Phosphonio-benzophospholide Zwitterions as Bridging 8e-Donor Ligands: Synthetic and Mechanistic Studies

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Dedicated to Professor Manfred Meisel on the Occasion of his 65th Birthday

Abstract. Reactions of the phosphonio-benzophospholide π -complexes **3a,b[Cr]** with [M(CO)₅(olefin)] or of the σ -complexes **2a,b[M]** (M = Cr, Mo, W) with [M(CO)₃(aren)] lead to the first binuclear complexes **4a,b[CrM]** featuring phosphonoio-benzophospholides as μ -bridging 8e-donor ligands to two group 6 metal atoms. The constitution of the products was determined by spectroscopic and X-ray diffraction studies. Mixed complexes with both group 6 and 7 metals were not accessible. Mechanistic studies showed that the reactions follow a complicated mechanism whose single steps may involve transfer of either M(CO)_n fragments or single CO ligands between complexes; the latter are associated with

a σ/π -coordination isomerization of the benzophospholide unit. Competition between both reaction channels can lead to the formation of product mixtures whose composition is controlled by the relative thermodynamic stabilities of the products. Computational studies suggest that in the more stable isomer of heterobimetallic complexes **4a,b[MM']** end-on coordination to the heavier and sideon coordination to the lighter metal atom is preferred.

Keywords: Phosphorus heterocycles; Benzophospholides; Binuclear complexes; Bridging ligands; Reaction mechanisms

Phosphonio-Benzophospholid-Zwitterionen als verbrückende 8e-Donorliganden: Synthetische und mechanistische Untersuchungen

Inhaltsübersicht. Reaktionen der Phosphonio-Benzophospholid- π -Komplexe **3a,b[Cr]** mit [M(CO)₅(olefin)] oder der σ -Komplexe **2a,b[M]** (M = Cr, Mo, W) mit [M(CO)₃(aren)] führten zu den ersten binuklearen Komplexen **4a,b[CrM]**, in denen Phosphonio-Benzophospholide als μ -verbrückende &e-Donorliganden gegenüber zwei Metallatomen der Gruppe 6 auftreten. Die Konstitution der Produkte wurde durch spektroskopische Untersuchungen und Röntgenstrukturanalysen bestimmt. Gemischte Komplexe mit Metallatomen der Gruppen 6 und 7 wurden nicht erhalten. Mechanistische Studien legten nahe, dass die Reaktionen einem komplexen Mechanismus folgen, dessen einzelne Schritte unter Übertra-

gung entweder eines $M(CO)_n$ -Fragments oder einzelner CO-Liganden zwischen Komplexen verlaufen; bei letzteren erfolgt gleichzeitig eine σ/π -Koordinationsisomerisierung der Benzophospholideinheit. Konkurrenz zwischen beiden Reaktionskanälen kann zur Bildung von Produktmischungen führen, deren Zusammensetzung durch die relativen thermodynamischen Stabilitäten der einzelnen Produkte bestimmt wird. Computerchemische Untersuchungen legen nahe, dass im stabileren Isomer heterobimetallischer Komplexe **4a,b**[MM'] end-on Koordination an das schwerere und side-on-Koordination an das leichtere Metallatom bevorzugt wird.

Introduction

We have recently shown that zwitterionic phosphonio-substituted benzo[c]phospholides are ambiphilic ligands and may bind to transition metal atoms "end on" via the phosphorus lone-pair (**A**, Scheme 1) or "side-on" via the π -electrons of the phosphole ring (**B**) [1, 2]. The "side-on" complexes resemble π -complexes of genuine phospholyl anions and the "end-on" complexes σ -complexes of phosphinins [3]. As both types of benzophospholide complexes still exhibit a free coordination site, they may themselves act as ligands [3] and support the formation of binuclear complexes. As first examples of such specimen we have recently reported on the formation of homobinuclear Mn- and Recompounds (C1, C2); here, each zwitterion acts as µ-bridging 4e-donor ligand that binds to one metal atom via the phosphorus lone-pair and to the second one via the π -electrons of a single PC bond in the phosphole ring [4]. In this work we report on studies directed at the synthesis of homo- and hetero-binuclear complexes in which the full 8edonating capacity of phosphonio-benzophospholides is exploited. In addition to the synthetic investigations, we will discuss the results of mechanistic studies which suggested that the formation of the target complexes via a deceptively

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Scheme 1 Dinuclear complexes with μ -bridging phosphonio-phospholide as 4e-donor ligands (M = Mn, Re).

simple ligand substitution may in fact involve more complicated reaction pathways.



Scheme 2 Molecular constitution of mono- and binuclear complexes of phosphonio-phospholides with group 6/7 metal carbonyl fragments. R = Ph (2a - 4a), Et (2b - 4b). M = Cr, Mo, W, Mn⁺ (for 3a).

Results and Discussion

Syntheses of homo- and heterobimetallic complexes with group 6 metals

By analogy to the reaction of $[Cr(CO)_5(coe)]$ (coe = cyclooctene) with triphenylphosphonio-benzo[c]phospholide **1a** to give **2a[Cr]** [1], treatment of $[Cr(CO)_5(coe)]$ with the π complex **3a[Cr]** afforded the binuclear species **4a[Cr**_2] (Scheme 2) as the only spectroscopically detectable reaction product. A similar sequence lead from the ligand **1b** via the π -complex **3b[Cr]** to **4b[Cr**_2]. The binuclear complexes were isolated as red crystalline solids that can be handled for short times in air and are moderately thermally stable; **4b[Cr**_2] decomposes slowly in boiling benzene with loss of the Cr(CO)₅ unit to give **3b[Cr]**.

As an extension to the reactions just described, treatment of **3a**[**Cr**] with a complex [M'(CO)₅(coe)] containing a different metal atom M' should allow selective access to heterobimetallic analogues of **4a**[**Cr**₂]. Whereas this proved true for the reaction of **3a**[**Cr**] with [W(CO)₅(coe)] to give **4a**[**Cr**,**W**], the analogous reaction with [Mo(CO)₅(coe)] produced according to a ³¹P NMR spectroscopic assay at least five different complexes with the ligand **1a**. Quite surprisingly, a mixture of identical composition was obtained when the π -complex **3a**[**Mo**] (prepared by analogy to **3a**[**Cr**] from **1a** and [Mo(CO)₃(tol)]; tol = toluene) was reacted with $[Cr(CO)_5(coe)]$. Although attempts to isolate any of the products failed, four components were identified by comparison of their spectral data with those of authentic samples as the mononuclear complexes 2a[Cr], 2a[Mo] (prepared by analogy to 2a[Cr] from 1a and $[Mo(CO)_5(coe)]$), 3a[Cr], and the binuclear complex $4a[Cr_2]$. The remaining species (which could not be independently prepared) was tentatively assigned as the hetero-binuclear complex 4a[Cr,Mo].

The unspecific outcome of the reactions of the π -complexes 3a[M] with $[M'(CO)_5(coe)]$ (M, M' = Cr, Mo) prompted us to study the possibility of transferring a 12e- $W(CO)_3$ -fragment from $[W(CO)_3(tol)]$ to the σ -complex 2a[Cr] as alternative access to a mixed binuclear complex. The reaction afforded indeed a single product which was. however, identified as the same complex 4a[Cr.W] as had been obtained from **3a[Cr]** and [W(CO)₅(coe)], and not the expected isomer $[W(CO)_3(\mu - \{\eta^5: W, \eta^1: Cr\} - 1a)Cr(CO)_5].$ The formal change of place of the two metal atoms suggested that the reaction involved a more complicated mechanism than a simple ligand substitution. This was verified by ³¹P NMR studies which allowed to detect several intermediates. Comparison of the change in relative product ratios with time disclosed that the starting complex 2a[Cr] reacted during the initial stages predominantly via formal loss of two CO-ligands to give the π -complex **3a**[Cr]. Both species then decayed at the expense of the homo-binuclear complex $4a[Cr_2]$ and the tungsten σ -complex 2a[W], until finally all intermediates were converted into 4a[Cr,W].

Attempts to prepare heterobimetallic complexes with group 6/7 metals

Considering that the free ligand **1a** forms σ -complexes with manganese carbonyls [4], we attempted as well the synthesis of mixed Cr/Mn-complexes by reaction of the π -complex **3a**[Cr] with [Mn(CO)₅Br] in THF. Surprisingly, a ³¹P NMR spectroscopic survey disclosed that no hetero-bimetallic complex was formed but that quantitative conversion of the starting material into the σ -complex **2a**[Cr] had occurred. Furthermore, the *homo*-bimetallic complex **4a**[Cr₂] was observed as an intermediate in the initial phase of the reaction and disappeared at the end. No further intermediates were detected when the reaction was conducted at 0 °C.

A hypothesis to rationalize the formation of the σ -complex **2a**[**Cr**] is to consider a transfer of two CO ligands from the manganese to the chromium carbonyl fragment, and concomitant η^5 - to η^1 -coordination isomerization [2] of the benzophospholide. As a possible source of the CO transferred, one can conceive formation of [Mn₂Br₂(CO)₈] [5] from Mn(CO)₅Br with loss of one CO per Mn-atom and, regarding that the chloride complex [Mn₂Cl₂(CO)₈] is known to loose two CO ligands in donating solvents to give [Mn₂Cl₂(CO)₆(solv)₂] [6], finally the formation of [Mn₂Br₂(CO)₆(THF)₂] with loss of a second CO per Mnatom. IR spectra of the product mixture formed from [Mn(CO)₅Br] and **3a**[**Cr**] displayed in the vCO region, be-



Scheme 3 Binuclear complexes via $Cr(CO)_5$ metathesis between σ and π -complexes.

side the bands of **2a**[Cr], three absorptions ($\bar{v} = 2046, 2011$, 1981 cm⁻¹; further bands in the 1960-1900 cm⁻¹ region would be hidden under the absorptions of **2a[Cr]**) that are close to the bands of an authentic sample of $[Mn_2Br_2(CO)_8]$ $(\bar{v} = 2042, 2011, 1976 \text{ cm}^{-1} \text{ in } \text{CH}_2\text{Cl}_2)$ and literature data for $[Mn_2Cl_2(CO)_6(THF)_2]$ ($\bar{v} = 2034, 2020, 1960,$ 1931 cm^{-1} [6]). Even if we interpret this finding as evidence for the presence of a binuclear complex with a $Mn_2(CO)_6$ core, uncertainties such as the solvent dependence¹⁾ of the spectrum of [Mn₂Br₂(CO)₈] and the unavailability of reference data for [Mn₂Br₂(CO)₆(THF)₂] make a more concise structural assignment unfeasible. The involvement of $[Mn_2Br_2(CO)_8]$ as possible source of CO was further substantiated by its reaction with an equimolar amount of 3a[Cr] which afforded likewise a quantitative yield of 2a[Cr]; ³¹P NMR studies revealed the transient occurrence of 4a[Cr₂] and the cation 3a[Mn⁺] (possibly with a Br⁻ or $[Mn(CO)_5]^-$ counter ion).

Although CO transfer from $[Mn(CO)_5Br]$ explains the conversion of **3a[Cr]** into **2a[Cr]**, it cannot account for the observation of the homo-binuclear complex **4a[Cr_2]**. The formation of this species can be rationalized, however, by metathesis of a $Cr(CO)_5$ fragment between **2a[Cr]** and **3a[Cr]** to give **4a[Cr_2]** and free ligand **1a** (Scheme 3). Conducting the appropriate control experiment revealed that the expected reaction indeed took place. Evaluation of relative signal intensities allowed to determine the equilibrium constant at a temperature of 303 K as K = 0.011(3), and the free enthalpy as $\Delta G = 3(1)$ kcal mol⁻¹ K⁻¹.

Spectroscopic studies

The novel binuclear complexes 4a[Cr₂], 4b[Cr₂], 4a[CrW] and the reference compounds 2a[Mo], 2a[W], and 3a[Mo] were unequivocally characterized by an extensive body of spectroscopic data (cf. experimental section). The most interesting piece of information, at least from the point of molecular structure elucidation, is the possibility to assign the benzophospholide coordination mode from easily accessible solution ³¹P NMR data. As is evident from the data in Table 1, different complex types differ clearly in the magnitudes of the coordination shift ($\Delta\delta^{coord}$) of the ring phosphorus atom and the coupling constant ²J_{PP} In particular, ranges of $\Delta\delta^{coord}$ are < -75 and > -140 for mononuclear complexes with η^{1} (P)- and $\eta^{5}(\pi)$ -bound ligands, respectively, and $-110 < \Delta \delta^{\text{coord}} < -135$ for binuclear complexes; coupling constants drop from approx. 90 Hz in the free ligands to 58 - 70 Hz in mononuclear complexes (without clear differentiation between σ - and π -complexes) and some 50 Hz in binuclear complexes. The increasing coordination shifts of σ -complexes with increasing atomic weight of the metal atom [8] and the high shielding of the phosphorus atoms in π -coordinated phosphole rings [3] reproduce known trends. Although the large coordination shifts in benzophospholide π -complexes can be related to population of the ligand π^* -orbital by $M \rightarrow L$ back donation [7], the qualitative arguments applied fail to give a satisfactory explanation for the observed decrease in $\Delta \delta^{\text{coord}}$ upon attachment of a second metal atom to the phosphorus atom in a π -complex 3[M].

The IR spectra of the compounds under study display in the carbonyl region patterns of three (2a[M], 3a,b[M]) or five bands (4a,b[M₂]), respectively. The assignment to vCO modes of $M(CO)_5$ and $M(CO)_3$ moieties is given in Table 2^{2}). The bands in both subspectra of the binuclear complexes 4[M₂] display small but consistent blue-shifts as compared to the mononuclear complexes 2a[M] and 3[M], respectively. We interpret this effect in terms of a synergistic enhancement of the π -acidity of the benzophospholide ligand which results from the larger drain in electron density associated with $L \rightarrow M$ charge transfer to two rather than one metal fragment. It had been pointed out previously [1] that the π -acceptor capacity of the phosphonio-benzophospholide **1a** in mononuclear $\eta^{1}(P)$ -complexes matches that of PPh₃ but is lower than those of trimethyl phosphite or 2,4,6-triphenylphosphinin, respectively.

Crystal structure determinations

The crystals of the $\sigma(P)$ -complexes **2a[Mo]**, **2a[W]** (both space group $P\bar{1}$) and the π -complex **3a[Mo]** (space group $P2_1/n$) are isotypic to those of the previously reported compounds **2a[Cr]** and **3a[Cr]**, respectively. Apart from deviations in metal-ligand distances which reflect the different size of the metal atoms, all bond distances and angles agree within experimental error with the corresponding data for **2a[Cr]** and **3a[Cr]** [1]. The deviations between analogous molecules affect in particular the M–P distances in the σ complexes **2a[M]** (2.504(1) Å for M = W and 2.513(1) for M = Mo vs. 2.376(1) Å for M = Cr [1]) and the distances between the metal atom and the centroid of the π -bound phosphole ring in **3a[M]** (2.064(4) Å for M = Mo vs. 1.874(3) Å for M = Cr [1]).

The molecular structure of $4a[Cr_2]$ (space group Pbca) is shown in Figure 1. The crystals of $4b[Cr_2]$ contain one solvent molecule (THF) per formula unit and crystallize in a

 $^{^{1)}}$ As judged by the deviation of the spectrum of a CH₂Cl₂ solution with respect to the reported literature data [5] which were obtained in CHCl₃.

²⁾ The low number of visible frequencies for $M(CO)_5$ fragments owes to the fact that not all IR active fundamentals are resolved whereas the observation of three bands for $M(CO)_3$ fragments indicates a perceptible perturbation of the local C_{3v} symmetry by the "unsymmetric" benzophospholide ligand.

	Formula	P(ring)		PR.		Ref
	1 of mala	δ ³¹ P	$\Delta \delta^{\text{coord a}}$	$\delta^{31}P$	$^{2}J_{\mathrm{PP}}$ /Hz	itel.
2a[Cr]	$[\{\eta^{1}(P)-\mathbf{1a}\}Cr(CO)_{5}]$	158.8	-30.0	14.1	67.4	[1]
2a[Mo]	$[\{\eta^{1}(P)-1a\}Mo(CO)_{5}]$	141.7	-46.1	14.3	69.3	
2a[W]	$[\{\eta^{1}(P)-1a\}W(CO)_{5}]$	113.1 ^{b)}	-74.7	13.7	67.4	
3a[Cr]	$[{\eta^{5}-1a}Cr(CO)_{3}]$	30.0	-157.8	21.5	66.1	[1]
3b[Cr]	$[\{\eta^{5}-1b\}Cr(CO)_{3}]$	28.0	-151.9	24.0	61.0	
3a[Mo]	$[\{\eta^{5}-1a\}Mo(CO)_{3}]$	47.1	-140.7	19.6	69.9	
3a[Mn ⁺] ^{c)}	$[{\eta^{5}-1a}Mn(CO)_{3}]^{+}$	29.3	-159.5	27.0	57.8	[4]
4a[Cr ₂]	$[\{\mu - \eta^{1}(P): \eta^{5}-1a\}Cr(CO)_{5}Cr(CO)_{3}]$	78.8	-110.0	17.7	51.5	
4b[Cr ₂]	$[\{\mu - \eta^{1}(P): \eta^{5} - \mathbf{1b}\}Cr(CO)_{5}Cr(CO)_{3}]$	75.5	-104.4	24.2	47.0	
4a[CrMo]	$[\{\mu - \eta^{1}(P): \eta^{5} - 1a\}Mo(CO)_{5}Cr(CO)_{3}]$	53.0	-135.8		48.0	
4a[CrW]	$[\{\mu-\eta^1(\mathbf{P}):\eta^5-\mathbf{1a}\}W(\mathbf{CO})_5\mathbf{Cr}(\mathbf{CO})_3]$	24.2 ^d)	-164.6	17.6	49.6	

Table 1 ³¹P NMR data of mono- and binuclear complexes of phosphonio-benzophospholides (at 30 °C in THF)

^{a)} $\Delta \delta^{\text{coord}} = \delta(\text{complex}) - \delta(\text{ligand});$ ^{b)} ${}^{1}J_{\text{WP}} = 232.4 \text{ Hz};$ ^{c)} $[\text{BF}_{4}]^{-}$ salt in CD₂Cl₂; ^{d)} ${}^{1}J_{\text{WP}} = 263.2 \text{ Hz}$

Table 2 IR spectra (vCO-region) of mono- and binuclear complexes of phosphonio-benzophospholides with group 6 metal atoms (in CH_2Cl_2).

		v(CO)	$/cm^{-1}$	Ref.
		M(CO) ₃	M'(CO) ₅	
2a[Cr]	M = -, M' = Cr		2064, 1942, 1913	[1]
2a[Mo]	M = -, M' = Mo		2073, 1948, 1918	
2a[W]	M = -, M' = W		2071, 1940, 1912	
3a[Cr]	M = Cr, M' = -	1925, 1835, 1826		[1]
3b[Cr]	M = Cr, M' = -	1924, 1839, 1821		
3a[Mo]	M = Mo, M' = -	1929, 1838, 1826		
4a[Cr ₂]	M = Cr, M' = Cr	1932, 1857, 1844	2071, 1954	
4b[Cr ₂]	M = Cr, M' = Cr	1932, 1857, 1834	2071, 1953	
4a[CrW]	M = Cr, M' = W	1938, 1857, 1843	2078, 1951	

different space group ($P\bar{1}$) but the molecular structure is quite similar and is not displayed³). A listing of important bond distances and angles for both compounds is given in Table 3.

The presence of different phosphonio groups in **4a.b[Cr**₂] leaves the remaining part of the molecules untouched and all bond lengths in the benzophospholide core and both metal carbonyl moieties are identical within experimental error. The intra-ligand bonds are further indistinguishable from those in mononuclear **3a[Cr]** [1], suggesting a similar extent of bond-lengthening in the phosphole ring by π -interaction with the M(CO)₃ fragment in all three compounds. A slant of the P1-Cr1 bond out of the mean plane of the phosphole ring induces a weak pyramidalization (sum of angles 355.5(3)°) at P1) in 4a[Cr₂] which is absent in $4b[Cr_2]$ (sum of angles $359.5(3)^\circ$) and is without doubt attributable to steric interference between the Cr(CO)₅ and $Ph_{3}P$ fragments. Both the P1-Cr1 (2.347(1), 2.352(1) Å) and Cr2-Ar distances (1.832(2), 1.839(5) Å) in 4a,b[Cr2] are shorter than in the mononuclear complexes 2a[Cr] (P1-Cr1 2.3760(5) Å [1]) and 3a[Cr] (Cr2-Ar 1.877(1) Å [1]), respec-



Fig. 1 Molecular structure of $4a[Cr_2]$. Thermal ellipsoids are drawn at 50 % probability level, and H atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 3.

tively. This observation allows certainly to rule out mutual steric interference between the two metal carbonyl moieties. It may further, in connection with the blue-shift of vCO bands in **4a,b[Cr₂]**, be interpreted as evidence for a strengthening of the metal-ligand bond by increased $M \rightarrow L$ back donation; however, conceding that the effect is very small, one should be careful as to avoid over-interpretation.

Mechanistic considerations and computational studies

The outcome of all reactions of phosphonio-benzophospholide complexes described in this work can be rationalized by a common mechanism involving sequences of two competing elementary steps, viz. transfer of intact $M(CO)_n$ fragments, or transfer of single CO ligands accompanied by σ/π -coordination isomerisation of the phosphonio-benzophospholide ligand. The formation of **4a[CrW]** from **2a[Cr]** and [W(CO)₃(tol)] is thus readily explained by a sequence

³⁾ A preliminary single crystal X-ray diffraction study of **4a[CrW]** confirmed the postulated structure with a $W(CO)_5$ and a $Cr(CO)_3$ unit and similar features as for the dichromium complexes. As successful refinement failed due to problems with modelling the disorder of two solvent molecules, the data are not discussed further.

Table 3 Selected bond distances (in Å) and angles (in °) for the binuclear complexes $4a[Cr_2]$ and $4b[Cr_2]$. The numbering scheme for all three compounds is identical to the one used in Figure 1.

	4a[Cr ₂]	4b[Cr ₂]
P1-C2	1.798(2)	1.801(4)
C2-C3	1.461(2)	1.458(6)
C3-C8	1.431(2)	1.442(6)
C8-C9	1.425(2)	1.416(6)
P1-C9	1.739(2)	1.728(4)
P2-C2	1.761(2)	1.762(4)
P1-Cr1	2.347(1)	2.352(1)
Cr1-C1A	1.884(2)	1.864(6)
Cr1-C1B	1.903(2)	1.908(6)
Cr1-C1C	1.909(2)	1.905(6)
Cr1-C1D	1.903(2)	1.896(5)
Cr1-C1E	1.909(2)	1.913(6)
Cr2-Ar a)	1.832(2)	1.839(5)
Cr2-C2A	1.827(2)	1.829(5)
Cr2-C2B	1.850(2)	1.819(5)
Cr2-C2C	1.838(2)	1.840(6)
$\Sigma_{angles(P1)}$	355.5(3)	359.5(3)

^{a)} Ar = Centroid of the phosphole ring

(Scheme 4) involving as the first step the loss of two CO ligands from 2a[Cr] to give 3a[Cr] and a tungsten complex (presumably [W(CO)₅(THF)], although this was not detected spectroscopically). Reaction of this species with 3a[Cr] affords the final product 4a[CrW] whereas transfer of a Cr(CO)₅ moiety from unreacted 2a[Cr] to 3a[Cr] produces 4a[Cr₂] and the free ligand 1a; the latter is immediately guenched by [W(CO)₅(THF)] to yield 2a[W]. The final conversion of all intermediates into 4a[CrW] requires that the intermediate steps are reversible. The same sequence can account as well for all products formed in the reactions of $3a[Cr] / [Mo(CO)_5(coe)]$ or $3a[Mo] / [Cr(CO)_5(coe)]$, respectively, and the observation of the same product distribution in both reactions further supports the idea of reversible reaction steps. It is reasonable to assume that the same processes may also occur during the deceptively simple "homonuclear" reactions involving only complexes with like metal atoms. Last, but not least, the involvement of CO transfer and Cr(CO)₅ exchange processes in the reaction of **3a[Cr]** with manganese complexes has already been mentioned.

Assuming reversible mutual transformations between benzophospholide complexes suggests that the final products are formed under thermodynamic control. The failure to obtain Mn-containing binuclear complexes with bridging benzophospholides, and the transfer of CO ligands from [Mn(CO)₅Br] to **3a**[Cr], may thus be assumed to reflect the known low stabilities of Mn-P [4] and Mn-CO [9][10] σbonds. Likewise, the observed formation of 4a[CrW] rather than the anticipated product with π -coordinated W(CO)₃ and $\eta^{1}(P)$ -bound Cr(CO)₅ fragments from [W(CO)₃(tol)] and 2a[Cr] could point to a higher stability of the former isomer. In order to evaluate a possible influence of the metal atoms on the stabilities of isomeric binuclear complexes we performed computational studies of the "intramolecular" and "intermolecular" ligand redistribution reactions (1) - (3) shown in scheme 5.

In order to cut down the cost of the computations, the ligand **1a** used in the experimental studies was modeled by the PH₃-substituted compound **1c**. All reaction energies were computed at the B3LYP/3-21g* level and are given in Scheme 5. The computation of ΔE_3 with M = M' = Cr was repeated at higher computational levels and also the Gibbs energy for this reaction was calculated, to give ΔG° values (at 293 K) of -0.5, 0.7, and 1.2 kcal mol⁻¹ K⁻¹ at the B3LYP/3-21G*, B3LYP/LAN2DZP, and B3LYP/6-311G* levels, respectively. All results are reasonably close together and to the experimentally determined value of ΔG for the corresponding reaction of **1a** (vide supra) if one considers that the computations were performed on model compounds in the gas phase.

The computed values of ΔE_3 are generally small, suggesting that the attachment of two metal carbonyl fragments to the same ligand does not introduce an exceedingly large amount of steric strain. The trends in $\Delta E_{1,2}$ reveal further a clear preference of the heavier metal for terminal and of the lighter metal for side-on coordination which is more pronounced for tungsten than for molybdenum. These findings suggest that the observed formation of **4a[CrW]** reflects indeed a higher stability relative to the other possible isomer, and prompted us as well to assign the constitution of the spectroscopically detectable, yet unisolable, complex **4a[CrMo]** accordingly.

Conclusions

It was demonstrated that treatment of mononuclear σ - or π complexes of phosphonio-benzophospholides with reagents capable of transferring appropriate M(CO)_n fragments gives rise to binuclear complexes with two group 6 metals and µ- $\{\eta^5: M, \eta^1: M'\}$ -bridging benzophospholide units. Mechanistic studies revealed that many of these reactions cannot be considered simple substitution processes but follow complicated mechanisms whose elementary steps involve either a transfer of intact M(CO)_n fragments or, alternatively, a transfer of single CO ligands and concomitant coordination isomerization of the benzophospholide moiety. Competition between both types of elementary reactions may yield product mixtures whose composition appears to be controlled by the relative thermodynamic stabilities of the components. As a consequence, unstable isomers or mixed binuclear complexes of group 6/7 metals remain inaccessible and the isolation of pure products is in principle restricted to cases where one exceedingly stable product is formed in large excess.

The results obtained here suggest further that side reactions via CO transfer and concomitant σ/π -isomerisation may as well complicate other reactions of carbonyl complexes of phosphonio-benzophospholide ligands (e.g. substitution or ligand redistribution with non-carbonyl compounds) and may restrict the use of these compounds in synthesis or catalysis. It can be envisaged that the mechanistic considerations presented here may also have importance for studies of complexes of other types of ligands that



Scheme 4 Proposed mechanism for the reaction of the π -complexes 3a[Cr] with [W(CO)₃(tol)].

[(CO) ₅ Μ (μ-η ¹ :Μ,η ² 4 c[MM]	:M'-1c)M'(CO) ₃ ']] 🚐	P	[(CO) ₅ M' (μ-η ¹ :Ν	$M', \eta^{5}: M-1c)M(CO)_{3} + \Delta E_{1}$ 4c[M'M]	(1)
$[M'(CO)_3(\eta^5-1c)] + 3c[M']$	· [M (CO) ₅ (η ¹ -1a 2c[M]	a)] 🚅		$\begin{matrix} [\mathbf{M'}(\mathrm{CO})_{5}(\eta^{1}\text{-}\mathbf{1c})\\ \mathbf{2c}[\mathbf{M'}] \end{matrix}$	$\mathbf{M} = [\mathbf{M}(\mathbf{CO})_3(\eta^5 - \mathbf{1c})] + \Delta \mathbf{E}$ $\mathbf{3c}[\mathbf{M}]$	E_2 (2)
		м	M'	ΔE_{\perp} [kcal mol ⁻¹]	ΔE_2 [kcal mol ⁻¹]	
		Cr	Mo	-3.3	-3.3	
		Mo	W	-8.5	-8.1	
		Cr	W	-11.8	-11.5	
			M			
			1.0	M' AE- Ike	al mol ⁻¹]	
			Cr	M' ΔE_3 [kc Cr 4	al mol ⁻¹]	
			Cr Cr	M' ΔE ₃ [kc Cr 4 Mo 4	al mol ⁻¹] .6 .9	
			Cr Cr Cr	M' ΔE ₃ [kc Cr 4 Mo 4 W 55	al mol ⁻¹] .6 .9 .1	
			Cr Cr Cr Mo	M' ΔE ₃ [kc Cr 4 Mo 4 W 5 Cr 4	al mol ⁻¹] .6 .9 .1 .9	
			Cr Cr Cr Mo Mo	$\begin{array}{ccc} M' & \Delta E_3 [kc \\ Cr & 4 \\ Mo & 4 \\ W & 5 \\ Cr & 4 \\ Mo & 5 \\ \end{array}$	al mol ⁻¹] .6 .9 .1 .9 .4	
			Cr Cr Cr Mo Mo Mo	$\begin{array}{cccc} M' & \Delta E_3 \ [kc \\ Cr & 4 \\ Mo & 4 \\ W & 5 \\ Cr & 4 \\ Mo & 5 \\ W & 6 \end{array}$	al mol ⁻¹] .6 .9 .1 .9 .4 .0	
			Cr Cr Cr Mo Mo W	$\begin{array}{cccc} M' & \Delta E_3 [kc \\ Cr & 4 \\ Mo & 4 \\ W & 5 \\ Cr & 4 \\ Mo & 5 \\ W & 6 \\ Cr & 5 \end{array}$	al mol ⁻¹] .6 .9 .1 .9 .4 .0 .4	
			Cr Cr Cr Mo Mo W W	M' ΔE ₃ [kc Cr 4 Mo 4 W 5 Cr 4 Mo 5 W 6 Cr 5 Mo 5 Mo 5 Mo 5 Mo 5	al mol ⁻¹] .6 .9 .1 .9 .4 .0 .4 .6	

Scheme 5 Computed energies (in kcal mol-1 at the B3LYP/3-21g* level) for ligand metathesis reactions. 1c denotes the parent 1-phos-phonio-benzo[c]phospholide.

are in principle capable to undergo σ/π -coordination isomerisation such as phosphinins or certain substituted pyridine derivatives.

Experimental Section

General Remarks: All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra: Bruker DPX 300 (¹H: 300.13 MHz, ³¹P 121.5 MHz, ¹³C: 75.3 MHz) in thf-D₈ at 30 °C; chemical shifts referenced to ext. TMS (¹H, ¹³C), 85 % H₃PO₄ ($\Xi = 40.480747$ MHz, ³¹P); positive

signs of chemical shifts denote shifts to lower frequencies, coupling constants are given as absolute values; prefixes *i*-, *o*-, *m*-, *p*- denote atoms of phenyl substituents and atoms in the benzophospholide ring are denoted as C-4, 5-H, etc. MS: Kratos Concept 1H, Xe-FAB, m-NBA matrix. IR spectra: Nicolet FT-IR Magna 550, NaCl cells. Elemental analysis: Perkin-Elmer 2400CHSN/O Analyser. Melting points were determined in sealed capillaries. IR and ³¹P NMR data are listed in Tables 1 and 2, respectively.

DFT calculations were carried out with the Gaussian 98 program package [11]. The molecular structures were energy optimized at the B3LYP/3-21G* level, using the experimental data available

from X-ray diffraction studies as starting points. The reaction energies and free reaction enthalpies for reaction (2) in Scheme 5 were recomputed at the B3LYP/3-21G*, B3LYP/LAN2DZP, and B3LYP/6-311G* levels, respectively, using molecular structures which were re-optimized at the same level of theory. The molecular structures obtained from these computations are minima on the potential energy surface (only positive eigenvalues of the Hessian matrix).

Complexes **2a**[**Cr**] and **3a**[**Cr**] were prepared as described earlier [1]. Complexes **2a**[**Mo**], **2a**[**W**], and **3a**[**Mo**] were prepared by analogy to the corresponding chromium complexes from **1a** and [$M(CO)_5(coe)$] (M = Mo, W) or [$MoCO)_3(toluene)$], respectively.

2a[Mo]: yield 81 %, mp. 159 °C (dec.); Anal. for $C_{31}H_{20}MoO_5P_2$: calcd. C 59.07 H 3.20 %; found: C 58.15 H 4.19 %.

¹H NMR: δ = 8.1 (dd, 1 H, ${}^{2}J_{PH}$ = 36.9 Hz, ${}^{4}J_{PH}$ = 5.9 Hz, 3-H), 7.89 – 7.58 (m, 15 H, Ph), 7.53 (m, 1 H, 6.5 – 6.6 (m, 2 H), 6.85 (m, 1 H, all 4-H – 7-H). –

2a[W]: yield 81 %, mp. 156 °C (dec.); Anal. for $C_{31}H_{20}O_5P_2W$: calcd. C 51.84 H 2.81 %; found: C 50.92 H 3.46 %.

¹**H** NMR: δ = 8.4 (dd, 1 H, ${}^{2}J_{PH}$ = 35.6 Hz, ${}^{4}J_{PH}$ = 5.8 Hz, 3-H), 7.5 – 6.8 (m, 15 H, Ph), 7.7 (m, 1 H, 6.8 – 6.5 (m, 3 H, all 4-H – 7-H). –

3a[Mo]: yield 92 %, mp. 212 °C (dec.); Anal. for $C_{29}H_{20}MoO_3P_2$: calcd. C 60.64 H 3.51 %; found: C 60.3 H 3.3 %.

¹**H** NMR: δ = 8.0 - 7.6 (m, 15 H, Ph), 7.0 - 6.8 (m, 4 H, all 4-H - 7-H), 6.0 (dd, 1 H, ${}^{2}J_{PH}$ = 39.4 Hz, ${}^{4}J_{PH}$ = 3.8 Hz, 3-H). -

1-Ethyldiphenylphosphonio-benzo[c]phospholide (1b) was prepared by reduction of 1a with two equivalents of sodium naphthalenide (2 h in THF at ambient temperature) and quenching of the resulting sodium 1-diphenylphosphino-benzophospholide with excess ethyl iodide. Solid NaI was filtered off, the reaction mixture concentrated in vacuum, and the product was precipitated by addition of hexane; yield 83 % after recrystallization from hexane; mp. 201 °C.

¹**H** NMR: δ = 7.9 (dd, 1 H, ${}^{2}J_{PH}$ = 42.8 Hz, ${}^{4}J_{PH}$ = 6.4 Hz, 3-H), 7.8 -7.5 (m, 10 H, Ph-H), 7.6-6.5 (m, 4 H, 4-H to 7-H), 3.05 (dq, 2 H, ${}^{2}J_{PH}$ = 12.7 Hz, ${}^{3}J_{HH}$ = 7.5 Hz, CH₂), 1.33 (dt, 3 H, ${}^{3}J_{HH}$ = 7.5 Hz, CH₃).

Complex 4a[Cr₂]. A mixture of **3a[Cr]** (100 mg, 0.19 mmol) and [Cr(CO)₅(coe)] (60 mg, 0.20 mmol) were dissolved in THF (10 ml). The resulting solution was stirred for 5 h at ambient temperature. The solution was then concentrated in vacuum to 0.5 ml and hexane (20 ml) was added. The dark red precipitate formed was filtered off, washed with little hexane, and dried in vacuum to yield 130 mg (yield 95 %) of product of mp. 219 °C. Anal. for $C_{34}H_{20}Cr_2O_8P_2$: calcd. C 56.52 H 2.79 %; found: C 56.95 H 3.06 %.

¹**H** NMR: δ = 8.3 – 7.7 (m, 15 H, Ph), 7.66 (m, 1 H), 7.05 (m, 1H), 6.72 (m, 1H), 6.36 (m, 1 H, 4-H to 7-H), 5.35 (dd, 1 H, ${}^{2}J_{PH}$ = 34.3 Hz, ${}^{4}J_{PH}$ = 2.6 Hz, 3-H). – ¹³C{¹H} NMR: δ = 235.7 (d, ${}^{2}J_{PC}$ = 3.1 Hz, 3 CO), 221.0 (d, ${}^{2}J_{PC}$ = 4.2 Hz, 1 CO), 214.5 (d, ${}^{2}J_{PC}$ = 15.1 Hz, 4 CO), 135.2 (d, ${}^{2}J_{PC}$ = 9.9 Hz, o-C), 134.9 (d, ${}^{4}J_{PC}$ = 2.9 Hz, p-C), 134.0 (dd, ${}^{1}J_{PC}$ = 50.5 Hz, ${}^{3}J_{PC}$ = 3.0 Hz, C-3), 130.2 (d, ${}^{3}J_{PC}$ = 12.4 Hz, m-C), 128.0 (dd, ${}^{3}J_{PC}$ = 1.8 Hz, ${}^{3}J_{PC}$ = 8.4 Hz, C-4/7), 125.8 (dd, ${}^{3}J_{PC}$ = 0.9 Hz, 7.6 Hz, C-3/7a), 124.0 (s, C-5/6), 124.7 (s, C-5/6), 123.0 (dd, ${}^{n}J_{PC}$ = 2.5 Hz, 2.5 Hz, C-4/7), 122.2 (dd, ${}^{1}J_{PC}$ = 89.7 Hz, ${}^{3}J_{PC}$ = 1.1 Hz, i-C), 113.6 (dd, ${}^{2}J_{PC}$ = 1.8 Hz, 13.6 Hz, C-3a/7a), 57.2 (dd, ${}^{1}J_{PC}$ = 35.7 Hz, 97.1 Hz, C-1). – MS (+)-Xe-FAB, mNBA): m/e(%) = 722 (25) [M⁺], 530 (60) [M⁺ - Cr(CO)₅], 446 (100) [M⁺ - Cr, -8 CO].

Complex 4b[Cr₂]. Ligand **1b** (150 mg, 0.43 mmol) and [Cr(CO)₃-(napth)] (114 mg, 0.43 mmol) were stirred in 30 ml of THF for 12 hours at room temperature. The reaction mixture was then concentrated to approx. 5 ml and hexane (20 ml) was added. The precipitate formed was filtered off and dried in vacuo. The product was identified as the π -complex **3b[Cr]** by ³¹P NMR spectroscopy. A

portion of the crude product (120 mg, 0.24 mmol) and $[Cr(CO)_5(coe)]$ (75 mg, 0.24 mmol) were then dissolved in THF (30 ml) and stirred for 2 hours at room temperature. The reaction mixture was concentrated to 5 ml and hexane (20 ml) was added. The precipitate formed was filtered off and dried in vacuum. Recrystallization from n-hexane/THF afforded 150 mg (91 %, with respect to **3a**[**Cr**]) of deep red crystals, mp. 208 °C (dec.).

¹H NMR: δ = 8.0–7.5 (m, 10 H, Ph), 7.21 (m, 1 H, 7-H), 6.98 (m, 1 H, 6-H), 6.81 (m, 1 H, 5-H), 6.46 (m, 1 H, 4-H), 5.37 (dd, 1 H, ${}^{2}J_{PH} = 35.0$ Hz, ${}^{4}J_{PH} = 2.8$ Hz, ${}^{4}J_{IH} = 0.8$ Hz, 3-H), 3.2 – 3.0 (m, 2H, CH₂), 1.2 (dt, 3 H, ${}^{3}J_{PH} = 19.7$ Hz, ${}^{3}J_{HH} = 7.5$ Hz). – 236.6 (d, ${}^{2}J_{PC} = 3.2$ Hz, 4 CO), 215.5 (d, ${}^{2}J_{PC} = 14.9$ Hz, CO), 213.7 (s, 3 CO), 135.5 (s, p-C), 135.4 (s, p-C), 135.3 (d, ${}^{2}J_{PC} = 9.8$ Hz, o-C), 135.1 (d, ${}^{2}J_{PC} = 9.8$ Hz, o-C), 130.7 (d, ${}^{3}J_{PC} = 2.3$ Hz, m-C), 129.3 (s, C-5/6), 126.1 (s, C-5/6), 124.0 (d, ${}^{3}J_{PC} = 8.4$ Hz, C-4/7), 122.7 (d, ${}^{3}J_{PC} = 2.9$ Hz, 2.6 Hz, C-4/7), 121.2 (d, ${}^{1}J_{PC} = 85.0$ Hz, i-C), 114.9 (dd, ${}^{n}J_{PC} = 6.8$ Hz, 1.3 Hz, C-3a/7a), 120. (dd, ${}^{1}J_{PC} = 32.3$ Hz, 94.4 Hz, C1), 23.1 (dd, ${}^{1}J_{PC} = 59.8$ Hz, ${}^{2}J_{PC} = 3.2$ Hz, CH₂), 7.5 (d, ${}^{2}J_{PC} = 5.2$ Hz, CH₃). – MS (+)-Xe-FAB, mNBA): m/ z(%): 674 (60) [M⁺], 482 (55) [M⁺-Cr(CO)₅], 398 (100) [M⁺-Cr, -8 CO].

Complex 4a[CrW]: Complex **3a[Cr]** (100 mg, 0.19 mmol) and [W(CO)₅(coe)] (78 mg, 0.19 mmol) were reacted as described above for **4a[Cr₂]**. Work-up yielded 180 mg (62 %) of a deep red crystalline solid, mp. 217 °C (dec.). Anal. for $C_{34}H_{20}CrO_8P_2W$: calcd. C 47.80 H 2.35 %; found: C 46.66 H 2.18 %.

¹H NMR: δ = 8.3 - 7.7 (m, 15 H, Ph), 7.0-7.2 (m, 2 H), 6.72 (m, 1 H), 6.32 (m, 1 H, all 4-H to 7-H), 5.39 (dd, 1 H, ${}^{2}J_{PH}$ = 34.6 Hz, ${}^{4}J_{PH}$ = 2.8 Hz, 3-H). - 235.8 (s, 3 CO), 197.8 (s, 4 CO), 194.6 (d, ${}^{2}J_{PC}$ = 8.0 Hz, CO), 144.7 (dm, ${}^{2}J_{PC}$ = 12.9 Hz, C-3a/7a), 143.6 (dm, ${}^{3}J_{PC}$ = 7.0 Hz, C-3a/7a), 135.2 (d, ${}^{2}J_{PC}$ = 9.7 Hz, o-C), 130.1 (d, ${}^{3}J_{PC}$ = 12.6 Hz, m-C), 128.8 (dd, ${}^{1}J_{PC}$ = 57.8 Hz, ${}^{3}J_{PC}$ = 3.1 Hz, C-3), 128.0 (dm, ${}^{3}J_{PC}$ = 8.8 Hz, C-4/7), 124.6 (s, C-5/6), 124.0 (s, C-5/6), 122.2 (dd, ${}^{1}J_{PC}$ = 89.8 Hz, ${}^{3}J_{PC}$ = 1.0 Hz, i-C), 121.5 (dd, ${}^{n}J_{PC}$ = 2.3 Hz, 2.6 Hz, C-4/7), 53.6 (dd, ${}^{1}J_{PC}$ = 26.9 Hz, 97.6 Hz, C-1). - MS (+)-Xe-FAB, mNBA): m/z (%) = 854 (80) [M⁺], 770 (65) [M⁺], 714 (30) [M⁺-5 CO], 662 (20) [M⁺-8 CO, -Cr].

Reactions of phosphonio-benzophospholide complexes with metal carbonyl complexes. The appropriate reactants (approx. 0.1 mmol each) were dissolved in 3 - 5 ml of THF. Part of the solution was then transferred to an NMR tube and the progress of the reaction monitored by ³¹P NMR spectroscopy.

Crystal structure determinations

2a[Mo]: yellow crystals, $C_{31}H_{20}MoO_5P_2$, M = 630.4, crystal size 0.40 x 0.30 x 0.25 mm, triclinic, space group $P\bar{I}$ (No. 2): a = 10.3519(2) Å, b = 11.1430(3) Å, c = 13.6726(4) Å, $\alpha = 110.688(2)^{\circ}$, $\beta = 93.005(2)^{\circ}$, $\gamma = 110.270(2)^{\circ}$, V = 1356.3(1) Å³, Z = 2, ρ (calcd) = 1.543 Mg m⁻³, F(000) = 636, m = 0.64 mm⁻¹, 19783 reflections (2 $\theta_{max} = 56.6^{\circ}$) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_{α} radiation ($\lambda = 0.71073$ Å), 6394 unique [R_{int} = 0.036] used for structure solution (Direct Methods, SHELXS-97 [12]) and refinement (full-matrix least-squares on F^2 , SHELXL-97 [12]) with 352 parameters, empirical absorption correction from multiple reflections, H-atoms with a riding model, R1 ($I > 2\sigma(I)$) = 0.023, wR2 = 0.056, largest diff. peak and hole 0.337 and -0.586 e Å⁻³.

2a[W]: yellow crystals, $C_{31}H_{20}O_5P_2W$, M = 718.3, crystal size 0.25 x 0.20 x 0.10 mm, triclinic, space group $P\bar{I}$ (No. 2): a = 10.3356(4) Å, b = 11.1304(4) Å, c = 13.6737(4) Å, $\alpha = 110.692(2)^{\circ}$, $\beta = 93.051(2)^{\circ}$, $\gamma = 110.313(2)^{\circ}$, V = 1352.0(1) Å³, Z = 2, ρ (calcd) = 1.764 Mg m⁻³, F(000) = 700, $\mu = 4.43$ mm⁻¹, 11233 reflections (2 $\theta_{max} = 50.0^{\circ}$) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_{α} radiation ($\lambda = 0.71073$ Å), 4715 unique [R_{int} = 0.044] used for structure solution (Direct

Methods, SHELXS-97 [12]) and refinement (full-matrix least-squares on F^2 , SHELXL-97 [12]) with 352 parameters, empirical absorption correction from multiple reflections, H-atoms with a riding model, R1 ($I > 2\sigma(I)$) = 0.023, wR2 = 0.055, largest diff. peak and hole 1.318 and -1.735 e Å⁻³.

3a[Mo]: yellow crystals, $C_{29}H_{20}MoO_3P_2$, M = 574.3, crystal size 0.15 x 0.10 x 0.05 mm, monoclinic, space group P2₁/n (No. 14): a = 8.6002(6) Å, b = 13.3527(12) Å, c = 21.3535(16) Å, $\beta = 97.847(5)^\circ$, V = 2429.2(3) Å³, Z = 4, ρ (calcd) = 1.570 Mg m⁻³, F(000) = 1160, $\mu = 0.70$ mm⁻¹, 11996 reflections (2 $\theta_{max} = 50.0^\circ$) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_{α} radiation ($\lambda = 0.71073$ Å), 4219 unique [R_{int} = 0.067] used for structure solution (Patterson Methods, SHELXS-97 [12]) and refinement (full-matrix least-squares on F^2 , SHELXL-97 [12]) with 316 parameters, H-atoms with a riding model, R1 ($I > 2\sigma(I)$) = 0.044, wR2 = 0.089, largest diff. peak and hole 0.584 and -0.373 e Å⁻³.

4a[**Cr**₂]: colorless crystals, $C_{34}H_{20}Cr_2O_8P_2$, M = 722.5, crystal size 0.18 x 0.12 x 0.06 mm, orthorhombic, space group Pbca (No. 61): a = 17.8340(3) Å, b = 15.7619(3) Å, c = 22.7827(3) Å, V = 6404.2(2) Å³, Z = 8, ρ (calcd) = 1.499 Mg m⁻³, F(000) = 2928, $\mu = 0.83$ mm⁻¹, 64905 reflections (2 $\theta_{max} = 56.6^{\circ}$) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_{α} radiation ($\lambda = 0.71073$ Å), 7910 unique [R_{int} = 0.049] used for structure solution (Direct Methods, SHELXS-97 [12]) and refinement (full-matrix least-squares on F^2 , SHELXL-97 [12]) with 415 parameters, H-atoms with a riding model, R1 ($I > 2\sigma(I) = 0.030$, wR2 = 0.077, largest diff. peak and hole 0.365 and -0.480 e Å⁻³.

4b[**Cr**₂]: colorless crystals, $C_{30}H_{20}Cr_2O_8P_2$ I thf, M = 746.5, crystal size 0.30 x 0.12 x 0.04 mm, triclinic, space group PĪ (No. 2): a = 11.2577(4) Å, b = 12.0239(4) Å, c = 13.0066(5) Å, $\alpha = 86.188(2)^\circ$, $\beta = 75.108(2)^\circ$, $\gamma = 83.558(2)^\circ$, V = 1689.4(1) Å³, Z = 2, ρ (calcd) = 1.467 Mg m⁻³, F(000) = 764, $\mu = 0.79$ mm⁻¹, 14140 reflections (2 $\theta_{max} = 50.0^\circ$) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_{α} radiation ($\lambda = 0.71073$ Å), 5881 unique [R_{int} = 0.082] used for structure solution (Direct Methods, SHELXS-97 [12]) and refinement (full-matrix least-squares on F^2 , SHELXL-97 [12]) with 424 parameters and 36 restraints, empirical absorption correction from multiple reflections, H-atoms with a riding model, R1 ($I > 2\sigma(I) = 0.056$, wR2 = 0.134, largest diff. peak and hole 0.972 and -0.692 e Å⁻³.

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-249089 (**2a[Mo]**), 249090 (**2a[W]**), 249091 (**3a[Mo]**), 249092 (**4a[Cr₂]**), 249093 (**4b[Cr₂]**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail:-teched@chemcrys.cam.ac.uk).

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