

phenyl carbons of **4**. The  $\Delta\Delta\delta$  is 0.08 ppm. The carbonyl and cyanide carbon resonances were not observed due to lower quality spectra in the presence of the Yb-Optishift. These results indicate that at least for the compounds studied here, shift reagents affect  $^1\text{H}$  nmr resonances considerably more than  $^{13}\text{C}$  nmr resonances.

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**Registry No.** 1, 53897-00-0; 2, 53897-01-1; 3, 53897-02-2; 4, 32757-48-5; 5, 12100-40-2; 6, 12099-18-2; 7, 53897-03-3; 8, 12078-28-3; 9, 12152-37-3;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^2\text{-C}_2\text{H}_4)]\text{BF}_4$ , 41560-74-1; **11**, 53897-04-4; NaOEt, 141-52-6; KCN, 151-50-8; NaBH<sub>4</sub>, 16940-66-2; Et<sub>3</sub>OPF<sub>6</sub>, 17950-40-2; Yb-Optishift, 38054-03-4.

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## Stereochemically Nonrigid Behavior in Transition Metal Complexes. Variable-Temperature Phosphorus-31 Nuclear Magnetic Resonance Studies of Diene and Dienyl Complexes of Manganese, Rhenium, Iron, and Ruthenium Containing Phosphite Ligands

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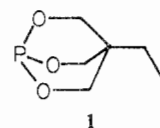
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The synthesis and characterization of a complete series of complexes of the types (diene) $\text{M}(\text{CO})_x(\text{EPTB})_{3-x}$  (where diene = cyclohexadiene, cycloheptadiene;  $\text{M} = \text{Fe}, \text{Ru}$ ;  $x = 0, 1, 2$ ) and (dienyl) $\text{M}(\text{CO})_x(\text{EPTB})_{3-x}$  (where dienyl = cyclopentadienyl, cyclohexadienyl, cycloheptadienyl;  $\text{M} = \text{Mn}, \text{Re}, \text{Fe}^+, \text{Ru}^+$ ;  $x = 1, 2$ ; and EPTB = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane) is described. Low-temperature  $^{31}\text{P}$  nmr studies of these complexes show that most of them exist as mixtures of ligand isomers and that these isomers are undergoing rapid interconversion at ambient temperatures. Computer simulation of the observed line shapes allowed the abstraction of kinetic parameters for the interconversion processes. Rates of ligand scrambling depend principally on the metal for both diene and dienyl species, decreasing in the order  $\text{Mn} \sim \text{Re} > \text{Fe}^+ > \text{Ru}^+$  for dienyl compounds and  $\text{Fe} > \text{Ru}$  for the diene complexes. Surprisingly, the formally five-coordinate diene complexes scramble only slightly faster than the formally six-coordinate dienyl complexes. The total range of rates is only a factor of about  $10^4$  at 220°K, suggesting that the phenomenon is probably quite general for transition metal  $\pi$  complexes. For the cycloheptadiene complexes, a second faster fluxional process involving equilibration of conformations of the methylene groups of the organic ligand was also observed.  $^{31}\text{P}$  nmr chemical shifts depend principally on the central metal atom, falling in the order  $\text{PMn}$  (-50 to -30 ppm) <  $\text{PFe}$  (-30 to -5 ppm) <  $\text{PRu}$  (-7 to +17 ppm) <  $\text{PRe}$  (+15 to +35 ppm) (shifts in ppm upfield of  $\text{P}(\text{OMe})_3$ ). Apical and basal ligands differ by about 10 ppm, with the basal ligands at higher field. Smaller effects of ring size, charge, and degree of substitution were also observed.

## Introduction

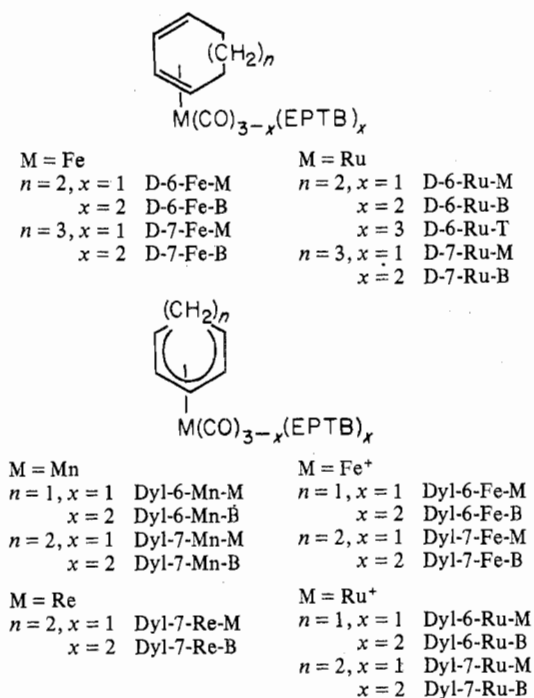
In connection with another problem, we had occasion to investigate the low-temperature  $^{31}\text{P}$  nmr spectrum of a fairly extensive series of cyclic diene and dienyl complexes of the type  $(\pi \text{ ligand})\text{M}(\text{CO})_x(\text{EPTB})_{3-x}$ , where  $\pi$  ligand =  $\eta^4$ -cyclohexadiene or  $\eta^4$ -cycloheptadiene,  $\text{M} = \text{Fe}$  or  $\text{Ru}$ , and  $x = 1, 2$ , or 3 or where  $\pi$  ligand =  $\eta^5$ -cyclohexadienyl or  $\eta^5$ -cycloheptadienyl,  $\text{M} = \text{Mn}, \text{Re}, \text{Fe}^+, \text{Ru}^+$ , and  $x = 1$  or 2 and where EPTB = 4-ethyl-1-phospha-2,6,7-

trioxabicyclo[2.2.2]octane, **1**. Most of these species show



interesting fluxional behavior, involving scrambling of the EPTB ligands among coordination sites at the metal, at rates which vary by a factor of about  $10^4$  at 220°K. In view of the

Scheme I. Diene Complexes



recent interest attracted by this kind of phenomenon, we here publish the results of this study, which in addition to being rather more extensive than previous work also describes the first examples to our knowledge of pentadienyl complexes which undergo intramolecular ligand-scrambling reactions. Related work has been carried out by Clark and coworkers,<sup>1,2</sup> Kruczynski and Takats,<sup>3a</sup> Giacometti, *et al.*,<sup>3b</sup> and Kreiter, Stüber, and Wachler<sup>4</sup> on diene iron complexes with PF<sub>3</sub> or CO ligands and by Kreiter and Lang<sup>5</sup> on cycloheptatriene complexes of chromium and molybdenum tricarbonyl.

### Experimental Section

**General Data.** While most of the compounds described here are not particularly air sensitive, all reactions involving organometallic species were performed under a nitrogen atmosphere, with reasonable precautions taken to exclude oxygen and water. These precautions included routine distillation of all solvents from drying agents prior to use. Saturated hydrocarbons were first stirred with concentrated sulfuric acid overnight, then distilled from KOH pellets, and stored over molecular sieves. Benzene was distilled from a blue suspension of sodium benzophenone ketyl and likewise stored over molecular sieves. Ethers (Et<sub>2</sub>O and THF) were freshly distilled under a nitrogen atmosphere from purple solutions of sodium benzophenone dianion. All solvents were degassed immediately prior to use by passing a stream of nitrogen through them for about 10 min.

Infrared spectra were routinely obtained using a Beckman IR8 infrared spectrophotometer. A few spectra were run on a Digilab FTS-20 fourier transform instrument. Proton spectra were obtained on Varian A-60A, Varian T-60, or JEOL MH100 spectrometers. High-resolution <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P nmr work was done using a Varian XL-100-15 spectrometer operating in the FT mode. All variable-temperature <sup>31</sup>P work was performed on acetone-*d*<sub>6</sub> solution using deuterium lock and proton decoupling on the XL-100-15 instrument.

Preparations involving photolysis were performed using light from a 450-W Hanovia medium-pressure mercury arc filtered through a Pyrex sleeve.

**Preparation of Tricarbonyl Complexes.** Most of the starting materials for the preparation of the complexes in Scheme I were known previous to this work. Cyclohexadienylmanganese tricarbonyl was prepared according to a slight modification of procedure of Winkhaus, Pratt, and Wilkinson;<sup>6</sup> cycloheptadienylmanganese tricarbonyl, by the procedure of Haque, *et al.*;<sup>7</sup> cyclopentadienylrhenium tricarbonyl, by the procedure of Green and Wilkinson;<sup>8</sup> and cyclohexadiene-ruthenium tricarbonyl, according to Cowles, *et al.*<sup>9</sup> The preparations of cyclohexadiene-<sup>10</sup> and cycloheptadieneiron<sup>11</sup> tricarbonyls were

performed by photolyzing the appropriate diene with iron penta-carbonyl. Distillation and chromatography gave materials identical with those described in the literature. Several attempts to prepare cyclohexadienylrhenium tricarbonyl by methods based on that used for the manganese compound failed.

**Preparation of  $\eta^5$ -Cycloheptadienylrhenium Tricarbonyl.** A mixture of Re<sub>2</sub>(CO)<sub>10</sub>, 652 mg (1 mmol), cycloheptadiene, 1.0 g (10.6 mmol), and 12 ml of mesitylene was refluxed under N<sub>2</sub> for 48 hr. Most of the mesitylene was removed by distillation under reduced pressure. The residue was chromatographed on alumina. Hexane-benzene mixtures eluted the product, which was isolated as a cream-colored solid, 712 mg (1.96 mmol, 98%). Sublimation (40°, 0.1 Torr) gave white crystals: mp 43°; ir (benzene) 2025, 1920 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ );  $\delta$  (benzene-*d*<sub>6</sub>) 5.34 (t,  $J = 5$  Hz, 1 H, H<sub>3</sub>), 4.92 (m, 2 H, H<sub>2</sub>, H<sub>4</sub>), 3.98 (broad d,  $J = 10$  Hz, 2 H, H<sub>6\beta</sub>, H<sub>7\beta</sub>), 1.89 (m, 4 H, H<sub>1</sub>, H<sub>5</sub>, H<sub>6\alpha</sub>, H<sub>7\alpha</sub>); mass spectrum  $m/e$  364.012 (calcd for C<sub>10</sub>H<sub>9</sub>O<sub>3</sub><sup>187</sup>Re 364.011).

*Anal.* Calcd for C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>Re: C, 33.05; H, 2.50; Re, 51.24. Found: C, 33.35; H, 2.59; Re, 50.90.

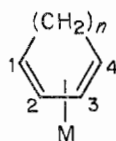
**Preparation of  $\eta^4$ -Cycloheptadienylruthenium Tricarbonyl.** Ruthenium dodecacarbonyl, 597 mg (0.93 mmol), cycloheptadiene, 2 ml (ca. 1.6 g, 17 mmol), and 15 ml of benzene were heated under reflux for 48 hr. Solvent was removed under reduced pressure, and the residue chromatographed on alumina. The product, eluted with hexane, was obtained as a pale yellow oil, 625 mg (81%); ir (hexane) 2065, 2000, 1990 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ );  $\delta$  (acetone-*d*<sub>6</sub>) 5.36 (m, 2 H, H<sub>2,3</sub>), 3.18 (m, 2 H, H<sub>1,4</sub>), 1.85 (m, 4 H, H<sub>5</sub>, H<sub>7</sub>), 1.42 (m, 2 H, H<sub>6</sub>); mass spectrum  $m/e$  279.98 (calcd for C<sub>10</sub>H<sub>10</sub>O<sub>3</sub><sup>102</sup>Ru 279.97).

**General Method for the Preparation of Neutral Complexes Containing EPTB Ligands.** A solution containing about 1 mmol of the neutral tricarbonyl complex and 3–5 mmol of EPTB<sup>12</sup> in about 85 ml of benzene was irradiated at ambient temperature in an annular well surrounding the water-cooled mercury arc. A continuous stream of N<sub>2</sub> was bubbled through the solution. The course of the reaction was monitored by ir spectra and thin-layer chromatography; when it appeared that the starting complex had been completely consumed (4–15 hr), the light was shut off and the solvent removed under reduced pressure. Chromatography on alumina allowed the separation of unreacted starting material and complexes with varying degrees of carbonyl substitution. Solvents used were hexane, benzene, ether, and ethyl acetate. Species obtained in this manner are listed in the format of compound (see Scheme I) (melting point, isolated yield), elution solvent, and high-resolution mass spectrum (calcd value): Dyl-5-Mn-M (10%), ethyl acetate,  $m/e$  338.011 (calcd for C<sub>13</sub>H<sub>16</sub>O<sub>5</sub>P<sup>55</sup>Mn 338.011); Dyl-5-Mn-B (38%), ethyl acetate,  $m/e$  472.061 (calcd for C<sub>18</sub>H<sub>27</sub>O<sub>2</sub>P<sub>2</sub><sup>55</sup>Mn 472.061); Dyl-6-Mn-M (mp 192°, 29%), 50% benzene-hexane,  $m/e$  352.029 (calcd for C<sub>14</sub>H<sub>18</sub>O<sub>5</sub>P<sup>55</sup>Mn 352.027); Dyl-6-Mn-B (mp 240° dec, 56%), benzene,  $m/e$  486.076 (calcd for C<sub>19</sub>H<sub>29</sub>O<sub>7</sub>P<sub>2</sub><sup>55</sup>Mn 486.077); Dyl-7-Mn-M (mp 150°, 4%), 50% benzene-hexane,  $m/e$  366.043 (calcd for C<sub>15</sub>H<sub>20</sub>O<sub>5</sub>P<sup>55</sup>Mn 366.043); Dyl-7-Mn-B (mp 248°, 64%), benzene,  $m/e$  500.085 (calcd for C<sub>20</sub>H<sub>31</sub>O<sub>7</sub>P<sub>2</sub><sup>55</sup>Mn 500.093); Dyl-5-Re-M (41%), ether,  $m/e$  470.029 (calcd for C<sub>13</sub>H<sub>16</sub>O<sub>5</sub>P<sup>187</sup>Re 470.029); Dyl-5-Re-B (15%), ethyl acetate,  $m/e$  604.078 (calcd for C<sub>18</sub>H<sub>27</sub>O<sub>7</sub>P<sub>2</sub><sup>187</sup>Re 604.079); Dyl-7-Re-M (mp 162°, 47%), benzene,  $m/e$  498.058 (calcd for C<sub>15</sub>H<sub>20</sub>O<sub>5</sub>P<sup>187</sup>Re 498.061); Dyl-7-Re-B (mp 215° dec, 13%), 50% ether-benzene,  $m/e$  632.108 (calcd for C<sub>20</sub>H<sub>31</sub>O<sub>7</sub>P<sub>2</sub><sup>187</sup>Re 632.110); D-6-Fe-M (mp 149°, 11%), 50% benzene-hexane,  $m/e$  354.031 (calcd for C<sub>14</sub>H<sub>19</sub>O<sub>5</sub>P<sup>56</sup>Fe 354.032); D-6-Fe-B (mp 178° dec, 50%), benzene, no molecular ion; D-7-Fe-M (mp 115°, 55%), 50% benzene-hexane,  $m/e$  368.047 (calcd for C<sub>15</sub>H<sub>21</sub>O<sub>5</sub>P<sup>56</sup>Fe 368.047); D-7-Fe-B (mp 207° dec, 42%), 75% benzene-hexane,  $m/e$  502.097 (calcd for C<sub>20</sub>H<sub>32</sub>O<sub>7</sub>P<sub>2</sub><sup>56</sup>Fe 502.097); D-6-Ru-M (mp 140°, 39%), benzene,  $m/e$  400.001 (calcd for C<sub>14</sub>H<sub>19</sub>O<sub>5</sub>P<sup>102</sup>Ru 400.001); D-6-Ru-B (mp 192°, 35%), 25% ether-benzene,  $m/e$  534.051 (calcd for C<sub>19</sub>H<sub>30</sub>O<sub>7</sub>P<sub>2</sub><sup>102</sup>Ru 534.050); D-6-Ru-T (11%), 50% ether-benzene,  $m/e$  668.100 (calcd for C<sub>24</sub>H<sub>41</sub>O<sub>9</sub>P<sub>3</sub><sup>102</sup>Ru 668.100); D-7-Ru-M (mp 118°, 35%), 50% benzene-hexane,  $m/e$  414.016 (calcd for C<sub>15</sub>H<sub>21</sub>O<sub>5</sub>P<sup>102</sup>Ru 414.016); D-7-Ru-B (mp 185°, 24%), 30% ether-benzene,  $m/e$  548.066 (calcd for C<sub>20</sub>H<sub>32</sub>O<sub>7</sub>P<sub>2</sub><sup>102</sup>Ru 548.066).

**General Method for the Preparation of Tetrafluoroborate Salts of the Dienyliron and -ruthenium Cations.** A solution of triphenylmethyl tetrafluoroborate in methylene chloride was allowed to react with a 5% molar excess of the diene complex dissolved in methylene chloride. The solution was stirred at room temperature until the carbonyl bands of the starting material had disappeared (0.5–20 hr). The methylene

Table I. Metal Carbonyl Stretching Frequencies

Compd	Solvent	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$	Compd	Solvent	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$
Diene Complexes					
D-6-Fe-M	Benzene	1990, 1925	D-6-Ru-M	Benzene	2010, 1941
D-6-Fe-B	Benzene	1930	D-6-Ru-B	Benzene	1941
D-7-Fe-M	Benzene	1985, 1930	D-7-Ru-M	Benzene	2015, 1940
D-7-Fe-B	Benzene	1925	D-7-Ru-B	Benzene	1945
Dienyl Complexes					
Dyl-5-Mn-M	Hexane	1955, 1888	Dyl-6-Fe-N	Acetone	2120, 2070
Dyl-5-Mn-B	$\text{CHCl}_3$	1885	Dyl-6-Fe-M	Acetone	2070, 2030
Dyl-6-Mn-M	$\text{CS}_2$	1955, 1875	Dyl-6-Fe-B	Acetone	2015
Dyl-6-Mn-B	$\text{CS}_2$	1883	Dyl-7-Fe-N	Acetone	2120, 2070
Dyl-7-Mn-M	Hexane	1950, 1890	Dyl-7-Fe-M	Acetone	2065, 2025
Dyl-7-Mn-B	Hexane	1885	Dyl-7-Fe-B	Acetone	2007
Dyl-5-Re-M	Hexane	1950, 1880	Dyl-6-Ru-M	Acetone	2085, 2045
Dyl-5-Re-B	$\text{CHCl}_3$	1888	Dyl-6-Ru-B	Acetone	2015
Dyl-7-Re-N	Hexane	2025, 1920	Dyl-7-Ru-M	Acetone	2087, 2040
Dyl-7-Re-M	Hexane	1953, 1886	Dyl-7-Ru-B	Acetone	2038
Dyl-7-Re-B	Hexane	1886			

Table II. Proton Chemical Shifts<sup>a</sup> for Diene Complexes

Compd	Solvent	$H_{2,3}^b$	$H_{1,4}^b$	EPTB		
				$\text{OCH}_2$	$\text{CH}_2\text{CH}_3$	Other
D-6-Fe-M	Benzene- $d_6$	4.99	3.08	3.35	0.17	1.67 ( $H_5, H_6$ )
D-6-Fe-B	Benzene- $d_6$	5.28	3.27	3.75	0.20	1.6–2.3 ( $H_5, H_6$ )
D-7-Fe-M	Benzene- $d_6$	5.08	3.07	3.60	0.23	1.95 ( $H_5, H_7$ ) 1.33 ( $H_6$ )
D-7-Fe-B	Benzene- $d_6$	5.23	3.10	3.78	0.20	2.24 ( $H_5, H_7$ ) 1.53 ( $H_6$ )
D-6-Ru-M	Benzene- $d_6$	5.18	3.13	3.53	0.10	1.79 ( $H_5, H_6$ )
D-6-Ru-B	Benzene- $d_6$	5.42	3.33	3.70	0.13	2.07 ( $H_5, H_6$ )
D-6-Ru-T	Acetone- $d_6$	4.74	2.56	4.00	1.15	1.3–1.8 ( $H_5, H_6$ )
D-7-Ru-M	Benzene- $d_6$	5.18	3.14	3.56	0.27	1.86 ( $H_5, H_7$ ) 1.40 ( $H_6$ )
D-7-Ru-B	Benzene- $d_6$	5.38	3.20	3.84	0.30	2.27 ( $H_5, H_7$ ) 1.77 ( $H_6$ )

<sup>a</sup> In  $\delta$ . <sup>b</sup> All signals multiplets.

chloride was evaporated, and the residue dissolved in a minimum volume of acetone. Dropwise addition of ether led to the precipitation of the dienyl salts in 48–99% yield. Analytical and spectral data are included in Tables I–IV.

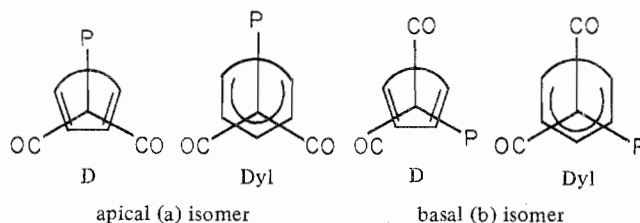
## Results

The compounds whose spectra we obtained are shown in Scheme I. Twenty-three compounds were prepared in all. These will be identified in the ensuing discussion by the mnemonics shown in Scheme I: the type of complex will be identified by the prefix D (diene) or Dyl (dienyl), followed by a numeral denoting the ring size of the organic ligand; the metal, by its symbol; and the number of EPTB ligands, by the letters N (none), M (monosubstituted), B (bis substituted), or T (tris substituted).

The neutral compounds were synthesized by photolysis of the corresponding tricarbonyl complex with an excess of the EPTB ligand dissolved in benzene. This treatment generally produced a mixture of mono- and bis-substituted complexes which could be easily separated by chromatography on alumina. The cationic species were generated by hydride abstraction with triphenylmethyl tetrafluoroborate in methylene chloride, followed by precipitation with ether. The compounds were characterized by their spectral properties, relevant features of which are shown in Tables I–III, elemental analysis (Table IV), and high-resolution mass spectra (see Experimental Section).

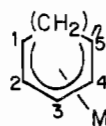
**Phosphorus Nmr Spectra.** The  $^{31}\text{P}$  nmr spectra of the

compounds in Scheme I generally consisted of singlets at ambient temperature. In the case of the mono-substituted species, as the temperature was lowered, this resonance usually broadened, and then split up into two peaks of unequal intensity, separated by about 10 ppm. These peaks are assigned to phosphorus atoms in each of the two possible chemical environments of the idealized tetragonal-pyramidal coordination geometry: apical (a) and basal (b)



Evidently, these two isomers interconvert rapidly on the nmr time scale at ambient temperature but more slowly at lower temperatures. The peak at higher field is assigned to the basal isomer on the basis of comparison to the bis and tris complexes (see below), where the apical and basal isomers can be unambiguously assigned.

Temperature-dependent spectra were observed for all of the mono-substituted complexes except D-6-Fe-M and D-7-Fe-M, where only one peak for each species was observed from  $-100$  to  $+35^\circ$ . In these complexes, either averaging remains rapid

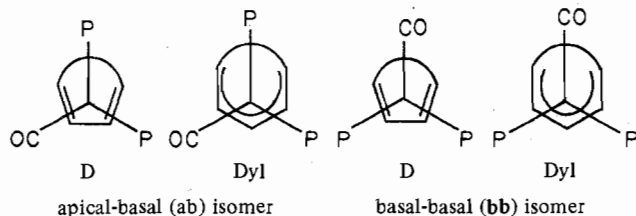
Table III. Proton Chemical Shifts<sup>a</sup> for Dienyl Complexes

Compd	Solvent	H <sub>3</sub>	H <sub>2,4</sub>	H <sub>1,5</sub>	EPTB		Other
					OCH <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub> <sup>b</sup>	
Dyl-5-Mn-M	Benzene- <i>d</i> <sub>6</sub>	4.38	4.38	4.38	3.63	0.2	
Dyl-5-Mn-B	Benzene- <i>d</i> <sub>6</sub>	4.61	4.61	4.61	3.76	0.2	
Dyl-6-Mn-M	Benzene- <i>d</i> <sub>6</sub>	5.52	4.45	2.58	3.58	0.2	2.00 (H <sub>6α</sub> )
Dyl-6-Mn-B	Benzene- <i>d</i> <sub>6</sub>	5.56	4.85	2.74	3.80	0.22	3.12 (H <sub>6β</sub> ) 2.30 (H <sub>6α</sub> ) 3.20 (H <sub>6β</sub> )
Dyl-7-Mn-M	Benzene- <i>d</i> <sub>6</sub>	5.41	4.80	3.76	3.53	0.2	1.50 (2H) 2.22 (2H)
Dyl-7-Mn-B	Benzene- <i>d</i> <sub>6</sub>	5.50	5.13	3.83	3.78	0.2	2.53 (2H) 1.73 (2H)
Dyl-5-Re-M	CDCl <sub>3</sub>	5.18	5.18	5.18	4.24	0.7-1.3	
Dyl-5-Re-B	CDCl <sub>3</sub>	5.02	5.02	5.02	4.20	0.7-1.4	
Dyl-7-Re-N	Benzene- <i>d</i> <sub>6</sub>	5.34	4.92	3.98			1.89 (2H) 1.88 (2H)
Dyl-7-Re-M	Benzene- <i>d</i> <sub>6</sub>	5.33	5.00	3.97	3.66	0.20	1.86 (2H) 1.94 (2H)
Dyl-7-Re-B	Benzene- <i>d</i> <sub>6</sub>	5.60	5.20	4.13	3.78	0.13	2.07 (2H) 2.20 (2H)
Dyl-6-Fe-M	CDCl <sub>3</sub>	7.01	5.79	4.06	4.55	0.10	2.78 (H <sub>6α</sub> ) 3.15 (H <sub>6β</sub> )
Dyl-6-Fe-B	Acetone- <i>d</i> <sub>6</sub>	6.50	5.43	3.33	4.46	0.13	2.84 (H <sub>6α</sub> ) 3.93 (H <sub>6β</sub> )
Dyl-7-Fe-M	Acetone- <i>d</i> <sub>6</sub>	6.80	5.95	4.81	4.60	0.12	1.85 (2H) 2.16 (2H)
Dyl-7-Fe-B	Acetone- <i>d</i> <sub>6</sub>	6.50	5.55	4.17	4.46	0.11	1.66 (2H) 2.48 (2H)
Dyl-6-Ru-M	Acetone- <i>d</i> <sub>6</sub>	6.75	5.55	4.14	4.65	0.11	3.25 (2H)
Dyl-6-Ru-B	Acetone- <i>d</i> <sub>6</sub>	5.51	4.80	2.84	4.48	0.11	1.60 (H <sub>6α</sub> ) 3.45 (H <sub>6β</sub> )
Dyl-7-Ru-M	Acetone- <i>d</i> <sub>6</sub>	6.75	6.04	5.88	4.62	0.11	2.00 (2H) 2.70 (2H)
Dyl-7-Ru-B	Acetone- <i>d</i> <sub>6</sub>	5.80	4.90	4.30	4.54	0.11	2.44 (2H) 3.14 (2H)

<sup>a</sup> in δ. <sup>b</sup> These protons appeared as an A<sub>2</sub>B<sub>3</sub> pattern, the center of which is reported.

at -100° or one isomer is favored to the exclusion of the other. On the basis of chemical shift considerations, the second possibility is favored, since the chemical shifts observed for these compounds (-19.00 and -15.10 ppm, respectively)<sup>13</sup> are similar to those observed for the basal ligands of the corresponding bis complexes D-6-Fe-B (-21.14 ppm) and D-7-Fe-B (-16.95 ppm). If scrambling were taking place between appreciable quantities of both apical and basal isomers, the averaged chemical shift would have been expected to be at somewhat lower field. The chemical shifts of the apical and basal isomers are given in Table V.

The low-temperature <sup>31</sup>P spectra of the bis-substituted species are somewhat more complex. Here again, two possible isomers exist: apical-basal (ab) and basal-basal (bb). While



the phosphorus atoms in the bb isomer are in identical environments and therefore give rise to a singlet in the <sup>31</sup>P spectrum, the ligands in the ab isomer are nonequivalent and also strongly coupled. The latter isomer therefore gives rise at sufficiently low temperature to a coupled AB pattern, with four lines. Again, however, as the temperature is increased

and the rate of interconversion of isomers increases, all five resonances broaden and eventually collapse to a single line at a chemical shift which is approximately the average of the three which characterize the low-temperature spectrum, weighted by the populations of the ab and bb isomers (the agreement of the calculated average and observed chemical shift in general was not exact due probably to minor changes in the chemical shifts with temperature or to shifts in populations with temperature or both). Three chemical shifts and a coupling constant are necessary to describe completely the low-temperature spectrum. It is possible to assign reasonably unambiguously the two chemical shifts of the ab isomer to the apical and basal ligands, because half of the coupled AB pattern, assigned to the basal ligand, invariably had a chemical shift similar to the singlet while the other occurred *ca.* 10 ppm to lower field. This observation also serves as a basis for the assignment of the peaks in the monoadduct spectra, where approximately the same chemical shift difference is observed between a and b isomers, and, for the same metal, charge, and ring size, similar shifts as well. The values obtained for the bis adducts are shown in Table VI. Also included in this table is the one tris adduct observed: D-6-Ru-T. This species gave rise to a coupled A<sub>2</sub>B spectrum at low temperature and a singlet at high temperature as expected if the same kind of ligand scrambling were occurring in this case as well.

The rates of isomer interconversion were determined by complete line shape analysis using one of several calculational schemes depending on the complexity of the spectrum to be simulated. For Dyl-6-Mn-B, Dyl-7-Mn-B, and Dyl-7-Re-B,

Table IV. Elemental Analyses

Compd		% C	% H	% metal
Dyl-6-Mn-M	Found	47.64	5.15	15.55
	Calcd for C <sub>14</sub> H <sub>18</sub> O <sub>5</sub> PMn	47.74	5.15	15.60
Dyl-6-Mn-B	Found	47.15	6.12	10.72
	Calcd for C <sub>19</sub> H <sub>29</sub> O <sub>7</sub> P <sub>2</sub> Mn	47.22	6.05	11.37
Dyl-7-Mn-M	Found	49.40	5.65	14.82
	Calcd for C <sub>15</sub> H <sub>20</sub> O <sub>5</sub> PMn	49.19	5.50	15.00
Dyl-7-Mn-B	Found	48.81	6.16	11.16
	Calcd for C <sub>20</sub> H <sub>31</sub> O <sub>7</sub> P <sub>2</sub> Mn	48.01	6.25	10.98
Dyl-7-Re-M	Found	36.47	4.10	14.78
	Calcd for C <sub>15</sub> H <sub>20</sub> O <sub>5</sub> Pre	36.21	4.05	37.43
Dyl-7-Re-B	Found	38.78	5.07	17.60
	Calcd for C <sub>20</sub> H <sub>31</sub> O <sub>7</sub> P <sub>2</sub> Re	38.03	4.95	29.48
D-6-Fe-M	Found	47.05	5.25	15.53
	Calcd for C <sub>14</sub> H <sub>18</sub> O <sub>5</sub> PFe	47.48	5.41	15.77
D-6-Fe-B	Found	46.78	6.23	11.28
	Calcd for C <sub>19</sub> H <sub>30</sub> O <sub>7</sub> P <sub>2</sub> Fe	46.74	6.19	11.44
D-7-Fe-B	Found	48.56	6.50	11.40
	Calcd for C <sub>20</sub> H <sub>32</sub> O <sub>7</sub> P <sub>2</sub> Fe	47.83	6.42	11.12
D-6-Ru-M	Found	42.57	4.96	24.62
	Calcd for C <sub>14</sub> H <sub>18</sub> O <sub>5</sub> PRu	42.11	4.80	25.31
D-6-Ru-B	Found	44.51	5.90	16.55
	Calcd for C <sub>19</sub> H <sub>30</sub> O <sub>7</sub> P <sub>2</sub> Ru	42.78	5.67	18.95
D-6-Ru-T	Found	41.73	6.04	15.59
	Calcd for C <sub>24</sub> H <sub>41</sub> O <sub>9</sub> P <sub>3</sub> Ru	43.18	6.19	15.14
D-7-Ru-M	Found	44.08	5.02	23.08
	Calcd for C <sub>15</sub> H <sub>21</sub> O <sub>5</sub> PRu	43.58	5.12	24.45
D-7-Ru-B	Found	44.71	6.07	15.74
	Calcd for C <sub>20</sub> H <sub>32</sub> O <sub>7</sub> P <sub>2</sub> Ru	43.88	5.89	18.46
Dyl-6-Fe-M	Found	38.01	4.24	12.83
	Calcd for C <sub>14</sub> H <sub>18</sub> O <sub>5</sub> PBF <sub>4</sub> Fe	37.88	4.09	12.58
Dyl-6-Fe-B	Found	38.71	5.17	9.62
	Calcd for C <sub>19</sub> H <sub>29</sub> O <sub>7</sub> P <sub>2</sub> BF <sub>4</sub> Fe	36.76	5.09	9.75
Dyl-7-Fe-M	Found	39.48	4.34	12.30
	Calcd for C <sub>15</sub> H <sub>20</sub> O <sub>5</sub> PBF <sub>4</sub> Fe	39.34	4.40	12.19
Dyl-7-Fe-B	Found	41.23	5.30	9.64
	Calcd for C <sub>20</sub> H <sub>31</sub> O <sub>7</sub> P <sub>2</sub> BF <sub>4</sub> Fe	40.85	5.31	9.50
Dyl-6-Ru-M	Found	33.40	3.72	11.95
	Calcd for C <sub>14</sub> H <sub>18</sub> O <sub>5</sub> PBF <sub>4</sub> Ru	34.66	3.74	20.83
Dyl-6-Ru-B	Found	34.30	4.63	11.13
	Calcd for C <sub>19</sub> H <sub>29</sub> O <sub>7</sub> P <sub>2</sub> BF <sub>4</sub> Ru	37.93	4.93	15.96
Dyl-7-Ru-M	Found	35.78	4.06	19.80
	Calcd for C <sub>15</sub> H <sub>20</sub> O <sub>5</sub> PBF <sub>4</sub> Ru	36.09	4.04	20.25
Dyl-7-Ru-B	Found	38.83	5.33	15.09
	Calcd for C <sub>20</sub> H <sub>31</sub> O <sub>7</sub> P <sub>2</sub> BF <sub>4</sub> Ru	37.93	4.93	15.96

Table V. <sup>31</sup>P Nmr Chemical Shifts<sup>a</sup> for Monoadducts

Compd	Temp, <sup>b</sup> °C	Apical (pop.) <sup>f</sup>	Basal (pop.)	Δ <sup>c</sup>
Diene Complexes				
D-6-Fe-M	-92	(0)	-19.00 <sup>d</sup> (1.0?)	
D-7-Fe-M	-92	(0)	-15.10 <sup>d</sup> (1.0?)	
D-6-Ru-M	-66	-0.79 (0.36)	+7.03 (0.64)	6.24
D-7-Ru-M	-86	+2.29 (0.22)	+9.49 <sup>e</sup> (0.52)	7.20
			+10.62 <sup>e</sup> (0.26)	8.33
Diényl Complexes				
Dyl-6-Mn-N	-96	-44.45 (0.32)	-34.86 (0.68)	9.59
Dyl-7-Mn-M	-96	-45.63 (0.13)	-33.04 (0.87)	12.59
Dyl-7-Re-M	-94	+21.84 (0.65)	+34.96 (0.35)	13.12
Dyl-6-Fe-M	-96	-17.3 (0.01)	-10.6 (0.99)	6.7
Dyl-7-Fe-M	-89	-18.55 (0.01)	-8.76 (0.99)	9.79
Dyl-6-Ru-M	-53	+8.31 (0.42)	+15.80 (0.58)	7.49
Dyl-7-Ru-M	-65	6.14 (0.39)	16.51 (0.61)	10.37

<sup>a</sup> In acetone-*d*<sub>6</sub>; ppm upfield from P(OMe)<sub>3</sub>. <sup>b</sup> Temperature of measurement. <sup>c</sup> Δ = δ(basal) - δ(apical). <sup>d</sup> Still possibly averaging (see text). <sup>e</sup> Resonances due to different ring conformations (see text). <sup>f</sup> Population given in parentheses.

where only the *ab* isomer is observed at low temperature, the equation derived by Heidberg and coworkers<sup>14</sup> was used; for all of the monoadducts, whose spectra consist of two singlets of unequal intensity, the equation of Gutowsky and Holm<sup>15</sup> was used. In both of these cases, the calculated line shapes were plotted using programs based on these equations written

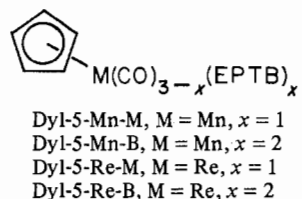
for a Wang 720C programmable calculator<sup>16</sup> equipped with a plotter. In the more complicated cases, line shapes were calculated using program DNMR.<sup>17</sup>

The accuracy of the results is limited in some cases by one of several considerations. The most important source of error occurred in the manganese and, to a lesser extent, rhenium complexes. Both of these elements include nuclei with large spins and quadrupole moments. The resulting coupling and relaxation effects introduce substantial *temperature-dependent* line-broadening effects. For example, the <sup>31</sup>P line widths in the manganese diényl complexes range from more than 150 Hz at 30° to about 5–10 Hz at -100° (see Figure 1). Experimentally, this phenomenon means that as the high-temperature limit is approached, the line width of the growing singlet goes through a minimum. Another complicating feature of these spectra is that the quadrupole broadening is not the same for the two ligand positions; thus, one set of resonances is broadened more than the other. This effect was *partially* corrected for by observing the phosphorus line widths in a series of manganese and rhenium cyclopentadiényl complexes as a function of temperature. Here rotation about the metal-ring axis is fast at all available temperatures, and the only effect on the line width is quadrupole broadening. The compounds studied are shown in the following structure. The <sup>31</sup>P chemical shifts (ppm, in acetone, with respect to P(OMe)<sub>3</sub>) of these species are as follows: Dyl-5-Mn-M, -44.48; Dyl-5-Mn-B, -46.45; Dyl-5-Re-M, +29.1; Dyl-5-Re-B, +26.65. The

Table VI.  $^{31}\text{P}$  Nmr Chemical Shifts<sup>a</sup> and Coupling Constants for Bis and Tris Adducts

Compd	$T, ^\circ\text{C}$	ab isomer				bb isomer	
		a	b	$J_{\text{pp}}^c$	Pop. <sup>d</sup>	b	Pop. <sup>d</sup>
Diene Complexes							
D-6-Fe-B	-93	-28.21	-21.14	34.1	0.65	-21.47	0.35
D-7-Fe-B	-102	-24.41	-16.95	30.0	0.69	-18.00 <sup>e</sup>	0.20
						-17.55 <sup>e</sup>	0.11
D-6-Ru-B	-91	-4.48	+4.79	35.0	0.89	+5.24 <sup>e</sup>	0.11
D-7-Ru-B	-80	-1.53	+8.72	31.3	0.67	+7.27 <sup>e</sup>	0.26
						+8.83 <sup>e</sup>	0.07
D-6-Ru-T	-80	-6.84 <sup>f</sup>	+3.28 <sup>g</sup>	38.0			
Dienyl Complexes							
Dyl-6-Mn-B	-97	-47.64	-35.15	91.0	1.0	<i>h</i>	0
Dyl-7-Mn-B	-72	-49.15	-33.34	89.7	1.0	<i>h</i>	0
Dyl-7-Re-B	-73	+15.35	+30.03	27.5	1.0	<i>h</i>	0
Dyl-6-Fe-B	-96	-22.65	-14.80	95.7	0.87	-5.95	0.13
Dyl-7-Fe-B	-95	-24.12	-13.40	94.2	0.72	-12.24	0.28
Dyl-6-Ru-B	-81	+4.35	+11.28	69.5	0.95	+12.95	0.05
Dyl-7-Ru-B	-81	+2.70	+10.86	69.7	0.95	+11.32	0.05

<sup>a</sup> In acetone- $d_6$ ; chemical shifts in ppm upfield of  $\text{P}(\text{OCH}_3)_3$ . <sup>b</sup> Temperature of observation. <sup>c</sup> Phosphorus-phosphorus coupling constant (Hz). <sup>d</sup> Population. <sup>e</sup> Chemical shifts of two ring conformers (see text). <sup>f</sup> A part of  $\text{AB}_2$  spectrum. <sup>g</sup>  $\text{B}_2$  part of  $\text{AB}_2$  spectrum. <sup>h</sup> None of this isomer detected.

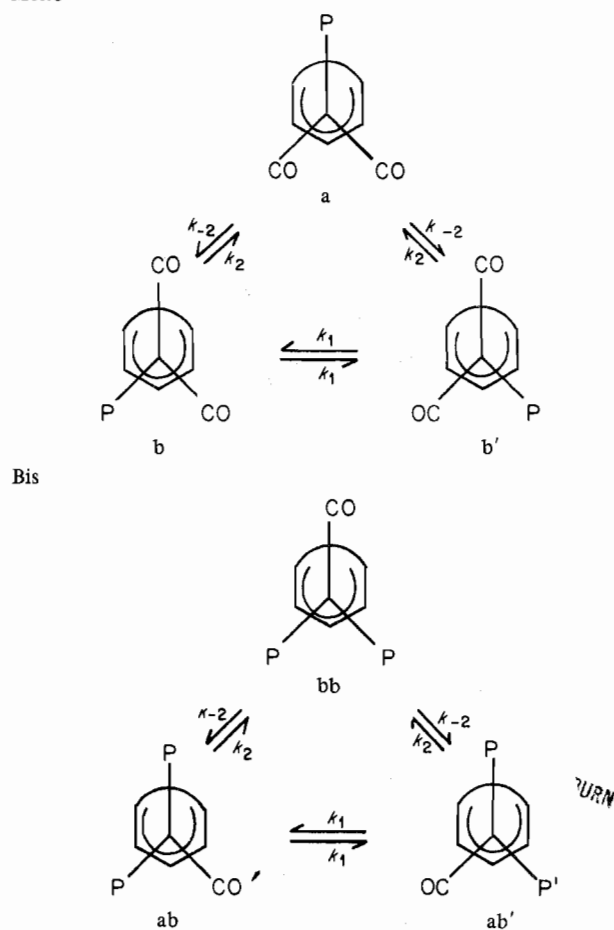


temperature dependence of their phosphorus line widths is shown in Figure 2. Line widths taken from this graph were used in the calculation of the line shapes for the manganese and rhenium complexes. Fortunately, in the region of greatest interest, around the coalescence temperature, the greatest contribution to the line shape is from exchange broadening, and the line shape is not very sensitive to the choice of natural line width. For this reason, rates derived from line shape fitting near coalescence are regarded as fairly accurate.

Another effect limiting the accuracy of the results arises in the monosubstituted series when the population of one isomer is high relative to the other. Under these circumstances, the line shape of the major isomer will be only slightly affected by the exchange, and in the region above coalescence there will therefore be only minor changes in line shape. In these cases, rates were derived principally from changes in the shape of the peak due to the minor isomer and thus were restricted to the region below coalescence.

A final limitation on the information derivable from the spectra is more fundamental. In order to characterize completely the kinetic behavior of the system in question three rate constants are necessary:  $k_1$ ,  $k_2$ ,  $k_{-2}$  (Scheme II). The ratio of  $k_2$  to  $k_{-2}$  is given by the population difference between a and b or ab and bb isomers. The magnitude of  $k_2$  or  $k_{-2}$  can be determined in all cases where appreciable quantities of both isomers are present, since interconversion of these isomers results in a change in the chemical environment of the phosphorus atom. Exchange *via*  $k_1$ , however, leads to no change in the observed spectrum, since the phosphorus nuclei are in identical chemical environments in both b and b' (which are enantiomeric). Only exchange *via*  $k_2$  is observable. In contrast, the rate constant  $k_1$  can be determined in the case of the bis adducts. Here exchange *via*  $k_1$  leads to the collapse of the coupled AB pattern; in the limit of no exchange *via* the symmetrical bb isomer a spectrum consisting of two singlets would result, one for the bb isomer and the other for the averaged ab isomer. On the other hand, exclusive exchange *via*  $k_2$  would lead to simultaneous collapse of all three signals.

Scheme II. Kinetic Scheme for Dienyl Complexes



The observed pattern of collapse is in fact intermediate between these two limits, and in order to simulate the observed spectra satisfactorily, different values of  $k_1$  and  $k_2$  were chosen by trial and error at each temperature. In the case of the bis adducts of Mn and Re, where none of the bb isomer can be observed, the observed rate constant measures the total rate of disappearance of the ab isomer by both  $k_1$  and  $k_2$ , and the two rate constants are not separable. Here again, only limited information can be derived from the spectra.

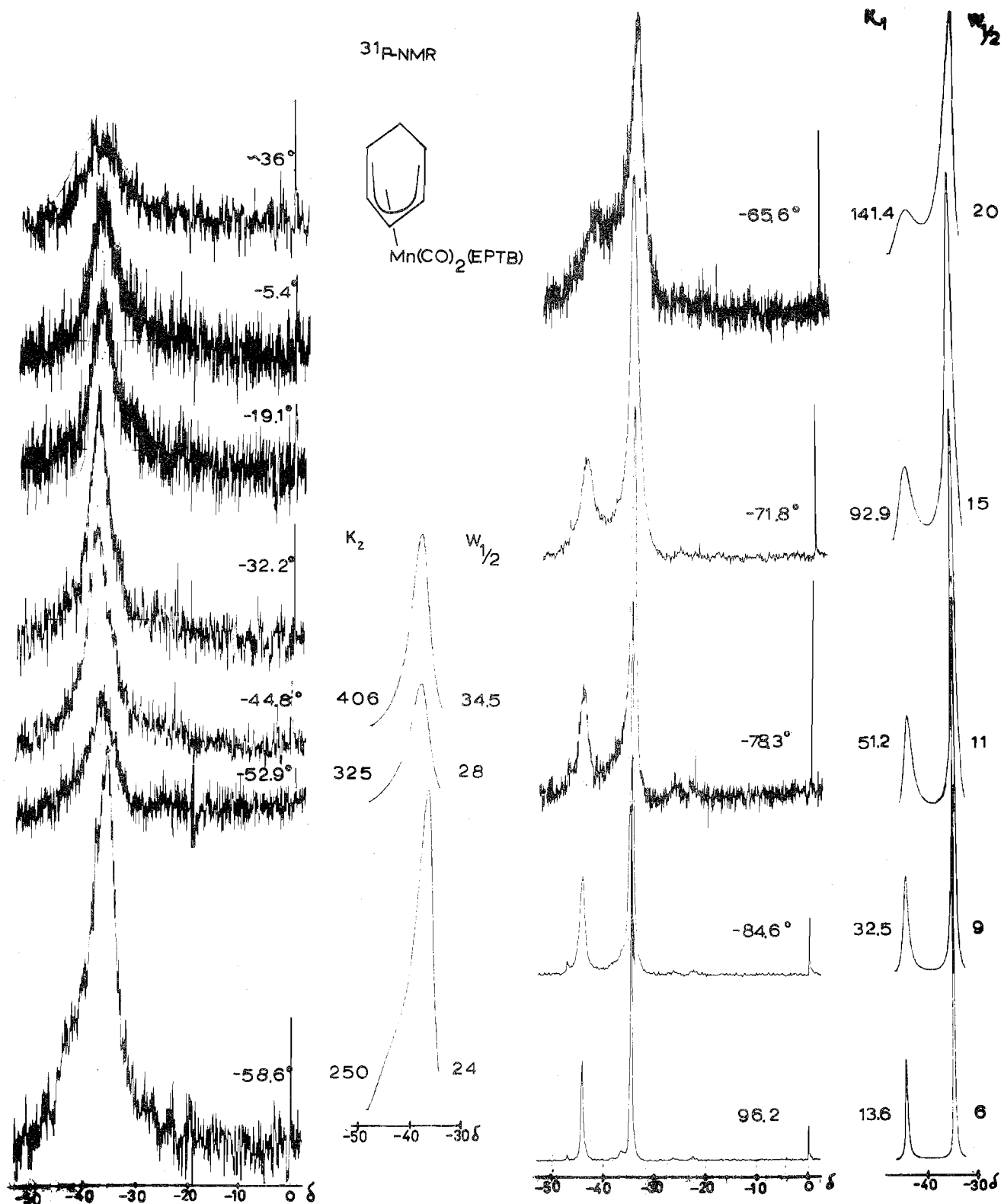


Figure 1. Temperature dependence of the  $^{31}\text{P}$  nmr spectrum of Dyl-6-Mn-M, proton decoupled. Note the effect of temperature-dependent quadrupolar line broadening. The spectra were simulated using line widths ( $W_{1/2}$ , Hz) taken from the graphs in Figure 2.

Typical spectra and simulations are shown in Figures 1, 3–5. Free energies of activation and rate constants at 220°K are given in Table VII. These values were determined by interpolation from results at other temperatures; the reference temperature was chosen to be one near the coalescence temperature for the maximum number of compounds so that large extrapolations were unnecessary. Limitations on the accuracy of the data discussed above do not warrant extraction

of the activation energies or frequency factors from our rates since good data were available only in a restricted temperature range near the coalescence temperature.

One entry in the table requires further comment. The fluxional nature of cyclohexadieneruthenium tricarbonyl, D-6-Ru-N, was investigated by  $^{13}\text{C}$  nmr using  $\text{Cr}(\text{acac})_3^{18}$  to enhance spin relaxation. As expected, two carbonyl resonances were observed at low temperature, and only one was observed

Table VII. Coalescence Temperatures, Free Energies of Activation at 220°K, and Rate Constants at 220°K for Ligand Scrambling

Compd	$T_c, ^\circ\text{C}$	$\Delta G^\ddagger_1, ^\text{b}$	$\Delta G^\ddagger_2, ^\text{b}$	$\Delta G^\ddagger_{-2}, ^\text{b}$	$k_1, ^\text{c}$	$k_2, ^\text{c}$	$k_{-2}, ^\text{c}$
Diene Complexes							
D-6-Fe-B	-78	9.9	8.5	8.6	710	15,600	14,300
D-7-Fe-B	-58	11.0	9.8	9.7	52	960	1,050
D-6-Ru-N	~-21	11.8 <sup>d</sup>	11.8 <sup>d</sup>	11.8 <sup>d</sup>			
D-6-Ru-M	-5		12.6	12.6		1.5	1.4
D-7-Ru-M	+4		13.2	13.0		0.3	0.6
D-6-Ru-B	-15	12.5	11.5	10.8	2.0	19.0	77.0
D-7-Ru-B	+5	13.2	11.9	11.9	0.4	7.3	7.5
D-6-Ru-T	-15	11.6	11.6	11.6	12.6	12.6	12.6
Dienyl Complexes							
Dyl-6-Mn-M			10.3	10.3		260	270
Dyl-7-Mn-M			10.6	10.1		123	404
Dyl-6-Mn-B		9.8			848 <sup>e</sup>		
Dyl-7-Mn-B		10.5			154 <sup>e</sup>		
Dyl-7-Re-M			11.0	11.5		58	16
Dyl-7-Re-B		10.3			263 <sup>e</sup>		
Dyl-6-Fe-M			12.1	10.5		4.7	165
Dyl-7-Fe-M			13.0	11.4		0.6	21
Dyl-6-Fe-B		9.8	10.5	10.0	886	175	595
Dyl-7-Fe-B		11.4	11.5	11.4	23	19	23
Dyl-6-Ru-M			12.8	13.0		0.9	0.6
Dyl-7-Ru-M			13.3	13.4		0.29	0.23
Dyl-6-Ru-B		12.8	13.0	12.1	0.94	0.52	4.7
Dyl-7-Ru-B		12.9	13.2	12.2	0.77	0.36	3.6

<sup>a</sup> Approximate coalescence temperature. <sup>b</sup> In kcal/mol; estimated precision  $\pm 0.2$  kcal/mol. <sup>c</sup> Determined from  $\Delta G^\ddagger(220^\circ\text{K})$ ; values in  $\text{sec}^{-1}$ . <sup>d</sup> From  $^{13}\text{C}$  nmr; see text. <sup>e</sup>  $k_{\text{obsd}} = k_1 + k_2$ ; see text.

Table VIII.  $^{13}\text{C}$  Nmr Chemical Shifts for D-6-Ru-N ( $-76.3^\circ$ )

Carbon atom	1,4	2,3	5,6	a	b
Chem shift <sup>a</sup>	+56.2	+88.2	+25.3	202.9	197.9
				200.1	

<sup>a</sup> In ppm downfield from tetramethylsilane.

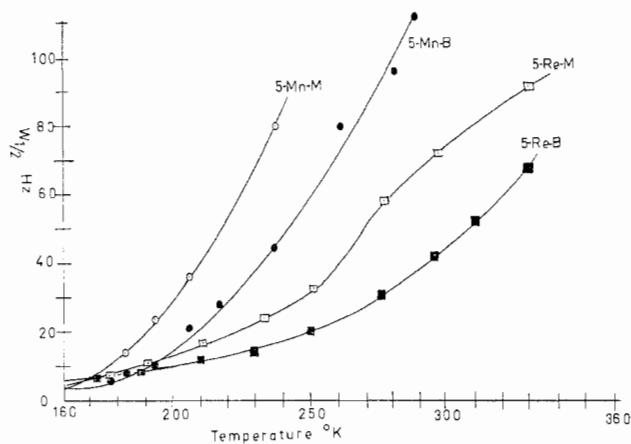
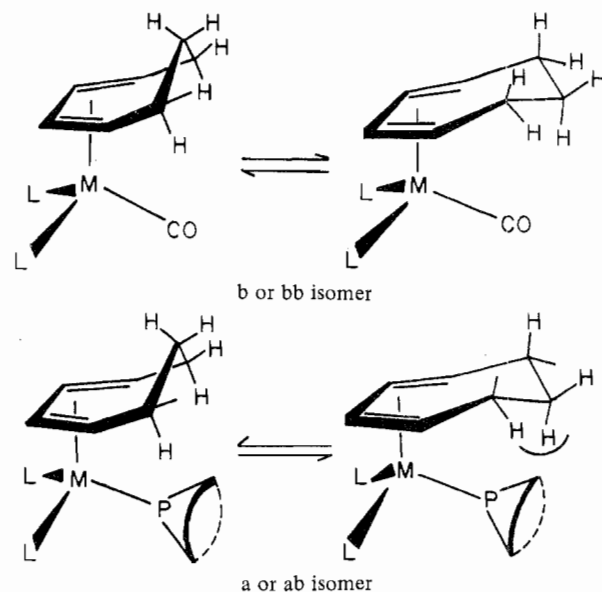


Figure 2. Temperature dependence of  $^{31}\text{P}$  nmr line widths for Dyl-5-Mn-M ( $\circ$ ), Dyl-5-Mn-B ( $\bullet$ ), Dyl-5-Re-M ( $\square$ ), and Dyl-5-Re-B ( $\blacksquare$ ).

at room temperature. The coalescence temperature of about  $21^\circ$  was used to evaluate  $\Delta G^\ddagger$ , giving the value shown in Table VII. Carbon-13 chemical shift parameters for D-6-Ru-N are given in Table VIII.

**Conformational Equilibria.** While ligand-scrambling reactions serve to provide an adequate explanation for the  $^{31}\text{P}$  nmr behavior of most of the molecules described here, in the cycloheptadiene complexes of iron and ruthenium still another fluxional process was observed. The type of behavior seen is illustrated in Figure 4 for D-7-Ru-M. Starting at  $47^\circ$ , successive spectra at lower temperatures show first broadening

Scheme III



and then, at about  $-7^\circ$ , the appearance of two singlets at 2.3 and 10.0 ppm, due to a and b isomers. The signal corresponding to the a isomer continues to sharpen, but the b isomer resonance reaches a maximum height at about  $-40$  and then collapses again, with a second coalescence temperature at about  $-80^\circ$ . Further cooling to  $-86^\circ$  leads finally to three singlets at 2.29, 9.49, and 10.62, corresponding to the apical isomer and two different b isomers. Similar phenomena were observed for D-7-Fe-B and D-7-Ru-B. Because this additional bridge was seen only for diene complexes containing a bridge with three methylene groups and because it was seen only for the isomer containing no large apical ligands, we assign this process to the rapid interconversion of two conformational isomers of the ring (Scheme III). As indicated there, the apical isomer exists essentially only in one conformer, a pseudoboat, because it has a sterically much larger ligand than CO in the apical position, where interference with the methylene group at C<sub>6</sub> is likely. In the isomers with CO apical, both ring conformers are accessible. Note that the interconversion of the pseudoboat



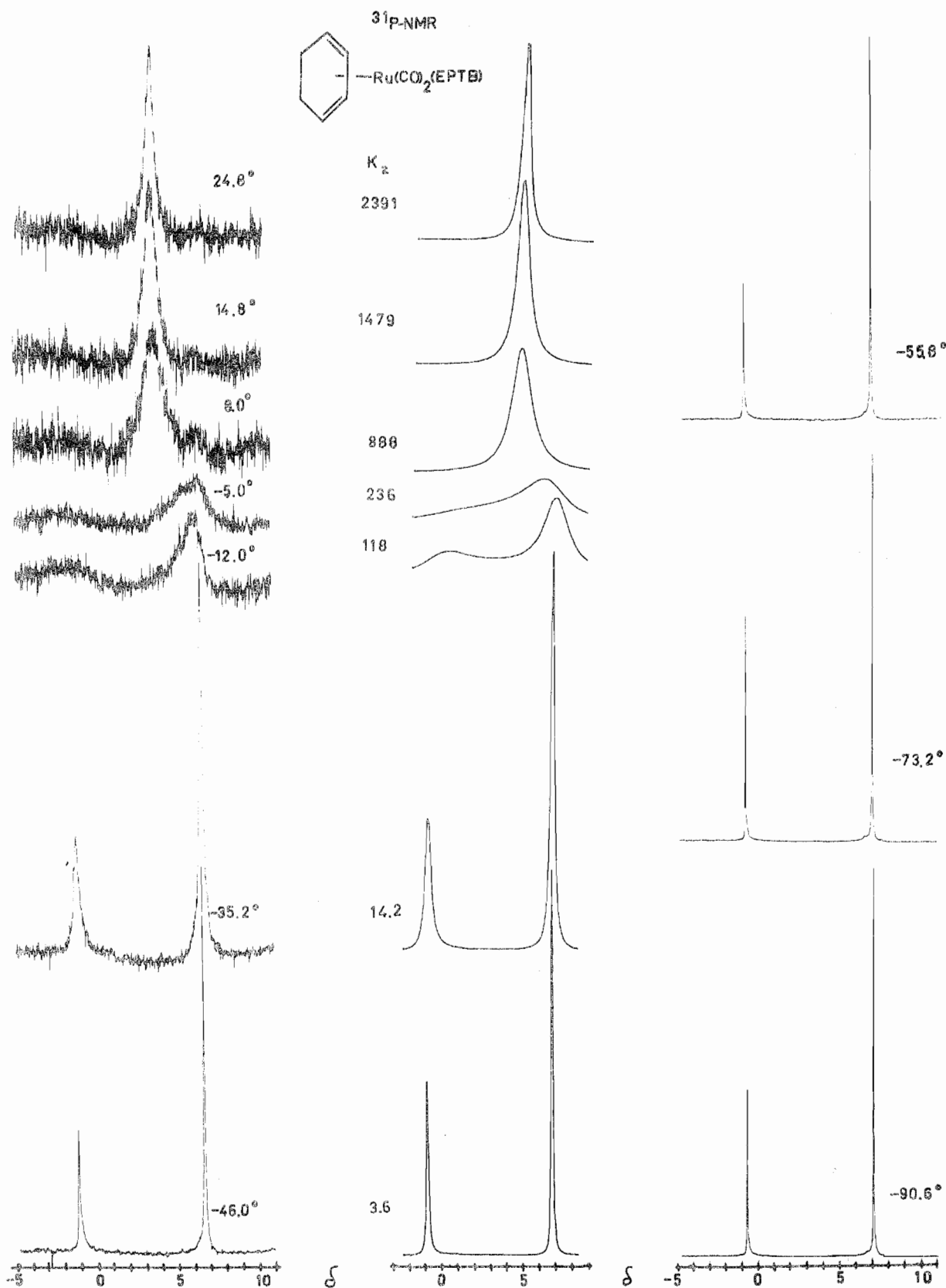


Figure 3. Temperature dependence of the  $^{31}\text{P}$  nmr spectrum of D-6-Ru-M, with proton decoupling.

and pseudochair ring conformations has not been included in the line shape calculation. This exclusion may introduce further uncertainty into the exact magnitude of the barrier to ligand scrambling in the cycloheptadiene series. Again, however, this effect is not expected to be serious near coalescence.

#### Discussion

**Fluxional Behavior.** Initially, it was expected that a large effect on the rate of stereochemically nonrigid behavior would be observed on changing from the formally  $d^8$ , five-coordinate iron and ruthenium diene complexes to the formally  $d^6$ ,

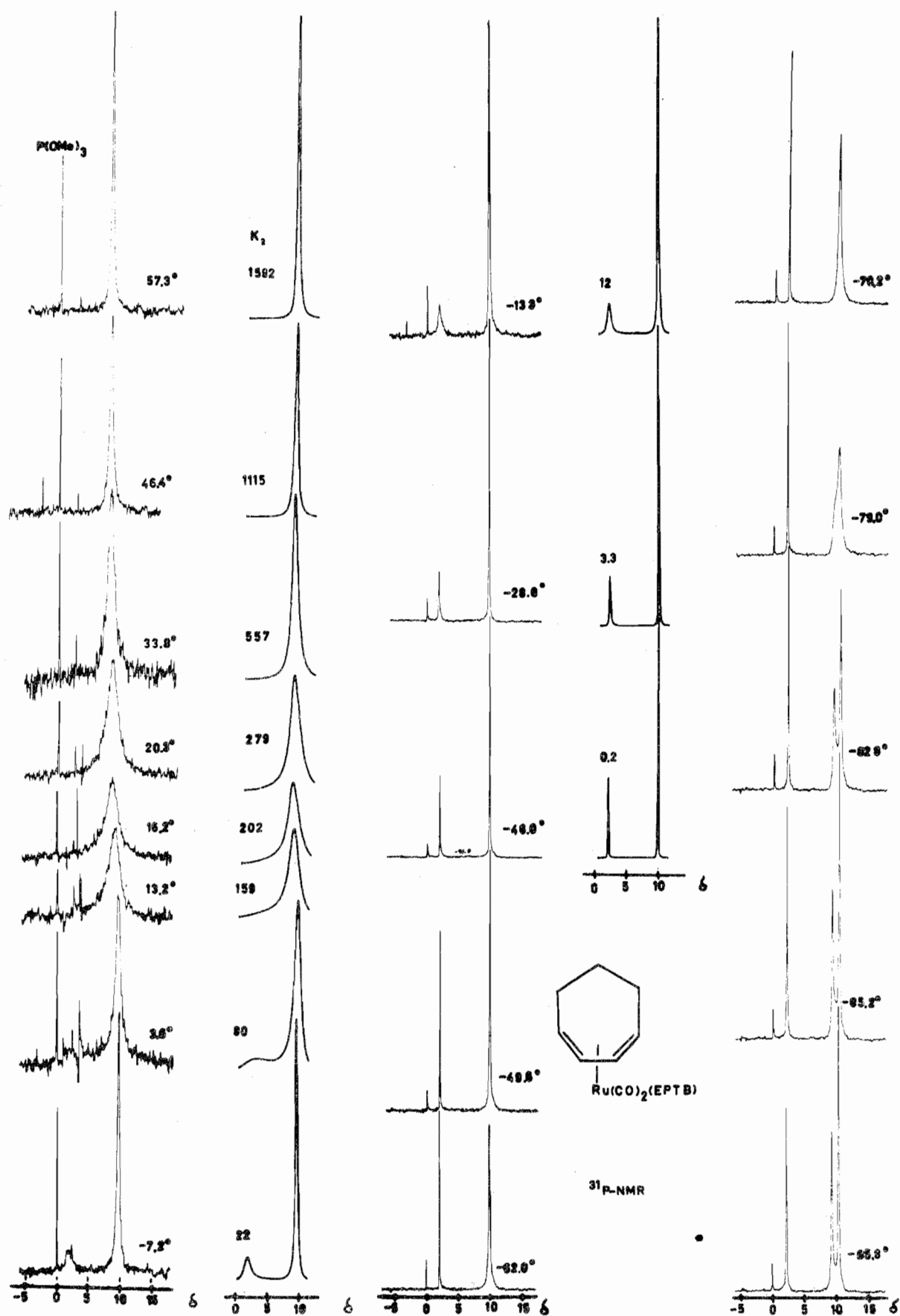


Figure 4. Temperature dependence of the  $^{31}\text{P}$  nmr spectrum of D-7-Ru-M. Simulations were carried out only for the metal-ring rotational process. Spectra below  $-46^\circ$  show the effect of ring conformational interchange (see text).

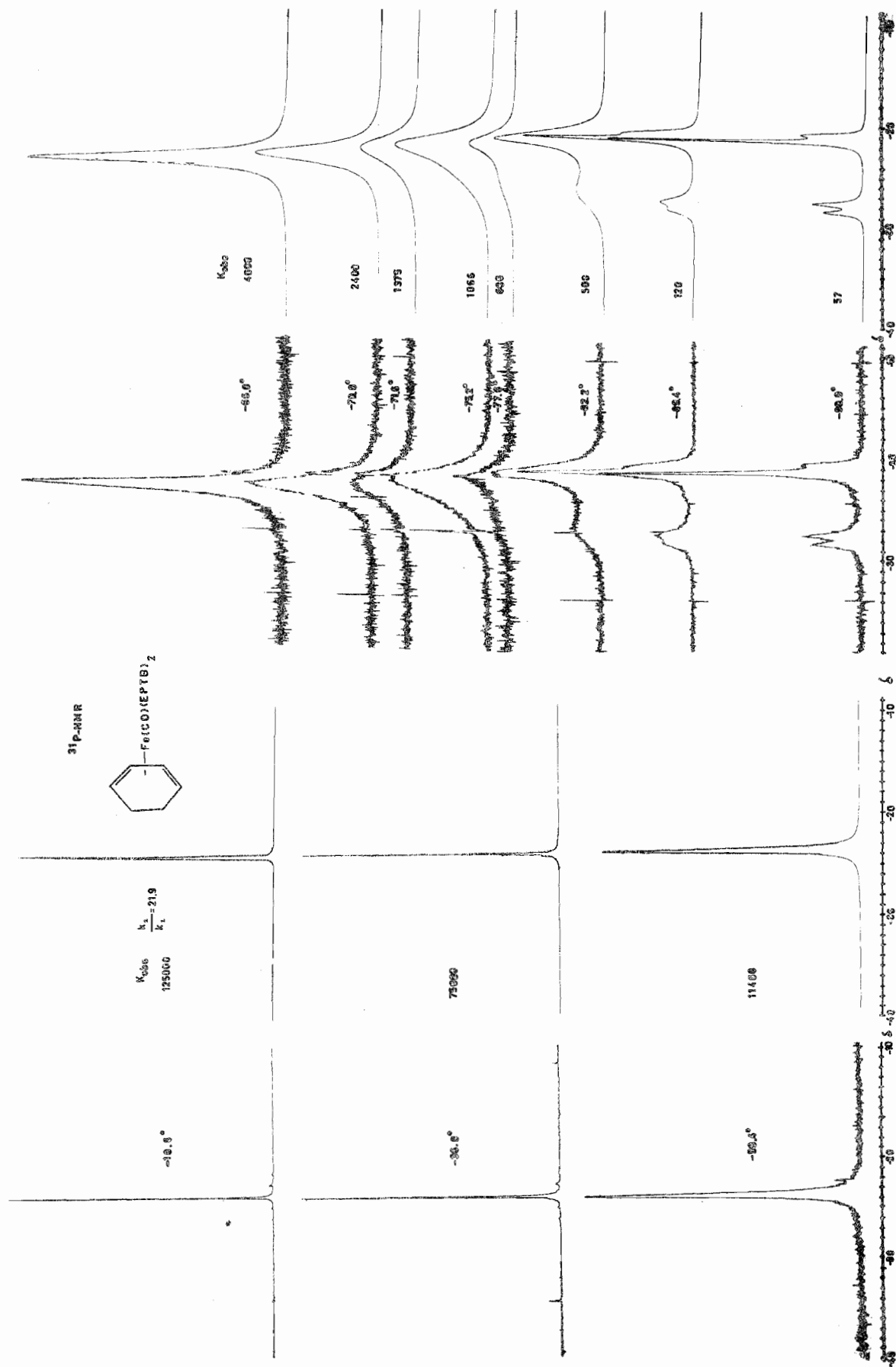


Figure 5. Temperature dependence of the <sup>31</sup>P NMR spectrum of D-6-Fe-B. Simulations were carried out with a constant ratio of  $k_2/k_1 = 21.9$ ;  $k_{obsd} = k_1 + k_2$  (the total rate of disappearance of the ab isomer).

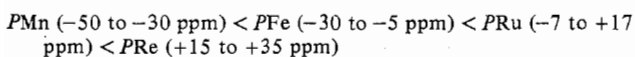
six-coordinate dienyl species, since fluxional behavior is common in five-coordinate, but much less so in six-coordinate, complexes. In fact, this effect is fairly small even in the iron compounds, where there is a maximum difference in the rates of disappearance of the *ab* isomer ( $k_1 + k_2$ ) of a factor of about 20 (between Dyl-6-Fe-B and D-6-Fe-B). The effect almost completely disappears in the ruthenium species, the maximum rate difference here being about a factor of 4 (Dyl-6-Ru-B and D-6-Ru-B).

Among the dienyl species, the rates are largely a function of the metal, decreasing in the order  $Mn \sim Re > Fe^+ > Ru^+$ . Increasing the ring size from 6 to 7 results in a decrease in the rate ( $k_1 + k_2$ ) by about an order of magnitude, presumably reflecting the increased rotational asymmetry as the C1-C5 distance is increased. Increasing the number of phosphite ligands apparently increases the rate of scrambling (as measured by  $k_2$ ) somewhat, with the effect being much more pronounced in the diene complexes (50-fold increase) than in the dienyl (maximum fivefold increase). Probably the most striking feature of the data presented here is the rather small difference produced by a wide variation of parameters. The maximum difference in activation free energies is only about 5 kcal/mol (between D-6-Fe-B and Dyl-7-Ru-M). Considering that this difference is the result of changes in ligand type, formal oxidation state, charge, and period of the central metal atom, it seems surprisingly small. A corollary of this observation is that the phenomenon is probably quite general among transition metal  $\pi$  complexes, as suggested by Kruczynski and Takats.<sup>3a</sup>

In most of the complexes investigated, both possible isomers were observed. Exceptions to this rule were the bis-substituted dienyl complexes of manganese and rhenium, where the *ab* isomer is the only one observed (as much as 1–2% of the *bb* isomer probably could have been detected), and probably the monosubstituted iron diene complexes as well, where either the basal isomer is the only one observed or the scrambling process was not frozen out (which we consider unlikely). From a statistical standpoint, there will be a 2:1 preference for the *b* (monoadducts) or *ab* (bis adducts) isomers, and most of the remaining compounds show essentially this population distribution. A maximum deviation of  $\pm 2$  kcal/mol in  $\Delta\Delta G$  between the two different isomers would serve to explain all of the results. A multitude of steric and/or electronic factors could produce interactions of this magnitude, and our data do not serve to distinguish adequately among them. Again probably the most striking observation is the *lack* of a major preference of the EPTB ligand for one position or another. This particular ligand is in fact expected to be reasonably similar to carbonyl, in that, as a phosphite, it is a fairly good  $\pi$  acceptor, and because of its bicyclic structure its steric bulk is appreciably smaller than, say, that of  $P(OEt)_3$  (cone angles:<sup>19,20</sup> EPTB, 101°;  $P(OEt)_3$ , 109°).

Apparently, the steric environments of the apical and basal positions are sufficiently similar that no marked steric preference for one position or the other is introduced. The larger size of EPTB relative to CO is however clearly seen in the effect of an apical EPTB ligand on the position of the ring conformation equilibrium in cycloheptadiene complexes as discussed above.

**Chemical Shifts.** Large phosphorus chemical shift differences were observed among the various complexes investigated. The principal determinant of chemical shift is the nature of the central metal atom. Thus chemical shifts fall in the order



increasing  
field

Table IX. <sup>31</sup>P Chemical Shift Ranges<sup>a</sup> for Apical and Basal EPTB Ligands

	a	b
Dyl-Mn	-49.15 to -44.45	-35.15 to -33.04
D-Fe	-28.21 to -24.41	-21.47 to -15.10
Dyl-Fe	-24.12 to -17.3	-14.80 to -5.95
D-Ru	-6.84 to +2.29	+3.28 to +10.62
Dyl-Ru	+2.70 to +8.31	+10.86 to +16.51
Dyl-Re	+15.35 to +21.84	+30.00 to +34.96

<sup>a</sup> Acetone-*d*<sub>6</sub>; ppm upfield of  $P(OMe)_3$ .

As pointed out previously, basal phosphite resonates at higher field than apical phosphite, ranges being as indicated in Table IX. Changing from a neutral diene complex to a positively charged dienyl species results in a small upfield shift (*ca.* 10 ppm) consistent with a slight decrease in electron density at the phosphorus atom (phosphorus chemical shifts are dominated by paramagnetic contributions and therefore increase with decreasing charge density). Changes of slightly smaller magnitude are produced by change in ring size ((6 → 7)-membered ring produces a 1–4-ppm *upfield* shift in the diene complexes and a somewhat smaller change in dienyl complexes) or substitution (increase in the number of phosphite ligands results in a 1–4-ppm *downfield* shift).

The phosphorus-phosphorus coupling constant in the dienyl complexes depends in a regular way on the atomic weight of the central atom, with first-row elements (Fe, Mn) having coupling constants around 90–95 Hz, second-row (Ru) around 70 Hz, and third-row (Re) around 28 Hz. The magnitude of the coupling in both iron and ruthenium diene complexes (30–35 Hz) is smaller than in the dienyls and shows no effect of atomic weight.

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**Registry No.** b-D-6-Fe-M, 53849-74-4; b-D-7-Fe-M, 53849-75-5; a-D-6-Ru-M, 53849-76-6; b-D-6-Ru-M, 53906-00-6; a-D-7-Ru-M, 53849-77-7; b-D-7-Ru-M, 53906-01-7; a-Dyl-6-Mn-M, 53849-78-8; b-Dyl-6-Mn-M, 53906-02-8; a-Dyl-7-Mn-M, 53849-79-9; b-Dyl-7-Mn-M, 53906-03-9; a-Dyl-7-Re-M, 53849-80-2; b-Dyl-7-Re-M, 53906-04-0; a-Dyl-6-Fe-M, 53849-82-4; b-Dyl-6-Fe-M, 53906-06-2; a-Dyl-7-Fe-M, 53849-84-6; b-Dyl-7-Fe-M, 53906-08-4; a-Dyl-6-Ru-M, 53849-86-8; b-Dyl-6-Ru-M, 53906-10-8; a-Dyl-7-Ru-M, 53849-88-0; b-Dyl-7-Ru-M, 53906-12-0; ab-D-6-Fe-B, 53849-89-1; bb-D-6-Fe-B, 53906-13-1; ab-D-7-Fe-B, 53849-90-4; bb-D-7-Fe-B, 53906-14-2; ab-D-6-Ru-B, 53906-15-3; bb-D-6-Ru-B, 53849-53-9; ab-D-7-Ru-B, 53849-54-0; bb-D-7-Ru-B, 53955-38-7; D-6-Ru-T, 53849-55-1; ab-Dyl-6-Mn-B, 53849-62-0; ab-Dyl-7-Mn-B, 53849-63-1; ab-Dyl-7-Re-B, 53849-61-9; ab-Dyl-6-Fe-B, 53849-65-3; bb-Dyl-6-Fe-B, 53905-97-8; ab-Dyl-7-Fe-B, 53849-67-5; bb-Dyl-7-Fe-B, 53905-99-0; ab-Dyl-6-Ru-B, 53849-57-3; bb-Dyl-6-Ru-B, 53955-35-4; ab-Dyl-7-Ru-B, 53849-59-5; bb-Dyl-7-Ru-B, 53905-89-8; Dyl-5-Mn-M, 53849-68-6; Dyl-5-Mn-B, 53849-69-7; Dyl-6-Fe-N, 53905-95-6; Dyl-7-Fe-N, 53905-93-4; D-6-Ru-N, 53905-91-2; Dyl-5-Re-M, 53849-70-0; Dyl-5-Re-B, 53849-71-1; Dyl-7-Re-N, 53849-60-8;  $\eta^4$ -cycloheptadieneruthenium tricarbonyl, 53905-90-1.

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## Metal Complexes of the Hexa(tertiary phosphine) *P,P,P',P'*-Tetrakis(2-diphenylphosphinoethyl)- $\alpha,\alpha'$ -diphospha-*p*-xylene

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The synthesis of a new sexadentate ligand, *P,P,P',P'*-tetrakis(2-diphenylphosphinoethyl)- $\alpha,\alpha'$ -diphospha-*p*-xylene (TDDX) and the preparation of its Ir(I), Rh(I), and Ru(II) complexes is described. The reaction of RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> or RhCl(PPh<sub>3</sub>)<sub>3</sub> with TDDX in boiling benzene gave the binuclear complex Rh<sub>2</sub>Cl<sub>2</sub>(TDDX). The reaction of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> with TDDX gave the complex Ir<sub>2</sub>Cl<sub>2</sub>(TDDX). The treatment of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> with TDDX formed the complexes Ru<sub>2</sub>Cl<sub>4</sub>(TDDX) and Ru(TDDX)(PF<sub>6</sub>)<sub>2</sub>. The reaction of hydrated ruthenium trichloride with TDDX in the presence of hexafluorophosphate gave Ru<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub>. A similar treatment of hydrated rhodium trichloride with TDDX gave the complex Rh<sub>2</sub>Cl<sub>6</sub>(TDDX) and Rh<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub>. The reaction of iridium trichloride with TDDX gave the complexes Ir<sub>3</sub>Cl<sub>9</sub>(TDDX) and Ir<sub>2</sub>Cl<sub>4</sub>(TDDX)(PF<sub>6</sub>)<sub>2</sub>. Reaction of the metal hexacarbonyls, M(CO)<sub>6</sub> (M = Cr, Mo), and diiron nonacarbonyl, Fe<sub>2</sub>(CO)<sub>9</sub>, with TDDX gave the binuclear complexes [M(CO)<sub>3</sub>]<sub>2</sub>(TDDX). The complexes have been characterized by elemental analysis and their infrared and nmr spectra.

### Introduction

Hexa(tertiary phosphines) are of special interest because of the possibilities of the preparation of sexadentate mononuclear or binuclear complexes. Binuclear complexes of d<sup>8</sup>, d<sup>6</sup>, and d<sup>5</sup> transition metal ions are of special significance because of the possibility that such complexes may act as bifunctional catalytic species. As a part of a general research program in this laboratory to synthesize and study polyfunctional catalysts it was considered of interest to design chelating agents that would form binuclear complexes with the metal-metal spacing needed to produce cooperative catalytic effects.

King, *et al.*,<sup>1</sup> have reported the preparation of complexes of the hexa(tertiary phosphine) 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane (hexaphos) which is analogous to EDTA in the relative disposition of the phosphorus donor atoms. In addition to hexaphos, an analogous sexadentate ligand, the poly(tertiary arsine) C<sub>6</sub>H<sub>4</sub>{As[CH<sub>2</sub>-CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>, is also known.<sup>2</sup> Because of the proximity of the phosphorus atoms of the 1,4-diphosphabutane moiety, hexaphos forms only a few binuclear derivatives. Molecular models indicate that a ligand such as *P,P,P',P'*-tetrakis(2-phenylphosphinoethyl)- $\alpha,\alpha'$ -diphospha-*p*-xylene (TDDX) would have a rigid aromatic ring separating the two potentially terdentate triphos moieties and thus would tend to act as a binucleating sexadentate ligand. Such a ligand would be well suited for the formation of binuclear complexes of d<sup>5</sup>, d<sup>6</sup>, and d<sup>8</sup> metal ions. The objective of this research was therefore to synthesize this new ligand and to study the properties of its metal complexes.

### Experimental Section

**Reagents.** All the complexes were prepared and the reactions conducted in a nitrogen atmosphere using Schlenk-tube techniques.

All solvents were AR grade reagents and were purged with purified nitrogen prior to their use. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz. The molecular weight determination of some of the complexes was done by the Australian Microanalytical Service, CSIRO, Australia. Infrared spectra of the ligand and its complexes were recorded in Nujol mull on a Beckman IR-12 spectrophotometer. The nmr spectra of the solution of some of the complexes in deuterated chloroform were recorded with a Varian T-60 spectrometer. The conductivity measurements were done in dimethylformamide solution at 30° with an Elico conductivity bridge.

The complexes Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>,<sup>3</sup> Rh(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>,<sup>4</sup> RhCl(PPh<sub>3</sub>)<sub>3</sub>,<sup>5</sup> and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub><sup>6</sup> were obtained by the appropriate published procedures. Ruthenium trichloride, rhodium trichloride, and iridium trichloride were purchased from Ventron-Alfa Inorganics. The metal carbonyls Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, and Fe<sub>2</sub>(CO)<sub>9</sub> were obtained from Pressure Chemical Co. Triethyl phosphite was obtained from Mobil Chemicals. Diphenylchlorophosphine was purchased from Eastern Chemical Co. Vinyl bromide and  $\alpha,\alpha'$ -dibromo-*p*-xylene were obtained from Aldrich Chemical Co. and used without further purification. Diphenylvinylphosphine was synthesized by the published procedure.<sup>7</sup> Yields, analytical data, molecular weights, and conductivity data are presented in Table I.

**Synthesis of TDDX.** The ligand was prepared by a modification of the procedure described for the preparation of hexaphos by King, *et al.*<sup>1</sup> The ester tetraethyl  $\alpha,\alpha'$ -*p*-xylenediphosphonate was obtained by the method of Issleib and Weichmann.<sup>8</sup> Twenty-six grams (100 mmol) of  $\alpha,\alpha'$ -dibromo-*p*-xylene was refluxed with 34.9 g (0.200 mol) of triethyl phosphite for about 4–6 hr. Ethyl bromide was distilled off and the product on cooling formed a colorless crystalline solid. The product was recrystallized from ether-petroleum ether to give 34-g (90%) yield of the diester (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(O)CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-P(O)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (mp 26°). *Anal.* Calcd for C<sub>16</sub>H<sub>28</sub>P<sub>2</sub>O<sub>6</sub>: C, 50.8; H, 7.4. Found: C, 50.01; H, 7.5. The diester is very soluble in water, ethanol, and ether and is very hygroscopic. The nmr spectrum of the diester (Figure 1) gave a peak corresponding to the aromatic protons at  $\tau$  2.8. The methylene proton of the ethyl groups gave a quartet centered at  $\tau$  6. The methylene protons of the *p*-xylene group gave