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Preliminary communication

A NONRIGID MIXED-CHELATE COMPLEX OF IRON(0)

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Summary

The reaction of $Fe(CO)(CH_2{=}CH{-}CH{=}CH_2)_2$ with $(Ph_2PCH_2)_2$ results in formation of a 4/1 mixture of two isomers of $Fe(CO)(CH_2{=}CH{-}CH{=}CH_2)$-$(Ph_2PCH_2CH_2PPh_2)$. NMR studies concerning the structures of these isomers and their dynamic behavior in solution are described.

Five-coordinate bis-butadiene complexes assume structures which are best characterized as square pyramidal. Thus, both $FeCO(C_4H_6)_2$ [1] and $RhCl(C_4H_6)_2$ [2] have four equivalent double bonds which occupy the basal positions in a square pyramid. $ML(Ph_2PCH_2CH_2PPh_2)_2$ complexes, on the other hand, are equatorially substituted trigonal bipyramids [3]. We report here the outcome of a competitive experiment which places one butadiene and one chelating phosphine in the same five-coordinate complex. The non-rigidity of this complex compares to that of $Fe(C_4H_6)(CO)_3$ [4] and its PF_3 derivatives [5].

Reaction of the bis-butadiene complex $FeCO(C_4H_6)_2$ [6] with $(Ph_2PCH_2)_2$, dpe, in refluxing benzene for 19 h produces a material of stoichiometry $FeCO(C_4H_6)$(dpe). Anal. Found: C, 68.55; H, 5.66; P, 11.43. $C_{31}H_{30}FeOP_2$ calcd.: C, 69.43; H, 5.60; P, 11.57%. In spite of the fact that this material shows only one CO stretching frequency both in Nujol (1905 cm^{-1}) and in acetone (1895 cm^{-1}), the ^{31}P NMR spectrum shows this to be a 4/1 mixture of two isomers. At —63° in acetone-d_6 (Fig. 1), one isomer (S) exhibits a singlet at 91.2 ppm**. The more abundant isomer, Q, is characterized by an AX pattern with ν_A = 102.1 ppm, ν_X = 91.3 ppm, and J_{AX} = 16.9 Hz. All resonances are unusually far downfield from the chemical shift of the free ligand (—12.5 ppm). Such a shift is characteristic of a five-membered chelate ring [7,8]. No trigonal bipyramidal structure for $FeCO(C_4H_6)$(dpe) has rigorously equivalent phosphorus nuclei. Structure I, a variant on the square

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[*] Contribution no. 2649.
[**] Positive chemical shifts are downfield from 85% H_3PO_4.

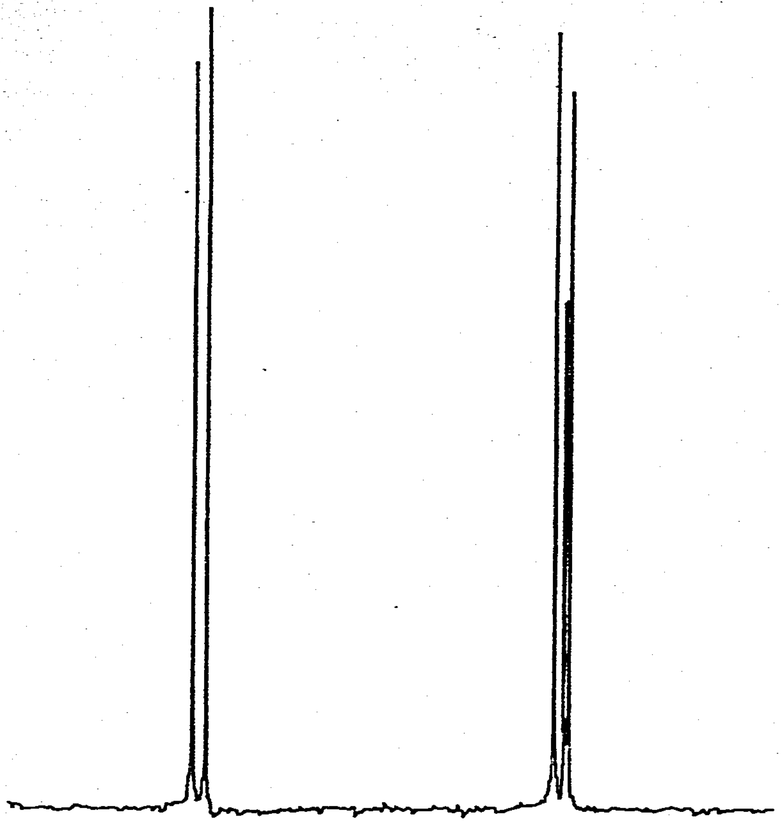
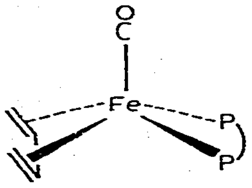
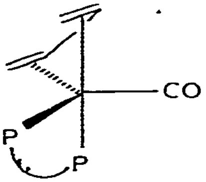


Fig.1. $^{31}P\{H\}$ NMR spectrum of $FeCO(C_4H_6)(dpe)$ in acetone-d_6 at −63°.

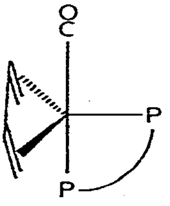
pyramidal structure adopted by $FeCO(C_4H_6)_2$, is consistent with the singlet spectrum observed for isomer S.



(I)



(II)



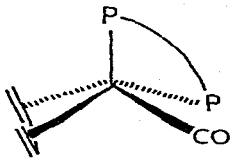
(III)

If isomer Q of $FeCO(C_4H_6)(dpe)$ is trigonal bipyramidal, the chelating phosphine must occupy axial and equatorial sites (II and III).

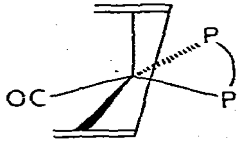
Structure III has several unattractive features. The strong π-acid CO would be more stable in an equatorial position [9]. Olefins in equatorial positions prefer to lie in, or nearly in, the equatorial plane rather than perpendicular to it [10]. Finally, butadiene has a relatively small "bite angle"

(~62°) [4], making it better suited to span axial—equatorial positions (II), rather than two equatorial positions (III).

Two square pyramidal forms, IV and V, have inequivalent phosphorus nuclei.



(IV)



(V)

The small (83°) bite angle of dpe will distort IV so that it is merely a variant of II (and vice versa). In fact, the actual structure of isomer Q will be a compromise between these idealizations and it is meaningless to focus on the trigonal and square extremes. Henceforth, all distinctions between II and IV will be dropped. Structure V is unfavorable with regard to the wide angle spanned by butadiene. The similarity of the *X* chemical shift of isomer Q and the chemical shift of isomer S can be rationalized if Q has structure IV and the 91 ppm chemical shift is that of a basal phosphorus.

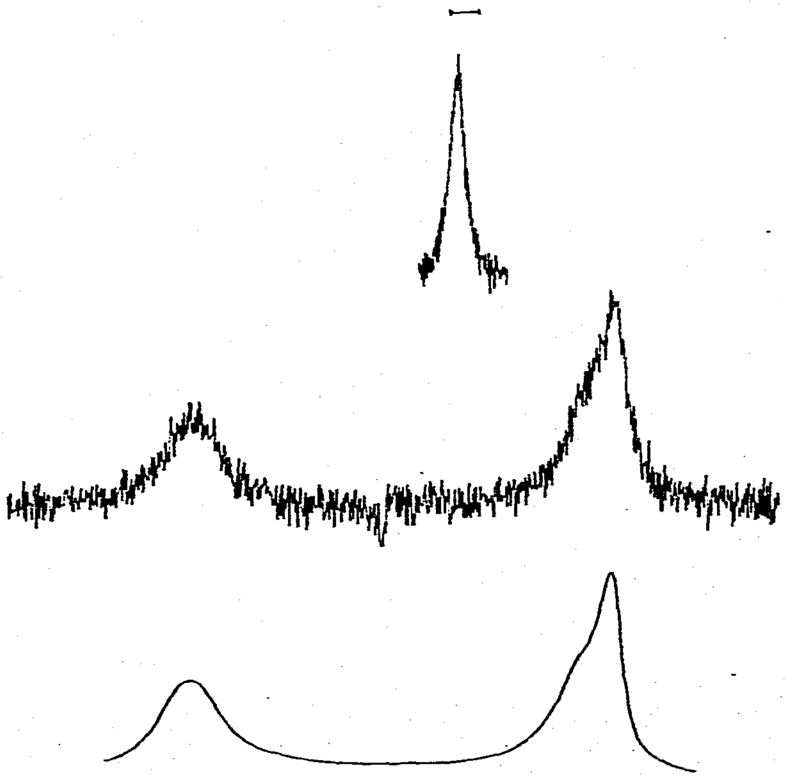
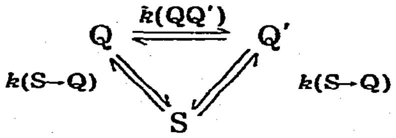


Fig.2. Variable-temperature $^{31}P\{H\}$ NMR spectrum of $FeCO(C_4H_6)(dpe)$. Upper: + 30° (calibration bar equals 162 Hz). Middle: − 8°. Lower: simulated spectrum at − 8° with $\nu_A = 101.3$, $\nu_X = 91.2$ and $\nu_S = 90.6$ (i.e., the chemical shifts are slightly temperature dependent).

Phosphorus NMR spectra recorded at higher temperatures (Fig. 2) show dynamic behavior typical of five-coordinate species. At −8°, the AX pattern has become two broad lines (peak width at half height 75 Hz), and at 30° these have collapsed to a single broad (100 Hz) line. At −8°, the singlet resonance due to S is sharper than the lines of the AX pattern, but clearly suffers some lifetime broadening; fortuitously, the singlet nearly superimposes on the upfield line of the AX pattern. Since a single broad resonance is evident at 30°, the two molecules are truly isomeric and interconvertible. Further, the chemical shift of the resonance at 30° is not simply the average of ν_A and ν_X', but is a weighted* average of ν_A', ν_X and the resonance frequency of the singlet species, S (see Fig. 2).

The ^{31}P NMR spectra were simulated using a model with three exchanging chemical configurations (see Scheme 1). Here S represents the isomer producing a singlet spectrum and Q is the isomer responsible for the quartet**.

SCHEME 1



Q' is related to Q by permutation of the inequivalent phosphorus nuclei. Since S contains equivalent phosphorus nuclei, it might be anticipated that this isomer is a necessary intermediate in the permutation of nuclei in Q. In terms of the chosen model, this limiting situation has Q converting to Q' only via S; this means $k(QQ') \ll k(Q\rightarrow S)$. Actual simulation shows such a model to be inconsistent with observation. In particular, this model results in a shorter lifetime for S than for Q or Q'. This is qualitatively different from Fig. 2, which shows S to have a narrower line than Q. The −8° spectrum can be reproduced with $k(QQ') = 200$ sec^{-1} and $k(S\rightarrow Q) = 45$ sec^{-1} (Fig. 2). This gives $\Delta G^{\ddagger}(QQ') = 12.6$ kcal/mol and $\Delta G^{\ddagger}(S\rightarrow Q) = 13.4$ kcal/mol at −8°. These parameters also yield the single-line spectrum observed at 30°, implying that the $\Delta G^{\ddagger}$ values are essentially temperature independent. Thus, contrary to our naive expectation, the main mechanism for site exchange ($Q \rightleftharpoons Q'$) is not via S. There is a path for direct interconversion of Q and Q' which is of lower activation energy than the path producing S.

The coexistence of observable populations of two isomeric five-coordinate complexes is exceptional. Equilibration between two geometrically or structurally isomeric five-coordinate structures has been observed for $IrH(CO)_2(PPh_3)_2$ [11], $HRuNO(PPh_2\text{-}i\text{-}Pr)_3$ [12] and $CF_3Co(CO)_3PF_3$ [13]. It is noteworthy that in the case at hand, as well as with $IrH(CO)_2(PPh_3)_2$, site exchange of inequivalent phosphorus nuclei within one isomer occurs faster than isomerization itself; the transition states for the two processes are therefore structurally distinct. $RuCO[S_2C_2(CF_3)_2]_2(PPh_3)_2$ also exists as two structural isomers in the solid state [14]. One isomer has equivalent phosphines

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*Isomer populations at −8° and 30° do not differ detectably from those at −63°.

**The rate constant for conversion of Q (or Q') to S is given by $k(Q\rightarrow S) = k(S\rightarrow Q)\,[S]\,[Q]^{-1}$

while the other should exhibit an AX phosphorus NMR pattern. In this case, however, we observe only a sharp singlet (45.1 ppm in CH_2Cl_2) down to $-89°$.

$FeCO(C_4H_6)(dpe)$ is stable to further substitution by $(Ph_2PCH_2)_2$, even under forcing conditions (excess chelate in refluxing *p*-xylene for 15 hours). After submission of this manuscript, Whitesides and Budnik [15] published an extensive series of observations on rearrangements like those observed here. Significantly, they observe cases where $k(S \rightarrow Q) > k(QQ')$.

Acknowledgements

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