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The solid-state, solution and gas—phase interactions of diphosphane monooxide spacers with heavier group 8,9 transition metals and gallium in novel organometallic assemblies: An experimental and computational study

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ABSTRACT

Six new mono-substituted carbonyl clusters $[M_3(CO)_{11}(DPMO)]$ (M = Os, Ru; 1–4) and $[Rh_6(CO)_{15}(DPMO)]$ (5, 6) were obtained from the reactions of non-symmetrical bifunctional diphosphane monoxides (DPMOs, $Ph_2P(CH_2)_nP(O)Ph_2$, n = 2, 3) with triangular clusters $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$, and octahedral cluster $[Rh_6(CO)_{15}(NCMe)]$ under mild conditions. 1–6 were then subjected to electrophilic reactions with GaCl₃, which resulted in coordination-based molecular assemblies $[M_3(CO)_{11}(DPMO)(GaCl_3)]$ (M = Ru, Os; 7–10) and $[Rh_6(CO)_{15}(DPMO)(GaCl_3)]$ (11, 12). 1–12 were characterised by ³¹P{¹H} NMR, IR spectroscopy, and FAB mass spectrometry. The crystal structures of 1, 2 and 7 were determined by single-crystal X-ray analysis. 7 is the first solid-state characterised Os–Ga bridged complex. The latter and its constitutive fragment, 1, were studied by density functional calculations in the gas phase and in solution in order to better understand their structural features. Two different rotameric structures related by rotation about the P–C–C–P linkage of the DPMO ligand were established for 1 and 7. The bonding properties of 7 were analysed by means of a quantitative energy decomposition analysis (EDA). The EDA revealed a predominant electrostatic character for the interactions between the three units (carbonyl cluster, gallium halide and spacer) constitutive of 7.

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1. Introduction

Coordination-based molecular assemblies with well-defined composition, specific properties and structures containing both main group elements and transition metals in different oxidation states attract considerable attention stimulated by purely academic and practical reasons. Their synthesis, structural characterisation and studies at the computational level are of high current interest in diverse branches of chemical science. Herein, we focus on organometallic complexes in which bridging ligands link metal centres of dramatically different nature. Such assemblies seem to have a good chance to display unusual physicochemical properties, catalytic properties [1] and to be precursors to a wide range of hybrid materials [2].

What types of constitutive molecular units were used to fabricate novel multifunctional coordination-based assemblies? The definite size, chemical properties, and structural features of *transition metal (TM) carbonyl clusters* give the possibility to use the latter as versatile building blocks for the synthesis of complicated macromolecules [3] and metal nanoparticles [4]. The Lewis acidic *main group metal salt* can form coordination complexes with electron-rich ligands. In its turn, an *organic linker* (or *spacer*) with two coordination sites at the beginning and at the end of the ligand chain makes use of the opportunity to link metal centres of two different species. Thus, molecular architectures can be constructed by design of such a relevant spacer.

The aim of this work is to explore new coordination-based molecular assemblies based on non-symmetrical bifunctional phosphanes DPMOs of the type $Ph_2P(CH_2)_nP(O)Ph_2$ (n = 2, 3) linking low-nuclear carbonyl clusters of the heavier group 8 and 9 transition metals (Ru, Os and Rh), namely [M₃(CO)₁₂] (M = Ru, Os) and [M₆(CO)₁₆] (M = Rh) and the group 13 element halide, GaCl₃. The choice of the spacers was dictated by the nature of both heterometallic centres. While the soft phosphane P-donors are usually bonded to the *d*-metals, the hard phosphane oxide O-donors are ideal to connect the group 13 metals [5–7].

It is also noteworthy that the structural chemistry of the organometallic TM^{VIII} -Ga (TM = Ru, Os) and TM^{Ix} -Ga (TM = Rh, Ir)

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mixed complexes is still not well developed. The experimental studies of the reactivity between the complexes of gallium and the heavier group 8 (Ru, Os) and 9 (Rh, Ir) transition metals mainly focus on the molecular RuGa and RhGa systems, respectively 31 and 36 crystal structures which are available in the Cambridge Crystallographic Data Centre, CCDC. The number of the crystal structures reported e.g. for the mixed IrGa complexes is much smaller with only 5 crystal structures. Concerning mixed-metal OsGa complexes, no synthesis or structural data are available up to now, nevertheless some theoretical works appeared [8]. Therefore, one of the main goals of our work was to synthesise and structurally characterise the first organometallic OsGa complex and to gain an insight into the nature of its metal–ligand interactions using the combination of experimental and computational tools.

2. Experimental

2.1. General Comments

All synthetic procedures were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were distilled under inert atmosphere over appropriate drying agents prior to use, and toluene was additionally stored over molecular sieve A4 during one week. The [Rh₆(CO)₁₅(NCMe)] cluster [9] was synthesised according to the literature procedure. Commercial grade [Ru₃(CO)₁₂], [Os₃(CO)₁₂] (Aldrich); 1,2-Bis(diphenylphosp hino)ethane monooxide. POPE and 1.3-Bis(diphenylphosphino) propane monooxide, POPP (ABCR GmbH & Co, KG) were used without further purification. Me₃NO \times 2H₂O (Aldrich) was dehvdrated in vacuo immediately before using. GaCl₃ (Aldrich) was sublimed immediately before using and packed in a glass capillary. Infrared spectra were recorded using Perkin Elmer 16PC FT-IR spectrometer. ³¹P{¹H} NMR spectra were recorded in CDCl₃ at room temperature using Bruker ACD-HD AV400 and AV600 instruments. The chemical shifts were referenced to the resonance in 85% H₃PO₄ agua solution. Elemental analysis was carried out in the Microanalytical Laboratory of the University of Heidelberg, FAB⁺ mass spectra were obtained on a JEOL JMS-700 instrument, Institute of Organic Chemistry, University of Heidelberg. 1-nitro-2-(octyloxy) benzene was used as the matrix. Theoretical isotope patterns were calculated using Sheffield ChemPuter program available free of charge online http://winter.group.shef.ac.uk/chemputer/.

2.2. Synthesis of 1-4

The solution of fresh sublimed Me₃NO (9 mg, 0.120 mmol) in an ethanol/CH₂Cl₂ mixture (10 mL) was added dropwise during 0.5 h to a solution of the $[M_3(CO)_{12}]$ (M = Os, Ru) cluster (0.110 mmol) and the POPE or POPP ligand (0.175 mmol) in CH₂Cl₂ (100 mL) at room temperature under vigorous stirring. After reaction completed, the solvents were removed *in vacuo* leaving yellow (for osmium) or orange (for ruthenium) oily material that was dissolved in a minimum volume of CH₂Cl₂ and separated out on the silica plate with the CH₂Cl₂/n-hexane/acetone = 40/40/15 mixture as an eluent. After the product was washed out from silica with acetone and diluted with heptane. The solvents were removed *in vacuo* leaving dry crystalline material.

2.2.1. [Os₃(CO)₁₁(POPE)], 1

Yield 79%. IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2107m, 2055s, 2031sh, 2018vs, 1987m, 1977sh, 1950sh. ³¹P{¹H} NMR (δ ppm, RT) –6.9 (d, ³J_{P-P} = 48, 1P, P–Os), 30.6 (d, ³J_{P-P} = 48, 1P, P=O). MS (FAB, *m*/*z*) 1294 (M⁺) C₃₇H₂₄O₁₂Os₃P₂, the signals (M⁺–nCO), *n* = 1–10 were observed in the spectrum. Anal. calcd for C₃₇H₂₄O₁₂Os₃P₂: C, 34.36; H, 1.87. Found: C, 34.47; H, 2.01. Single crystals of **1** suitable for X- ray structure determination were grown from a dichloroethane/ acetone/octane mixture at +4 °C.

2.2.2. [Os₃(CO)₁₁(POPP)], 2

Yield 78%. IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2106m, 2054s, 2032sh, 2017vs, 1987m, 1974sh, 1950sh. ³¹P{¹H} NMR (δ ppm, RT) –9.5 (d, ⁴J_{P-P} = 2, 1P, P–Os), 31.8 (broad s, 1P, P=O). MS (FAB, *m*/*z*) 1308 (M⁺) C₃₈H₂₆O₁₂Os₃P₂, the signals (M⁺–nCO), *n* = 1–8 were observed in the spectrum. Anal. calcd for C₃₈H₂₆O₁₂Os₃P₂: C, 34.91; H, 2.00. Found: C, 34.87; H, 2.05. Single crystals of **2** suitable for X-ray structure determination were grown from a CH₂Cl₂/acetone/ heptane mixture at +4 °C.

2.2.3. [Ru₃(CO)₁₁(POPE)], **3**

Yield 49%. IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2097m, 2046s, 2028sh, 2013vs, 1985sh. ³¹P{¹H} NMR (δ ppm, RT) 30.2 (d, ³*J*_{P-P} = 45, 1P, P–Ru), 31.3 (d, ³*J*_{P-P} = 45, 1P, P=O). MS (FAB, *m*/*z*) 1343 (M⁺) C₃₇H₂₄O₁₂P₂Ru₃, the signals (M⁺–nCO), *n* = 1–9 were observed in the spectrum. Anal. calcd for C₃₇H₂₄O₁₂P₂Ru₃: C, 43.32; H, 2.36. Found: C, 43.46; H, 2.57.

2.2.4. [Ru₃(CO)₁₁(POPP)], 4

Yield 37%. IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2097m, 2046s, 2028sh, 2013vs, 1985sh. ³¹P{¹H} NMR (δ ppm, RT) 26.8 (d, ⁴J_{P-P} = 2, 1P, P–Ru), 31.4 (d, ⁴J_{P-P} = 2, 1P, P=O). MS (FAB, *m*/*z*) 1040 (M⁺) C₃₈H₂₆O₁₂P₂Ru₃, the signals (M⁺–nCO), *n* = 1–10 were observed in the spectrum. Anal. calcd for C₃₈H₂₆O₁₂P₂Ru₃: C, 43.90; H, 2.52. Found: C, 43.88; H, 2.61.

2.3. Synthesis of 5 and 6

The complex [Rh₆(CO)₁₅(NCMe)] (0.039 mmol) was dissolved in CH₂Cl₂ (40 mL) and the solid POPE or POPP ligand (0.048 mmol) was added under vigorous stirring. The reaction mixture immediately got a dark-red colour. After stirring for 15 min n-hexane was added to the reaction mixture and the solvents were removed *in vacuo* leaving dry brown material. The latter was dissolved in a minimum volume of CH₂Cl₂ and the product was separated on TLC silica plate with the CH₂Cl₂/n-hexane/acetone = 30/30/15 mixture as an eluent and then washed out from silica with acetone. Heptane was added to the acetone solution and the solvents were removed *in vacuo* leaving brown crystalline precipitate of the product.

2.3.1. [Rh₆(CO)₁₅(POPE)], 5

Yield 59%. IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2100m, 2065vs, 2035m, 2025sh, 2008sh, 1793brm. ³¹P{¹H} NMR (δ ppm, RT) 21.2 (ddm, ¹J_{Rh-P} = 135, ³J_{P-P} = 38, ²J_{Rh-P} = 4, 1P, P-Rh), 30.6 (d, ³J_{P-P} = 38, 1P, P=O). MS (FAB, *m*/*z*) 1452 (M⁺) C₄₁H₂₄O₁₆P₂Rh₆, the signals (M⁺-nCO), *n* = 1–14 were observed in the spectrum. Anal. calcd for C₄₁H₂₄O₁₆P₂Rh₆: C, 33.91; H, 1.67. Found: C, 33.97; H, 2.01.

2.3.2. [Rh₆(CO)₁₅(POPP)], 6

Yield 59%. IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2100m, 2065vs, 2034m, 2024sh, 2008sh, 1793brm. ³¹P{¹H} NMR (δ ppm, RT) 18.2 (dm, ¹J_{Rh-P} = 134, ²J_{Rh-P} = 3, 1P, P–Rh), 31.5 (s, 1P, P=O). MS (FAB, *m*/*z*) 1466 (M⁺) C₄₂H₂₆O₁₆P₂Rh₆, the signals (M⁺–nCO), *n* = 1–14 were observed in the spectrum. Anal. calcd for C₄₂H₂₆O₁₆P₂Rh₆: C, 34.41; H, 1.79. Found: C, 34.50; H, 1.99.

2.4. Synthesis of 7–10

In a typical procedure, complex 1-4 (0.043 mmol) was dissolved in toluene and cooled in dry ice/isopropanol bath. The tube with GaCl₃ (*ca* 0.057 mmol) was then broken inside of the reaction flask in the argon stream and under high stirring. After stirring for 1 h the reaction mixture was allowed to warm to room temperature, and the solvent was removed *in vacuo* to give an oily material that was washed by hexane and dried *in vacuo*. Resulting substance was dissolved in CH_2Cl_2 and passed through short silica column using the CH_2Cl_2/n -hexane/acetone = 40/40/15 mixture as an eluent. Heptane was added to the solution and the solvents were removed *in vacuo* resulting in the formation of light orange (for ruthenium) or yellow (for osmium) wax material. Satisfactory elemental analysis results and yield values (the yields of **7**–**12** are estimated as 75–80%) for **7–12** were not obtained because of an unremovable admixture of gallium compounds.

2.4.1. [Os₃(CO)₁₁(POPE)(GaCl₃)], 7

IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2150m, 2122w, 2107s, 2083s, 2066vs, 2046m, 2025s. ³¹P{¹H} NMR (δ ppm, RT) –12.0 (d, ³J_{P-P} = 44, 1P, P–Os), 52.6 (d, ³J_{P-P} = 44, 1P, P=O). MS (FAB, *m/z*) 1470 (M⁺) C₃₇H₂₄Cl₃GaO₁₂Os₃P₂, the signals (M⁺–nCO), *n* = 1–6 were observed in the spectrum. Single crystals of **7** suitable for X-ray structure determination were grown in a NMR tube from CDCl₃ solution at +4 °C.

2.4.2. [Os₃(CO)₁₁(POPP)(GaCl₃)], 8

IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2149m, 2121w, 2106s, 2081s, 2064vs, 2043s, 2025s. ³¹P{¹H} NMR (δ ppm, RT) –13.3 (d, ⁴J_{P-P} = 4, 1P, P–Os), 53.4 (d, ⁴J_{P-P} = 4, 1P, P=O). MS (FAB, *m*/*z*) 1484 (M⁺) C₃₈H₂₆Cl₃GaO₁₂Os₃P₂, the signals (M⁺–nCO), *n* = 1–5 were observed in the spectrum.

2.4.3. [Ru₃(CO)₁₁(POPE)(GaCl₃)], 9

IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2143m, 2130sh, 2104s, 2081s, 2067vs, 2052vs, 2034s, 1974w. ³¹P{¹H} NMR (δ ppm, RT) 22.4 (d, ³J_{P-P} = 40, 1P, P–Ru), 52.9 (d, ³J_{P-P} = 40, 1P, P=O). MS (FAB, m/z), 1201 (M⁺) C₃₇H₂₄Cl₃Ga₁O₁₂P₂Ru₃; the signals (M⁺–nCO), n = 1-8 were observed in the spectrum.

2.4.4. [Ru₃(CO)₁₁(POPP)(GaCl₃)], 10

IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2143w, 2130sh, 2103s, 2080s, 2065vs, 2052sh, 2031s, 1975vw. ³¹P{¹H} NMR (δ ppm, RT) 20.4 (d, ⁴*J*_{P-P} = 4, 1P, P–Ru), 53.5 (d, ⁴*J*_{P-P} = 4, 1P, P=O). MS (FAB, *m/z*) 1216 (M⁺) C₃₈H₂₆Cl₃Ga₁O₁₂P₂Ru₃, the signals (M⁺–nCO), *n* = 1–6 were observed in the spectrum.

2.5. Synthesis of 11 and 12

In a typical procedure, complex **5** or **6** (0.021 mmol) was dissolved in *ca.* 20 mL of toluene and the tube with the GaCl₃ (*ca.* 0.057 mmol) was broken inside of the reaction flask under high stirring. After stirring for 1 h all volatile components were removed *in vacuo* to result in brown oil. This substance was dissolved in CHCl₃ and passed through silica column using the CH₂Cl₂/nhexane/acetone = 40/40/15 mixture as an eluent leaving some brown start. Heptane was added to the solution and the solvents were removed *in vacuo*, resulting in the formation of brown wax substance. The latter was washed by hexane and then dried *in vacuo* leaving brown paste material.

2.5.1. [Rh₆(CO)₁₅(POPE)(GaCl₃)], 11

IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2101m, 2090w, 2066vs, 2035m, 2008sh, 1796brm. ³¹P{¹H} NMR (δ ppm, RT) 19.8 (ddm, ¹J_{Rh-P} = 133, ³J_{P-P} = 39, ²J_{Rh-P} = 4, 1P, P–Rh), 53.9 (d, ³J_{P-P} = 39, 1P, P=O). MS (FAB, *m*/*z*) 1628 (M⁺) C₄₁H₂₄Cl₃GaO₁₆P₂Rh₆, the signals (M⁺–nCO), *n* = 3–14 were observed in the spectrum.

2.5.2. [Rh₆(CO)₁₅(POPP)(GaCl₃)], 12

IR (CH₂Cl₂, cm⁻¹, ν_{CO}) 2100m, 2089w, 2065vs, 2035m, 2026sh, 2006sh, 1795brm. ³¹P{¹H} NMR (δ ppm, RT) 17.9 (dm, ¹J_{Rh-P} = 129,

 ${}^{2}J_{Rh-P} = 3$, 1P, P–Rh), 55.4 (s, 1P, P=O). MS (FAB, m/z) 1642 (M⁺) C₄₂H₂₆Cl₃GaO₁₆P₂Rh₆, the signals (M⁺–nCO), n = 1–14 were observed in the spectrum.

2.6. X-ray crystal structure determination

Single crystals of compounds 1, 2, and 7 suitable for X-ray diffraction studies were mounted with perfluorinated polvether oil on the tip of a glass fibre and cooled down to 200 K immediately on the goniometer head. Data collection was performed on a STOE IPDS I diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). Structures were solved and refined with the Bruker AXS SHELXTL 5.1 program package. Refinement was in full matrix against F^2 . All hydrogen atoms were included as riding models with fixed isotropic U values in the final refinement. Due to the rather small size and low quality of the crystals of 1 only Os and P atoms were refined anisotropically, C(1)O(1) carbonyl ligand in the structure of 1 is disordered over two crystallographically non-equivalent halfoccupied positions with the total site-occupation factor (s.o.f.) equal to 1.0. There is also a partial disordering in the C(20)-C(25)ring. Thus, three carbon atoms C(23), C(24) and C(25) of the ring disordered over two non-equivalent half-occupied positions with the total s.o.f. equal to 1.0. In the structure of **7** there is the H[GaCl₄] complex. Crystal structure of 7 also contains crystallographically disordered over two non-equivalent positions CHCl₃ molecule with the s.o.f. equal 0.50 and 0.25 for C(A)Cl(A)Cl(C)Cl(D) and C(B)Cl(B) Cl(E)Cl(F) parts, respectively. For further data refer to Table 1.

2.7. Computational details

Density functional theory (DFT) geometry optimisations were firstly performed in the gas phase using the Gaussian 09 program

Table 1

Crystal data and	structure refinement	t details for	12	and 7
Crystal uata allu	structure reinfemen	L UCLAIIS IUI	1, 2,	anu 7.

	1	2	7
Empirical formula	C ₃₇ H ₂₄ O ₁₂ Os ₃ P ₂	$C_{38}H_{26}O_{12}Os_3P_2$	C _{37.75} H ₂₄ Cl _{9.25} Ga ₂ O ₁₂ Os ₃ P ₂
Formula mass [g/mol]	1293.10	1307.13	1769.46
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> −1	P 2 ₁ /c	$P 2_1/n$
a [Å]	8.7588(18)	15.244(3)	9.6141(19)
b [Å]	13.607(3)	22.996(5)	19.213(4)
c [Å]	16.869(3)	11.348(2)	29.691(6)
α [°]	77.96(3)	90.00	90.00
β[°]	83.60(3)	101.92(3)	91.23(3)
γ [°]	73.75(3)	90.00	90.00
V [Å ³]	1884.7(7)	3892.3(13)	5483.1(19)
Ζ	2	4	4
Calculated density [g/cm ³]	2.279	2.231	2.144
F(000) [e]	1200	2432	3295
Crystal size [mm ³]	0.18 imes 0.08	$\textbf{0.246} \times \textbf{0.038}$	$\textbf{0.24} \times \textbf{0.23}$
	× 0.07	× 0.034	× 0.15
θ range for data collection [°]	5.84 ÷ 26.37	1.77 ÷ 24.21	2.12 ÷ 24.00
Index ranges	$-10 \le h \le 10$	$-17 \leq h \leq 17$	$-11 \le h \le 11$
	$-17 \leq k \leq 17$	$-26 \le k \le 26$	$-21 \leq k \leq 21$
	$-21 \le l \le 21$	$-13 \le l \le 13$	$-33 \le l \le 32$
Collected reflections	15 505	25 262	34 949
Unique reflections	7082	6229	8535
Data/restraints/ parameters	7082/88/263	6229/108/496	8535/6/601
Goodness of fit on F^2	0.938	0.890	0.903
Final R indices	R1 = 0.0709	R1 = 0.0641	R1 = 0.0470
$(I > 2\sigma(I))$	wR2 = 0.1553	wR2 = 0.1214	wR2 = 0.0870
R indices (all data)	R1 = 0.1462	R1 = 0.1552	R1 = 0.0663
	wR2 = 0.1832	wR2 = 0.1423	wR2 = 0.0926
Residual electronic density, [e/Å ³]	1.919/-2.818	2.034/-4.596	1.327/-0.960

package [10] and energy minima were verified to be equilibrium structures through vibrational analysis. The equilibrium structures were obtained from the DFT computations using the threeparameter exchange functional of Becke [11] with gradientcorrected correlation functional of Lee, Yang, and Parr (B3LYP) [12]. We used Los Alamos National Laboratory 2 (LANL2) relativistic effective core potentials (RECPs) [13] to describe the core electrons of Os. Ru. Rh and Ga atoms and split-valence (double- ζ) guality basis sets to describe their valence electrons. For the heavier group 8 and 9 transition metals (Os, Ru, Rh), the LANL2DZ basis sets were augmented by adding one set of *f* polarisation functions (orbital exponents 0.886 for Os, 1.235 for Ru, and 1.350 for Rh) [14]. For Ga, the LANL2DZ basis set was augmented by one set of d polarisation functions (orbital exponent 0.16, as used by Timoshkin et al. in [15]). For the non-metal atoms Cl, P, O, C, and H, all-electron splitvalence 6-311G(d,p) basis sets were employed [16]. The combination of all these basis sets is denoted as Basis Set System I (BS-I).

Energy decomposition analyses (EDA) [17] were performed using the Amsterdam Density Functional (ADF) program developed by Baerends and others [18-20]. The numerical integration was performed using the procedure developed by te Velde et al. [19] The molecular orbitals (MOs) were expanded in a large uncontracted set of Slater-type orbitals (STOs): TZ2P (no Gaussian functions are involved) [20]. The basis set of triple- ζ quality was used for all nonand metal atoms and augmented with two set of polarisation functions on each atom (e.g. for non-metal atoms: 2p and 3d on H; 3d and 4f on C. O. P. and Cl). An auxiliary set of s. p. d. f and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field cycle. All energies were calculated at the B3LYP level (20% Hartree-Fock exchange); electron correlation was treated in the Vosko-Wilk-Nusair (VWN5) parameterisation [21]. Scalar relativistic effects were accounted for using the zeroth-order regular approximation (ZORA) [22].

In order to take into account the environment continuum medium effects modeling the situation in solution, the B3LYP functional was combined with the Polarisable Continuum Model (PCM) in toluene ($\varepsilon = 2.3741$) and chloroform ($\varepsilon = 4.7113$). The gasphase geometries were thus re-optimised in corresponding solutions using the Gaussian 09 program package. The radii and non-electrostatic terms were taken from the SMD solvation model developed by Truhlar and co-workers [23]. The optimised geometries were verified through vibrational analysis to undertake their characterisation as true minima (number of imaginary frequencies, NImag = 0), transition states (NImag = 1) or higher order saddle points (NImag = 2, 3, etc.).

3. Results and discussion

3.1. Synthesis and structural characterisation of $[M_3(CO)_{11}(DPMO)]$ (M = Os, Ru; 1-4) and $[Rh_6(CO)_{15}(DPMO)]$ (5–6)

We found that the reactions of transition metal carbonyl cluster compounds $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ in the presence of Me₃NO and the labile cluster $[Rh_6(CO)_{15}(NCMe)]$ with a slight excess of the DPMO, Ph₂P(CH₂)_nP(O)Ph₂ (n = 2, POPE; n = 3, POPP), result in the formation of mono-substituted cluster complexes $[Os_3(CO)_{11}(-POPE)]$ (**1**), $[Os_3(CO)_{11}(POPP)]$ (**2**), $[Ru_3(CO)_{11}(POPE)]$ (**3**), $[Ru_3(CO)_{11}(POPP)]$ (**4**), $[Rh_6(CO)_{15}(POPE)]$ (**5**), and $[Rh_6(CO)_{15}(-POPP)]$ (**6**) under mild conditions. Complexes **1**–**6** are moderately air-stable and not destroyed on silica.



 $TMC = [Ru_3(CO)_{11}], [Os_3(CO)_{11}], [Rh_6(CO)_{15}]$

The single crystals of **1** and **2** were isolated from corresponding solvents/mixtures (see Experimental) at +4 °C. The solid-state structures of the compounds were established by single-crystal X-ray diffraction analyses. Compound **1** crystallises in the triclinic space group P - 1, whereas **2** crystallises in the monoclinic space group $P 2_1/c$. Molecular structures of **1** and **2** are illustrated in Fig. 1; crystallographic data are collected in Table 1; selected structural parameters are given in Table 2.

The molecular structures of **1** and **2** are very similar and consist of 11 terminal CO groups and a DPMO ligand coordinated to the triangular Os₃ skeleton in a terminal manner through the phosphorus atom. The Os–Os bond lengths in **1** and **2** fall in the range from 2.847(2) to 2.9255(2) Å and the Os(1)–P(1) bond lengths are equal to 2.352(5) and 2.361(6) Å, respectively. As a result, the observed values of the bond lengths are comparable to those in other previously reported $[Os_3(CO)_{11}(PR_3)]$ clusters with terminal



Fig. 1. Molecular structures of complexes 1 (left) and 2 (right).

 Table 2

 Selected bond lengths [Å] for 1, 2, and 7.

	1	2	7
Os(1)-Os(3)	2.8893(13)	2.876(2)	2.8596(8)
Os(2) - Os(1)	2.9255(12)	2.847(2)	3.0306(9)
Os(3)-Os(2)	2.8822(15)	2.867(2)	2.8687(8)
Os(1)-P(1)	2.352(5)	2.361(6)	2.344(3)
P(1) - C(12)	1.853(17)	1.83(2)	1.825(9)
C(13)-C(12)	1.50(3)	1.55(3)	1.510(13)
C(13)-P(2)	1.815(15)		1.787(9)
C(13)-C(38)		1.53(4)	
C(38)-P(2)		1.79(3)	
P(2)-O(12)	1.459(13)	1.48(2)	1.515(6)
O(12) - Ga(1)			1.843(6)
C(1) - O(1)	1.154(5)	1.23(3)	1.150(13)
C(2) - O(2)	1.12(2)	1.17(4)	1.147(13)
C(3)-O(3)	1.22(3)	1.19(4)	1.129(13)

coordinated phosphanes [24–26]. The DPMO ligand in **1** and **2** occupies an equatorial position on the osmium triangle. The values of its P=O bond lengths, 1.459(13) in **1** and 1.48(2) Å in **2**, are similar to those found in free phosphane oxides [27,28]. In addition, **1** and **2** comprise coordination sites at the O(12) atom of the DPMO that are accessible for further electrophilic attack of a Lewis acid.

The structures of compounds 1–6 in solution were characterised by spectroscopic and spectrometric methods. The data obtained were shown to be very similar for the pairs of complexes 1-2, 3-4, and 5–6 due to minor differences in the ligand construction of the DPMO. The FAB⁺ mass spectra of **1–6** display the signals of corresponding molecular ions. The observed isotopic distribution pattern of each molecular ion is in excellent accordance with their calculated one (see Supplementary Information; denoted as SI below). The ³¹P NMR and IR spectroscopic data of **5** are identical to the data published by Tunik et al. [29] for the rhodium cluster complex $[Rh_6(CO)_{15}(Ph_2P(CH_2)_2P(O)Ph_2)]$. The ³¹P NMR spectrum of each complex, 1–6, contains two signals of the equal intensity (Table 3). Firstly, the high-field signal is assigned to the phosphorus atom P(1) coordinated to the metal core. The chemical shift position of P(1) along with typical ${}^{1}J_{Rh-P}$ coupling constants obtained for **5** and **6** confirms such an assignment. The signal of the P(1)

Table 3

³¹ P NMR data of 1–12

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3
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atom has a considerable low-field shift with respect to the phosphorus resonance in a free ligand. Such a behaviour is typical for a phosphane coordinated in the ligand environment of Os_3 [25,26], Ru₃ [24,26,30,31], and Rh₆ clusters [29,32]. Secondly, the low-field signal is assigned to the phosphorus atom P(2) of "dangling" phosphane oxide [29,33]. The observed coupling constants are due to interaction of the phosphorus atoms in the POPE and the POPP.

While the IR spectra of **1**–**4** in CH₂Cl₂ solutions show only the peaks corresponding to the terminal CO ligands in the carbonyl region, the IR spectra of **5** and **6** in CH₂Cl₂ display bands associated with the stretching vibrations of both a terminal and μ_3 -bridging CO group in the same region (see Experimental and SI). Relative positions and intensities of the observed signals are in good agreement with those obtained for the mono-substituted [Os₃(CO)₁₁(PR₃)] [25,26], [Ru₃(CO)₁₁(PR₃)] [24,26,30], and [Rh₆(CO)₁₅(PR₃)] clusters [34]. As a result, the structures of compounds **3**–**4** can be described as metal triangles surrounded by 11 terminal carbonyl groups and terminal phosphane ligands, POPE or POPP, coordinated to the metal skeleton through the phosphorus atom in an equatorial position likewise **1** and **2**. Clusters **5**–**6** are Rh₆ octahedrons with 11 terminal CO and 4 face-bridging CO groups, and a terminal phosphane ligand.

3.2. Synthesis and structural characterisation of $[M_3(CO)_{11}(DPMO)(GaCl_3)]$ (M = Os, Ru; 7-10) and $[Rh_6(CO)_{15}(DPMO)(GaCl_3)]$ (11–12)

Transition metal cluster complexes **1–6** react with GaCl₃ in toluene solution to yield coordination-based molecular assemblies **7–12**, respectively, in which a diphosphane monoxide linker connects both the transition metal cluster core and the main group metal centre. The reactions of **5** or **6** with GaCl₃ occur at room temperature without measurable cluster core decomposition, whereas the reactions between **1–4** and GaCl₃ need a lower temperature to prevent the metal skeleton deconstruction. Compounds **7**, **8**, **11**, and **12** are moderately air-stable and they are not destroyed on short silica column. Compounds **9** and **10** have relatively short life time in solution as well as in the solid state.



 $TMC = [Ru_3(CO)_{11}], [Os_3(CO)_{11}], [Rh_6(CO)_{15}]$

The single crystals of **7** were isolated from CDCl₃ solution at +4 °C and its solid-state structure was established by X-ray diffraction analysis. Compound **7** crystallises in the monoclinic space group $P 2_1/n$. The structural representation of **7** is shown in Fig. 2; crystallographic data are collected in Table 1; and selected structural parameters are given in Table 2.

The molecular structure of **7** consists of two main units involving the complex structural fragment **1** and GaCl₃. The latter is coordinated to **1** *via* the oxygen atom O(12). In contrast to the trigonal planar configuration of a non-coordinated GaCl₃ molecule, the gallium atom in the {OGaCl₃} fragment of **7** displays a tetrahedral coordination environment (Fig. 2). The Os–Os bond lengths in



Fig. 2. Molecular structure of 7.

7 fall in the range 2.8596(8)–3.0306(9) Å. The POPE ligand occupies an equatorial position on the osmium triangle likewise **1**. The Os(1)-P(1) bond length is equal to 2.344(3) Å and it is thus slightly shorter than that in **1**. The P(2)–O(12) bond length in **7** is elongated to 1.515(6) Å with respect to that in **1** and accordingly to the one in a free phosphane oxide [28]. A somewhat analogous scenario is observed for the mononuclear gallium complexes with the terminal and chelate phosphane oxides [6,7].

The structures of 7–12 in solutions were characterised by spectroscopic and spectrometric methods. The data obtained were shown to be very similar for the pairs of complexes 7-8, 9-10 and 11-12 like in the previous case (see Section 3.1). According to spectroscopic data obtained for 7-12, the latter preserve their overall structural composition as well as the structure of transition metal carbonyl cluster skeleton after the electrophilic coordination of GaCl₃ to the spacer. The FAB⁺ mass spectra of compounds 7–12 display the signals of their corresponding molecular ions. The observed isotopic distribution pattern of each molecular ion is in excellent accordance with their calculated one (see SI). The ³¹P NMR spectrum of each complex, 7–12, contains two signals of the equal intensity (Table 3). Firstly, the presence of the low-field resonance in the ³¹P NMR spectrum is compatible with the structural pattern mentioned above. The P(2) signal is substantially down-shifted when compared to that in the ³¹P NMR spectra of **1–6**, in accordance with literature data [7]. This indicates a relatively high acidity of the Ga coordination centre in 7-12 that elongates the P(2)-O(12) bonds, as observed e.g. in the crystal structure of 7 (Table 2). Secondly, the high-field resonance is assigned to the phosphorus atom P(1) coordinated to the metal core. Interestingly, the P(1)resonance in **7–10** is up-shifted when compared to that in the ³¹P NMR spectra of **1–4**. This means that the electronic density on the P(1) atom bonded to the Os₃ or Ru₃ metal cores increases when Ga is coordinated to the opposite site (to the O(12) atom) of the DPMO ligand. The IR spectra of 7–10 in CH₂Cl₂ solutions show only the peaks corresponding to the terminal CO ligands in the carbonyl region. Furthermore, their frequencies are shifted to high energy field compared to those in 1-4 (see Experimental and SI). Overall, the spectral behaviour of the studied molecular systems is complex, but somewhat similar, albeit we observe some non-typical changes in the IR spectra of 7-10 with respect to 1-4. Moreover, from analysis of the electron density distribution for 1-10 it can be concluded that only minor charge transfer effects operate when the three units (carbonyl cluster, GaCl₃, and spacer) assemble together (see SI, Tables S1, S2).

In the case of cluster compounds **11** and **12**, their ³¹P NMR and IR spectroscopic data are very similar to those of **5** and **6** with the exception of the observed low-field shift of the P(2) atom resonance. In contrast to the complexes with a triangular core, the ³¹P NMR and IR spectra of **11** and **12** demonstrate no high-field shifts for the P(1) atom and the CO groups, respectively (see Table 3, Experimental and SI). This may be indicative of the fact that the coordination of GaCl₃ to the DPMO ligand of **5** and **6** activates no change in the electron structure of the {Rh₆(CO)₁₅P} fragment. Furthermore, such a behaviour might be related to the three-dimensional aromaticity of the closed-face octahedral rhodium cluster system [35] that stabilises the octahedral Rh₆ architecture towards any external electron influences.

3.3. Quantum chemical calculations

The B3LYP optimised gas-phase structures of $[M_3(CO)_{11}(PO-PE)(GaCl_3)]$ with M = Os (**7**), Ru (**9**) and $[Rh_6(CO)_{15}(POPE)(GaCl_3)]$ (**11**) complexes are represented in Fig. 3. As we can see, the constitution of the equilibrium geometries **7**_{comput} and **9**_{comput} is not influenced by the nature of the transition metal (M = Os, Ru). The values of their dihedral M(1)-P(1)-P(2)-Ga angles are around -69° ; the M–M and M(1)-P(1) bond lengths change only insignificantly, whereas the values of the P(2)–O and Ga–O bonds do not change at all. The experimental value of the dihedral Os(1)-P(1)-P(2)-Ga angle in **7** is equal to -48.9° . This shows that the structure of complex **7** is somewhat influenced by crystal packing effects; the solid-state structure thus becomes more reduced in its volume. The constitution of **11**_{comput}, in its turn, differs from the previous ones (Fig. 3). The dihedral Rh(1)-P(1)-P(2)-Ga angle is



Fig. 3. The equilibrium gas-phase structures 7_{comput} (left), 9_{comput} (centre), and 11_{comput} (right) and their structural parameters.



Fig. 4. The B3LYP optimised gas-phase structures of rotamers $1A_{\rm comput}$ (left) and $1B_{\rm comput}$ (right).

ca. 171° and the Rh(1)–P(1), P(2)–O, and Ga–O bond lengths slightly increase compared to those in **7**_{comput} and **9**_{comput}. As a result, the metal–metal bond distances in these three studied assemblies moderately elongate when going down the heavier group 8 transition metals (from Ru to Os) and shorten when going left to right across the period 5 transition metals (from Ru to Rh).

In order to examine the influence of homogeneous solvent medium on the structure and properties of **7**, we re-optimised the "relaxed" gas-phase geometry of the latter in a toluene and CHCl₃ solvent shell. The results obtained for the equilibrium structure **7**_{comput} indicate that: (*i*) the dihedral Os(1)–P(1)–P(2)–Ga angle is slightly reduced towards lower value of *ca.* -62° in both toluene and CHCl₃; (*ii*) the Ga–O bond lengths moderately shorten with an increase in the polarity of the solvent (d_{Ga–O} = 1.875 Å and 1.858 Å in toluene and CHCl₃, respectively); (*iii*) in contrast, the Os(1)–P(1) and P(2)–O bond lengths elongate monotonically (d_{Os(1)}–P₍₁₎ = 2.428 Å, d_{P(2)–O} = 1.546 Å in toluene; d_{Os(1)}–P₍₁₎ = 2.430 Å, d_{P(2)–O} = 1.551 Å in CHCl₃); (*iv*) the HOMO–LUMO gap of **7**_{comput} in both solutions does not increase. In addition, the equilibrium structure **7**_{comput} is energetically more favourable by 2.5 kcal mol⁻¹ (incl. zero-point energy, ZPE, correction) in CHCl₃ than in toluene.

Elimination of GaCl₃ from **7** leads to a very interesting situation in complex **1**. According to our DFT calculations, the latter exhibits two equilibrium isostructures, **1**A_{comput} and **1**B_{comput}, which are the rotamers related by rotation about the P(1)–C–C–P(2) linkage (Fig. 4). The energy difference between these rotameric structures in the gas phase is only –1.2 kcal mol⁻¹ (incl. ZPE correction). The more stable **1**B_{comput} structure matches the experimental one (**1**; Fig. 1).

The situation becomes more complex by coordination of Ga to the oxygen atom of the diphosphane monoxide ligand (POPE) of **1**. As observed by X-ray crystallography, complex **7** in the solid-state



Fig. 5. The B3LYP optimised structures of rotamers 7_{comput} (left) and 7^(unfd)_{comput} (right). 7_{comput} corresponds to the experimental structure of 7 observed in the solid state, whereas 7^(unfd)_{comput} is the more stable structure in the gas phase.



Fig. 6. The gas-phase interactions between the units constitutive of coordination-based molecular assembly 7_{comput} studied by means of a quantitative energy decomposition analysis (EDA). Top: interaction of $[Os_3(CO)_{11}]$ with (POPE)GaCl₃. Bottom: interaction of $[Os_3(CO)_{11}(POPE)]$ (**1B**_{comput}) with GaCl₃.

Table 4

Energy decomposition analysis (in kcal mol^{-1}) of the interactions between the units constitutive of the equilibrium structure 7_{comput} .

EDA ^a	[Os ₃ (CO) ₁₁ (POPE)(GaCl ₃)], 7 _{comput}		
	$[Os_3(CO)_{11}] + (POPE)GaCl_3$	$[Os_3(CO)_{11}(POPE)] + GaCl_3$	
ΔE_{int}^{b}	-42.9	-41.4	
ΔE_{Pauli}	164.7	101.1	
ΔV_{elstat}	-132.6 (63.9%)	-86.5 (60.7%)	
ΔE_{oi}	-75.0 (36.1%)	-56.0 (39.3%)	
ΔE_{prep}	5.1	16.5	
D_e^{c}	37.8	24.9	

^a At ZORA-B3LYP/TZ2P.

 $\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}}.$

 $\Delta E (= -D_e) = \Delta E_{int} + \Delta E_{prep}.$

favours more compact (or "folded") molecular structure (corresponds to 7_{comput}) in its volume (see Figs. 2 and 5). In their turn, the results obtained from the structural optimisations of 7 in the gas phase and in solution reveal that the "unfolded" structural shape of this complex (referred to as $7_{comput}^{(unfd)}$) is energetically more stable by 3.3 kcal mol⁻¹ in the gas phase, and by 1.1 kcal mol⁻¹ in toluene and 0.2 kcal mol⁻¹ in CHCl₃ than the "folded" one of 7_{comput} according to the relative energies (incl. ZPE correction) calculated at their equilibrium structures (Fig. 5). The observation of the two rotameric structures, 7_{comput} and $7_{comput}^{(unfd)}$, is related to that fact that the potential energy surface of the studied Os–Ga bridged complex is fairly flat.

The dissimilarities observed between the gas and solution phases clearly demonstrate the importance of the continuum medium effects not only on the geometric shape of the coordination-based molecular assembly **7** but also on its energetic features. Thus, the phase differences are expected to have an effect on **7** of which constitution may, furthermore, be influenced by the crystallisation conditions (solvent, temperature, etc.). For example, a more polar solvent (e.g. CDCl₃) should facilitate the rotation about the P(1)–C–C–P(2) linkage due to the possible weakening of the interconstitutive Os(1)–P(1) and P(2)–O bonds. In addition, **7**_{comput} should obviously be better stabilised by non-specific intermolecular interactions in the crystal structure than **7**_{comput}.

In order to gain further insight into the nature of the interconstitutive metal–ligand interactions in **7**, energy decomposition analyses (EDA) of the equilibrium gas-phase structure **7**_{comput} were performed for two models constructed from different fragments: (*i*) $[Os_3(CO)_{11}]$ and (POPE)GaCl₃, and (*ii*) $[Os_3(CO)_{11}(POPE)]$ (**1B**_{comput}) and GaCl₃ (Fig. 6, Table 4). The EDA shows that the interaction energies, ΔE_{int} , of $[Os_3(CO)_{11}]$ with (POPE)GaCl₃ and of **1B**_{comput} with GaCl₃ are very small (*ca.* –40 kcal mol⁻¹). This is indicative of a relatively low strength of binding between the units. Furthermore, these interconstitutive interactions are predominantly electrostatic in nature (ΔV_{elstat} is approx. 60% of all bonding interactions, i.e. $\Delta V_{elstat} + \Delta E_{oi}$), albeit the orbital interaction terms, ΔE_{oi} (approx. 40%), also significantly contribute to the attractive interactions between the building units of **7**_{comput}. Even though strong Pauli repulsion, ΔE_{Pauli} , liable for the destabilising interactions is observed, the strongly attractive or stabilising electrostatic interactions outweigh quantum mechanical ones, i.e. $\Delta E_{oi} + \Delta E_{Pauli}$, [36] and are mainly responsible for the binding between the considered fragments (Table 4).

The preparation energy, ΔE_{prep} , which is the energy difference between the equilibrium structures of the fragments illustrated in Fig. 6 and the energies of those in the geometries that they acquire in the equilibrium structure 7_{comput}, is only negligible for the interaction between [Os₃(CO)₁₁] and (POPE)GaCl₃. This contrasts with ΔE_{prep} of **7**_{comput} obtained from the interaction of [Os₃(CO)₁₁(POPE)] $(1B_{comput})$ with GaCl₃ (Fig. 6). Interestingly, the major energy contribution to this ΔE_{prep} term comes from the GaCl₃ moiety which changes its trigonal planar geometry to a distorted tetrahedral one by coordination to $1B_{comput}$. The values of the bond dissociation energies (BDEs), D_e , calculated from the two models for 7_{comput} reveal that the studied interactions are relatively weak and can be easily broken (Fig. 6, Table 4). Overall, the Os(1)-P(1) bond formed by the interaction of $[Os_3(CO)_{11}]$ and $(POPE)GaCl_3$ is more stable than the Ga–O bond originated from the interaction between 1B_{comput} and GaCl₃. It is also noteworthy that the fairly low stability of complexes 7, 9, and 11 observed from their solid-state behaviour might be the result of the relatively low HOMO-LUMO gaps [37] found for $\mathbf{7}_{comput}$ (0.94 eV), $\mathbf{9}_{comput}$ (0.92 eV), and $\mathbf{11}_{comput}$ (0.91 eV) as well as of the low BDEs as shown in the case of 7_{comput} .

4. Conclusions

We showed that reactions of the triangular clusters $[M_3(CO)_{12}]$ (M = Ru, Os), and the octahedral cluster $[Rh_6(CO)_{15}(NCMe)]$ with nonsymmetrical bifunctional diphosphane monoxides (DPMOs) led to the formation of new mono-substituted carbonyl cluster complexes $[M_3(CO)_{11}(DPMO)]$ (M = Ru, Os; 1–4) and $[Rh_6(CO)_{15}]$ (DPMO)] (5, 6), respectively. We demonstrated that phosphane coordination to the metal cluster (1-6) can be followed by functionalisation of the pendant phosphane-oxide moiety with GaCl₃ to fabricate novel heterometallic coordination-based molecular assemblies [M₃(CO)₁₁(DPMO)(GaCl₃)] (7-10) and [Rh₆(CO)₁₅(DP-MO)(GaCl₃)](11–12)(Fig. 7). The crystal structures of compounds 1, 2, and 7 were determined by single-crystal X-ray diffraction. As a result, we were able to synthesise and structurally characterise the first organometallic osmium-gallium mixed complex, 7. On the basis of experimental data and quantum chemical calculations, we established that (i) the condensed media (crystal, solution) have an effect on the structure of 7, (ii) the latter is influenced by the type of solvent (a more polar solvent leads to almost isoenergetic rotameric structures), and (iii) the nature of the interconstitutive metal-ligand



TMC = $[Ru_3(CO)_{11}], [Os_3(CO)_{11}], [Rh_6(CO)_{15}];$ **DPMO** $= Ph_2P(CH_2)_nP(O)Ph_2, n = 2, 3; L = CO, NCMe$

Fig. 7. Two-step synthesis of heterometallic coordination-based molecular assemblies 7-12.

interactions in **7** is predominantly electrostatic. From the experimental and computational analyses of complexes 1-12, it can be concluded that their molecular structures are evidently maintained not only in the solid state and the gas phase but also in solution. Although, the three units (*i*) carbonyl cluster, (*ii*) GaCl₃, and (*iii*) spacer assemble together without modifying their individual properties (that is being supported by inspection of analytical and computational protocols), the authors are very encouraged to see a detailed theoretical analysis of the other linked molecular systems in which metallic elements of different nature and properties will be combined in order to seek out the very promising intramolecular electron transport effects. Our work opens a prospect for further comprehensive investigations of the types of assemblies herein presented.

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Appendix A. Supplementary material

CCDC 772727, 772728, 780727 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2012.03.003.

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