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# Synthesis, characterization, and reactivity of half-sandwich Ru(II) complexes containing phosphine, arsine, stibine, and bismutine ligands

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**Abstract**

The synthesis and some reactions of the Ru(II) and Ru(IV) half-sandwich complexes $[RuCp(EPh_3)(CH_3CN)_2]^+$ (E = P, As, Sb, Bi) and $[RuCp(EPh_3)(\eta^3\text{-}C_3H_5)Br]^+$ have been investigated. The chemistry of this class of compounds is characterized by a competitive coordination of $EPh_3$ either via a Ru–E or a $\eta^6$-arene bond, where the latter is favored when the former is weaker, that is in going down the series. Thus in the case of Bi, the starting material $[RuCp(CH_3CN)_3]^+$ does not react with $BiPh_3$ to give $[RuCp(BiPh_3)(CH_3CN)_2]^+$ but instead gives only the $\eta^6$-arene species $[RuCp(\eta^6\text{-}PhBiPh_2)]^+$ and $[(RuCp)_2(\mu\text{-}\eta^6,\eta^6\text{-}Ph_2BiPh)]^{2+}$. Similarly, the $EPh_3$ ligand can be replaced by an aromatic solvent or an arene substrate. Thus, the catalytic performance of $[RuCp(EPh_3)(CH_3CN)_2]^+$ for the isomerization of allyl-phenyl ethers to the corresponding 1-propenyl ethers is best with E = P, while the conversion drops significantly using the As and Sb derivatives. By the same token, only $[RuCp(PPh_3)(CH_3CN)_2]^+$ is stable in a non-aromatic solvent, whereas both $[RuCp(AsPh_3)(CH_3CN)_2]^+$ and $[RuCp(SbPh_3)(CH_3CN)_2]^+$ rearrange upon warming to $[RuCp(\eta^6\text{-}PhEPh_2)]^+$ and related compounds. In addition, the potential of $[RuCp(EPh_3)(CH_3CN)_2]^+$ as precatalysts for the transfer hydrogenation of acetophenone and cyclohexanone has been investigated. Again aromatic substrates are clearly less suited than non-aromatic ones due to facile $\eta^6$-arene coordination leading to catalyst's deactivation. 

*Keywords:* Ruthenium; Arsines; Stibines; Bismutines; Arene coordination; Allyl complexes

## 1. Introduction

We have recently shown [1] that the complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = Me, Ph, Cy) are easily available in high yields by treating $[RuCp(CH_3CN)_3]PF_6$ with one equivalent of the respective tertiary phosphine. These complexes are intriguing compounds because of the versatile reactivity patterns under mild conditions with respect to substitution and oxidative addition reactions. Preliminary studies have revealed that these complexes: (i) promote C–C coupling of acetylenes to give novel allyl, allenyl, and butadienyl carbene complexes [2] and (ii) are able to efficiently catalyze the redox isomerization of allyl alcohols [3].

In the present contribution we turn to the preparation of the Group-15 element congeners $[RuCp(EPh_3)(CH_3CN)_2]PF_6$ with E = As, Sb, and Bi. The scope is to study the accompanying changes in structure, reactivity, and catalytic activity. A preliminary account of the reactivity of $[RuCp(SbPh_3)(CH_3CN)_2]^+$ towards alkynes has appeared in a recent communication [4].

## 2. Results and discussion

### 2.1. Synthesis and reactivity of $[RuCp(EPh_3)(CH_3CN)_2]^+$ (E = P, As, Sb)

Treatment of $[RuCp(CH_3CN)_3]PF_6$ (**1**) with one equivalent of the monodentate ligands $EPh_3$ (E = P, As,

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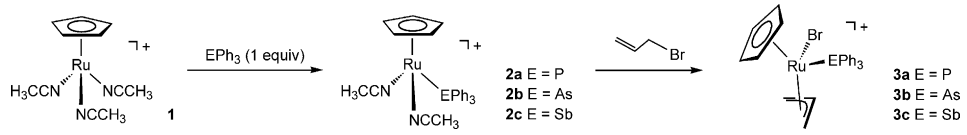



Scheme 1.

Sb) at room temperature affords the cationic complexes $[RuCp(EPh_3)(CH_3CN)_2]PF_6$ (**2a**–**c**) in essentially quantitative yields as monitored by $^1$H-NMR spectroscopy (Scheme 1). The synthesis of $[RuCp(PPh_3)(CH_3CN)_2]$-$PF_6$ (**2a**) has been reported previously [1]. All these complexes are stable to air in the solid state but decompose slowly in solution on exposure to air. The characterization was accomplished by $^1$H-, $^{13}C\{^1H\}$-NMR and IR spectroscopies as well as elemental analysis. The spectra do not comprise unusual features and, therefore, are not discussed here.

The complexes **2a**–**c** undergo facile oxidative addition reactions with allyl bromide to give the Ru(IV) $\eta^3$-allyl complex complexes $[RuCp(\eta^3\text{-}CH_2CHCH_2)$-$(EPh_3)Br]PF_6$ (**3a**–**c**) in high isolated yields (Scheme 1), which are air stable both in solution and in the solid state. The $^1$H-NMR spectra show the expected singlet resonances of the Cp ligand in the range 5.87–6.07 ppm, and the characteristic doublet and multiplet resonances of the allyl ligands. In the $^{13}C\{^1H\}$-NMR spectrum, the Cp carbon atoms give rise to singlets between 94.5 and 92.9 ppm (cf. 77.1, 76.0, and 75.6 ppm in **2a**–**c**). The downfield chemical shifts point to an increased oxidation state of the Ru center.

The solid state structures of **2b**, **2c**, **3a**–**3c** have been determined by single-crystal X-ray diffraction studies. The structural views of representative examples are depicted in Figs. 1 and 2.

Selected bond distances and angles of the compounds are given in Table 1. Together with the data of **2a** from Ref. [1], a structural comparison of the Ru(II)– and Ru(IV)–$EPh_3$ complexes becomes feasible. All complexes adopt a three-legged piano stool conformation. The Ru–Cp(av) distance is shorter by 0.054 Å in the Ru(II) series compared to the corresponding Ru(IV) compounds. Furthermore, the Ru–Cp(av) distances decrease in both series from P to Sb by 0.017 Å. The reverse trend is found for the Ru–E bond lengths. These increase from P to Sb by 0.260 and 0.199 Å, respectively, for the Ru(II) and Ru(IV) series. It is noteworthy that complexes **2a**–**2c** are isostructural and crystallize in triclinic unit cells of space group $P\bar{1}$, each with two formula moieties per asymmetric unit. The three structures are pseudo-monoclinic. The numerical data for **2a**–**2c** as given in Table 1 are mean values of the independent Ru complexes in each structure. In contrast to the bisacetonitrile complexes the allyl bromides **3a**–**3c** do not form a complete isostructural series, only **3b** and **3c** being isostructural. All three were found to readily form crystalline solvates also (e.g. with acetone) which will be reported elsewhere.

It should be emphasized that in the case of E = Bi the reactions took a different course. Thus, treatment of $[RuCp(CH_3CN)_3]PF_6$ (**1**) with one equivalent of $BiPh_3$ at room temperature did not afford the cationic complex $[RuCp(BiPh_3)(CH_3CN)_2]PF_6$ but instead a mixture of two compounds exhibiting both $\eta^6$-coordinated phenyl rings of the $BiPh_3$ ligand as detected by $^1$H- and $^{13}C\{^1H\}$-NMR spectroscopy (Scheme 2).

Since $[RuCp(\eta^6\text{-}PhBiPh_2)]PF_6$ (**4a**) could not be isolated in pure form, it was characterized by NMR spectroscopy in a mixture with $[(RuCp)_2(\mu\text{-}\eta^6,\eta^6\text{-}$ $Ph_2BiPh)](PF_6)_2$ (**4b**). This was feasible, because the

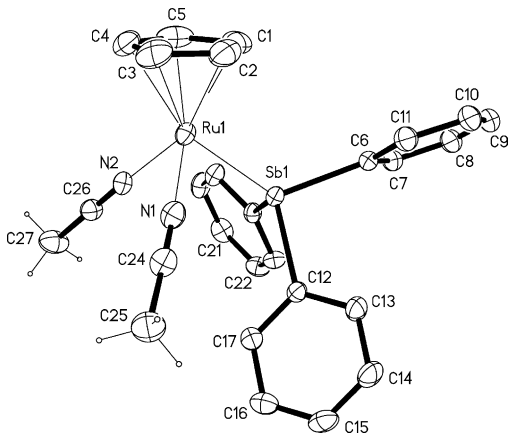



Fig. 1. Structural view of $[RuCp(SbPh_3)(CH_3CN)_2]PF_6$ (**2c**) showing 20% thermal ellipsoids (aromatic H atoms and $PF_6^-$ omitted for clarity).

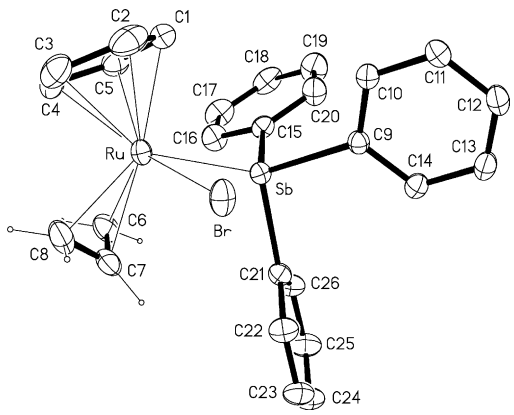
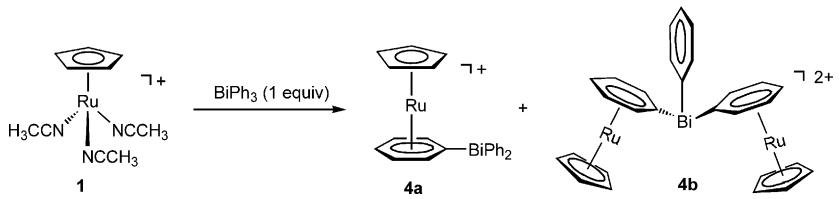



Fig. 2. Structural view of $[RuCp(SbPh_3)(\eta^3\text{-}C_3H_5)Br]PF_6$ (**3c**) showing 20% thermal ellipsoids (aromatic H atoms and $PF_6^-$ omitted for clarity).

Table 1
Selected bond distances (Å) and bond angles (°) for complexes **2a**–**2c** and **3a**–**3c**

| | **2a** [a] E = P | **2b** E = As | **2c** E = Sb | **3a** E = P | **3b** E = As | **3c** E = Sb |
|---|---|---|---|---|---|---|
| *Bond lengths* | | | | | | |
| Ru–Cp(av) | 2.173(5) | 2.158(4) | 2.155(5) | 2.225(3) | 2.211(3) | 2.209(4) |
| Ru–N(1) | 2.057(4) | 2.062(3) | 2.068(4) | | | |
| Ru–N(2) | 2.060(4) | 2.065(3) | 2.069(3) | | | |
| Ru–E | 2.323(2) | 2.438(1) | 2.583(1) | 2.414(1) | 2.498(1) | 2.613(1) |
| Ru–Br | | | | 2.544(1) | 2.534(1) | 2.540(1) |
| Ru–C(6) | | | | 2.234(2) | 2.225(3) | 2.237(3) |
| Ru–C(7) | | | | 2.180(2) | 2.165(3) | 2.170(4) |
| Ru–C(8) | | | | 2.253(3) | 2.234(3) | 2.224(4) |
| E–C(av) | 1.838(5) | 1.950(3) | 2.133(3) | 1.828(2) | 1.942(3) | 2.123(3) |
| *Bond angles* | | | | | | |
| E–Ru–N(1) | 91.1(1) | 89.6(1) | 89.1(1) | | | |
| E–Ru–N(2) | 88.6(1) | 87.1(1) | 86.8(1) | | | |
| N(1)–Ru–N(2) | 85.2(1) | 85.1(1) | 84.8(1) | | | |
| E–Ru–Br | | | | 83.50(2) | 81.75(1) | 79.23(1) |

[a] Ref. [1].




Scheme 2.

latter could be prepared independently by the reaction of $[RuCp(CH_3CN)_3]PF_6$ with 0.5 equivalent of $BiPh_3$ at elevated temperature and characterized by NMR spectroscopy and elemental analysis. In addition, its structure was determined by X-ray crystallography with the ORTEP plot shown in Fig. 3. Apparently, two $RuCp^+$ fragments coordinate in a $\eta^6$-fashion to two phenyl rings of the $BiPh_3$ molecule. Selected bond lengths and angles are given in Fig. 3.

Subsequently, we investigated the thermal stability of **2a** and **2c** at elevated temperature in a non-coordinating solvent. For this purpose we heated these complexes at 80 °C for 4 h in nitromethane. Whereas **2a** did not undergo a significant decomposition, **2c** underwent several rearrangement reactions leading to a mixture of different products, viz. $[RuCp(SbPh_3)_2(CH_3CN)]PF_6$ (**5c**) [5], $[RuCp(CH_3CN)_3]PF_6$ (**1**), $[RuCp(\eta^6\text{-}PhSbPh_2)]PF_6$ (**6**), and $[CpRu\{(\eta^6\text{-}PhSbPh_2)RuCp\}(SbPh_3)(CH_3CN)](PF_6)_2$ (**7**) as monitored by $^1$H-NMR spectroscopy (Scheme 3).

Upon heating **2c** in nitromethane for 6 h at 80 °C mainly **7** is formed, which could be isolated and characterized. It should be mentioned that **2b** behaved very similar to **2c**, but we did not investigate the decomposition products in more detail.

When benzene was used as the solvent instead of nitromethane, the complexes **2a**–**c** underwent clean ligand substitution reactions. After heating for 72 h at 80 °C, **2a** converted according to Scheme 4 giving a 1:1 mixture of the known complexes $[RuCp(\eta^6\text{-benzene})]^+$ (**8**) [6] and $[RuCp(PPh_3)_2(CH_3CN)]^+$ (**5a**) [7]. Already after 30 min, complexes **2b** and **2c** gave the corresponding 1:1 mixture of **8** and known $[RuCp(EPh_3)_2(CH_3CN)]^+$ (**5b**, E = As; **5c**, E = Sb) [5]. While under these reaction conditions virtually no difference in reactivity between **2b** and **2c** could be observed, at a

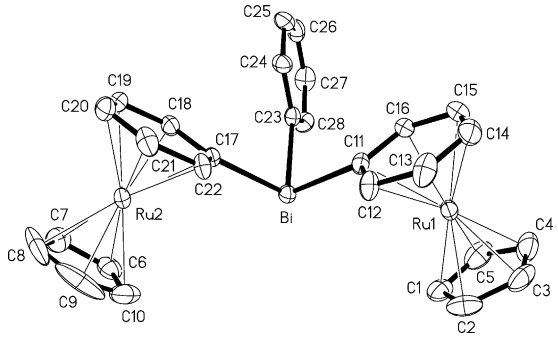
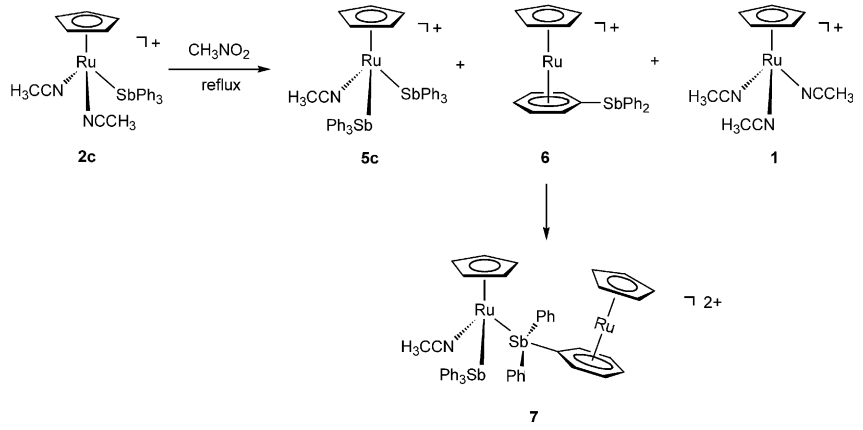
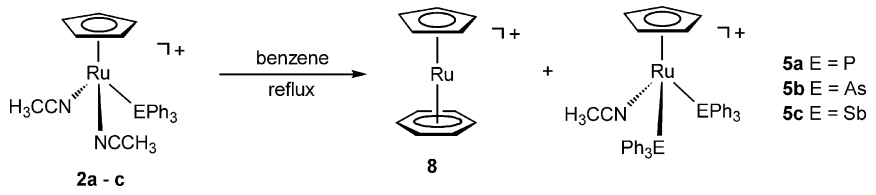



Fig. 3. Structural view of $[(RuCp)_2(\mu\text{-}\eta^6,\eta^6\text{-}Ph_2BiPh)](PF_6)_2$ (**4b**) showing 20% thermal ellipsoids ($PF_6^-$ omitted for clarity). Selected bond lengths (Å) and angles (°): Ru1–C(1–5)$_m$ 2.173(7), Ru2–C(6–10)$_m$ 2.155(7), Ru1–C(11–16)$_m$ 2.198(5), Ru2–C(17–22)$_m$ 2.200(5), Bi–C(11) 2.294(4), Bi–C(17) 2.279(4), Bi–C(23) 2.242(6), C(11)–Bi–C(17) 94.4(2), C(11)–Bi–C(23) 92.2(2), C(17)–Bi–C(23) 91.6(2).




Scheme 3.




Scheme 4.

reaction temperature lowered to 50 °C it was revealed that **2c** is slightly more reactive than **2b**. This follows from the observation that after 30 min 30% of **2c** but only 10% of **2b** were consumed. It is reasonable to attribute the differences in reactivity between **2a** and **c** to the different Ru–E bond strength decreasing in the order Ru–P ≫ Ru–As > Ru–Sb [8]. It is safe to assume that the thermodynamic stabilities of complexes **2a**–**c** decrease in the same order.

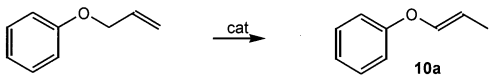
### 2.2. Catalytic activity of *2a*–*c*

Compounds **2a**–**c** have been tested in two catalytic model reactions, viz. the isomerization of phenyl-allyl ether and the transfer hydrogenation of ketones. While there are large number of catalysts available that promote isomerizations [9], the stereoselective preparation of *E*- or *Z*-aryl-prop-1-enyl ethers remains still an attractive goal.

During our studies we found that **2a** catalyzes the isomerization of phenylprop-2-enylether to phenyl-*E*-prop-1-enylether with a stereoselectivity exceeding 99%. Therefore we tested $[RuCp(L)(CH_3CN)_2]^+$ (L = $CH_3CN$, $AsPh_3$, $SbPh_3$) compounds for their catalytic performance. In the experimental procedure chosen we heated 0.047–0.008 mmol catalyst (3–0.25 mol% with respect to phenylallyether) in 4 ml of THF or acetone for 24 h using an oil-bath at a temperature of 80 °C. The results are summarized in Table 2. While as expected $[RuCp(CH_3CN)_3]PF_6$ proved to be inactive, the stereoselectivity of the reaction catalyzed by $[RuCp(L)(CH_3CN)_2]^+$ (L = $PPh_3$, $AsPh_3$, $SbPh_3$) is promising. However, the yield of products decreases dramatically in the series. This observation is consistent with the findings described above and is explained in terms of an increasing Ru–L lability with concurrent $\eta^6$-coordination of a phenyl ring stemming from the ligand or the substrate and concomitant formation of $[RuCp(EPh_3)_2(CH_3CN)]^+$ (**5b** and **5c**). Acetone seems to promote the catalyst deactivation in contrast to THF obviously due to different stabilities of solvated intermediates such as $[RuCp(solvent)_3]^+$. Among other decomposition products the complexes $[RuCp(\eta^6\text{-}C_6H_5\text{–}O\text{–}CH_2\text{–}CH{=}CH_2)]PF_6$ (**10**) and **5b**, **c** were identified by running a catalytic reaction and investigating the fate of the catalyst after removal of the volatiles by NMR spectroscopy. Noteworthy, complex **9** is also formed directly by heating **1** in the presence of phenylallylether (Scheme 5). The deactivation pathway delineated here is also operative in the case of **2a**, explaining the deactivation of the catalyst after ca. 300 turnovers. Therefore, despite the excellent stereoselectivity for the *E*-product, **2a** is unfortunately not an attractive catalyst for the present purpose. It may be mentioned that the isomerization of benzylallylether has also been studied, but was found to suffer from the same problems in addition to the poorer stereoselectivity of the catalysis (97% *E*-product with 0.008 mmol of **2a**, 200 μl of benzylallylether, in 4 ml of THF, conversion 100%, reaction time 5.5 h under reflux).

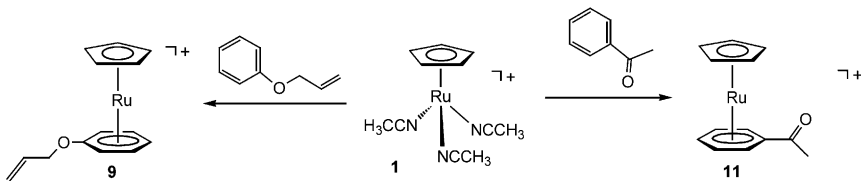
We have also investigated whether the complexes $[RuCp(EPh_3)(CH_3CN)_2]^+$ are suitable precatalysts for

Table 2
Reaction of phenylprop-2-enylether in the presence of various precatalysts




| Catalyst + 200 μl substrate | Catalyst (mg) | Catalyst (mmol) | Time (h) | Solvent | Conversion (%) | *E*/*Z* **10a**/**10b** | TON |
|---|---|---|---|---|---|---|---|
| **2a** | 5 [a] | 0.008 | 5.5 | THF | 83 | >99:1 | 303 |
| **2a** | 6 | 0.009 | 5.5 | THF | 100 | >99:1 | 162 |
| **2a** | 20 | 0.031 | 24 | THF | 100 | >99:1 | 47 |
| **2a** | 20 | 0.031 | 24 | Acetone | 74 | >99:1 | 35 |
| **2b** | 20 | 0.029 | 24 | THF | 29 | >99:1 | 15 |
| **2b** | 20 | 0.029 | 24 | Acetone | 34 | >99:1 | 17 |
| **2c** | 20 | 0.027 | 24 | THF | 25 | >99:1 | 14 |
| **2c** | 20 | 0.027 | 24 | Acetone | 4 | >99:1 | 2 |
| $[RuCp(CH_3CN)_3]PF_6$ | 15 | 0.035 | 24 | THF | 0 | – | – |
| $[RuCp(CH_3CN)_3]PF_6$ | 15 | 0.035 | 24 | Acetone | 0 | – | – |

[a] Reaction with 400 μl (2.916 mmol).




Scheme 5.

the transfer hydrogenation of aliphatic and aromatic ketones. We therefore compared the conversions of the two substrates cyclohexanone and acetophenone under the same reaction conditions (**2a**: 5 mg, 0.008 mmol, ketone: 4.8 mmol, in 10 ml *i*-PrOH with 5 mg *i*-PrONa at 82 °C for 24 h). Whereas cyclohexanone is reduced quantitatively to cyclohexanol, only 71% of acetophenone is converted to 1-phenyl ethanol. In the latter case, the catalyst transforms into known **5a** (as seen by $^{31}P\{^1H\}$-NMR) and $[RuCp(\eta^6\text{-}C_6H_5\text{–}CO\text{–}CH_3)]^+$ (**11**). Complex **11** has been unequivocally identified by comparison with an authentic sample prepared directly from **1** and acetophenone (Scheme 5).

### 2.3. Conclusions

With the exception of E = Bi, the complexes $[RuCp(EPh_3)(CH_3CN)_2]PF_6$ (E = P, As, Sb) are readily accessible in very high yields. As the Ru–E bond strength decreases in the order P > As > Sb > Bi, the dissociation of the $EPh_3$ ligand takes place easily at elevated temperatures particularly in the case of As and Sb. This favors both $\eta^6$-arene coordination as well as the formation of substitutionally inert bis-$EPh_3$ complexes $[RuCp(EPh_3)_2(CH_3CN)]PF_6$. Therefore, the $[RuCp(EPh_3)(CH_3CN)_2]PF_6$ complexes are unsuitable catalysts particularly if the substrate has an arene functionality.

## 3. Experimental

### 3.1. General procedures

All manipulations were performed under an inert atmosphere of Ar by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [10]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. TLC was performed on Riedel-de-Haen TLC-sheets silica gel 60 F 254 (layer thickness 0.2 mm). For column chromatography, silica gel grade 60, 70–230 mesh, 60 Å purchased from Merck, or neutral MN-aluminum oxide, purchased from Macherey-Nagel was used. $[RuCp(CH_3CN)_3]PF_6$ (**1**) [11] $[RuCp(PPh_3)(CH_3CN)_2]PF_6$ (**2a**), and $[RuCp(\eta^3\text{-}CH_2CHCH_2)(PPh_3)Br]PF_6$ (**3a**) [1] were prepared according to the literature. $^1H$-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded in a Bruker Avance-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $Me_4Si$ and $H_3PO_4$ (85%). Infrared spectra were recorded in a Perkin–Elmer 16PC FTIR spectrometer.

### 3.2. Syntheses

#### 3.2.1. $[RuCp(AsPh_3)(CH_3CN)_2]PF_6$ (**2b**)

A solution of **1** (240 mg, 0.552 mmol) and $AsPh_3$ (169 mg, 0.552 mmol) in $CH_2Cl_2$ (5 ml) has been stirred at room temperature (r.t.) for 2 h. After that time the volume of the solution was reduced to about 0.5 ml. Upon addition of $Et_2O$ (5 ml) a yellow precipitate was formed, which was collected on a glass frit, washed twice with $Et_2O$, and dried under vacuum. Yield: 365 mg (95%). Anal. Calc. for $C_{27}H_{26}AsF_6N_2PRu$: C, 46.36; H, 3.75; N, 4.01. Found: C, 46.38; H, 3.80; N, 3.98%. $^1$H-NMR ($\delta$, acetone-$d_6$, 20 °C): 7.74–7.20 (m, 15H, Ph), 4.43 (s, 5H, Cp), 2.41 (s, 6H, $CH_3$). $^{13}C\{^1H\}$-NMR ($\delta$, acetone-$d_6$, 20 °C): 135.3 (6C, $Ph^{2,6}$), 133.9 (d, 3C, $Ph^1$), 130.9 (3C, $Ph^4$), 129.7 (6C, $Ph^{3,5}$), 129.3 (2C, N≡*C*), 74.1 (5C, Cp), 3.3 (2C, *C*$H_3$). IR (KBr, $cm^{-1}$): $\nu_{CN}$ 2284 (m).

#### 3.2.2. $[RuCp(SbPh_3)(CH_3CN)_2]PF_6$ (**2c**)

This complex has been prepared analogously to **2b** with **1** (240 mg, 0.552 mmol) and $SbPh_3$ (195 mg, 0.552 mmol) as the starting materials. Yield: 380 mg (92%). Anal. Calc. for $C_{27}H_{26}F_6N_2PRuSb$: C, 43.45; H, 3.51; N, 3.75. Found: C, 43.41; H, 3.57; N, 3.81%. $^1$H-NMR ($\delta$, $CDCl_3$, 20 °C): 7.51–7.41 (m, 15H, Ph), 4.59 (s, 5H, Cp), 2.20 (s, 6H, $CH_3$). $^{13}C\{^1H\}$-NMR ($\delta$, acetone-$d_6$, 20 °C): 136.3 (6C, $Ph^{2,6}$), 132.2 (3C, $Ph^1$), 131.1 (3C, $Ph^4$), 130.3 (6C, $Ph^{3,5}$), 130.2 (2C, N*C*–$CH_3$), 72.6 (5C, Cp), 3.6 (2C, *C*$H_3$). IR (KBr, $cm^{-1}$): $\nu_{CN}$ 2283 (m).

#### 3.2.3. $[RuCp(\eta^3\text{-}CH_2CHCH_2)(AsPh_3)Br]PF_6$ (**3b**)

To a solution of **2b** (100 mg, 0.143 mmol) in 5 ml of $CH_2Cl_2$ was slowly added $BrCH_2CH{=}CH_2$ (13.6 μl, 0.157 mmol). The mixture was stirred at r.t. for 5 h. The solvent was then removed in vacuo and the residue redissolved in $CH_2Cl_2$ (0.5 ml). On slow addition of *n*-hexane (5 ml) an orange precipitate was formed, which was collected on a glass frit, washed with *n*-hexane (4 × 1 ml), and dried in vacuo. Yield: 102 mg (97%). Anal. Calc. for $C_{26}H_{25}AsBrF_6PRu$: C, 42.30; H, 3.41. Found: C, 42.38; H, 3.38%. $^1$H-NMR ($\delta$, acetone-$d_6$, 20 °C): 7.70–7.36 (m, 15H, Ph), 6.21 (s, 5H, Cp), 4.82 (d, $^3J_{trans} = 11.0$ Hz, 1H, C$H_2$CHCH$_2$), 4.54 (dd, $^3J_{cis} = 6.3$ Hz, $^4J_{allyl} = 2.8$ Hz, 1H, C$H_2$CHCH$_2$), 4.23–4.04 (m, 1H, CH$_2$C*H*CH$_2$), 3.96 (dd, $^3J_{cis} = 6.3$ Hz, $^4J_{allyl} = 2.6$ Hz, 1H, CH$_2$CHC$H_2$), 3.78 (d, $^3J_{trans} = 11.1$ Hz, 1H, CH$_2$CHC$H_2$). $^{13}C\{^1H\}$-NMR ($\delta$, acetone-$d_6$, 20 °C): 134.2 (6C, $Ph^{2,6}$), 133.8 (3C, $Ph^1$) 132.5 (3C,$Ph^4$), 130.4 (6C, $Ph^{3,5}$), 97.3 (1C, CH$_2$*C*HCH$_2$), 94.3 (5C, Cp) 67.1 (1C, *C*H$_2$CHCH$_2$), 53.7 (1C, CH$_2$CH*C*H$_2$).

#### 3.2.4. $[RuCp(\eta^3\text{-}CH_2CHCH_2)(SbPh_3)Br]PF_6$ (**3c**)

This complex has been prepared analogously to **3b** with **2c** (100 mg, 0.134 mmol) and $BrCH_2CH{=}CH_2$ (12.7 μl, 0.147 mmol) as the starting materials. Yield: 90 mg (86%). Anal. Calc. for $C_{26}H_{25}BrF_6PRuSb$: C, 39.77; H, 3.21. Found: C, 39.79; H, 3.24%. $^1$H-NMR ($\delta$, acetone-$d_6$, 20 °C): 7.66–7.50 (m, 15H, Ph), 6.26 (s, 5H, Cp), 4.74 (d, $^3J_{trans} = 10.7$ Hz, 1H, C$H_2$CHCH$_2$), 4.36 (dd, $^3J_{cis} = 6.3$ Hz, $^4J_{allyl} = 2.7$ Hz, 1H, C$H_2$CHCH$_2$), 4.33–4.20 (m, 1H, CH$_2$C*H*CH$_2$), 4.16 (dd, $^3J_{cis} = 6.3$ Hz, $^4J_{allyl} = 2.7$ Hz, 1H, CH$_2$CHC$H_2$), 3.50 (d, $^3J_{trans} = 10.7$ Hz, 1H, CH$_2$CHC$H_2$). $^{13}C\{^1H\}$-NMR ($\delta$, acetone-$d_6$, 20 °C): 136.5 (6C, $Ph^{2,6}$), 136.1 (3C, $Ph^1$), 132.6 (3C, $Ph^4$), 130.8 (6C, $Ph^{3,5}$), 96.1 (1C, CH$_2$*C*HCH$_2$), 92.5 (5C, Cp) 63.6 (1C, *C*H$_2$CHCH$_2$), 48.9 (1C, CH$_2$CH*C*H$_2$).

#### 3.2.5. $[RuCp(\eta^6\text{-}PhBiPh_2)]PF_6$ (**4a**)

Compound **4a** could not be isolated and was characterized by NMR spectroscopies from a mixture of **4a** and **4b** from the reaction of **1** with one equivalent of $BiPh_3$ at r.t. $^1$H-NMR ($\delta$, $CD_3NO_2$, 20 °C): 7.92 (d, $^3J_{HH} = 8.0$ Hz, 4H, $Ph^{2,6}$), 7.56 (t, $^3J_{HH} = 8.0$ Hz, 4H, $Ph^{3,5}$), 7.44 (d, $^3J_{HH} = 8.0$ Hz, 2H, $Ph^4$), 6.46–6.16 (m, 5H, $\eta^6$-Ph), 5.26 (s, 5H, Cp). $^{13}C\{^1H\}$-NMR ($\delta$, $CD_3NO_2$, 20 °C): 138.5 (4C, $Ph^{2,6}$), 132.1 (4C, $Ph^{3,5}$), 129.6 (2C, $Ph^4$), not observed (2C, $Ph^1$), 94.1 (2C, $\eta^6$-$Ph^{2,6}$), 88.9 (2C, $\eta^6$-$Ph^{3,5}$), 85.8 (1C, $\eta^6$-$Ph^4$), not observed (1C, $\eta^6$-$Ph^1$), 81.2 (5C, Cp).

#### 3.2.6. $[(RuCp)_2(\mu\text{-}\eta^6,\eta^6\text{-}Ph_2BiPh)](PF_6)_2$ (**4b**)

A solution of **1** (100 mg, 0.230 mmol) and $BiPh_3$ (51 mg, 0.115 mmol) in nitromethane (4 ml) was stirred for 4 h at 80 °C. After that time the volume of the solution was reduced to about 0.1 ml. Upon addition of $Et_2O$ (5 ml) a yellow precipitate was formed, which was collected on a glass frit, washed with $Et_2O$, and dried under vacuum. Yield: 106 mg (86%). Anal. Calc. for $C_{28}H_{25}BiF_{12}P_2Ru_2$: C, 31.65; H, 2.37. Found: C, 31.42; H, 2.35%. $^1$H-NMR ($\delta$, $CD_3NO_2$, 20 °C): 8.07 (d, $^3J_{HH} = 7.3$ Hz, 2H, $Ph^{2,6}$), 7.71 (t, $^3J = 7.3$ Hz, 2H, $Ph^{3,5}$), 7.53 (d, $^3J = 7.3$ Hz, 1H, $Ph^4$), 6.46–6.16 (m, 10H, $\eta^6$-Ph), 5.33 (s, 10H, Cp). $^{13}C\{^1H\}$-NMR ($\delta$, $CD_3NO_2$, 20 °C): 138.4 (2C, $Ph^{2,6}$), 132.7 (2C, $Ph^{3,5}$), 130.5 (1C, $Ph^4$), not observed (1C, $Ph^1$), 94.2, 93.9 (4C, $\eta^6$-$Ph^{2,6}$), 89.6, 89.3 (4C, $\eta^6$-$Ph^{3,5}$), 86.3 (2C, $\eta^6$-$Ph^4$), not observed (2C, $\eta^6$-$Ph^1$), 81.7 (10C, Cp).

#### 3.2.7. $[RuCp(PPh_3)_2(CH_3CN)]PF_6$ (**5a**)

A solution of **2a** (100 mg, 0.153 mmol) in benzene (4 ml) was stirred for 72 h at 80 °C. The solvent was removed in vacuum and the residue was purified by column chromatography (eluent $CH_2Cl_2$–$Me_2CO$ 10:1 (v/v) sampling the yellow band). Removal of the solvent and drying in vacuum gave a yellow powder. Yield: 47 mg (35%) [7].

*3.2.8. [RuCp(AsPh$_3$)$_2$(CH$_3$CN)]PF$_6$ (**5b**)*

A solution of **2b** (100 mg, 143 mmol) in benzene (4 ml) was stirred for 30 min at 80 °C. The solvent was removed in vacuum and the residue was purified by column chromatography (eluent $CH_2Cl_2$–$Me_2CO$ 10:1 (v/v) sampling the yellow band). Removal of the solvent and drying in vacuum gave a yellow powder. Yield: 45 mg (33%) [5].

*3.2.9. [RuCp(SbPh$_3$)$_2$(CH$_3$CN)]PF$_6$ (**5c**)*

A solution of **2c** (100 mg, 0.134 mmol) in benzene (4 ml) was stirred for 10 min at 80 °C. The solvent was removed in vacuum and the residue was purified by column chromatography (eluent $CH_2Cl_2$–$Me_2CO$ 10:1 (v/v) sampling the yellow band). Removal of the solvent and drying in vacuum gave a yellow powder. Yield: 41 mg (29%) [5].

*3.2.10. [RuCp($\eta^6$-PhSbPh$_2$)]PF$_6$ (**6**)*

A solution of **2c** (210 mg, 0.281 mmol) in nitromethane (4 ml) was stirred for 4 h at 80 °C. The solvent was removed in vacuum and the residue was purified by column chromatography (neutral $Al_2O_3$; eluent $CH_2Cl_2$–$Me_2CO$ 10:1 (v/v) sampling the yellow band giving **5c**, followed by neat $Me_2CO$ as eluent giving pure **6**). Removal of the solvent and drying in vacuum gave a yellow powder. Yield: 15 mg (9%) Anal. Calc. for $C_{23}H_{20}F_6PRuSb$: C, 41.59; H, 3.04. Found: C, 41.35; H, 3.17%. $^1$H-NMR ($\delta$, $CDCl_3$, 20 °C): 7.53–7.44 (m, 10H, Ph), 6.29 (d, $^3J_{HH} = 5.8$ Hz, 1H, $\eta^6$-Ph$^4$), 6.18 (t, $^3J_{HH} = 5.8$ Hz, 2H, $\eta^6$-Ph$^{3,5}$), 5.96 (d, $^3J_{HH} = 5.3$ Hz, 1H, $\eta^6$-Ph$^{2,6}$), 5.23 (s, 5H, Cp). $^{13}$C{$^1$H}-NMR ($\delta$, $CDCl_3$, 20 °C): 135.4, 133.2, 132.2, 131.6, 130.8, 130.4, 129.9, 129.2 (10C, SbPh), 91.3, 90.8, 90.3, 88.2, 87.2, 81.4 (6C, $\eta^6$-Ph), 81.6 (5C, Cp).

*3.2.11. [CpRu{($\eta^6$-PhSbPh$_2$)RuCp}(SbPh$_3$)(CH$_3$CN)](PF$_6$)$_2$ (**7**)*

A solution of **2c** (200 mg, 0.268 mmol) in nitromethane (4 ml) was stirred for 6 h at 80 °C. The solvent was then removed and the product was purified by column chromatography ($Al_2O_3$ discarding a first yellow band eluted with $CH_2Cl_2$ and finally sampling the second yellow band with neat $Me_2CO$). Removal of the solvent and drying in vacuum afforded a yellow powder. Yield: 238 mg (65%). Anal. Calc. for $C_{48}H_{43}F_{12}NP_2Ru_2Sb_2$: C, 42.10; H, 3.17; N, 1.02. Found: C, 41.42; H, 3.46; N, 0.91%. $^1$H-NMR ($\delta$, acetone-$d_6$, 20 °C): 7.74–7.21 (m, 25H, Ph), 6.44–6.22 (m, 5H, $\eta^6$-Ph), 5.29 (s, 5H, Cp), 5.11 (s, 5H, Cp), 2.17 (s, 3H, NC–C$H_3$). $^{13}$C{$^1$H}-NMR ($\delta$, acetone-$d_6$, 20 °C): 135.8, 135.7, 135.6, 133.2, 132.9, 132.2, 132.0, 131.8, 131.6, 131.5, 130.8, 130.4, 129.9, 129.1 (31C, SbPh, NC–$C$H$_3$), 92.3, 91.9, 91.2, 87.3, 87.2, 81.6 (6C, $\eta^6$-Ph), 81.6 (5C, Cp), 75.2 (5C, Cp), 3.7 (NC–$C$H$_3$).

*3.3. Catalyses*

*3.3.1. Typical reaction conditions for the isomerization of phenylallylether*

A mixture of 0.047–0.008 mmol catalyst (3–0.25 mol% with respect to phenylallyether) and phenylallyether in THF or $Me_2CO$ (4 ml) was heated for 5.5–24 h using an oil-bath at a temperature of 80 °C. The reaction mixture was evaporated to dryness under reduced pressure (10 mbar) and the crude product was examined by NMR spectroscopy. The organic material has been separated by column chromatography ($SiO_2$, eluent: $Et_2O$).

*3.3.2. [RuCp($\eta^6$-C$_6$H$_5$–O–CH$_2$–CH=CH$_2$)]PF$_6$ (**9**)*

During a typical run of the reaction with **1** (30 mg, 0.069 mmol) as the pre-catalyst (solvent: 4 ml of THF) and phenylallylether as the substrate (24 h; 80 °C) no catalytic reaction has been observed. THF and the phenylallylether were removed in vacuum resulting in an oily residue, which was precipitated upon addition of $Et_2O$. The resulting off-white powder was collected on a glass frit, washed with $Et_2O$ (4 × 2 ml), and dried under vacuum. Yield: 24 mg (78%). Anal. Calc. for $C_{14}H_{15}F_6OPRu$: C, 37.76; H, 3.40. Found: C, 37.69; H, 3.45%. $^1$H-NMR ($\delta$, $CDCl_3$, 20 °C): 6.14 (d, $^3J_{HH} = 5.4$ Hz, 2H, Ph$^{2,6}$), 6.05 (m, 2H, Ph$^{3,5}$), 5.96–5.79 (m, 2H, Ph$^4$, $CH_2$–C$H$=$CH_2$), 5.39 (d, $^3J_{HH} = 16.2$ Hz, $CH_2$–CH=C$H_2$), 5.29 (s, 5H, Cp) 5.24 (d, $^3J_{HH} = 10.0$ Hz, $CH_2$–CH=C$H_2$), 4.45 (d, 2H, $^3J_{HH} = 5.4$ Hz, C$H_2$–CH=$CH_2$). $^{13}$C{$^1$H}-NMR ($\delta$, $CDCl_3$, 20 °C): 133.8 (1C, Ph$^1$), 131.1 (1C, $CH_2$–$C$H=$CH_2$), 119.8 (1C, $CH_2$–CH=$C$H$_2$), 84.5 (1C, Ph$^4$), 80.3 (5C, Cp), 79.9 (2C, Ph$^{3,5}$), 75.0 (2C, Ph$^{2,6}$), 70.8 (1C, $C$H$_2$–CH=$CH_2$).

*3.3.3. Phenyl-E-propenylether (**10a**)*

$^1$H-NMR ($\delta$, $CDCl_3$, 20 °C): 7.40 (dd, $^3J_{HH} = 8.8$ Hz, $^3J_{HH} = 7.4$ Hz, 2H, Ph$^{3,5}$), 7.14 (t, $^3J_{HH} = 7.4$ Hz, 2H, Ph$^4$), 7.08 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ph$^{2,6}$), 6.52 (dq, $^3J_{HH} = 12.1$ Hz, $^4J_{HH} = 1.7$ Hz, 1H, C$H$=CH–CH$_3$), 5.48 (dq, $^3J_{HH} = 12.1$ Hz, $^4J_{HH} = 6.9$ Hz, 2H, CH=C$H$–CH$_3$), 1.77 (dd, $^3J_{HH} = 6.9$ Hz, $^3J_{HH} = 1.7$ Hz, 3H, C$H$=CH–C$H_3$). $^{13}$C{$^1$H}-NMR ($\delta$, $CDCl_3$, 20 °C): 157.7 (1C, Ph$^1$), 142.3 (1C, O–$C$H=CH–CH$_3$), 129.8 (2C, C$^{3,5}$), 122.7 (1C, C$^4$), 116.6 (2C, C$^{2,6}$), 108.5 (1C, O–CH=$C$H–CH$_3$), 12.5 (1C, O–CH=CH–$C$H$_3$).

*3.3.4. Benzyl-E-propenylether (**10b**)*

$^1$H-NMR ($\delta$, $CDCl_3$, 20 °C): 7.40–7.34 (m, 5H, Ph), 6.36 (dq, $^3J_{HH} = 12.2$ Hz, $^3J_{HH} = 1.5$ Hz, 1H, C$H$=CH–CH$_3$), 4.93 (dq, $^3J_{HH} = 12.2$ Hz, $^3J_{HH} = 6.6$ Hz, 1H, CH=C$H$–CH$_3$), 4.73 (s, 2H, Ph–C$H_2$–O), 1.61 (dd, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.5$ Hz, 3H, CH=CH–$CH_3$). $^{13}$C{$^1$H}-NMR ($\delta$, $CDCl_3$, 20 °C): 146.9 (1C, O–$C$H=CH–CH$_3$), 138.0 (1C, Ph$^1$), 129.0 (2C, C$^{3,5}$), 128.2 (1C, C$^4$), 128.0 (2C, C$^{2,6}$), 99.8 (1C,

O–CH=*C*H–$CH_3$), 71.5 (1C, Ph–$CH_2$–O), 12.5 (1C, O–CH=CH–$CH_3$).

### 3.3.5. Typical reaction conditions for the transfer hydrogenation catalysis

A mixture of precatalyst **2a** (5 mg, 0.008 mmol) and 4.8 mmol ketone in 10 ml *i*-PrOH with 5 mg *i*-PrONa was heated for 24 h using an oil-bath at a temperature of 85 °C. The reaction mixture was evaporated to dryness under reduced pressure (5 mbar) and the crude product was examined by NMR spectroscopy. The organic product has been separated by column chromatography ($SiO_2$, eluent: $Et_2O$).

### 3.3.6. [RuCp($\eta^6$-$C_6H_5$–CO–$CH_3$)]$PF_6$ (11)

To a solution of **1** (50 mg, 0.115 mmol) in nitromethane (3 ml) acetophenone (12.5 μl, 0.138 mmol) was added and stirred for 1 h at 80 °C. After removal of the solvent an oily residue was obtained. An off-white precipitate was formed upon addition of $Et_2O$ which was collected on a glass frit, washed with $Et_2O$ (4 × 2 ml), and dried under vacuum. Yield: 36 mg (73%). Anal. Calc. for $C_{13}H_{13}F_6OPRu$: C, 36.21; H, 3.04. Found: C, 36.00; H, 3.32%. $^1$H-NMR ($\delta$, acetone-$d_6$, 20 °C): 6.84 (m, 2H, Ph$^{2,6}$), 6.51 (m, 3H, Ph$^{3,4,5}$), 5.57 (s, 5H, Cp), 2.64 (s, 3H, $CH_3$). $^{13}$C{$^1$H}-NMR ($\delta$, acetone-$d_6$, 20 °C): 197.0 (1C, *C*O), 93.4 (1C, Ph$^1$), 87.7 (1C, Ph$^4$), 87.1, 85.8 (4C, Ph$^{2,3,5,6}$), 82.2 (5C, Cp), 25.9 (1C, $CH_3$).

### 3.4. X-ray structure determination

Crystals of **2b**, **2c**, **3a**–**3c**, and **4b** were obtained by diffusion of $Et_2O$ into $CH_2Cl_2$ solutions. Crystal data and experimental details are given in Table 3. X-ray data were collected in a Bruker AXS Smart CCD area detector diffractometer (graphite monochromated Mo–$K_\alpha$ radiation, $\lambda = 0.71073$ Å, 0.3° $\omega$-scan frames covering complete spheres of the reciprocal space). Corrections for Lorentz and polarization effects, for

Table 3
Crystal data and structure refinement parameters for **2b**, **2c**, **3a**–**3c**, and **4b**

| | **2b** | **2c** | **3a** | **3b** | **3c** | **4b** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{27}H_{26}AsF_6N_2PRu$ | $C_{27}H_{26}F_6N_2PRuSb$ | $C_{26}H_{25}BrF_6P_2Ru$ | $C_{26}H_{25}AsBrF_6PRu$ | $C_{26}H_{25}BrF_6PRuSb$ | $C_{28}H_{25}BiF_{12}P_2Ru_2$ |
| Formula weight | 699.46 | 746.29 | 694.38 | 738.33 | 785.16 | 1062.54 |
| Crystal size (mm) | 0.22 × 0.32 × 0.44 | 0.18 × 0.42 × 0.70 | 0.28 × 0.65 × 0.75 | 0.20 × 0.32 × 0.64 | 0.30 × 0.38 × 0.45 | 0.06 × 0.18 × 0.48 |
| Space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | $C2/c$ (No. 15) | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | $C2/c$ (No. 15) |
| Unit cell dimensions | | | | | | |
| $a$ (Å) | 10.533(3) [a] | 10.530(2) [a] | 28.422(8) | 10.079(2) | 10.211(2) | 17.030(3) |
| $b$ (Å) | 16.374(4) | 16.457(4) | 13.690(4) | 10.459(2) | 10.805(2) | 13.349(2) |
| $c$ (Å) | 17.762(4) | 18.176(4) | 13.865(4) | 13.498(2) | 13.420(3) | 27.349(5) |
| $\alpha$ (°) | 72.26(1) | 72.21(1) | | 103.22(1) | 104.39(1) | |
| $\beta$ (°) | 82.23(1) | 82.31(1) | 106.07(1) | 96.54(1) | 97.81(1) | 93.30(1) |
| $\gamma$ (°) | 90.07(1) | 90.07(1) | | 99.69(1) | 99.90(1) | |
| $V$ (Å$^3$) | 2894(1) | 2969(1) | 5184(3) | 1348.1(4) | 1387.8(5) | 6207(1) |
| $Z$ | 4 | 4 | 8 | 2 | 2 | 8 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.606 | 1.669 | 1.779 | 1.819 | 1.879 | 2.274 |
| $T$ (K) | 297(2) | 297(2) | 223(2) | 297(2) | 297(2) | 297(2) |
| $\mu$ (mm$^{-1}$) (Mo–$K_\alpha$) | 1.790 | 1.528 | 2.328 | 3.396 | 3.069 | 6.812 |
| $F$(000) | 1392 | 1464 | 2752 | 724 | 760 | 4016 |
| Absorption correction | SADABS | SADABS | SADABS | SADABS | SADABS | SADABS |
| Transmission factors min/max | 0.60/0.72 | 0.28/0.72 | 0.28/0.46 | 0.25/0.60 | 0.40/0.53 | 0.39/0.69 |
| $\theta_{max}$ (°) | 30 | 30 | 30 | 30 | 30 | 27 |
| Number of reflections measured | 42 231 | 43 290 | 25 177 | 14 503 | 20 062 | 36 872 |
| Number of unique reflections | 16 465 | 16 904 | 7452 | 7436 | 7853 | 6749 |
| Number of reflections $I > 2\sigma(I)$ | 11 446 | 12 835 | 6404 | 5916 | 6743 | 5358 |
| Number of parameters | 690 | 690 | 325 | 363 | 363 | 407 |
| $R_1$ ($I > 2\sigma(I)$) | 0.035 | 0.040 | 0.031 | 0.030 | 0.030 | 0.032 |
| $R_1$ (all data) | 0.059 | 0.057 | 0.038 | 0.042 | 0.036 | 0.046 |
| $wR_2$ (all data) | 0.103 | 0.099 | 0.084 | 0.080 | 0.078 | 0.085 |
| Difference Fourier peaks min/max (e Å$^{-3}$) | −0.69/0.77 | −0.75/1.78 | −0.66/1.40 | −0.55/0.50 | −0.61/0.61 | −0.88/0.81 |

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

[a] Triclinic unit cells not reduced in order to maintain the same setting as for the unit cell of the isostructural phosphine **2a**, Ref. [1].

crystal decay, and for absorption were applied. All structures were solved by direct methods using the program SHELXS97 [12]. Structure refinement on $F^2$ was carried out with program SHELXL97 [13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

## 4. Supporting material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 175155–175160 for compounds **2b**, **2c**, **3a**–**3c**, and **4b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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