

group  $P2_1/n$ . The coordinates of the scandium atom were obtained from a Patterson map; locations of the other non-hydrogen atoms were determined from successive structure factor–Fourier calculations. Hydrogen atom positions for the methyl groups and for the heterometalacyclic ring were determined from difference maps and were refined along with their isotropic  $B$  values. The full least-squares matrix, consisting of coordinates for all of the atoms, anisotropic  $U_{ij}$  values for the non-hydrogen atoms, isotropic  $B$  values for the hydrogen atoms, an extinction parameter, and a scale factor, contained 380 parameters. A final difference Fourier map showed deviations ranging from  $-0.61$  to  $0.63 \text{ eÅ}^{-3}$ . The refinement converged with an  $R$  factor of  $0.117$  ( $0.051$  for  $F_o^2 > 3\sigma(F_o^2)$ ) and a goodness of fit of  $1.34$  for all 3855 reflections.

**Structure Determination for  $\text{Cp}^*_2\text{ScN}(\text{H})\text{C}(\text{CH}_3)\text{NNMe}_2$ .** A colorless crystal grown from a petroleum ether solution of the complex cooled at  $-60^\circ \text{C}$  was mounted in a thin-walled glass capillary under  $\text{N}_2$ . The crystal was centered on a CAD-4 diffractometer. Unit cell parameters and an orientation matrix were obtained by a least-squares calculation from the setting angles of 24 reflections with  $35^\circ < 2\theta < 39^\circ$ . Two equivalent intensity data sets to a  $2\theta$  value of  $40^\circ$  were collected, corrected for absorption (transmission coefficient  $0.889\text{--}0.956$ ) and a slight decay, reduced to  $F_o^2$  values, and merged to yield the final data set. Systematic absences led to the choice of space group  $P2_1/n$ . Coordinates of the scandium atom were obtained from a Patterson map; locations of the other non-hydrogen atoms were determined from successive structure factor–Fourier calculations. Hydrogen atom positions were determined from difference maps for the methyl groups and by calculation for the other one. All hydrogen atoms were given isotropic  $B$  values 20% greater

than that of the attached atom; no hydrogen atom parameters were refined. The full least-squares matrix, consisting of coordinates and anisotropic  $U_{ij}$  values for the non-hydrogen atoms and a scale factor, contained 253 parameters. A final difference Fourier map showed deviations ranging from  $-0.30$  to  $0.38 \text{ eÅ}^{-3}$ . The refinement converged with an  $R$  factor of  $0.0640$  ( $0.0416$  for  $F_o^2 > 3\sigma(F_o^2)$ ) and a goodness of fit of  $1.78$  for all 2267 reflections.

All calculations were carried out on a VAX 11/750 computer using the CRYM system of programs and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference.<sup>18</sup>

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**Supplementary Material Available:** For  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScN}(\text{H})\text{C}(\text{CH}_3)\text{NNH}_2$  and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScN}(\text{H})\text{C}(\text{CH}_3)\text{NNMe}_2$ , tables of crystal and intensity collection data, complete distances and angles, anisotropic thermal displacement parameters, and hydrogen atom coordinates and displacement parameters (9 pages); tables of observed and calculated structure factors for 3 and 4 (27 pages). Ordering information is given on any current masthead page.

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## Synthesis and Structure of $\text{FeCl}(\text{C}\equiv\text{CPh})(\text{DMPE})_2$

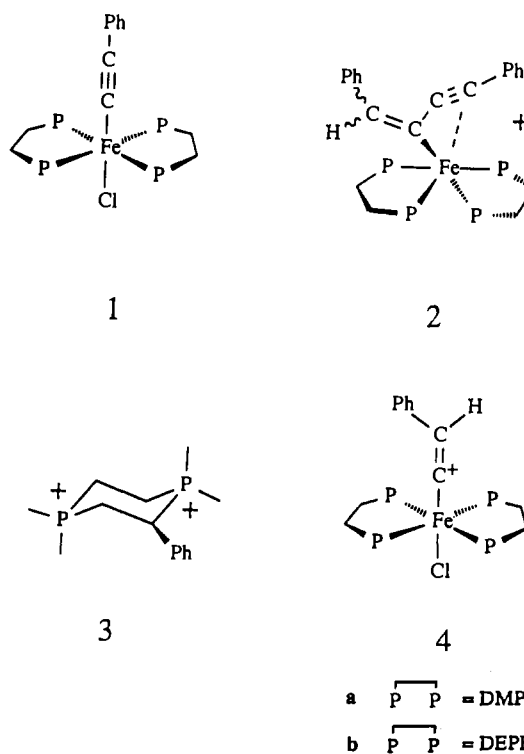
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The reaction of  $\text{FeCl}_2(\text{DMPE})_2$  with phenylacetylene in methanol solution forms three phosphorus-containing products: two complexes,  $\text{FeCl}(\text{C}\equiv\text{CPh})(\text{DMPE})_2$  and  $[\text{Fe}(\eta^3\text{-C}(\text{CHPh})\text{C}_2\text{Ph})(\text{DMPE})_2][\text{PF}_6]$ , and a cyclic diposponium salt,  $[\text{Me}_2\text{PCHPhCH}_2\text{P}(\text{CH}_2\text{CH}_2)\text{Me}_2][\text{Cl}]_2$ . Crystals of  $\text{FeCl}(\text{C}\equiv\text{CPh})(\text{DMPE})_2$  are monoclinic, space group  $P2_1/n$ , with  $a = 9.038$  (3) Å,  $b = 8.852$  (2) Å,  $c = 30.675$  (9) Å,  $\beta = 96.34$  (2)°,  $Z = 4$ , and  $R = 0.042$  (2262  $F$  values).

The first metal acetylide complex was isolated in the 1950s, and since that time, a wide variety of alkynyl complexes of transition metals or metal clusters displaying a range of coordination types have been isolated.<sup>1</sup> The synthesis of such compounds has usually involved the reaction of acetylide salts or Grignard reagents with a metal halide<sup>2</sup> or a metal triflate,<sup>3</sup> though the action of acetylene on a metal halide in the presence of triethylamine and a copper(I) iodide catalyst has also been reported.<sup>4</sup> Aryldiacetylides have been used in the preparation of conjugated poly-yne metal dimers and oligomers,<sup>5</sup> enroute to organic conducting polymers.<sup>6</sup> The formation of metal acetylide complexes indirectly provides one route to vinylidene complexes<sup>1</sup> and may also be used to functionalize alkynes.<sup>7</sup> The vinylidene complexes (formally metal carbenes) were isolated as early as 1966,<sup>8,9</sup> and since then, there has been considerable activity devoted to their study.<sup>10</sup>

During our investigation of the reaction of acetylenes and acetylides with iron complexes of the type  $\text{FeL}_2(\text{PP})_2$  [ $L = \text{H}, \text{Cl}$ ;  $\text{PP} = \text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ ;  $\text{R} = -\text{CH}_3$  (DMPE),  $-\text{CH}_2\text{CH}_3$  (DEPE)], we found that phenylacetylene reacted directly with  $\text{FeCl}_2(\text{PP})_2$  in methanol solvent to give a number of products. With  $\text{FeCl}_2(\text{DMPE})_2$ , phenylacetylene afforded a solid product, which, after recrystallization from ethanol, was identified as the acetylide chloride complex, *trans*- $\text{FeCl}(\text{C}\equiv\text{CPh})(\text{DMPE})_2$  (1). Two other products were also isolated from this reaction and identified as the cationic complex 2 (isolated as its  $[\text{PF}_6^-]$  salt) and the cyclic diposponium salt 3. Bellerby and Mays<sup>9</sup> have



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previously reported that the reaction of phenylacetylene with  $\text{FeCl}_2(\text{DEPE})_2$  afforded the vinylidene complex 4b.

**Table I.** Crystal Data for *trans*-FeCl(C≡CPh)(DMPE)<sub>2</sub> (1)

space group	$P2_1/n$	empirical formula	$C_{20}H_{37}ClFeP_4$
$a, \text{Å}$	9.038 (3)	$Z$	4
$b, \text{Å}$	8.852 (2)	abs coeff, $\text{cm}^{-1}$	9.44
$c, \text{Å}$	30.675 (9)	$t, ^\circ\text{C}$	21
$\beta, \text{deg}$	96.34 (2)	$\lambda, \text{Å}$	0.710 69
$V, \text{Å}^3$	2439 (1)	$R(F_o)$	0.042
fw	492.71	$R_w$	0.046
$D_{\text{calcd}}, \text{g cm}^{-3}$	1.342		

### Experimental Section

NMR spectra were recorded on a Bruker WM400 NMR spectrometer operating at 400.1 MHz for <sup>1</sup>H observation, 100.6 MHz for <sup>13</sup>C observation, and 162.0 MHz for <sup>31</sup>P observation. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to residual solvent resonances, and <sup>31</sup>P NMR spectra were referenced to external, neat trimethyl phosphite, taken to be 140.85 ppm at the temperature quoted.

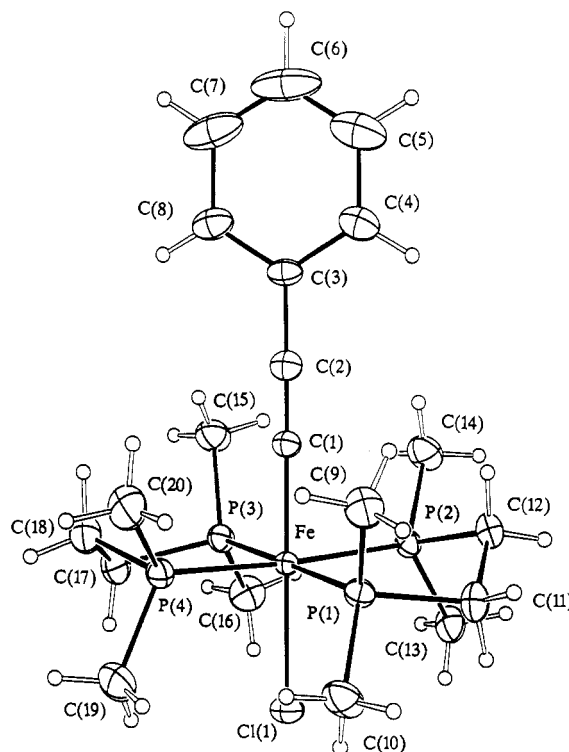
All solvents and phenylacetylene were of reagent quality and were rigorously dried, distilled, and degassed before use. DMPE was prepared by a literature method,<sup>11</sup> and this was reacted with anhydrous iron(II) chloride in benzene<sup>12</sup> to yield FeCl<sub>2</sub>(DMPE)<sub>2</sub> as a green crystalline solid.

**Reaction of FeCl<sub>2</sub>(DMPE)<sub>2</sub> with Phenylacetylene.** Phenylacetylene (0.5 mL, 4.9 mmol) was added to a solution of *trans*-FeCl<sub>2</sub>(DMPE)<sub>2</sub> (1 g, 2.4 mmol) in dry methanol (10 mL). The solution was warmed for 6 h at approximately 60 °C, during which time a precipitate formed. The mixture was maintained at room temperature for 16 h before the solid was removed by filtration and washed with cold methanol. The precipitate was recrystallized from ethanol to give *trans*-FeCl(C≡CPh)(DMPE)<sub>2</sub> (1) as a light brown crystalline solid. Mp: 279–80 °C dec. Anal. Calcd for FeC<sub>20</sub>H<sub>37</sub>P<sub>4</sub>Cl: C, 48.73; H, 7.51. Found: C, 48.6; H, 7.8. <sup>31</sup>P{<sup>1</sup>H} NMR: (dimethyl-*d*<sub>6</sub> sulfoxide, 300 K)  $\delta$  66.3 (very broad singlet,  $W_{1/2} = 174$  Hz); (dichloromethane-*d*<sub>2</sub>, 220 K)  $\delta$  63.5 (very broad singlet,  $W_{1/2} = 260$  Hz). <sup>1</sup>H NMR: (dimethyl-*d*<sub>6</sub> sulfoxide, 330 K)  $\delta$  1.35 (12 H, b s, CH<sub>3</sub>), 1.5 (12 H, b s, CH<sub>3</sub>), 1.9 (8 H, b s, CH<sub>2</sub>), 6.7 (3 H, b s, Ar H), 7.2 (2 H, b s, Ar H); (dichloromethane-*d*<sub>2</sub>, 300 K)  $\delta$  1.3 (12 H, s, CH<sub>3</sub>), 1.4 (12 H, s, CH<sub>3</sub>), 1.8 (8 H, b s, CH<sub>2</sub>), 6.65 (3 H, b m, Ar H), 7.1 (2 H, m, Ar H). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (dichloromethane-*d*<sub>2</sub>, 300 K):  $\delta$  13.2 (CH<sub>3</sub>), 15.5 (CH<sub>3</sub>), 29.7 (CH), 124.1 (CH), 127.8 (CH), 132.8 (CH). UV-vis (THF) [ $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 247 (3.20), 358 (3.18), 466 nm (1.52)]. IR (Nujol),  $\nu$  2044, 1585  $\text{cm}^{-1}$ .

Potassium hexafluorophosphate (approximately 0.5 g) was added to the filtrate, and the solvent was removed. The residue was recrystallized from ethanol to yield red needles of [Fe( $\eta^3$ -C(CHPh)<sub>2</sub>Ph)(DMPE)<sub>2</sub>][PF<sub>6</sub>] (2). Mp: >320 °C dec. Anal. Calcd for FeC<sub>28</sub>H<sub>43</sub>P<sub>5</sub>F<sub>6</sub>: C, 47.73; H, 6.11. Found: C, 48.0; H, 6.3. <sup>31</sup>P{<sup>1</sup>H} NMR (methanol):  $\delta$  49.5 (1 P, m), 56.3 (1 P, m), 62.9 (1 P, m), 63.2 (1 P, m). <sup>1</sup>H NMR (methanol-*d*<sub>4</sub>):  $\delta$  0.80 (3 H, d,  $J_{\text{PH}} = 8.6$  Hz, CH<sub>3</sub>), 0.92 (3 H, d,  $J_{\text{PH}} = 8.8$  Hz, CH<sub>3</sub>), 1.35 (1 H, m, CH<sub>2</sub>), 1.38 (3 H, d,  $J_{\text{PH}} = 8.0$  Hz, CH<sub>3</sub>), 1.38 (3 H, d,  $J_{\text{PH}} = 8.0$  Hz, CH<sub>3</sub>), 1.50 (3 H, d,  $J_{\text{PH}} = 8.5$  Hz, CH<sub>3</sub>), 1.53 (3 H, d,  $J_{\text{PH}} = 8.3$  Hz, CH<sub>3</sub>), 1.69 (3 H, d,  $J_{\text{PH}} = 7.2$  Hz, CH<sub>3</sub>), 1.75 (4 H, m, CH<sub>2</sub>), 2.05 (3 H, m, CH<sub>2</sub>, CH), 2.15 (3

**Table II.** Positional Parameters ( $\times 10^4$ ) for *trans*-FeCl(C≡CPh)(DMPE)<sub>2</sub> (1)

	$x$	$y$	$z$
Fe(1)	90 (1)	2637 (1)	1379 (1)
C(1)	-1343 (6)	4113 (6)	1198 (2)
C(2)	-2306 (6)	5037 (7)	1087 (2)
C(3)	-3475 (6)	6082 (7)	968 (2)
C(4)	-4011 (8)	6324 (8)	525 (3)
C(5)	-5163 (10)	7315 (11)	411 (4)
C(6)	-5803 (10)	8102 (11)	715 (5)
C(7)	-5334 (10)	7881 (9)	1155 (5)
C(8)	-4152 (7)	6889 (8)	1278 (3)
P(1)	1462 (2)	3390 (2)	864 (1)
P(2)	-1056 (2)	1146 (2)	868 (1)
P(3)	-1254 (2)	1845 (2)	1894 (1)
P(4)	1112 (2)	4254 (2)	1875 (1)
C(9)	1126 (9)	5237 (8)	612 (2)
C(10)	3483 (7)	3330 (10)	953 (3)
C(11)	1084 (8)	2143 (8)	384 (2)
C(12)	-595 (7)	1791 (8)	333 (2)
C(13)	-581 (9)	-862 (7)	859 (2)
C(14)	-3073 (7)	1077 (9)	776 (3)
C(15)	-3172 (7)	2457 (10)	1887 (3)
C(16)	-1396 (9)	-169 (8)	2011 (3)
C(17)	-424 (9)	2603 (8)	2426 (2)
C(18)	27 (9)	4239 (9)	2350 (2)
C(19)	2989 (8)	3898 (11)	2139 (3)
C(20)	1173 (11)	6255 (8)	1764 (3)
Cl(1)	1895 (2)	752 (2)	1609 (1)

**Figure 1.** ORTEP plot of FeCl(C≡CPh)(DMPE)<sub>2</sub> (1). Thermal ellipsoids are at 30% probability.

H, d,  $J_{\text{PH}} = 8.6$  Hz, CH<sub>3</sub>), 7.20 (1 H, m, Ar H), 7.38 (2 H, m, Ar H), 7.40 (1 H, s, CH), 7.4–7.5 (5 H, m, Ar H), 7.88 (2 H, m, Ar H). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (acetone-*d*<sub>6</sub>):  $\delta$  10.2 (CH<sub>3</sub>), 10.8 (CH<sub>3</sub>), 16.9 (CH<sub>3</sub>), 18.4 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.7 (2 C, CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 28.0 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 34.2 (CH<sub>2</sub>), 52.0 (C≡), 108.4 (C≡), 126.9 (2 C, CH), 127.7 (CH), 129.8 (CH), 130.1 (2 C, CH), 130.7 (2 C, CH), 131.1 (2 C, CH), 131.1 (Ar C), 134.0 (CH), 139.6 (Ar C), 155.8 (Fe–C). UV-vis (THF) [ $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ): 274 (3.40), 413 nm (3.00)].

The solvent was removed from the filtrate from the recrystallization of 1, and the residue was washed with benzene to leave a white powder, 1,4-diphosphonia-2-phenyl-1,1,4,4-tetramethylcyclohexane dichloride (3). Mp: 260 °C dec. Anal. Calcd for C<sub>14</sub>H<sub>24</sub>P<sub>2</sub>Cl<sub>2</sub>: C, 51.69; H, 7.38. Found: C, 51.9; H, 7.8. <sup>31</sup>P{<sup>1</sup>H} NMR: (dimethyl-*d*<sub>6</sub> sulfoxide)  $\delta$  26.8 (1 P, d,  $J = 15$  Hz, P(4)), 28.4 (1 P, d,  $J = 15$  Hz, P(1)); (methanol-*d*<sub>4</sub>)

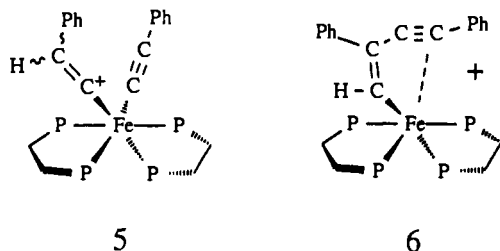
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$\delta$  25.8 (1 P, d,  $J = 15$  Hz), 27.2 (1 P, d,  $J = 15$  Hz); (*N,N*-dimethylformamide-*d*<sub>7</sub>)  $\delta$  31.0 (1 P, d,  $J = 15$  Hz), 32.8 (1 P, d,  $J = 15$  Hz). <sup>1</sup>H{<sup>31</sup>P} NMR (dimethyl-*d*<sub>6</sub> sulfoxide):  $\delta$  1.99 (3 H, s,  $J_{PH} = 15.0$  Hz, CH<sub>3</sub>P(1)), 2.10 (3 H, s,  $J_{PH} = 14.1$  Hz, CH<sub>3</sub>P(1)), 2.22 (3 H, s,  $J_{PH} = 15.6$  Hz, CH<sub>3</sub>P(4)), 2.37 (3 H, s,  $J_{PH} = 14.9$  Hz, CH<sub>3</sub>P(4)), 2.9–3.2 (4 H, m, CH<sub>2</sub>), 3.09 (1 H, m), 3.90 (1 H, dd,  $J = 15.1, 13.0$  Hz), 5.11 (1 H, d,  $J = 13.0$  Hz), 7.45 (2 H, m, Ar H), 7.5–7.6 (3 H, m, Ar H). <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P} NMR (dimethyl-*d*<sub>6</sub> sulfoxide):  $\delta$  5.1 (CH<sub>3</sub>), 8.4 (CH<sub>3</sub>), 9.2 (CH<sub>3</sub>), 11.0 (CH<sub>3</sub>), 17.8 (CH<sub>2</sub>), 18.5 (CH<sub>2</sub>), 24.0 (CH<sub>2</sub>), 34.9 (CH), 131.4 (2 C, CH), 131.9 (CH), 132.1 (2 C, CH), 134.7 (Ar C).

**Crystallography.** Cell constants were determined by a least-squares fit to the setting values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table I. Data were reduced, and Lorentz, polarization, and decomposition corrections were applied by use of the Enraf-Nonius Structure Determination Package.<sup>13</sup> The structure was solved by direct methods using SHELXS-86<sup>14</sup> and was refined by full-matrix least-squares analysis with SHELX-76.<sup>15</sup> All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated sites (C–H = 0.97 Å) with individual isotropic thermal parameters. Scattering factors and anomalous dispersion corrections used for Fe were taken from ref 16, and all others were those supplied in SHELX-76.<sup>15</sup> Non-hydrogen atom coordinates are listed in Table II. The atomic nomenclature is defined in Figure 1.<sup>17</sup> Listings of H atom coordinates, anisotropic thermal parameters, close intermolecular contacts, torsion angles, details of least-squares planes calculations, and observed and calculated structure factor amplitudes have been deposited as supplementary material.

## Discussion

**Spectroscopic Characterization of 1–3.** The structure of **2** was established by <sup>31</sup>P, <sup>13</sup>C, and <sup>1</sup>H NMR spectroscopy. The complex cation is diamagnetic and has no axis or plane of symmetry. Integration of the proton spectrum indicated that it contained two different monosubstituted phenyl groups, two DMPE ligands, and a single methine proton (at  $\delta$  7.40). There are three possible isomeric structures, **2**, **5**, and **6**, consistent with the required molecular formula.



The <sup>31</sup>P NMR spectrum of the cation consists of four well-resolved multiplets, typical of a *cis*-FeL'L''(DMPE)<sub>2</sub> complex. The <sup>13</sup>C NMR spectrum has resonances for three nonaromatic quaternary carbons at  $\delta$  52.0, 108.4, and 155.8 ppm and a vinyl C–H carbon whose chemical shift occurs well into the aromatic region. Of the quaternary resonances, only the one at 155.8 ppm exhibits coupling to <sup>31</sup>P.

The <sup>13</sup>C chemical shifts observed for the quaternary carbon atoms are not consistent with those expected for metal acetylides or metal vinylidenes,<sup>18</sup> and this eliminates structure **5**. Isomers **2** and **6** can be distinguished by careful examination of the phosphorus-coupled and phosphorus-decoupled <sup>13</sup>C spectra (proton

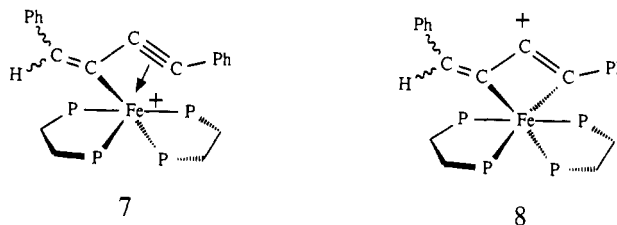
**Table III.** Bond Lengths (Å) for *trans*-FeCl(C≡CPh)(DMPE)<sub>2</sub> (1)

C(1)–Fe(1)	1.880 (5)	P(1)–Fe(1)	2.216 (2)
P(2)–Fe(1)	2.216 (2)	P(3)–Fe(1)	2.213 (2)
P(4)–Fe(1)	2.217 (2)	Cl(1)–Fe(1)	2.386 (2)
C(2)–C(1)	1.216 (8)	C(3)–C(2)	1.421 (8)
C(4)–C(3)	1.407 (9)	C(8)–C(3)	1.385 (9)
C(5)–C(4)	1.377 (11)	C(6)–C(5)	1.343 (16)
C(7)–C(6)	1.383 (15)	C(8)–C(7)	1.403 (12)
C(9)–P(1)	1.819 (7)	C(10)–P(1)	1.818 (6)
C(11)–P(1)	1.842 (7)	C(12)–P(2)	1.828 (6)
C(13)–P(2)	1.830 (6)	C(14)–P(2)	1.815 (7)
C(15)–P(3)	1.814 (6)	C(16)–P(3)	1.827 (7)
C(17)–P(3)	1.845 (7)	C(18)–P(4)	1.842 (7)
C(19)–P(4)	1.824 (7)	C(20)–P(4)	1.805 (7)
C(12)–C(11)	1.541 (9)	C(18)–C(17)	1.529 (10)

**Table IV.** Bond Angles (deg) for *trans*-FeCl(C≡CPh)(DMPE)<sub>2</sub> (1)

P(1)–Fe(1)–C(1)	90.2 (2)	P(2)–Fe(1)–C(1)	87.3 (2)
P(2)–Fe(1)–P(1)	86.0 (1)	P(2)–Fe(1)–C(1)	90.9 (2)
P(3)–Fe(1)–P(1)	178.9 (1)	P(3)–Fe(1)–P(2)	93.8 (1)
P(4)–Fe(1)–C(1)	88.6 (2)	P(4)–Fe(1)–P(1)	94.1 (1)
P(4)–Fe(1)–P(2)	175.9 (1)	P(4)–Fe(1)–P(3)	86.2 (1)
Cl(1)–Fe(1)–C(1)	179.6 (1)	Cl(1)–Fe(1)–P(1)	90.2 (1)
Cl(1)–Fe(1)–P(2)	92.5 (1)	Cl(1)–Fe(1)–P(3)	88.7 (1)
Cl(1)–Fe(1)–P(4)	91.6 (1)	C(2)–C(1)–Fe(1)	177.8 (5)
C(3)–C(2)–C(1)	177.5 (6)	C(4)–C(3)–C(2)	121.0 (6)
C(8)–C(3)–C(2)	122.1 (6)	C(8)–C(3)–C(4)	117.0 (6)
C(5)–C(4)–C(3)	120.7 (9)	C(6)–C(5)–C(4)	121.8 (10)
C(7)–C(6)–C(5)	119.6 (9)	C(8)–C(7)–C(6)	119.6 (9)
C(7)–C(8)–C(3)	121.3 (9)	C(9)–P(1)–Fe(1)	119.5 (3)
C(10)–P(1)–Fe(1)	121.0 (3)	C(10)–P(1)–C(9)	102.0 (4)
C(11)–P(1)–Fe(1)	108.7 (2)	C(11)–P(1)–C(9)	101.1 (3)
C(11)–P(1)–C(10)	101.4 (4)	C(12)–P(2)–Fe(1)	108.2 (2)
C(13)–P(2)–Fe(1)	119.9 (2)	C(13)–P(2)–C(12)	102.3 (3)
C(14)–P(2)–Fe(1)	120.9 (3)	C(14)–P(2)–C(12)	101.2 (3)
C(14)–P(2)–C(13)	101.4 (4)	C(15)–P(3)–Fe(1)	119.7 (3)
C(16)–P(3)–Fe(1)	120.4 (3)	C(16)–P(3)–C(15)	101.9 (4)
C(17)–P(3)–Fe(1)	108.4 (2)	C(17)–P(3)–C(15)	101.4 (4)
C(17)–P(3)–C(16)	102.2 (4)	C(18)–P(4)–Fe(1)	108.7 (2)
C(19)–P(4)–Fe(1)	119.3 (3)	C(19)–P(4)–C(18)	101.4 (4)
C(20)–P(4)–Fe(1)	121.5 (3)	C(20)–P(4)–C(18)	100.7 (4)
C(20)–P(4)–Fe(1)	102.0 (4)	C(12)–C(11)–P(1)	107.2 (4)
C(11)–C(12)–P(2)	107.0 (4)	C(18)–C(17)–P(3)	107.4 (5)
C(17)–C(18)–P(4)	107.6 (5)		

decoupled in both cases). The data are consistent with structure **2** and not isomer **6**, where phosphorus coupling to the vinyl CH and not a quaternary carbon would be expected. A complex analogous to **2**, [Os( $\eta^3$ -C(CHPh)<sub>2</sub>Ph)(PMe<sub>3</sub>)<sub>4</sub>][PF<sub>6</sub>], has been reported<sup>19</sup> and crystallographically characterized, and this sets a precedent for the unusual type of structure. The bonding in this complex may be rationalized in terms of the contributing structures **7** and **8**.



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- (18) We have found the acetylene carbon atoms in *trans*-Fe(C≡CPh)<sub>2</sub>(DMPE)<sub>2</sub> possess chemical shifts of 133 and 140 ppm, and the metal-bound carbon atom in vinylidene complexes has been reported to resonate at very low field (between 300 and 450 ppm).<sup>10</sup>

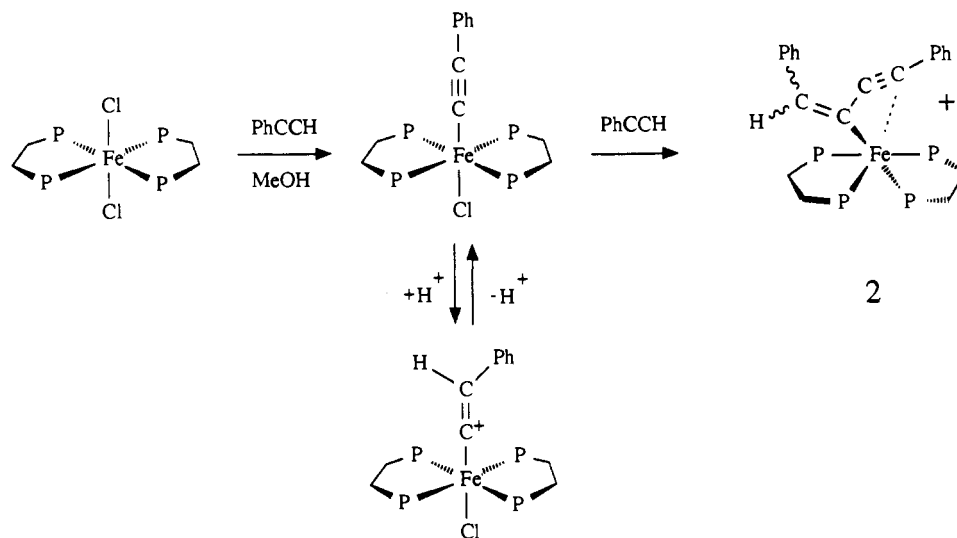
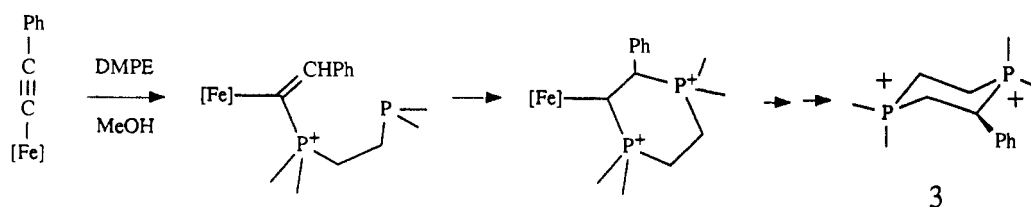
The structure of the cyclic phosphonium salt **3** was established by homonuclear and heteronuclear NMR experiments.

Complex **1** was difficult to examine by NMR spectroscopy. Both the <sup>31</sup>P and <sup>1</sup>H NMR spectra were broad, with the line width of the resonances being solvent and temperature dependent. This behavior indicates paramagnetism in the complex, but the possible presence of trace amounts of oxidized material could not be excluded. The <sup>13</sup>C spectrum was obtained (CD<sub>2</sub>Cl<sub>2</sub> solvent); however, despite all attempts, the quaternary resonances of the carbon atoms along the central axis of the molecule were not observed.

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**Table V.** Comparison of Bond Lengths (Å) in Iron Acetylide and Chloride Complexes

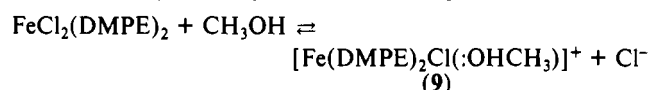
	Fe—C	C≡C	C—C(Ph)	Fe—Cl	Fe—P	ref
Fe(C≡CPh) <sub>2</sub> (DMPE) <sub>2</sub>	1.925 (6)	1.209 (9)	1.438 (9)			20
FeCl(C≡CPh)(DMPE) <sub>2</sub>	1.880 (5)	1.216 (8)	1.421 (8)	2.386	2.216	this work
Fe(cp)(C≡CPh)(CO) <sub>2</sub>	1.920 (6)	1.201 (9)	1.444 (9)			21
FeCl <sub>2</sub> (DMPE) <sub>2</sub>				2.352	2.235	22

**Scheme I****Scheme II**

**X-ray Crystallography.** The structure of **1** (Figure 1) consists of the neutral *trans*-FeCl(C≡CPh)(DMPE)<sub>2</sub> complex with no contacts between molecules shorter than the sum of the van der Waals radii. Selected bond lengths and bond angles are listed in Table III and IV. Of particular interest are the Fe—C and Fe—Cl bond lengths and whether or not these show any evidence of a d-p π overlap in the Fe—C bond. The Fe—C distance in the present structure is shorter (ca. 0.04 Å) than in the other two structures with comparable bonds<sup>20,21</sup> (Table V). The shortening of the Fe—C bond is associated with a lengthening of the C≡C bond and a shortening of the C—C(Ph) bond, though these changes are at a marginal level of significance. The length of the Fe—C bond is evidently affected by the nature of the group *trans* to it. The Fe—Cl bond length of 2.386 (2) Å is longer than those in FeCl<sub>2</sub>(DMPE)<sub>2</sub>, FeCl<sub>2</sub>(DEPE)<sub>2</sub>, and FeCl<sub>2</sub>(DPrPE)<sub>2</sub> (2.345 (2)–2.352 (1) Å).<sup>22,23</sup> These effects suggest that both the chloro and acetylide ligands are involved in π-bonding with the Fe atom. Fe—P bond lengths (average 2.216 Å) are shorter than those in FeCl<sub>2</sub>(DMPE)<sub>2</sub> (2.235 Å).<sup>22</sup>

The phenyl group of the phenylacetylide is planar to within 0.012 Å, and the entire ligand is planar to within 0.031 Å. The Fe atom lies significantly (0.175 Å) out of the latter plane. This is in contrast to the situation in the related structure Fe(C≡CPh)<sub>2</sub>(DMPE)<sub>2</sub>, where the Fe is within 0.001 Å of the phenylacetylide planes.<sup>20</sup> The Fe—C≡C—C grouping shows small deviations from linearity with the Fe—C≡C and C≡C—C angles both about 178°.

**The Course of the Reaction of Phenylacetylene with FeCl<sub>2</sub>(PP)<sub>2</sub>.** In methanol solution, FeCl<sub>2</sub>(DMPE)<sub>2</sub> is known to be in equilibrium with the solvolyzed complex **9**, where the equilibrium lies far to



the right.<sup>24</sup> The solvent is loosely coordinated, and this effectively provides a source of the coordinatively unsaturated [FeCl(DMPE)<sub>2</sub>]<sup>+</sup>, which may add to a terminal acetylene to give the acetylide chloride complex **1** and H<sup>+</sup>. Metal acetylides are readily protonated at the β-carbon<sup>10</sup>, and in this reaction mixture, **1** would be in equilibrium with its protonated form **4a**; however **1** is less soluble and crystallizes from the solution. Complex **2** is probably formed by attack of phenylacetylene (or phenylacetylide) at the electrophilic α-carbon of the vinylidene complex **4a** with displacement of chloride by the π-system of the neighboring alkyne (Scheme I). Alternatively, **2** could be formed by oxidative coupling from the diacetylide Fe(C≡CPh)<sub>2</sub>(DMPE)<sub>2</sub> in a mechanism analogous to that proposed by Werner<sup>19</sup> for the formation of [Os(η<sup>3</sup>-C(CHPh)<sub>2</sub>C<sub>2</sub>Ph)(PMe<sub>3</sub>)<sub>4</sub>][PF<sub>6</sub>]. However, this is unlikely, since there is no evidence for the formation of Fe(C≡CPh)<sub>2</sub>(DMPE)<sub>2</sub> and this bis(phenylacetylide) complex is known to be a stable crystalline compound.<sup>20</sup>

Complex **2** is only formed in significant amounts when the phenylacetylene substrate is present in excess. Instances where alkynes are added to a coordinated vinylidene ligand have been reported.<sup>25</sup> If the reaction mixture is concentrated by evaporation of the solvent, the complex decomposes unless the counterion [Cl<sup>-</sup>]

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is replaced by a less reactive species, e.g.  $[\text{PF}_6^-]$ .

The formation of the cyclic diphosphonium salt **3** may result from the initial quaternization of free DMPE (from some complex decomposition) with an activated (metal-bound) alkyne (Scheme II). Subsequent cyclization with loss of the metal would give the observed product. In the absence of  $\text{FeCl}_2(\text{DMPE})_2$ , phenylacetylene and DMPE do not react to give **3**; however, the reaction of tertiary phosphines with acetylenes to give vinylphosphonium salts is well-known.<sup>26</sup> Instances in which a tertiary phosphine, or other  $n$  donor ligands, attack the electrophilic carbene carbon of a vinylidene complex have also been noted.<sup>10,27</sup>

$\text{FeCl}_2(\text{DEPE})_2$  reacts with excess phenylacetylene in a protic solvent at a slower rate than  $\text{FeCl}_2(\text{DMPE})_2$  to give the  $[\text{Fe}$

$(\eta^3\text{-C}(\text{CHPh})\text{C}_2\text{Ph})(\text{DEPE})_2]^+$  complex and the corresponding cyclic diphosphonium salt. This is in contrast to the findings of Bellerby and Mays,<sup>9</sup> who reported the formation of vinylidene cation  $[\text{FeCl}(\text{CCHPh})(\text{DEPE})_2]^+$  from this reaction.

### Conclusion

The reaction of  $\text{FeCl}_2(\text{DMPE})_2$  with phenylacetylene in methanol solution forms a stable, crystalline acetylide chloride complex,  $\text{FeCl}(\text{C}\equiv\text{CPh})(\text{DMPE})_2$ . Additionally, products formed from further attack of phenylacetylene or free DMPE on  $\text{FeCl}(\text{C}\equiv\text{CPh})(\text{DMPE})_2$  are found in the reaction mixture and these can be rationalized by the activation of the  $\alpha$ -carbon of the coordinated acetylide toward nucleophilic attack.

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**Supplementary Material Available:** Tables of full crystallographic details, details of least-squares planes, anisotropic thermal parameters, and hydrogen atom positional and thermal parameters for **1** (4 pages); tables of calculated and observed structure factors for **1** (14 pages). Ordering information is given on any current masthead page.

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## Synthesis and Characterization of (Nitro)ruthenium Complexes That Utilize Identical Trans-Positioned Tertiary Phosphine Ligands

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We report the synthesis and characterization of a variety of complexes with the form  $[\text{Ru}(\text{NO}_2)(\text{PR}_3)_2(\text{trpy})](\text{ClO}_4)$  ( $\text{trpy} = 2,2':6',2''$ -terpyridine and  $\text{PR}_3 =$  tertiary phosphine ligand, where R = ethyl,  $n$ -propyl,  $n$ -butyl, phenyl, and benzyl) and  $[\text{Ru}(\text{NO})(\text{PR}_3)_2(\text{trpy})](\text{ClO}_4)_3$ . Two routes toward the synthesis of the  $[\text{Ru}(\text{NO}_2)(\text{PR}_3)_2(\text{trpy})](\text{ClO}_4)$  complexes, starting from  $\text{Ru}(\text{Cl})_3 \cdot 3\text{H}_2\text{O}$ , will be discussed. One method involves a five-step synthesis, with the stepwise addition of the phosphine ligands. The other route, a three-step synthesis, involves a novel one-pot incorporation of two phosphine ligands into the trans positions of a ruthenium coordination center. Characterization of the  $[\text{Ru}(\text{NO}_2)(\text{PR}_3)_2(\text{trpy})](\text{ClO}_4)$  complexes was accomplished through elemental analysis, IR, UV-visible,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopies, and cyclic voltammetry. Notably, variations in the phosphine ligands resulted in cyclic voltammograms that ranged from reversible to irreversible, where the utilization of trimethylphosphine resulted in the greatest reversibility. The irreversible voltammograms indicated that the electrochemically generated  $[\text{Ru}(\text{NO}_2)(\text{PR}_3)_2(\text{trpy})]^{2+}$  complexes were unstable and that the analogous  $[\text{Ru}(\text{NO})(\text{PR}_3)_2(\text{trpy})]^{3+}$  complexes were the decomposition products. In this regard, we also report the synthesis and characterization of  $[\text{Ru}(\text{NO})(\text{PR}_3)_2(\text{trpy})](\text{ClO}_4)_3$  complexes, where the complexes were characterized by elemental analysis, IR and UV-visible spectroscopies, and cyclic voltammetry.

There has been considerable interest in low-valent (phosphine)ruthenium complexes, where a common use of these complexes has been in the area of homogeneous catalysis.<sup>1-7</sup> However, the utilization of phosphine ligands with high-oxidation-state ruthenium centers is much less common, possibly due to the well-documented ease of oxidation of phosphine compounds.<sup>8-10</sup> Thus, we have focused our attention on the tertiary phosphine ligand effects on the stabilization and reactivity of high-oxidation-state ruthenium complexes.<sup>11-22</sup> We have observed that

tertiary phosphine ligands stabilize (oxo)ruthenium(IV) centers and that the phosphine ligands confer interesting properties on (oxo)(phosphine)ruthenium complexes,<sup>13-15</sup> where the reactivities of these complexes are strongly affected by the phosphine ligand.<sup>16-18</sup>

Recently, Mukaida reported the first (nitro)ruthenium(III) complex which is stable in the solid state.<sup>23</sup> However, his complex

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