Phosphinomethanide *versus* phosphinoenolate: thermodynamical preference for a three- instead of a five-membered chelate ring

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The phosphinoenolate complex 4, which is prepared stepwise from [(mes)RuCl$_2$]$_2$ 1 *via* the neutral and cationic compounds 2 and 3 as isolated intermediates, rearranges slowly in benzene to the thermodynamically more stable phosphinomethanide isomer 5; the presence of a three-membered RuCP ring in the latter is confirmed by X-ray crystallography.

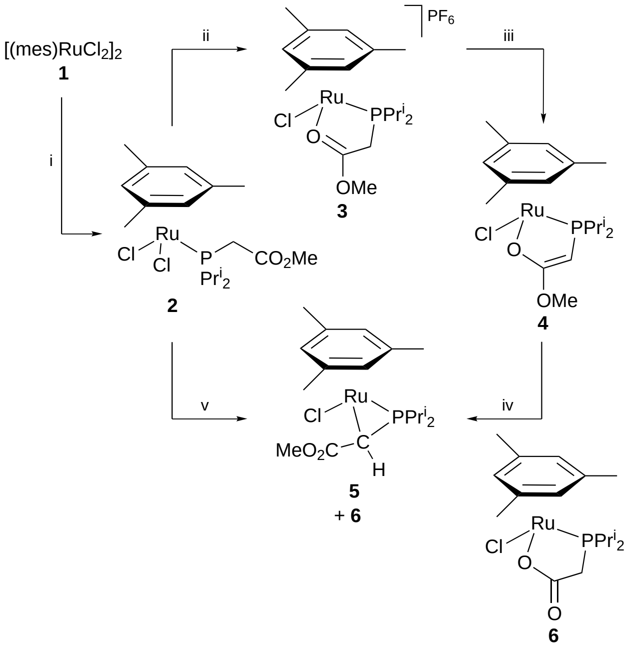
Following the development of the Shell Higher Olefin Process (SHOP),[1] the chemistry of phosphinoenolate metal complexes has become a focus of general interest.[2] While it has been shown by numerous examples that both β-phosphinoketones and β-phosphinoesters are easily converted to ligands of general composition $R_2PCH{=}C(R)O^-$ in the coordination sphere of transition metals,[3] we discovered more recently that from functional phosphines such as $Pr^i_2PCH_2CO_2R$ (R = Me, Et) phosphinomethanide units $Pr^i_2PCHCO_2R^-$ can also be generated.[4] However, it was not known which of the isomeric forms $Pr^i_2PCH{=}C(OR)O^-$ and $Pr^i_2PCHCO_2R^-$, the first forming a five-membered and the second a three-membered chelate ring, is more stable in a particular metal–ligand environment and whether the two types of ligands can be transformed into each other.

The half-sandwich-type complex **2**, which by analogy to previous work[5] was prepared from **1** and $Pr^i_2PCH_2CO_2Me$, reacts with an equimolar amount of $AgPF_6$ in CH_2Cl_2 to give the chelate compound **3** (Scheme 1) in almost quantitative yield.† The IR spectrum of the orange–red, nearly air-stable solid displays a C=O stretching frequency at 1618 cm^{-1} (in CH_2Cl_2), which is lower by about 110 cm^{-1} if compared with the frequency of $Pr^i_2PCH_2CO_2Me$.[6] This supports the assumption that the functional phosphine is coordinated *via* phosphorus and oxygen to the metal.

Treatment of the PF_6^- salt **3** with $KOBu^t$ in THF led to a rapid change of colour from deep red to bright red and gave, after recrystallization from CH_2Cl_2–hexane (1 : 3), the phosphinoenolate complex **4** in 78% yield. The most characteristic features of the NMR spectroscopic data of **4** are the signal at δ 3.19 [*J*(PH) 3.7 Hz] for the vinylic proton and the two resonances at δ 180.5 (CO_2) and 44.5 (=CH) for the carbon atoms of the chelate ring, which display a strong P–C coupling of 28.6 and 70.6 Hz, respectively.

While phosphinoenolate complexes, such as those used for the oligomerization and polymerization of alkenes,[1,7] seem to be quite stable, compound **4** is thermally labile and slowly rearranges in benzene at room temp. to isomer **5**. After 3 d the reaction is complete. There is, to the best of our knowledge, no precedence for this type of isomerisation process which is probably driven by the conversion of the C=C double into a C–C single bond and the re-formation of the intact CO_2Me unit. The IR spectrum of **5** (in KBr) displays a C=O stretch at 1661 cm^{-1}, the ^{1}H NMR spectrum a doublet at δ 2.71 [*J*(PH) 3.1 Hz] for the C*H*CO$_2$Me proton and the ^{13}C NMR spectrum a singlet at δ 10.0 for the carbon atom of the RuPC three-membered ring.

The X-ray crystal structure analysis of **5** (Fig. 1) confirmed the structural proposal outlined in Scheme 1.‡ The ruthenium is coordinated by the mesitylene ring, one chloride and the P,C-



Scheme 1 *Reagents and conditions*: i, $Pr^i_2PCH_2CO_2Me$, CH_2Cl_2, 25 °C, 3 h, 91%; ii, $AgPF_6$, CH_2Cl_2, 25 °C, 45 min, 90%; iii, $KOBu^t$, THF, 25 °C, 15 min, 78%; iv, C_6H_6, 25 °C, 3 d, 88%; v, Al_2O_3/NaH, THF, 25 °C, 45 min, 15% (for **5**) and 80% (for **6**)

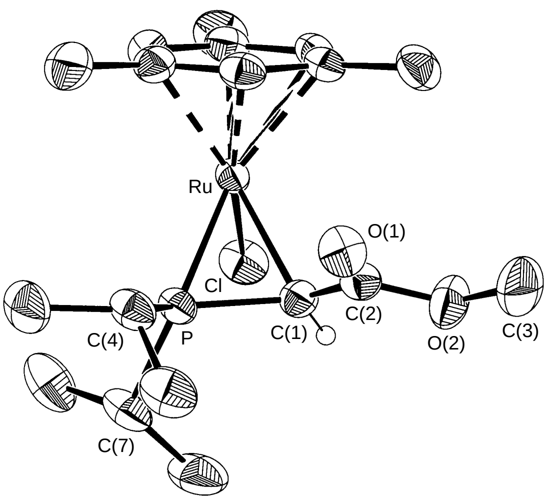


Fig. 1 Molecular structure (ORTEP drawing) of **5**. Selected bond distances (Å) and angles (°): Ru–P 2.269(1), Ru–Cl 2.410(1), Ru–C(1) 2.201(2), P–C(1) 1.761(2), P–C(4) 1.832(2), P–C(7) 1.847(2), C(1)–C(2) 1.455(3), C(2)–O(1) 1.208(3), C(2)–O(2) 1.363(3); P–Ru–Cl 88.97(3), P–Ru–C(1) 46.37(6), C(1)–Ru–Cl 84.97(6), Ru–P–C(1) 64.77(7), Ru–C(1)–P 68.86(7), P–C(1)–C(2) 125.5(2), Ru–C(1)–C(2) 116.5(1), C(1)–C(2)–O(1) 128.6(2), C(1)–C(2)–O(2) 110.0(2), O(1)–C(2)–O(2) 121.3(2).

bonded phosphinomethanide ligand, the CO_2Me substituent of which is pointing away from the Ru–Cl axis. The bond angles of the three-membered ring are comparable to those found in the osmium analogue of **5**[4] and in various [$L_nM\{\kappa^2$(P,C)-$Ph_2PCH_2\}$] complexes.[8] The distance P–C(1) is shorter by *ca.* 0.08 Å than the distances P–C(4) and P–C(7) indicating a substantial double-bond character of the phosphorus–carbon bond in the RuCP unit.

The phosphinomethanide and not the isomeric phosphinoenolate compound is also formed, although as the minor component, on treatment of **2** with Al_2O_3/NaH in THF (Scheme 1). The main product of this reaction is the phosphinocarboxylate complex **6**, which has been characterized by elemental analysis and spectroscopic techniques. Both the IR and ^1H NMR data are similar to those of [(mes)RuCl$\{\kappa^2$(P,O)-$Ph_2PCH_2C(O)O\}$], obtained by acid hydrolysis of [(mes)-$RuCl_2(Ph_2PCH_2CO_2Bu^t)$] (mes = $C_6H_3Me_3$-1,3,5).[9] We note that in contrast to **2**, the related osmium compound [(mes)-$OsCl_2(Pr^i{}_2PCH_2CO_2Me)$] reacts with Al_2O_3/NaH in THF to give the corresponding phosphinomethanide complex [(mes)-OsCl$\{\kappa^2$(P,O)-$Pr^i{}_2PCHCO_2Me\}$] almost quantitatively.[4]

In conclusion, the present work has shown that, in connection with [(mes)RuCl] as a building block, a three-membered chelate ring of a phosphinomethanide complex is thermodynamically more stable than a five-membered ring of the phosphinoenolate metal isomer. At present, we are investigating whether an analogous isomerisation (as that of **4** to **5**) also occurs if the CH fragment of the $RuOC_2P$ five-membered ring is replaced, *e.g.* by a CC(O)NHR unit which is formed by insertion of an isocyanate into the C–H bond.[2a]

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Footnotes and References

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† All new compounds gave satisfactory elemental analyses. **2**: orange–red solid, mp 160 °C (decomp.). **3**: orange–red solid, mp 89 °C (decomp.), equiv. conductivity (CH_3NO_2) Λ 68 cm^2 Ω^{-1} mol^{-1}. **4**: light red solid, mp 85 °C (decomp.). **5**: yellow crystals, mp 174 °C. **6**: pale yellow solid, mp 198 °C.

‡ *Crystal data* for **5**: crystals from hexane; $C_{18}H_{30}ClO_2PRu$, $M = 445.91$; monoclinic, space group $P2_1/n$ (no. 14), $Z = 4$, $a = 9.195(3)$, $b = 15.398(3)$, $c = 14.193(5)$ Å, $\beta = 94.69(2)°$, $U = 2002.7(10)$ Å^3; $D_c = 1.479$ g cm^{-3}; $T = 293(2)$ K; max $2\theta = 48°$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). 3117 unique data were obtained and 2776 of these with $I > 2\sigma(I)$ were used in the refinement; $R_1 = 0.0178$, $wR_2 = 0.0522$ [$I > 2\sigma(I)$]; $R_1 = 0.0251$, $wR_2 = 0.0726$ (all data); reflection/parameter ratio 14.15; residual electron density 0.245/−0.212. CCDC 182/637.

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