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1,3,4-Azadiphospholides as building blocks for scorpionate and bidentate ligands in multinuclear complexes†

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Annulated oxy-substituted 1,3,4-azadiphospholides such as the anion in Na[1] are readily accessible phosphorus heterocycles made from the phosphaehtynolate anion (OCP)[−] and 2-chloropyridines. The sodium salt Na[1] reacts with oxophilic element halides such as OPCL₃, PhSiCl₃, PhBCl₂ and CpTiCl₃ at room temperature to form exclusively the oxygen bound tris-substituted compounds E(1)₃ (with E = OP, PhSi, PhB[−] or CpTi). Six equivalents of Na[1] with group four metal chlorides MCL₄ (M = Ti, Zr, Hf) form cleanly the hexa-substituted dianions (Na₂[M(1)₆]) which are isolated in excellent yields. The titanium complexes are deeply coloured species due to ligand to metal charge transfer (LMCT) excitations. In all complexes, the phosphorus atoms of the azadiphosphole moieties are able to coordinate to a soft metal center as shown in their reactions with [Mo(CO)₃Mes], yielding complexes in which the Mo(CO)₃ binds in a *fac* manner. Functionalization of the oxy group with amino phosphanes allows isolation of tridentate ligands, which have been used as synthons for macrocyclic molybdenum carbonyl complexes.

Received 14th April 2020,
Accepted 26th May 2020

DOI: 10.1039/d0dt01864c

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Introduction

One of the world's most famous dyes is Prussian blue, an iron cyanide complex with the formula [Fe(CN)₆]₃Fe₄.¹ The different oxidation states of the iron centers in the polynuclear complex allow charge transfer processes which cause the dark blue color of the complex. Polynuclear metal complexes often show luminescence² or even phosphorescence making them potential triplet emitters in light emitting diodes.³ Assemblies of metal complexes with unpaired electrons can form single molecule magnets.^{4–10} Not only small linear linkers¹¹ such as cyanates^{12–14} or azides¹⁵ have been applied but also anionic rings such as triazoles,¹⁶ tetrazoles¹⁷ or phosphorus containing heterocycles¹⁸ have been used to generate scorpionate type ligands which serve as ligands in a very broad range of metal complexes^{19–21} and as components in opto-electronic materials.²² The phosphaehtynolate anion (OCP)[−] is an excellent building block for a wide variety of organophosphorus

compounds.^{23–26} Due to its ambident nucleophilic character, it binds to soft centers^{27–32} *via* the phosphorus atom (M–P=C=O) and hard centers *via* the oxygen atom (M–O–C≡P).^{33–39} Furthermore, phosphaketenes ([M]–P=C=O) with [M] = main group element or transition metal fragment show a tendency to lose carbon monoxide which allows to prepare mono- and polynuclear metal phosphides.^{23,33,40–47} There are very few examples which show a bridging OCP-unit between two metal centers.^{42,48–51} A high yield multigram synthesis of annulated oxy functionalized 1,3,4-azadiphospholides such as Na[1] (Scheme 1) from Na(OCP) and 2-chloropyridines was developed.^{52,53} These anionic heterocycles contain a OCP-functionality stabilized within the aromatic scaffold of the 1,3,4-azadiphosphole and therefore no elimination of carbon monoxide is expected.

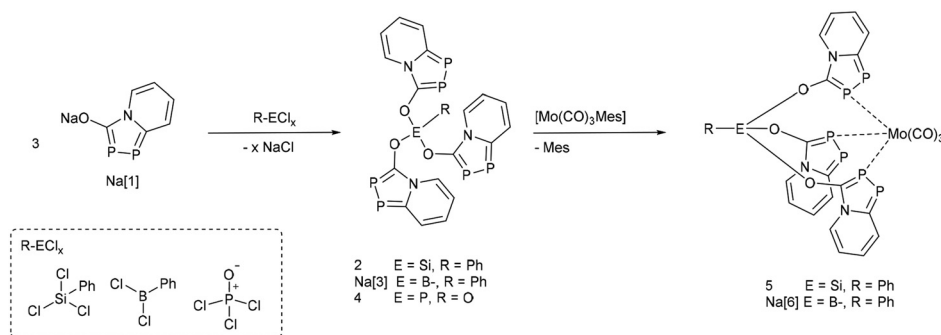
Results and discussion

In this paper, we report the use of Na[1] as anionic building block to form tridentate scorpionate-type ligands containing low-coordinated λ³,σ²-phosphorus atoms as donor sites. The electronic properties of these polydentate ligands can be modified easily by varying the central oxophilic linker.

To form a neutral tridentate ligand, three equivalents of the azadiphospholide Na[1] were added to the phenyl trichlorosilane PhSiCl₃ in THF. The reaction mixture turned yellow

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†Electronic supplementary information (ESI) available: Containing synthetic procedures and experimental details. CCDC 1494716, 1494717, 1494718, 1494719, 1494720, 1494721, 1494722, 1494723, 1494802, 1495143, 1495146 and 1495123. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt01864c



Scheme 1 Synthesis of main group substituted scorpionates **2**, Na[**3**] and **4** from Na[**1**] and the corresponding molybdenum complexes **5** and Na[**6**].

immediately and a white precipitate was formed. Isolation of the pure compound **2** was possible by recrystallization. In CD₂Cl₂ as solvent, the product exhibits two doublet resonances with very similar chemical shifts (³¹P δ = 118.8 and 123.0 ppm, ¹J_{PP} = 442.3 Hz). The similarly tris(substituted) but anionic boron analogue Na[**3**] has been isolated in the reaction of three equivalents of Na[**1**] with PhBCl₂. However, similar reactions with PCl₃ only formed a mixture of products and copious amounts of a brown precipitate, which could not be identified. The reaction of three equivalents of Na[**1**] with phosphoryl chloride POCl₃ on the other hand formed one major product, which was unambiguously identified by X-ray crystallography as the expected tris(substituted) phosphine oxide compound **4** (Fig. 1). The ³¹P{¹H}-NMR spectrum in CD₂Cl₂ shows three different phosphorus resonances. The resonance for the P=O atom is observed at low frequency (³¹P δ = -20.8 ppm), comparable to (Ph-O)₃P=O (³¹P δ = -17.3 ppm in CDCl₃),⁵⁴ and does not show any coupling to the phosphorus atoms of the azadiphospholide substituents. The ¹J_{PP} coupling in the azadiphosphole ring (¹J_{P1,P2} = 446.5 Hz) is comparable to that in the silicon species **2** (¹J_{PP} = 442.3 Hz) and significantly larger than that in the sodium salt Na[**1**] (¹J_{P1,P2} = 424.7 Hz).

To study the suitability of these compounds as ligands in transition metal complexes, one equivalent of the molybdenum complex [Mo(Mes)(CO)₃] dissolved in THF was added to a solution of **2**, Na[**3**], or **4**, respectively. Upon standing at room temperature for 16 hours, dark yellow single crystals suit-

able for X-ray crystal diffraction studies of the silicon complex **5** and boron species Na[**6**], grew from the reaction mixtures (Fig. 2). The complexes show the expected κ³P-coordination mode of the tridentate ligands **2** and Na[**3**]. No clean product was isolated from the reaction of [Mo(Mes)(CO)₃] with **4**.

In the next step, the use of oxophilic transition metal halides as central connecting node was tested. Therefore CpTiCl₃ and three equivalents of Na[**1**] were suspended in toluene to instantly form a deep purple solution. The mixture was left at room temperature for 72 hours without stirring to give a dark purple product **7** as crystalline solid. This procedure only produces a low yield due to the formation of several side products. When a large excess of Na[**1**] was added to CpTiCl₃, a dark green solution was obtained from which dark green crystals were isolated and identified as the dianionic hexa-substituted compound Na₂[**8_{Ti}**] (Scheme 2). In this reaction not only the chloride but also the cyclopentadienide (Cp⁻) became substituted by an azadiphospholide group. Both compounds, **7** and Na₂[**8_{Ti}**], have been unambiguously identified by single crystal X-ray diffraction methods and plots are shown in Fig. 5.

The titanium species Na₂[**8_{Ti}**] can be synthesized directly in the reaction of six equivalents of the sodium salt of Na[**1**] with TiCl₄(THF)₂. This route gives very good yields (>95%) and pure and single crystalline material can be isolated on a multi-gram scale. The analogous dianions (Na₂[**8_{Zr}**] and Na₂[**8_{Hf}**]) with the heavier group four metals zirconium and hafnium were synthesized using a similar procedure (ESI† for details).

The salts containing the heavier group four metals in the center show a significant blue shift of the longest wave absorption compared to the titanium species (Fig. 3).

Solutions of **7** are dark purple and Na₂[**8_{Ti}**] are coloured dark green, whereas the zirconium and hafnium complexes yield yellow to orange solutions, respectively. To elucidate the excitation processes, TD-DFT calculations (on the B3LYP/6-31G* level of theory) were performed on optimized structures of the titanium compound **7** and [**8_{Ti}**]²⁻ including a PCM solvent model with THF. Complex **7** exhibits an absorption maximum at λ_{max} = 498 nm in THF, which agrees well with the calculated values. The most intense absorption of the ones at lower energies is calculated to be at 464 nm with weaker

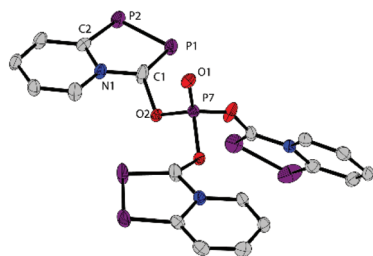


Fig. 1 Crystal structure of compound **4**. Anisotropic thermal displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and the solvent molecules are omitted for clarity reasons. Average interatomic distances (Å) summarized in Table 1.



Table 1 Averaged interatomic bond distances in Å and standard deviations (σ) for compounds **4**, **5**, **Na[6]**, **7**, **Na₂[8_{Tl}]**, **9**, **Na₂[10_{Hf}]**. For clarity, all bond distances and standard deviations are averaged over all azadiphosphole units in the same compound, because these are chemically identical and show only minor differences in the crystal structures. Italics indicate compounds without Mo(CO)₃ fragments. E...Mo indicates the distance between the bridgehead atom (E) and the Mo center

	4	5	Na[6]	7	σ	Na ₂ [8 _{Tl}]	σ	9	σ	Na ₂ [10 _{Hf}]	Σ
P1 P2	2.1092	2.100	2.1004	2.118	0.0017	2.1223	0.002	2.1029	0.0014	2.1024	0.0006
P1 C1	1.710	1.705	1.710	1.732	0.005	1.741	0.005	1.730	0.003	1.7242	0.0018
P2 C2	1.742	1.746	1.744	1.741	0.005	1.730	0.005	1.752	0.003	1.7413	0.0018
N1 C1	1.369	1.386	1.391	1.379	0.006	1.397	0.006	1.388	0.004	1.384	0.002
N1 C2	1.395	1.401	1.400	1.397	0.006	1.400	0.006	1.398	0.004	1.397	0.002
O1 C1	1.44 ^a	1.358	1.340	1.332	0.006	1.304	0.005	1.322	0.005	1.306	0.002
C≡O _{carbonyl}	—	1.144	1.269	—	—	—	—	1.154	0.004	1.148	0.002
E...Mo	—	4.498	4.485	—	—	—	—	4.817	—	5.087	—
P...Mo	—	2.467	2.475	—	0.0012	—	—	2.4813	0.0009	2.472	0.0005

^a Significant disorder around the phosphine oxide unit resulting in a low bond accuracy and potentially a large error.

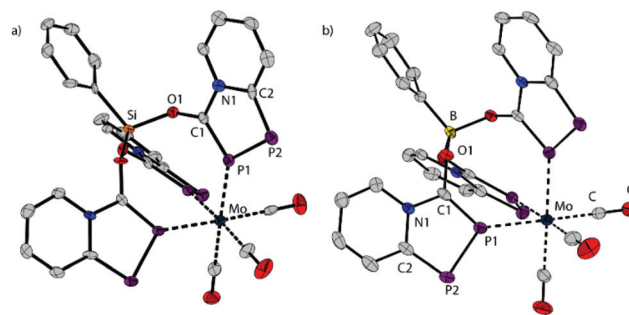
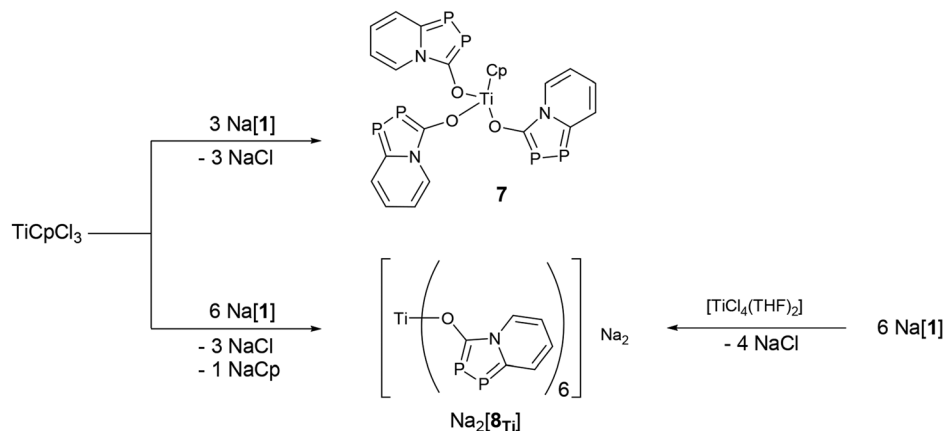


Fig. 2 Solid state structure of **5** (a) and the anion in **Na[6]** (b), anisotropic thermal displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and the sodium ion in **[6][−]** are omitted for clarity. Average interatomic distances are summarized in Table 1.

absorptions up to 504 nm. Analogously **[8_{Tl}]^{2−}** possesses a λ_{max} of 520 nm in THF with a broad shoulder up to 700 nm in the UV-VIS spectrum (Fig. 3) which matches well with the absorptions found by TD-DFT at $\lambda_{\text{max}} = 544\text{--}547$ nm with weaker ones up to 608 nm. Contours of the frontier molecular orbitals for compound **[8_{Tl}]^{2−}** are depicted in Fig. 4 and show that the occupied orbitals are mainly ligand centered. On the other hand, the unoccupied acceptor orbitals are metal centered d-orbitals. Consequently, these absorptions are best described as ligand to metal charge transfer (LCMT) bands and the fact that these occur at rather low energies support the fact that azadiphospholides **Na[1]** are electron rich molecules. A related charge transfer process was observed for the anions of the cyano-substituted azadiphospholides of **Na[1]**, which have absorption maxima ranging from $\lambda_{\text{max}} = 525$ to 596 nm.⁵² In these anions, the azadiphospholide acts as a donor and the cyano substituent as the electron accepting group causing strongly coloured species. The absorption maxima of the heavier group four metals dianions, **Na₂[8_{Zr}]** ($\lambda_{\text{max}} = 422.5$ nm) and **Na₂[8_{Hf}]** ($\lambda_{\text{max}} = 409.0$ nm) are blue shifted compared to **Na₂[8_{Tl}]** which is explained by the lack of LCMT bands (Fig. 3). The reason for this are the energetically higher lying acceptor orbitals at the heavier group four metals resulting in a poor overlap with the occupied ligand orbitals.

In analogy to the reaction with compound **5**, compound **7** was added to a THF solution of the molybdenum precursor complex **[Mo(Mes)(CO)₃]**. After 24 hours dark red crystals were obtained from the reaction mixture and the product was identified as the bimetallic complex **9** (Fig. 5). Due to the low solubility in common organic solvents, no NMR spectra could be recorded but the purity of the complex was proven by elemental analysis. Reactions of **Na₂[8_{Tl}]** with two equivalents of **[Mo(Mes)(CO)₃]** did form an insoluble microcrystalline solid. In the IR-spectrum, two distinct CO stretching vibrations at $\nu = 1925$ cm^{−1} and $\nu = 1829$ cm^{−1} are observed indicating a similar coordination environment around the molybdenum center as observed in compounds **5** or **9**, respectively. Addition of two equivalents of **[Mo(Mes)(CO)₃]** to a solution containing 18-crown-6 (18C6) and **Na₂[8_{Hf}]** in DCM yielded single crystals suitable for X-ray diffraction analysis. This species was identi-



Scheme 2 Synthesis of compounds **7** and $\text{Na}_2[\mathbf{8-Ti}]$.

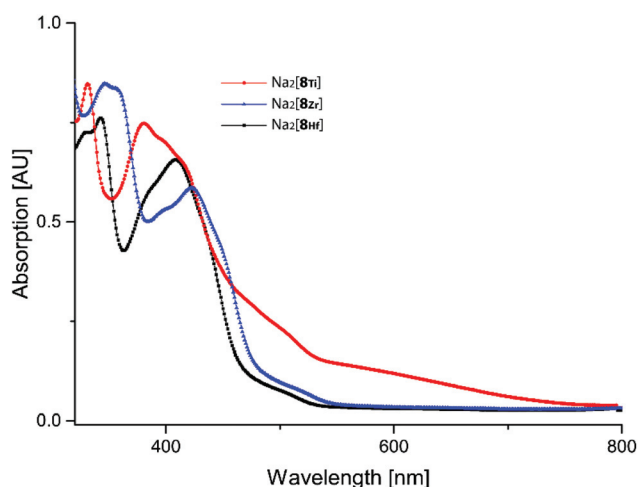


Fig. 3 UV-VIS absorption spectra of the complexes $\text{Na}_2[\mathbf{8-Ti}]$, $\text{Na}_2[\mathbf{8-Zr}]$, $\text{Na}_2[\mathbf{8-Hf}]$ in THF. The wavelength in nm is plotted against the absorption in arbitrary units.

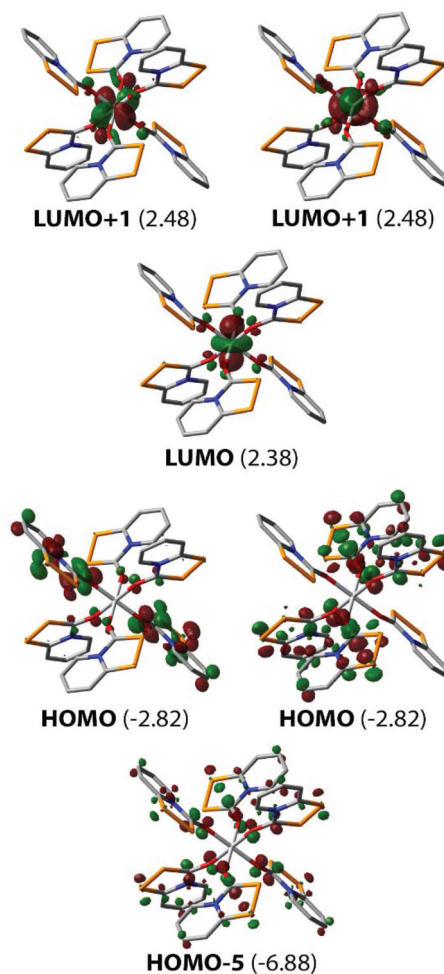


Fig. 4 Selected molecular orbitals of complex $[\mathbf{8-Ti}]^{2-}$ which are involved in the absorption processes at low energies. Energies are given in eV and orbitals are depicted at an isovalue of 0.04.

fied as the trinuclear heterobimetallic complex $\text{Na}_2[\mathbf{10-Hf}]$ which contains one Hf^{4+} in the center and two $\text{Mo}(\text{CO})_3$ units bound to the outer-sphere *via* the six phosphorus donor sites of the azadiphospholide units (Fig. 5). Once crystallized, compound $\text{Na}_2[\mathbf{10-Hf}]$ is also only sparingly soluble in common organic solvents.

The three compounds **4** (Fig. 1), **7** and $\text{Na}_2[\mathbf{8-Ti}]$ (Fig. 5) which do not contain a $\text{Mo}(\text{CO})_3$ fragment show similar characteristics in the solid state. The “hard” P(v) or Ti(iv) centers are, as expected, bound to the oxygen atoms of the azadiphospholide unit which for steric reasons adopt a paddle wheel arrangement around the oxophilic centers. Upon complexation to $\text{Mo}(\text{CO})_3$, the azadiphospholide units are rotated inwards such that in every case the P1 centers form a tridentate pocket to which the $\text{Mo}(\text{CO})_3$ can bind in a facial fashion; that is every CO group is positioned *trans* to a P1 center. This feature can be seen in complexes **5** and $\text{Na}[\mathbf{6}]$ (Fig. 2). The coordination sphere around the molybdenum centers is

slightly distorted octahedral with Mo–P bond distances (Mo-P_{av} 2.475 Å) in the expected range.⁵⁵ A comparison between the structures of **7** and **9** indicates that the structural parameters



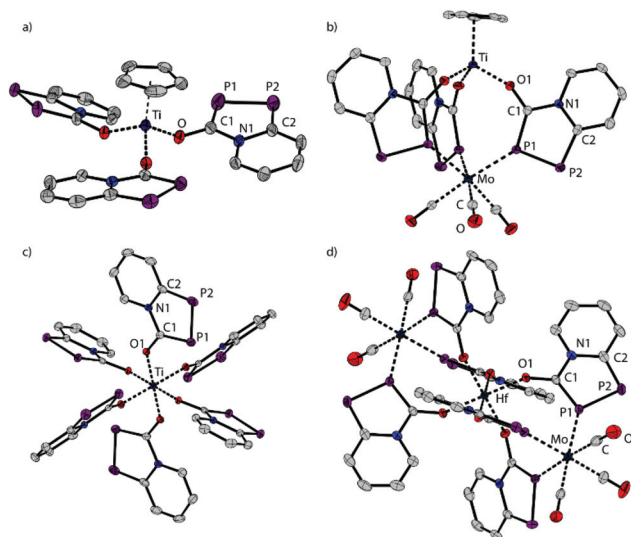


Fig. 5 Plots of the structures of (a): **7**; (b): **9**; (c): $\text{Na}_2[\mathbf{8}_{\text{Ti}}]$, and (d): $\text{Na}_2[\mathbf{10}_{\text{Hf}}]$. Anisotropic thermal displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, solvent molecules are omitted for clarity. The two sodium cations in $\text{Na}_2[\mathbf{8}_{\text{Ti}}]$ and $\text{Na}_2[\mathbf{10}_{\text{Hf}}]$ are not shown. Average interatomic distances are summarized in Table 1.

of the azadiphospholide rings does not change significantly upon coordination to $\text{Mo}(\text{CO})_3$ and specifically the P1–P2 distance varies very little (**7**: 2.118 Å; **9**: 2.1029 Å).

The only remarkable structural differences between these complexes are associated with the P1–C1, P2–C2, and C1–O1 distances. In compounds **4**, **5**, and $\text{Na}[\mathbf{6}]$, which do not contain a transition metal in the center, the P1–C1 bond adjacent to the C1–O1 group (av. 1.345 Å) is in the range of 1.705–1.710 Å. This is significantly shorter than the P2–C2 bond (1.742–1.746 Å). This feature is opposite to what is observed in the salt $\text{Na}[\mathbf{1}]$ – with the “free” azadiphospholide anion – where the P1–C1 bond [1.760(3) Å] is longer than the P2–C2 distance [1.725(4) Å] and the short C1–O1 bond [1.268(3) Å] indicates significant C–O multiple bond character.⁵² In the compounds **7**, $\text{Na}_2[\mathbf{8}_{\text{Ti}}]$, **9**, and $\text{Na}_2[\mathbf{10}_{\text{Hf}}]$ with a M(IV) center (M = Ti, Hf) the P1–C1 and P2–C2 bonds are almost equally long and the C1–O1 bond slightly shortened (1.302–1.332 Å) with respect to **4**, **5**, and $\text{Na}[\mathbf{6}]$. We attribute these effects to the more pronounced polarization of the $\text{C1}^{\delta+}\text{--O1}^{\delta-}$ bond which makes the azadiphospholide units in the Ti(IV) and Hf(IV) compounds more “anion like” such that adopt a structure which is closer to $[\mathbf{1}]^-$. The partial charge transfer from the azadiphospholide units to the Ti(IV), which is the reason for the red shifted long wave absorptions, is not reflected in the structural parameters. In all compounds containing $\text{Mo}(\text{CO})_3$ fragments, the distance between the Mo centers and the central atom is far above 4 Å and excludes any electronic through space interactions.

In order to evaluate the electronic properties of the new tris(azadiphospholide) ligands $\text{Na}[\mathbf{3}]$, **4** as well as the titanium compound **7** and hafnium derivative $\text{Na}_2[\mathbf{8}_{\text{Hf}}]$, Table 2 lists the carbonyl stretching frequencies, ν_{CO} [cm^{-1}], of the $\text{Mo}(\text{CO})_3$

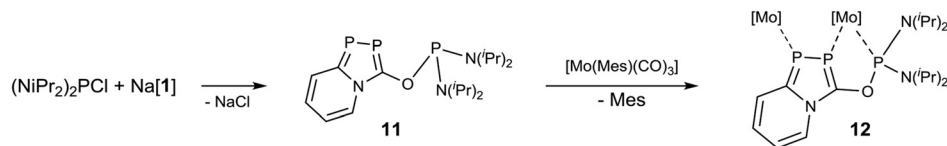
Table 2 IR frequencies in cm^{-1} for the carbonyl groups in the molybdenum metal complexes compared with literature known species

Compound	ν [cm^{-1}]	ν [cm^{-1}]
$\text{Mo}(\text{CO})_6$	1967.1	
$[\text{Mo}(\text{Mes})(\text{CO})_3]^{60}$	1973	1900
$[\text{Mo}(\text{triphos})(\text{CO})_3]^{56}$	1930	1905
$[\text{Mo}(\text{PMe}_3)_3(\text{CO})_3]^{61}$	1923	1821
$[\text{Mo}\{\text{HB}(\text{pyr})_3\}(\text{CO})_3]^{-62}$	1897	1761
5	1960	1871
$[\mathbf{6}]^-$	1939	1844
9	1943	1863
$[\mathbf{10}_{\text{Hf}}]^{2-}$	1930	1817

complexes synthesized in this work. For comparison, the ν_{CO} of a number of $[\text{Mo}(\text{L})_x(\text{CO})_3]$ complexes including $[\text{Mo}(\text{CO})_6]$ are given. As expected, all complexes with a facial arrangement of the three CO groups show two ν_{CO} stretching vibrations. Strongly σ -electron donating and poor π -accepting ligands like PMe_3 or especially the anionic tris(pyrazolyl)borate shift the ν_{CO} to lower wave numbers below 1900 cm^{-1} and 1800 cm^{-1} , respectively, for the latter. Strong σ -donation increases the electron density at the Mo center which consequently increases the electron back donation in the π^* orbital of the CO groups. On the contrary, a strong π -acceptor ligand like 1,3,5-tri(methyl)benzene (*i.e.* mesitylene = Mes) diminishes the M \rightarrow CO back donation and hence the ν_{CO} increases. As Table 2 shows, the neutral tris(azadiphospholes) **2** and **7** have a smaller σ -donor: π -acceptor ratio when compared to phosphines like PMe_3 or triphos ($\text{Me-C}\{\text{CH}_2\text{PPh}_2\}_3$).⁵⁶ That is they behave as comparatively weaker σ -donors but stronger π -acceptors, a property which is well established for phosphinines, PC_5R_5 , the phosphorus analogues of pyridines.^{57–59} As expected the mono-anionic ligand $[\mathbf{3}]^-$ or dianionic ligand $[\mathbf{8}_{\text{Hf}}]^{2-}$ give the lowest ν_{CO} in the series of complexes described in this paper and are coming very close to $[\text{Mo}(\text{PMe}_3)_3(\text{CO})_3]$.⁶⁰ It is, however, remarkable that replacement of the PhSi group in **5** by the CpTi unit in **9** has a significant influence on ν_{CO} and shifts the frequency 16 cm^{-1} to lower wavenumbers. This shows that the electron donation in the tridentate azadiphospholide ligands can be sensitively tuned by the remotely placed connecting node in the center of the ligand.

Finally, we studied the suitability of the azadiphospholide salt $\text{Na}[\mathbf{1}]$ as building block for bidentate ligands. Earlier work showed that related alkoxy functionalized phosphinines⁶³ react with chlorophosphanes, R_2PCl , to form such bidentate ligands which could be successfully used in the synthesis of photo-luminescent complexes.^{64,65} However, reactions of $\text{Na}[\mathbf{1}]$ with chloro-phosphanes such as PCl_3 , PhPCl_2 and Ph_2PCl only formed brown insoluble precipitates. On the other hand, the reaction of $\text{Na}[\mathbf{1}]$ with bis(diisopropylamino)chlorophosphane, $(\text{iPr}_2\text{N})_2\text{PCl}$, proceeded cleanly to form compound **11** (Scheme 3). This substitution is accompanied by a colour change of the reaction mixture from orange to dark yellow and the precipitation of an off-white solid. $^{31}\text{P}\{\text{H}\}$ NMR spectroscopic analysis revealed the formation of one major product with three inequivalent phosphorus nuclei, forming a AMX





Scheme 3 Synthesis of **11** and the reaction with $[\text{Mo}(\text{Mes})(\text{CO})_3]$ to form complex **12**.

spin system: ^{31}P δ (ppm) = 134.4 (dd, $^1J_{\text{P3,P1}} = 121.7$ Hz, $^2J_{\text{P2,P3}} = 19.1$ Hz), 121.7 (dd, $^1J_{\text{P2,P1}} = 425.6$ Hz, $^2J_{\text{P2,P3}} = 19.1$ Hz), 109.0 (dd, $^1J_{\text{P1,P2}} = 425.6$ Hz, $^1J_{\text{P1,P3}} = 121.7$ Hz). The coupling constant between the two phosphorus atoms in the azadiphosphole ring ($J_{\text{PP}} = 426$ Hz) is comparable to the one in $\text{Na}[\mathbf{1}]$ ($J_{\text{P,P}} = 424.7$ Hz) indicating that the substitution took place at the oxygen atom. The coupling constant $J_{\text{P1,P3}} = 121.7$ Hz is relatively large for a 3J -through bond coupling, and may be caused by the alignment of the two lone pairs at P1 and P3 causing a strong through space coupling.⁶⁶ This assignment was supported by a structure determination through X-ray diffraction methods using a single crystal of **11** (Fig. 6).

In **11**, the two phosphorus atoms P1 and P3 form a bidentate binding site ($\text{P1}\cdots\text{P3}$ 3.299 Å) which is ideally suited to bind a metal center in a κ^2 -fashion. Furthermore, the phosphorus center P2 may bind to an additional metal center which opens the possibility of preparing multinuclear complexes. This idea was tested in the reaction of equimolar amounts of **11** and $[\text{Mo}(\text{Mes})(\text{CO})_3]$ which upon loss of mesitylene opens up three coordination sites. Dark orange crystals were isolated directly from the reaction mixture after about 12 hours at room temperature and the product was analysed by X-ray diffraction analysis. Indeed, a tetranuclear molybdenum complex of the composition $[\text{Mo}_4(\mathbf{11})_4(\text{CO})_{12}]$ (**12**) was formed (Fig. 7). Elemental analysis proved the purity of the compound, which is insoluble in all common deuterated solvents. The IR spectrum exhibits two major carbonyl bands at

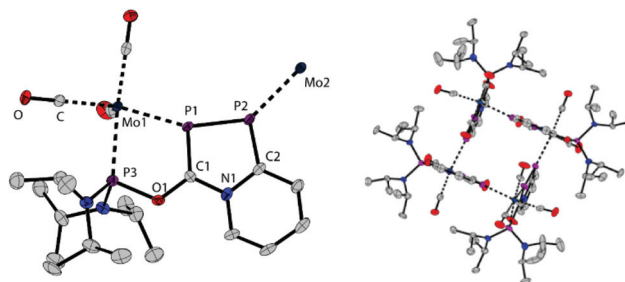


Fig. 7 Crystal structure of the organometallic macrocycle **12**. Anisotropic thermal displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and three DCM molecules are omitted for clarity reasons. Average interatomic distances (Å): Mo1 P1 2.4816(17), Mo1 P3 2.5357(17), P2 Mo2 2.5042(15), P2 P1 2.100(2), P2 C2 1.740(7), P1 C1 1.722(7), C1 O1 1.347(8), C1 N1 1.372(9), C2 N1 1.397(8).

ν_{CO} [cm^{-1}] = 1950, 1849 in the same range as observed in the complexes mentioned above.

Complex $[\text{Mo}_4(\mathbf{11})_4(\text{CO})_{12}]$ crystallizes in the orthorhombic space group $Fdd2$, with two azadiphosphole and molybdenum centers per asymmetric unit. The individual bond lengths and angles within the azadiphosphole units are comparable to the ones observed in the complexes discussed above. Upon coordination to Mo, the distance between the two phosphorus atoms P1 and P3 is slightly diminished to 3.132 Å. In the solid state, the $[\text{Mo}_4(\mathbf{11})_4(\text{CO})_{12}]$ macrocycles stack above each other such that channels with a diameter of about 5.6 Å are formed (diagonal Mo–Mo distance 7.276 Å).

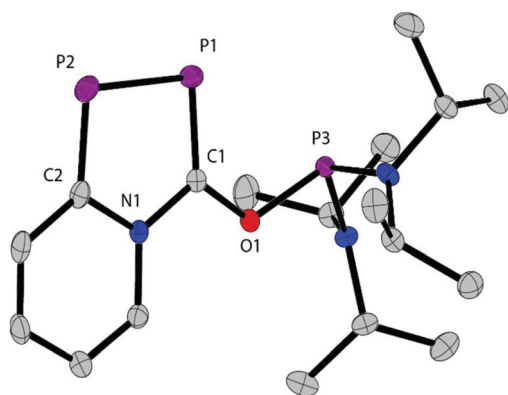


Fig. 6 Crystal structure of compound **11**. Anisotropic thermal displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and the solvent molecules are omitted for clarity. Average interatomic distances (Å): P1 P2 2.1284(5), P2 C2 1.7373(15), P1 C1 1.7308(14), O1 C1 1.3496(16), N1 C1 1.3773(17), N1 C2 1.4074(17), P3 P1 3.299.

Conclusions

The salt $\text{Na}[\mathbf{1}]$ containing the azadiphospholide anion is a versatile reagent for the synthesis of a range of new multidentate ligands. These are accessed *via* nucleophilic substitutions reactions with various main group and transition metal halides and in all cases studied so far, the “hard” oxygen center in $[\mathbf{1}]^-$ binds to the electrophilic center E in R_nECl_m (E = B, Si, P, Ti, Zr, Hf). The azadiphospholides form strongly coloured complexes with d^0 -titanium centers which is explained by LMCT excitations which indicate that the 1,3,4-azadiphospholes are rather electron rich heterocycles. The two adjacent phosphorus centers in the azadiphospholide ring possess each a lone pair of electrons which can be further engaged in the coordination to a transition metal center. This property was exploited in reactions $[\text{Mo}(\text{Mes})(\text{CO})_3]$ and allowed to synthesize bi- and trinuclear heterobimetallic complexes. The reaction between



(iPr₂N)₂PCl and Na[1] leads cleanly to a molecule with a P–O–C–P scaffold which is suitable as ligand for the synthesis of polynuclear macromolecular metalloheterocycles. In the crystalline state, these compounds form channels which eventually may be used for the encapsulation or adsorption of guest molecules. The preliminary results reported in this paper let hope that an especially rich coordination chemistry can be developed with these kind of polydentate phosphorus compounds which are moreover easily synthesized on a multi-gram scale.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the ETH Zürich (project 0-20406-18), and the Swiss National Science Foundation (SNF) (project 2-77199-18). Further support came from the NKFIH Grant (PD 116329), a Janos Bolyai Research Fellowship, and a UNKP Grant (UNKP-19-4-BME-422).

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