

IRONTETRACARBONYL-COMPLEXES OF SYN- AND ANTI-9-SUBSTITUTED  
9-PHOSPHABICYCLO[4.2.1]NONATRIENES: COMPLEXATION WITH INVERSION  
AND RETENTION OF CONFIGURATION AT PHOSPHORUS

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Summary: anti-9-Substituted 9-phosphabicyclo[4.2.1]nonatrienes complex with  $\text{Fe}_2(\text{CO})_9$  under retention, whereas the corresponding syn-isomers complex via inversion at phosphorus.

Metal carbonyl complexes of phosphorus compounds and of olefins have received considerable attention<sup>1)</sup>; however, unsaturated phosphines have been relatively neglected as ligands. Stereochemical aspects of complexation seem to have been widely ignored and is generally assumed to proceed via retention of the configuration at phosphorus.

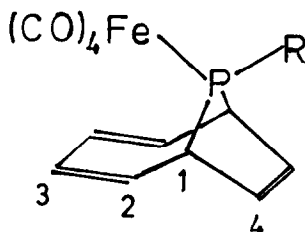
Our studies on irontetracarbonyl-complexes of syn- and anti-9-substituted 9-phosphabicyclo [4.2.1]nonatrienes reported here partly invalidate the above assumption. Both the syn- and anti-isomers were synthesized from magnesium-cyclooctatetraene and substituted dichlorophosphines and characterized, among others, by their respective NMR spectra, which show distinct differences between the epimers<sup>2)</sup>. In the  $^{31}\text{P}$  NMR spectra, the syn-compounds show a very large upfield shift (70 - 80 ppm) relative to the corresponding anti-isomers, and the stereochemical difference is also reflected in differing in their  $^1\text{H}$  NMR spectra.

The  $^1\text{H}$  NMR spectra of the  $\text{Fe}(\text{CO})_4$ -complexes formed with the anti-9-tert.butyl-9-phospha-bicyclo [4.2.1] nonatriene (1a), the anti- and syn-9-phenyl-compounds 2a and 2b, and the syn-9-(bisdiethylamino)-compound 3b are strikingly similar (see table 1), suggesting that the products have the same stereochemistry. The  $^{31}\text{P}$  NMR spectra also show some unexpected features: Whereas the anti-ligands 1a and 2a give rise to the expected downfield shift on complexation of  $\Delta\delta = 55 \text{ ppm}$ <sup>3)</sup>, the syn-isomers 2b and 3b exhibit an abnormally large downfield shift of 120 and 140 ppm. In addi-

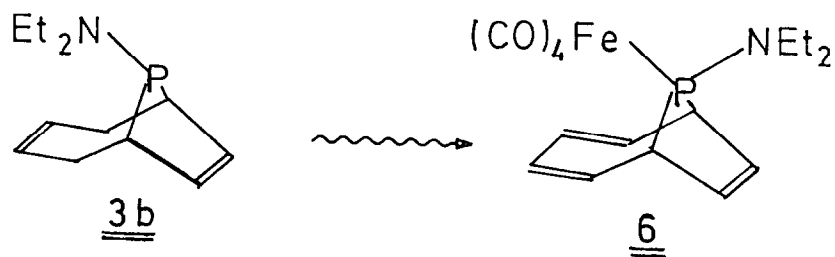
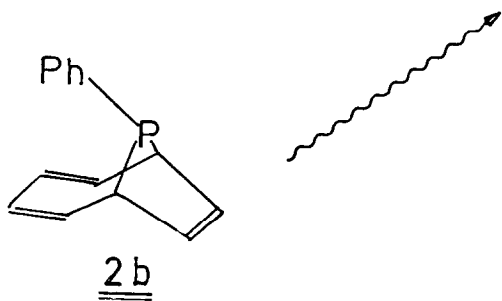
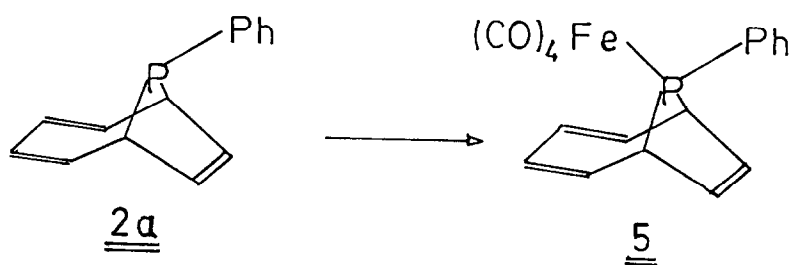
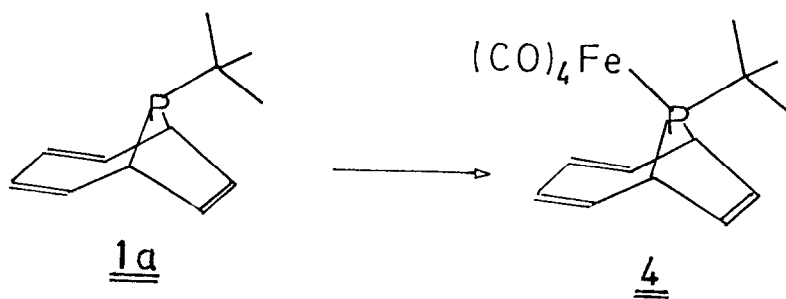
tion, the syn- and anti-isomers of 2 lead to the same iron complex 5. Detailed analysis of the  $^1\text{H}$  NMR spectra of complex 4, including NOE experiments <sup>4)</sup>, confirmed that the tert.butyl group faces the olefinic double bond. Consequently the  $\text{Fe}(\text{CO})_4$ -group must face the butadiene moiety, but is not complexed to it. Thus the complexation has indeed occurred with retention of the configuration at phosphorus without significant participation of the diene <sup>5,6)</sup>.

Table 1.  $^1\text{H}$ -NMR chemical shifts ( $\text{C}_6\text{D}_6$ , TMS as internal standard) for 4 - 6

Comp.	R	H <sup>1</sup>	H <sup>2</sup> , H <sup>3</sup>	H <sup>4</sup>	H <sup>R</sup>
<u>4</u>	tert.butyl	2.73 $J_{\text{P}} = 0$ $J_{1,2} = 3.0$	5.71, 5.79 $J_{1,2} = 8.5$ $J_{3,4} = 12.3$	4.80 $J_{\text{P}} = 15.2$	0.79 ( $\text{C}(\text{CH}_3)_3$ ) $J_{\text{P}} = 14.6$
<u>5</u>	phenyl	3.31	5.25, 5.66	5.19 $J_{\text{P}} = 20.5$	7.05, ~7.2 ( $\text{C}_6\text{H}_5$ )
<u>6</u>	diethylamine	3.11	~5.6	4.92 $J_{\text{P}} = 21.5$	2.5, 0.81, 1.01 ( $\text{Et}_2\text{N}$ ) $J_{\text{P}} = 9.5$



Since the  $^1\text{H}$  NMR spectra of the complexes 4 to 6 are very similar, we conclude that all the complexes have the  $\text{Fe}(\text{CO})_4$ -group facing the butadiene unit irrespective of the initial stereochemistry of the phosphine. Consequently, net 'inversion' at the bridgehead phosphorus atom must have occurred in the syn-compounds 2b and 3b at some stage of the reaction, generating in all cases the anti-ligands prior to final complex formation. This is also consistent with the apparently very large  $^{31}\text{P}$  complexation shifts, because inversion of the phosphine is associated with a large change in shift. When compared with the shift of the phosphine of the appropriate stereochemistry, the complexation shifts fall in the expected range. The epimerization at bridgehead phosphorus is not without precedence: Katz<sup>7)</sup> noted a syn- to anti-isomerization of the phenyl-compound 2b upon treatment with  $\text{HCl}$  in  $\text{CHCl}_3$ , 2a being thermodynamically favoured. With a similar class of compounds, the 7-methyl-7-phosphanorborenes, Mesch and Quin<sup>8)</sup> observed a syn- to anti-isomerization upon reaction with methanol. Again, the anti-isomer is favoured, and is accompanied by a large downfield



shift in the  $^{31}\text{P}$  NMR spectrum ( 66.3 ppm ). Since direct pyramidal inversion at phosphorus is energetically ruled out, it is most likely that a pentacoordinate intermediate is involved in the reaction path allowing a facile Berry-pseudorotation prior to final complexation.

Our findings cast new light on the complexation behaviour of strained phosphines, and suggest that they tend to isomerize to thermodynamically more stable phosphines before complexation.

- 1) C. A. McAuliffe and W. Levason in "Phosphine, Arsine, and Stibine Complexes of the Transition Elements" (Studies in Inorganic Chemistry; 1), Elsevier Scientific Publ. Comp., 1979.
- 2) W. J. Richter, Chem. Ber. 1984, in print.
- 3) M. Crutchfield, C. Dungan, J. Letcher, and J. R. Van Wazer, Topics in Phosphorus Chemistry, 5, 227 (1967).
- 4) Collection of NMR data, MPI f. Kohlenforschung.
- 5) The compounds were prepared from equimolar amounts of  $\text{Fe}_2(\text{CO})_9$  and the corresponding phosphines 1 - 3 in dry toluene. Selected data:  
4: mp :  $160^\circ\text{C}$  (dec.); IR ( $\nu_{\text{C=O}}$ ) 1930, 1940, 1965,  $2045\text{ cm}^{-1}$ ;  
 $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ ) +63.6 ppm; mass spectrum, m/e: 360 ( $\text{M}^+$ ), 332, 304, 276, 248 (70%), 192 (100%), 134. 5: mp :  $106^\circ\text{C}$ ; IR ( $\nu_{\text{C=O}}$ ) 1930, 1940, 1970,  $2045\text{ cm}^{-1}$ ;  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ ) +42.9 ppm; mass spectrum: m/e: 380 ( $\text{M}^+$ ), 352, 324, 296, 268 (100%), 190 (50%), 165.  
6: mp :  $70^\circ\text{C}$ ; IR ( $\nu_{\text{C=O}}$ ) 1930, 1940, 1960,  $2040\text{ cm}^{-1}$ ;  
 $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ ) +102.8 ppm; mass spectrum, m/e: 375 ( $\text{M}^+$ ), 347, 319, 291, 263 (100%), 192 (50%).
- 6) R. B. King, and K. H. Pannell, Inorg. Chem. 7, 273 (1968); stereochemistry of 5 not assigned.
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