51-8; **15d**, 126796-50-7; **15e**, 126796-52-9; **16a**, 126796-54-1; **16f**, 126796-56-3; **18c**, 137203-90-8; **18d**, 137203-87-3; **18e**, 126796-39-2; **19a**, 126796-41-6; **19b**, 126796-42-7; **19f**, 126796-44-9; **24**, 137203-92-0; **25**, 137203-94-2; **26c**, 137203-95-3; **26d**, 137203-97-5; **26e**, 137203-86-2; **27a**, 137203-96-4; **27b**, 137203-89-5; **27f**, 137203-91-9; **30**, 137203-98-6; **31**, 137203-99-7; **32**, 137204-00-3; **33**, 137204-01-4; **34**, 137204-02-5; **35**, 137204-03-6; **37**, 137259-47-3; **38**, 137204-04-7.

# *Notes*

## Preparation of Electron-Rich Cationic Complexes of the Type $[(\eta^5\text{-}C_5Me_5)Ru(bipyridine)L]^+$

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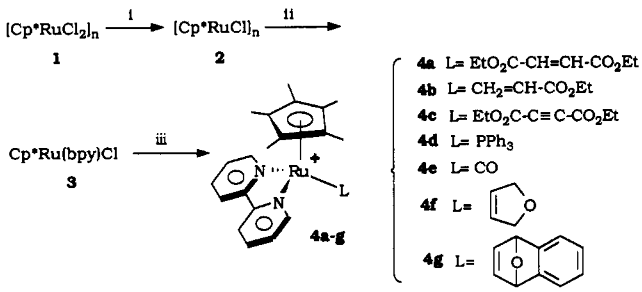
*Summary:* Reaction of Cp*Ru(bpy)Cl (Cp* = $C_5Me_5$, bpy = 2,2′-bipyridine) with various monodentate two-electron donor ligands (L) in the presence of $NH_4PF_6$ gives $[Cp^*Ru(bpy)L]^+PF_6^-$ (L = $EtO_2C—CH{=}CH—CO_2Et$; $CH_2{=}CH—CO_2Et$; $EtO_2C—C{\equiv}C—CO_2Et$; 1,4-epoxy-1,4-dihydronaphthalene; 2,5-dihydrofuran; CO; $PPh_3$). The molecular structure of the ethyl maleate complex determined by X-ray diffraction studies is described.

Transition-metal complexes containing electron-rich ligands have been the focus of recent studies in the field of organometallic chemistry of group VIII metals. These metal complexes are known to be stable in high formal oxidation states, which, in some cases, has proven valuable to promote C–H activation reactions.

The very strong σ-donor ligands phenanthroline and bipyridine have been extensively used in the coordination chemistry of ruthenium where they play a key role.[1] However, the development of the organometallic chemistry of ruthenium complexes containing such ligands is still rather limited. Singleton et al.[2] recently reported the synthesis of several cyclopentadienylruthenium complexes including $[(\eta^5\text{-}C_5H_5)Ru(diamine)Cl]$ where diamine = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy).

Pentamethylcyclopentadiene (Cp*), another electron-rich ligand, was used by Bercaw et al.[3] for the synthesis of $[Cp^*RuCl_2]_n$. This compound is a precursor for a number of complexes containing the (Cp*Ru) unit.[4]

Scheme I



[a] Key: (i) Zn, THF, room temperature; (ii) bpy (1 equiv), THF, room temperature; (iii) $NH_4PF_6$, L (5 equiv or 1 atm (CO)), MeOH.

So far, Cp*Ru(bpy)X (X = halide, $OCH_3$)[5] are the only known examples of ruthenium complexes where both electron-rich ligands, $C_5Me_5$ and bipyridine, are simultaneously coordinated to ruthenium. To the best of our knowledge, no X-ray structure for any of these compounds has been previously reported in the literature.

Here we describe the synthesis of various $[Cp^*Ru(bpy)L]^+PF_6^-$ complexes (Scheme I) and the molecular structure determination of the ethyl maleate complex [L = $EtO_2C—CH{=}CH—CO_2Et$] by X-ray diffraction.

### Results and Discussion

The chloride $[(\eta^5\text{-}C_5Me_5)Ru(bpy)Cl]$ (**3**) was prepared in 91% yield by modified published procedures[5,6] using THF as solvent. Treatment of the chloride **3** with an excess (5 equiv) of a ligand L (L = diethyl maleate, ethyl acrylate, diethyl acetylenedicarboxylate, $PPh_3$, or CO) in methanol in the presence of ammonium hexafluorophosphate, results in the rapid displacement of the chloride ion and affords the cationic $[Cp^*Ru(bpy)L]^+PF_6^-$ complexes **4a–e**.

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[†] Contribution from the Laboratoire de Chimie Organique des Elements de Transition associated with the CNRS (URA 255).

[‡] Laboratoire de Physique des Solides associated with the CNRS (URA 2).

(1) Cotton and Wilkinson. *Advances Inorganic Chemistry*, 4th ed.; J. Wiley & Sons: New York, p 922.

(2) (a) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Singleton, E. *Organometallics* **1987**, *6*, 2179. (b) Albers, M. O.; Robinson, D. J.; Singleton, E. *J. Organomet. Chem.* **1986**, *311*, 207.

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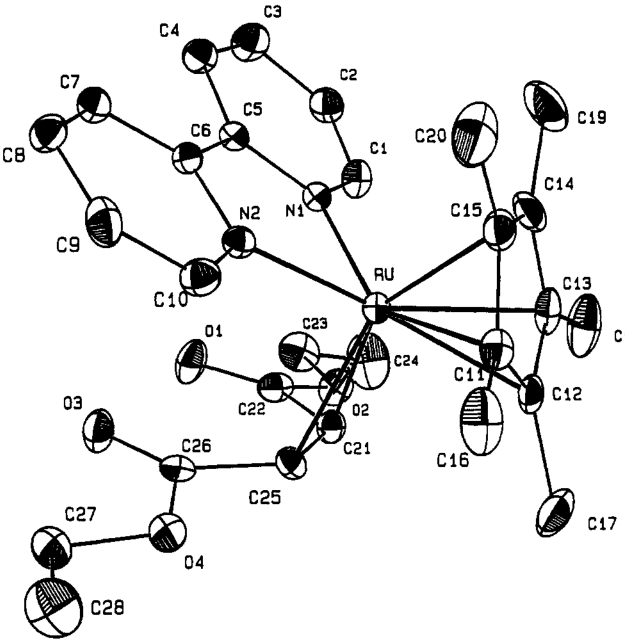

**Figure 1.** ORTEP drawing of the molecule **4a**. The thermal ellipsoids enclose 15% of the electron density.

The infrared absorption of the carbonyl group of **4e** ($\nu_{CO}$ = 1928 cm$^{-1}$, Nujol) occurs at a frequency lower than those reported for [Cp*Ru(PMe$_3$)$_2$CO]$^+$PF$_6^-$ ($\nu_{CO}$ = 1935 cm$^{-1}$, Nujol)[3] and [CpRu(phenanthroline)CO]$^+$BPh$_4^-$ ($\nu_{CO}$ = 1948 cm$^{-1}$, Nujol)[2a] and that we found for [CpRu(bpy)CO]$^+$PF$_6^-$ ($\nu_{CO}$ = 1963 cm$^{-1}$, Nujol) (see Experimental Section, complex **5**). These differences are due to the enhanced electron-donating ability of the [Cp*Ru(bpy)] moiety compared to [Cp*Ru(PMe$_3$)$_2$], [CpRu(bpy)], or [CpRu(phen)] moieties. The high-field chemical shift of the carbonyl carbon in the $^{13}$C NMR spectrum of **4e** ($\delta$ = 199.3 ppm) reflects this property.

All efforts to obtain complexes with unsaturated hydrocarbons bearing no electron-withdrawing groups, such as ethylene, cyclohexene, ethyl vinyl ether, *Z*- or *E*-stilbene, diphenylacetylene and bis(trimethylsilyl)acetylene were unsuccessful. The failure of these reactions is likely due to a weak back-bonding interaction of the electron-rich system [Cp*Ru(bpy)] with the $\pi^*$ orbitals of the electron-rich olefins or alkynes.

However, it was possible to obtain in good yields complexes of alkenes bearing an oxygen atom in the allylic position such as 2,5-dihydrofuran or 1,4-epoxy-1,4-dihydronaphthalene. We originally hoped that the intriguing ruthenium complex [Cp*Ru(bpy)O]$^+$ could be obtained after elimination of naphthalene from the complex **4g**. However complex **4g** remained unchanged even after refluxing in the THF for 24 h.

An X-ray structure determination was carried out for [Cp*Ru(bpy)(EtO$_2$C—CH=CH—CO$_2$Et)]$^+$PF$_6^-$ (**4a**). Single crystals of **4a** were obtained by allowing slow diffusion of cyclohexane into a dichloromethane solution of **4a** at ambient temperature.

The asymmetric unit of the centrosymmetrical triclinic unit cell contains two independent complexes A and B. Both molecules have the same geometrical shape therefore only the distances and angles of molecule A are discussed here.

An ORTEP drawing of **4a** is given in Figure 1. Experimental details are given in Table I, and positional and thermal parameters are in Table II. Table III lists some of the relevant bond distances and bond angles.

**Table I. Experimental Data for the X-ray Study of [Cp*Ru(bpy)(EtO$_2$C—CH=CH—CO$_2$Et)]$^+$PF$_6^-$ (4a)**

| | |
|---|---|
| molecular formula | C$_{28}$H$_{35}$F$_6$N$_2$O$_4$PRu |
| fw | 709.63 |
| cryst syst | triclinic |
| space group | $P\bar{1}$ |
| $a$, Å | 14.726 (4) |
| $b$, Å | 16.969 (2) |
| $c$, Å | 14.547 (2) |
| $\alpha$, deg | 98.75 (1) |
| $\beta$, deg | 104.69 (1) |
| $\gamma$, deg | 114.15 (1) |
| $V$, Å$^3$ | 3070.9 |
| $Z$ | 4 |
| $d$(calc), g·cm$^{-3}$ | 1.53 |
| $\mu$, cm$^{-1}$ | 6.2 |
| no. of params refined | 683 |
| resid density, e·Å$^{-3}$ | 0.66 |
| $R$,[a] % | 7.9 |
| $R_w$,[b] % | 10.5 |
| goodness of fit | 2.098 |
| final shift/error | 0.0 |

[a] $R = \sum |K|F_o| - |F_c|| / \sum K|F_o|$. [b] $R_w = [\sum w(K|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. $w = 1/\sigma^2(|F_o|)$. $\sigma^2(F_o) = \sigma^2(I) + (pF_o^2)^2/4F_o^2$.

**Table II. Positional Parameters and Their Estimated Standard Deviations for [Cp*Ru(bpy)(EtO$_2$C—CH=CH—CO$_2$Et)]$^+$PF$_6^-$[a] (4a)**

| atom | $x$ | $y$ | $z$ | $B$(eq), Å$^2$ |
|---|---|---|---|---|
| Ru | 0.27236 (6) | 0.47514 (5) | 0.20244 (6) | 3.33 (2) |
| O1 | 0.2095 (6) | 0.3260 (6) | 0.3638 (5) | 6.3 (3) |
| O2 | 0.0514 (6) | 0.3116 (5) | 0.2809 (5) | 5.3 (2) |
| O3 | 0.3713 (6) | 0.3209 (5) | 0.3010 (5) | 5.4 (2) |
| O4 | 0.3879 (6) | 0.3109 (5) | 0.1507 (5) | 5.0 (2) |
| N1 | 0.2780 (6) | 0.5194 (5) | 0.3472 (6) | 3.7 (2) |
| N2 | 0.4304 (6) | 0.5195 (5) | 0.2912 (6) | 3.7 (2) |
| C1 | 0.1947 (8) | 0.5179 (7) | 0.3713 (8) | 4.9 (3) |
| C2 | 0.2064 (8) | 0.5586 (7) | 0.4636 (8) | 5.0 (3) |
| C3 | 0.3052 (9) | 0.6012 (8) | 0.5389 (9) | 6.0 (4) |
| C4 | 0.3911 (9) | 0.6003 (7) | 0.5176 (8) | 4.7 (3) |
| C5 | 0.3760 (8) | 0.5590 (6) | 0.4203 (7) | 3.7 (3) |
| C6 | 0.4617 (8) | 0.5591 (6) | 0.3884 (7) | 3.6 (3) |
| C7 | 0.5655 (8) | 0.5930 (7) | 0.4499 (8) | 4.5 (3) |
| C8 | 0.6403 (8) | 0.5902 (7) | 0.4107 (8) | 4.7 (3) |
| C9 | 0.6076 (9) | 0.5514 (8) | 0.312 (1) | 6.0 (4) |
| C10 | 0.5042 (9) | 0.5157 (7) | 0.2525 (8) | 4.8 (3) |
| C11 | 0.2862 (8) | 0.5073 (7) | 0.0650 (8) | 4.2 (3) |
| C12 | 0.1806 (8) | 0.4543 (6) | 0.0473 (7) | 4.1 (3) |
| C13 | 0.1457 (8) | 0.4980 (8) | 0.1091 (8) | 5.3 (3) |
| C14 | 0.234 (1) | 0.5830 (7) | 0.1634 (9) | 6.2 (3) |
| C15 | 0.3194 (9) | 0.5894 (7) | 0.1352 (9) | 5.5 (3) |
| C16 | 0.345 (1) | 0.486 (1) | 0.004 (1) | 8.4 (5) |
| C17 | 0.105 (1) | 0.365 (1) | −0.0316 (9) | 8.0 (5) |
| C18 | 0.033 (1) | 0.463 (1) | 0.111 (1) | 9.2 (5) |
| C19 | 0.232 (1) | 0.6561 (9) | 0.234 (1) | 12.1 (5) |
| C20 | 0.427 (1) | 0.672 (1) | 0.173 (1) | 12.4 (6) |
| C21 | 0.1683 (8) | 0.3381 (6) | 0.1972 (7) | 4.2 (3) |
| C22 | 0.1497 (9) | 0.3252 (7) | 0.2912 (8) | 4.6 (3) |
| C23 | 0.018 (1) | 0.3004 (9) | 0.366 (1) | 7.0 (4) |
| C24 | −0.092 (1) | 0.284 (1) | 0.340 (1) | 10.8 (6) |
| C25 | 0.2516 (7) | 0.3370 (6) | 0.1650 (7) | 3.7 (3) |
| C26 | 0.3400 (8) | 0.3235 (6) | 0.2158 (8) | 4.0 (3) |
| C27 | 0.4797 (9) | 0.2990 (8) | 0.1874 (9) | 5.8 (3) |
| C28 | 0.530 (1) | 0.303 (1) | 0.115 (1) | 8.3 (5) |

[a] The form of the anisotropic displacement parameters is $\exp[-(h^2B(1,1) + k^2B(2,2) + l^2B(3,3) + hkB(1,2) + hlB(1,3) + klB(2,3))]$.

The lengthening of the carbon–carbon double bond in complex **4a** (1.43 Å) compared to free maleate (1.34 Å)[7] is somewhat greater than usually observed in the com-

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(7) The structure of free diethyl maleate was calculated by a geometrical optimization in a force field (MM2). (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8172. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

**Table III. Selected Bond Distances (Å) and Angles (deg) for [Cp*Ru(bpy)(EtO$_2$C—CH=CH—CO$_2$Et)]$^+$PF$_6^-$ [a]**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Ru–N1 | 2.094 (6) | Ru–N2 | 2.097 (6) |
| Ru–C11 | 2.187 (8) | Ru–C12 | 2.206 (7) |
| Ru–C13 | 2.223 (8) | Ru–C14 | 2.233 (9) |
| Ru–C15 | 2.240 (9) | Ru-centroid-Cp* | 1.873 (1) |
| Ru–C21 | 2.175 (8) | Ru–C25 | 2.197 (7) |
| C21–C25 | 1.43 (1) | | |
| | Bond Angles | | |
| N1–Ru–N2 | 75.8 (2) | C21–Ru–C25 | 38.1 (3) |
| Ru–N1–C1 | 124.8 (5) | Ru–N2–C10 | 122.4 (5) |
| Ru–C25–C26 | 116.8 (5) | Ru–C21–C22 | 116.2 (6) |
| C11–Ru–C12 | 36.3 (3) | C11–Ru–C15 | 37.0 (3) |
| C12–Ru–C13 | 36.9 (3) | C13–Ru–C14 | 36.9 (4) |
| C14–Ru–C15 | 36.1 (4) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

plexation of olefin. This reflects the strong back-bonding which is further confirmed by the disappearance of the infrared absorption of the carbon–carbon double bond in **4a**, which was at 1640 cm$^{-1}$ in the free ligand. This also explains the large chemical shift toward high field of the NMR signal. Atoms of the double bond give signals at $\delta$ = 3.60 ppm for $^1$H and $\delta$ = 54.3 ppm for $^{13}$C in the complex (see Experimental Section) compared to $\delta$ = 6.21 ppm and $\delta$ = 130.0 ppm, respectively, in the free ligand. The structure of **4a** (Figure 1) shows that ethyl carboxylate substituents are located on the less sterically hindered side, i.e., opposite to the C$_5$Me$_5$ unit. The failure of diethyl fumarate complexation, which has electronic requirements similar to diethyl maleate, is undoubtedly due to the steric repulsion between the bulky C$_5$Me$_5$ ligand and one of the ethyl carboxylate substituents.

In conclusion, we report in this paper a variety of new cationic ruthenium complexes obtained in high yields from the very electron-rich [Cp*Ru(bpy)]$^+$ parent unit and the appropriate ligand L. The [Cp*Ru(bpy)]$^+$ unit promises to be a useful precursor to stable Ru$^{IV}$ organometallic complexes and work in this field is in progress.

## Experimental Section

**Crystallographic Structure Determination for the Complex 4a.** An orange crystal of **4a** (0.30 × 0.16 × 0.16 mm$^3$) was mounted on an Enraf-Nonius CAD4-F diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Cell parameters were determined by a least-square refinement of angular coordinates of 23 reflections. Data were collected at room temperature by the $\omega$–$\theta$ scan technique [scan width (0.75 + 0.35 tan $\theta$)°]. A total of 17232 independent reflections was measured in the range $1° \le \theta \le 30°$ ($+h,\pm k,\pm l$), of which 6228 with $I \ge 3\sigma(I)$ were used in the subsequent refinements.

Of particular note is the presence of two independent complexes A and B in the asymmetric unit. Weissenberg and precession photographs revealed no systematic extinction or other indications of a unit cell and space group of higher symmetry. There was no evidence either for any correlations between any atom of A and B in the least-squares refinements. Some correlations were identified however in single atoms between the anisotropic parameters in the last cycles of refinement. Albeit rather faint, observation of the expected extinctions by examination of single crystals with polarized light suggests the absence of significant twinning. Nevertheless this latter possibility cannot be totally excluded.

Data were corrected for absorption[8] (transmission factor: 0.998 max, 0.935 min) and Lorentz–polarization effects. Calculations were performed on a Micro VAX computer using the Enraf-Nonius Structure Determination Package.[9] The structure was solved by a combination of direct methods and Fourier techniques. The two independent cations in the asymmetric unit were refined anisotropically, and the hexafluorophosphate anions, isotropically. Hydrogen atoms were included in structure factor calculations at idealized positions. Fractional atomic coordinates of nonhydrogen atoms are given in Table II.

**Synthesis.** Syntheses were performed under an inert atmosphere (nitrogen or argon) with Schlenk tube techniques. Solvents were dried by standard methods, freshly distilled, and degassed before use. The nuclear magnetic resonance spectra were recorded on a Brucker AC 200 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer (4000–200 cm$^{-1}$) using Nujol mulls or KBr pellets. [Cp*RuCl$_2$]$_n$[3,4a] and CpRu(bpy)Cl[2b] were prepared by literature methods.

**Cp*Ru(bpy)Cl (3).** A suspension of 1.536 g (5.0 mmol) of [Cp*RuCl$_2$]$_n$ and 8.17g (25 equiv) of zinc in THF leads to rapid dissolution of the ruthenium complex and appearance of a green coloration which totally disappears after 15 min.[6] The solution was stirred during 2 h and filtered; 0.781 g (1 equiv) of 2,2′-bipyridine was then added to the solution. Solvent was removed after 1 h, and the residue was extracted with CH$_2$Cl$_2$. After removal of the solvent, the solid was washed twice with ether and dried. The yield was 1.95 g (91%). NMR and IR spectral data were in accordance with ref 5.

**[Cp*Ru(bpy)(EtO$_2$C—CH=CH—CO$_2$Et)]$^+$PF$_6^-$ (4a).** To a solution of 0.50 g (1.2 mmol) of Cp*Ru(bpy)Cl and 0.95 g (5.8 mmol) of NH$_4$PF$_6$ in methanol (40 mL) was added 1.9 mL (6 mmol) of diethyl maleate. After 1.5 h, the solvent was removed and the residue extracted with CH$_2$Cl$_2$. After evaporation to dryness, a yellow crystalline solid is obtained, which is washed with ether and recrystallized from CH$_2$Cl$_2$–cyclohexane. The yield was 0.71 g (85.7%). $^1$H NMR (CD$_2$Cl$_2$, $\delta$): 8.62 (H$_a$) (2 H, dd, $J$(H$_a$,H$_b$) = 5.6 Hz, $J$(H$_a$,H$_c$) = 1.4 Hz), 8.28 (H$_d$) (2 H, dd, $J$(H$_c$,H$_d$) = 8.1 Hz, $J$(H$_b$,H$_d$) = 1.2 Hz), 8.06 (H$_c$) (2 H, br t), 7.57 (H$_b$) (2 H, br t), 3.60 (CH$_2$) (4 H, q, $J$(H,H) = 7.1 Hz), 3.60 (CH) (2 H, s), 1.42 (Cp*) (15 H, s), 1.02 (CH$_3$) (6 H, t). $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$): 170.4 (CO), 155.7 (C$_{bridge}$), 154.3 (C$_a$), 138.9 (C$_c$), 126.3 (C$_b$), 124.0 (C$_d$), 98.4 (Cp*, cycle), 60.5 (CH$_2$), 54.3 (CH), 14.1 (CH$_3$), 8.0 (Cp*, methyl). IR (KBr): $\nu_{CO}$ = 1734 cm$^{-1}$. Anal. Calcd for C$_{28}$H$_{35}$F$_6$N$_2$O$_4$PRu: C, 47.39; H, 4.97; N, 3.95. Found: C, 46.99; H, 4.73; N, 3.90.

**[Cp*Ru(bpy)(CH$_2$=CH—CO$_2$Et)]$^+$PF$_6^-$ (4b).** Prepared as described above for **4a**, using CH$_2$=CH—CO$_2$Et as ligand L. Yield: 87.3%. $^1$H NMR (CD$_2$Cl$_2$, $\delta$): 8.70 (H$_a$, H$_a'$) (2 H, m), 8.32 (H$_d$, H$_d'$) (2 H, m), 8.02 (H$_b$, H$_b'$) (2 H, m), 7.60 (H$_c$, H$_c'$) (2 H, m), 3.55 (H$_{1cis}$) (1 H, m), 3.28 (H$_2$) (1 H, d, $J$(H$_2$, H$_{1cis}$) = 8.4 Hz), 3.05 (H$_{1trans}$, CH$_2$) (3 H, m), 1.42 (Cp*) (15 H, s), 0.76 (CH$_3$) (3 H, t). $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$): 172.5 (CO), 155.3 (C$_{bridge}$), 154.8 and 154.2 (C$_a$, C$_a'$), 138.7 and 138.1 (C$_c$, C$_c'$), 127.0 and 126.0 (C$_b$, C$_b'$), 123.4 and 123.1 (C$_d$, C$_d'$), 95.4 (Cp*, cycle), 59.7 ($C$H$_2$CH$_3$), 57.8 ($C$H$_2$=CHR), 56.3 (CH), 13.9 (CH$_3$), 8.1 (Cp*, methyl). IR (KBr): $\nu_{CO}$ = 1691 cm$^{-1}$. Anal. Calcd for C$_{25}$H$_{31}$F$_6$N$_2$O$_2$PRu: C, 47.10; H, 4.90; N, 4.39. Found: C, 47.04; H, 4.86; N, 4.24.

**[Cp*Ru(bpy)(EtO$_2$C—C≡C—CO$_2$Et)]$^+$PF$_6^-$ (4c).** Prepared as described above for **4a**, using EtO$_2$C—C≡C—CO$_2$Et as ligand L. Yield: 87.5%. $^1$H NMR (CDCl$_3$, $\delta$): 9.05 (H$_a$) (2 H, br d, $J$(H$_a$,H$_b$) = 5.3 Hz), 8.47 (H$_d$) (2 H, br d, $J$(H$_c$,H$_d$) = 8.5 Hz), 8.10 (H$_c$) (2 H, br t), 7.65 (H$_b$) (2 H, br t), 4.22 (CH$_2$) (4 H, q, $J$(H,H) = 7.0 Hz), 1.52 (Cp*) (15 H, s), 1.25 (CH$_3$) (6 H, t). $^{13}$C NMR (CDCl$_3$, $\delta$): 155.5 (C$_{bridge}$), 154.8 (C$_a$), 139.2 (C$_c$), 126.4 (C$_b$), 124.5 (C$_d$), 99.2 (Cp*, cycle), 62.5 (CH$_2$), 14.3 (CH$_3$), 8.6 (Cp*, methyl). The CO and C≡C resonances were not observed. IR (KBr): $\nu_{CO}$ = 1694 cm$^{-1}$. Anal. Calcd for C$_{28}$H$_{33}$F$_6$N$_2$O$_4$PRu: C, 47.53; H, 4.70; N, 3.96. Found: C, 47.08; H, 4.48; N, 3.68.

**[Cp*Ru(bpy)PPh$_3$]$^+$PF$_6^-$ (4d).** Prepared as described above for **4a**, using PPh$_3$ as ligand L. Yield: 78.0%. $^1$H NMR (CD$_2$Cl$_2$, $\delta$): 8.86 (H$_a$) (2 H, d, $J$(H$_a$,H$_b$) = 5.7 Hz), 7.73 (H$_c$, H$_d$) (4 H, m), 7.39–7.34 (H$_b$, H$_{para}$) (5 H, m), 7.22 (H$_{meta}$) (6 H, m), 6.90 (H$_{ortho}$) (6 H, m), 1.39 (Cp*) (15 H, s). $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$): 155.5 (C$_{bridge}$), 152.9 (C$_a$), 135.9 (C$_c$), 133.3 and 133.1 (C$_{ortho}$), 131.6 ($C$–P) ($J$(P,C) = 38.6 Hz), 130.2 (C$_{para}$), 128.6 and 128.4 (C$_{meta}$), 126.1 (C$_b$), 122.9 (C$_d$), 87.7 (Cp*, cycle), 9.1 (Cp*, methyl). Anal. Calcd for

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$C_{38}H_{38}F_6N_2P_2Ru$: C, 57.07; H, 4.79. Found: C, 56.49; H, 4.69.

**[Cp*Ru(bpy)CO]$^+$PF$_6^-$ (4e).** Carbon monoxide was bubbled through a methanol solution of ($\eta^5$-$C_5Me_5$)Ru(bpy)Cl (0.5 g, 1.2 mmol) and $NH_4PF_6$ (0.95 g, 5.8 mmol). After 1 h, the solvent was removed and the residue was extracted with methylene chloride, followed by evaporation to dryness. The yellow solid obtained was washed with ether and recrystallized from $CH_2Cl_2$–pentane. The yield was 0.45 g (71.6%). $^1$H NMR ($CDCl_3$, $\delta$): 8.70 ($H_a$) (2 H, br d, $J(H_a,H_b)$ = 4.3 Hz), 8.47 ($H_d$) (2 H, br d, $J(H_c,H_d)$ = 7.9 Hz), 8.14 ($H_c$) (2 H, br t), 7.67 ($H_b$) (2 H, br t), 1.68 (Cp*) (15 H, s). $^{13}$C NMR ($CDCl_3$, $\delta$): 199.3 (CO), 155.7 ($C_{bridge}$), 154.1 ($C_a$), 139.5 ($C_c$), 127.3 ($C_b$), 124.2 ($C_d$), 94.1 (Cp*, cycle), 9.4 (Cp*, methyl). IR (Nujol mulls): $\nu_{CO}$ = 1928 cm$^{-1}$. Anal. Calcd for $C_{21}H_{23}F_6N_2OPRu$: C, 44.61; H, 4.10; N, 4.95. Found: C, 44.64; H, 4.11; N, 4.95.

**[Cp*Ru(bpy)($C_4H_6O$)]$^+$PF$_6^-$ (4f).** Prepared as described above for **4a**, using 2,5-dihydrofuran as ligand L. Yield: 45%. $^1$H NMR ($CD_2Cl_2$, $\delta$): 8.78 ($H_a$) (2 H, dd, $J(H_a,H_b)$ = 5.8 Hz, $J(H_a,H_c)$ = 1.4 Hz), 8.19 ($H_d$) (2 H, dd, $J(H_c,H_d)$ = 7.9 Hz, $J(H_b,H_d)$ = 1.4 Hz), 8.00 ($H_c$) (2 H, br t), 7.64 ($H_b$) (2 H, br t), 3.82 ($CH_1H_1'$) (2 H, s), 3.63 ($CH_1H_1'$) (2 H, d, $J(H_1,H)$ = 10 Hz), 2.70 (CH) (2 H, d), 1.43 (Cp*) (15 H, s). $^{13}$C NMR ($CD_2Cl_2$, $\delta$): 153.8 ($C_a$), 153.0 ($C_{bridge}$), 137.4 ($C_c$), 126.8 ($C_b$), 123.1 ($C_d$), 94.2 (Cp*, cycle), 70.7 (CH), 65.1 ($CH_2$), 8.0 (Cp*, methyl).

**[Cp*Ru(bpy)($C_{10}H_8O$)]$^+$PF$_6^-$ (4g).** Prepared as described above for **4a**, using 2,5-epoxy-2,5-dihydronaphthalene as ligand L. Yield: 82%. $^1$H NMR ($CD_2Cl_2$, $\delta$): 9.00 ($H_a$) (2 H, dd, $J(H_a,H_b)$ = 5.4 Hz, $J(H_a,H_c)$ = 0.8 Hz), 8.22 ($H_d$) (2 H, dd, $J(H_c,H_d)$ = 7.9 Hz, $J(H_b,H_d)$ = 0.9 Hz), 8.04 ($H_c$) (2 H, br t), 7.69 ($H_b$) (2 H, br t), 7.13 and 6.93 ($CH_{Ar}$) (2 × 2 H, m), 4.25 ($CH_{ether}$) (2 H, s), 3.54 ($CH_{ethylene}$) (2 H, s), 1.40 (Cp*) (15 H, s). $^{13}$C NMR ($CD_2Cl_2$, $\delta$): 156.0 ($C_{bridge}$), 153.8 ($C_a$), 148.6 ($C_{Ar,bridge}$), 137.7 ($C_c$), 126.2 ($C_b$), 125.8 ($C_{meta}$), 123.3 ($C_d$), 120.3 ($C_{ortho}$), 95.6 (Cp*, cycle), 82.6 ($CH_{ethylene}$), 68.4 ($CH_{ether}$), 8.0 (Cp*, methyl). Anal. Calcd for $C_{30}H_{31}F_6N_2OPRu$: C, 52.86; H, 4.58; N, 4.11. Found: C, 52.22; H, 4.53; N, 4.30.

**[CpRu(bpy)CO]$^+$PF$_6^-$ (5).** Prepared as described above for **4e**, using CpRu(bpy)Cl as reagent. Yield: 45%. $^1$H NMR ($CD_2Cl_2$, $\delta$): 8.96 ($H_a$) (2 H, br d, $J(H_a,H_b)$ = 5.4 Hz), 8.33 ($H_d$) (2 H, br d, $J(H_c,H_d)$ = 8.1 Hz), 8.14 ($H_c$) (2 H, br t), 7.53 ($H_b$) (2 H, br t), 5.22 (Cp) (5 H, s). $^{13}$C NMR ($CD_2Cl_2$, $\delta$): 197.6 (CO), 157.7 (Ca), 156.5 ($C_{bridge}$), 139.6 ($C_c$), 126.9 ($C_b$), 124.2 ($C_d$), 89.5 (Cp). IR (Nujol mulls): $\nu_{CO}$ = 1963 cm$^{-1}$.

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**Registry No.** **3**, 119886-13-4; **4a**, 137365-61-8; **4b**, 137365-63-0; **4c**, 137365-65-2; **4d**, 137365-67-4; **4e**, 137365-69-6; **4f**, 137365-71-0; **4g**, 137365-73-2; **5**, 137365-75-4; CpRu(bpy)Cl, 93966-27-9; [Cp*RuCl$_2$]$_n$, 92390-47-1.

**Supplementary Material Available:** Tables of atomic coordinates and anisotropic thermal parameters, all bond lengths and angles, and root mean square amplitudes (23 pages); a listing of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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# New Access to 1,3-Diphospholyl Anions. Application to the Synthesis of the First Phosphorus Analogue of a Ferrocenophane

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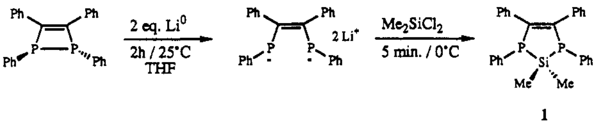
*Summary:* The reaction of acyl chlorides RC(O)Cl with a 2-sila-1,3-diphosphacyclopent-4-ene gives the corresponding 2-R-2-siloxy-1,3-diphosphacyclopent-4-enes via the formal replacement of the silicon by the acyl carbon in the five-membered ring. The substituents at P1, P3, and C2 in the resulting heterocycles are all cleaved by an excess of lithium in THF to afford the 1,3-diphospholyl anions. The dianion obtained from glutaryl dichloride, $ClC(O)C(CH_2)_3C(O)Cl$, reacts with a bis($\eta^6$-*p*-xylene)iron(II) salt, ([(*p*-xylene)$_2$Fe][PF$_6$]$_2$, to give the corresponding 2,2′-trimethylene-1,1′,3,3′-tetraphosphaferrocene, {[(PhC)$_2$P$_2$CCH$_2$]$_2$CH$_2$}Fe (**9**), whose structure has been established by X-ray crystallography. **9** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a$ = 18.913 (1) Å, $b$ = 11.362 (1) Å, $c$ = 29.621 (3) Å, $\beta$ = 106.49 (1)°, and $d_{calcd}$ = 1.396 g cm$^{-3}$ for $Z$ = 8. Least-squares refinement based on 2441 observed reflections with intensities $F_o \geq 3\sigma(F)$ in the range of $2° \leq 2\theta \leq 50°$ converged at $R$ = 4.5% ($R_w$ = 5.6%).

In a recent paper,[1] we have described the first general synthesis of 1,3-diphospholyl anions. Compared to earlier syntheses of the 2,4,5-tris-*tert*-butyl-1,3-diphospholyl anion,[2] the new method produces these species free from other phosphorus-containing products and allows for various substitution schemes on carbons $C_4$ and $C_5$. It has one major drawback, however; the substitution on carbon $C_2$ is not possible. Thus, we have looked for access to those anions that would circumvent this limitation.

## Results and Discussion

We chose the readily available 1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphete[3] as our starting product. Lithium cleavage of the P–P bond followed by reaction with dimethyldichlorosilane afforded the corresponding 1-sila-2,5-diphosphacyclopent-3-ene (1) as a single isomer according to the $^{31}$P NMR spectrum of the reaction mixture (eq 1).



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(1)

The crude product was used as such without further purification due to its very high sensitivity toward oxygen

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