to a reduced catalytic viability of the complex.

Conclusions

(1) Although each ligand (**1c**, **4a**, and **5**) associates strongly with Zn^{2+}, the complexes are probably not exclusively tricoordinated under conditions where catalysis is evident since NMR studies show a dynamic behavior.

(2) The visible absorption spectra of **5**·Co(II)–Cl_x show formation of two different tetrahedral complexes as a function of pH. The spectrum is also anion dependent, indicating that these associate with the metal to form tetrahedral or 5-coordinate complexes. The **4a**·Co(II) absorption spectrum shows only a small amount of tetrahedral species.

(3) Catalytically the Zn^{2+} complexes of **1c**, **4a**, and **5** accelerate the attainment of $HCO_3^- \rightleftarrows CO_2$ equilibrium. The maximum catalytic rate constants are 900 $M^{-1}\ s^{-1}$, 1500 $M^{-1}\ s^{-1}$, and 2700 $M^{-1}\ s^{-1}$, respectively, and show that accessibility of $HCO_3^-(CO_2)$ to the Zn^{2+} and a hydrophobic metal environment are both important features for catalysis. Anions inhibit the reaction by associating with the metal which prevents access of the reactants.

(4) The rate of attainment of equilibrium increases as a function of $[HCO_3^-]$ in a manner indicative of a saturation behavior.

(5) Initial rate measurements to determine the rate constant for HCO_3^- cannot be made due to the inability to obtain the buffer factors under the experimental conditions.

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Registry No. 4a, 89210-50-4; **4b**, 89210-51-5; **5**, 89210-52-6; 6, 84802-87-9; CA, 9001-03-0; *N*-(dimethoxymethyl)-4,5-diisopropylimidazole, 74483-01-5; chlorobis(*N*-dimethoxymethyl)-4,5-diisopropyl-2-imidazolyl)phosphine, 89210-53-7; *N*-(diethoxymethyl)-4,5-di-*n*-propylimidazole, 89210-54-8; 4,5-di-*n*-propylimidazole, 24363-69-7; bicarbonate, 71-52-3.

Communications to the Editor

Mills–Nixon Effect, a Resolution: Clear Evidence for No Significant π-Bond Localization in Small Ring Annelated Aromatics. The Synthesis and Diatropicity of Cyclobutane Annelated Dihydropyrenes[1]

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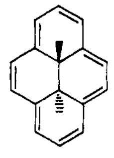
Received September 22, 1983

Mills and Nixon postulated over 50 years ago[3] that the strain of fusing a five-membered ring onto a benzene ring caused partial π-bond localization in the aromatic system. This hypothesis initiated many synthetic and spectroscopic papers attempting to prove or disprove the effect.[4] The problem was given new impetus by theoretical predictions,[5] and this led to the synthesis of a variety of benzocyclopropenes[4e] and benzocyclobutenes,[4g] including bis- and tris-annelated derivatives,[4g,h,l] annelated heterocyclic aromatics,[4f,j] and annelated naphthalenes.[4i,k] These have been subject of considerable analysis, for example, by ^1H and ^{13}C NMR, both coupling constants and chemical shifts,[4b,c,g,i,l] by ultraviolet spectroscopy,[4g,i,l] and by X-ray crystallography,[4d,h,k] and have also been the subject of theoretical calculations.[4c]

Although changes in both the physical and chemical properties of such compounds were observed and have been explained on the basis of rehybridization,[6] no experiment has yet shown whether a measurable degree of double bond localization occurs. This is in part due to the fact that a molecule such as benzene or naphthalene is not very readily probed in terms of π-electron delocalization.



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Dimethyldihydropyrene **1** on the other hand is.[7] The chemical shift of the internal methyl groups of **1** (δ −4.25) is very sensitive to the degree of delocalization in the macrocyclic ring, and we have shown[8] that the chemical shift shielding (Δδ) of the internal methyl protons of **1** is related to the average deviation in π-SCF bond order (Δ*r*)[9] by eq 1. While this equation was derived by

$$\Delta\delta = 5.533 - 0.02752\Delta r \qquad (1)$$

study of a number of benzannelated annulenes, we have conclusively shown[8] that the anisotropy effects of the annelating rings are small relative to effects caused by changes in delocalization. Moreover, dihydropyrenes with only external alkyl groups or saturated annelated rings would not be expected to cause sub-

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[1] Annelated annulenes Part 10. For part 9, see: Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Org. Chem.* **1982**, *47*, 5210.

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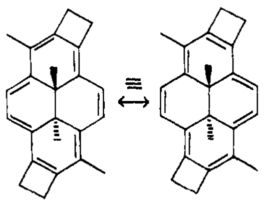
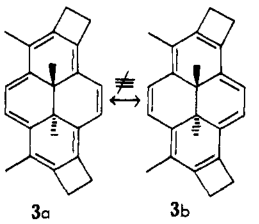
[7] Mitchell, R. H.; Carruthers, R. J.; Mazuch, L.; Dingle, T. W. *J. Aam. Chem. Soc.* **1982**, *104*, 2544.

[8] Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571.

[9] Δ*r* is defined[8] as $\Delta r = (\sum m|(P_\mu - 642)|)/m$ where P_μ = π-SCF bond order x 10^3 of the μth bond, and *m* is the number of bonds in the macrocycle (= 14 in **1**).

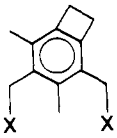
stantial anisotropy effects on the internal methyl groups (a hypothesis we have checked by synthesis). Moreover, meta fusion of two small rings as in **3a,b** should enhance the Mills–Nixon

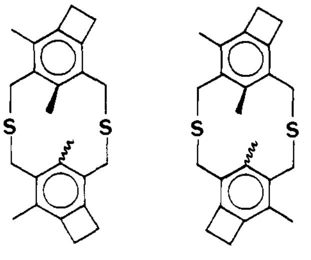

2a 2a'


3a 3b

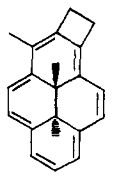
effect, whereas para fusion as in **2a,a'** should eliminate it;[4g,m] thus comparison of the ^{1}H NMR spectra of **2** with **3** should provide a real indication of any π-bond localization.

A synthesis of **2** and **3** was therefore undertaken. Pyrolysis of tris(chloromethyl)mesitylene at 550 °C led to the cyclobutane **4** in 10% yield.[10] Thiourea and then KOH readily converted **4** into the dithiol **5**, mp 57–58 °C in 62% yield. Cyclization[11] of **4** and **5** yielded 35% of a mixture of four thiacyclophanes **6a,b** and **7a,b**. The less soluble anti cyclophanes **6a** and **7a** could be obtained free of the syn cyclophanes **6b** and **7b** by chromatography and crystallization. The internal methyl protons of anti **6a** and **7a** appear shielded[12] at δ 1.23 and 1.30 with those of **7a** probably being at δ 1.30.[13] Despite considerable efforts (chromatography, HPLC, crystallization), we were unable to obtain these compounds free of each other. Likewise we were not ablve to separate the syn isomers, internal methyl protons at δ 2.40 and 2.44. A Wittig rearrangement–Hofmann elimination sequence[11] on the mixture of anti isomers **6a** and **7a** then led to a 5% yield of the desired dihydropyrenes **2** and **3**. Again despite extensive efforts, **2** could not be separated from **3**. However, the internal methyl protons of **2** and **3** appears as sharp sinlgets at δ −4.09 and −4.21, and fortunately we are only concerned with the difference in chemical shift of the internal protons of **2** and **3**, which is 0.12 ppm. The external methyl and cyclobutane protons appear coincidently as broad singlets at δ 3.0 and 3.75, respectively, and the aromatic protons as a multiplet at δ 8.2–8.9. (The related monocyclobutane annelated compound, **8**, could be obtained pure, mp 177–178 °C, internal methyl protons at δ −4.23).


4: X = Cl
5: X = SH


anti: 6a 7a
syn: 6b 7b

Thus from the observed chemical shift difference of 0.12 ppm for the internal methyl protons of **2** and **3**, we can calculate from eq 1 a maximum average bond-order deviation of 0.0044 between **2** and **3** from those of **1**. This we believe to be insignificant. Calculations, based on π-bond orders for benzocyclobutene,[4c] predict a value at least 10 times greater, and thus we at this point have no difficulty in claiming that there is *no* significant π-bond localizing Mills–Nixon effect. Investigation of the effects on the σ-bond system of **1**, **2**, and **8** will be carried out by determination of X-ray structures and designed synthesis of only **2** or **3** and will be reported in due course.


8

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for support of this work.

Registry No. **2a**, 89088-72-2; **3a**, 89088-73-3; **8**, 89088-74-4.

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[11] For a review, see: Mitchell, R. H. *Heterocycles* **1978**, *11*, 563.

[12] For a review see: Mitchell, R. H. In "Cyclophanes"; Keehn, P., Rosenfeld, S., Eds.; Academic Press: New York, 1983; Chapter 4.

[13] Fractional crystallisaion enhances this peak somewhat. Comparison with previous systems would suggest this is the *transoid* isomer; see: Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2560.

Activation of a C–H Bond in an Iron Phosphoranide Adduct. Unprecedented Rearrangement and Migration of a Phosphorus-Bound Allyl Group into an Iron-Bound Vinyl Group

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In the line of our current studies on the interplay between transition metals and phosphorus-based ligands, and specifically with the aim of developing new, metal-induced, phosphorus chemistry, we investigated the reactivity of metal derivatives with systems that are potentially capable of displaying phosphorane/phosphane tautomeric equilibria.[1]

This led us to obtain, from complexes **2**, under the action of methyllithium, the first transition-metal phosphoranides **4a,b**[2] and **5a,b**,[3] the coordination adduct of the phosphane form, **2**, serving both as a straightforward way of forming the P–M bond and as a relay to facilitate the abstraction of the proton initially located on phosphorus in **1**. The same approach proved effective in the synthesis of metal cyclamphosphoranides.[4]

On the other hand, the iron chelate **2c**, when treated in similar conditions, led to the unexpected and reversible (under the action of an acid) migration of the phenyl group between phosphorus and iron (**2c** ⇄ **6**) (Scheme I).[5] The mechanism of this reaction was elucidated by introducing a chemically labeled phenyl group

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