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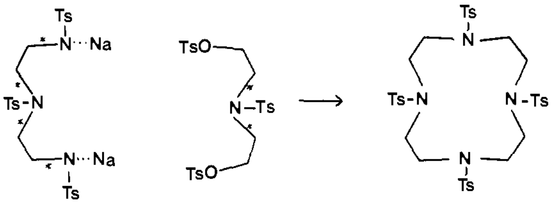
Formation of Large Rings, Internal Metalation Reactions, and Internal Entropy Effects

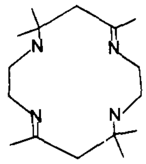
Sir:

In order to induce long open-chains with α- and ω-functional groups to condense internally into large rings it is generally necessary to use either (1) a dilution technique or (2) a template effect, otherwise long open-chain structures are formed.[1,2] However, there are a few instances where large rings are preferentially formed in the absence of either (1) or (2) and which have not been explained hitherto. Three examples, (a), (b), and (c), where this occurs are as follows. (a) The 12-membered ring derivative of 1,4,7,10-tetraazacyclododecane (**1**, Ts = p-toluenesulfonyl) is formed in 80% yield from **2** and **3**. Many analogs were similarly synthesized, no dilution being necessary, and a template effect was ruled out since tetramethylammonium could be used as a cation in place of sodium.[3] (b) Similarly the 14-membered ring (**4**) is formed in high (75%) yield from mesityl oxide and ethylenediamine monoperchlorate.[4] (c) It has been shown that long chain diphosphines, t-Bu$_2$P(CH$_2$)$_n$P-t-Bu$_2$ ($n = 9$, 10, or 12) give large ring metal chelate compounds (12- to 45-membered rings) in preference to open-chain polynuclear species even after long reaction times under vigorous conditions (12 hr, 125°). Analogous diphosphines with less bulky end groups (e.g., Ph) preferentially give open-chain polynuclear complexes.[5]



2 3 1

Enthalpy, external entropy, and internal entropy effects will influence whether a large ring is formed or not. In particular internal entropy is lost on cyclization and if the loss is large it will tend to favor the formation of open-chain products. It is suggested that the factor which distinguishes examples (a), (b), or (c) from the great majority of cases where cyclization is not preferred is the unusually small internal entropy of the open-chain intermediates and therefore the unusually small loss on cyclization.[6] Thus in (a) the bulky p-toluenesulphonyl groups in **2** and **3** restrict rotation about the six bonds marked with an asterisk and therefore the loss in internal entropy on cyclization to **1** is small. Similarly one would expect the *gem*-dimethyl and methyl substituents and the C=N double bonds to restrict rotation in the open-chain intermediates involved in the formation of **4**.[7] A small loss in internal entropy could also be an important factor in the conversion of α,ω-diacetylenes to macrocycles by oxidative coupling since the internal entropy of the linear C⋮CC or -CC⋮C-C⋮CC- systems is low.[8]



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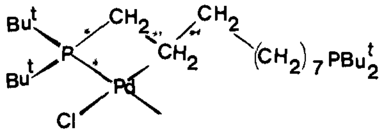

5

There is abundant ^{31}P and ^{1}H NMR evidence for restricted rotation about P-metal bonds in P-t-Bu$_2$R-metal complexes.[9,10] Space filling molecular models show that on complexing one end of a diphosphine such as t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$ to a metal halide such as PdCl$_2$ there will be severely restricted rotation around the bonds marked with an asterisk (**5**) and that the preferred orientation around the bonds marked with a double asterisk or asterisk (**5**) is the same as that found for the structures of *trans*-[IrCl(CO){t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$}][11] or *trans*-[PdCl$_2${t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$}]$_2$[12] and *trans*-[RhCl(CO)-t-Bu$_2$P(CH$_2$)$_{10}$P-t-Bu$_2$]$_2$[11] by X-ray diffraction. Similar restrictions would occur at the other end of a CH$_2$CH$_2$P-t-Bu$_2$-metal system. These effects would favor cyclization. In the formation of very large ring binuclear (or trinuclear) species, similar arguments would apply.

The above arguments are in part extensions of some which have been put forward,[13,14] to explain the so-called "Thorpe-Ingold" or "*gem*-dimethyl" effect for small (≤seven-membered) rings.[15,16] It is now well-established that *gem*-dimethyl or similar groups cause remarkable stabilization of small rings and also increase the rate at which small rings are formed.[15,16] For similar steric effects to operate with an atom much larger than carbon, such as phosphorus, one would expect more bulky groups such as *tert*-butyl to be necessary; i.e., for phosphorus we would have "a *gem*-*tert*-butyl" effect.

We have also demonstrated that steric effects are important in internal metalation reactions of tertiary phosphines or tertiary arsines;[17] e.g., -P-t-Bu$_2$- or -As-t-Bu$_2$- derivatives are readily metalated under conditions where the corresponding -PMe$_2$- or -AsMe$_2$- derivatives are not—another example of a "*gem*-di-*tert*-butyl" effect. Similarly

Me_2NCH_2Ph is rapidly metalated in the ortho position by the chloropalladate(II) ion whereas H_2NCH_2Ph is not metalated,[18] a "*gem*-dimethyl" effect. In these metalation reactions the formation of four-, five-, or six-membered rings is presumably promoted by enthalpy, entropy, and conformational effects which are analogous to those of the "Thorpe–Ingold" or "*gem*-dimethyl" effect. Masters[19] has shown that 3,3-dimethyl-pent-1-ene undergoes platinum catalyzed hydrogen/deuterium exchange at position 5. This presumably involves metalation of carbon atom 5 which could have been promoted by the *gem*-dimethyl group.

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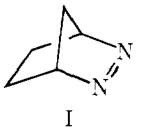
An Electron Spin Resonance Study of Matrix Isolated 1,3-Cyclopentadiyl, a Localized 1,3-Carbon Biradical[1]

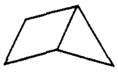
Sir:

Short-chain localized carbon biradicals, particularly 1,3- and 1,4-biradicals, have been postulated as reaction intermediates with increasing frequency during the last decade.[2] In spite of their importance in mechanistic chemistry no direct detection of these molecules by physical methods has been reported.[3] In this communication we wish to present the results of an electron spin resonance study of a biradical of this type, 1,3-cyclopentadiyl (II).



I

II



III

When a dilute solution (~1% w/v) of 2,3-diazabicyclo[2.2.1]heptene-2 (I) in cyclohexane is rapidly frozen to a glassy matrix and irradiated at 5.5°K with ultraviolet light, a well defined ESR spectrum can be observed (Figure 1, upper trace).[4] At that temperature the spectrum persists after irradiation has been ceased although the intensity diminishes with a half-life of ~30 min. The ESR transitions can be described by the usual spin Hamiltonian for triplet states with fine structure parameters of $D/hc = -0.084$ cm^{-1} and $E/hc = \pm 0.0020$ cm^{-1}.[5] In addition to fine structure, hyperfine structure is also evident, particularly in the half-field transition. The assignment of the carrier of the spectrum to II is based on the zero-field splitting parameters and the change of the hyperfine structure with deuteration of I. The zero-field splitting parameters were calculated for an idealized planar structure of II with a bond angle of 110° at the carbon separating the two trivalent carbon atoms, and a C–C bond length of 1.52 Å. Including only the two-center interaction and using the semiempirical method suggested by van der Waals and Ter Maten for the evaluation of the integral, one obtains $D/hc = -0.106$ and $E/hc = 0.0055$ cm^{-1}.[6,7]

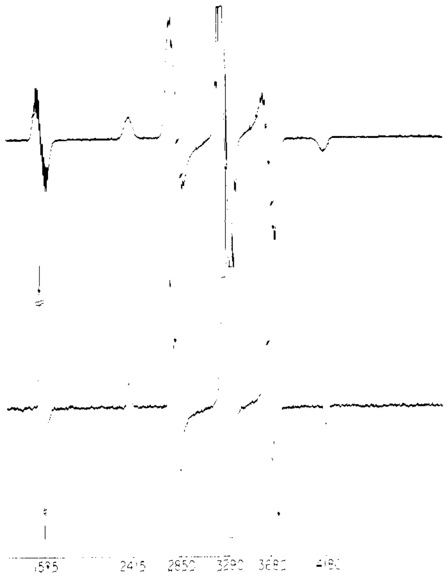


Figure 1. ESR spectra of II (upper trace) and II-d_8 (lower trace). Klystron frequency 9.204 GHz. In each case, the strong monoradical absorption at 3290 G was produced from the biradical by a secondary photoprocess.

The reasonable agreement between experiment and calculation for *D* is strong support for II being the carrier of the spectrum. As is usually the case the agreement for *E* is much poorer.[6] This discrepancy is at least partly due to the approximations inherent in the calculation but might also be caused by a slight deviation from planarity.

Although a large number of hyperfine lines are resolved, there are too many protons to obtain an unambiguous assignment of the coupling constants. To eliminate the possibility of a biradical derived from I in which only one C–N bond has been cleaved the spectrum of II-d_8 was examined (Figure 1, lower trace). The observed narrowing of the fine structure transitions is completely accounted for by replacing proton hyperfine with deuterium hyperfine coupling, thus eliminating any possibility of sizable nitrogen coupling.

The spectrum of II persists down to 1.3°K making it highly probable that II has a triplet ground state. In this connection it is of interest that preliminary CIDNP results obtained on benzophenone sensitized photolysis of I in solution at 300°K also support a triplet ground state for II. This conclusion is based on the observation of enhanced absorption for all NMR transitions of bicyclo[2.1.0]pentane (III), indicating predominant mixing of the upper Zeeman level of the triplet state with the singlet state of II.[8]

The decay kinetics of II and II-d_8 are highly unusual.[9] In several matrices, including microcrystalline I, the decay of the ESR signal is nonexponential over the whole tempera-