Figure 2. Proposed structure of $Co_4(CO)_{11}P(OCH_3)_3$. It is uncertain which of the two possible terminal positions on a basal Co is occupied by $P(OCH_3)_3$.

strongly resembles in gross outlines the solution spectrum in the 2100–1800-cm^{-1} region. (The absorptions are too broad for detailed comparisons.) The ir results thus do not support the hypothesis that there exists a mixture of two forms.

Thus, the evidence presently available leads to the conclusion that $Co_4(CO)_{12}$ is almost surely of C_{3v} symmetry in solution. The sole piece of contrary evidence is the relative intensities of the ^{13}C NMR lines in solution. Evans et al. allude to the difficulties in interpretation of the relative intensities in cobalt carbonyl systems, as a result of the scalar relaxation of ^{13}C spins resulting from rapid ^{59}Co quadrupolar relaxation. However, we experienced no difficulties in assigning reasonable relative intensities in the $Co_4(CO)_{11}P(OCH_3)_3$ spectrum. The origin of the ^{13}C NMR intensity anomaly remains unclear.

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(5) The sample was enriched by stirring, at room temperature, a hexane solution of $Co_4(CO)_{11}P(OCH_3)_3$ under 1 atm of 29% enriched ^{13}CO for 7 days. The Ir showed no sign of reversion to $Co_4(CO)_{12}$ during enrichment.
(6) Spectra were recorded using a Varian Associates XL-100 FT NMR spectrometer. The ^{13}C lines of $Co_4(CO)_{11}P(OCH_3)_3$ broaden and apparently lose intensity at higher temperatures. The spectrum becomes essentially unobservable above −5°. However, it is not possible to conclude reliably from the observed line shape changes that exchange is occurring.
(7) We have examined the ^{13}C NMR spectrum of 12% ^{13}CO enriched $Co_4(CO)_{12}$ in $HCFCl_2$–CD_2Cl_2 mixed solvent in the temperature range −95 to −30°. In agreement with Evans et al., we observe three peaks of approximately equal intensity at 244.0, 196.0, and 192.0 ppm. At higher temperatures the lines broaden and eventually become unobservable at about −20°. The line at 244 ppm broadens less rapidly than the other two. Unfortunately, it is not possible to state with any certainty that any of the observed line shape behavior is due to effects other than scalar relaxation of the second kind.^{8,9}
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1-Amino-2-azadienes from the Thermolysis of 2-Amino-1-azirines. New Reagents for the Construction of Pyridine and Dihydropyridine Rings

Sir:

As part of our studies on the reactivity and synthetic uses of 2-amino-1-azirines,[1-3] we have observed a smooth thermal isomerization of 2-dimethylamino-3,3-dimethyl-1-azirine (**1**) to 1-dimethylamino-3-methyl-2-azabutadiene (**2**), an activated isoprene which is a useful reagent for the synthesis of pyridines or dihydropyridines.

Slow evaporation of **1** through an 80-cm hot glass tube (340°, 0.1 Torr) filled with glass beads gave a colorless liquid (97%) which was shown by NMR to be **2** (purity 95%). The NMR spectrum (100 Mhz, $CDCl_3$) showed signals at δ 7.40 (s, 1 H), 4.12 and 4.24 (m, 2 H, J_{gem} = 2 Hz), 2.93 (s, 6 H), and 1.87 (3 H, J_{allyl} = 1.5 Hz). The structure of **2** was confirmed by mass spectral (M^+, m/e 112) and ir data (strong bands at 1633 and 1610 cm^{-1}) as well as by hydrolysis to acetone and N,N-dimethylformamidine (identified as its picrate).
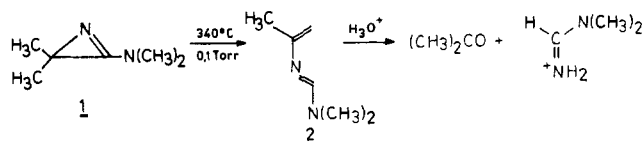
The aminoazirine, **3**, exhibited an analogous behavior and rearranged in high yields (>95%) at 400° to diene **4**: M^+, m/e = 152; ir (CCl_4) 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.38 (s, 1 H), 5.07 (m, 1 H), 2.90 (s, 6 H), 2.10, and 1.63 (m, 8 H).
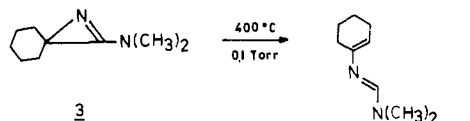
These thermal rearrangements are similar to that of 2-phenyl-3,3-dimethyl-1-azirine reported[4] by Wendling and Bergman but occur at lower temperatures (already from

**Table I.** Reactions of 1-Amino-2-azadienes with Olefins and Acetylenes

Diene	Dienophile	T, °C	Product[a]	Yields, %[b]
2	MeOOCC≡CCOOMe	−20		58
2	MeOOCC≡CH	−20		72
2		0		35
2	MeOOC C=C COOMe H H	−20		43
4	MeOOCC≡CH	20		30

[a] All spectral data (NMR, ir, mass) of the isolated products were consistent with the assigned structures. Elemental analysis within 0.3% have been obtained for each adduct. [b] Yields were determined by VPC.

250°) and in higher yields. They are of preparative interest since they provide a simple and efficient route to reactive heterodienes[5] from starting materials **1** and **3**, which are readily available in large quantities from tertiary carboxamides (overall yield, four steps: 60–70%).[1,3a]

The synthetic potential of 1-amino-2-azadienes, **2** and **4**, is illustrated by their facile cycloadditions to electrophilic olefins and acetylenes followed by loss of dimethylamine to yield dihydropyridine or pyridine rings (Table I).

In a typical experiment, 0.654 g (5.84 mmol) of crude **2** directly obtained from the pyrolysis of **1** was slowly introduced into 1.66 g (11.7 mmol) of dimethylacetylene dicarboxylate in 20 ml of CH_3CN at −20°. After 1 hr, the dark brown reaction mixture was concentrated in vacuo. The yield as shown by GLPC analysis was 58%. Bulb to bulb distillation followed by fractional crystallization from benzene–cyclohexane gave pure 2-methyl dimethylcinchomerate (0,572 g, 47%).
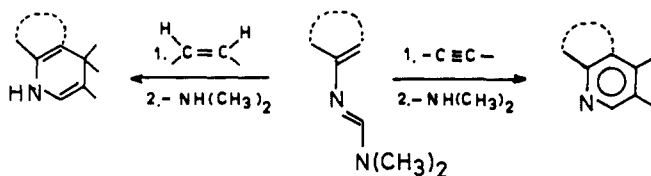
Further investigations concerning the synthesis of 1-amino-2-azadienes through rearrangements 2-amino-2H-azirines and their use as cycloaddition partners are in progress and will be described in future publications.

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Received March 11, 1975

Carbon-13 Magnetic Resonance of Allyl, Pentadienyl, and Arylmethyl Carbanions. Empirical Calculation of π-Electron Densities

Sir:

Proton[1,2] and carbon[1,3-6] chemical shifts have been found to be proportional to π-electron densities in aromatic systems. For proton shifts, the proportionality constant is approximately 10 ppm/electron. This constant has been used to estimate the π-densities at the ortho, meta, and para positions for arylmethyllithiums, and they agree well with the values derived from SCF calculations.[7] For carbon-13 shifts, the proportionality constant is approximately 160 ppm/electron.[1,3,5,6,8] For the cyclic, aromatic systems used
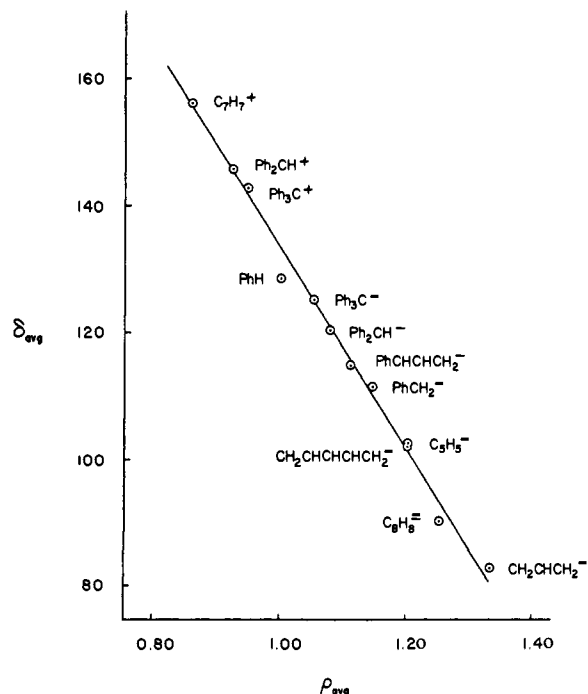

Figure 1. Correlation of average carbon-13 chemical shift with π-electron density.

in the correlation, the π-electron density at the equivalent carbons is defined as the number of π-electrons divided by the number of π-carbons (e.g., $C_5H_5^-$, $\rho = 1.20$; C_6H_6, $\rho = 1.00$; $C_7H_7^+$, $\rho = 0.86$). It has been implied that this linear shift relationship is applicable only to sp^2 carbons in cyclic, aromatic systems. However, theoretical calculations indicate that it might be more widely applied to sp^2 hybridized carbons in planar, conjugated systems.[10]

We wish to report the carbon-13 shift values for allylpotassium, pentadienylpotassium, 1-phenylallylpotassium, benzylpotassium, diphenylmethylpotassium, and triphenylmethylpotassium. Allylpotassium, pentadienylpotassium, 1-phenylallylpotassium, and benzylpotassium were prepared in ~0.5 M solutions in tetrahydrofuran (THF) by direct metalation of propene, 1,4-pentadiene, allylbenzene, and toluene with trimethylsilylmethylpotassium as previously described.[11] Diphenylmethylpotassium and triphenylmethylpotassium were prepared by the reaction of the hydrocarbons with potassium sand in THF. The carbon-13 shifts for these carbanions are presented in Table I.

The spectrum of allylpotassium shows two resonances, one at δ 52.8 for the terminal carbons and one at δ 144.0 for the central carbon. The spectrum of benzylpotassium shows upfield shifts for the ortho and para carbons, a downfield shift for the substituted ring carbon, and only slight change for the meta carbons when compared to the corresponding shifts for toluene. Similar chemical shift trends are seen for pentadienylpotassium, 1-phenylallylpotassium, diphenylmethylpotassium, and triphenylmethylpotassium (see Table I). The changes in the aryl carbons indicate a substantial amount of charge delocalization into the ring(s). The benzylic carbon of benzylpotassium is observed at δ 52.7, a 31.2 ppm downfield shift compared to the methyl of toluene. Further, the ortho carbons are nonequivalent for benzylpotassium compounds in which the benzylic substituents are not the same such as 1-phenylallylpotassium, α-methylbenzylpotassium,[13] and α-trimethylsilylbenzylpotassium.[11] These results show that the benzylic and allylic carbons in these carbanions are most probably sp^2 hybridized and that there is considerable double bond character in the benzyl carbon–aryl carbon bond.