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Reactivity of the dimer [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] towards diphosphines and diphosphine-monoxides: synthesis and characterization of novel (2,7-dimethylocta-2,6-diene-1,8-diyl)-ruthenium(IV) complexes

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Dedicated to Professor Rafael Usón with great admiration for his outstanding contributions to modern inorganic chemistry

Abstract

Treatment of complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-P-$Ph_2PCH_2PPh_2$)] (**2**) with $AgBF_4$ yields the chelate derivative [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-P,P-$Ph_2PCH_2PPh_2$)][BF_4] (**3**). Attempts to generate species structurally related to **2** by reaction of the bis(allyl)-ruthenium(IV) dimer [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (**1**) with diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$, 3, 4) failed, obtaining instead the dinuclear compounds [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2${μ-$Ph_2P(CH_2)_nPPh_2$}] ($n = 2$ (**4a**), 3 (**4b**), 4 (**4c**)). In contrast, mononuclear neutral species [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2{κ^1-P-$Ph_2P(CH_2)_nP(=O)Ph_2$}] ($n = 1$ (**5a**), 2 (**5b**), 3 (**5c**), 4 (**5d**)) have been easily prepared by reaction of **1** with the corresponding diphosphine-monoxide $Ph_2P(CH_2)_nP(=O)Ph_2$ ($n = 1$, 2, 3, 4). Treatment of **5a**,**b** with $AgBF_4$ allows the formation of cationic derivatives [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-P,O-$Ph_2P(CH_2)_nP(=O)Ph_2$}][BF_4] ($n = 1$ (**6a**), 2 (**6b**)).

Keywords: η^3:η^3-Octadienediyl complexes; Bis(allyl) complexes; Diphosphines; Diphosphine-monoxides; Ruthenium(IV) complexes

1. Introduction

Although the dimeric chloro-bridged bis(allyl)-ruthenium(IV) complex [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (**1**) has been known for many years [1], its chemistry has been scarcely developed. This fact is rather surprising given the profusion of studies on the structurally related ruthenium(II) dimers [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] [2]. Complex **1** and some of its derivatives possess a number of features which make them particularly appealing. These include: (i) remarkable stability and water solubility [3]; (ii) catalytic activity in ROMP of cycloolefins [3b,4] and butadiene polymerization [5]; (iii) the chirality of the metal coordinated 2,7-dimethylocta-2,6-diene-1,8-diyl ligand (in solution complex **1** has been shown to exist in two diasteromeric forms; see Fig. 1) [6]; and (iv) the high reactivity derived from the chloro-bridged structure. The later feature has disclosed wide series of derivatives of the type: [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2L] [6,7], [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-L–L)] [3a,8], [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-L-L)] [7d,9] and [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl-(μ-L)}$_2$] [7e,10], generated by the bridging cleavage using monodentate and bidentate ligands. In addition, cationic species [Ru(η^3:η^3-$C_{10}H_{16}$)ClL_2]$^+$ and [Ru(η^3:η^3-$C_{10}H_{16}$)L_3]$^{2+}$ have been also prepared by treatment of **1** with $AgBF_4$ in the presence of monodentate ligands [4d,7c,d,8f,9b].

In spite of this versatile reactivity, studies focused on the preparation of bis(allyl)-ruthenium(IV) complexes containing chelating diphosphines starting from dimer **1** have been almost neglected. To the best of our knowledge only the complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-P,P-$^iPr_2PCH_2P^iPr_2$)][BF_4] is known [11]. This prompted

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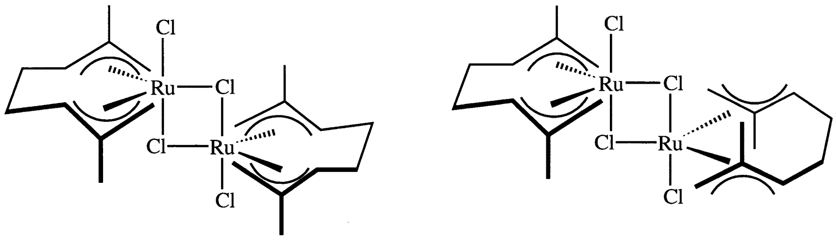


C_i isomer **C_2 isomer**

Fig. 1. The two diastereomeric forms of $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**).

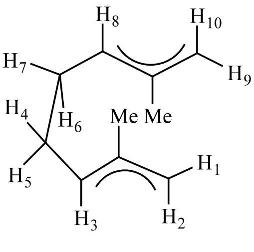
us to study the reactivity of $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**) towards the chelating bis(diphenylphosphino)alkane ligands $Ph_2P(CH_2)_nPPh_2$ (dppm, dppe, dppp and dppb), as well as their hemilabile diphosphine-monoxide counterparts $Ph_2P(CH_2)_nP({=}O)Ph_2$ (dppmO, dppeO, dpppO and dppbO).

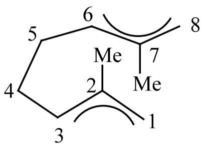
2. Experimental

2.1. General information

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**) [5], $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2PPh_2)]$ (**2**) [9a], dppmO [12], dppeO [12], dpppO [12] and dppbO [12] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The C and H analyses were carried out with a Perkin–Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^1H), 121.44 MHz (^{31}P) or 75.47 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported.

The numbering for protons and carbons of the octadienediyl skeleton is as follows:





2.2. Preparations

2.2.1. $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,P\text{-}Ph_2PCH_2PPh_2)][BF_4]$ (3)

Method A: a suspension of 0.200 g (0.289 mmol) of $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2PPh_2)]$ (**2**) and 0.058 g (0.298 mmol) of $AgBF_4$ in 10 ml of dichloromethane was stirred in the dark, at room temperature (r.t.), for 30 min. The reaction mixture was then filtered through Kieselguhr and the filtrate evaporated to dryness. The resulting yellow solid residue was washed with diethyl ether (3 × 20 ml) and dried in vacuo. Yield 0.187 g (87%). *Anal.* Calc. for $RuC_{35}H_{38}F_4P_2BCl$ (744.12 g mol^{-1}): C, 56.51; H, 5.15. Found: C, 56.26; H, 4.89%. IR (KBr, cm^{-1}): $\nu = 3055$ (m), 2915 (m), 1628 (m), 1484 (m), 1435 (s), 1385 (w), 1060 (vs), 998 (m), 741 (s), 696 (s), 532 (m), 510 (m), 483 (s); $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) $\delta = -33.70$ and -15.84 (d, $J(P,P) = 58.2$ Hz) ppm; ^1H NMR ($(CD_3)_2CO$) $\delta = 1.87$ (dd, 3H, $J(H,P) = 1.7$ Hz, $J(H,P) = 1.7$ Hz, CH_3), 2.40 (dd, 1H, $J(H,P) = 15.0$ Hz, $J(H,P) = 4.5$ Hz, H_2 or H_{10}), 2.51 (d, 3H, $J(H,P) = 2.0$ Hz, CH_3), 2.61 (dd, 1H, $J(H,P) = 9.1$ Hz, $J(H,P) = 4.5$ Hz, H_2 or H_{10}), 2.75, 3.03, 3.24 and 3.40 (m, 1H each, H_4, H_5, H_6 and H_7), 3.51 (dd, 1H, $J(H,P) = 3.9$ Hz, $J(H,P) = 3.9$ Hz, H_1 or H_9), 3.85 and 4.92 (m, 1H each, H_3 and H_8), 4.14 (dd, 1H, $J(H,P) = 4.3$ Hz, $J(H,P) = 4.3$ Hz, H_1 or H_9), 5.34 (m, 2H, PCH_2P), 6.50–8.30 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$) $\delta = 19.24$ (dd, $J(C,P) = 3.8$ Hz, $J(C,P) = 1.3$ Hz, CH_3), 19.74 (d, $J(C,P) = 1.3$ Hz, CH_3), 31.06 and 37.84 (s, C_4 and C_5), 38.82 (dd, $J(C,P) = 28.0$ Hz, $J(C,P) = 28.0$ Hz, PCH_2P), 67.99 (dd, $J(C,P) = 5.7$ Hz, $J(C,P) = 2.5$ Hz, C_1 or C_8), 69.05 (d, $J(C,P) = 5.7$ Hz, C_1 or C_8), 98.18 (dd, $J(C,P) = 3.5$ Hz, $J(C,P) = 1.6$ Hz, C_3 and C_6), 113.46 (dd, $J(C,P) = 2.5$ Hz, $J(C,P) = 2.5$ Hz, C_2 or C_7), 116.56 (s, C_2 or C_7), 117.00–133.00 (m, Ph) ppm.

Method B: a suspension of 0.200 g (0.324 mmol) of $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**), 0.250 g (0.650 mmol) of dppm and 0.126 g (0.650 mmol) of $AgBF_4$ in 10 ml of dichloromethane was stirred in the dark, at r.t. for 30 min. The reaction mixture was then filtered through Kieselguhr and the filtrate evaporated to dryness. The resulting yellow solid residue was washed with diethyl ether (3 × 20 ml) and dried in vacuo. Yield 0.410 g (85%).

2.2.2. *$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ ($n = 2$ (**4a**), 3 (**4b**), 4 (**4c**))*

A solution of 0.200 g (0.324 mmol) of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**) in 10 ml of dichloromethane was treated at r.t. with the corresponding diphosphine (0.325 mmol). After stirring for 5 min, the solvent was removed under vacuum and the resulting solid residue washed with hexanes (3 × 20 ml) and dried in vacuo. **4a**: yellow solid; yield 0.319 g (97%). *Anal.* Calc. for $Ru_2C_{46}H_{56}Cl_4P_2$ (1014.85 g mol^{-1}): C, 54.44; H, 5.53. Found: C, 53.96; H, 5.25%. IR (KBr, cm^{-1}): $\nu = 3052$ (m), 2853 (m), 1587 (w), 1432 (s), 1383 (s), 1311 (w), 1185 (m), 1087 (m), 1023 (m), 969 (m), 861 (m), 749 (m), 694 (vs), 529 (s), 519 (s), 491 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta =$ 24.97 and 25.30 (s) ppm; ^1H NMR (CD_2Cl_2) $\delta = 2.06$ (s, 12H, CH_3), 2.34 and 2.70 (m, 2H each, $P(CH_2)_2P$), 2.59 (m, 4H, H_4 and H_6), 2.97 and 3.01 (br, 2H each, H_2 and H_{10}), 3.37 (m, 4H, H_5 and H_7), 3.96 and 4.03 (d, 2H each, $J(H,P) = 7.7$ Hz, H_1 and H_9), 5.05 (m, 4H, H_3 and H_8), 7.30–7.65 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 20.87$ (s, CH_3), 22.84 (m, $P(CH_2)_2P$), 36.95 and 36.99 (s, C_4 and C_5), 66.77 (s, C_1 and C_8), 108.23 and 108.37 (d, $J(C,P) = 5.4$ Hz, C_3 and C_6), 124.90 (d, $J(C,P) = 7.0$ Hz, C_2 and C_7), 127.00–136.00 (m, Ph) ppm. **4b**: orange solid; yield 0.313 g (94%). *Anal.* Calc. for $Ru_2C_{47}H_{58}Cl_4P_2$ (1028.87 g mol^{-1}): C, 54.87; H, 5.68. Found: C, 54.81; H, 5.64%. IR (KBr, cm^{-1}): $\nu = 3054$ (m), 2908 (m), 1672 (m), 1433 (s), 1382 (s), 1186 (m), 1087 (m), 1019 (m), 959 (s), 857 (m), 789 (w), 742 (s), 695 (vs), 525 (s), 493 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 16.05$ and 16.69 (s) ppm; ^1H NMR (CD_2Cl_2) $\delta =$ 1.30 (m, 2H, $CH_2\mathit{CH_2}CH_2$), 2.11 and 2.13 (s, 6H each, CH_3), 2.63 (m, 4H, H_4 and H_6), 2.81 (m, 4H, PCH_2), 2.94 and 3.03 (d, $J(H,P) = 2.9$ Hz, H_2 and H_{10}), 3.41 (m, 4H, H_5 and H_7), 4.03 and 4.05 (d, 2H each, $J(H,P) = 9.2$ Hz, H_1 and H_9), 5.09 (m, 4H, H_3 and H_8), 7.25–7.75 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 20.06$ (s, $CH_2\mathit{C}H_2CH_2$), 20.87 (s, CH_3), 27.72 (dd, $J(C,P) = 26.5$ Hz, $J(C,P) = 12.2$ Hz, PCH_2), 37.01 (s, C_4 and C_5), 66.74 (s, C_1 and C_8), 108.09 and 108.21 (d, $J(C,P) = 9.8$ Hz, C_3 and C_6), 124.90 (s, C_2 and C_7), 127.00–137.00 (m, Ph) ppm. **4c**: yellow solid; yield 0.321 g (95%). *Anal.* Calc. for $Ru_2C_{48}H_{60}Cl_4P_2$ (1042.91 g mol^{-1}): C, 55.28; H, 5.79. Found: C, 54.99; H, 5.73%. IR (KBr, cm^{-1}): $\nu = 3055$ (m), 2902 (m), 2853 (m), 1573 (w), 1462 (m), 1434 (s), 1381 (s), 1183 (w), 1159 (w), 1096 (m), 1047 (w), 1022 (m), 962 (w), 859 (m), 846 (m), 748 (s), 696 (vs), 523 (s), 495 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 17.73$ and 17.83 (s) ppm; ^1H NMR (CD_2Cl_2) $\delta =$ 1.00–1.40 and 2.49 (m, 4H each, $P(CH_2)_4P$), 2.11 (s, 12H, CH_3), 2.61 (m, 4H, H_4 and H_6), 3.05 (d, 4H, $J(H,P) = 3.2$ Hz, H_2 and H_{10}), 3.40 (m, 4H, H_5 and H_7), 4.09 (d, 4H, $J(H,P) = 9.4$ Hz, H_1 and H_9), 5.09 (m, 4H, H_3 and H_8), 7.30–7.70 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 20.92$ (s, CH_3), 26.45 (d, $J(C,P) = 27.3$ Hz, PCH_2), 26.46 (d, $J(C,P) = 5.7$ Hz, $PCH_2\mathit{C}H_2$), 37.04 (s, C_4 and C_5), 66.77 (d, $J(C,P) = 5.7$ Hz, C_1 and C_8), 108.17 (d, $J(C,P) = 9.5$ Hz, C_3 and C_6), 124.93 (s, C_2 and C_7), 127.50–137.00 (m, Ph) ppm.

2.2.3. *$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\{\kappa^1\text{-}P\text{-}Ph_2P(CH_2)_nP(=O)Ph_2\}]$ ($n = 1$ (**5a**), 2 (**5b**), 3 (**5c**), 4 (**5d**))*

A solution of 0.400 g (0.648 mmol) of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**) in 10 ml of dichloromethane was treated at r.t. with the corresponding diphosphine-monoxide (1.298 mmol). After stirring for 5 min, the solvent was removed under vacuum and the resulting solid residue washed with diethyl ether (3 × 20 ml) and dried in vacuo. **5a**: orange solid; yield 0.883 g (96%). *Anal.* Calc. for $RuC_{35}H_{38}Cl_2P_2O$ (708.61 g mol^{-1}): C, 59.32; H, 5.40. Found: C, 59.15; H, 5.41%. IR (KBr, cm^{-1}): $\nu = 3050$ (w), 2854 (w), 1587 (w), 1483 (m), 1434 (s), 1383 (m), 1310 (m), 1202 (vs), 1173 (s), 1115 (vs), 1024 (m), 996 (w), 920 (w), 851 (w), 802 (s), 736 (vs), 691 (vs), 615 (w), 552 (m), 506 (s), 487 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 18.61$ (d, $J(P,P) = 29.5$ Hz, Ph_2P), 22.80 (d, $J(P,P) = 29.5$ Hz, $Ph_2P{=}O$) ppm; ^1H NMR (CD_2Cl_2) $\delta = 2.14$ (s, 6H, CH_3), 2.64 (m, 2H, H_4 and H_6), 3.29 (d, 2H, $J(H,P) = 3.1$ Hz, H_2 and H_{10}), 3.47 (m, 2H, H_5 and H_7), 3.79 and 4.15 (m, 1H each, $PCH_2P{=}O$), 4.24 (d, 2H, $J(H,P) = 9.6$ Hz, H_1 and H_9), 5.20 (m, 2H, H_3 and H_8), 7.00–7.80 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 20.86$ (s, CH_3), 26.13 (dd, $J(C,P) = 61.8$ Hz, $J(C,P) = 18.5$ Hz, $PCH_2P{=}O$), 36.89 (s, C_4 and C_5), 68.45 (d, $J(C,P) = 4.9$ Hz, C_1 and C_8), 107.85 (d, $J(C,P) = 10.3$ Hz, C_3 and C_6), 125.73 (d, $J(C,P) = 1.2$ Hz, C_2 and C_7), 127.10–136.40 (m, Ph) ppm. **5b**: orange solid; yield 0.853 g (91%). *Anal.* Calc. for $RuC_{36}H_{40}Cl_2P_2O$ (722.64 g mol^{-1}): C, 59.83; H, 5.58. Found: C, 59.56; H, 5.80%. IR (KBr, cm^{-1}): $\nu = 3057$ (m), 2855 (m), 1590 (w), 1483 (m), 1434 (s), 1381 (m), 1278 (w), 1198 (s), 1174 (vs), 1121 (s), 1085 (s), 1026 (m), 967 (m), 881 (m), 860 (m), 788 (m), 733 (vs), 692 (vs), 545 (s), 517 (s), 501 (s), 482 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 20.19$ (d, $J(P,P) = 39.1$ Hz, Ph_2P), 31.79 (d, $J(P,P) = 39.1$ Hz, $Ph_2P{=}O$) ppm; ^1H NMR (CD_2Cl_2) $\delta = 2.14$ (s, 6H, CH_3), 2.21 and 3.44 (m, 2H each, $P(CH_2)_2P{=}O$), 2.64 (m, 2H, H_4 and H_6), 2.99 (m, 2H, H_5 and H_7), 3.07 (d, 2H, $J(H,P) = 3.5$ Hz, H_2 and H_{10}), 4.17 (d, 2H, $J(H,P) = 9.4$ Hz, H_1 and H_9), 5.13 (m, 2H, H_3 and H_8), 7.36–7.77 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 19.49$ (dd, $J(C,P) = 25.4$ Hz, $J(C,P) = 3.1$ Hz, PCH_2), 20.86 (s, CH_3), 24.90 (dd, $J(C,P) = 68.0$ Hz, $J(C,P) = 4.5$ Hz, $CH_2P{=}O$), 37.04 (s, C_4 and C_5), 66.56 (d, $J(C,P) = 5.4$ Hz, C_1 and C_8), 108.74 (d, $J(C,P) = 9.9$ Hz, C_3 and C_6), 125.14 (d, $J(C,P) = 1.2$ Hz, C_2 and C_7), 128.00–137.00 (m, Ph) ppm. **5c**: yellow solid; yield 0.937

g (98%). *Anal.* Calc. for $RuC_{37}H_{42}Cl_2P_2O$ (736.66 g mol^{-1}): C, 60.33; H, 5.75. Found: C, 60.34; H, 5.20%. IR (KBr, cm^{-1}): $\nu = 3052$ (m), 2914 (m), 1586 (w), 1483 (m), 1435 (s), 1382 (m), 1310 (w), 1243 (w), 1187 (vs), 1160 (s), 1118 (s), 1101 (m), 1021 (m), 951 (m), 859 (m), 791 (w), 743 (s), 716 (vs), 697 (vs), 522 (s), 521 (s), 482 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 17.53$ (d, $J(P,P) = 1.9$ Hz, Ph_2P), 31.04 (d, $J(P,P) = 1.9$ Hz, $Ph_2P{=}O$) ppm; ^1H NMR (CD_2Cl_2) $\delta = 1.39$ and 1.58 (m, 1H each, $CH_2C\mathit{H}_2CH_2$), 2.10 (s, 6H, CH_3), 2.25 and 2.84 (m, 2H each, PCH_2 and $CH_2P{=}O$), 2.61 (m, 2H, H_4 and H_6), 3.01 (d, 2H, $J(H,P) = 3.1$ Hz, H_2 and H_{10}), 3.40 (m, 2H, H_5 and H_7), 4.08 (d, 2H, $J(H,P) = 9.4$ Hz, H_1 and H_9), 5.09 (m, 2H, H_3 and H_8), 7.20–7.80 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 17.72$ (dd, $J(C,P) = 3.8$ Hz, $J(C,P) = 3.8$ Hz, $CH_2\mathit{C}H_2CH_2$), 20.89 (s, CH_3), 27.72 (dd, $J(C,P) = 26.1$ Hz, $J(C,P) = 12.7$ Hz, PCH_2), 30.89 (dd, $J(C,P) = 70.6$ Hz, $J(C,P) = 12.1$ Hz, $CH_2P{=}O$), 37.03 (s, C_4 and C_5), 66.78 (d, $J(C,P) = 5.7$ Hz, C_1 and C_8), 108.19 (d, $J(C,P) = 9.5$ Hz, C_3 and C_6), 125.04 (s, C_2 and C_7), 128.00–136.00 (m, Ph) ppm. **5d**: orange solid; yield 0.935 g (96%). *Anal.* Calc. for $RuC_{38}H_{44}Cl_2P_2O$ (750.69 g mol^{-1}): C, 60.80; H, 5.91. Found: C, 60.65; H, 6.00%. IR (KBr, cm^{-1}): $\nu = 3054$ (w), 2902 (w), 1591 (w), 1482 (m), 1451 (w), 1436 (m), 1379 (m), 1311 (w), 1291 (w), 1242 (w), 1197 (s), 1117 (s), 1087 (s), 1071 (m), 1024 (m), 995 (m), 965 (m), 921 (w), 886 (w), 857 (m), 839 (m), 789 (m), 781 (m), 745 (s), 720 (s), 714 (s), 699 (s), 551 (s), 517 (s), 488 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 17.42$ (s, Ph_2P), 30.78 (s, $Ph_2P{=}O$) ppm; ^1H NMR (CD_2Cl_2) $\delta = 0.87$–1.65 (m, 6H, $P(CH_2)_4P{=}O$), 2.15 (s, 6H, CH_3), 2.63 (m, 2H, H_4 and H_6), 2.80 (m, 2H, $P(CH_2)_4P{=}O$), 3.14 (br, 2H, H_2 and H_{10}), 3.44 (m, 2H, H_5 and H_7), 4.13 (d, 2H, $J(H,P) = 9.3$ Hz, H_1 and H_9), 5.16 (m, 2H, H_3 and H_8), 7.30–7.70 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 20.96$ (s, CH_3), 23.39 (dd, $J(C,P) = 12.8$ Hz, $J(C,P) = 2.4$ Hz, $\mathit{C}H_2CH_2P{=}O$), 26.05 (dd, $J(C,P) = 15.9$ Hz, $J(C,P) = 4.9$ Hz, $PCH_2\mathit{C}H_2$), 26.56 (d, $J(C,P) = 26.9$ Hz, PCH_2), 29.60 (d, $J(C,P) = 70.8$ Hz, $CH_2P{=}O$), 37.06 (s, C_4 and C_5), 66.75 (d, $J(C,P) = 4.9$ Hz, C_1 and C_8), 108.21 (d, $J(C,P) = 9.8$ Hz, C_3 and C_6), 124.95 (s, C_2 and C_7), 128.00–137.00 (m, Ph) ppm.

2.2.4. *$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl\{\kappa^2\text{-}P,O\text{-}Ph_2P(CH_2)_nP({=}O)Ph_2\}][BF_4]$ ($n = 1$ (6a), 2 (6b))*

Method A: a suspension of complexes **5a**,**b** (1.141 mmol) and 0.224 g (1.150 mmol) of $AgBF_4$ in 10 ml of dichloromethane was stirred in the dark at r.t. for 30 min. The reaction mixture was then filtered through Kieselguhr and the filtrate concentrated to dryness. The resulting solid residue was washed with diethyl ether (3 × 20 ml) and dried in vacuo. **6a**: orange solid; yield 0.720 g (83%). *Anal.* Calc. for $RuC_{35}H_{38}F_4P_2BClO$ (759.96 g mol^{-1}): C, 55.31; H, 5.04. Found: C, 55.05; H, 4.85%. IR (KBr, cm^{-1}): $\nu = 3054$ (w), 2859 (m), 1623 (w), 1485 (d), 1438 (s), 1388 (w), 1134 (vs), 1058 (vs), 859 (w), 786 (m), 742 (s), 699 (s), 547 (s), 514 (s), 465 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 26.19$ (d, $J(P,P) = 28.3$ Hz, Ph_2P), 72.08 (d, $J(P,P) = 28.3$ Hz, $Ph_2P{=}O$) ppm; ^1H NMR (CD_2Cl_2) $\delta = 1.70$ and 2.18 (s, 3H each, CH_3), 2.57 (d, 1H, $J(H,P) = 5.4$ Hz, H_2 or H_{10}), 3.02 (m, 2H, H_4 and H_6), 3.31 (d, 1H, $J(H,P) = 2.8$ Hz, H_2 or H_{10}), 3.73 (m, 2H, H_5 and H_7), 3.95 (d, 2H, $J(H,P) = 9.4$ Hz, H_1 and H_9), 4.29 (m, 2H, $PCH_2P{=}O$), 5.01 and 5.31 (m, 1H each, H_3 and H_8), 7.30–8.05 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 20.52$ and 20.78 (s, CH_3), 28.08 (dd, $J(C,P) = 67.1$ Hz, $J(C,P) = 15.9$ Hz, $PCH_2P{=}O$), 36.96 and 37.77 (s, C_4 and C_5), 68.25 (d, $J(C,P) = 3.2$ Hz, C_1 or C_8), 68.32 (d, $J(C,P) = 3.0$ Hz, C_1 or C_8), 109.59 (dd, $J(C,P) = 7.9$ Hz, $J(C,P) = 2.5$ Hz, C_3 or C_6), 118.04 (d, $J(C,P) = 10.8$ Hz, C_3 or C_6), 125.99 (d, $J(C,P) = 1.9$ Hz, C_2 or C_7), 126.35 (d, $J(C,P) = 1.3$ Hz, C_2 or C_7), 129.00–136.00 (m, Ph) ppm. **6b**: yellow solid; yield 0.750 g (85%). *Anal.* Calc. for $RuC_{36}H_{40}F_4P_2BClO$ (773.99 g mol^{-1}): C, 55.86; H, 5.21. Found: C, 55.64; H, 5.38%. IR (KBr, cm^{-1}): $\nu = 3054$ (m), 2859 (m), 1589 (w), 1486 (m), 1437 (s), 1383 (m), 1280 (w), 1128 (s), 1062 (vs), 978 (s), 860 (w), 742 (s), 724 (s), 693 (s), 551 (s), 509 (s), 485 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 9.33$ (d, $J(P,P) = 2.3$ Hz, Ph_2P), 52.53 (d, $J(P,P) = 2.3$ Hz, $Ph_2P{=}O$) ppm; ^1H NMR (CD_2Cl_2) $\delta = 1.59$ and 2.19 (s, 3H each, CH_3), 2.78 (m, 2H, H_4 and H_6), 2.83 (d, 1H, $J(H,P) = 3.7$ Hz, H_2 or H_{10}), 2.93 (d, 1H, $J(H,P) = 3.1$ Hz, H_2 or H_{10}), 3.12 (m, 2H, H_5 and H_7), 3.33 and 3.74 (m, 2H each, $P(CH_2)_2P{=}O$), 4.25 (d, 1H, $J(H,P) = 9.9$ Hz, H_1 or H_9), 4.49 (d, 1H, $J(H,P) = 11.1$ Hz, H_1 or H_9), 5.04 and 5.32 (m, 1H each, H_3 and H_8), 7.20–8.10 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 16.42$ (dd, $J(C,P) = 28.0$ Hz, $J(C,P) = 5.7$ Hz, PCH_2), 18.93 (d, $J(C,P) = 66.7$ Hz, $CH_2P{=}O$), 20.45 (s, CH_3), 21.92 (d, $J(C,P) = 0.6$ Hz, CH_3), 36.98 and 38.17 (s, C_4 and C_5), 67.96 (d, $J(C,P) = 3.8$ Hz, C_1 or C_8), 68.03 (d, $J(C,P) = 3.2$ Hz, C_1 or C_8), 111.33 (d, $J(C,P) = 7.0$ Hz, C_3 or C_6), 118.17 (d, $J(C,P) = 10.2$ Hz, C_3 or C_6), 127.06 (d, $J(C,P) = 1.3$ Hz, C_2 or C_7), 127.99 (d, $J(C,P) = 1.9$ Hz, C_2 or C_7), 128.50–134.50 (m, Ph) ppm.

Method B: a suspension of 0.200 g (0.324 mmol) of $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ (**1**), the corresponding diphosphine-monoxide (0.650 mmol) and 0.126 g (0.650 mmol) of $AgBF_4$ in 10 ml of dichloromethane was stirred in the dark at r.t. for 30 min. The reaction mixture was then filtered through Kieselguhr and the filtrate evaporated to dryness. The resulting solid residue was washed with diethyl ether (3 × 20 ml) and dried in vacuo. **6a**: yield 0.394 g (80%). **6b**: yield 0.411 g (82%).

3. Results and discussion

3.1. Reactivity of [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (**1**) towards diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1–4$)

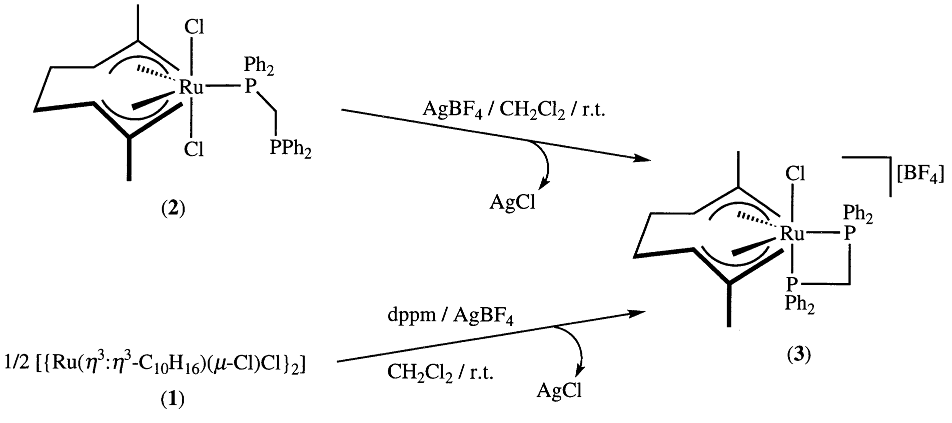
A preliminary account on the reactivity of the dimeric bis(allyl)-ruthenium(IV) complex [{Ru(η^3:η^3-$C_{10}H_{16}$)-(μ-Cl)Cl}$_2$] (**1**) towards bis(diphenylphosphino)methane (dppm) was reported by Toerien and van Rooyen in 1991 [9a]. They reported that the dinuclear derivative [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-$Ph_2PCH_2PPh_2$)], bearing a bridging dppm unit, or the mononuclear adduct [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-$Ph_2PCH_2PPh_2$)], in which dppm is acting as a monodentate ligand, can be selectively obtained depending exclusively on the molar ratio used.

We have found that [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-$Ph_2PCH_2PPh_2$)] (**2**) reacts with an stoichiometric amount of $AgBF_4$, in dichloromethane at room temperature, to afford the cationic chelate complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P*,*P*-$Ph_2PCH_2PPh_2$)][BF_4] (**3**) which is isolated from the reaction mixture after filtration of the AgCl formed (87% yield; Scheme 1). Alternatively, **3** can be also prepared directly from [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (**1**) by treatment with 2 equiv. of dppm and $AgBF_4$ in dichloromethane.

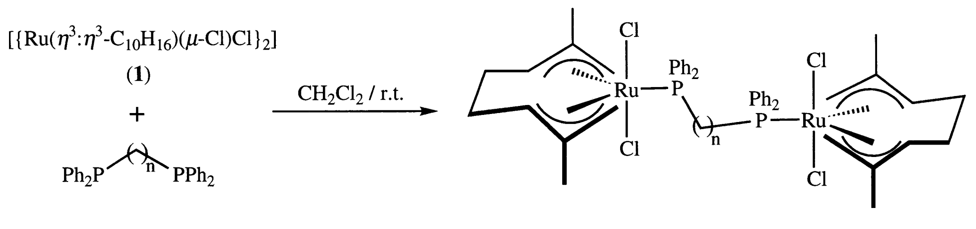
Characterization of **3** was achieved unequivocally by means of standard spectroscopic techniques (IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR) as well as elemental analyses (see Section 2). Thus, the $^{31}P\{^1H\}$ NMR spectrum exhibits resonances consistent with an AB spin system (δ −33.70 and −15.84 ppm ($J_{PP} = 58.2$ Hz)), the highly shielded chemical shifts observed being comparable to those recently reported for the related complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P*,*P*-$^iPr_2PCH_2P^iPr_2$)]-[BF_4] [11]. The ^1H NMR spectrum displays a characteristic four-line pattern for the terminal allylic protons (δ 2.40, 2.61, 3.51 and 4.14 ppm) and two separated signals for the methyl substituents (δ 1.87 and 2.51 ppm) of the bis(allyl) unit indicative of inequivalent axial sites on the trigonal-bipyramidal ruthenium atom. $^{13}C\{^1H\}$ NMR spectrum also shows clearly that the two halves of the octadienediyl ligand are in inequivalent environments since nine different signals are observed (see Section 2).

To extend the scope of this reactivity we decided to use the commercially available related diphosphines 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb). However, the treatment of **1** with 2 equiv. of these ligands, in dichloromethane at room temperature, does not afford the desired mononuclear derivatives [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2{κ^1-*P*-$Ph_2P(CH_2)_nPPh_2$}] ($n = 2$, 3, 4) obtaining instead reaction mixtures containing the dinuclear species [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2${μ-$Ph_2P(CH_2)_nPPh_2$}] ($n = 2$ (**4a**), 3 (**4b**), 4 (**4c**)) and the corresponding unreacted diphosphine. Similar results were also observed when a large excess (ca. 10 equiv.) of the ligands was used. As expected, complexes **4a**–**c** can be properly prepared working under stoichiometric conditions (94–97% yield; Scheme 2).

Compounds **4a**–**c** are air stable in the solid state and soluble in polar solvents (e.g. dichloromethane or acetone). They have been characterized by elemental analyses and IR and NMR ($^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$) spectroscopy (for details see Section 2) being their dimeric nature confirmed by the relative intensities of the octadienediyl and diphosphine resonances (2:1) in the ^1H NMR spectra. Significantly, a closer examination of the NMR data of **4a**–**c** reveals the presence of two different isomers in solution. This fact is clearly evidenced from: (a) the $^{31}P\{^1H\}$ NMR spectra which show in all the cases the presence of two singlet signals in ca. 1:1 ratio (**4a**: 24.97 and 25.30 ppm; **4b**: 16.05 and 16.69 ppm; **4c**: 17.73 and 17.83 ppm); and (b) the ^1H and $^{13}C\{^1H\}$ NMR spectra in which a doubling of some proton and carbon resonances is observed for the octadienediyl ligand (see Section 2). We note that similar results have been previously reported for the analogous complexes [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppm)] [9a] and



Scheme 1. Synthesis of the complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ_2-*P*,*P*-dppm)][BF_4] (**3**).



n = 2 (**4a**), 3 (**4b**), 4 (**4c**)

Scheme 2. Synthesis of the dinuclear complexes [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2${μ-$Ph_2P(CH_2)_nPPh_2$}] (**4a**–**c**).

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppf)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) [9c] which has been attributed, on the basis of variable-temperature NMR experiments, to the presence of two conformational isomers in solution.

It is apparent that the selective formation of the complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-$Ph_2PCH_2PPh_2$)] (**2**) versus the dinuclear species [{Ru(η^3:η^3-$C_{10}H_{16}$)-Cl_2}$_2${μ-$Ph_2P(CH_2)_nPPh_2$}] (*n* = 2 (**4a**), 3 (**4b**), 4 (**4c**)) indicates a different coordination ability of the diphosphines, probably due to the steric requirements of the bulky η^3:η^3-octadienediyl-Ru(IV) fragment. It seems that the relatively close proximity of both metallic fragments for dppm does not facilitate the formation of dinuclear species, i.e. [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppm)] [9a], which however can be readily formed for the longer chain diphosphines dppe, dppp and dppb. In accordance with this hypothesis we have found that, while **4a**–**c** are unreactive towards PPh_3, [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppm)] readily reacts with 1 equiv. of PPh_3, in dichloromethane at room temperature, to afford an equimolar mixture containing complex [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-$Ph_2PCH_2PPh_2$)] (**2**) and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(PPh_3)] [7a] via partial dissociation of the dppm ligand in [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2}$_2$(μ-dppm)].

Finally, we note that all attempts to prepare cationic species [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P*,*P*-$Ph_2P(CH_2)_n$-PPh_2}][BF_4] (*n* = 2, 3, 4) by treatment of dimer **1** with 2 equiv. of the appropriate diphosphine and $AgBF_4$ in dichloromethane, acetone or acetonitrile have been unsuccessful obtaining instead complicated mixtures of uncharacterized products. Apparently, the tendency of dppe, dppp and dppb to act as bridging ligands prevents the formation of the desired chelate complexes.

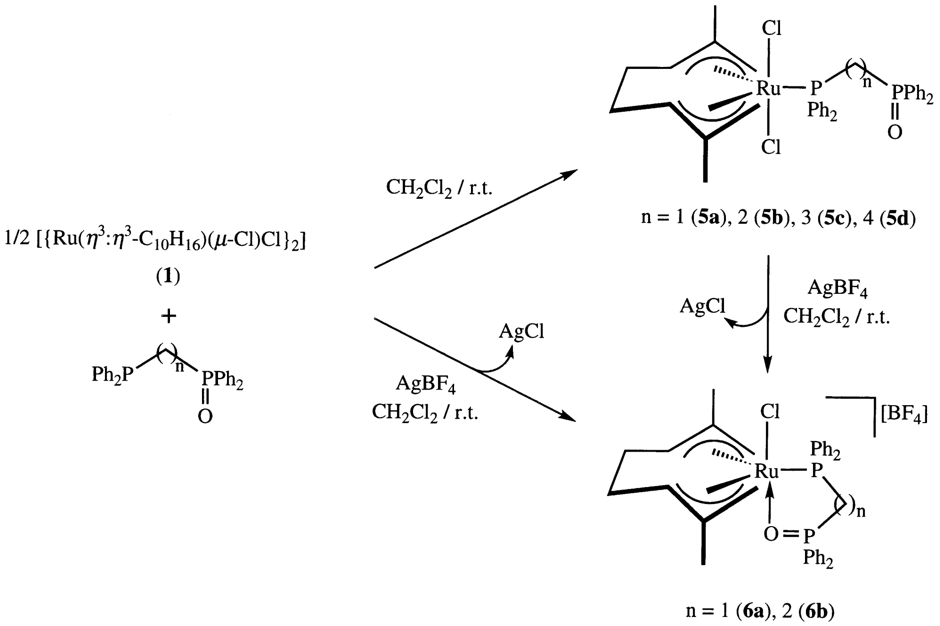
3.2. Reactivity of [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (1) towards diphosphine-monoxides $Ph_2P(CH_2)_nP(=O)Ph_2$ (n = 1–4)

Taking into account the lower ability of diphosphine-monoxides to act as intermetallic bridging ligands when compared to the corresponding diphosphines, we became interested in studying the reactivity of dimer **1** towards the monoxides derived from dppm, dppe, dppp and dppb. Moreover, the presence in these ligands of both a soft (P) and a hard (O) donor center confers hemilabile properties to their metal complexes of interest in homogeneous catalysis [13].

As expected, complex **1** reacts with a twofold excess of $Ph_2P(CH_2)_nP(=O)Ph_2$ (dppmO (*n* = 1), dppeO (*n* = 2), dpppO (*n* = 3) and dppbO (*n* = 4)), in dichloromethane at room temperature, to generate the neutral mononuclear adducts [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2{κ^1-*P*-Ph_2P-$(CH_2)_nP(=O)Ph_2$}] (*n* = 1 (**5a**), 2 (**5b**), 3 (**5c**), 4 (**5d**)) as the result of the selective coordination of the diphenylphosphino group on the Ru(IV) center (91–98% yield; Scheme 3). It is worth mentioning that no dinuclear bridged products were detected even when the reactions were carried out with only 1 equiv. of the diphosphine-monoxides obtaining instead equimolar mixtures of **5a**–**d** and the precursor complex **1**.

Complexes **5a**–**d** have been isolated as yellow–orange air-stable solids and are soluble in chlorinated solvents and tetrahydrofuran. They have been characterized by elemental analyses and IR and NMR ($^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$) spectroscopy being all the data fully consistent with the proposed formulations (see Section 2). Significant features are: (i) ($^{31}P\{^1H\}$ NMR) the expected doublet ($J_{PP} = 1.9$–39.1 Hz; **5a**–**c**) or singlet (**5d**) resonances for the Ph_2P and $Ph_2P{=}O$ groups in the ranges δ 17.42–20.19 and 22.80–31.79 ppm, respectively, and (ii) (^1H and $^{13}C\{^1H\}$ NMR) the presence of a single set of signals for the two allylic moieties of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand (i.e. only five resonances are observed in $^{13}C\{^1H\}$ NMR spectra) indicative of the formation of a simple equatorial adduct [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2L] with a local C_2-symmetry for the octadienediyl chain [6].

Treatment of dichloromethane solutions of complexes **5a**,**b** with 1 equiv. of $AgBF_4$ results in the formation of cationic derivatives [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P*,*O*-$Ph_2P(CH_2)_nP(=O)Ph_2$}][BF_4] (*n* = 1 (**6a**; 83% yield), 2 (**6b**; 85% yield); Scheme 3). These complexes can be also prepared in similar yields from **1** by reaction with 2 equiv. of the diphosphine-monoxide and $AgBF_4$ in dichloromethane at room temperature. NMR spectroscopic data (see Section 2 for details) provide significant structural information. Thus, in the $^{31}P\{^1H\}$ NMR spectra the chelating coordination of the diphosphine-



Scheme 3. Synthesis of the complexes [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P*,*O*-$Ph_2P(CH_2)_nP(=O)Ph_2$}][BF_4] (**6a**,**b**).

monoxide ligands is marked by a large downfield shift in the phosphoryl group resonances from the parent compounds **5a**,**b** (**6a**: 72.08 ppm ($J_{PP} = 28.3$ Hz); **6b**: 52.53 ppm ($J_{PP} = 2.3$ Hz)) in spite of the fact that this phosphorus is not directly bound to the metal. This behaviour, which has been previously observed in other metallic fragments [13c–h], can be attributed to delocalization of electron density in the –P=O–Ru– framework. In contrast, the ^{31}P NMR chemical shifts for the directly bound Ph_2P phosphorus atoms are less affected by the ring closure appearing at δ 26.19 (**6a**) and 9.33 (**6b**) ppm. ^{1}H NMR spectra of **6a**,**b** indicate that the two halves of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand are inequivalent, as expected for the loss of the C_2-symmetry (see Section 4). This is also clearly evidenced from the ^{13}C{^{1}H} NMR spectra in which ten separate signals are observed for the bis(allyl) unit.

Significantly, all attempts to form the corresponding cationic derivatives [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P*,*O*-$Ph_2P(CH_2)_nP(=O)Ph_2$}][BF_4] ($n = 3$, 4) by treatment of **5c**,**d** with $AgBF_4$ or starting directly from **1** have been unsuccessful obtaining instead mixtures of uncharacterized products. This behaviour can be attributed to the lower thermodynamic stability of the seven and eight-membered rings with respect to those of only five and six members (**6a**,**b**).

4. Conclusions

In summary, it has been demonstrated that cationic mononuclear bis(allyl)-ruthenium(IV) complexes containing chelating P–P and P–O ligands, i.e. [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P*,*P*-$Ph_2PCH_2PPh_2$)][BF_4] and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{κ^2-*P*,*O*-$Ph_2P(CH_2)_nP(=O)Ph_2$}][BF_4] ($n = 1$, 2), can be obtained from the readily available dimer [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] via initial chloride bridging cleavage to form neutral mononuclear species, i.e. [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-$Ph_2PCH_2PPh_2$)] and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2{κ^1-*P*-$Ph_2P(CH_2)_nP(=O)Ph_2$}] ($n = 1$, 2), and subsequent chloride extraction using silver(I) tetrafluoroborate. The former process is clearly the key step on this synthetic procedure since the formation of undesirable dinuclear ligand-bridged species, i.e. [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2{κ^1-*P*-$Ph_2P(CH_2)_nPPh_2$}] ($n = 2$, 3, 4), avoids the chelation of the ligand.

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