

**Synthesis and Characterization of Soluble Polycationic Ruthenium Polystyrene Derivatives [PSTRuL]CF<sub>3</sub>SO<sub>3</sub>, (L = C<sub>5</sub>Me<sub>5</sub>, Ru:[PhC<sub>2</sub>H<sub>3</sub>] = 0.5 : 1; L = C<sub>8</sub>H<sub>11</sub>, Ru:[PhC<sub>2</sub>H<sub>3</sub>] > 0.9 : 1) and [PSTRuH(PCy<sub>3</sub>)<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub> [PST = Polystyrene, PCy<sub>3</sub> = P(c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>]**

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Protonation of the ruthenium derivatives Ru(COD)(COT) (COD = 1,5-C<sub>8</sub>H<sub>12</sub>, COT = 1,3,5-C<sub>8</sub>H<sub>10</sub>), [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)RuOMe]<sub>2</sub>, and RuH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> [PCy<sub>3</sub> = P(c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>] in the presence of polystyrene leads to the polymeric materials [PSTRu(η<sup>5</sup>-C<sub>8</sub>H<sub>11</sub>)]CF<sub>3</sub>SO<sub>3</sub> (**4**), [PSTRu(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)]CF<sub>3</sub>SO<sub>3</sub> (**2**), and [PSTRuH(PCy<sub>3</sub>)<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub> (**7**) in which the ruthenium fragments are bonded to over 90, 50, and 25%, respectively, of the phenyl rings of polystyrene; compounds (**2**) and (**4**) are air-stable, soluble in acetone and methanol, and have been characterized by microanalytical and spectroscopic methods; (**7**) is slightly air-sensitive and has been characterized by comparison with [(η<sup>6</sup>-PhMe)RuH(PCy<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (**6**).

The preparation of polymer-attached soluble organometallic derivatives is a synthetic challenge with important applications. Modified polymers, in particular those containing phosphine groups, have been used to link homogeneous catalysts but loss of metal was frequently observed during catalysis runs.<sup>1</sup> Direct linkage to the phenyl groups of cheap aromatic polymers like polystyrene is an attractive target,<sup>2-5</sup> but good preparative methods have not been found so far. Some chromium compounds have been attached to polystyrene (PST) but the products were not well characterized<sup>2</sup> or difficult to prepare<sup>3</sup> and were not very reactive. Vitulli and Pertici have described the incorporation of ruthenium into polystyrene by hydrogenation of Ru(COD)(COT) (COD = 1,5-C<sub>8</sub>H<sub>12</sub>, COT = 1,3,5-C<sub>8</sub>H<sub>10</sub>) but found later that in fact ruthenium colloids were formed.<sup>5</sup>

We now describe the facile preparation and characterization of polycationic polystyrene ruthenium complexes includ-

ing the first hydrido derivative of a transition metal in which up to 25, 50, or >90% of the phenyl rings are bound to ruthenium, depending upon the other ligand on the metal.

We have reported recently the high affinity towards arenes of the '(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru<sup>+</sup>' fragment which can be prepared either by zinc reduction of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)RuCl]<sub>2</sub>,<sup>6</sup> or by protonation of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)RuOMe]<sub>2</sub>.<sup>7</sup> Unusual π-pyridine<sup>6</sup> and zwitterionic π-benzoate<sup>7</sup> derivatives could be obtained by these methods. The fragment '(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru<sup>+</sup>' obtained by reaction of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)RuCl]<sub>4</sub> with AgOSO<sub>2</sub>CF<sub>3</sub> has also been shown recently to co-ordinate to aromatic compounds of different shapes and lead to interesting physical properties.<sup>8</sup> We find now that in CH<sub>2</sub>Cl<sub>2</sub> the '(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru<sup>+</sup>' fragment {prepared by protonation of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)RuOMe]<sub>2</sub> (**1**) with CF<sub>3</sub>SO<sub>3</sub>H} with one equivalent of polystyrene (based on one monomeric unit) leads to the precipitation of a yellow material in high yield (76% based on polymer) (**2**). This material is

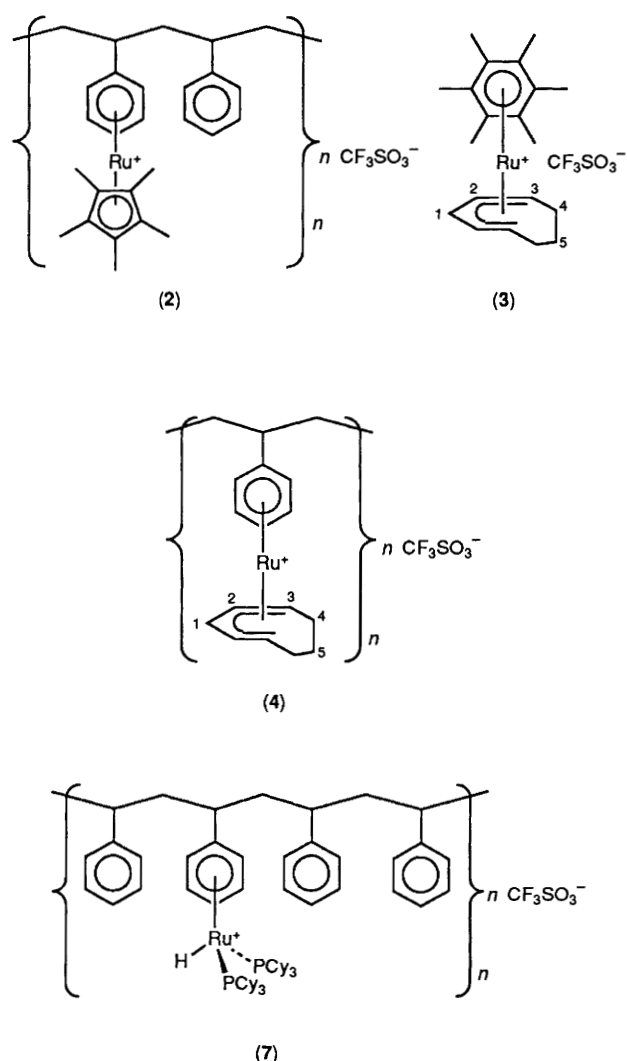


Figure 1. Proposed structures for compounds (2), (3), (4), and (7).

soluble in methanol and acetone and can be reprecipitated upon addition of ether. Slow evaporation of a methanol solution at the surface of mercury leads to the formation of a film through which IR spectra were recorded. Microanalysis, NMR data ( $^1\text{H}$  and  $^{13}\text{C}$ ), and the formation of the same material for a Ru : PST ratio of 1 : 2 are in agreement with one  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}^+$  fragment per two monomeric units of PST.

It has been shown that the protonation of  $\text{Ru}(\text{COD})(\text{COT})$  in benzene leads to  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta^5\text{-C}_8\text{H}_{11})]^+$ .<sup>9</sup> We obtained the same product upon protonation of  $\text{Ru}(\text{COD})(\text{COT})$  in  $\text{CH}_2\text{Cl}_2$  and subsequent addition of one equivalent of benzene. The reaction with a solid aromatic compound  $\text{C}_6\text{Me}_6$  leads similarly to  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\eta^5\text{-C}_8\text{H}_{11})]\text{CF}_3\text{SO}_3$  (3)<sup>10</sup> (see NMR data in Table 1).

The same reaction in the presence of polystyrene in  $\text{CH}_2\text{Cl}_2$  led to the precipitation of a yellow polymeric material (4) which was very soluble in acetone and slightly soluble in methanol, and which was shown to contain over 90%  $(\text{C}_8\text{H}_{11})\text{Ru}^+$  fragment per phenyl ring of PST.

Recently, we have studied the chemistry of the bisdihydrogen derivative  $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$  [ $\text{PCy}_3 = \text{P}(\text{C-C}_6\text{H}_{11})_3$ ] (5)<sup>11</sup> and in particular its protonation<sup>12</sup> as part of a study of the stability of co-ordination of dihydrogen to a transition metal.

Table 1. Relevant spectroscopic data for compounds (2), (3), (4), and (7).

Compound	$^1\text{H}$ NMR	$^{13}\text{C}$ NMR
(2)	7.35; 6.88 (br., 5H) <sup>b</sup> 6.00; 5.50 (br., 5H) <sup>c</sup> 1.98 (br., 15H) 1.70 (m, 2H) <sup>d</sup>	130.7; 129 <sup>b</sup> 98.5 (s, $\text{C}_5\text{Me}_5$ ) 88; 87 <sup>c</sup> 44; 39 (t, $\text{CH}_2$ ) <sup>d</sup> 12.3 (q, $\text{C}_5\text{Me}_5$ )
(3)	6.25 (t, $\text{H}_1$ ) 4.29 (t, $2\text{H}_2$ ) 3.42 (m, $2\text{H}_3$ ) 2.20 (s, 18H) 1.81 (m, $4\text{H}_4$ ) 1.21 (m, $\text{H}_{5\text{exo}}$ ) 0.04 (m, $\text{H}_{5\text{endo}}$ )	106.3 (d, $\text{C}_1$ ) 104.8 (s, $\text{C}_6\text{Me}_6$ ) 84.2 (d, $\text{C}_2$ ) 60.9 (d, $\text{C}_3$ ) 27.0 (t, $\text{C}_4$ ) 19.1 (t, $\text{C}_5$ ) 15.7 (q, $\text{C}_6\text{Me}_6$ )
(4)	7.40 (m, $\text{H}_1$ ) 6.70 (br., 5H) <sup>c</sup> 5.01 (m, $2\text{H}_2$ ) 4.71 (m, $2\text{H}_3$ ) 2.01 (m, $4\text{H}_4$ ) 1.56 (m, $\text{H}_{5\text{exo}}$ ) 0.24 (m, $\text{H}_{5\text{endo}}$ )	108.3 (d, $\text{C}_1$ ) 92.9 (m) <sup>c</sup> 82.3 (d, $\text{C}_2$ ) 56.9 (d, $\text{C}_3$ ) 44; 37 (m, $\text{CH}_2$ ) <sup>d</sup> 18.9 (t, $\text{C}_5$ )
(7)	7.20; 6.80 (br., 15H) <sup>b</sup> 6.00; 4.20 (br., 5H) <sup>c</sup> 2.00 (br., $6\text{C}_6\text{H}_{11}$ ) -9.8 (t, 1H, $J_{\text{PH}}$ 37 Hz)	

<sup>a</sup>  $^1\text{H}$  NMR of (2), (4), and (7) in  $(\text{CD}_3)_2\text{CO}$  and (3) in  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR of (2) in  $\text{CD}_3\text{OD}$ , (3) in  $\text{CDCl}_3$ , and (4) in  $(\text{CD}_3)_2\text{CO}$ . <sup>b</sup> Free phenyl group of PST. <sup>c</sup> Co-ordinated phenyl group of PST. <sup>d</sup> Alkyl group of PST.

When (5) is reacted with  $\text{HBF}_4$  in the presence of toluene, a  $\pi$ -arene derivative  $[(\eta^6\text{-PhMe})\text{RuH}(\text{PCy}_3)_2]\text{BF}_4$  (6) is obtained. A similar protonation reaction of  $\text{RuH}(\text{OAc})(\text{PPh}_3)_3$  had been shown by Wilkinson *et al.* to lead to the same type of complexes.<sup>13</sup> In the presence of polystyrene, (5) reacts with  $\text{CF}_3\text{SO}_3\text{H}$  in  $\text{CH}_2\text{Cl}_2$  to yield  $[\text{PSTRuH}(\text{PCy}_3)_2]\text{CF}_3\text{SO}_3$  (7) in which 25% of the phenyl rings are linked to ruthenium. Compound (7) is soluble in acetone,  $\text{CH}_2\text{Cl}_2$ , and methanol but can be precipitated upon addition of diethyl ether.

The microanalytical data for (2) and (7) calculated respectively for one ruthenium per two phenyl rings and one ruthenium per four phenyl rings are in good agreement with the experimental values whereas the data for (4), calculated for one ruthenium per phenyl ring, show a small deficit in Ru. However, the assumption that only 90% of the phenyl rings are linked to ruthenium leads to calculated data in good agreement with the experimental data.<sup>†</sup> Some residual  $\text{CH}_2\text{Cl}_2$  is present as shown by  $^1\text{H}$  NMR spectroscopy, about 0.25 from integration. This leads to excellent agreement with the experimental analytical data.

The NMR spectra of (2), (4), and (7) are broad, like that of PST itself, but are very clear and in accordance with the structures illustrated in Figure 1 (see Table 1), allowing unambiguous characterization of the complexes. We note (i) a shift to high field of the co-ordinated rings of polystyrene as observed for mononuclear compounds (*ca.* 1 ppm in  $^1\text{H}$  NMR,

<sup>†</sup> Satisfactory microanalytical data were obtained for compounds (2) (yield 76%), (3) (>80%), and (7). Calcd. for compound (4)  $\{\text{RuC}_{17}\text{H}_{19}\text{SO}_3\text{F}_3\}_n$ : C, 44.25; H, 4.12; Ru, 21.91; (4) (with 90% complexation): C, 45.43; H, 4.21; Ru, 21.37; (4) (with 90% complexation + 0.25  $\text{CH}_2\text{Cl}_2$ ): C, 43.94; H, 4.12; Ru, 20.35. Found: C, 44.87; H, 4.24; Ru, 19.96. Yield 73%.

40 ppm in  $^{13}\text{C}$  NMR), (ii) the  $^{13}\text{C}$  NMR spectrum of (4) which shows very clearly the different carbons of the co-ordinated cyclo-octadienyl ligand, and (iii) the observation of a triplet for the hydrides in (7) as for (6).

The observation that roughly 25, 50, or 100% of phenyl rings can be covered with ruthenium according to the ligand is most probably related to steric effects since the two  $\text{PCy}_3$  ligands are more bulky than  $\text{C}_5\text{Me}_5$ , the latter being more bulky than  $\text{C}_8\text{H}_{11}$ . We attempted an anion exchange reaction with tetracyanoquinodimethane ( $\text{TCNQ}$ ) $^-$  in order to see whether an order could exist in the structure. However we only succeeded in substituting half of the trifluoromethanesulphonate (triflate) anions and obtained a green paramagnetic material of composition  $[\{\text{PST}(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\}_2(\text{CF}_3\text{SO}_3)(\text{TCNQ})(\text{CH}_2\text{Cl}_2)]_n$ . The presence of both triflate and  $\text{TCNQ}$  in the polymer is attested by the IR spectra of films obtained at the surface of mercury. Owing to the paramagnetism a good NMR spectrum was not obtained, and only the presence of  $\text{CH}_2\text{Cl}_2$  was attested. The EPR spectrum shows a typical signal for  $\text{TCNQ}^-$  at 3356 G ( $1\text{G} = 10^{-4}\text{ T}$ ) ( $g\ 2.004$ ).

We have described the facile synthesis of soluble polycationic polymers which are also well defined organometallic complexes. The preparation of an air-stable material containing 20% of ruthenium and of the first polymer supported hydrido derivative of a transition metal are of particular interest. The physical and chemical properties of these polymers are presently under investigation.

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