

Preliminary Communication

The preparation and reactions of $(\eta^3\text{-allyl})_2\text{Ru}[\text{Pr}_2^i\text{P}(\text{CH}_2)_n\text{PPr}_2^i]$ complexes

S. Holle, P.W. Jolly*, J. Kuhnigk

Max-Planck-Institut für Kohlenforschung, D-45466 Mülheim an der Ruhr, Germany

Received 7 March 1997

Abstract

The title compounds have been prepared either by reacting $(\text{cod})(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Ru}$ with the appropriate bisphosphine or $\text{Ru}(\text{Pr}_2^i\text{P}(\text{CH}_2)_n\text{PPr}_2^i)\text{Cl}_2$ with allylmagnesium chloride. In contrast to the analogous iron compounds, the $\eta^3\text{-allyl-Ru}$ compounds react with 1,5-hexadiene to give $(\eta^5\text{-1-hexadienyl})\text{RuH}$ complexes irrespective of the length of the methylene chain joining the two P atoms in the bidentate ligand. The $\eta^3\text{-C}_3\text{H}_5$ -containing compounds react more selectively than the $\eta^3\text{-2-MeC}_3\text{H}_4$ -containing compounds and the product of the reaction of the former with acetic acid has been shown by X-ray crystallography to be the ionic complex $[\text{Ru}(\text{Pr}_2^i\text{PC}_2\text{H}_4\text{PPr}_2^i)_2\text{OAc}]^+\text{OAc}^-$. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; $\eta^3\text{-allyl}$; $\eta^5\text{-1-hexadienyl}$; Acetate

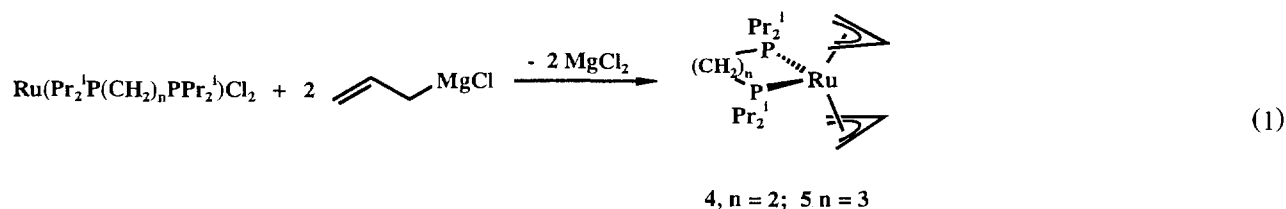
Although organometallic complexes of ruthenium are currently attracting increasing attention as catalyst-precursors for a variety of organic syntheses [1] the application of $(\eta^3\text{-allyl})_2\text{RuL}_2$ species, which might be anticipated to be a convenient source of the $\text{L}_2\text{Ru}(0)$ moiety through coupling of the two allyl groups, is limited to hydrogenation [2–7] and the addition of carboxylic acids to alkynes [8–10]. The ruthenium species investigated generally involve bidentate ligands containing aryl-substituted P atoms, e.g. binap, $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$. We were interested in preparing compounds containing alkyl-substituted bidentate phosphines since related investigations involving iron had shown that the chemistry of the $(\text{Pr}_2^i\text{P}(\text{CH}_2)_n\text{PPr}_2^i)\text{Fe}(0)$ species is dictated by steric effects which are influenced by the length of the methylene chain joining the two P atoms [11–13].

The ruthenium compounds studied previously have almost invariably involved the $\eta^3\text{-2-MeC}_3\text{H}_4$ group and we decided to attempt to prepare analogous compounds containing the $\eta^3\text{-C}_3\text{H}_5$ group in the anticipation that these might be more reactive. As far as we are aware, the only known examples of this class of compound are $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{PPh}_3)_2$ [14] and $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{CO})_2$ [15,16] and no compounds have been reported containing bidentate ligands.

The $\eta^3\text{-2-MeC}_3\text{H}_4$ -containing compounds are in general prepared by reacting $(\text{cod})(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Ru}$ with the appropriate ligand [2–10,15,17,18] and we have also used this route to prepare $(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Ru}(\text{Pr}_2^i\text{P}(\text{CH}_2)_n\text{PPr}_2^i)$ (**1**, $n = 1$; **2**, $n = 2$; **3**, $n = 3$) [19]. However, this approach does not give satisfactory results when applied to the $\eta^3\text{-C}_3\text{H}_5$ -stabilized species – mainly because $(\text{cod})(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}$ is less easy to prepare and manipulate [20] – and examples of these compounds (**4**, **5**) have been prepared by reacting $(\text{cod})\text{RuCl}_2$ [21] with the bisphosphine in

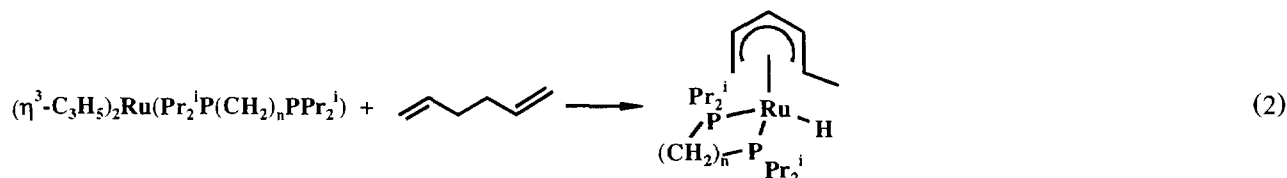
* Corresponding author. Fax: +49-208-3062980.

refluxing ethanol to give $[\text{Ru}(\text{Pr}_2^i\text{P}(\text{CH}_2)_n\text{PPr}_2^i)\text{Cl}_2]_2$ followed by treatment with allylmagnesium chloride [22] Eq. (1).



The NMR spectra of both the η^3 -2-MeC₃H₄ and η^3 -C₃H₅-containing compounds **1–5** [19,22] indicate that in solution they all have the same pseudo-tetrahedral geometry, with the meso-C atoms of the allyl groups pointing away from the metal atom (C₂-symmetry), which has been observed for the related Fe compounds [11] and which has been confirmed by X-ray diffraction for $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{PPh}_3)_2$ [14].

In contrast to the analogous reaction involving iron, we have observed no significant difference in the behaviour of the η^3 -C₃H₅-Ru compounds stabilized by bis(diisopropylphosphino)ethane (dippe) or bis(diisopropylphosphino)propane (dipp) with 1,5-hexadiene: in both cases $(\eta^5$ -1-hexadienyl)RuH-species are formed [23] Eq. (2).



The product of the analogous reaction with iron is either $(\eta^{2,2}$ -1,5-hexadiene)Fe(dipp) or $(\eta^5$ -1-hexadienyl)Fe(dippe)H [12,13]. We attribute this difference in behaviour to the larger size of the Ru atom which reduces the significance of steric effects associated from the metal-bonded bidentate ligand.

Although the η^3 -C₃H₅-Ru complexes (**4**, **5**) are not obviously more reactive than the corresponding η^3 -2-MeC₃H₄-Ru complexes (**1–3**), they do react in a more selective manner. For example, the reaction of 1,5-hexadiene with $(\eta^3$ -2-MeC₃H₄)₂Ru(PrⁱPC₃H₆PPrⁱ) leads to a complex mixture of products while the same species react with

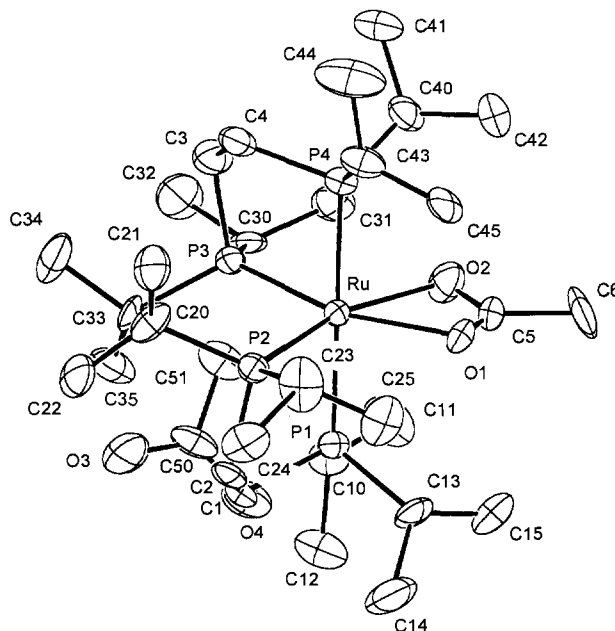
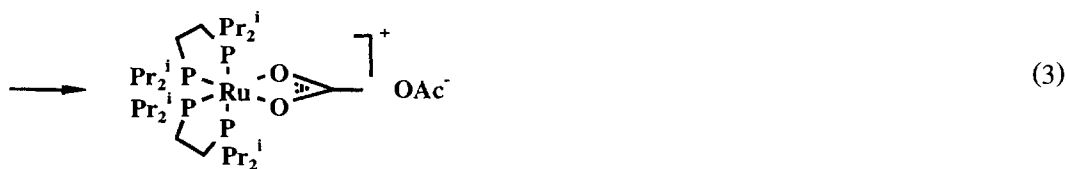
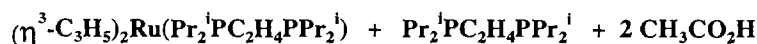


Fig. 1. The molecular structure of $[\text{Ru}(\text{Pr}_2^i\text{PC}_2\text{H}_4\text{PPr}_2^i)_2\text{OAc}]^+\text{OAc}^-$ (**6**). Selected interatomic distances (Å) and angles (deg): Ru–P1 2.385(4), Ru–P2 2.316(3), Ru–P3 2.331(3), Ru–P4 2.396(4), Ru–O1 2.220(8), Ru–O2 2.234(9), O1–C5 1.18(1), O2–C5 1.32(1), P1–Ru–P4 179.6(1), P1–Ru–P2 83.6(1), P3–Ru–P4 83.5(1), P1–Ru–P3 96.7(1), P1–Ru–O2 91.2(2), O1–Ru–P1 89.7(2), O1–Ru–O2 58.5(3), O1–C5–O2 120.6(7).

acetic acid and one equivalent of bisphosphine to give a mixture of mono- and bis-acetate–Ru species. In contrast $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{Pr}_2^i\text{P}(\text{CH}_2)_n\text{PPr}_2^i)$ reacts to give the ionic compound $[\text{Ru}(\text{Pr}_2^i\text{P}(\text{CH}_2)_n\text{PPr}_2^i)_2\text{OAc}]^+\text{OAc}^-$ (**6**, $n = 2$) in high yield [24] Eq. (3).



6

The ionic nature of **6** has been confirmed by a crystal structure determination [25] and the molecular structure is shown in Fig. 1. The Ru atom lies at the centre of a distorted octahedron and is bonded to the P atoms of the bidentate ligands and to the O atoms of the chelating acetate group. The structure is similar to that observed for $[\text{Ru}(\text{PPh}_2\text{Me})_4\text{OAc}]^+\text{PF}_6^-$ [26], $[\text{Ru}(\text{PMe}_2\text{Ph})_4\text{OAc}]^+\text{PF}_6^-$ [27], $[\text{Ru}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{OAc}]^+\text{BPh}_4^-$ [28] and $[\text{Ru}(\text{PPh}_3)_2(\text{NCMe})_2\text{OAc}]^+\text{ClO}_4^-$ [29] with the P–Ru bonds *cis* to the O-atoms significantly longer (Ru–P1/P2 2.39 Å) than those in a *trans* position (Ru–P2/P3 2.32 Å).

References

- [1] B.M. Trost, *Angew. Chem.* 107 (1995) 285.
- [2] J.P. Genêt, S. Mallart, C. Pinel, S. Juge, J.A. Laffitte, *Tetrahedron: Asymmetry* 2 (1991) 43.
- [3] J.P. Genêt, C. Pinel, S. Mallart, S. Juge, S. Thorimbert, J.A. Laffitte, *Tetrahedron: Asymmetry* 2 (1991) 555.
- [4] J.P. Genêt, S. Juge, J.A. Laffitte, C. Pinel, S. Mallart, *Soc. Nat. Elf. Aquitaine, Fr. Demande FR 2,671,079* (1992); *Chem. Abs.* 118 (1993) 146948s.
- [5] J.P. Genêt, C. Pinel, S. Mallart, S. Juge, N. Cailhol, J.A. Laffitte, *Tetrahedron Lett.* 33 (1992) 5343.
- [6] J.P. Genêt, X. Pfister, V. Ratovelomanana-Vidal, C. Pinel, J.A. Laffitte, *Tetrahedron Lett.* 35 (1994) 4559.
- [7] J.P. Genêt, *Acros Organics Acta* 1 (1995) 4.
- [8] J. Höfer, H. Doucet, C. Bruneau, P.H. Dixneuf, *Tetrahedron Lett.* 32 (1991) 7409.
- [9] H. Doucet, B. Martin-Vaca, C. Bruneau, P.H. Dixneuf, *J. Org. Chem.* 60 (1995) 7247.
- [10] H. Doucet, J. Höfer, N. Derrien, C. Bruneau, P.H. Dixneuf, *Bull. Soc. Chim. Fr.* 133 (1996) 939.
- [11] B. Gabor, S. Holle, P.W. Jolly, R. Mynott, *J. Organometal. Chem.* 466 (1994) 201.
- [12] B. Gabor, R. Goddard, S. Holle, P.W. Jolly, C. Krüger, R. Mynott, W. Wisniewski, *Z. Naturforsch. B* 50 (1995) 503.
- [13] S. Geier, R. Goddard, S. Holle, P.W. Jolly, C. Krüger, F. Lutz, *Organometallics* 16 (1997) 1612.
- [14] A.E. Smith, *Inorg. Chem.* 11 (1972) 2306.
- [15] M. Cooke, R.J. Goodfellow, M. Green, G. Parker, *J. Chem. Soc. A* (1971) 16.
- [16] E.W. Abel, S. Moorhouse, *J. Chem. Soc., Dalton Trans.* (1973) 1706.
- [17] J. Powell, B.L. Shaw, *J. Chem. Soc. A* (1968) 159.
- [18] J.P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, S. Mallart, X. Pfister, M.C. Cano de Andrade, J.A. Laffitte, *Tetrahedron: Asymmetry* 5 (1994) 665.
- [19] $(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Ru}(\text{Pr}_2^i\text{PCH}_2\text{PPr}_2^i)$ (**1**). Prepared by reacting $(\text{cod})(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Ru}$ with the bidentate ligand in refluxing hexane for 8 h. Yield 57%. Satisfactory elemental analyses have been obtained for all compounds reported. MS (80°C): m/e 460 (M^+). IR (KBr): ν 3060, 1365. ^{31}P NMR (d_8 -toluene): δ 15.5. ^1H NMR (d_8 -toluene): δ 2.83 (m, H-3 syn), 2.09 (s, 2-Me)–2-MeC₃H₄; 2.93, 1.9, 1.6, 1.2–0.8 (dippm). ^{13}C NMR (d_8 -toluene): δ 93.44 (C-2), 35.31 (C-3, *J*(P,C) 20.0), 32.21 (C-1, *J*(P,C) 6.1), 26.09 (Me)–2-MeC₃H₄; 37.97 (*J*(P,C) 12.5), 29.38 (*J*(P,C) 15.7), 26.72 (*J*(P,C) 7.9), 20.75, 20.17, 19.86, 18.80 – dippm. $(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Ru}(\text{Pr}_2^i\text{PC}_2\text{H}_4\text{PPr}_2^i)$ (**2**). Prepared as described above in 61% yield. MS (80°C): m/e 474 (M^+). IR (KBr): ν 3070. ^{31}P NMR (d_8 -toluene): δ 72.21. ^1H NMR (d_8 -toluene): δ 2.16 (2-Me)–2-MeC₃H₄; 2.13, 1.97, 1.80, 1.28, 1.13, 0.89 (2-MeC₃H₄/dippe). ^{13}C NMR (d_8 -toluene): δ 92.93 (C-2), 35.93/35.57 (C-3, *J*(C,P) 18.3/19.2), 31.82 (C-1, *J*(C,P) 7.9), 26.30 (Me)–2-MeC₃H₄; 33.4 (*J*(C,P) 21.8), 27.94 (*J*(C,P) 40.1), 25.38 (*J*(C,P) 6.1), 20.9, 20.4, 19.7 – dippe. The compound can also be prepared by reacting 2-methylallylmagnesium chloride with $\text{Ru}(\text{dippe})\text{Cl}_3$ (yield 66%) or $\text{Ru}(\text{dippe})\text{Cl}_2$ (yield 69%) in diethyl ether. $(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Ru}(\text{Pr}_2^i\text{PC}_3\text{H}_6\text{PPr}_2^i)$ (**3**). Prepared as described above in 73% yield. MS (60°C): m/e 488 (M^+), 432 ($\text{M}^+ - \text{C}_4\text{H}_8$), 376 ($\text{M}^+ - 2\text{C}_4\text{H}_8$). IR (KBr): ν 3020. ^{31}P NMR (d_8 -toluene): δ 27.23. ^1H NMR (d_8 -toluene): δ 2.1 (Me)–2-MeC₃H₄; 2.5, 2.09–1.5, 1.3–0.8 (dipp/2-MeC₃H₄). ^{13}C NMR (d_8 -toluene): δ 92.8 (C-2), 39.6 (C-3, *J*(C,P) 21), 33.2 (C-1, *J*(C,P) 8.2), 26.6 (Me)–2-MeC₃H₄; 29.4 (*J*(C,P) 21.0), 26.4 (*J*(C,P) 7.0), 23.4 (*J*(C,P) 25), 21.0, 20.6, 20.5, 20.2, 19.9 – dipp. The compound can also be prepared (yield 69%) by reacting $\text{Ru}(\text{dipp})\text{Cl}_2$ with 2-methylallylmagnesium chloride in diethyl ether.
- [20] M.O. Albers, E. Singleton, J.E. Yates, *Inorg. Synth.* 26 (1989) 249.
- [21] J. Müller, E.O. Fischer, *J. Organometal. Chem.* 5 (1966) 275.

- [22] $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{Pr}_2^i\text{PC}_2\text{H}_4\text{PPr}_2^i)$ (**4**). Prepared by reacting $\text{Ru}(\text{dippe})\text{Cl}_2$ (prepared in 84% yield by reacting $(\text{cod})\text{RuCl}_2$ [21] with dippe in refluxing EtOH) with allylmagnesium chloride in diethyl ether at room temperature overnight. The reacting mixture was evaporated to dryness and the residue extracted with pentane. Evaporation of the extract gave the compound as a beige solid in 51% yield. MS (50°C): m/e 446 (M^+). IR (KBr): ν 3040, 1219, 1006. ^{31}P NMR (d_8 -toluene): δ 85.7. ^1H NMR (d_8 -toluene): δ 3.32 (m, H-2), 2.58 (d, H-1 syn, J 6.9), 1.76 (d, H-1 anti, J 6.9), 1.30 (d, H-3 syn, J 7.2) – C_3H_5 ; 1.99, 1.91, 1.58, 1.22, 1.18, 1.16, 1.02, 0.75 (dippe). ^{13}C NMR (d_8 -toluene): 83.19 (C-2), 32.75 (C-3, $J(\text{C},\text{P})$ 29.8), 30.45 (C-1, $J(\text{C},\text{P})$ 7.9) – C_3H_5 ; 32.53 ($J(\text{C},\text{P})$ 26.3), 25.34 ($J(\text{C},\text{P})$ 41.4), 24.06 ($J(\text{C},\text{P})$ 10.6), 20.18, 19.91, 19.67, 19.01 (dippe). The compound can also be prepared (yield 63%) by reacting $\text{Ru}(\text{dippe})\text{Cl}_3$ with allylmagnesium chloride in diethyl ether at -30°C . $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{Pr}_2^i\text{PC}_3\text{H}_6\text{PPr}_2^i)$ (**5**). Prepared as described above in THF/diethyl ether in 56% yield. MS (75°C): m/e 460 (M^+). IR (KBr): ν 3047. ^{31}P NMR (d_8 -toluene): δ 30.41. ^1H NMR (d_8 -toluene): δ 4.05 (m, H-2), 2.80 (m, H-1 syn), 1.38 (d, H-1 anti, J 8.4), 1.31 (H-3 syn), 0.96 (H-3 anti) – C_3H_5 ; 2.1–2.0, 1.6, 1.1–0.7 (dippe). ^{13}C NMR (d_8 -toluene): δ 81.82/79.05 (C-2), 35.04 (C-1, $J(\text{C},\text{P})$ 7.9), 31.61 (C-3, $J(\text{C},\text{P})$ 18.3) – C_3H_5 ; 30.26 ($J(\text{C},\text{P})$ 21.8), 26.73 ($J(\text{C},\text{P})$ 9.6), 23.30 ($J(\text{C},\text{P})$ 22.7), 20.56, 20.33, 20.26, 19.93 (dippe).
- [23] $(\eta^5\text{-1-Hexadienyl})\text{Ru}(\text{Pr}_2^i\text{PC}_2\text{H}_4\text{PPr}_2^i)_2\text{H}$. $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{dippe})$ (**4**) (0.23 g, 0.52 mmol) was dissolved in toluene (60 ml) and treated with 1,5-hexadiene (0.12 ml, 1.04 mmol). The solution was heated to 100°C and stirred for 16 h. The toluene was evaporated and the residue washed with pentane to give the compound as a yellow solid. Yield 0.08 g (35%). Insufficient material was available for elemental analyses and the compound was characterized spectroscopically. MS (30°C): m/e 446 (M^+). IR (KBr): ν 3037, 1916 (RuH). ^{31}P NMR (d_8 -toluene): δ 77.53, 74.70, $J(\text{P}, \text{P})$ 18.2. ^1H NMR (d_8 -toluene): δ 5.85, 5.09, 4.37, 2.43, 1.87, -0.61 – $1\text{-MeC}_3\text{H}_6$; the spectrum is practically identical with that of $(\eta^5\text{-1-hexadienyl})\text{Fe}(\text{dippe})\text{H}$ [12].
- [24] $[\text{Ru}(\text{Pr}_2^i\text{PC}_2\text{H}_4\text{PPr}_2^i)_2\text{OAc}]^+\text{OAc}^-$ (**6**). $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{dippe})$ (0.55 g, 1.24 mmol) was dissolved in diethyl ether (50 ml), treated with dippe (0.39 ml, 1.24 mmol) and MeCO_2H (141 μl , 2.47 mmol) at room temperature and stirred for 16 h. The resulting yellow-orange solution was evaporated to dryness and the residue washed with pentane at -78°C and dried under high vacuum. Yield 0.81 g (88%). The compound was recrystallized from toluene. Found: C, 51.6; H, 9.0; P, 15.9; Ru 17.5. $\text{C}_{32}\text{H}_{70}\text{O}_4\text{P}_4\text{Ru}$ calculated: C, 51.7; H, 9.4; P, 16.7; Ru, 13.6%. MS (ESI, acetone): m/e 744 (M^+), 685 ($\text{M}^+ - \text{MeCO}_2$, 100%). IR (KBr): ν (OAc) 1577, 1454, 1421. ^{31}P NMR (d_6 -acetone): δ (A_2B_2 spin system) 79.8, 79.6, 60.8, 60.5, $J(\text{P},\text{P})$ 17.8. ^1H NMR (d_6 -acetone): δ 1.6, 1.4, 1.2 (m, Me/OAc); 2.7, 2.6, 2.4 (CH/CH₂), 1.84, 1.76 (Me) (dippe). ^{13}C NMR (d_6 -acetone): δ 186.8/165.9, 25.9/22.5 ($J(\text{C},\text{P})$ 5.4) (OAc); 35.1 ($J(\text{C},\text{P})$ 19.9), 32.5 ($J(\text{C},\text{P})$ 20.4), 28.5 ($J(\text{C},\text{P})$ 23.6), 24.1 ($J(\text{C},\text{P})$ 15.3), 23.1, 20.6, 20.1, 20.0, 19.5, 19.3, 18.8 (dippe). Crystal structure: see Fig. 1. The same compound can also be prepared (yield 75%) by reacting $(\text{cod})\text{RuCl}_2$ with dippe and NaOAc in ethanol at 75°C .
- [25] Crystal data for $[\text{Ru}(\text{Pr}_2^i\text{PC}_2\text{H}_4\text{PPr}_2^i)_2\text{OAc}]^+\text{OAc}^-$ (**6**): $\text{C}_{32}\text{H}_{70}\text{O}_4\text{P}_4\text{Ru}$, monoclinic, space group Cc(No. 9), $a = 18.7380(14)$ Å, $b = 12.1777(5)$ Å, $c = 18.5902(9)$ Å, $\beta = 105.365(6)^\circ$, $V = 4090.4(4)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.209$ Mg m⁻³, 5046 measured reflections, 4814 independent reflections, 4161 reflections with $I \geq 2\sigma(I)$ used in refinement, structure solved by the heavy atom method, $R = 0.0476$, $R_w = 0.1536$ [$w = 1/\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P$], EOF = 1.365, residual electron density 1.956 and -0.467 e Å⁻³. The structure was solved using SHELXS-86 and the final refinement was carried out with the programme SHELXL-93.
- [26] T.V. Ashworth, M.J. Nolte, E. Singleton, S. Afr. J. Chem. 31 (1978) 155.
- [27] T.V. Ashworth, M.J. Nolte, E. Singleton, J. Chem. Soc., Dalton Trans. (1976) 2184.
- [28] E.P. Boyar, P.A. Harding, S.D. Robinson, C.P. Brock, J. Chem. Soc., Dalton Trans. (1986) 1771.
- [29] B.K. Das, A.R. Chakravarty, Ind. J. Chem. A 31 (1992) 408.