mixed anhydride can occur to a minor (20%) extent, if at all.

In conclusion, the use of optically active dehydrating agents permits the detection of acylating agents other than anhydrides and provides a new method for kinetic resolution. Applied to the carbodiimide reaction, the results emphasize that the actual acylating agent is very much a function of reaction conditions. Alternatively, the use of polymer-bound reagents allows the detection of anhydrides (and other reaction intermediates[10]) and shows the symmetrical anhydride to be the acylating agent in the acid–isocyanate reaction.

Acknowledgment. This work was supported by NIH Grant GM 22044.

References and Notes

(1) R. B. Merrifield, A. R. Mitchell, and J. E. Clarke, *J. Org. Chem.*, **39**, 660 (1974).

(2) J. Rebek in "Peptides, 1974", Proceedings of the 13th European Peptide Symposium, Y. Wolman, Ed., in press.

(3) Satisfactory elemental analyses and expected spectroscopic features were obtained for all new compounds. The carbodiimide derived from the (+) amine boils at 120° (bath temp) (04 mm) and shows $[\alpha]^{25}\mathrm{D}$ −14.5° (*c* 2, acetone).

(4) The first reaction reflects conditions of solid phase peptide synthesis; the second has been recommended for solid phase synthesis in cases where diketopiperazine formation is a competing reaction (B. F. Gisin and R. B. Merrifield, *J. Am. Chem. Soc.*, **94**, 3012 (1972)); the final conditions are those of peptide synthesis in solution.

(5) Control experiments established that no fractionation of racemate and enantiomer occurred during the isolation of the benzamide product (distillation). The benzamide of (+)-α-phenylethylamine (L. Skulski, G. Palmer, and M. Calvin, *Rocz. Chem.*, **38**, 789 (1964)) showed $[\alpha]^{25}\mathrm{D}$ −104° (*c* 1, DMF).

(6) The *O*-benzoylisourea reacts preferentially with the amine of the same absolute configuration.

(7) For a review see S. Goldschmidt and H. Krauss in "Newer Methods of Preparative Organic Chemistry", W. Foerst, Ed., Academic Press, New York, N.Y., 1963, p 31.

(8) Resins of differing mesh size were used and separated after reaction by screening. Direct reactions between the two solid phases have been shown to be negligible in related cases, and acyl transfer to P_2 occurs even when the two resins are separated by a glass frit.

(9) Our preference for the anhydride (rather than the acyl pyridinium species) in Scheme III is based on the observation of acyl transfer between the two resins even when toluene is used as a solvent. However, the acylpyridinium species is quite likely in the solvent shown.

(10) J. Rebek and F. Gavina, *J. Am. Chem. Soc.*, **96**, 7112 (1974); J. Rebek, D. Brown, and S. Zimmerman, *ibid.*, **97**, 454 (1975).

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The Structures of $Co_4(CO)_{12}$ and $Co_4(CO)_{11}P(OCH_3)_3$ in Solution[1]

Sir:

The recent discussion by Evans et al.[2] of the structure of $Co_4(CO)_{12}$ in solution prompts us to report data recently obtained. The question at hand is whether $Co_4(CO)_{12}$ has C_{3v} or D_{2d} molecular symmetry in solution. In the solid state the structure corresponds to idealized C_{3v} point group symmetry.[3] On the other hand, the low temperature ^{13}C NMR spectrum reported by Evans et al. consists of only three lines of roughly equal intensity, corresponding to one bridging and two terminal environments. These results are consistent only with a structure possessing D_{2d} symmetry.

We have prepared ^{13}CO enriched (~13%) $Co_4(CO)_{11}P(OCH_3)_3$,[4,5] and examined its ^{13}C NMR spectrum. The spectrum in CD_2Cl_2 at −82° is shown in Figure 1A.[6] Comparison with the previously reported ^{13}C NMR spectrum of $Co_4(CO)_{12}$[2,7] is displayed in Table I.[7]

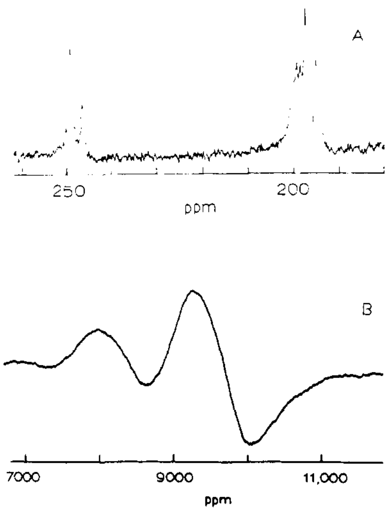

Figure 1. (A) ^{13}C FT NMR spectrum of $Co_4(CO)_{11}P(OCH_3)_3$ in CD_2Cl_2 at −82°. (B) ^{59}Co NMR spectrum of $Co_4(CO)_{12}$ in hexane at room temperature.

Table I. ^{13}C Chemical Shifts[a] in $Co_4(CO)_{11}P(OCH_3)_3$ and $Co_4(CO)_{12}$

$Co_4(CO)_{11}P(OCH_3)_3$ (−82°)			$Co_4(CO)_{12}$ (−60°)[2]
Shift	Rel int	Assignment	Shift
248.2	2	Bridging	243.1
245.6	1		
198.0 197.2	3	Basal, terminal	
196.1	3	Apical	195.9
193.7	2	Basal, terminal	191.9

[a] Downfield of TMS.

The most unequivocal result from the spectrum shown in Figure 1A is that the bridging CO resonances are in the relative intensity ratio 3:8 with respect to all the other CO's. Secondly, there are two bridging CO groups in the ratio 1:2. This strongly suggests that $Co_4(CO)_{11}P(OCH_3)_3$ is derived from the C_{3v} structure of $Co_4(CO)_{12}$, with a terminal CO group of one of the basal Co atoms replaced by $P(OCH_3)_3$, Figure 2. Furthermore, the bridging CO furthest removed from the substitution, relative intensity 1, is very close in chemical shift to the bridging CO groups of $Co_4(CO)_{12}$. Because the chemical shifts of the remaining CO groups are rather closely grouped, additional correlations between the two compounds are uncertain.

The ^{59}Co NMR spectrum of $Co_4(CO)_{12}$ has been reported twice previously.[10,11] Because of discrepancies in the reported chemical shifts we have obtained the ^{59}Co NMR spectrum at 30° in the saturated hexane solution at a higher field (~0.2 T) than previously, using a Varian WL-115 spectrometer. The spectrum is shown in Figure 1B. It is evident that there are two distinct Co resonances in roughly 1:3 intensity ratio. These occur at chemical shifts of 8400 and 9670 ppm upfield relative to $Co(NH_3)_6Cl_3$ in saturated aqueous solution as external standard.[12] These results strongly suggest that the C_{3v} form is predominant at room temperature.

An alternative possibility is that the two ^{59}Co absorptions correspond to C_{3v} and D_{2d} forms, present in roughly 1:3 ratio, respectively. This interpretation, however, is inconsistent with ir evidence. The ir spectrum of $Co_4(CO)_{12}$ in hexane at room temperature[13] shows six terminal and two bridging CO stretching absorptions. The matrix isolation spectra in Ar or N_2 at 30 K[14] are essentially identical with the room temperature solution spectra. For a C_{3v} species molecule a total of eight ir-active CO stretching modes is predicted. Finally, a KBr pellet spectrum of $Co_4(CO)_{12}$

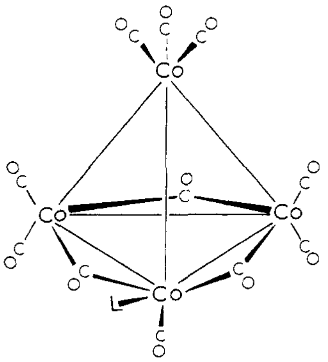

Figure 2. Proposed structure of $Co_4(CO)_{11}P(OCH_3)_3$. It is uncertain which of the two possible terminal positions on a basal Co is occupied by $P(OCH_3)_3$.

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.

References and Notes

(1) This research was supported by the National Science Foundation through Research Grant MPS-71-03201.

(2) J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Am. Chem. Soc.*, **97**, 1245 (1975).
(3) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).
(4) (a) D. Labroue and R. Poilblanc, *C.R. Acad. Sci.*, **271**, 1585 (1970); (b) D. Labroue and R. Poilblanc, *Inorg. Chim. Acta*, **6**, 387 (1972).
(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]
(8) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961, Chapter 8.
(9) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y., 1971, p 60.
(10) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).
(11) H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **29**, 693 (1967). The shift data reported in Table I of this reference are low by a factor of ten. The spectrum in Figure 2 of the reference is, however, correct except for a sign error in the shift scale. The corrected values for $Co_4(CO)_{12}$ are 8490 and 9820 ppm, relative to $Co(NH_3)_6Cl_3$.
(12) R. L. Martin and A. H. White, *Nature* (*London*), **223**, 394 (1969).
(13) G. Bor, *Spectrochim. Acta*, **19**, 1209 (1963).
(14) R. Sweany and T. L. Brown, unpublished observations.

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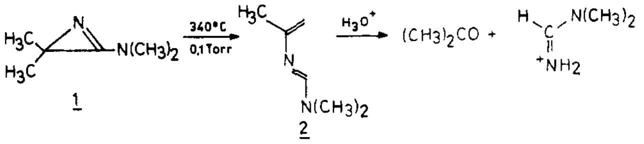
1-Amino-2-azadienes from the Thermolysis of 2-Amino-1-azirines. New Reagents for the Construction of Pyridine and Dihydropyridine Rings

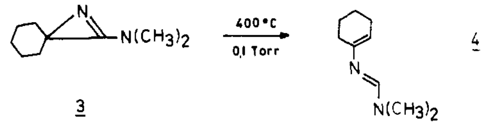
Sir:

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** (purity95%). 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).

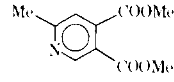
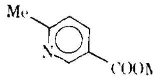
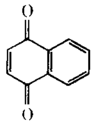
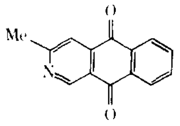
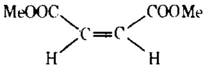
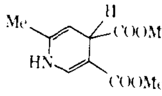
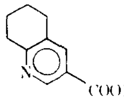


The aminoazirine, **3**, exhibited an analogous behavior and rearranged in high yields (>95%) at 400° to diene **4**: M^+, *m/e* = 152; ir (CCl_4) 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.38 (s, 1 H), 5.07 (m, 1 H), 2.90 (s, 6 H), 2.10, and 1.63 (m, 8 H).



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	$MeOOCC\equiv CCOOMe$	−20		58
2	$MeOOCC\equiv CH$	−20		72
2		0		35
2		−20		43
4	$MeOOCC\equiv CH$	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.