A. *J. Am. Chem. Soc.* 1961, *83*, 949–954.

(17) The PMe₃ adduct exhibited the best-resolved ^{1}H NMR spectrum (toluene-d_8): δ 4.85 (s, 5 H), 4.55 (d, J = 0.5 Hz, 5 H), 0.61 (d, J = 10 Hz, 9 H).

(18) ^{1}H NMR of PPh₃ adduct: (THF-d_8, -30 °C) δ 4.78, 4.65.

(19) T_c = 10 ± 5 °C, $\Delta G^\ddagger$ = 14.2 ± 0.3 kcal/mol.

(20) We are aware of only two examples of stepwise addition of dative ligands to multiple metal–metal bonded systems; in neither of these is the overall bond order reduced, and in at least one[20b] the mechanism is dissociative: (a) Wachter, J.; Mitschler, A.; Reiss, J. G. *J. Am. Chem. Soc.* 1981, *103*, 2121–2123. (b) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H. *Ibid.* 1981, *103*, 3953–3955.

(21) Leonhard, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 649–650.

of the reactions of **2** with phosphines indicate that a complicated mechanism, probably involving two phosphine-trappable intermediates in thermal equilibrium with **2**, is operative. Significantly, the reaction of **2** with phosphines is the first dimetallacycle transformation we have found in which the organometallic fragment is extruded in dinuclear form. This result provides a unique opportunity to employ crossover experiments to determine whether the two metal centers remain associated with each other during the reaction; i.e., whether the *o*-xylylene extrusion is truly a dinuclear elmination reaction. The outcome and interpretation of these experiments will be reported in a full paper.

ESR Detection of the Dimethyl Ether Radical Cation

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Despite their great importance as reaction intermediates, comparatively few oxygen-centered radicals have been characterized by ESR spectroscopy.[1,2] Here we report the radical cation of dimethyl ether, $(CH_3)_2O^+$, which is isoelectronic with the dimethyl aminyl radical $(CH_3)_2N$.[3-5] As far as we are aware, this is the first example of an oxygen-centered radical cation where the unpaired electron is not delocalized into an aromatic ring system as in the case of the anisole[6] and dimethoxybenzene[7] radical cations.

Bearing in mind the high reactivity of alkoxyl radicals in hydrogen atom abstraction reactions,[8] the dimethyl ether cation radical would be expected to react avidly with any potential hydrogen donor. This expectation is borne out by the very large rate constant of 1.9×10^{-9} cm^3 molecule^{-1} s^{-1} (1.1×10^{12} L mol^{-1} s^{-1}) measured for the gas-phase ion–molecule reaction of $(CH_3)_2O^+$ with $(CH_3)_2O$ to form the dimethyloxonium cation $(CH_3)_2OH^+$,[9] the reaction occurring essentially on every collision. Thus, $(CH_3)_2O^+$ would probably be difficult to detect if generated in a hydrogen-containing solvent or matrix. This problem has been avoided by using a γ-irradiation technique[10-12] which allows the radical cation to be generated through positive charge transfer from a Freon matrix to the dimethyl ether solute, the method satisfying the requirement that the $(CH_3)_2O^+$ species be trapped in a chemically inert environment.

Figure 1 shows the first-derivative and second-derivative ESR spectra obtained from a γ-irradiated solid solution of dimethyl
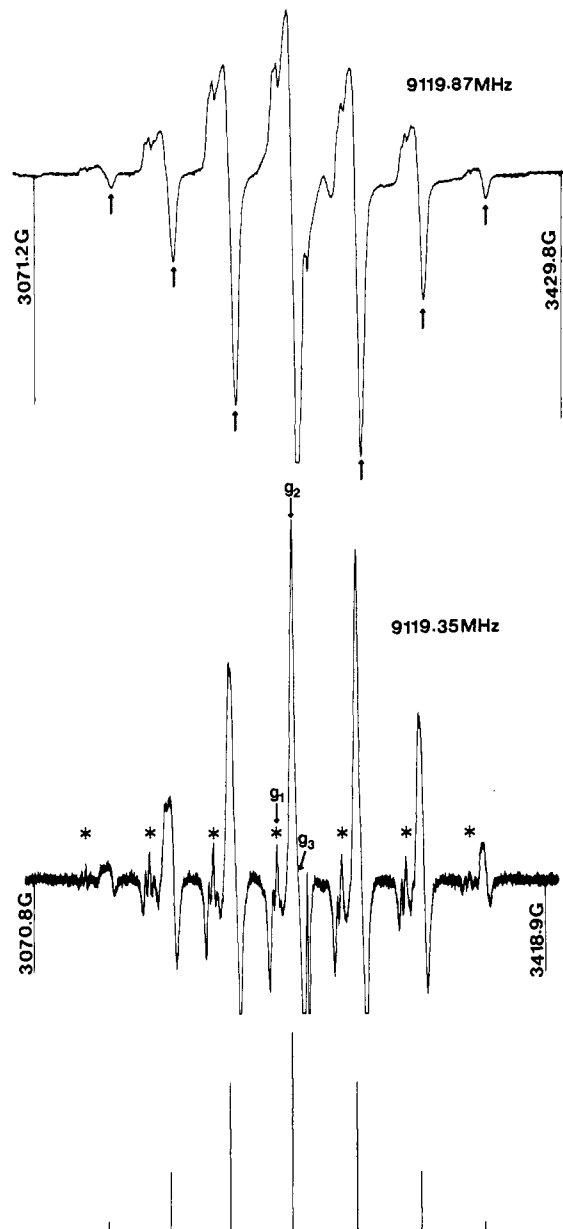

Figure 1. First-derivative (upper) and second-derivative (lower) ESR spectra of a γ-irradiated solid solution of 5 mol % dimethyl ether in trichlorofluoromethane recorded at 97 K after irradiation (dose, 1 M rad) at 77 K. The stick diagram shows the seven hyperfine components from the dimethyl ether radical cation, the anisotropy in the line positions extending between the two sets of features marked by asterisks (lower spectrum) and arrows (upper spectrum). The larger signal amplitudes for the high-field lines are due to a line-narrowing effect resulting from $g_1 > g_3$ and $A_1 > A_3$ (see text).

Table I. ESR Parameters for the Dimethyl Ether Radical Cation in a Freon 11 Matrix at 97 K

components of g tensor and g_{iso}	^{1}H hyperfine couplings, G
$g_1 = 2.0138$	$A_1 = 43.6$
$g_2 = 2.0072$	$A_2 = 42.8$
$g_3 = 2.0045$	$A_3 = 42.5$
$g_{iso} = 2.0085$	$a_\beta(6H)^a = 43.0$

^{a} Isotropic coupling = $(1/3)(A_1 + A_2 + A_3)$.

ether in trichlorofluoromethane (Freon 11) at 97 K. The first-derivative spectrum consists of seven lines with approximately binomial intensity ratios (1:6:15:20:15:6:1) as expected for hyperfine interaction with six equivalent ^{1}H ($I = ^1/_2$) nuclei. Each line in the binomial pattern is asymmetrically broadened, and this

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(10) Grimison, A.; Simpson, G. A. *J. Phys. Chem.* **1968**, *72*, 1176.
(11) (a) Shida, T.; Nosaka, Y.; Kato, T. *J. Phys. Chem.* **1978**, *82*, 695. (b) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963.
(12) Wang, J. T.; Williams, F. *J. Phys. Chem.* **1980**, *84*, 3156.