

Group 6 Metal Carbonyl Complexes of *cyclo*-(P₅Ph₅)

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Abstract: Group 6 metal (Cr, Mo, W) carbonyl complexes react with *cyclo*-(P₅Ph₅) to afford the phosphorus-rich complexes [Cr(CO)₅{*cyclo*-(P₅Ph₅)-κP¹}] (**1**), [{Cr(CO)₅}₂{μ-*cyclo*-(P₅Ph₅)-κP¹,P³}] (**2**), [M(CO)₄{*cyclo*-(P₅Ph₅)-κP¹,P³}] (with M = Cr (**3**), Mo (**4**), W (*exo*-**5**, *endo*-**5**)) depending on the reaction conditions. Complexes **1–5** were characterised by ³¹P{¹H} NMR and IR spectroscopy, elemental analysis, and X-ray crystallography. The cyclopentaphosphane remains intact and acts as monodentate (**1**), bridging (**2**) or bidentate (**3–5**) ligand. Compounds *exo*-**5** and *endo*-**5** are configurational isomers and essentially differ in the orientations adopted by the phenyl rings attached to the uncoordinated phosphorus atoms. The ³¹P{¹H} NMR spectra show five multiplets for an ABCDE spin system. Theoretical calculations showed that *exo*-**5** and *endo*-**5** are practically isoenergetic, which is in good agreement with the observed equilibrium in solution between *exo*-**5** and *endo*-**5**. The thermal properties of the complexes have also been evaluated.

Keywords: Density functional calculations, Group 6 carbonyls, P ligands, Phosphorus, Thermolysis.

1 Introduction

Scientific interest in the fundamental chemistry of cyclophosphanes *cyclo*-(P_nR_n) and cyclophosphanides *cyclo*-(P_nR_{n-1})⁻ (n = 3-6) has gone from a period of intense research between 1960 and 1990, to a period of low activity in the past two decades but has renewed interest lately.[1] These compounds, which display diverse reactivity with transition metal carbonyls, have been used for the synthesis of phosphorus-rich main group and transition metal complexes.[1] The synthesis as well as the structural characterisation of *cyclo*-(P_nR_n) (R = Me, n = 3, 5;[2-4] Et, n = 3, 5;[2-4] Cy, n = 3, 4;[2,5] Bu, n = 5;[2,3] Ph, n = 3-5;[2,3,6,7] *i*Pr, n = 3, 4;[8] ^tBu, n = 3, 4;[9-11] 1-Ad, n = 3, 4;[9-12] CF₃, n = 4, 5;[13,14] 2,4,6-Me₃C₆H₂ (Mes), n = 6;[15] *etc*) with three to six phosphorus ring atoms have been reported.[16] Also, some main group and transition metal complexes of *cyclo*-(P_nR_n) (n = 3,[5,17-23] 4,[23-27] 5,[26,28-30] 6,[29,31] 7-9[32-34]) are known in the literature. Among the cyclophosphanes, *cyclo*-(P₅Ph₅) is a versatile starting material in the preparation of phosphorus-rich transition metal complexes.[35-40] Reactions of *cyclo*-(P₅R₅) (R = Me, Et, Ph) with triosmium or triruthenium carbonyls have afforded several cluster derivatives [M₃(CO)₁₀{*cyclo*-(P₅R₅)-κP¹,P³}] (with M = Os, Ru, R = Ph; [35,38] R = Et;[41]), [Os₃(CO)₁₁{*cyclo*-(P₅Ph₅)-κP¹}] and [{Os₃(CO)₁₁}₂{μ-*cyclo*-(P₅Ph₅)-κP¹,P³}] [38,39] in which the ring remains intact. The cyclopentaphosphanes *cyclo*-(P₅R₅) (R = Me, Et, Ph) have also been shown to react with group 6 metal hexacarbonyls to yield compounds of the type [M(CO)_n{*cyclo*-(P₅R₅)}] (M = Cr, Mo, W; n = 3-5) in which the ring coordinates as a mono- (κP¹) or bidentate ligand, usually in a κP¹,P³ and rarely in a κP¹,P² manner.[30,38,42,43] In contrast, *cyclo*-(P₄Ph₄) was shown to react with low-valent molybdenum and tungsten hexacarbonyls at high temperatures (>120°C) to yield complexes in which the ring size had changed from a four-membered to a five-membered phosphorus ring.[42] Although the complexes [M(CO)_n{*cyclo*-(P₅R₅)}] (M = Cr, Mo, W; n = 3-5; R = Me, Et, Ph) have been synthesised and characterised especially using IR spectroscopy and mass spectrometry,[29,42,44] the single crystal X-ray structures of only two complexes have been reported, [Cr(CO)₅{*cyclo*-(P₅Ph₅)-κP¹}][36,37] and [Mo(CO)₄{*cyclo*-(P₅Et₅)-κP¹,P³}][28,45]. Furthermore, the structures of [M(CO)₅{*cyclo*-(P₄Ph₄)-κP¹}] (M = Cr, W),[24,25] and [W(CO)₄{*cyclo*-(P₆Me₆)-κP¹,P³}][29] are known.

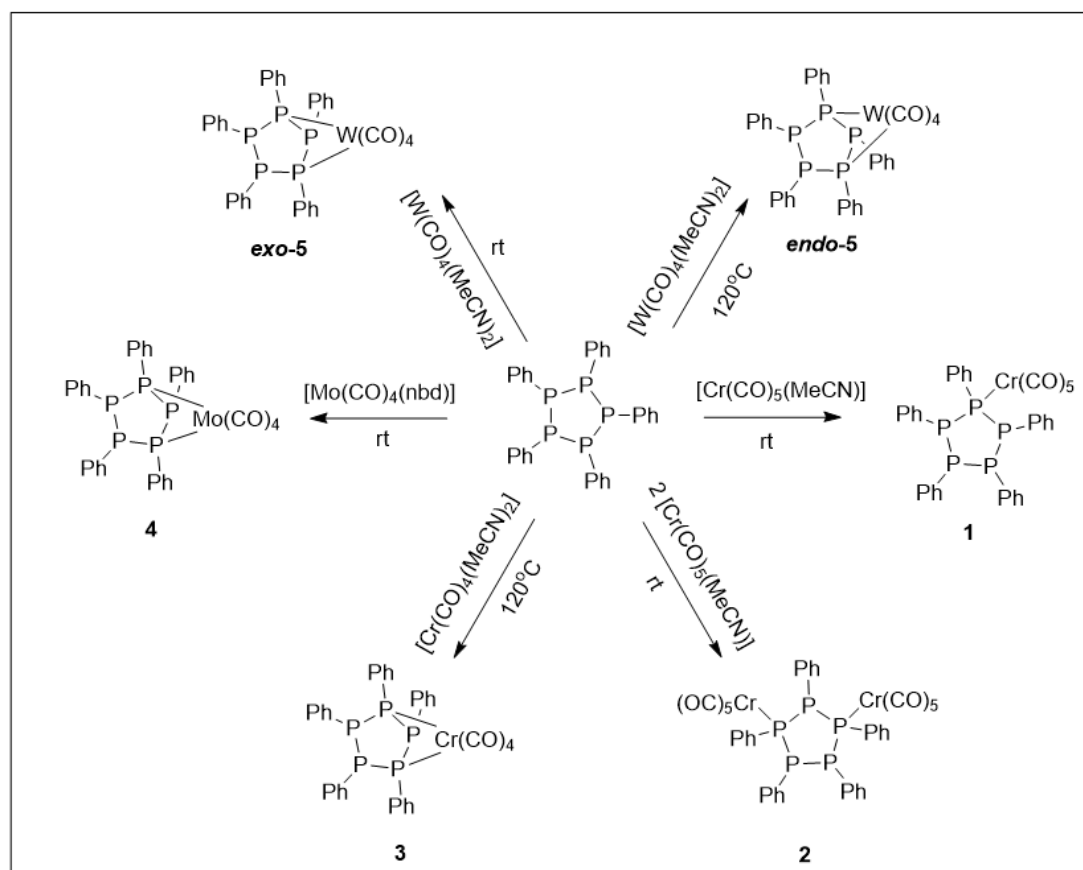
Recently, we embarked on a systematic study of the syntheses, structural properties and reactivity of cyclophosphanes with the specific aim of exploring their application as building blocks for phosphorus-rich metal complexes which could serve as precursors for phosphorus-rich nanoparticles M_xP_y (y>x).[46,47] Herein, we describe a study of the reactions of *cyclo*-(P₅Ph₅) with [Cr(CO)_x(MeCN)_y] (x = 5, y = 1; x = 4, y = 2), [Mo(CO)₄(nbd)] (nbd = norbornadiene) and [W(CO)₄(MeCN)₂]. Single crystal X-ray

crystallography and solution $^3\text{P}\{^1\text{H}\}$ NMR spectroscopic studies are employed to elucidate the influence of coordination on the conformation of the *cyclo*-(P_5R_5) ring in the solid state and in solution.

2 Results and Discussion

The phosphorus-rich complexes $[\text{Cr}(\text{CO})_5\{\textit{cyclo}\text{-}(\text{P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1\}]$ (**1**), $[\{\text{Cr}(\text{CO})_5\}_2\{\mu\text{-}\textit{cyclo}\text{-}(\text{P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$ (**2**), $[\text{M}(\text{CO})_4\{\textit{cyclo}\text{-}(\text{P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$ (with $\text{M} = \text{Cr}$ (**3**), Mo (**4**), W (*exo*- and *endo*-**5**)) were obtained in stoichiometric reactions (1:1 or 2:1) of the group 6 carbonyls with *cyclo*-(P_5Ph_5) in toluene or dichloromethane at room temperature (Scheme 1) and fully characterized. Complexes **1–5** are air-stable at room temperature for at least one day. Single crystals of **1–5** were obtained by recrystallisation from suitable solvents at low temperatures. Crystallographic data for **2–5** are given in Table S1 (ESI), selected bond lengths (\AA) and angles ($^\circ$) in Table 1.

$[\text{Cr}(\text{CO})_5\{\textit{cyclo}\text{-}(\text{P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1\}]$ (**1**) has been structurally characterised before at 293 K, in a monoclinic ($P2_1/c$)[36] as well as a triclinic ($P\bar{1}$)[37] modification (Table S2, ESI, shows the comparative crystallographic data).



Scheme 1: Preparation of compounds **1–5**

The bonding mode of *cyclo*-(P_5Ph_5) in **1** is similar to that in $[\text{Os}_3(\text{CO})_{11}\{\textit{cyclo}\text{-}(\text{P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1\}]$. [38] However, NMR data have not been reported and are, therefore, discussed here. The $^3\text{P}\{^1\text{H}\}$ NMR spectrum of **1** (in C_6D_6) (Fig. S2, ESI) shows five multiplets for an ABCDE spin system, centred at 41.3, 2.7, -7.1 , -18.5 and -24.5 ppm, consistent with five magnetically inequivalent phosphorus atoms. The $^1J(\text{P},\text{P})$ coupling constants are in the expected range for P–P single bonds (Table 3)[41] and show that the ring remains intact in solution. The P_5 ring has an envelope conformation in the solid state. [36]

In compound **2** (Fig. 1), *cyclo*-(P_5Ph_5) acts as a bridging ligand between two $\text{Cr}(\text{CO})_5$ moieties. The metal complex fragments are coordinated by the two phosphorus atoms in 1- and 3-position and occupy the equatorial positions of the five-membered ring. A similar coordination mode was observed in $[\{\text{Os}_3(\text{CO})_{11}\}_2\{\mu\text{-}\textit{cyclo}\text{-}(\text{P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$. [38] The P–P bonds (Table 1) in **2** are in the

typical range for P–P single bonds[38,40,48], including *cyclo*-(P₅Ph₅),[48] with two bonds (P2–P3 (2.208(2) and P4–P5 (2.205(2) Å) being slightly shorter than the other P–P bonds (2.226(2)–2.233(2) Å).

The Cr–P bond lengths (2.417(2), 2.400(2) Å) are in the same range as in [Cr(CO)₅{*cyclo*-(P₄R₄)}] (R = Cy, Cr–P 2.4375(6) Å;[27] R = Ph, Cr–P 2.3921(5) Å)[25]. The *cyclo*-(P₅Ph₅) ligand has an envelope conformation with P(4), P(5), P(1) and P(2) being almost coplanar (torsion angle P(4)–P(5)–P(1)–P(2) 8.5(1)°) and P(3) located 0.948 Å above this plane. The Ph substituents at P3 and P4 have a cis arrangement.[16,40,49,50] The P–P–P bond angles (100.36(8) to 109.10(8)°) are similar to those in *cyclo*-(P₅Ph₅)[51] with P(2)–P(3)–P(4) being the smallest.

The ³¹P{¹H} NMR spectrum of **2** in C₆D₆ (Fig. S3, ESI) shows five multiplets for the ABCDE spin system at about 54.1, 40.8, 26.7, 10.1 and 4.3 ppm. This is similar to the spin system observed for [{Os₃(CO)₁₁]₂{*cyclo*-(P₅Ph₅)-κP^l,P³}]. [38] The chemical shifts and coupling constants (Table 3) were extracted from the experimental data. The coupling constants ¹J(P,P) are in the range observed for P–P single bonds.[52]

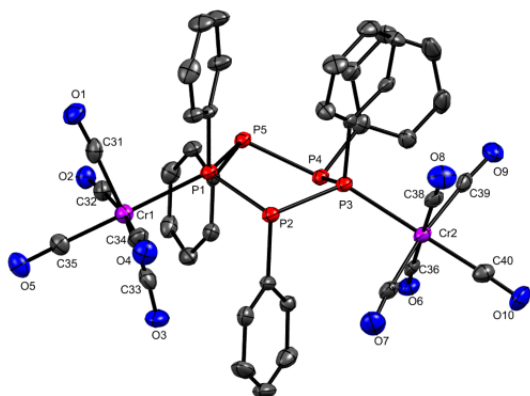


Fig. 1: Molecular structure and atom-labelling scheme for **2** with ellipsoids drawn at 30% probability level. H atoms are omitted for clarity.

Tab. 1: Selected bond lengths (Å) and angles (°) for **2–5**.

	2	3	4	<i>exo-5</i>	<i>endo-5</i>				
P1-P5	2.226(2)	P1-P5	2.2101(5)	P1-P5	2.215(2)	P1-P5	2.210(1)		
P1-P2	2.232(2)	P1-P2	2.2416(5)	P1-P2	2.2388(6)	P1-P2	2.241(1)	P1-P2	2.235(1)
P1-Cr1	2.417(2)	P1-Cr1	2.3826(4)	P1-Mo1	2.5249(4)	P1-W1	2.5099(9)	P1-W1	2.5072(9)
P2-P3	2.209(2)	P2-P3	2.2339(5)	P2-P3	2.2362(6)	P2-P3	2.224(1)	P2-P3	2.235(1)
P3-P4	2.233(2)	P3-P4	2.2338(5)	P3-P4	2.2378(6)	P3-P4	2.216(1)	P3-P4	2.234(1)
P4-P5	2.206(2)	P4-P5	2.2124(5)	P4-P5	2.2118(6)	P4-P5	2.266(1)	P4-P5	2.212(1)
		P4-Cr1	2.3782(4)	P4-Mo1	2.5219(4)	P4-W1	2.516(1)	P4-W1	2.5102(8)
P5-P1-Cr1	121.83(8)	P4-Cr1-P1	68.589(1)	P4-Mo1-P1	65.86(1)	P5-P1-P2	95.53(5)	P5-P1-P2	99.06(5)
P5-P1-P2	109.10(8)	P5-P1-P2	98.69(2)	P2-P1-Mo1	100.44(2)	P5-P1-W1	102.08(4)	P5-P1-W1	92.81(4)
P2-P1-Cr1	114.20(7)	P2-P1-P4	81.87(2)	P3-P2-P1	93.91(2)	P2-P1-W1	106.91(4)	P2-P1-W1	114.17(4)
P3-P2-P1	103.36(8)	P3-P2-P1	94.81(2)	P2-P3-P4	95.49(2)	P1-W1-P4	65.33(3)	P1-P2-P3	95.34(5)
P2-P3-P4	100.36(8)	P4-P3-P2	93.10(2)	P5-P4-P3	99.10(2)	P4-P3-P2	94.95(5)	P4-P3-P2	93.62(4)
P2-P3-Cr2	118.06(7)	P5-P4-P3	113.34(2)	P5-P4-Mo1	92.53(2)	P3-P4-P5	90.91(5)	P5-P4-P3	113.24(5)
P4-P5-P1	101.49(8)	P5-P4-P1	52.62(1)	P3-P4-Mo1	113.91(2)	P3-P4-W1	114.49(5)	P5-P4-W1	92.69(4)
P5-P4-P3	105.81(8)	P3-P4-P1	83.62(2)	P4-P5-P1	76.63(2)	P5-P4-W1	100.44(4)	P3-P4-W1	100.79(4)
P4-P3-Cr2	112.61(7)	P1-P5-P4	74.68(2)	P5-P1-Mo1	92.42(2)	P1-P5-P4	74.49(5)	P1-P5-P4	76.05(4)
P3-Cr2-M2	2.400(2)					P3-P2-P1	97.01(5)	P1-W1-P4	65.76(3)

The complex [W(CO)₄{*cyclo*-(P₅Ph₅)-κP^l,P³}] (*exo-5*) (Fig. 2) crystallises in the monoclinic space group *P*2₁/*c* with four molecules in the unit cell. The complexes [M(CO)₄{*cyclo*-(P₅Ph₅)-κP^l,P³}] (M = Cr (**3**, Fig. S1, ESI), Mo (**4**, Fig. S1, ESI), W (*endo-5*, Fig. 2)) are isostructural, all are *endo* isomers. They crystallise in the triclinic space group *P* $\bar{1}$ with two molecules in the unit cell.

The coordination mode of *cyclo*-(P₅Ph₅) is similar to that observed in [Os₃(CO)₁₀{*cyclo*-(P₅Ph₅)-κPⁱ,P³}].[38,39,45] The P–P bond lengths (2.2101(6)–2.2416(6) Å) are typical for P–P single bonds.[48]

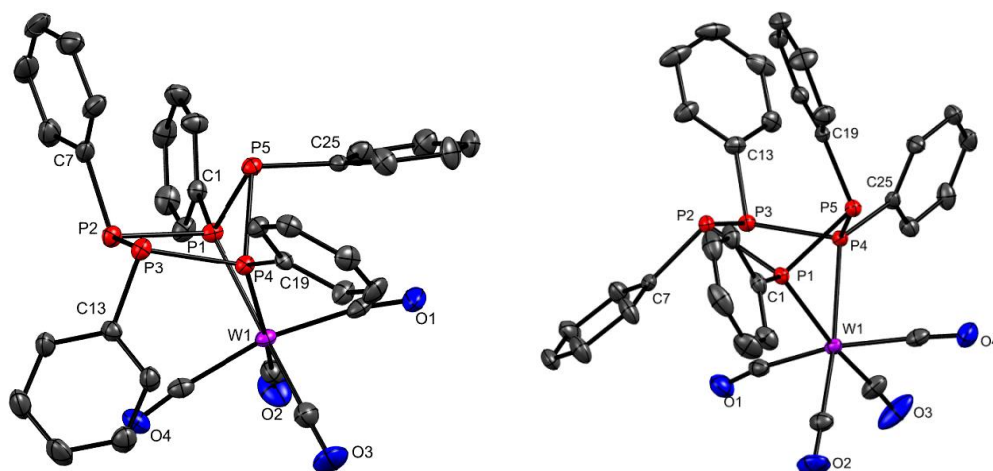


Fig. 2: Molecular structure and atom-labelling scheme for *exo*-**5** (left) and *endo*-**5** (right) with ellipsoids drawn at 30% probability level. H atoms are omitted for clarity.

Tab. 2: Conformation of the P₅ ring in complexes **2–5**.

	2	3	4	<i>exo</i> - 5	<i>endo</i> - 5
Plane	P2,P1,P5,P4	P1,P2,P3,P4	P1,P2,P3,P4	P1,P2,P3,P4	P1,P2,P3,P4
Average distance of coplanar P atoms from the plane (in Å)	0.06	0.195	0.195	0.081	0.194
Distance of P3 (in 2) or P5 (in 3–5) to the plane	0.948	1.558	1.520	1.760	1.529

In complexes **2–5**, the P₅ rings have an envelope conformation in the solid state, with four of the phosphorus atoms being almost coplanar and one phosphorus atom located above the plane (Table 2). The phenyl groups of the two phosphorus atoms ((P4, P5) for **2** and (P2, P3) for **3–5**) between the coordinating phosphorus atoms have a *trans* arrangement while the phenyl groups of the coordinating phosphorus atoms ((P1 and P3) for **2** and P1 and P4 for **3–5**) are in equatorial positions with the group 6 metal in the axial positions. The Cr–P (2.3782(4), 2.3826(4) Å), Mo–P (2.5249(4), 2.5219(4) Å) and W–P (2.5072(9), 2.5102(8) Å) bond lengths are in the range as observed for similar complexes (Cr: 2.3921(5);[25] Mo: 2.51(1) Å;[45] W: 2.502(7) Å[29]).

Complexes *endo*- and *exo*-**5** (Fig. 2) differ only in the orientation of the phenyl group at P5, resulting in formation of an *exo* and an *endo* isomer, similar to the *endo–exo* isomerism found in organic compounds with a substituent on a bridged ring system. This phenomenon had previously been observed in the cluster [Os₃(CO)₁₀{*cyclo*-(P₅Ph₅)-κPⁱ,P³}].[35,38] The P–W bond lengths in *exo*-**5** and *endo*-**5** are similar (2.5072(9) to 2.516(1) Å) and are consistent with values of P–W single bonds (2.50 ± 0.02 Å) found in the literature.[53,54]

The ³¹P{¹H} NMR spectra of **3–exo-5** (Fig. 3 and Figs. S4-S7, ESI) in C₆D₆ show five multiplets for the expected ABCDE spin system. The chemical shifts and coupling constants of **3**, **4** and *exo*-**5** were extracted from these spectra by simulation (Table 3). The coordinating phosphorus atoms in these complexes exhibit a significant downfield shift compared to the free ligand. The P atom between the coordinating ones experiences a slightly larger upfield shift compared to the ligand.[55] The ¹J(P,P) coupling constants fall within the range of P–P single bonds.[52] The differences in the ¹J(P,P) coupling constants for the complexes indicate a difference in the stereochemical orientation around the coupled ³¹P nuclei. Crystal structures of these complexes confirm an asymmetric conformation in the solid state with the *cis–trans* arrangement of the phenyl groups (and hence lone pair of electrons).[14,50] For complexes **4** and *exo*-**5**, the respective coupling constants ¹J(P_C,P_D) = –79.77(4) and ¹J(P_C,P_D) = –76.48(1) are smaller than the expected values though a similar value has been reported for [PtCl{*cyclo*-(P₄tBu₃)PtBu}(PMe₂Ph)].[52] While we

cannot yet explain this observation, there is no evidence that these molecules are different in solution. The large $^2J(\text{P},\text{P})$ coupling constants for **4** and *exo-5*, $^2J(\text{P}_\text{A},\text{P}_\text{D}) = +175.45(4)$ and $^2J(\text{P}_\text{A},\text{P}_\text{D}) = +177.35(2)$, respectively, can be attributed to through-space coupling in which the lone pairs of electrons are pointing towards each other.[56,57] Complex **4** gradually interconverts in solution to another isomer (probably the *exo* isomer, Fig. S8, ESI). Attempts to crystallise this isomer were not successful. The very strong higher order effects in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *endo-5* in combination with its poor quality prevented the successful simulation.

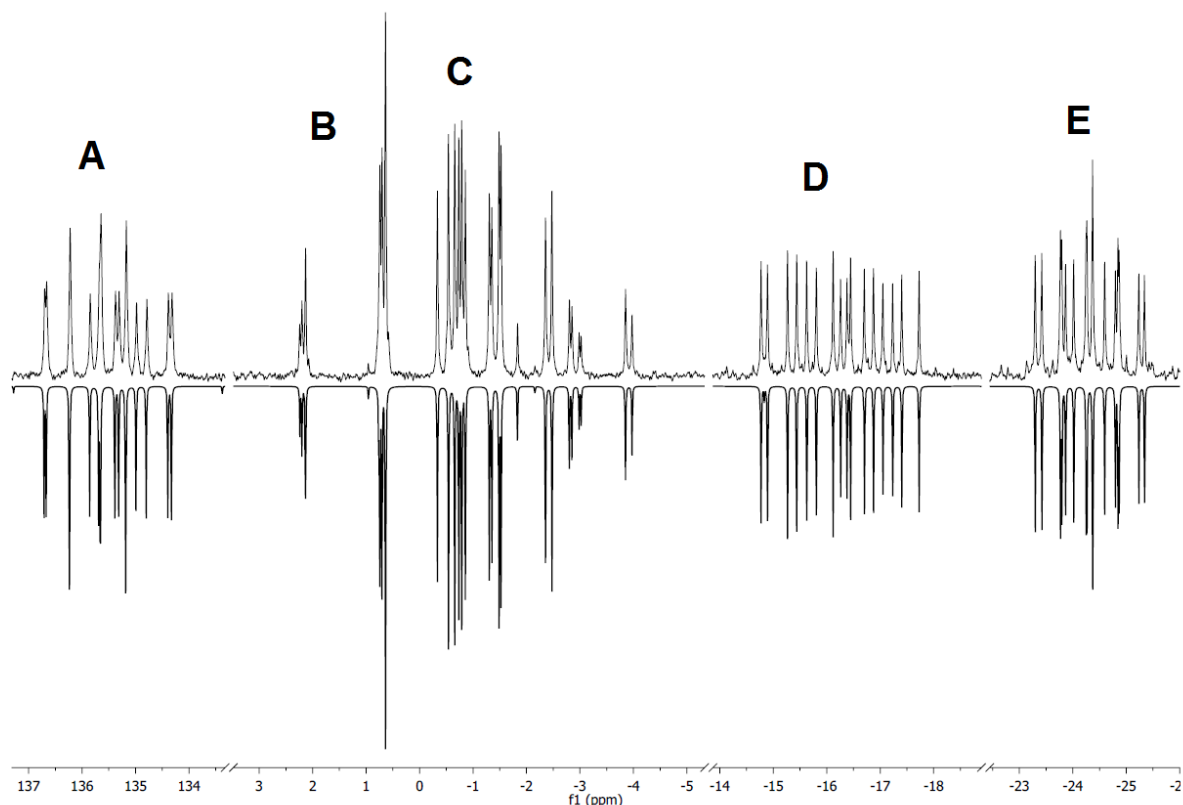


Fig. 3: Experimental (top) and simulated (bottom) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex *exo-5* in C_6D_6 (for details see Table 3).

Pure complexes *exo-5* and *endo-5* also gradually interconvert in solution to give a mixture of both isomers (*endo/exo*) as shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Fig. S9, ESI). This process occurs even faster at elevated temperature. Theoretical calculations showed that *exo-5* and *endo-5* are practically isoenergetic (**Fehler! Verweisquelle konnte nicht gefunden werden.**). This is in good agreement with the observed equilibrium between both complexes in solution. The activation energy for the inversion should be low as the isomerisation already occurs at room temperature. Though the inversion barrier in tertiary phosphines is usually high (30–38 kcal/mol),[58] it has been shown to be lower (18.5 kcal/mol) for polycyclic phosphines.[16] Furthermore, the coordination of cyclic phosphines to metals, coupled with steric and electronic effects, has resulted in even lower inversion barriers (11–13 kcal/mol)[58] which matches the experimental observation for *exo-5* and *endo-5*. Our calculations however show that the isomerisation does not proceed through a classical inversion *i.e.* a transition state with planar P atom (Fig. 4). The barrier was calculated to be 32.8 kcal/mol, which is too high for the inversion to occur spontaneously. Consequently, we considered an alternative mechanism, which includes an oxidative insertion. However, even though we were not able to locate the transition state, the relative energy of the optimised intermediate **5-IM** (Fig. 4) suggests a similarly high barrier. It is thus unclear how the isomerisation of **5** occurs and future studies are needed.

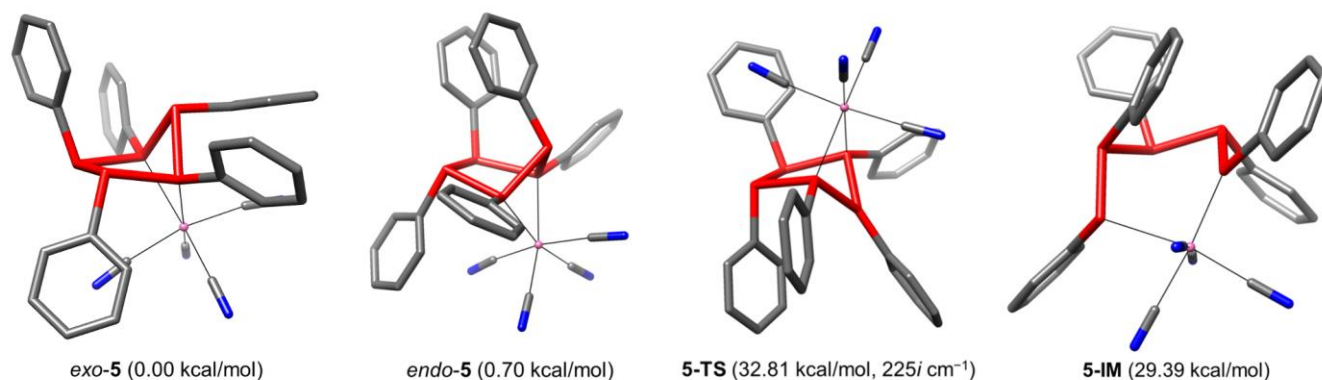


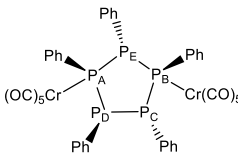
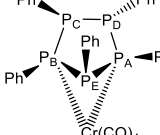
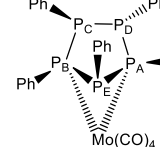
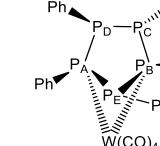
Fig. 4: Optimised geometries of the two isomers of **5**; the transition state for the classical inversion (**5-TS**) and the intermediate for the alternative mechanism (**5-IM**). C: grey, P: red, O: blue, W: pink. Relative Gibbs free enthalpy values and the imaginary frequency value of **5-TS** are also given. Hydrogen atoms are omitted for clarity.

The IR spectra (Fig. S10, ESI) and data (cm⁻¹) of complexes **1**, **2**, **4** and *exo-5* in the carbonyl region are summarised in Table S3 (ESI). Three IR-active bands are expected for [M(CO)₅L] (M = Cr, Mo, W) with local C_{4v} symmetry, but in the IR spectra of **1** and **2**, only one sharp and one broad CO stretching vibration were observed.[59] The IR spectra of **4** and *exo-5* each show terminal CO stretching bands with frequencies typical of *cis*-[M(CO)₄L₂] complexes of Cr, Mo and W with local C_{2v} symmetry, assigned to the B₂, B₁, A₁¹, A₁² vibrational modes.[44,59–62] In some cases, the B₁ mode was obscured because of overlap with the B₂ and A₁¹ modes, and only three bands were reported as is also observed for complex *exo-5*. [61,63]

The thermal properties of complexes **2**, **4** and *exo-5* were studied by simultaneous TG/DTA/MS analyses in the temperature range 30–900°C under an argon atmosphere (Figs. S11–S13 and Table S4, ESI). Two endothermic peaks are observed at ~200°C, and ~300°C in the DTA. The first decomposition step up to 260°C is attributed to the loss of ten CO (for **2**) or two CO (for **4** and *exo-5*). This step is followed by the loss of further CO (for **4** and *exo-5*) and some of the phenyl moieties (as C₆H₅[·]) between 260 and 460°C. A broad exothermic peak observed in **2** (360–420°C), **4** (400–500°C) and *exo-5* (400–600°C) can be attributed to the decomposition of the phenyl substituents within this range. The loss of two (for **2** and **4**) or three (for *exo-5*) phosphorus atoms occurs at higher temperatures. The PXRD patterns of the residues (Fig. S14, ESI) indicate that they are poorly crystalline, and the very low intensity peaks could not be indexed to any phase. The percent weight of the experimentally obtained residues (30.27%, 55.00% and 46.67%, respectively) differ a lot from the calculated amounts for the potential phosphorus-rich metal phosphides (Cr₂P₃ (21.29%), MoP₃ (25.24%) and WP₂ (29.39%)), indicating the presence of impurities, probably carbon. The observed decomposition patterns of these compounds render them unsuitable as precursors for phosphorus-rich metal phosphides.

Tab. 3: ³¹P{¹H} NMR data (δ (ppm) and J (Hz)) of compounds **1–5** in C₆D₆ at 25°C.

[Cr(CO) ₅ { <i>cyclo</i> -(P ₅ Ph ₅)-κP ¹ }] (1) (ABCDE spin system)		δ _A (P _A) = 41.26 δ _B (P _B) = 2.68 δ _C (P _C) = -7.12 δ _D (P _D) = -18.50 δ _E (P _E) = -24.50
		¹ J(P _D ,P _B) = -329.33(1) ² J(P _B ,P _C) = 77.01(1) ¹ J(P _D ,P _E) = -280.26(1) ¹ J(P _A ,P _B) = -153.35(1) ² J(P _D ,P _C) = 6.95(1) ¹ J(P _C ,P _E) = -260.68(1) ² J(P _D ,P _A) = 10.06(1) ² J(P _A ,P _E) = 5.40(1) ² J(P _B ,P _E) = -6.17(1) ¹ J(P _A ,P _C) = -196.10(1)

<p>$[[\text{Cr}(\text{CO})_5]_2\{\mu\text{-cyclo-(P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$ (2) (ABCDE spin system)</p>	 <p> $\delta_A(\text{P}_A) = 54.06$ $\delta_B(\text{P}_B) = 40.77$ $\delta_C(\text{P}_C) = 26.71$ $\delta_D(\text{P}_D) = 10.07$ $\delta_E(\text{P}_E) = 4.30$ </p> <p> ${}^2J(\text{P}_C, \text{P}_E) = -8.66(6)$ ${}^1J(\text{P}_A, \text{P}_E) = -368.20(6)$ ${}^1J(\text{P}_B, \text{P}_C) = -295.88(6)$ ${}^2J(\text{P}_D, \text{P}_E) = 4.54(6)$ ${}^2J(\text{P}_A, \text{P}_C) = 65.41(6)$ ${}^2J(\text{P}_A, \text{P}_B) = -3.59(6)$ ${}^1J(\text{P}_C, \text{P}_D) = -280.72(6)$ ${}^2J(\text{P}_B, \text{P}_D) = -3.68(6)$ ${}^1J(\text{P}_B, \text{P}_E) = -289.81(6)$ ${}^1J(\text{P}_A, \text{P}_D) = -169.20(6)$ </p>
<p>$[\text{Cr}(\text{CO})_4\{\text{cyclo-(P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$ (3) (ABCDE spin system)</p>	 <p> $\delta_A(\text{P}_A) = 63.57$ $\delta_B(\text{P}_B) = 37.00$ $\delta_C(\text{P}_C) = 20.88$ $\delta_D(\text{P}_D) = 17.94$ $\delta_E(\text{P}_E) = 9.03$ </p> <p> ${}^2J(\text{P}_C, \text{P}_E) = 28.95(1)$ ${}^1J(\text{P}_B, \text{P}_C) = -202.73(9)$ ${}^2J(\text{P}_D, \text{P}_E) = 17.19(7)$ ${}^2J(\text{P}_A, \text{P}_C) = 16.39(9)$ ${}^1J(\text{P}_B, \text{P}_E) = -235.04(2)$ ${}^2J(\text{P}_B, \text{P}_D) = 10.29(1)$ ${}^1J(\text{P}_A, \text{P}_E) = -353.59(1)$ ${}^1J(\text{P}_A, \text{P}_D) = -273.69(1)$ ${}^1J(\text{P}_C, \text{P}_D) = -210.16(3)$ ${}^2J(\text{P}_A, \text{P}_B) = -11.99(9)$ </p>
<p>$[\text{Mo}(\text{CO})_4\{\text{cyclo-(P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$ (4) (ABCDE spin system)</p>	 <p> $\delta_A(\text{P}_A) = 125.79$ $\delta_B(\text{P}_B) = 9.47$ $\delta_C(\text{P}_C) = 4.89$ $\delta_D(\text{P}_D) = -4.08$ $\delta_E(\text{P}_E) = -9.26$ </p> <p> ${}^1J(\text{P}_B, \text{P}_C) = -141.73(4)$ ${}^2J(\text{P}_A, \text{P}_B) = -8.22(4)$ ${}^1J(\text{P}_C, \text{P}_D) = -79.77(4)$ ${}^1J(\text{P}_B, \text{P}_E) = -256.15(4)$ ${}^2J(\text{P}_A, \text{P}_C) = 175.45(4)$ ${}^1J(\text{P}_A, \text{P}_D) = -166.28(4)$ ${}^2J(\text{P}_C, \text{P}_E) = -3.71(4)$ ${}^2J(\text{P}_D, \text{P}_E) = -5.95(6)$ ${}^2J(\text{P}_B, \text{P}_D) = 70.96(4)$ ${}^1J(\text{P}_A, \text{P}_E) = -241.41$ </p>
<p><i>exo</i>-$[\text{W}(\text{CO})_4\{\text{cyclo-(P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$ (<i>exo-5</i>) (ABCDE spin system)</p>	 <p> $\delta_A(\text{P}_A) = 135.51$ $\delta_B(\text{P}_B) = 0.44$ $\delta_C(\text{P}_C) = -1.95$ $\delta_D(\text{P}_D) = -16.22$ $\delta_E(\text{P}_E) = -24.30$ </p> <p> ${}^1J(\text{P}_A, \text{P}_D) = -138.58(1)$ ${}^2J(\text{P}_A, \text{P}_B) = -8.4(1)$ ${}^1J(\text{P}_C, \text{P}_D) = -76.48(1)$ ${}^1J(\text{P}_A, \text{P}_E) = -251.88(1)$ ${}^2J(\text{P}_B, \text{P}_D) = 177.35(2)$ ${}^1J(\text{P}_B, \text{P}_C) = -168.63(1)$ ${}^2J(\text{P}_D, \text{P}_E) = -5.67(1)$ ${}^2J(\text{P}_C, \text{P}_E) = -5.63(1)$ ${}^2J(\text{P}_A, \text{P}_C) = 80.54(1)$ ${}^1J(\text{P}_B, \text{P}_E) = -243.19(1)$ </p>
<p><i>endo</i>-$[\text{W}(\text{CO})_4\{\text{cyclo-(P}_5\text{Ph}_5)\text{-}\kappa\text{P}^1, \text{P}^3\}]$ (<i>endo-5</i>) (ABCDE spin system)</p>	<p> $\delta_A = 32.51$ (m) $\delta_B = 25.31$ (m) $\delta_C = 19.37$ (m) $\delta_D = 16.82$ (m) $\delta_E = -11.45$ (m) </p>

2.1 Conclusions

Group 6 metal carbonyls react with *cyclo*-(P₅Ph₅) under mild conditions to form the phosphorus-rich complexes [Cr(CO)₅{*cyclo*-(P₅Ph₅)-κP¹}] (**1**), [[Cr(CO)₅]₂{μ-*cyclo*-(P₅Ph₅)-κP¹, P³}] (**2**), *endo*-[M(CO)₄{(*cyclo*-P₅Ph₅)-κP¹, P³}] with M = Cr (**3**), Mo (**4**) and *endo*- and *exo*-[W(CO)₄{(*cyclo*-P₅Ph₅)-κP¹, P³}] (*endo*- and *exo-5*) in which the P₅ ring remains intact. The ³¹P{¹H} NMR spectra of these complexes present an ABCDE spin system. While the crystal structures of the chromium complexes **1–3** are consistent with spectroscopic data obtained in solution, the molybdenum and tungsten complexes **4** and **5** slowly interconvert in solution at room temperature to form a pair of *endo* and *exo* isomers. Theoretical calculations showed that *exo-5* and *endo-5* are practically isoenergetic. Thermal decomposition of **2**, **4** and *exo-5* occurs in three steps starting at ca. 220°C and being completed at 600°C. The decomposition products indicate that these complexes are not suitable as precursors for the synthesis of phosphorus-rich metal phosphides.

3 Experimental

All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and freshly distilled under nitrogen and kept over molecular sieve 4 Å. The NMR spectra were recorded at 25°C with a Bruker AVANCE DRX 400 spectrometer (^1H NMR: 400.13 MHz, ^{31}P NMR: 161.97 MHz). TMS was used as internal standard for ^1H NMR spectra. ^{31}P NMR (161.9 MHz): 85% H_3PO_4 was used as external standard. The chemical shifts and coupling constants were obtained with the simulation program SpinWorks 4.[64] Mass spectrometry measurements were carried out as ESI-MS with a BRUKER Daltonics FT-ICR-MS spectrometer (Type APEX II, 7 Tesla). IR spectra: KBr pellets were prepared in a nitrogen-filled glovebox and the spectra were recorded on a Perkin–Elmer System 2000 FTIR spectrometer in the range 350–4000 cm^{-1} . Elemental analyses for C, H, N and O were performed on a FlashEA1112 element analyser. Thermogravimetric (TG) and differential thermal analysis (DTA) curves, coupled with mass spectrometry, were obtained using a NETZSCH STA449F1 thermoanalyzer in a dynamic argon atmosphere (heating rate 10°C·min $^{-1}$, flow rate 25 mL/min, aluminium oxide crucible, mass 20 mg, and temperature range from room temperature up to 900°C).

3.1 Materials

$[\text{Cr}(\text{CO})_y(\text{MeCN})_x]$ ($x = 1, y = 5; x = 2, y = 4$),[65] $[\text{Mo}(\text{CO})_4(\text{nbd})]$ (nbd = norbornadiene), [66] $[\text{W}(\text{CO})_4(\text{MeCN})_2]$,[65] and *cyclo*-(P_5Ph_5)[30] were synthesized according to literature methods. *Cyclo*-(P_5Ph_5) was recrystallised from hot toluene to obtain crystals of higher purity and quality.

3.2 Synthesis of the Complexes

3.2.1 Synthesis of 1

At room temperature, a solution of $[\text{Cr}(\text{CO})_5(\text{MeCN})]$ (0.280 g, 1.2 mmol) in toluene (15 mL) was added dropwise to a solution of *cyclo*-(P_5Ph_5) (0.541 g, 1 mmol) in toluene (15 mL). The colour of the solution gradually changed from cream white to reddish brown. The reaction mixture was stirred at room temperature overnight, filtered and the volume of the filtrate was reduced to ca. 10 mL. At 0°C **1** was obtained as cream white crystals (384.2 mg, 52.4%): ^1H NMR (C_6D_6 , 25°C): $\delta = 8.36\text{--}6.85$ (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): see Table 4. IR (KBr): $\tilde{\nu} = 2062\text{s}, 1987\text{sh}, 1949\text{vs}, 1948\text{vs}, 1938\text{vs}$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{35}\text{H}_{25}\text{CrO}_5\text{P}_5$ (732.4): C 57.39, H 3.44; found: C 57.71, H 3.46.

3.2.2 Synthesis of 2

At room temperature, a solution of $[\text{Cr}(\text{CO})_5(\text{MeCN})]$ (0.536 g, 2.3 mmol) in toluene (15 mL) was added dropwise to a solution of *cyclo*-(P_5Ph_5) (0.541 g, 1 mmol) in toluene (15 mL). The colour of the solution changed to reddish brown during the addition. The reaction mixture was stirred at room temperature overnight, filtered and the volume of the filtrate was reduced to ca. 10 mL. Crystallisation from toluene at -15°C afforded compound **2** as yellow needle-like crystals (687.6 mg, 74.3%): m.p.: 190°C; ^1H NMR (C_6D_6 , 25°C): $\delta = 8.47\text{--}6.85$ (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): see Table 4. IR (KBr): $\tilde{\nu} = 2058\text{s}, 1992\text{sh}, 1983\text{sh}, 1927\text{vs}, 1958\text{sh}$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{25}\text{Cr}_2\text{O}_{10}\text{P}_5$ (924.45): C 51.97, H 2.73; found: C 52.94, H 2.43.

3.2.3 Synthesis of 3

At room temperature, a solution of $[\text{Cr}(\text{CO})_4(\text{MeCN})_2]$ (0.542 g, 2.2 mmol) in toluene (20 mL) was added dropwise a solution of *cyclo*-(P_5Ph_5) (0.541 g, 1 mmol) in toluene (20 mL). The colour of the solution changed to reddish brown during the addition. The reaction mixture was stirred at room temperature for 30 minutes and then refluxed overnight at 120°C to give a dark brown mixture. The solvent was removed in vacuum and the resulting brown solid was dissolved in CH_2Cl_2 and carefully layered with *n*-hexane. Light orange crystals of **3** were obtained by recrystallisation from CH_2Cl_2 /*n*-hexane (10 mL 8:2) at -15°C (227.1 mg, 32.3%) which were also suitable for single-crystal X-ray diffraction: ^1H NMR (C_6D_6 , 25°C): $\delta = 8.33\text{--}6.52$ (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): see Table 4. Elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{25}\text{CrO}_4\text{P}_5$ (704.39): C 57.97, H 3.44; found: C 57.54, H 3.58.

3.2.4 Synthesis of **4**

At room temperature, a solution of [Mo(CO)₄(nbd)] (0.159 g, 0.5 mmol) in CH₂Cl₂ (15 mL) was added dropwise to a solution of *cyclo*-(P₅Ph₅) (0.270 g, 0.5 mmol) in CH₂Cl₂ (15 mL). The colour of the solution changed to yellow during the addition. The reaction mixture was refluxed overnight, cooled to room temperature, filtered and the volume of the filtrate was reduced to ca. 10 mL. At 0°C **4** as bright yellow crystals (292.2 mg, 78.1%): ¹H NMR (C₆D₆, 25°C): δ = 8.2-6.6 (m, Ph); ³¹P{¹H} NMR (C₆D₆, 25°C): see Table 4. IR (KBr): $\tilde{\nu}$ = 2016s, 1916vs, 1915vs, 1873vs cm⁻¹; elemental analysis calcd (%) for C₃₄H₂₅MoO₄P₅ (748.33): C 54.57, H 3.37; found: C 54.59, H 3.06.

3.2.5 Synthesis of *exo*-**5**

At room temperature, a solution of [W(CO)₄(MeCN)₂] (0.201 g, 0.5 mmol) in toluene or CH₂Cl₂ (15 mL) was added dropwise to a solution of *cyclo*-(P₅Ph₅) (0.270 g, 0.5 mmol) in toluene (15 mL). The colour of the solution changed from cream white through orange to reddish brown during the addition. The reaction mixture was stirred at room temperature overnight, filtered and the volume of the filtrate was reduced to ca. 10 mL. At -15°C *exo*-**5** was obtained as bright yellow crystals (284.5 mg, 68.0%): m.p.: 214°C; ¹H NMR (C₆D₆, 25°C): δ = 8.2-6.6 (m, Ph); ³¹P{¹H} NMR (C₆D₆, 25°C): see Table 4. IR (KBr): $\tilde{\nu}$ = 2011s, 1904vs, 1867vs cm⁻¹; elemental analysis calcd (%) for C₃₄H₂₅O₄P₅W (836.24): C 48.83, H 3.01; found: C 49.13, H 3.08.

3.2.6 Synthesis of *endo*-**5**

At room temperature, a solution of [W(CO)₄(MeCN)₂] (0.201 g, 0.5 mmol) in toluene (15 mL) was added dropwise to a solution of *cyclo*-(P₅Ph₅) (0.270 g, 0.5 mmol) in toluene (15 mL). The colour of the solution changed from cream white through orange to reddish brown during the addition. The reaction mixture was stirred at room temperature for 30 minutes and then refluxed overnight at 120°C to give a greenish black mixture. The solvent was removed *in vacuo* and the resulting greenish black solid was dissolved in CH₂Cl₂ and layered with *n*-hexane. Cooling to -15°C afforded *endo*-**5** as dark yellow crystals (101.6 mg, 24.3%): elemental analysis calcd (%) for C₃₄H₂₅O₄P₅W (836.24): C 48.83, H 3.01; found: C 48.78, H 2.82.

3.3 DFT Calculations

Computations were carried out with ORCA 3.0.3.[67,68] Geometry optimisations were carried out with the BP functional using the all-electron TZV-ZORA basis set.[69] Numerical frequency calculations were carried out in order to identify whether the optimised geometries are minima or saddle points. Density fitting techniques, also called resolution-of-identity approximation (RI),[70,71] were used to speed up the BP/TZV-ZORA calculations. The dispersion corrections using Becke-Johnson damping has been employed to improve the BP/TZV-ZORA results.[72,73] Single point energy calculations with the B3P hybrid functional has been carried out on the RI-BP-D3BJ/TZV-ZORA geometries in order to verify the predicted trends.[74] The RIJONX method was used to speed up the B3P/TZV-ZORA calculations. The dispersion corrections have been discarded, since the B3P functional has not been parameterised for the D3 method. Toluene solvent effects were accounted for with the COSMO solvent model, as implemented in ORCA 3.0.3. All figures were rendered with the UCSF Chimera package.[75]

3.4 Data Collection and Structure Refinement

X-ray data were collected with a GEMINI CCD diffractometer (Rigaku Inc.), $\lambda(\text{Mo-}K_{\alpha}) = 0.71073 \text{ \AA}$, $T = 130(2) \text{ K}$, empirical absorption corrections with SCALE3 ABSPACK.[76] All structures were solved by dual space methods with SIR-92.[77] Structure refinement was done with SHELXL-2016[78,79] by using full-matrix least-square routines against F^2 . All hydrogen atoms were calculated on idealised positions. The pictures were generated with the program Mercury.[80] CCDC 1862041 (**2**), CCDC 1862044 (**3**), CCDC 1862040 (**4**), CCDC 1862038 (*exo*-**5**) and CCDC 1862046 (*endo*-**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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