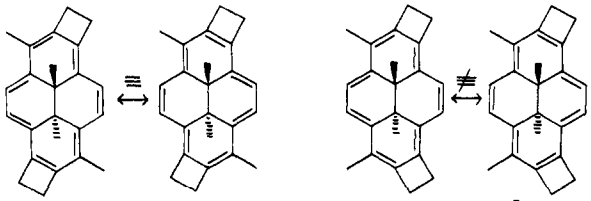
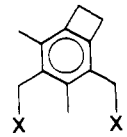
stantial anisotropy effects on the internal methyl groups (a hypothesis we have checked by synthesis). Moreover, meta fusion of two small rings as in **3a,b** should enhance the Mills-Nixon



2a **2a'** **3a** **3b**

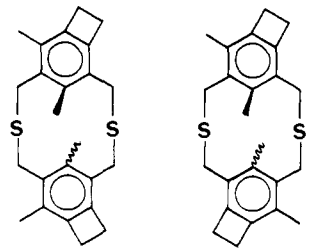
effect, whereas para fusion as in **2a,a'** should eliminate it;[4g,m] thus comparison of the ^{1}H NMR spectra of **2** with **3** should provide a real indication of any π-bond localization.

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**



4: X = Cl
5: X = SH

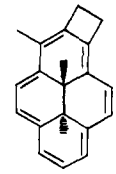
into the dithiol **5**, mp 57-58 °C in 62% yield. Cyclization[11] of **4** and **5** yielded 35% of a mixture of four thiacyclophanes **6a,b** and **7a,b**. The less soluble anti cyclophanes **6a** and **7a** could be



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

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).

Thus from the observed chemical shift difference of 0.12 ppm for the internal methyl protons of **2** and **3**, we can calculate from



8

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.

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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(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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Received October 26, 1983

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** $\rightleftarrows$ **6**) (Scheme I).[5] The mechanism of this reaction was elucidated by introducing a chemically labeled phenyl group

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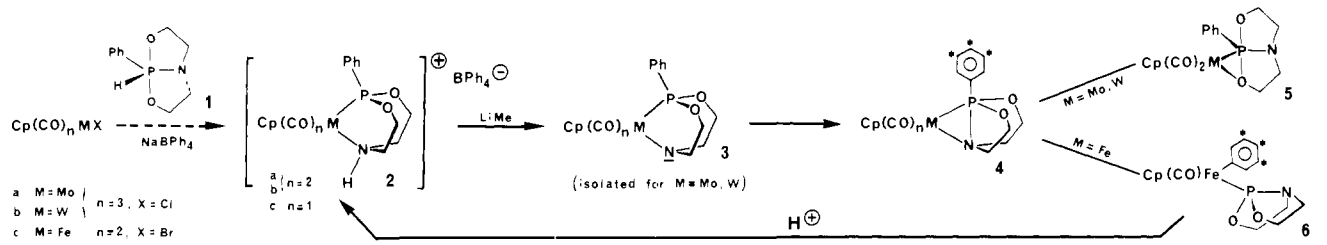
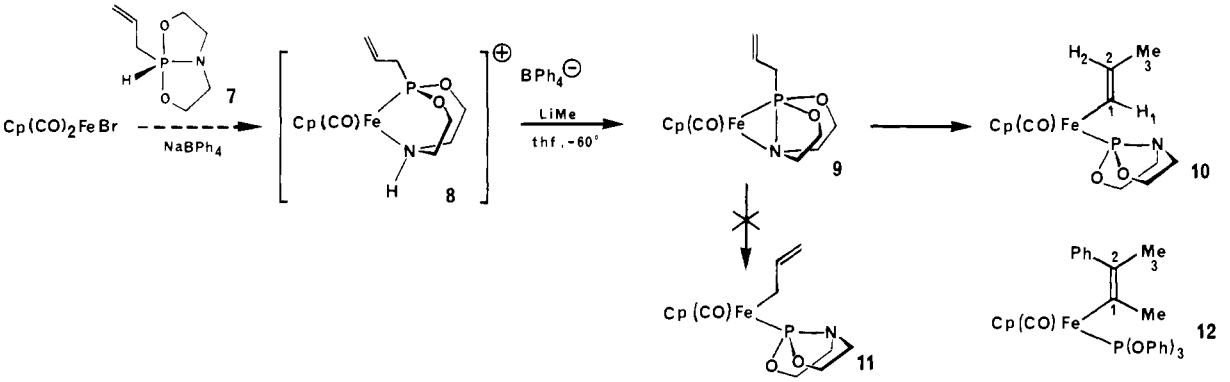
Scheme I



Scheme II



in the phosphorane and shown to consist in a 1,2-nucleophilic transfer of the phenyl group in the iron phosphoranide adduct **4c** rather than an orthometalation reaction: it is the same carbon atom that is alternately bound to phosphorus and to iron.[6]

The question thus arose as to what the extent of this reactivity pattern was and whether advantage could be taken of it as a means of forming metal–carbon bonds. We therefore investigated the behavior of bicyclic phosphoranes similar to **1**, but having other substituents than a phenyl group.

An unexpected behavior was observed in the case of the allylaminophosphorane **7**, which led to the (σ-vinyl)iron compound **10** instead of the (σ-allyl)iron derivative **11** (Scheme II), which would have been anticipated if the same reaction as with the phenyl group had taken place.

Under the action of LiMe (1.1 molar equiv) in THF, the cationic adduct **8** is first converted, quantitatively, at −60 °C, into the iron phosphoranide **9**. The ν(CO) vibration of **8** at 1965 cm^{-1} is seen to disappear within minutes, while a new absorption develops at 1910 cm^{-1}. Concomitantly, the low-field ^{31}P resonance of **8** at 222 ppm is replaced by an upfield signal at 80 ppm. This considerable variation in chemical shift ($\Delta\delta$ = 142 ppm) is comparable in amplitude to those that accompany the formation of the molybdenum and tungsten phosphoranides **4** from the corresponding adduct **2** ($\Delta\delta$ = 154 and 142 ppm, respectively),[2,3] therefore indicating the formation of the phosphoranide **9** rather than that of an amidophosphane iron chelate analogous to **3**. The formation of such an amidophosphane complex was indeed found, in the molybdenum and tungsten series, to be accompanied by downfield $\Delta\delta$'s of -8 and -13 ppm only, the ^{31}P chemical shift thus staying as expected within the 160–220 ppm range characteristic of M(II)–phosphane adducts.

Complex **9** is only stable in solution and at temperatures lower than 0 °C. At or above room temperature a new carbonyl stretching vibration progressively appears at 1930 cm^{-1}; at 60 °C the transformation is complete within 1 h. Adduct **10** was isolated as a yellow powder in 40% yield by column chromatography (SiO_2/Et_2O) of the crude reaction product. Its structure is unambiguously established by its spectroscopic characteristics, which also exclude its being the initially expected (σ-allyl)iron adduct **11**. The conversion of the phosphoranide ligand into the aminophosphane ligand as in **6**, for which it has been proven by an X-ray structure determination,[5] is indicated by the downfield $\Delta\delta$ of 136 ppm to δ 216 and by the ^{13}C resonances of the NCH_2 and OCH_2 groups at 54.5 and 69.1 ppm, respectively, these being very close to those found for **6**.

The rearrangement of the P-bound allyl group into a Fe-bound vinyl group is clearly attested by the ^1H and ^{13}C NMR data. The off-resonance ^{13}C spectra of **10** displays two vinylic carbons at 133 (C_1) and 138 (C_2) ppm, each coupled with one proton, while the third carbon, at 24.8 ppm, belongs to a methyl group. This definitely establishes a CH=CH-CH_3 pattern. Both these chemical shifts and the coupling constants with phosphorus (J_{C_1P} = 38, $J_{C_2P} \sim 0$, and J_{C_3P} = 5 Hz) are also consistent with those published for the related compound **12** (δ ^{13}C) 136.5, 152.4, and 23.8; J_{CP} = 37, ~0, and 3 Hz, respectively), whose structure has been confirmed by X-ray diffraction analysis.[7] The trans configuration on the double bond is confirmed by the magnitude of the $J_{H_1H_2}$ coupling of 16 Hz.[8] The fact that only the trans isomer is isolated is, however, not indicative of a stereoselective process since thermal cis → trans isomerisations assigned to steric effects have been reported to occur in mild conditions for analogous σ-vinylic iron derivatives.[7] In contrast to the phenyl group migration, which is reversible,[5] the migration of the vinyl group back from iron to phosphorus under the action of HCl was not observed.

No evidence has been found for a two-step process comprising, first, the S_N2 (or S_N2') migration of the allyl group (anticipated by analogy with the previously observed phenyl migration, to give the (σ-allyl)iron species **11**) followed by a σ-allyl to σ-vinyl isomerization. An H^+-catalyzed isomerization, as was observed for $Ir^{III}CH_2CMe{=}CH_2$ (but not for $Ir^{III}CH_2CH{=}CH_2$)[9] but during chromatography on SiO_2, is excluded since the products before and after chromatography exhibit quasi-identical NMR and IR patterns. In addition, protonation of σ-allyliron complexes, when observed, leads to π-olefinic cationic derivatives.[10,11] A base-catalyzed isomerization due to the 10% excess LiMe used

(6) The asterisks stand for methyl groups in the labeled complexes. Vierling, P.; Riess, J. G., unpublished results.

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is also unlikely since the same reaction occurs, and at a similar rate, with less than 1 equiv of LiMe. On the other hand, if the breaking of the P–C bond were the first step of the process, one would expect the benzyl group to migrate too, and even faster, in the benzyl-P analogue of **9**; this was not observed. So far the only rearrangement reported for a (σ-allyl)iron derivative, as in η^5-CpFe(CO)(PPh_3)(σ-allyl), is its thermal σ/π rearrangement, leading to the stable η^5-CpFe(CO)(π-allyl), which implies the dissociation of the phosphane complex.[11]

Thus the mechanism of the process reported here most likely consists in the insertion of iron into an allylic or a terminal vinylic C–H bond followed by a 1,3-proton shift to the terminal olefinic or allylic carbon atom, respectively, with concomitant P–C bond cleavage. This reactivity pattern differs both from the previously found phenyl group migration between phosphorus and iron, which implies only the breaking of a P–C bond, and from an ortho-metalation reaction, which implies only the insertion of a metal into a C–H bond. The basicity of the metal is known to play a determining role in the activation of C–H bonds; low oxidation states are usually required. In the present case, the anionic phosphoranide ligand in **9** is likely to increase the charge density on iron, and hence its basicity.

This unprecedented phenomenon is a further indication that the recently discovered phosphoranide ligands employed here promise to lead to new reactivity patterns.

Orientational Order in Phospholipid Bilayers. ^2H NMR Study of Selectively Deuterated Palmitic Acids in Unilamellar Vesicles

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Received December 5, 1983

We have addressed the current controversy on whether the orientational order of acyl chains in unilamellar vesicles, whose surface is highly curved, is the same or different from acyl chains in multilamellar systems (where the surface has a much lower curvature). Finer,[1] Stockton et al.,[2] and Bloom et al.[3] have stated that the order is essentially the same in both systems, whereas Petersen and Chan[4] and, more recently, Fuson and Prestegard[5] suggest that the order is lower in the vesicle system. We present evidence which shows that the C–D order parameter of ≈5 mol % selectively deuterated palmitic acids incorporated into unilamellar vesicles composed of 15% w/v egg phosphatidylcholine/bovine brain sphingomyelin (85:15 w/w) in deuterium-depleted water are *significantly lower* than the values[2] found in multilamellar liposomes at comparable reduced temperatures.

Fatty acids are considered to be reliable probes of the phospholipid acyl chain in model membranes.[2,6] In fact, Pauls et al.[7] examined the fidelity of deuterated fatty acids used as probes of dipalmitoylphosphatidylcholine bilayers and concluded that, even at 20 mol % incorporation, the acids reflect the order of the membrane to within 10%.

The unilamellar vesicles were prepared by codissolving 300 mg of egg phosphatidylcholine (isolated from fresh eggs[8,9]), 52 mg of bovine brain sphingomyelin (Sigma Chemical Co.), and 6 mg of the selectively deuterated palmitic acid in chloroform. The solvent was removed in a stream of dry nitrogen followed by vacuum pumping overnight to leave a thin lipid film. Deuterium-depleted water (2.5 mL) was added and the mixture rapidly agitated on a vortex mixer until the solution appeared homogeneous (approximately 5–10 min). Vesicles were prepared by sonication for 15 min at ~4 °C under a stream of nitrogen using a Biosonic III probe-type sonicator. The sonicated dispersion was centrifuged 20–25 min on a Clay–Adams clinical centrifuge to remove titanium fragments and undispersed lipid. The vesicles were then filtered through glass wool into an NMR sample tube, and ^2H NMR spectra were determined immediately on a

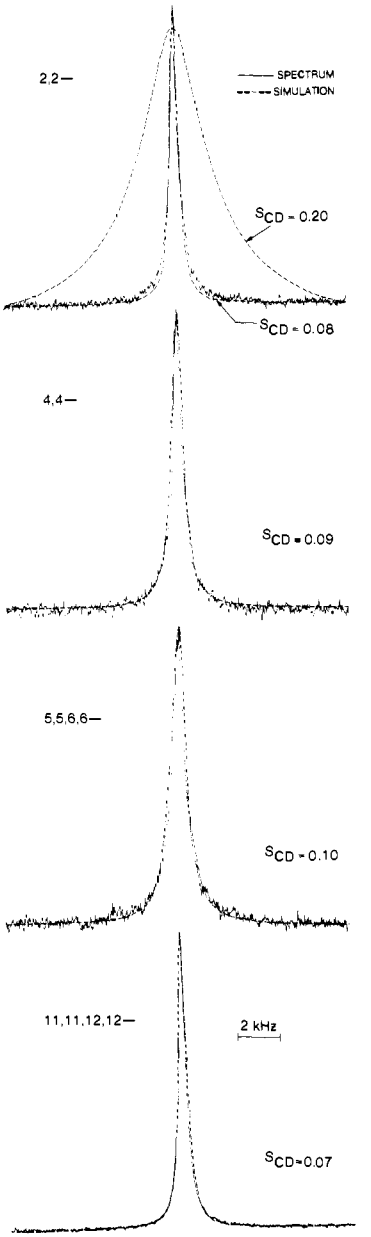

Figure 1. Deuterium NMR spectra (solid lines) of approximately 5 mol % selectively deuterated palmitic acids in unilamellar vesicles of 15% w/v egg phosphatidylcholine/beef brain sphingomyelin (85:15 w/w) in deuterium-depleted water. Position of selective deuteration is indicated to the left of each spectrum. Spectral parameters: sweep width = 50 kHz (16 kHz plotted), pulse width = 8 μs (90° flip angle), data set = 8K, delay before acquisition = 10 μs, line broadening = 20 Hz. The dotted lines are the best fit superposition of Lorentzian lines simulating the spectrum by using the order parameter S_{CD} indicated (see text for details).

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