Axial ⇌ Basal Isomer Distributions in Cyclic and Acyclic (η^4-diene)$Fe(CO)_2PPh_3$ Complexes

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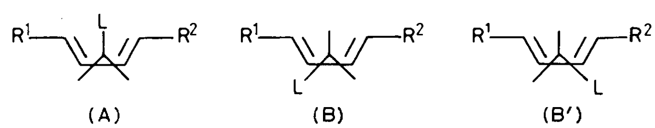
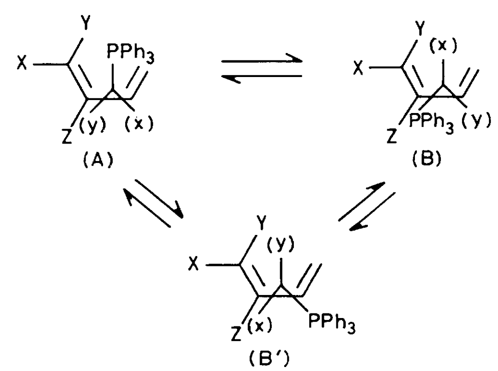
(Diene)$Fe(CO)_2PPh_3$ complexes exist in solution as isomeric mixtures with phosphine in the axial or basal position of the square pyramidal structure, methyl substitution at the internal diene carbon or *trans*-disubstitution at the terminal diene carbon increasing the concentration of axial isomer; *cis*- or *trans*-monosubstitution or *cis*-disubstitution at the terminal carbon increases the concentration of basal isomer.

Cyclic and acyclic (diene)$Fe(CO)_3$ and [(dienyl)$Fe(CO)_3$]X complexes constitute useful intermediates for stoicheiometric organic synthesis, primarily because of the high stereo- and regio-specificity observed on reaction with both nucleophiles and electrophiles.[1a—c] Recent improved syntheses[2a—c] also make the analogous (diene)$Fe(CO)_2PR_3$ complexes attractive candidates, relative to the $Fe(CO)_3$ derivative, since both increased reactivity towards electrophiles[3] and pronounced differences in the regiospecificity of nucleophilic attack[2b] have been observed. Additionally, use of optically active PR_3 ligands presents the possibility of asymmetric induction in reactions with both electrophiles and nucleophiles.[4]

A monosubstituted (diene)$Fe(CO)_2L$ complex can exist as three isomers (A)—(B′) which may interconvert *via* formal diene rotation; (B′) and (B) form an enantiomeric pair when $R^1 = R^2$, but are potentially distinguishable by n.m.r. methods where R^1 and R^2 are different. Little information exists on isomer distributions in such complexes; the most complete data on a series of acyclic (diene)$Fe(CO)_2PF_3$ complexes shows only isomer (A) regardless of diene substitution.[5a,b] We report here a much more profound influence of



(A) = axial; (B), (B′) = basal



Scheme 1

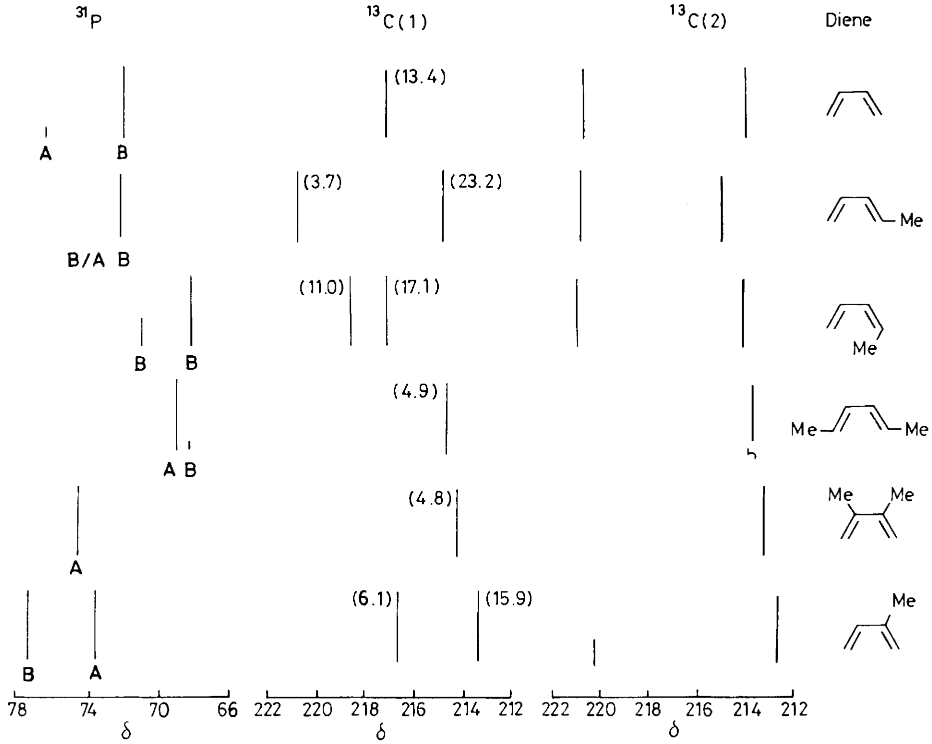


Figure 1. Schematic representation of the ^{13}C (carbonyl only) and ^{31}P n.m.r. spectra of (diene)$Fe(CO)_2PPh_3$ complexes in CD_2Cl_2–CH_2Cl_2 solution with J/Hz values in parentheses. ^{31}P spectra, in p.p.m. from 85% H_3PO_4, at −85 °C; $^{13}C(1)$ at 0 °C and $^{13}C(2)$ at −85 °C, with respect to $SiMe_4$.

diene substituent on isomer distribution in (diene)Fe-$(CO)_2PPh_3$ derivatives.

Schematic representations of the ^{31}P and ^{13}C (carbonyl only) n.m.r. spectra of (butadiene)$Fe(CO)_2PPh_3$ and a series of internal and terminal methyl substituted complexes are shown in Figure 1.† In all but the 2,3-dimethylbutadiene complex, low temperature (−85 °C) ^{31}P spectra show two resonances of varying relative intensity which are averaged to a single resonance at high temperature (0 °C). Axial–basal assignments may be made with the aid of ^{13}C n.m.r. spectra, which fall into three general classes.

(i) Spectra of complexes of symmetric dienes which exist exclusively or almost exclusively as isomer (A). Thus, the 2,3-dimethylbutadiene and *trans,trans*-hexa-2,4-diene complexes show a single high temperature resonance at δ *ca.* 214 which remains unchanged at low temperature.‡ The small amount of basal isomer observable in the ^{31}P spectrum of the *trans,trans*-hexa-2,4-diene complex is undetectable in the low temperature ^{13}C spectrum.

(ii) Spectra of complexes of symmetric and asymmetric dienes which exist as axial–basal mixtures. The high temperature spectrum of the *trans*-penta-1,3-diene complex shows two resonances at δ *ca.* 214 and 221 which remain unchanged on cooling. As shown in Scheme 1, formal diene rotation in an asymmetric diene complex does not result in total carbonyl scrambling. Thus, except under quite specific conditions,§ *two* averaged high temperature resonances will be observed, representing a weighted average of chemical shift and J(P–C) values for carbonyls (x) and (y) in the three isomers. If, as in the *trans*-penta-1,3-diene complex (X = Me, Y = Z = H), only one isomer is substantially populated, high- and low-temperature spectra will be indistinguishable. On the basis of previous work, the major basal isomer is assigned as (B′) rather than (B).[5a]

The 2-methylbutadiene complex (X = Y = H, Z = Me) exists as a 1:1 axial–basal mixture, the most likely basal candidate being (B′). Consideration of the above scheme shows that (A) $\rightleftharpoons$ (B′) exchange is accompanied by axial–basal averaging of (y), but (x) is averaged only between basal positions. Thus, the low temperature spectrum consists of two resonances at δ 214 and 221 in the intensity ratio of 3:1 which coalesce to two resonances of equal intensity at high temperature whose averaged chemical shifts and J(P–C) values are in agreement with a 1:1 (A)/(B′) ratio.¶

For a symmetric diene, carbonyls (x) and (y) are completely scrambled by diene rotation; thus, the butadiene complex, which exists predominantly as the basal isomer, shows two low

† Complexes were prepared either by photolysis of $Fe(CO)_4PPh_3$–diene mixtures[4] or Me_3NO substitution of (diene)$Fe(CO)_3$ [2a] and gave satisfactory analytical and spectroscopic data.

‡ Normal temperature-broadening of signals obscures J(P–C) values at low temperature (−85 °C) and makes individual axial and basal resonances for (A)–(B′) or (B)–(B′) mixtures indistinguishable.

§ A *single* averaged resonance might be expected for an equimolar mixture of (A)–(B)–(B′) or an equimolar (B)–(B′) mixture, assuming degeneracy of axial and equatorial carbonyl resonances in the three isomers.

¶ Assuming chemical shifts for axial and basal CO resonances of δ 221 and 214 and coupling constants of $J(P_{axial}–CO_{basal})$ ~5 Hz, $J(P_{basal}–CO_{axial})$ ~4 Hz and $J(P_{basal}–CO_{basal})$ ~25 Hz. The reversed ordering of the axial and basal ^{31}P shifts [relative to (butadiene)$Fe(CO)_2PPh_3$] has been confirmed using data for (2-methylbutadiene)-$Fe(CO)_2PPh_xMe_{3-x}$ (x = 1—3) complexes.

temperature resonances of equal intensity at δ 214 and 221 which coalesce to a *single* averaged high temperature resonance.

(iii) Spectra of complexes of asymmetric dienes which exist as mixtures of (B) and (B′). The *cis*-penta-1,3-diene complex (X = Z = H, Y = Me), exists as a 2.5 : 1 mixture of the two basal isomers, though which is the more abundant is not obvious. Consideration of Scheme 1 shows that (B) ⇌ (B′) exchange is accompanied by axial–basal exchange of *both* carbonyls (x) and (y). Thus, the low temperature spectrum shows two resonances of *equivalent* intensity at δ *ca.* 214 and 221 which coalesce to two high temperature resonances of equivalent intensity whose chemical shifts and *J*(P–C) values are in agreement with the 2.5 : 1 distribution.

The effect of diene substitution may be summarized as follows. (i) Internal methyl substitution alters the axial–basal ratio in the order butadiene (1 : 6) < 2-methylbutadiene (1 : 1) < 2,3-dimethylbutadiene (>100 : 1), with only one of the two possible basal isomers observed for an asymmetric diene. (ii) Terminal methyl substitution alters the axial–basal ratio in the order *cis*-pentadiene (<1 : 100) < *trans*-pentadiene (1 : 18) < butadiene (1 : 6) < *trans,trans*-hexa-2,4-diene (52 : 1). For *trans*-terminal substitution, only one basal isomer is observed; the axial isomer is absent in *cis*-terminally substituted complexes, but both basal isomers are populated for an asymmetric diene. Complexes of cyclic dienes (which may be regarded as *cis,cis*-terminally substituted) adopt only the basal structure. Thus, although a limiting low temperature spectrum cannot be obtained, the spectrum of (cyclohexadiene)Fe$(CO)_2PPh_3$ at 0 °C is essentially identical to that of the butadiene complex, and a crystal structure determination confirms the basal structure in the solid state.[6] Asymmetric cyclic diene complexes such as (cycloheptatriene)- and (tropone)-$Fe(CO)_2PPh_3$ exist as (B)/(B′) mixtures.[7]

Calculations indicate only small differences in electronic preference of phosphine for the axial or basal position in the distorted square-pyramidal structure characteristic of (diene)$Fe(CO)_3$ complexes;[8] thus, the dramatic changes observed in isomer distribution seem best attributed to steric factors. We are currently undertaking crystallographic studies of the axial and basal configurations, and are examining possible differences in chemical reactivity or regiospecificity between the two isomeric forms.

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