

## Preliminary communication

Protonation of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuC}\equiv\text{CPh}$ : Formation of cationic phenylacetylene and phenylvinylidene complexes and subsequent reaction with ethylene oxide to form the net [2 + 3] cycloadduct

$$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{CCH}(\text{Ph})\text{CH}_2\text{CH}_2\text{O}]^+$$

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## Abstract

Protonation of the alkynyl complex  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuC}\equiv\text{CPh}$  (**1**) at low temperature affords quantitatively the vinylidene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{C}=\text{CH}(\text{Ph})]^+$  (**3**), which upon warming to room temperature forms an equilibrium with the  $\eta^2$ -phenylacetylene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\eta^2\text{-HC}\equiv\text{CPh})]^+$  (**4**), with the latter predominating. Subsequent reaction with ethylene oxide yields the cyclic oxacarbene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{CCH}(\text{Ph})\text{CH}_2\text{CH}_2\text{O}]^+$  (**5**), which can be regarded as the result of a net [3 + 2] cycloaddition reaction between **3** and ethylene oxide. Deprotonation of **5** affords the corresponding neutral cyclic vinyl complex  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{C}(\text{Ph})\text{CH}_2\text{CH}_2\text{O}$  (**6**), which can in turn be protonated to regenerate **5** in a diastereoselective manner. The structures of complexes **5** and **6** were determined by X-ray crystallography.

**Keywords:** Ruthenium; Cyclopentadienyl; Vinylidene complex; Acetylene complex; Isomerism; Carbene complex

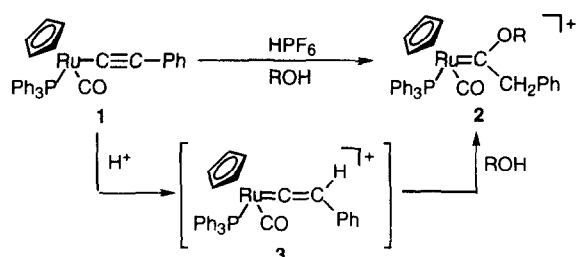
Vinylidene complexes typically undergo nucleophilic addition to the central  $\alpha$ -carbon atom and electrophilic addition to the terminal  $\beta$ -carbon atom [1], and there are several examples of what are formally cycloaddition reactions across the vinylidene  $\text{C}_\alpha=\text{C}_\beta$  bond [2]. In addition, some cationic vinylidene complexes have been shown to possess an  $\alpha$ -carbon atom electrophilic enough to interact with acyclic ethers and eventually cleave them through retro-ene-like reactions [3]. In view of these observations and following investigations of acetylide and vinylidene complexes directed towards cyclic Fischer-type carbenes [2c,4], we thought it of interest to investigate the reactivity of the cationic vinylidene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{C}=\text{CH}(\text{Ph})]^+$  [**5**] towards ethylene oxide.

Bruce and co-workers [5] reported that protonation of the alkynyl complex  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuC}\equiv\text{CPh}$  (**1**) by  $\text{HPF}_6$  in the presence of an alcohol ROH ( $\text{R} = \text{Me}, \text{Et}$ ,

$i\text{Pr}$ ) affords the alkoxycarbene derivatives  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{C}(\text{OR})\text{CH}_2\text{Ph}]^+$  (**2**). The reaction was thought to proceed via the intermediacy of the vinylidene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{C}=\text{CH}(\text{Ph})]^+$  (**3**), which, however was not isolated (Scheme 1).

In our hands, the protonation of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuC}\equiv\text{CPh}$  (**1**) by  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  in diethyl ether at room temperature gave a beige precipitate [6]. An NMR spectroscopic analysis revealed this to be a mixture of the vinylidene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}=\text{C}=\text{CH}(\text{Ph})]^+$  (**3**, minor) and the  $\eta^2$ -phenylacetylene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\eta^2\text{-HC}\equiv\text{CPh})]^+$  (**4**, major), in a 9:91 ratio (Scheme 2). The  $^{13}\text{C}$  NMR spectrum of the mixture clearly shows the acetylenic carbon atoms of the coordinated phenylacetylene in **4** at 70.8 (d,  $^2J_{\text{CH}} = 37$  Hz) and 57.2 ppm (dd,  $^1J_{\text{CH}} = 252$  Hz,  $^2J_{\text{CP}} = 7$  Hz), while the  $^1\text{H}$  NMR spectrum shows the acetylenic proton as a doublet at 4.81 ppm ( $J_{\text{PH}} = 15.0$  Hz) [7]. The presence of **3** is indicated in the  $^1\text{H}$  spectrum by a doublet at 6.12 ppm ( $^4J_{\text{HP}} = 4$  Hz) attributable the proton attached to the terminal carbon atom of the vinylidene fragment.

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Scheme 1.

When the protonation of **1** is conducted at  $-80^\circ\text{C}$  ( $\text{CD}_2\text{Cl}_2$  solution, NMR tube), the vinylidene complex **3** is formed selectively. The  $\alpha$ - and  $\beta$ -carbon atoms of the vinylidene fragment are observed in the  $^{13}\text{C}$  NMR spectra at 372.0 ( $^2J_{\text{CP}} = 12$  Hz) and 119.2 ppm ( $^1J_{\text{CH}} = 152$  Hz,  $^3J_{\text{CP}} = 15$  Hz) ppm, respectively [7]. When the solution is warmed to room temperature, the complex readily isomerizes to give a 9:91 mixture of **3** and **4**. We found this result surprising, since the protonation of the closely related complex  $\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{RuC}\equiv\text{CPh}$  leads exclusively to the vinylidene complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{CH}(\text{Ph})]^+$  [8] and, in addition, most of the earlier examples of transition metal acetylene–vinylidene interconversion were concerned with the isomerization of terminal alkynes to their thermodynamically favoured  $\eta^1$ -vinylidene isomers [1,9]. In some instance, however, the two forms had been found to be in equilibrium, but with the  $\eta^1$ -vinylidene form usually predominating [10]. In detailed studies, Bly et al. [11] found that the cationic Fe(II) dicarbonyl vinylidene complexes  $[\text{Cp}(\text{CO})_2\text{Fe}=\text{C}=\text{CRR}']^+$  readily isomerize to the corresponding  $\eta^2$ -alkyne complexes  $[\text{Cp}(\text{CO})_2\text{Fe}(\eta^2\text{-RC}\equiv\text{CR}')]^+$  [3b,11]. On the basis of electronic considerations, Bly et al. suggested that the less electron-rich the metal centre, the more the  $\eta^1$ -vinylidene ligands should tend to rearrange to  $\eta^2$ -alkyne ligands. Such a trend is, indeed, observed if one compares the difference in behaviour of the disubstituted phosphine complex  $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\eta^2\text{-HC}\equiv\text{CPh})]^+$  (which is in fact too unstable to be isolated and spontaneously rearranges to  $[\text{Cp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{CH}(\text{Ph})]^+$  [8]) and the

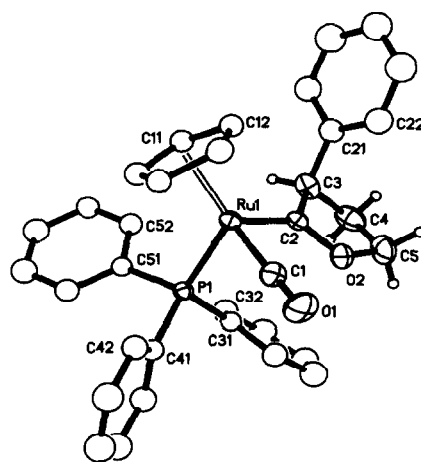
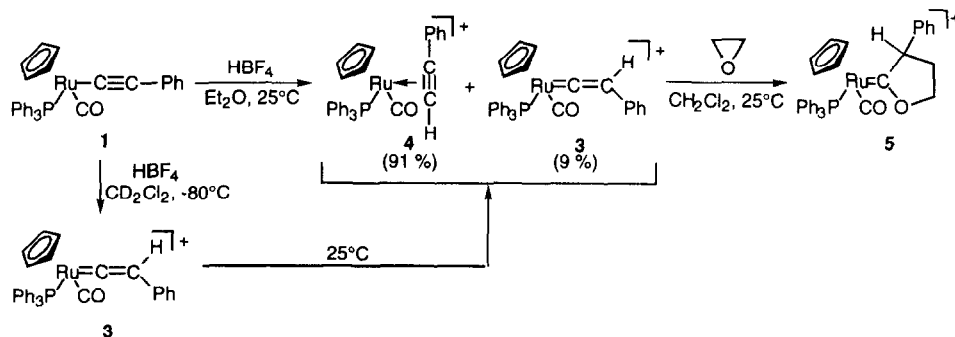


Fig. 1. Perspective view of  $[\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Ru}=\text{CCH}(\text{Ph})\text{CH}_2\text{CH}_2\text{O}]^+$  (**5**). Selected bond lengths (Å) and angles ( $^\circ$ ): Ru(1)–P(1) = 2.335(2); Ru(1)–C(1) = 1.860(8); Ru(1)–C(2) = 1.946(8); C(2)–O(2) = 1.312(9); C(2)–C(3) = 1.503(10); C(3)–C(4) = 1.536(12); C(4)–C(5) = 1.490(15); C(5)–O(2) = 1.462(11); P(1)–Ru(1)–C(1) = 90.5(3); P(1)–Ru(1)–C(2) = 91.1(2); C(1)–Ru(1)–C(2) = 88.9(3); O(2)–C(2)–C(3) = 109.0(6); C(2)–O(2)–C(5) = 112.9(6); C(2)–C(3)–C(4) = 102.8(6); C(3)–C(4)–C(5) = 103.2(7); O(2)–C(5)–C(4) = 103.9(8).

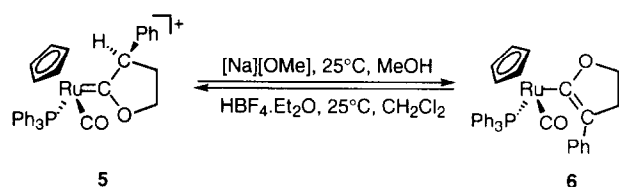
less electron-rich monosubstituted phosphine complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\eta^2\text{-HC}\equiv\text{CPh})]^+$  (**4**), which predominates in solution at the expense of  $[\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{CH}(\text{Ph})]^+$  (**3**). The fact that the metal centre in **4** is less hindered than  $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\eta^2\text{-HC}\equiv\text{CPh})]^+$  may also contribute to the stability of the former [12].

In solution in dichloromethane, the mixture of **3** and **4** reacts at room temperature with an excess of ethylene oxide to give the cationic complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Ru}=\text{CCH}(\text{Ph})\text{CH}_2\text{CH}_2\text{O}]^+$  (**5**) as the main product (Scheme 2). Complex **5** was isolated as a pale yellow solid in 32% yield after recrystallization of the product mixture from acetone–hexane, and spectroscopically and crystallographically characterized [7,13].

As shown in Fig. 1, complex **5** contains a five-membered cyclic oxacarbene ligand bonded to a  $\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Ru}$  moiety. As expected on electronic grounds [14], the mean plane of the cyclic carbene ligand is



Scheme 2.



Scheme 3.

orthogonal to the Ru(1)–P(1) vector. In addition, the cycle is oriented in such a way that the phenyl ring attached to C(3) points away from the bulky PPh<sub>3</sub> group, and the oxygen atom O(2) is in a cisoid position relative to the carbonyl ligand C(1)O(1). Both the metal centre and the carbon atom C(3) are chiral, and Fig. 1 shows that it was the *RR*–*SS* pair that was isolated. The complexity of the NMR spectra of the crude reaction mixture did not allow us, however, to find out whether this diastereoisomer was the only one formed in the reaction.

Deprotonation of **5** gave the cyclic vinyl complex Cp(CO)(PPh<sub>3</sub>)RuC=C(Ph)CH<sub>2</sub>CH<sub>2</sub>O (**6**) (Scheme 3), which was isolated in 73% yield after chromatography a silica gel column.

Compound **6** was characterized by the usual spectroscopic techniques [7] and its structure determined by X-ray crystallography [13]. Fig. 2 shows that, as in **5**, the mean plane of the cyclic vinyl ligand is perpendicular to the Ru(1)–P(1) vector, but in this case, the oxygen atom O(2) within the cycle is in transoid position relative to the carbonyl ligand C(1)O(1).

Upon protonation at room temperature of the vinyl complex **6** with a slight excess of HBF<sub>4</sub> · Et<sub>2</sub>O, complex **5** is quantitatively regenerated (Scheme 3). Examination of the crude product mixture showed that **5** had been formed as a single pair of diastereoisomers corresponding to that isolated from the reaction of **3/4** with ethylene oxide (Scheme 2). From the structure of **6**, this pair of diastereoisomer would indeed be expected if the protonation of C(3) occurs from the less hindered side of the cyclic vinyl fragment, away from the bulky triphenylphosphine ligand.

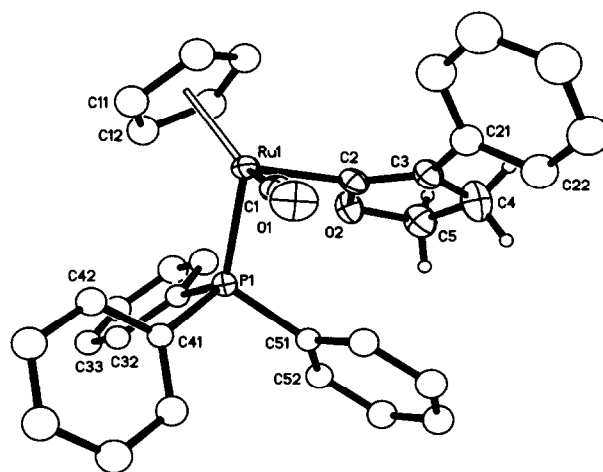
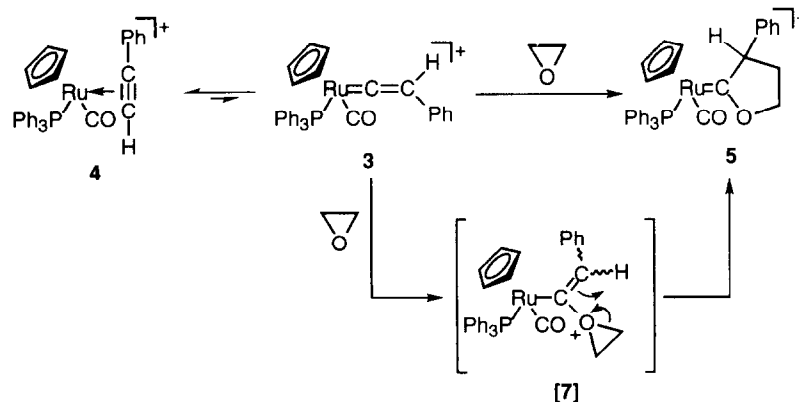


Fig. 2. Perspective view of Cp(CO)(PPh<sub>3</sub>)RuC=C(Ph)CH<sub>2</sub>CH<sub>2</sub>O (**6**). Selected bond lengths (Å) and angles (°): Ru(1)–P(1) = 2.298(2); Ru(1)–C(1) = 1.846(7); Ru(1)–C(2) = 2.058(6); C(2)–O(2) = 1.401(8); C(2)–C(3) = 1.349(9); C(3)–C(4) = 1.499(12); C(4)–C(5) = 1.525(11); C(5)–O(2) = 1.438(9); P(1)–Ru(1)–C(1) = 90.1(2); P(1)–Ru(1)–C(2) = 87.7(2); C(1)–Ru(1)–C(2) = 92.3(3); O(2)–C(2)–C(3) = 110.8(6); C(2)–O(2)–C(5) = 109.9(5); C(2)–C(3)–C(4) = 110.1(6); C(3)–C(4)–C(5) = 103.3(6); O(2)–C(5)–C(4) = 105.8(6).

In conclusion, we note that although there have been many reports of the formation of cyclic oxacarbene complexes [15], such complexes are typically formed either by reaction of alkylalkoxycarbene anions with epoxides [16], or by rearrangement of  $\eta^2$ -alkynol complexes [17]. In the present work it is likely that the formation of **5** is the result of the reaction between the epoxide and the vinylidene complex **3**, as depicted in Scheme 4.

Initial nucleophilic addition of the epoxide to the electrophilic  $\alpha$ -carbon of the vinylidene ligand in **3** would lead to a cationic vinyl complex such as **7**, which would rearrange by epoxide ring opening to afford **5** [18]. Although the  $\eta^2$ -alkyne complex **4** is the major compound observed in solution upon protonation of **1** at room temperature, reaction of **3** would drive the equilib-



Scheme 4.

rium  $4 \leftrightarrow 3$  to the right. Thus, the overall reaction sequence can be seen as a net  $[3 + 2]$  cycloaddition reaction between an epoxide and the  $C_\alpha = C_\beta$  bond of a vinylidene complex to form an oxacarbene complex.

## References and notes

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- [6] To a vigorously stirred suspension of  $Cp(CO)(PPh_3)Ru \equiv CPh$  (200 mg) in  $Et_2O$  (15 ml) was added an excess of  $HBF_4 \cdot Et_2O$  (0.1 ml). A beige precipitate formed during a period of 30 min. The precipitate was allowed to settle and the supernatant liquid was removed through a canula. The solid was washed twice with  $Et_2O$  ( $2 \times 15$  ml) and dried under vacuum to give 220 mg of a 91:9 mixture (by NMR analysis) of  $[Cp(CO)(PPh_3)Ru(\eta^2-HC \equiv CPh)]^+$  (**4**) and  $[Cp(CO)(PPh_3)Ru=C=CH(Ph)]^+$  (**3**) (yield 95%).
- [7] Selected spectroscopic data for the new compounds. **3**: NMR ( $CD_2Cl_2$ )  $^1H$  (300 MHz, 193 K)  $\delta$  6.12 (d, 1H,  $J_{HP} = 4$  Hz,  $=C(H)Ph$ ),  $^{13}C$  (75 MHz, 193 K)  $\delta$  372.0 (d,  $J_{CP} = 12.2$  Hz,  $C=C(H)Ph$ ), 119.2 (dd,  $J_{CH} = 152$  Hz,  $J_{CP} = 15$  Hz,  $C=C(H)Ph$ );  $^{31}P\{^1H\}$  (32 MHz, 193 K)  $\delta$  43.62. **4**: IR ( $CH_2Cl_2$ )  $\nu_{C=O}$  2005(s)  $cm^{-1}$ . NMR ( $CD_2Cl_2$ )  $^1H$  (300 MHz)  $\delta$  4.81 (d, 1H,  $J_{PH} = 15.0$  Hz,  $PhC \equiv CH$ );  $^{13}C$  (75 MHz)  $\delta$  200.6 (d,  $J_{PC} = 19$  Hz, CO), 70.8 (d,  $J_{CH} = 37$  Hz,  $PhC \equiv CH$ ), 57.2 (dd,  $J_{CH} = 252$  Hz,  $J_{CP} = 7$  Hz,  $PhC \equiv CH$ );  $^{31}P\{^1H\}$  (32 MHz)  $\delta$  44.39. MS (FAB $^+$ ):  $m/z = 559$  ( $M^+$ ), 457 ( $M^+ - PhC \equiv CH$ ), 429 ( $M^+ - PhC \equiv CH - CO$ ). **5**: IR ( $CH_2Cl_2$ )  $\nu_{C=O}$  1995  $cm^{-1}$ . NMR ( $CD_2Cl_2$ )  $^1H$  (300 MHz)  $\delta$  4.98 (dd,  $H_4$ ,  $J_{H_4,H_1} = 8.9$  Hz,  $J_{H_4,H_1'} = 3.3$  Hz,  $-C(H)Ph-$ ), 4.64 (ddt,  $H_3$ ,  $J_{H_3,P} = 1.2$  Hz,  $J_{H_3,H_1} = 10.5$  Hz,  $J_{H_3,H_1'} = 6.7$  Hz,  $J_{H_3,H_2} = 10.5$  Hz,  $-OCH_2-$ ), 4.08 (ddd,  $H_2$ ,  $J_{H_2,H_1} = 9.2$  Hz,  $J_{H_2,H_1'} = 2.7$  Hz,  $J_{H_2,H_3} = 10.5$  Hz,  $-OCH_2-$ ), 1.84 (m,  $H_1$  and  $H_{1'}$ ,  $J_{H_1,H_1'} = 12.9$  Hz,  $J_{H_1,H_2} = 9.2$  Hz,  $J_{H_1,H_3} = 10.5$  Hz,  $J_{H_1,H_4} = 8.9$  Hz,  $J_{H_1',H_2} = 2.7$  Hz,  $J_{H_1',H_3} = 6.7$  Hz,  $J_{H_1',H_4} = 3.3$  Hz,  $-CH_2CH(Ph)-$ );  $^{13}C\{^1H\}$  (50 MHz)  $\delta$  306.4 (s(br),  $Ru=C$ ), 200.6 (d, CO,  $J_{CP} = 17$  Hz), 83.8 ( $-OCH_2-$ ), 75.2 ( $-CH_2CH(Ph)-$ ), 31.6 ( $-CH_2CH(Ph)-$ );  $^{31}P\{^1H\}$  (32 MHz)  $\delta$  47.96. MS (FAB $^+$ ):  $m/z = 603$  ( $M^+$ ), 575 ( $M^+ - CO$ ). Anal. Calc. for  $C_{34}H_{30}BF_4O_2PRu$ : C, 59.23; H, 4.39. Found: C, 58.49; H, 4.31%. **6**: IR ( $CH_2Cl_2$ )  $\nu_{C=O}$  1995  $cm^{-1}$ . NMR ( $CD_2Cl_2$ )  $^1H$  (300 MHz)  $\delta$  4.98 (dd,  $H_4$ ,  $J_{H_4,H_1} = 8.9$  Hz,  $J_{H_4,H_1'} = 3.3$  Hz,  $-C(H)Ph-$ ), 4.64 (ddt,  $H_3$ ,  $J_{H_3,P} = 1.2$  Hz,  $J_{H_3,H_1} = 10.5$  Hz,  $J_{H_3,H_1'} = 6.7$  Hz,  $J_{H_3,H_2} = 10.5$  Hz,  $-OCH_2-$ ), 4.08 (ddd,  $H_2$ ,  $J_{H_2,H_1} = 9.2$  Hz,  $J_{H_2,H_1'} = 2.7$  Hz,  $J_{H_2,H_3} = 10.5$  Hz,  $-OCH_2-$ ), 1.84 (m,  $H_1$  and  $H_{1'}$ ,  $J_{H_1,H_1'} = 12.9$  Hz,  $J_{H_1,H_2} = 9.2$  Hz,  $J_{H_1,H_3} = 10.5$  Hz,  $J_{H_1,H_4} = 8.9$  Hz,  $J_{H_1',H_2} = 2.7$  Hz,  $J_{H_1',H_3} = 6.7$  Hz,  $J_{H_1',H_4} = 3.3$  Hz,  $-CH_2CH(Ph)-$ );  $^{13}C\{^1H\}$  (50 MHz)  $\delta$  206.6 (d, CO,  $J_{CP} = 17$  Hz), 173.5 (s(br),  $Ru=C$ ), 142–121 ( $C_6H_5$  and  $=C(Ph)-$ ) 70.2 ( $-OCH_2CH_2-$ ), 36.1 ( $-OCH_2CH_2-$ );  $^{31}P\{^1H\}$  (32 MHz)  $\delta$  47.96. MS (EI):  $m/z = 602$  ( $M^+$ ), 574 ( $M^+ - CO$ ). Anal. Calc. for  $C_{34}H_{29}O_2PRu$ : C, 67.88; H, 4.86. Found: C, 67.18; H, 5.37%.
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- [13] Crystal data. **5**:  $C_{34}H_{30}BF_4O_2PRu$ ,  $F_w = 689.46$ , monoclinic,  $I2/a$ ,  $a = 20.409(2)$ ,  $b = 13.595(2)$ ,  $c = 21.965(2)$  Å,  $\beta = 95.99(1)^\circ$ ,  $V = 6061(1)$  Å $^3$ ,  $Z = 8$ ,  $\rho_{calc} = 1.511$  g  $cm^{-3}$ ,  $\mu = 6.12$   $cm^{-1}$ , Mo  $K\alpha$  radiation,  $T = 22^\circ C$ ,  $R = 0.047$ ,  $R_w = 0.050$  (from 2921 observations ( $F_o^2 > 3\sigma(F_o^2)$ ) to  $2\theta_{max}$   $45^\circ$ , and 197 variable parameters). **6**:  $C_{34}H_{29}O_2PRu$ ,  $F_w = 601.64$ , monoclinic,  $C2/c$ ,  $a = 23.347(5)$ ,  $b = 12.626(1)$ ,  $c = 19.141(2)$  Å,  $\beta = 97.54(2)^\circ$ ,  $V = 5594(2)$  Å $^3$ ,  $Z = 8$ ,  $\rho_{calc} = 1.429$  g  $cm^{-3}$ ,  $\mu = 6.33$   $cm^{-1}$ , Mo  $K\alpha$  radiation,  $T = 22^\circ C$ ,  $R = 0.045$ ,  $R_w = 0.046$  (from 2806 observations ( $F_o^2 > 3\sigma(F_o^2)$ ) to  $2\theta_{max}$   $44^\circ$ , and 152 variable parameters). Structure solution and refinement. Structure solution by direct method (G.M. Sheldrick, *SHELXS-86 Program for Crystal Structure Solution*, University of Göttingen, Göttingen, 1986), full-matrix least-squares refinement (G.M. Sheldrick, *SHELX-76 Program for Crystal Structure Determination*, University of Cambridge, Cambridge, 1976), Cp and Ph rings refined as rigid groups with isotropic temperature factors, all other non-hydrogen atoms refined with anisotropic temperature factors, absorption correction by empirical  $\Psi$ -scan method (A.C.T., North, D.C. Phillips and F.S. Mathew *Acta Crystallogr., Sect. A*, **24** (1968) 351), all hydrogen atoms set in idealized position ( $C-H = 0.97$  Å) and entered in the last cycle of refinement. Tables of atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.
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