

## Syntheses of Olefin and Acetylene Complexes, $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2(\text{un})]\text{PF}_6$

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Reactions of  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  with various olefins and acetylenes, followed by  $\text{NH}_4\text{PF}_6$  addition, have produced the compounds  $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2(\text{un})]\text{PF}_6$  ( $\text{un} = \text{CH}_2=\text{CHPh}$ ,  $\text{CH}_2=\text{CHCN}$ ,  $\text{CH}_2=\text{CHCH}_3$ ,  $\text{trans-ClCH}=\text{CHCl}$ ,  $\text{cis-EtO}_2\text{CCH}=\text{CHCO}_2\text{Et}$ ,  $\text{PhC}\equiv\text{CPh}$ ,  $\text{EtC}\equiv\text{CEt}$ ,  $\text{MeO}_2\text{CC}=\text{CCO}_2\text{Me}$ ) The same reaction with 1,5-cyclooctadiene gave  $[\{\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\}_2\text{C}_8\text{H}_{12}](\text{PF}_6)_2$ . Similar reactions of  $\text{PhC}\equiv\text{CH}$  or  $\text{PhC}\equiv\text{CSiMe}_3$  gave the carboalkylidene complex  $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2(\text{C}=\text{CHPh})]\text{PF}_6$ .

### Introduction

Recently, we described the synthesis of  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  from the reaction  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}$  and  $\text{PMe}_3$  in toluene [1]. This compound was used as a precursor for a number of  $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{L}]^+$  complexes, taking advantage of the propensity of this precursor toward halide displacement. As we pointed out in this earlier work, this type of reactivity is anticipated for electron-rich complexes [2].

We have now taken further advantage of this feature of  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  to prepare ruthenium complexes of olefins and acetylenes (= un) having the formula  $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2(\text{un})]^+$ . These complexes were isolated as hexafluorophosphate salts, and characterized by analyses and by nmr and ir spectroscopy.

Similar olefin complexes of ruthenium have not been reported prior to this work. There are known, however, several olefin complexes of iron, including  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{dmpe})(\text{un})]\text{BF}_4$  ( $\text{un} = \text{EtO}_2\text{CCH}=\text{CHCO}_2\text{Et}$  and  $\text{CH}_2=\text{CHCO}_2\text{Me}$ ) [3] and  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{P}(\text{OPh})_3)_2(\text{C}_2\text{H}_4)]\text{BF}_4$  [4]. In addition a few monocarbonyl complexes,  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})(\text{P}(\text{OPh})_3)(\text{un})]^+$  were described recently [5]. Dicarbonyl iron species have been known for some time; and their syntheses and chemical behavior have been well studied [6].

### Experimental

The following starting materials were prepared according to literature procedures:  $\text{PMe}_3$  [7],  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  [1] and  $\text{PhC}\equiv\text{CSiMe}_3$  [8]. Other reagents were obtained commercially. Reagent

grade solvents were used without purification. Petroleum ether refers to the commercial saturated hydrocarbon mixture Skelly B, boiling range 60–80 °C. All reactions were routinely carried out under nitrogen.

Proton nmr spectra were run on a JEOL NM-MH-100 spectrometer, and where indicated, on a Bruker WH-270 spectrometer. Unless otherwise designated DMSO- $d_6$  was used as a solvent, and chemical shift values ( $\delta$ ) are given relative to an internal TMS standard. Infrared data (KBr disc spectra) were obtained with a Beckman Acculab-7 spectrometer. Elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee.

#### $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2(\text{CH}_2=\text{CHPh})]\text{PF}_6$

A mixture of 0.50 g (1.41 mmol)  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  and 3.0 ml (25.9 mmol) styrene in 100 ml MeOH was heated for 17 hr at reflux. The solution was filtered; addition of a methanol solution of  $\text{NH}_4\text{PF}_6$  to the filtrate gave a precipitate. This was separated and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the product (0.41 g, 51%) as a light yellow powder, mp 215–218 °C. Found: C, 40.29; H, 5.61; P, 16.43%.  $\text{C}_{19}\text{H}_{31}\text{F}_6\text{P}_3\text{Ru}$  calcd: C, 40.22; H, 5.51; P, 16.38%. NMR (acetone- $d_6$ , 270 MHz):  $\delta$  1.69d ( $\text{PMe}_3$ ,  $J_{\text{P-H}} = 9.2$  Hz) 1.75 d ( $\text{PMe}'_3$ ,  $J_{\text{P-H}} = 9.6$  Hz); 2.16 m ( $\text{CHPh}$ ); 3.87 m ( $\text{CH}_2=$ ); 4.90 s ( $\text{C}_5\text{H}_5$ ); 7.13–7.40 m ( $\text{C}_6\text{H}_5$ ).

#### $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2(\text{CH}_2=\text{CHMe})]\text{PF}_6$

A 0.50 g (1.41 mmol) sample of  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  was dissolved in 100 ml MeOH and the solution heated at reflux temperature for 3 hr while  $\text{CH}_2=\text{CHMe}$  was bubbled in. After cooling the solution was filtered and 1.0 g (6.13 mmol)  $\text{NH}_4\text{PF}_6$  added. The solvent was removed and the residue remaining extracted with  $\text{CH}_2\text{Cl}_2$ . Addition of petroleum ether to the  $\text{CH}_2\text{Cl}_2$  extract caused precipitation of a white powder which was recrystallized from the same solvents, 0.51 g (72%); mp 276 °C (d). Found: C, 33.00; H, 5.58; P, 18.19%.  $\text{C}_{14}\text{H}_{29}\text{F}_6\text{P}_3\text{Ru}$  calcd: C, 33.27; H, 5.78; P, 18.39%. NMR (270 MHz):  $\delta$  1.46 d ( $\text{PMe}_3$ ,  $J_{\text{P-H}} = 9.2$  Hz); 1.54 d ( $\text{PMe}'_3$ ,  $J_{\text{P-H}} = 9.2$  Hz); 1.61 d (Me,  $J_{\text{H-CH}_3} = 5.9$  Hz); 1.75–1.91 m (2H) and 2.99 d (1 H,  $J = 11.4$ ) olefinic  $\text{CH}_2=\text{CH}$ ; 5.12 s ( $\text{C}_5\text{H}_5$ ).

*Reaction of Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl and CH<sub>2</sub>=CHCN*

A filtered solution containing 1.0 g (6.0 mmol) NH<sub>4</sub>PF<sub>6</sub> in 100 ml methanol was added to 0.50 g (1.4 mmol) Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl. Acrylonitrile (0.50 ml, 7.6 mmol) was then added and the solution heated at reflux for 1 hr. Partial evaporation of the solvent caused the precipitation of yellow crystals. These were separated; extraction using CH<sub>2</sub>Cl<sub>2</sub> left a white solid, 0.05 g (7%); mp: color changes from white to yellow ~ 210–235 °C, melts 280–283 °C. Found: C, 32.44; H, 4.90; P, 17.86%. C<sub>14</sub>H<sub>26</sub>F<sub>6</sub>NP<sub>3</sub>Ru calcd: C, 32.57; H, 5.08; P, 18.00%. IR: ν(CN) at 2320 w, 2200 w cm<sup>-1</sup>. NMR (270 MHz): δ 1.45 d (PMe<sub>3</sub>, J<sub>P-H</sub> = 10.1 Hz); 1.88 d of d (CHCN, J<sub>H-H</sub>, *cis* = 8.6 Hz, J<sub>H-H</sub>, *trans* = 13.0 Hz); 2.44 d (H *cis* to CN, J = 13 Hz), 3.53 d (H *trans* to CN, J = 8.6 Hz), 5.34 s (C<sub>5</sub>H<sub>5</sub>).

After partially evaporating the CH<sub>2</sub>Cl<sub>2</sub> solution, addition of Et<sub>2</sub>O caused the precipitation of a yellow crystalline solid. This was recrystallized from the same solvent mixture, 0.39 g (53%); mp. 287–290 °C. This is the N-bonded isomer.

Found: C, 32.41; H, 4.98; P, 18.08%. C<sub>14</sub>H<sub>26</sub>F<sub>6</sub>NP<sub>3</sub>Ru calcd: C, 32.57; H, 5.08; P, 18.00%. IR: ν(CN) at 2236 m cm<sup>-1</sup>; NMR: δ 1.58 virtual triplet (PMe<sub>3</sub>, J<sub>P-H</sub> = 5 Hz); 4.92 s (C<sub>5</sub>H<sub>5</sub>); 6.32 m (three olefinic hydrogens).

*[Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(trans-CICH=CHCl)]PF<sub>6</sub>*

This white crystalline product was prepared in a manner similar to the styrene compound; it was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 24%, mp 168 °C (d). Found: C, 27.96; H, 4.65; P, 16.78%. C<sub>13</sub>H<sub>25</sub>Cl<sub>2</sub>F<sub>6</sub>P<sub>3</sub>Ru calcd: C, 27.87; H, 4.50; P, 16.59%. NMR: δ 1.49 d (PMe<sub>3</sub>, J<sub>P-H</sub> = 10 Hz); 1.75 d (PMe<sub>3</sub>, J<sub>P-H</sub> = 10 Hz) 5.48 s (two olefinic hydrogens + C<sub>5</sub>H<sub>5</sub>).

*[Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(cis-EtO<sub>2</sub>CCH=CHCO<sub>2</sub>Et)]PF<sub>6</sub>*

A solution of 0.50 g (1.4 mmol) Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl, 1.0 g (6.0 mmol) NH<sub>4</sub>PF<sub>6</sub> and 3.0 ml (3.2 g, 18 mmol) diethyl maleate in 150 ml MeOH was heated at reflux for 12 hrs. Solvent was removed and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub>. Partial evaporation and then addition of Et<sub>2</sub>O gave a white precipitate of the product, 0.78 g (87%); mp 185–189 °C. Found: C, 35.85; H, 5.33; P, 14.56%. C<sub>19</sub>H<sub>35</sub>F<sub>6</sub>O<sub>4</sub>P<sub>3</sub>Ru calcd: C, 35.91; H, 5.55; P, 14.62%. IR: ν(CO) at 1735 s, 1716 s cm<sup>-1</sup>. NMR: δ 1.22 t (CH<sub>3</sub>, J<sub>H-H</sub> = 7 Hz); 1.57 t (PMe<sub>3</sub>, J<sub>P-H</sub> = 5 Hz); 2.70 t (olefinic hydrogens, J = 8 Hz), 4.02 q (CH<sub>2</sub>, J<sub>H-H</sub> = 7 Hz), 5.23 s (C<sub>5</sub>H<sub>5</sub>).

*[{Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(1,5-C<sub>8</sub>H<sub>12</sub>)](PF<sub>6</sub>)<sub>2</sub>*

This compound was prepared using a method similar to that of the previous preparation. Note that excess 1,5-cyclooctadiene (an approximately 3:1 molar ratio) was used. The product was a greenish-white solid (82% based on Ru), mp 267–270 °C (d).

Found: C, 34.80; H, 5.26; P, 17.87%. C<sub>30</sub>H<sub>58</sub>F<sub>12</sub>P<sub>6</sub>Ru<sub>2</sub> calcd: C, 34.82; H, 5.65, P, 17.96%. NMR (CD<sub>3</sub>CN): δ 1.48 m (PMe<sub>3</sub> and HC=CH-), 2.58 m (CH<sub>2</sub>), 4.88 s (C<sub>5</sub>H<sub>5</sub>).

*[Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(PhC≡CPh)]PF<sub>6</sub>*

Prepared in the same manner, bright yellow crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, 74%; mp 221–224 °C. Found: C, 46.73; H, 5.10; P, 14.53%. C<sub>25</sub>H<sub>33</sub>F<sub>6</sub>P<sub>3</sub>Ru calcd: C, 46.81; H, 5.19; P, 14.48%. IR: ν(C≡C) at 1890 w, br cm<sup>-1</sup>. NMR (acetone-d<sub>6</sub>): δ 1.55 t (PMe<sub>3</sub>, J = 5 Hz); 5.82 s (C<sub>5</sub>H<sub>5</sub>); 7.42–7.90 m (C<sub>6</sub>H<sub>5</sub>).

*[Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(EtC≡CEt)]PF<sub>6</sub>*

The product, obtained in a similar procedure, was a yellow powder, 70%; mp. 245–248 °C. Found: C, 37.54; H, 5.75; P, 16.83%. C<sub>17</sub>H<sub>33</sub>F<sub>6</sub>P<sub>3</sub>Ru calcd, C, 37.44; H, 6.10; P, 17.04%. IR: ν(C≡C) at 1874 m cm<sup>-1</sup>. NMR: δ 1.32 t (CH<sub>3</sub>, J<sub>H-H</sub> = 7 Hz); 1.51 t (PMe<sub>3</sub>, J = 4 Hz); 2.90 q (CH<sub>2</sub>, J<sub>H-H</sub> = 7 Hz); 5.25 s (C<sub>5</sub>H<sub>5</sub>).

*[Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me)]PF<sub>6</sub>*

Prepared in the same manner, bright yellow crystals (69%); mp. 185–187 °C. Found: C, 33.70; H, 4.91; P, 15.39%. C<sub>17</sub>H<sub>29</sub>F<sub>6</sub>O<sub>4</sub>P<sub>3</sub>Ru calcd: C, 33.73; H, 4.83; P, 15.35%. IR ν(C≡C) at 1870 m, ν(CO) at 1702 s cm<sup>-1</sup>. NMR (acetone-d<sub>6</sub>): δ 1.75 t (PMe<sub>3</sub>, J = 5 Hz); 3.95 s (CH<sub>3</sub>), 5.67 (C<sub>5</sub>H<sub>5</sub>).

*Reaction of Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl and PhC≡CH*

A solution of 0.43 g (1.2 mmol) Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl, 1.0 g (6.0 mmol) NH<sub>4</sub>PF<sub>6</sub>, and 0.50 ml (4.6 mmol) PhC≡CH in 100 ml MeOH was heated at reflux for 1 hr. Partial evaporation of the solution caused precipitation of pink crystals which were recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, 0.57 g (83%), mp. 236–238 °C. Found: C, 40.58; H, 5.37; P, 16.59%. C<sub>19</sub>H<sub>29</sub>F<sub>6</sub>P<sub>3</sub>Ru calcd: C, 40.36; H, 5.17; P, 16.43%. IR: ν(C=C) at 1656 s cm<sup>-1</sup>. NMR (acetone-d<sub>6</sub>): δ 1.82 m, (PMe<sub>3</sub>); 5.80 t (=CHPh, J<sub>P-H</sub> = 2 Hz), 5.94 s (C<sub>5</sub>H<sub>5</sub>); 7.26 m (C<sub>6</sub>H<sub>5</sub>).

The same product was obtained from a similar reaction using PhC≡CSiMe<sub>3</sub> (82%). Because of this result we carried out the following reaction using a non-protonic solvent and mild conditions.

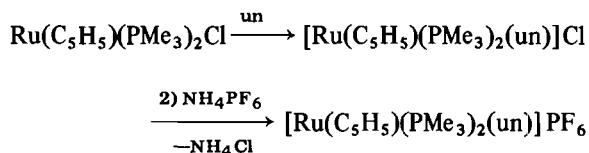
*Reaction of Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl, AgBF<sub>4</sub>, and PhC≡CSiMe<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>*

A sample of AgBF<sub>4</sub> (0.285 g, 1.46 mmol) was added to a solution of 0.52 g (1.4 mmol) Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl and 1.0 g (5.7 mmol) of PhC≡CSiMe<sub>3</sub> in 75 ml CH<sub>2</sub>Cl<sub>2</sub>. Silver chloride precipitated in a few seconds and the solution became yellow but then turned pink during 18 hrs. Workup yielded the product [Ru(C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(C=CHPh)]BF<sub>4</sub> (mp. 215–217 °C) in ~ 85% yield, identified by IR and

NMR. Another reaction was run for 0.5 hr, being terminated while the solution was still yellow. Work-up gave a crude yellow-orange product, but recrystallization in  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  again gave the pink carbonyl complex. It was not possible to obtain a good sample of the intermediate species for study.

## Results and Discussion

As anticipated, the chloride ion in  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  was displaced by a variety of olefins and acetylenes:



(un = various olefins and disubstituted acetylenes)

These reactions were carried out in methanol at reflux temperature. They were found to be generally slow, usually requiring less than an hour for completion. Progress of the reaction could be determined by monitoring the color of the solution; orange color for the starting material gradually fades to the pale yellow of the products. Chloride complexes were converted as  $\text{PF}_6^-$  salts by metathetical reaction with  $\text{NH}_4\text{PF}_6$ . The procedure to obtain the final  $\text{PF}_6^-$  complexes was sometimes simplified by adding  $\text{NH}_4\text{PF}_6$  to the initial reaction mixture, allowing the synthesis to be run in one step rather than two. It is noted that  $\text{NH}_4\text{PF}_6$ , which is known to serve as a halide acceptor in other reactions, is not a requirement for the halide displacement reaction.

The products are white to pale yellow solids, very stable, and not noticeably reactive with moisture or air. Solubility in polar solvents was found, as expected, for ionic species.

In a reaction with 1,5-cyclooctadiene a product was obtained containing two metal atoms per diolefin. The structure of this complex is assumed to be one in which the individual  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2$  groups bonded to each of the olefinic groups of the ligand. It is significant that even though an excess of the olefin was used, this was the only product.

The reaction of a terminal acetylene,  $\text{PhC}\equiv\text{CH}$ , with  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  gave the pink alkylidene complex  $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{C}=\text{CHPh}]^+$  also isolated as a  $\text{PF}_6^-$  salt. A reaction with  $\text{PhC}\equiv\text{CSiMe}_3$  gave the same product although a yellow intermediate color was detected. Presumably this intermediate is the expected  $\eta^2$ -acetylene complex. This could not be isolated however, all attempts to work up this mixture giving only the alkylidene complex. The preparation of alkylidene complexes in the reaction of  $\text{PhC}\equiv\text{CH}$

is not particularly surprising. A similar complex was reported earlier in the reaction of  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}$  with this acetylene [9].

The reaction of  $\text{Ru}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}$  with  $\text{CH}_2=\text{CHCN}$  deserves comment in that two isomeric products are obtained. A white product was characterized as the  $\eta^2$ -olefin complex while the second isomer, a yellow complex, is the N bonded species. Identification of the two isomers was made based on nmr data. There is no evidence of interconversion of the two isomers on standing at room temperature, although the former apparently converts to the latter upon melting ( $> 200^\circ\text{C}$ ). Slow interconversion accords well with the general kinetic stability of ruthenium(II) complexes. We commented on this fact earlier, noting that the syntheses of these complexes was a relatively slow process.

Proton nmr spectra of the olefin complexes were run. For complexes of monosubstituted olefins ( $\text{CH}_2=\text{CHR}$ , R = Me, Ph, CN) and the complex of a *trans* disubstituted olefin the phosphines are in dissimilar environments (structures I and II below).



Rotation of the olefin about the metal-olefin axis cannot interconvert these ligand environments. Hence, two resonances are seen for the protons associated with the  $\text{PMe}_3$  ligands. In contrast, in the complexes of symmetric acetylenes and *cis*-olefins, and in the complex of N-bonded  $\text{CH}_2=\text{CHCN}$ , phosphine protons are in equivalent environments; thus for these species a single proton resonance for  $\text{PMe}_3$  groups is found.

Noteworthy, also, is the relatively low  $\nu(\text{C}\equiv\text{C})$  frequency observed for the acetylene complexes. This infrared absorption occurs around  $1870\text{ cm}^{-1}$  (between  $1856$  and  $1890\text{ cm}^{-1}$  in the three examples presented here). A substantial shift to lower frequency, on the order of  $350\text{ cm}^{-1}$ , has occurred on coordination to the metal. This shift resembles the shift upon coordination to zerovalent metals (in complexes like  $\text{Pt}(\text{L})_2(\text{acetylene})$ ). This shift in frequency is related to the extent to which the metal donates negative charge to these ligands through  $\pi$  bonding [10]. This level of backbonding is expected for an electron-rich system.

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