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# Ruthenium(II) complexes with a new potentially trifunctional phosphinoester and its enolate as ligands†

**Jürgen Bank, Paul Steinert, Bettina Windmüller, Werner Wolfsberger and Helmut Werner***

*Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*

Both $RuCl_3 \cdot nH_2O$ and $[RuCl_2(PPh_3)_3]$ reacted with $PBu^t(CH_2CO_2Me)_2$ to give a mixture of two isomeric ruthenium(II) complexes $[RuCl_2\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)\text{-}\kappa^2P,O\}_2]$ **1a** and **1b** (ratio 3:1) which contain two molecules of the ester as bidentate chelating ligands. Treatment of **1a**, **1b** with $AgPF_6$ led, after abstraction of one chloride ligand, to the cationic complex $[RuCl\{PBu^t[CH_2C(OMe)=O]_2\text{-}\kappa^3P,O,O\}\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)\text{-}\kappa^2P,O\}]PF_6$ **2** in which one molecule of the phosphinoester is a bi- and the other a tri-dentate ligand. Reaction of **2** with $KOBu^t$ or $NaN(SiMe_3)_2$ yielded the neutral phosphinoenolate-ruthenium(II) compound $[RuCl\{PBu^t[CH=C(OMe)O][CH_2C(OMe)=O]\text{-}\kappa^3P,O,O\}\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)\text{-}\kappa^2P,O\}]$ **3** which, by cleavage of the Ru–O(ester) bonds, reacted with CO or CNMe to give the corresponding monocarbonyl or bis(isocyanide) complexes $[RuCl(CO)\{PBu^t[CH=C(OMe)O](CH_2CO_2Me)\text{-}\kappa^2P,O\}\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)\text{-}\kappa^2P,O\}]$ **4** or $[RuCl(CNMe)_2\{PBu^t[CH=C(OMe)O](CH_2CO_2Me)\text{-}\kappa^2P,O\}\{PBu^t(CH_2CO_2Me)_2\text{-}\kappa P\}]$ **5** respectively. On treatment with PhNCO compound **3** underwent an insertion reaction of the isocyanate into the C–H bond of the metal enolate to give the ring-substituted derivative $[RuCl\{PBu^t[C(CONHPh)=C(OMe)O][CH_2C(OMe)=O]\text{-}\kappa^3P,O,O\}\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)\text{-}\kappa^2P,O\}]$ **6**. While compound **3** reacted with water in tetrahydrofuran to yield almost quantitatively the phosphino(monoester)acetate complex $[RuCl\{PBu^t[CH_2C(O)O][CH_2C(OMe)=O]\text{-}\kappa^3P,O,O\}\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)\text{-}\kappa^2P,O\}]$ **7**, reaction of **3** with $CNBu^t$, in the presence of water, yielded the bis(isocyanide) adduct $[RuCl(CNBu^t)_2\{PBu^t[CH_2C(O)O](CH_2CO_2Me)\text{-}\kappa^2P,O\}\{PBu^t(CH_2CO_2Me)_2\text{-}\kappa P\}]$ **8**. Treatment of **3** with HCl or PhSH reconverted the phosphinoenolate into the phosphinoester moiety with concomitant formation of compounds **1a**, **1b** and $[RuCl(SPh)\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)\text{-}\kappa^2P,O\}_2]$ **9**, respectively. The molecular structures of **1a** and **3** have been determined by X-ray crystallography.

Owing to their important role in homogeneous catalysis,[1,2] an impressive number of transition-metal complexes containing potentially bidentate phosphines has been investigated in recent years.[3] In most of these studies, bifunctional P,O-chelating ligands such as phosphino-ethers, -esters and -ketones have been employed.[4] Since little is known about the corresponding complexes with tridentate tertiary phosphines of the general type $PRX_2$ [X = $(CH_2)_nOMe$, $(CH_2)_nCO_2R'$ or $(CH_2)_nC(=O)R'$],[5] we developed a preparative route for phosphinoesters $RP(CH_2CO_2R')_2$ and started to investigate their co-ordinating abilities. In this paper we describe the synthesis of a series of ruthenium(II) complexes with $PBu^t(CH_2CO_2Me)_2$ as a mono-, bi- or tri-dentate ligand and the facile formation of a phosphinoenolate ruthenium compound which undergoes addition as well as insertion reactions.

## Results and Discussion

### Preparation and molecular structure of $[RuCl_2\{PBu^t(CH_2CO_2Me)_2\}_2]$

The phosphinoester, which was prepared according to a recently published method[6] by heating $PBu^t(SiMe_3)_2$ with 2 equivalents of $ClCH_2CO_2Me$ in benzene, readily reacts with $RuCl_3 \cdot nH_2O$ in methanol or with $[RuCl_2(PPh_3)_3]$ in dichloromethane to give a mixture of two isomeric products **1a** and **1b** in about 60% yield. The ratio of **1a** and **1b** is approximately 3:1 and does not depend on the synthetic route used. While attempts to separate the two isomers by chromatographic techniques failed, fractional crystallization led to the isolation of red-brown crystals of **1a** which, as confirmed by NMR spectroscopy, correspond to the main component of the mixture of products. The structural analysis of **1a** reveals a distorted-octahedral geometry [P(1)–Ru–P(2) 108.18(8) and P(1)–Ru–O(1) 81.8(2)°] with *trans* chloride ligands and two coplanar P,O-chelates, the two phosphorus and the two oxygen atoms being *cis* disposed (Fig. 1). Both chloride ligands are bent away from the phosphorus atoms, thereby minimizing steric interactions with the tertiary butyl groups. The identical Ru–Cl(1) and Ru–Cl(2) distances of 2.406(3) Å and the very similar Ru–P(1) and Ru–P(2) bond lengths of 2.252(3) and 2.247(2) Å are in the range found for *trans* Cl–Ru–Cl and *cis* P–Ru–P arrangements in other phosphine ruthenium(II) complexes.[7]

The stereochemistry of the second isomer **1b** is not yet clear. Since NMR spectroscopic measurements in the presence of the shift reagent $[Eu(tfc)_3]$ {tfc = [3-hydroxy(trifluoromethyl)-methylene]-(+)-camphorate; camphor = 1,7,7-trimethylbicyclo[2.2.1]heptane-2-one} confirm that a pair of enantiomers (and not a *meso* form) is present, the two configurations **A** and **B** (Scheme 1) are possible. Owing to the similarity of the $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopic data for the two isomers (for details see Experimental section), we prefer **A** for **1b** since in this geometry as in **1a** the phosphorus atoms are in *cis* disposition. We note that a *cis* arrangement of the phosphine groups is not only found in **1a** but also in the related octahedral ruthenium(II) complexes $[RuCl_2(PPr^i_2CH_2CO_2R\text{-}\kappa^2P,O)_2]$ (R = Me or Et) and the corresponding dibromo and diiodo derivatives.[8]

### Generation and bonding ability of a new phosphinoenolate

Treatment of the isomeric mixture of **1a**, **1b** with 1 equivalent of

† *Non-SI unit employed:* eV ≈ 1.60 × $10^{-19}$ J.

$AgPF_6$ in dichloromethane at −78 °C leads to the abstraction of one chloride ligand and to the formation of the cationic complex **2** (Scheme 2) in which one of the phosphinoesters is bidentate and one tridentate. The composition of **2**, which is a yellow, only moderately air-sensitive solid, has been confirmed both by elemental analysis and conductivity measurements. As would be expected, its NMR spectra are more complicated than those of **1a** (or **1b**) and display, for example, four signals for the $OCH_3$ protons and carbon atoms as well as four signals for the C=O carbons of the ester groups. The $^{31}P$ NMR spectrum shows two signals at δ 77.6 and 73.3 with a relatively small P–P coupling of 34.9 Hz which supports the assumption that the two phosphorus atoms are *cis* disposed. Based on the spectroscopic data, three different stereochemical arrangements for **2** are possible of which that shown in Scheme 2 is the most reasonable one.

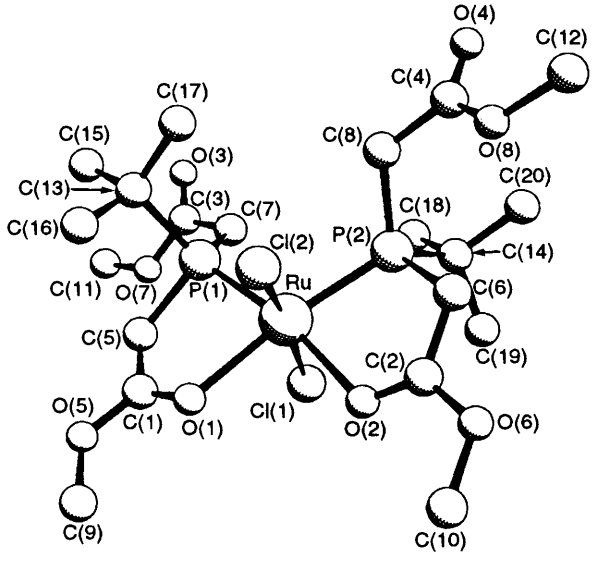
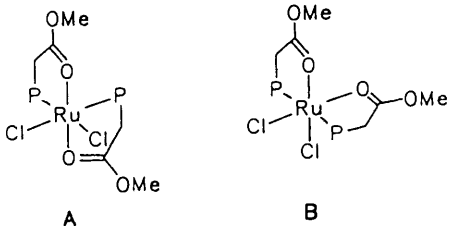



**Fig. 1** Molecular structure of compound **1a**. Selected bond lengths (Å) and angles (°): Ru–Cl(1) 2.406(3), Ru–Cl(2) 2.406(3), Ru–P(1) 2.252(3), Ru–P(2), 2.247(2), Ru–O(1) 2.202(6), Ru–O(2) 2.187(7), P(1)–C(5) 1.861(8), C(1)–C(5) 1.49(1), C(1)–O(1) 1.21(1), C(1)–O(5) 1.32(1), P(2)–C(6) 1.86(1), C(2)–C(6) 1.52(1), C(2)–O(2) 1.21(1) and C(2)–O(6) 1.31(1); Cl(1)–Ru–Cl(2) 169.59(9), Cl(1)–Ru–P(1) 87.4(1), Cl(1)–Ru–P(2) 98.85(9), Cl(1)–Ru–O(1) 84.6(2), Cl(1)–Ru–O(2) 88.7(2), Cl(2)–Ru–P(1) 98.76(9), Cl(2)–Ru–P(2) 87.22(8), Cl(2)–Ru–O(1) 88.0(2), Cl(2)–Ru–O(2) 83.8(2), P(1)–Ru–P(2) 108.18(8), P(1)–Ru–O(1) 81.8(2), P(1)–Ru–O(2) 169.6(1), P(2)–Ru–O(1) 169.5(2), P(2)–Ru–O(2) 82.0(2), O(1)–Ru–O(2) 88.3(2), Ru–P(1)–C(5) 99.1(3), P(1)–C(5)–C(1) 108.5(7), O(1)–C(1)–C(5) 124.5(8), Ru–O(1)–C(1) 116.8(6), O(1)–C(1)–O(5) 122.8(9), Ru–P(2)–C(6) 100.2(3), P(2)–C(6)–C(2) 108.4(6), O(2)–C(2)–C(6) 124.2(9), Ru–O(2)–C(2) 117.6(5) and O(2)–C(2)–O(6) 122.9(7)



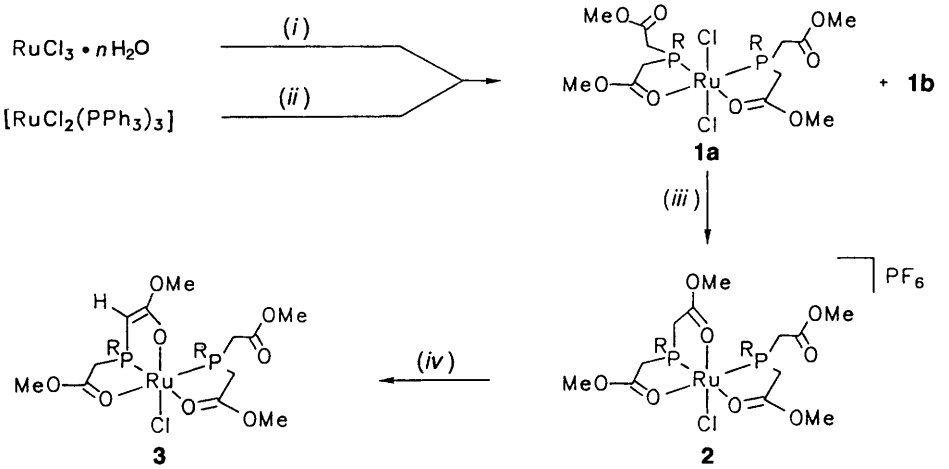

**Scheme 1** Possible stereoisomers of **1b** (the other substituents on the phosphorus atoms are omitted for clarity)

Reaction of compound **2** with sterically demanding bases such as $KOBu^t$ or $NaN(SiMe_3)_2$ affords the neutral phosphinoenolate complex **3**. Although it is possible to prepare **3** directly by treatment of **1** with $KOBu^t$ in tetrahydrofuran (thf), the route *via* **2** as intermediate gives the product in higher yield. The $^{31}P$ NMR spectrum of the yellow, moisture-sensitive compound displays two doublets at δ 83.0 and 68.8 with a P–P coupling of 40 Hz and thus indicates that in **3** as in **2** the two phosphine groups are *cis* to each other.

This proposition has been confirmed by a crystal structure analysis of compound **3**. The SCHAKAL [9] structure plot (Fig. 2) reveals that the ruthenium atom is in a slightly distorted octahedral environment, with the bite angles of the chelate rings [O(1)–Ru–P(1), O(2)–Ru–P(1) and O(3)–Ru–P(2)] close to 82–83°. The five-membered phosphinoenolate metal unit is almost planar showing P–C, C–C and C–O bond lengths similar to those in related ring systems.[10,11] The distances between the metal and the ester C=O oxygen atoms [O(2) and O(3)] are nearly the same as those found for **1a** while the Ru–O(1) bond length is significantly shorter; this is almost identical to the Ru–O distances in the recently described anionic complex $[Ru\{Ph_2PCHC(Ph)O\text{-}\kappa^2P,O\}_3]^-$.[12]

Whereas treatment of the phosphinoenolate compound **3** with CO results in substitution of one of the co-ordinated ester functions to yield the monocarbonyl derivative **4**, reaction with an excess of CNMe leads to the formation of the bis(isocyanide) complex **5** in good yield. In contrast to **3** the phosphorus atoms in the carbonyl and isocyanide complexes are thought to be *trans* disposed, an assignment based on the large P–P coupling of the two signals in the $^{31}P$ NMR spectra of **4** and **5** (308.5 and 298.5 Hz). We also note that compound **4** is highly fluxional in solution on the NMR time-scale. The isomer shown in Scheme 3 is one of the five possible stereoisomers having a co-ordination sphere in which two chelate units are bonded to the metal centre.

Compound **3** reacts with phenyl isocyanate to give the ring-substituted derivative **6** which formally results from the addition of the C–H bond of the phosphinoester enolate across the C=N bond of the substrate. Such an insertion reaction is not without precedent and has been studied in detail with other




**Scheme 2** R = Bu$^t$. (*i*) $PBu^t(CH_2CO_2Me)_2$, MeOH; (*ii*) $PBu^t(CH_2CO_2Me)_2$, $CH_2Cl_2$; (*iii*) $AgPF_6$, −78 °C; (*iv*) $KOBu^t$

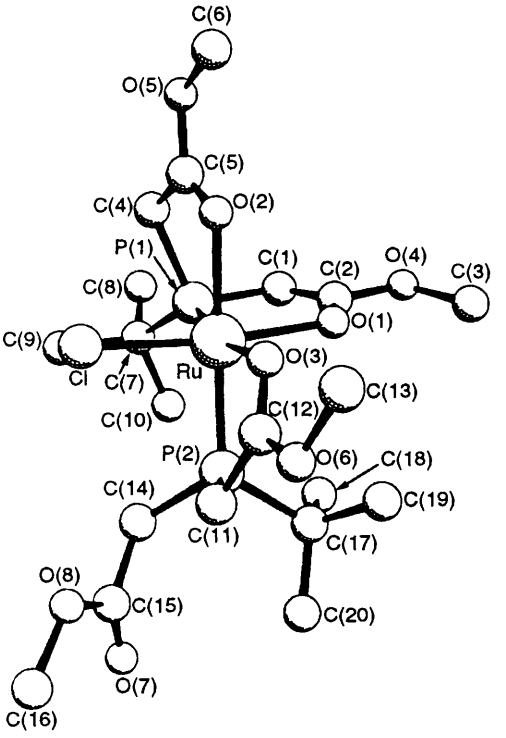
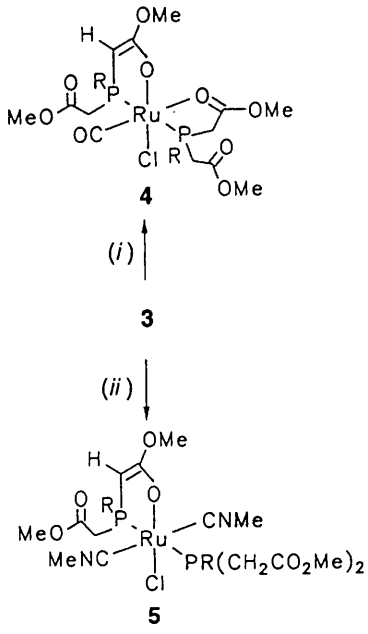



**Fig. 2** Molecular structure of compound **3**. Selected bond lengths (Å) and angles (°): Ru–Cl 2.397(1), Ru–P(1) 2.227(1), Ru–P(2) 2.225(1), Ru–O(1) 2.103(3), Ru–O(2) 2.174(3), Ru–O(3) 2.215(3), P(1)–C(1) 1.748(4), C(1)–C(2) 1.349(6) and O(1)–C(2) 1.293(5); Cl–Ru–P(1) 97.16(4), Cl–Ru–P(2) 89.80(4), Cl–Ru–O(1) 172.77(8), Cl–Ru–O(2) 87.55(8), Cl–Ru–O(3) 89.70(8), P(1)–Ru–P(2) 108.51(4), P(1)–Ru–O(1) 83.12(8), P(1)–Ru–O(2) 81.56(8), P(1)–Ru–O(3) 167.32(7), P(2)–Ru–O(1) 96.97(8), P(2)–Ru–O(2) 169.84(8), P(2)–Ru–O(3) 82.05(8), O(1)–Ru–O(2) 85.3(1), O(1)–Ru–O(3) 88.7(1), O(2)–Ru–O(3) 88.1(1), Ru–P(1)–C(1) 101.8(2), P(1)–C(1)–C(2) 113.3(3), O(1)–C(2)–C(1) 126.8(4) and Ru–O(1)–C(2) 114.9(3)

phosphinoenolate transition-metal compounds particularly by Braunstein, Matt and their co-workers.[13] The structural proposal for complex **6** (Scheme 4) is not only supported by elemental analysis but also by mass spectral, NMR {$\delta_H$(NH) 8.69 (s); $\delta_C$[C(O)N] 166.05 (s)} and IR data of which the N–H frequency at 3385 $cm^{-1}$ is most typical for those systems.[13a] We note that whereas phosphinoenolate palladium complexes react smoothly and reversibly with $CO_2$,[10] compound **3** is completely inert towards carbon dioxide.

In the presence of water (in thf solution), hydrolysis of the enolate function of compound **3** takes place and the phosphinoacetate complex **7** is formed almost quantitatively. A related metal-assisted transformation of a P-bonded phosphinoester to a chelated phosphinoacetate ligand has recently been observed, and the structure of the corresponding iridium compound has been determined by X-ray crystallography.[14] Contrary to the reaction of **3** with CNMe which yields the 1:2 adduct **5** (Scheme 3), on treatment of the phosphinoenolate complex with CNBu$^t$, in the presence of small amounts of water, the phosphinoacetate derivative **8** is obtained. In contrast to **7**, the $^{13}C$ NMR spectrum of **8** displays only one resonance at δ 179.59 for the carbon atom of a co-ordinated OCO unit and three very narrow signals at δ 169.88, 169.61 and 169.50 for the corresponding carbons of unco-ordinated OCO ester moieties.

A reconversion of the phosphinoenolate ligand to the intact phosphinodiester unit occurs either on treatment of compound **3** with HCl or PhSH (Scheme 5). Whereas the reaction of **3** with gaseous HCl in toluene yields a mixture of the dichloro isomers **1a** and **1b** in the same ratio as found during their preparation from $RuCl_3 \cdot nH_2O$ or $[RuCl_2(PPh_3)_3]$ (Scheme 2), only one product with the analytical composition corresponding to **9** is




**Scheme 3** R = Bu$^t$. (*i*) CO; (*ii*) CNMe

formed from **3** and benzenethiol. Since the $^{31}P$ NMR spectrum of **9** displays two signals (AB system) with a $^2J_{PP}$ which is very similar to that found for **3**, **6** or **7**, we assume that the phosphorus atoms of the two phosphinoester ligands are in *cis* disposition. In contrast to **1**, the $^{13}C$ NMR spectrum of **9** displays two resonances at δ 181.89 and 181.52 for the carbon atoms of the co-ordinated OCO units and four signals at δ 36.01, 35.47, 32.49 and 30.53 for the $PCH_2$ carbons of the phosphinoester moieties. We therefore favour the proposal that the chloride and the benzenethiolate ligands are *cis* to each other and consider the two configurations shown in Scheme 5 as the most appropriate.

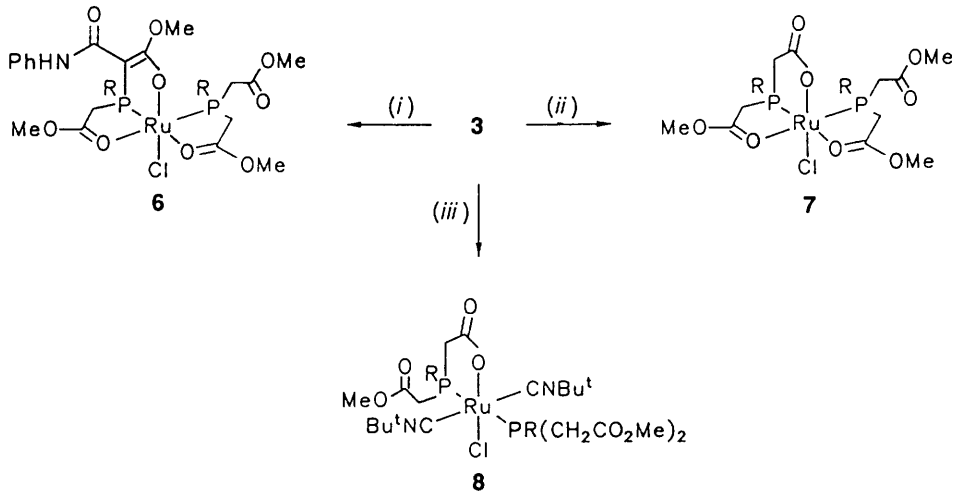
Current work is concerned with the further modification of the P,O,O-tripodal phosphane and the investigation into the catalytic activity of the various ruthenium complexes containing bi- or tri-dentate hemilabile-chelate ligands. Moreover, it is an attractive synthetic target to convert the anionic unit of **6** into an unsymmetrical (possibly chiral) phosphane and to study the reactivity of the respective transition-metal complexes.

## Experimental

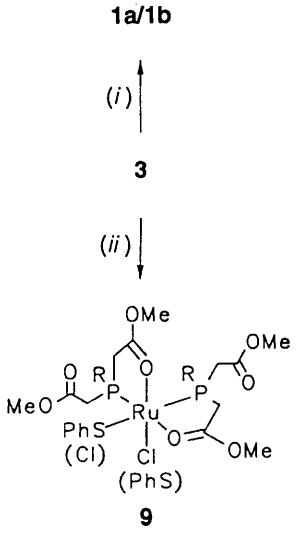
All reactions were carried out under an atmosphere of argon by using Schlenk-tube techniques. All solvents were analytical grade and distilled under argon from sodium–benzophenone (toluene, diethyl ether, thf), sodium–potassium (pentane, hexane), $P_2O_5$ (dichloromethane) or NaH (Bu$^t$OH). The starting materials PBu$^t$$(CH_2CO_2Me)_2$,[6] $[RuCl_2(PPh_3)_3]$[15] and CNMe[16] were prepared as described in the literature. The NMR spectra were recorded at room temperature on JEOL FX 90 Q, Bruker AC 200 and AMX 400 spectrometers (s = singlet, d = doublet, t = triplet, vt = virtual triplet, spt = septet, m = multiplet), the IR spectra on a Perkin-Elmer 1420 spectrophotometer, and the mass spectra on Varian CH7 MAT and Finnigan 90 MAT instruments. The conductivity Λ was measured in nitromethane with a Schott Konduktometer CG 851 instrument, and melting and decomposition points were determined by differential thermal analysis.

### Preparations

**$[RuCl_2\{PBu^t[CH_2C(OMe)=O](CH_2CO_2Me)$-$\kappa^2P,O\}_2]$ 1a, 1b.** A solution of $[RuCl_2(PPh_3)_3]$ (1.0 g, 1.04 mmol) in $CH_2Cl_2$ (20 $cm^3$) was treated with PBu$^t$$(CH_2CO_2Me)_2$ (611 mg,



**Scheme 4** R = Bu$^t$. (*i*) PhNCO; (*ii*) $H_2O$, thf; (*iii*) CNBu$^t$, $H_2O$



**Scheme 5** R = Bu$^t$. (*i*) HCl; (*ii*) PhSH

2.61 mmol) and stirred for 2 h at room temperature. The solution was concentrated to *ca.* 0.5 $cm^3$ *in vacuo*, and the concentrate chromatographed on $Al_2O_3$ (neutral, activity grade III). With $CH_2Cl_2$ a red-brown fraction was eluted from which the solvent was removed *in vacuo*. The oily residue was converted into a red-brown microcrystalline solid by stirring with diethyl ether (3 $cm^3$). According to the intensities of the $^1H$ NMR signals, the ratio of the two isomers **1a**/**1b** is 3:1: yield 427 mg (64%), decomp. 207 °C (Found: C, 37.80; H, 6.10. Calc. for $C_{20}H_{38}Cl_2O_8P_2Ru$: C, 37.50; H, 6.00%). Mass spectrum (70 eV): *m*/*z* 640 ($M^+$). IR (KBr): $\nu(CO)_{unco\text{-}ord}$ 1727, $\nu(CO)_{co\text{-}ord}$ 1647 $cm^{-1}$. NMR ($CDCl_3$): $^1H$ (400 MHz), **1a**, δ 4.04 and 3.66 (both s, 12 H, $OCH_3$), 4.04–2.83 (m, 8 H, $PCH_2$), and 1.20 [d, *J*(PH) 14.5, 18 H, $PCCH_3$]; **1b**, δ 4.05 and 3.65 (both s, 12 H, $OCH_3$), 4.04–2.83 (m, 8 H, $PCH_2$), 1.25 [d, *J*(PH) 14.6 Hz, 18 H, $PCCH_3$]; $^{13}C$ (100.6 MHz), **1a**, δ 182.35 (m, $OCO_{co\text{-}ord}$), 169.56 (m, $OCO_{unco\text{-}ord}$), 55.21 and 51.87 (both s, $OCH_3$), 35.28 (m, $PCH_2$), 34.93 (m, $PCCH_3$), 31.52 (m, $PCH_2$), and 26.24 (s, $PCCH_3$); **1b**, δ 182.08 (m, $OCO_{co\text{-}ord}$), 51.96 (s, $OCH_3$), 35.67 and 30.41 (both m, $PCH_2$), 26.60 (s, $PCCH_3$); the other signals were hidden by those of the major isomer **1a**; $^{31}P$ (162.0 MHz), **1a**, δ 71.6 (s); **1b**, δ 69.0 (s).

**[RuCl{PBu$^t$[$CH_2C$(OMe)=O]}$_2$-κ$^2$*P*,*O*,*O*}{PBu$^t$[$CH_2C$(OMe)=O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}]$PF_6$ 2.** A solution of compound **1** (244 mg, 0.38 mmol) in $CH_2Cl_2$ (20 $cm^3$) was cooled to −78 °C and then treated with $AgPF_6$ (96 mg, 0.38 mmol). After the reaction mixture was warmed to room temperature it was stirred for 1 h in the absence of light. A change from red to yellow occurred and a white solid (AgCl) precipitated. The solution was filtered with Celite, and the filtrate brought to dryness *in vacuo*. The remaining yellow solid was repeatedly washed with diethyl ether and dried: yield 280 mg (98%), decomp. 258 °C (Found: C, 32.30; H, 5.10. Calc. for $C_{20}H_{38}ClF_6O_8P_3Ru$: C, 32.05; H, 5.10%) Λ 67 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. IR (KBr): $\nu(CO)_{unco\text{-}ord}$ 1729, $\nu(CO)_{co\text{-}ord}$ 1635 and 1608, ν(PF) 842 $cm^{-1}$. NMR ($CD_2Cl_2$): $^1H$ (200 MHz), δ 5.20, 5.09, 4.86, 4.69 (all s, 12 H, $OCH_3$), 5.02–3.97 (m, 8 H, $PCH_2$), 2.34 [d, *J*(PH) 16.5, 9 H, $PCCH_3$] and 2.13 [d, *J*(PH) 15.0, 9 H, $PCCH_3$]; $^{13}C$ (50.3 MHz), δ 184.93 [d, *J*(PC) 12.0, $OCO_{co\text{-}ord}$], 184.03 [d, *J*(PC) 10.2, $OCO_{co\text{-}ord}$], 182.80 [d, *J*(PC) 9.2, $OCO_{co\text{-}ord}$], 168.53 [d, *J*(PC) 1.1, $OCO_{unco\text{-}ord}$], 56.80, 56.63, 56.56 and 52.79 (all s, $OCH_3$), 36.62 [d, *J*(PC) 25.9, $PCH_2$], 35.24 [d, *J*(PC) 27.8, $PCH_2$], 34.39 [d, *J*(PC) 26.8, $PCCH_3$], 34.00 [d, *J*(PC) 25.0, $PCH_2$], 30.50 [d, *J*(PC) 31.5, $PCCH_3$], 30.39 [d, *J*(PC) 31.5, $PCH_2$], 26.27 [d, *J*(PC) 3.7, $PCCH_3$] and 26.15 [d, *J*(PC) 4.6 Hz, $PCCH_3$]; $^{31}P$ (81.0 MHz), δ 77.6 and 73.3 [both d, *J*(PP) 34.9, 2 P, Bu$^t$P($CH_2CO_2Me$)$_2$] and −142.9 [spt, *J*(PF) 706.2 Hz, 1 P, $PF_6$].

**[RuCl{PBu$^t$[CH=C(OMe)O][$CH_2C$(OMe)=O]-κ$^3$*P*,*O*,*O*}-{PBu$^t$[$CH_2C$(OMe)=*O*](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}] 3.** A suspension of compound **2** (286 mg, 0.38 mmol) in toluene–Bu$^t$OH (20 $cm^3$, 1:1) was treated with KOBu$^t$ (43 mg, 0.38 mmol) and stirred for 1 h at room temperature. The solvent was removed *in vacuo*, and the residue extracted with diethyl ether (20 $cm^3$). After the extract was brought to dryness *in vacuo*, the remaining yellow solid was washed with pentane (0 °C) and dried: yield 147 mg (64%), decomp. 104 °C (Found: C, 39.60; H, 5.90. Calc. for $C_{20}H_{37}ClO_8P_2Ru$: C, 39.75; H, 6.20%). Mass spectrum (70 eV): *m*/*z* 604 ($M^+$). IR ($C_6H_6$): $\nu(CO)_{unco\text{-}ord}$ 1728, $\nu(CO)_{co\text{-}ord}$ 1648, ν(CO), ν(C=C) 1515 $cm^{-1}$. NMR ($C_6D_6$): $^1H$ (200 MHz), δ 4.36 [dd, *J*(HH) 17.1, *J*(PH) 10.8, 1 H, $PCH_2$], 4.05 [dd, *J*(HH) 14.4, *J*(PH) 13.0, 1 H, $PCH_2$], 3.71 [dd, *J*(HH) 15.6, *J*(PH) 7.0, 1 H, $PCH_2$], 3.59 [d, *J*(PH) 2.0, 1 H, PCH], 3.42 [dd, *J*(HH) 17.1, *J*(PH) 10.3, 1 H, $PCH_2$], 3.53, 3.30, 3.29 and 3.24 (all s, 12 H, $OCH_3$), 3.03–2.90 (m, 2 H, $PCH_2$), 1.10 and 1.07 [both d, *J*(PH) 14.6 Hz, 18 H, $PCCH_3$]; $^{13}C$ (100.6 MHz), δ 183.18 [d, *J*(PC) 7.7, $OCO_{co\text{-}ord}$], 182.06 [d, *J*(PC) 10.0, $OCO_{co\text{-}ord}$], 181.85 [d, *J*(PC) 8.3, $OCO_{co\text{-}ord}$], 169.53 [d, *J*(PC) 12.2, $OCO_{unco\text{-}ord}$], 54.38, 54.22 and 51.46 (all s, $OCH_3$), 52.01 [d, *J*(PC) 1.0, $OCH_3$], 50.32 [d, *J*(PC) 63.5, PCH], 39.06 [d, *J*(PC) 16.4, $PCH_2$], 35.52 [d, *J*(PC) 24.0, $PCH_2$], 34.92 [d, *J*(PC) 24.7, $PCCH_3$], 31.62 [d, *J*(PC) 12.6, $PCH_2$], 29.68 [d, *J*(PC) 40.7, $PCCH_3$], 26.81 [d, *J*(PC) 3.7, $PCCH_3$] and 26.21 [d, *J*(PC) 4.6 Hz, $PCCH_3$]; $^{31}P$ (81.0 MHz), δ 83.0 and 68.8 [both d, *J*(PP) 40.0 Hz].

**[RuCl(CO){PBu$^t$[CH=C(OMe)O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}{P-Bu$^t$[CH$_2$C(OMe)=O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}] 4.** A solution of compound **3** (50 mg, 0.08 mmol) in benzene (10 cm$^3$) was stirred for 20 min at room temperature under a carbon monoxide atmosphere. The solvent was removed *in vacuo*, the oily residue was dissolved in diethyl ether (2 cm$^3$) and hexane (10 cm$^3$) was added. After the solution was concentrated *in vacuo* to *ca.* 2 cm$^3$ a bright-yellow solid precipitated which was washed with pentane (0 °C) and dried: yield 44 mg (87%), decomp. 111 °C (Found: C, 39.65; H, 5.70. Calc. for $C_{21}H_{37}ClO_9P_2Ru$: C, 39.90; H, 5.90%). IR ($CH_2Cl_2$): ν(C≡O) 1950, ν(CO)$_{unco\text{-}ord}$ 1728, ν(CO)$_{co\text{-}ord}$ 1634, ν(CO), ν(C=C) 1509 cm$^{-1}$. NMR ($CDCl_3$, −20 °C): $^1$H (89.6 MHz), δ 3.92–2.90 (m, 7 H, $PCH_2$ and PCH), 3.79 (s, 3 H, $OCH_3$), 3.61 (s, 6 H, $OCH_3$), 3.39 (s, 3 H, $OCH_3$) and 1.32–1.15 (m, 18 H, $PCCH_3$]; $^{31}$P (36.2 MHz), δ 34.8 and 15.2 [AB system, *J*(PP) 308.5 Hz].

**[RuCl(CNMe)$_2${PBu$^t$[CH=C(OMe)O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}{PBu$^t$(CH$_2$CO$_2$Me)$_2$-κ*P*}] 5.** A solution of compound **3** (35 mg, 0.06 mmol) in benzene (10 cm$^3$) was treated with CNMe (4.8 mg, 0.12 mmol) and stirred for 24 h at room temperature. The solvent was removed *in vacuo*, the remaining pale yellow solid was washed with pentane (0 °C) and dried: yield 27 mg (68%), decomp. 140 °C (Found: C, 42.10; H, 6.40; N, 3.70. Calc. for $C_{24}H_{43}ClN_2O_8P_2Ru$: C, 42.00; H, 6.30; N, 4.10%). IR ($CH_2Cl_2$): ν(C≡N) 2140, ν(CO)$_{unco\text{-}ord}$ 1721, ν(CO), ν(C=C) 1516 cm$^{-1}$. NMR ($CDCl_3$): $^1$H (200 MHz), δ 3.84–3.36 (m, 7 H, $PCH_2$ and PCH), 3.50, 3.49, 3.42, 3.36 (all s, 12 H, $OCH_3$), 2.85 and 2.53 (both s, 6 H, $CNCH_3$), 1.51–1.33 (m, 18 H, $PCCH_3$); $^{31}$P (81.0 MHz), δ 38.5 and 37.6 [AB system, *J*(PP) 298.5 Hz].

**[RuCl{PBu$^t$[C(CONHPh)=C(OMe)O][CH$_2$C(OMe)=O]-κ$^3$*P*,*O*,*O*}{PBu$^t$[CH$_2$C(OMe)=O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}] 6.** A solution of compound **3** (55 mg, 0.09 mmol) in thf (10 cm$^3$) was treated with an excess of PhNCO (0.3 cm$^3$) and stirred for 30 min at room temperature. The solvent was removed *in vacuo*, the remaining ochre-yellow solid was repeatedly washed with hexane (0 °C) and dried: yield 50 mg (76%), decomp. 130 °C (Found: C, 45.05; H, 5.50; N, 2.35. Calc. for $C_{27}H_{42}ClNO_9P_2Ru$: C, 44.85; H, 5.85; N, 1.95%). Mass spectrum (70 eV): *m*/*z* 723 ($M^+$). IR (KBr): ν(NH) 3385, ν(CO)$_{unco\text{-}ord}$ 1720, ν(CO)$_{co\text{-}ord}$ 1631 cm$^{-1}$. NMR ($CDCl_3$): $^1$H (400 MHz), δ 8.69 (s, 1 H, NH), 7.48–6.95 (m, 5 H, $C_6H_5$), 4.31 (m, 1 H, $PCH_2$), 4.02 (m, 1 H, $PCH_2$), 3.50 (m, 3 H, $PCH_2$), 2.83 [d, *J*(HH) 14.7, 1 H, $PCH_2$], 4.10, 3.96, 3.70 and 3.66 (all s, 12 H, $OCH_3$), 1.35 [d, *J*(PH) 16.3, 9 H, $PCCH_3$] and 1.02 [d, *J*(PH) 14.5 Hz, 9 H, $PCCH_3$]; $^{13}$C (50.3 MHz), δ 183.97 [d, *J*(PC) 7.4, OCO$_{co\text{-}ord}$], 182.49 [d, *J*(PC) 10.2, OCO$_{co\text{-}ord}$], 177.43 [d, *J*(PC) 31.4, OCO$_{co\text{-}ord}$], 169.40 [d, *J*(PC) 13.0, OCO$_{unco\text{-}ord}$], 166.05 [s, C(O)N], 139.76, 130.44, 124.41, 120.55 (all s, $C_6H_5$), 71.99 [d, *J*(PC) 56.4, P*C*=C], 55.35, 55.04, 52.56 and 52.06 (all s, $OCH_3$), 35.85 [d, *J*(PC) 12.0, $PCH_2$], 35.35 [d, *J*(PC) 13.9, $PCH_2$], 34.51 [d, *J*(PC) 24.1, P*C*$CH_3$], 33.02 [d, *J*(PC) 37.0, P*C*$CH_3$], 30.69 [d, *J*(PC) 13.0, $PCH_2$], 28.93 [d, *J*(PC) 5.6, PC*C*$H_3$], 26.18 [d, *J*(PC) 4.6 Hz, PC*C*$H_3$]; $^{31}$P (81.0 MHz), δ 75.9 and 72.9 [both d, *J*(PP) 35.6 Hz].

**[RuCl{PBu$^t$[CH$_2$C(O)O][CH$_2$C(OMe)=O]-κ$^3$*P*,*O*,*O*}-{PBu$^t$[CH$_2$C(OMe)=O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}] 7.** A few drops of water were added to a solution of compound **3** (36 mg, 0.06 mmol) in thf (10 cm$^3$) and the mixture was stirred for 24 h at room temperature. The solvent was removed, the remaining bright-yellow solid was repeatedly washed with diethyl ether and dried: yield 30 mg (86%), decomp. 117 °C (Found: C, 38.70; H, 5.80. Calc. for $C_{19}H_{35}ClO_8P_2Ru$: C, 38.70; H, 6.00%). IR ($CH_2Cl_2$): ν(CO)$_{unco\text{-}ord}$ 1723, ν(CO)$_{co\text{-}ord}$ 1637 and 1617 cm$^{-1}$. NMR ($CDCl_3$): $^1$H (400 MHz), δ 4.10, 4.04, 3.66 (all s, 9 H, $OCH_3$), 3.44–2.45 (m, 8 H, $PCH_2$), 1.25 [d, *J*(PH) 15.3, 9 H, $PCCH_3$] and 1.12 [d, *J*(PH) 15.2 Hz, 9 H, $PCCH_3$]; $^{13}$C (100.6 MHz) δ 182.52 [d, *J*(PC) 11.6, OCO$_{co\text{-}ord}$], 181.34 [d, *J*(PC) 9.5, OCO$_{co\text{-}ord}$], 179.17 [d, *J*(PC) 8.9, OCO$_{co\text{-}ord}$], 168.96 [d, *J*(PC) 11.6, OCO$_{unco\text{-}ord}$], 55.76, 55.66 and 52.17 (all s, $OCH_3$), 36.30 [d, *J*(PC) 21.4, $PCH_2$], 34.96 [d, *J*(PC) 25.6, $PCH_2$], 34.61 [d, *J*(PC) 25.4, P*C*$CH_3$], 32.93 [d, *J*(PC) 24.1, $PCH_2$], 30.78 [d, *J*(PC) 14.4, $PCH_2$], 29.59 [d, *J*(PC) 28.9, P*C*$CH_3$], 26.30 [d, *J*(PC) 3.6, PC*C*$H_3$] and 25.95 [d, *J*(PC) 4.0, PC*C*$H_3$]; $^{31}$P (81.0 MHz), δ 79.4 and 66.3 [both d, *J*(PP) 37.5 Hz].

**[RuCl(CNBu$^t$)$_2${PBu$^t$[CH$_2$C(O)O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}-{PBu$^t$(CH$_2$CO$_2$Me)$_2$-κ*P*}] 8.** A solution of compound **3** (51 mg, 0.08 mmol) in benzene (10 cm$^3$) was treated with CNBu$^t$ (17.5 mg, 0.24 mmol) and a few drops of water, and the mixture was stirred for 12 h at room temperature. The solvent was removed *in vacuo*, the oily residue dissolved in thf (2 cm$^3$) and the solution chromatographed on $Al_2O_3$ (neutral, activity grade III). With thf a yellow fraction was eluted which was brought to dryness *in vacuo*. The oily residue was dissolved in diethyl ether (1 cm$^3$) and after addition of hexane (5 cm$^3$) a bright-yellow solid precipitated: yield 46 mg (71%), decomp. 156 °C (Found: C, 45.60; H, 6.95; N, 3.85. Calc. for $C_{29}H_{53}ClN_2O_8P_2Ru$: C, 46.05; H, 7.05; N, 3.70%). IR (KBr): ν(C≡N) 2105, ν(CO)$_{unco\text{-}ord}$ 1727, ν(CO)$_{co\text{-}ord}$ 1616 cm$^{-1}$. NMR ($CDCl_3$): $^1$H (400 MHz), δ 3.69, 3.66 and 3.65 (all s, 9 H, $OCH_3$), 3.69–2.78 (m, 8 H, $PCH_2$), 1.60 and 1.56 (both s, 18 H, $NCCH_3$), 1.34 and 1.28 [both d, *J*(PH) 13.7 Hz, 18 H, $PCCH_3$]; $^{13}$C (50.3 MHz), δ 179.59 [dd, *J*(PC) 12.0 and 5.6, OCO$_{co\text{-}ord}$] 169.88 [d, *J*(PC) 7.4, OCO$_{unco\text{-}ord}$], 169.61 [d, *J*(PC) 6.5, OCO$_{unco\text{-}ord}$], 169.50 [d, *J*(PC) 4.6 Hz, OCO$_{unco\text{-}ord}$), 57.76 and 57.34 (both s, N*C*$CH_3$), 52.10, 52.06 and 51.99 (all s, $OCH_3$), 34.80 and 33.24 (both m, P*C*$CH_3$), 31.35, 29.54, 28.06 and 27.73 (all m, $PCH_2$), 30.45 and 30.36 (both m, NC*C*$H_3$), 26.60 and 26.04 (both m, PC*C*$H_3$), signals of *C*NBu$^t$ not located; $^{31}$P (81.0 MHz), δ 41.1 and 38.1 [AB system, *J*(PP) 300.8 Hz].

**[RuCl(SPh){PBu$^t$[CH$_2$C(OMe)=O](CH$_2$CO$_2$Me)-κ$^2$*P*,*O*}$_2$] 9.** A solution of compound **3** (140 mg, 0.23 mmol) in toluene (10 cm$^3$) was cooled to −78 °C and then treated with PhSH (26 mg, 0.23 mmol). After the reaction mixture was warmed to room temperature it was stirred for 2 h. A change from yellow to orange-red occurred. The solvent was removed *in vacuo*, and the remaining orange solid washed with hexane (0 °C) and dried: yield 131 mg (79%), decomp. 61 °C (Found: C, 43.85; H, 6.05; Ru, 13.65; S, 4.20; Calc. for $C_{26}H_{43}ClO_8P_2RuS$: C, 43.75; H, 6.05; Ru, 14.15; S, 4.50%). IR (KBr): ν(CO)$_{unco\text{-}ord}$ 1718, ν(CO)$_{co\text{-}ord}$ 1634 cm$^{-1}$. NMR: $^1$H (400 MHz, $C_6D_6$), δ 7.51 (m, 2 H, $C_6H_5$), 6.81 (m, 3 H, $C_6H_5$), 4.07–3.72 (m, 4 H, $PCH_2$), 3.85, 3.59, 3.56 and 3.48 (all s, 12 H, $OCH_3$), 3.13–2.69 (m, 4 H, $PCH_2$), 1.13 and 1.09 [both d, *J*(PH) 14.1 Hz, 18 H, $PCCH_3$]; $^{13}$C (100.6 MHz, $CDCl_3$), δ 181.89 [d, *J*(PC) 11.0, OCO$_{co\text{-}ord}$], 181.52 [d, *J*(PC) 11.6, OCO$_{co\text{-}ord}$], 170.07 [d, *J*(PC) 9.6, OCO$_{unco\text{-}ord}$], 145.15, 134.15, 126.98, 122.60 (all s, $C_6H_5$), 55.04 and 51.96 (both s, $OCH_3$), 36.01 [d, *J*(PC) 28.4, $PCH_2$], 35.47 [d, *J*(PC) 25.0, $PCH_2$], 32.49 [d, *J*(PC) 17.0, $PCH_2$], 30.53 [d, *J*(PC) 18.3, $PCH_2$], 26.79 and 26.46 [d, *J*(PC) 3.5 Hz, PC*C*$H_3$], the signals of P*C*$CH_3$ accidently coincide with the $PCH_2$ signals; $^{31}$P (81.0 MHz, $C_6D_6$), δ 74.2 and 72.4 [AB system, *J*(PP) 39.7 Hz].

### Reaction of compound 3 with HCl

A slow stream of HCl was passed through a solution of compound **3** (27 mg, 0.04 mmol) in toluene (10 cm$^3$) for *ca.* 10 s at room temperature. A quick change from yellow to orange-red occurred. After the reaction mixture was stirred for 5 min the solvent was removed *in vacuo*. The $^1$H NMR spectrum of the red-brown residue confirmed that isomers **a**, **b** of complex **1** were formed in the ratio of 3:1.

**Table 1** Crystallographic data for compounds **1a** and **3***

| | **1a** | **3** |
|---|---|---|
| Formula | $C_{20}H_{38}Cl_2O_8P_2Ru$ | $C_{20}H_{37}ClO_8P_2Ru$ |
| $M$ | 640.44 | 603.98 |
| Crystal size/mm | 0.2 × 0.25 × 0.45 | 0.13 × 0.20 × 0.40 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) |
| For cell dimensions | 23 reflections, $10 < \theta < 13°$ | 23 reflections, $10 < \theta < 12°$ |
| $a$/Å | 15.125(9) | 10.457(3) |
| $b$/Å | 9.897(3) | 10.816(4) |
| $c$/Å | 20.43(1) | 12.604(4) |
| $\alpha$/° | | 73.61(3) |
| $\beta$/° | 111.3(2) | 82.53(2) |
| $\gamma$/° | | 84.80(3) |
| $U$/Å$^3$ | 2850(3) | 1354(1) |
| $Z$ | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.50 | 1.48 |
| $\mu$/cm$^{-1}$ | 9.3 | 8.2 |
| $2\theta_{max}$/° | 48 | 52 |
| Total reflections scanned | 4962 | 5617 |
| Unique reflections | 4564 | 4999 |
| Observed reflections [$F_o > 3\sigma(F_o)$] | 4046 | 3818 |
| $R$ | 0.061 | 0.036 |
| $R'$ | 0.082 | 0.040 |
| Parameters | 298 | 329 |
| Reflection/parameter ratio | 13.58 | 11.60 |
| Residual electron density/e Å$^{-3}$ | +1.30, −1.11 | +0.75, −0.82 |

* The positions of all hydrogen atoms were calculated according to an ideal geometry ($d_{CH}$ = 0.95 Å) and were used only in structure-factor calculations. Details in common: Enraf-Nonius CAD4 diffractometer; zirconium filtered (factors 16.4 and 15.4), graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ 0.709 30 Å); 20 ± 1 °C; $\omega$–$\theta$ scans; $w = 1/\sigma^2$ where $\sigma = \sigma(F_o)$.

**Table 2** Positional parameters for compound **1a** and their estimated standard deviations (e.s.d.s)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru | −0.006 01(5) | 0.038 97(8) | 0.239 04(3) |
| Cl(1) | −0.104 8(2) | 0.232 2(3) | 0.233 7(1) |
| Cl(2) | 0.080 9(2) | −0.152 4(3) | 0.221 5(1) |
| P(1) | −0.073 7(1) | −0.059 2(2) | 0.308 7(1) |
| P(2) | 0.134 2(1) | 0.125 7(2) | 0.307 9(1) |
| O(1) | −0.132 9(4) | −0.043 2(8) | 0.156 2(3) |
| O(2) | 0.034 2(4) | 0.130 7(8) | 0.156 5(3) |
| O(3) | −0.130 0(5) | 0.007 6(9) | 0.478 2(3) |
| O(4) | 0.362 3(5) | 0.036(1) | 0.468 1(4) |
| O(5) | −0.280 7(5) | −0.117 9(8) | 0.128 2(3) |
| O(6) | 0.151 4(5) | 0.190 6(9) | 0.121 8(3) |
| O(7) | −0.236 1(4) | 0.019 5(9) | 0.369 9(3) |
| O(8) | 0.356 9(4) | 0.031 8(8) | 0.359 5(3) |
| C(1) | −0.199 3(6) | −0.073(1) | 0.173 3(5) |
| C(2) | 0.117 5(6) | 0.153(1) | 0.169 6(4) |
| C(3) | −0.148 4(6) | 0.020(1) | 0.416 2(5) |
| C(4) | 0.317 1(6) | 0.027(1) | 0.406 3(5) |
| C(5) | −0.199 0(6) | −0.062 0(9) | 0.246 3(5) |
| C(6) | 0.193 8(6) | 0.141(1) | 0.242 8(4) |
| C(7) | −0.076 6(6) | 0.043(1) | 0.383 2(4) |
| C(8) | 0.211 9(6) | 0.011(1) | 0.375 6(5) |
| C(9) | −0.287(1) | −0.124(2) | 0.056 0(5) |
| C(10) | 0.084(1) | 0.191(2) | 0.051 0(6) |
| C(11) | −0.311 7(7) | −0.003(2) | 0.396 4(6) |
| C(12) | 0.458 6(7) | 0.049(1) | 0.383 7(6) |
| C(13) | −0.052 8(6) | −0.236(1) | 0.340 7(5) |
| C(14) | 0.150 2(6) | 0.296 3(9) | 0.348 1(5) |
| C(15) | −0.110 8(8) | −0.275(1) | 0.385 4(5) |
| C(16) | −0.083 6(7) | −0.328(1) | 0.275 4(5) |
| C(17) | 0.053 2(8) | −0.255(1) | 0.383 6(6) |
| C(18) | 0.093 6(7) | 0.304(1) | 0.397 7(5) |
| C(19) | 0.112 6(8) | 0.399(1) | 0.289 4(5) |
| C(20) | 0.254 6(8) | 0.328(1) | 0.389 4(6) |

**Table 3** Positional parameters for compound **3** and their e.s.d.s

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru | 0.238 27(4) | 0.272 72(3) | 0.354 07(3) |
| Cl | 0.038 7(1) | 0.240 6(1) | 0.473 1(1) |
| P(1) | 0.209 1(1) | 0.485 2(1) | 0.284 47(9) |
| P(2) | 0.164 0(1) | 0.176 0(1) | 0.242 18(9) |
| O(1) | 0.423 5(3) | 0.303 6(3) | 0.267 1(3) |
| O(2) | 0.314 8(3) | 0.333 0(3) | 0.482 9(2) |
| O(3) | 0.306 5(3) | 0.072 7(3) | 0.435 0(3) |
| O(4) | 0.564 6(4) | 0.445 9(4) | 0.159 8(3) |
| O(5) | 0.330 1(4) | 0.487 7(3) | 0.564 3(3) |
| O(6) | 0.300 2(4) | −0.135 9(3) | 0.445 2(3) |
| O(7) | −0.115 3(5) | 0.113 2(5) | 0.107 0(3) |
| O(8) | −0.129 9(4) | 0.039 3(4) | 0.290 2(3) |
| C(1) | 0.357 7(5) | 0.524 3(4) | 0.205 9(4) |
| C(2) | 0.443 5(5) | 0.422 2(5) | 0.213 4(4) |
| C(3) | 0.653 0(7) | 0.339 6(7) | 0.156 0(6) |
| C(4) | 0.206 3(5) | 0.539 1(4) | 0.413 0(4) |
| C(5) | 0.287 6(5) | 0.444 1(5) | 0.488 0(4) |
| C(6) | 0.402 4(6) | 0.395 7(6) | 0.644 2(4) |
| C(7) | 0.080 6(5) | 0.592 2(4) | 0.212 1(4) |
| C(8) | 0.107 5(6) | 0.733 7(5) | 0.194 8(5) |
| C(9) | −0.051 4(5) | 0.565 2(6) | 0.280 7(5) |
| C(10) | 0.079 0(6) | 0.567 6(5) | 0.098 8(4) |
| C(11) | 0.156 2(5) | 0.010 4(4) | 0.334 6(4) |
| C(12) | 0.261 4(5) | −0.013 7(4) | 0.409 1(4) |
| C(13) | 0.394 9(6) | −0.165 3(6) | 0.522 6(5) |
| C(14) | −0.004 5(5) | 0.216 4(4) | 0.209 6(4) |
| C(15) | −0.085 7(5) | 0.116 7(5) | 0.193 3(4) |
| C(16) | −0.211 3(6) | −0.059 4(6) | 0.285 5(5) |
| C(17) | 0.262 7(5) | 0.155 7(5) | 0.112 5(4) |
| C(18) | 0.289 7(6) | 0.289 3(5) | 0.034 6(4) |
| C(19) | 0.389 3(6) | 0.083 6(6) | 0.146 2(5) |
| C(20) | 0.195 3(7) | 0.080 5(5) | 0.050 7(4) |
| H(1) | 0.375(6) | 0.605(6) | 0.166(5) |

### Structure determinations of compounds 1a and 3

Single crystals of compound **1a** were grown from $CH_2Cl_2$–hexane and those of **3** from $Et_2O$. Crystal-data-collection parameters are summarized in Table 1. All calculations were performed on a Micro-VAX computer using the program package SDP.[17] Intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (**1a**) or by the Patterson method (**3**), respectively (SHELXS 86).[18] Atomic coordinates (Tables 2 and 3) and

anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of the hydrogen atoms [with exception of H(1) in **3**] were calculated according to ideal geometry (C–H 0.95 Å) and were taken for the structure-factor calculation (**1a**). In the case of **3** the hydrogen atoms were refined by the riding method.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59071, the names of the authors, and the journal citation.

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## References

1 W. Keim, *J. Mol. Catal.*, 1989, **52**, 19; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235; G. J. P. Britovsek, W. Keim, S. Mecking, D. Sainz and T. Wagner, *J. Chem. Soc., Chem. Commun.*, 1993, 1632; W. Keim, H. Maas and S. Mecking, *Z. Naturforsch., Teil B*, 1995, **50**, 430.

2 E. Lindner, S. Meyer, P. Wegner, B. Karle, A. Sickinger and B. Steger, *J. Organomet. Chem.*, 1987, **335**, 59; P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. De Cian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1994, 2203; D. Matt, M. Huhn, M. Bonnet, I. Tkatchenko, U. Englert and W. Kläui, *Inorg. Chem.*, 1995, **34**, 1288.

3 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.

4 J. C. Jeffrey and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, 2658; P. Braunstein, T. M. G. Carneiro, D. Matt, F. Balegroune and D. Grandjean, *Organometallics*, 1989, **8**, 1737; H. Werner, A. Hampp, K. Peters, L. Walz and H. G. von Schnering, *Z. Naturforsch., Teil B*, 1990, **45**, 1548; M. Schulz and H. Werner, *Organometallics*, 1992, **11**, 2790; E. Lindner, A. Möckel, H. A. Mayer, H. Kühbauch, R. Fawzi and M. Steimann, *Inorg. Chem.*, 1993, **32**, 1266; B. Demersemann, R. Le Lagadec, B. Guilbert, C. Renouard, P. Crochet and P. H. Dixneuf, *Organometallics*, 1994, **13**, 2269; B. Weber, P. Steinert, B. Windmüller, J. Wolf and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1994, 2595.

5 E. Lindner, H. A. Mayer and P. Wegner, *Chem. Ber.*, 1986, **119**, 2619.

6 W. Wolfsberger, W. Burkart, S. Bauer, A. Hampp, J. Wolf and H. Werner, *Z. Naturforsch., Teil B*, 1994, **49**, 1659.

7 L. M. Wilkes, J. H. Nelson, J. P. Mitchener, M. W. Babich, W. C. Riley, B. J. Helland, R. A. Jacobson, M. Y. Cheng, K. Seff and L. B. McCusker, *Inorg. Chem.*, 1982, **21**, 1376; P. Braunstein, D. Matt and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 2043; E. Lindner, U. Schober, R. Fawzi, W. Hiller, U. Englert and P. Wegner, *Chem. Ber.*, 1987, **120**, 1621.

8 H. Werner, A. Stark, M. Schulz and J. Wolf, *Organometallics*, 1992, **11**, 1126; H. Werner, A. Stark, P. Steinert, C. Grünwald and J. Wolf, *Chem. Ber.*, 1995, **128**, 49.

9 E. Keller, SCHAKAL 92, a Fortran Program for the Graphic Representation of Molecular and Crystallographic Models, University of Freiburg, 1992.

10 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**, 5115.

11 E. M. Georgiev, H. tom Dieck, G. Fendesak, G. Hahn, G. Petrov and M. Kirilov, *J. Chem. Soc., Dalton Trans.*, 1992, 1311.

12 P. Braunstein, Y. Chauvin, J. Nähring, Y. Dusausoy, D. Bayeul, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc., Dalton Trans.*, 1995, 851.

13 (*a*) S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1988, **27**, 2279; (*b*) P. Braunstein and D. Nobel, *Chem. Rev.*, 1989, **89**, 1927.

14 P. Steinert and H. Werner, *Organometallics*, 1994, **13**, 2677.

15 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.

16 R. E. Schuster, J. E. Scott and J. Casanova, jun., *Org. Synth.*, 1973, Coll. Vol. V, 772.

17 B. A. Frenz, The Enraf-Nonius CAD 4 SDP, a real time system for concurrent X-ray data collection and structure determination, in *Computing in Crystallography*, Delft University Press, Delft, 1978; pp. 64–71.

18 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986.

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