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# Retention of Phosphorus Configuration on Forming Irontetracarbonyl Complexes with Phosphines in the 9-Phosphabicyclo[4.2.1]nonatriene and 7-Phosphanorbornene Systems

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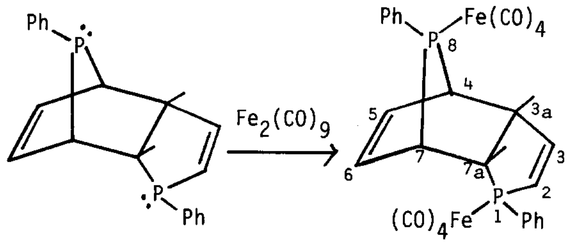
Abstract. Dimers of phospholes with syn or anti configuration at the bridging phosphorus react with $Fe_2(CO)_9$ to give complexes, $R_3PFe(CO)_4$, with complete retention of configuration. Contrary to a report in the literature, isomers of 9-phenylbicyclo[4.2.1]nonatriene also formed complexes with complete retention of configuration.

Included in our studies of the properties of phosphines having the 7-phosphanorbornene structure, first synthesized in 1980 as a component of the phosphole dimer framework[1], is their behavior as ligands in coordination compounds. It was shown[2] that syn and anti isomers at the bridging phosphorus in the phosphole dimers form complexes with methylcobaloxime that have retained the original configuration at phosphorus. These isomeric complexes have distinctly different $^{31}P$ chemical shifts and $^{31}P$-$^{31}P$ coupling constants, and exhibit the same pronounced differences in stereodependent $^{31}P$-$^{13}C$ coupling constants that are found in the phosphine ligands[3]. We have now found that complexes of the types $R_3PFe(CO)_4$ form readily with the phosphole dimers, again with complete retention of phosphorus configuration. Our results are of special significance in that they differ from a suggestion made in a recent report[4] in this journal "that [strained phosphines] tend to isomerize to thermodynamically more stable phosphines before complexation". A reexamination of the complexes on which this statement is based has been performed, and a different result is reported here.

Phosphole dimers 1[3] and 2[3] were reacted with $Fe_2(CO)_9$ (two molar equivalents) for 16 hrs at 25°C in hexane solution to give complexes 3 and 4, respectively. There was no indication of the formation of isomeric products in the complexation reaction, nor any tendency for interconversion between isomers 3 and 4. Characterizing data are provided in footnote 5. Of special note is the different magnitude of $\delta$ $^{31}P$ (+176.5 and +142.3, respectively) at the bridging phosphorus, and the significantly different $^{31}P$-$^{31}P$ coupling constant (31.7 and 14.7 Hz, respectively). Similar effects were also observed[2] for the cobaloxime complexes, and are found in the free ligands as well[3], where they serve as decisive indicators of stereochemistry.



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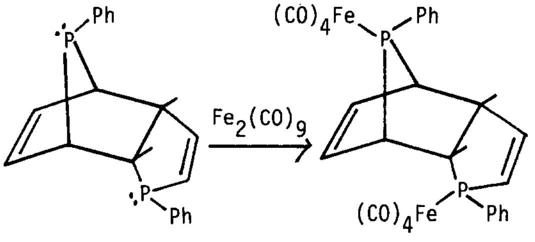

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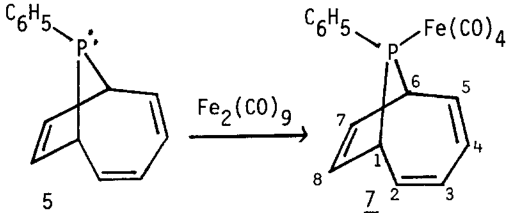
The $^{13}$C NMR spectra (Table 1) display important differences that also arise from stereochemical effects. In the phosphines, the correlation is present that $^2J_{PC}$ is large when the lone pair is close to the carbon, but small when remote. This effect is preserved even when a complexing metal (e.g., Co[2]) is present, as is evident from the data in Table 1 for the Fe(CO)$_4$ complexes. For example, $^2J_{P_8-C_5}$ is 7.0 Hz when Fe is close to C-5 (in 4) but 0 when remote (in 3). Conversely Fe is remote from C-3a in 4 ($^2J$ = 6.6Hz) but close in 3 ($^2J$ = 19.6 Hz).

These results seemed rather surprising since it had been reported that an inversion of configuration in the least stable member of a <u>syn</u>, <u>anti</u> pair probably could be expected when Fe$_2$(CO)$_9$ is used as the complexing agent[4]. We felt it necessary to examine the original reaction on which this suggestion was based, namely, the reaction between phosphines 5 and 6 with Fe$_2$(CO)$_9$. The individual phosphines[6] were reacted with Fe$_2$(CO)$_9$ in toluene or hexane at 25°C. Each gave a <u>single product</u> (7 and 8, respectively) with <u>distinctly different</u> physical and spectral properties (footnote 7 and Table 1). We call special attention to features of the $^{13}$C NMR spectra (Figure 1 and Table 1) that are compelling in showing that the isomers differ in configuration at P, while at the same time revealing their structures. The two-bond coupling to ring carbons 7,8 are quite different in the two isomers (0 and 11.0 Hz, respectively), just as they are in the free phosphines (2.4 and 16.9 Hz[8]). As noted above, a similar retention of stereospecificity of $^2J_{PC}$ in the phosphines is observed on complexing the phosphole dimers (3 and 4).



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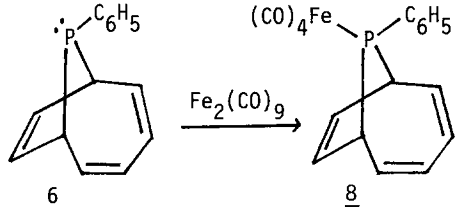

6 8

In the report of the results with the same phosphines from another laboratory [4], it was stated that phosphine 5 gave a complex with $\delta$ $^{31}$P +42.9 in C$_6$D$_6$ and m.p. 106°C. Since we find $\delta$ $^{31}$P(C$_6$D$_6$) +50.1 and m.p. 83-86°C for this complex, and $\delta$$^{31}$P +43.7 and m.p. 107-109°C for the complex of phosphine 6, a reconsideration of the earlier structure assignment[4] is desirable. This report[4] also claimed that phosphine 6 gave the same complex as did phosphine 5, as a result of a preliminary isomerization of 6 by $Fe_2(CO)_9$. We see no indication of this process, nor did we detect isomerization with the more highly strained phosphole dimers, even though isomerization of 1 to 3 is known to occur for the dimers in some media[9,10].

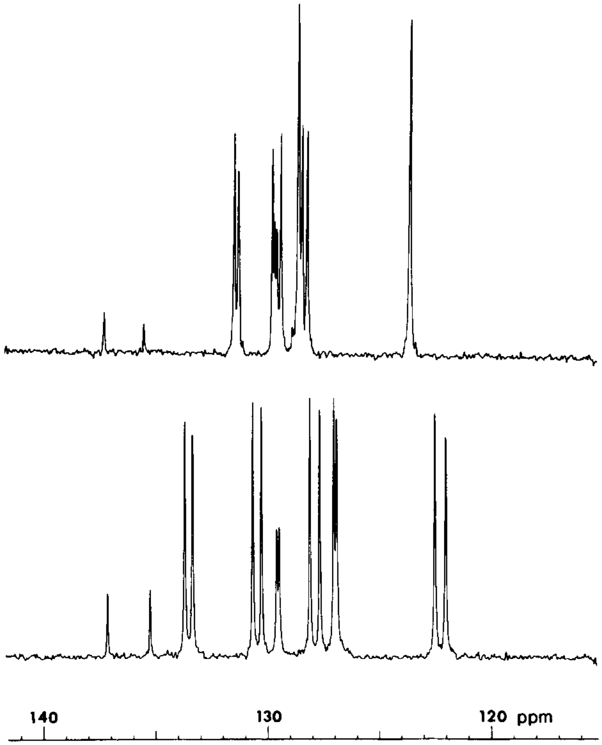

Fig. 1. $^{13}C$ NMR Spectra of Complex 7 (top) and 8 (bottom) obtained at an operating frequency of 22.50 MHz.

We must conclude that there is no experimental basis for the suggestion[4] that a strained bicyclic phosphine can be isomerized by $Fe_2(CO)_9$ before complexation; the complexations so far examined are stereospecific with retention of configuration at phosphorus.

## Acknowledgement

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Table 1. $^{13}C$ NMR Data[a] for Complexes

| Carbon | $3^b$ | $4^b$ | Carbon | $7^d$ | $8^d$ |
|---|---|---|---|---|---|
| 2 | 127.75(43.0)( 3.3) | c | 1,6 | 45.6(20.2) | 45.8(24.2) |
| 3 | 149.37( 5.9)(10.1) | 146.51( 6.0)( 6.0) | 2,5 | 131.3( 4.0) | 133.4( 7.7) |
| 3a | 56.78( 4.8)(19.6) | 57.82( 4.4)( 6.6) | 3,4 | 128.5( 4.0) | 126.8( 3.3) |
| 4 | 48.42( 0.0)(28.7) | 46.78( 0.0)(27.4) | 7,8 | 123.5( 0.0) | 122.1(11.0) |
| 5 | 135.43( 0.0)( 0.0) | 131.10( 0.0)(13.2) | ipso | 136.4(39.6) | 136.0(44.0) |
| 6 | 134.86( 4.9)( 0.0) | 134.39( 5.5)(11.0) | ortho | 129.5( 8.7) | 130.3( 8.8) |
| 7 | 48.03( 4.6)(25.3) | 46.75( 3.8)(23.5) | meta | 128.4( 9.4) | 127.7( 9.9) |
| 7a | 47.98(34.2)(20.8) | 49.22(31.3)( 5.0) | para | 129.6( 2.0) | 129.4( 3.2) |

[a] In $CDCl_3$, except 3 ($CD_3C(O)CD_3$ at -10°C). Chemical shifts referenced to tetramethylsilane.

[b] Phenyl carbons omitted for brevity. Values in parentheses are $J_{^{13}C-^{31}P-1}$, and $J_{^{13}C-^{31}P-8}$ respectively.

[c] Obscured.

[d] Values in parentheses are $J_{^{13}C-^{31}P}$.

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3. L.D. Quin, K.C. Caster, J.C. Kisalus, and K.A. Mesch, J. Am. Chem. Soc. 106, 7021 (1984).
4. W.J. Richter, Tetrahedron Lett. 26, 1039 (1985).
5. Compound 4 was purified by sublimation (140°C, 0.3 torr) or crystallization from cold hexane. Compound 3 decomposed upon sublimation but was purified by crystallization from hexane at -80°C. Anal. Calcd for $C_{28}H_{18}Fe_2O_8P_2$: C, 51.26; H, 2.77; P, 9.44. Found for 3: C, 51.27; H, 3.04; P, 9.90. $\delta\,^{31}P[^1H]$ ($CDCl_3$), $P_8$ +176.5; $P_1$ +88.8; $^3J_{PP}$ = 31.7 Hz.; mp 160°C (dec.); Found for 4: C, 50.94; H, 3.10; P, 9.16. $\delta\,^{31}P\ [^1H]$ ($CDCl_3$), $P_8$ +142.3; $P_1$ +86.5; $^3J_{PP}$ = 14.7 Hz.; mp 180°C (dec.).
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7. Both 7 and 8 were purified by sublimation at 120°C at 0.3 torr. Anal. Calcd for $C_{18}H_{13}FeO_4P$: C, 56.72; H, 3.70; P, 8.13; Found for 7: C, 57.04; H, 3.92; P, 8.37; $\delta\,^{31}P\ [^1H]$ ($C_6D_6$), +50.14; mp 83-86°C. Found for 8: C, 56.85; H, 3.90; P, 8.21; $\delta\,^{31}P[^1H]$ ($C_6D_6$), +43.74; mp 107-109°C.
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9. K.A. Mesch and L.D. Quin, Tetrahedron Lett., 4791 (1980).
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