Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Dalton Trans.*, 2023, **52**, 3308

The coordination chemistry of 2,4,6-oxy functionalised 1,3,5-triphosphinines†

Anne Sofie Abels,[a] Frederik Eiler,[a] Grégoire Le Corre,[a] Pascal Jurt,[a] Michael Wörle,[a] René Verel,[a] Zoltan Benkő[b] and Hansjörg Grützmacher*[a]

Received 7th January 2023,
Accepted 2nd February 2023

DOI: 10.1039/d3dt00057e

rsc.li/dalton

A number of stable group 6 metal complexes bearing 2,4,6-oxy functionalised 1,3,5-triphosphinines, phosphorus containing heterocyclic ligands with a central C_3P_3 core, were synthesised such that a complete series of $[M\{P_3C_3(OX)_3\}(CO)_3]$ compounds is obtained [M = Cr(0), Mo(0), W(0); X = H, Si*t*BuPh$_2$, B(ipc)$_2$]. In all complexes, the triphosphinine coordinates in a η^6-binding mode *via* the delocalized 6π-system of the ring. The ligand properties can be tuned by changing the substituent on the oxygen centre. The π-electron accepting properties of the ligand increases in the following order: $P_3C_3(OH)_3 < P_3C_3(OSi^tBuPh_2)_3 < P_3C_3(OB(ipc)_2)_3$. This trend is reflected in the structures determined by X-ray crystallography, and the ν(CO) stretching frequencies determined by IR spectroscopy. The collected data raise questions with respect to the frequently made assumption that phosphinines act as stronger π-acceptors with respect to arenes and thereby deplete electron density at the metal centres. With $P_3C_3(OH)_3$ as an η^6-coordinated ligand further molecules can be coordinated in the second coordination sphere *via* hydrogen bonds, which may be of interest for the construction of coordination polymers.

Introduction

Since Märkl and Ashe successfully prepared the first monophosphinines,[1,2] these phosphorus heterocycles and their coordination chemistry have been studied extensively.[3–10] Nowadays, these compounds serve as ligands in transition metal complexes that are active homogeneous catalysts, for example in hydroformylation, hydrogenation and oligomerisation reactions.[6,9,11] In contrast to monophosphinines, the chemistry of phosphinines containing three phosphorus centres, namely triphosphinines, is much less developed.[12,13] Generally, 1,3,5-triphosphinines are obtained by transition metal mediated trimerisation of kinetically stabilised phosphaalkynes.[14–17] The range of reported 1,3,5-triphosphinines is rather limited and most carry tertiary butyl, *t*Bu, substituents or related bulky hydrocarbon groups attached to the C atom of the ring. In combination, these studies led to the assumption that phosphorus-containing heterocycles have strong π-accepting properties with respect to arenes, making them excellent ligands for binding low-valent electron rich metal centres in a η^6-coordination mode.[4,18–26]

In 2017, Grützmacher and co-workers reported on a new synthetic route to access functionalized triphosphinines by the reaction of sodium phosphaethynolate, [Na(OCP)], with commercially available (−)-B-chlorodi(isopinocampheyl)borane, $(ipc)_2B\text{-}Cl$, forming the boryloxy-functionalised phosphaalkyne $(ipc)_2B\text{–}O\text{–}C{\equiv}P$ as slightly thermodynamically preferred product that trimerises in absence of a catalyst to form a 1,3,5-triphosphinine with a central six-membered P_3C_3 ring (Scheme 1, P_3C_3–B) on a multi-gram scale.[27] This compound is the first triphosphinine that can readily be derivatised and thereby the electronic properties can be tuned by changing the substituent at the oxygen atom. Treatment of triphosphinine P_3C_3–B with an excess of alcohol yields the deprotected tris(hydroxyl) triphosphinine $P_3C_3(OH)_3$ (P_3C_3–H), the phosphorus analogue of cyanuric acid. But unlike cyanuric acid, $P_3C_3(OH)_3$ is rather labile, therefore could not be isolated and was only stable in solution.

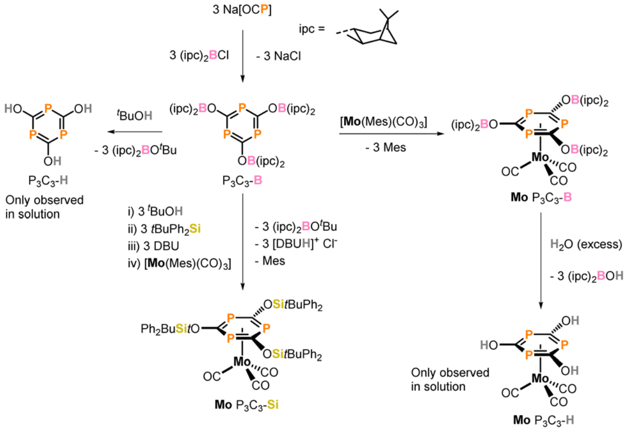
Cyanuric acid is an industrially useful chemical and finds use in the production of herbicides,[28,29] dyes[30] and flame retardants.[31–33] Furthermore, its trimeric structure and the ability to form hydrogen bonds makes cyanuric acid an attractive precursor for cross linkers in polymers[34,35] and an building block in supramolecular networks.[36–41] The formation of a stable $P_3C_3(OH)_3$ compound may therefore be of interest. Furthermore, these type of P_3C_3 rings have shown that they are

---

[a] *Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog Weg 1, Hönggerberg, 8093 Zürich, Switzerland. E-mail: hgruetzmacher@ethz.ch, abelsa@inorg.chem.ethz.ch*

[b] *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, 1111 Budapest, Műegyetem rakpart 3, Hungary. E-mail: benko.zoltan@vbk.bme.hu*

† Electronic supplementary information (ESI) available. CCDC 2234729–2234735. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3dt00057e



Scheme 1 Previous synthesis of borylated compound P_3C_3–B from the reaction of Na[OCP] with $(ipc)_2BCl$, the formation of the phosphorus analogue of cyanuric acid (P_3C_3–H) and the synthesis of molybdenum 2,4,6-oxy functionalised 1,3,5-triphosphinine complexes.

excellent ligands and coordinate in a η^6-binding mode through the π-system of the ring to a molybdenum centre (Scheme 1). However, the molybdenum complex with $P_3C_3(OH)_3$ as ligand could not be isolated, therefore key structural information and spectroscopic data is missing.

In this study we investigated the coordination chemistry of these 2,4,6-oxy functionalised 1,3,5-triphosphinines with group 6 metals in depth and we were able to isolate and analyse the phosphorus analogue of cyanuric acid as ligand in coordination compounds. This series of group 6 metal 2,4,6-tri-oxy-1,3,5-triphosphinine complexes bearing different substituents on the oxygen centre allowed us to study the physical properties of this class of compounds in detail by single-crystal X-ray structure determinations (XRD's), IR-, and NMR-spectroscopic analyses.

Results and discussion

The Mo(0) complexes $[Mo\{P_3C_3[OB(ipc)_2]_3\}(CO)_3]$ **Mo**–P_3C_3–B and $[Mo\{P_3C_3[O(SitBuPh_2)]_3\}(CO)_3]$ **Mo**–P_3C_3–Si were previously synthesised from $[Mo(Mes)(CO)_3]$ and isolated in crystalline form. The complex $[Mo\{P_3C_3(OH)_3\}(CO)_3]$ **Mo**–P_3C_3–H could only be spectroscopically observed in solution.[27] In straightforward ligand exchange reactions, the analogous tricarbonyl chromium and tungsten complexes of P_3C_3–B were synthesised from $[M(NCMe)_3(CO)_3]$ (M = Cr and W) (Fig. 1). Single crystals of **Cr**–P_3C_3–B and **W**–P_3C_3–B were grown by slow evaporation of *n*-hexane solutions and analysed by single crystal diffraction. The silyloxy-substituted compound $P_3C_3[O(SitBuPh_2)]_3$, P_3C_3–Si, was prepared in solution[27] and addition of the group 6 metal precursor to the reaction mixture yielded compounds **Cr**–P_3C_3–Si and **W**–P_3C_3–Si (Fig. 1). The reaction time varied from 1 hour for **Cr**–P_3C_3–Si to 5 days for **W**–P_3C_3–Si, the latter was heated to 40 °C to accelerate the reaction. The use of multiple reagents explains the rather low isolated yields (10–11%) in these one-pot syntheses of **M**–P_3C_3–Si (M = Cr, W) and it proved to be difficult to separate the desired complexes from a number of side products. Slow evaporation of *n*-hexane solutions of **Cr**–P_3C_3–Si and **W**–P_3C_3–Si gave single crystals suitable for X-ray diffraction studies.

To obtain the tris(hydroxyl)triphosphinine complexes, the group 6 metal tricarbonyl complexes of P_3C_3–B were dissolved in *n*-hexane and an excess of methanol was added to give a biphasic system. After shaking the reaction flask, the subsequently formed $P_3C_3(OH)_3$ complexes could be isolated as orange (M = Cr) or yellow (M = Mo, W) solids from the methanol phase. The *n*-hexane phase contains the methoxyborane-$(ipc)_2B(OMe)$, which could easily be separated. Coordination of the $P_3C_3(OX)_3$ rings [X = $B(ipc)_2$: $\delta(^{31}P)$ = 182.7 ppm, X = $SitBuPh_2$: $\delta(^{31}P)$ = 177.5 ppm; X = H: $\delta(^{31}P)$ = 133.7 ppm][27] leads to a significant coordination shift $\Delta\delta = \delta(P_3C_3[OX]_3) - \delta([M\{P_3C_3[OX]_3(CO)_3\}])$ of the ^{31}P NMR resonances to lower frequencies in the range of 161 to 198 ppm, which is especially pronounced in case of the parent tris(hydroxyl)triphosphinine $P_3C_3(OH)_3$ (see Table 1, first entry). The $\Delta\delta$ values increase slightly in the order Cr < Mo < W within each series of ligand and $SitBuPh_2$ < $B(ipc)_2$ < H with respect of the group X bound to the oxygen centres of the $P_3C_3(OX)_3$ ring. Comparable strong coordination shifts ($\Delta\delta$ > 160 ppm to lower frequencies) were also observed when 2,4,6-triphenyl-phosphinine, $PC_5H_2(Ph)_3$, or 2,4,6-*tert*-butyltriphosphinine, $P_3C_3(tBu)_3$, are η^6-coordinated to a $M(CO)_3$ fragment.[42]

Single crystals of **Cr**–P_3C_3–B, **W**–P_3C_3–B, **Cr**–P_3C_3–Si, and **W**–P_3C_3–Si were grown by slow evaporation of *n*-hexane solutions and analysed by single crystal diffraction (XRD) (Fig. 1). Single crystals of the coordinated $P_3C_3(OH)_3$ group 6 complexes were obtained by cooling a concentrated *n*-hexane solution of **Cr**–P_3C_3–H, **Mo**–P_3C_3–H, or **W**–P_3C_3–H in the presence of *t*BuOH. The structures of the P_3C_3–H metal complexes determined by XRD show interactions of the OH groups of the ring with the OH groups of *t*BuOH *via* hydrogen bonding. Related O–H⋯O hydrogen bonding was previously postulated for **Mo**–P_3C_3–H in THF solution.[27] Table 1 summarises selected spectroscopic data and bond lengths and angles of the solid state structures of the nine different chromium, molybdenum and tungsten triphosphinine complexes, bearing different functionalities at the oxygen centres in 1,3,5 position of the P_3C_3 ring.

In these piano stool complexes, the P_3C_3 ring is planar and binds in an η^6-coordination mode to the metal centre (Fig. 1). The P–C bond lengths (1.76–1.78 Å) of the coordinated P_3C_3 rings are slightly elongated compared to the uncoordinated triphosphinine ring (1.736 Å).[27] Compared to $P_3C_3[OB(ipc)_2]_3$ (C–P–C_{av}: 104°; P–C–P_{av} 136°), the C–P–C angles become slightly more acute (P–C–P_{av} 101.9°) while the P–C–P angles widen up slightly (P–C–P_{av} 138.0°) upon coordination to a $M(CO)_3$ fragment. Within the complexes, these values vary rather little [C–P–C 100.6(3)–102.9(3)°; P–C–P 137.0(3)–140.2(4)], but independently of M, the boryloxy substituted complexes show the smallest C–P–C (largest P–C–P) angle, while the hydroxyl substituted show the largest C–P–C (smallest P–C–P) angle.

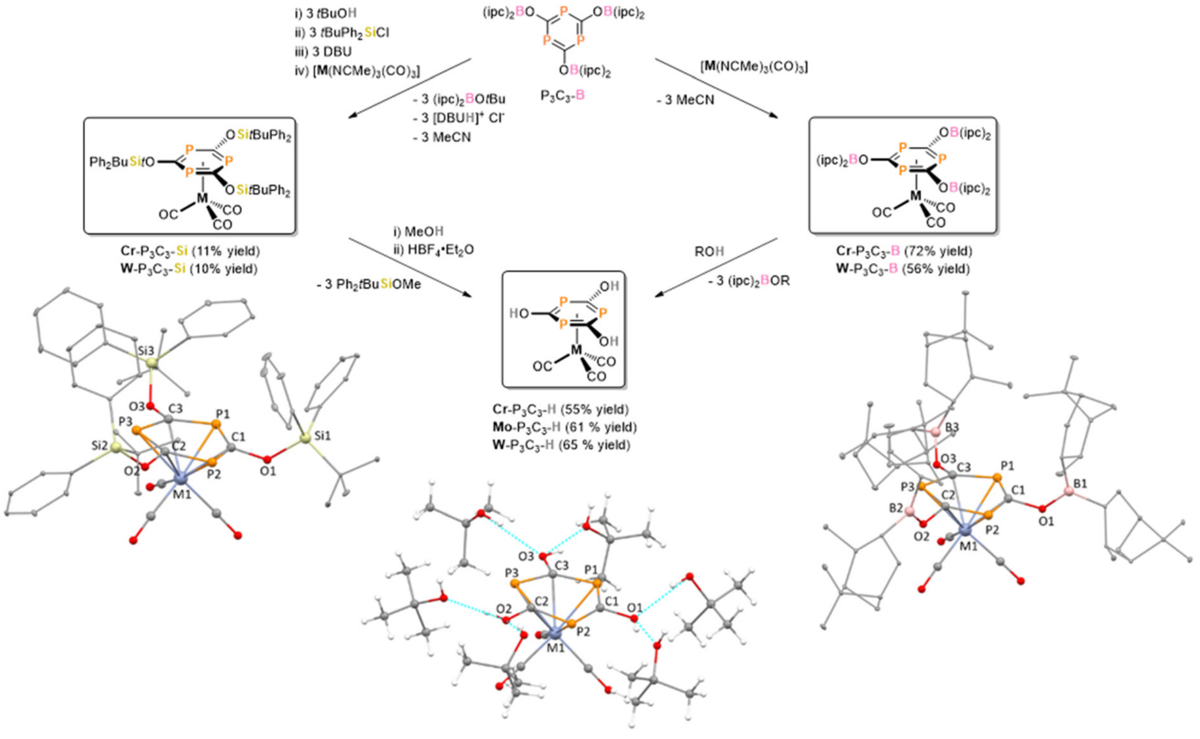


Fig. 1 Synthesis of complexes **M**–P_3C_3–B (M = Cr, W), **M**–P_3C_3–Si (M = Cr, W) and **M**–P_3C_3–H (M = Cr, Mo, W). The crystal structures of **W**–P_3C_3–B, **W**–P_3C_3–Si and **W**–P_3C_3–H are given below the respective chemical structures. Hydrogen atoms and solvent molecules are omitted for clarity. Average interatomic distances are summarised in Table 1. The crystal structures of **Cr**–P_3C_3–B, **Cr**–P_3C_3–Si, **Cr**–P_3C_3–H and **Mo**–P_3C_3–H are included in the ESI.†

Table 1 Selected average bond distances [Å] and angles [°] for **M**–P_3C_3–B, **M**–P_3C_3–Si and **M**–P_3C_3–H (**M** = Cr, Mo, W) obtained from XRD data with single crystals. Coordination shifts Δδ in the ^{31}P NMR spectra are defined by δ($P_3C_3[OX]_3$) – δ([M{$P_3C_3[OX]_3$}(CO)$_3$] and are given in ppm

	Cr–P_3C_3–B	**Cr**–P_3C_3–Si	**Cr**–P_3C_3–H	**Mo**–P_3C_3–B	**Mo**–P_3C_3–Si	**Mo**–P_3C_3–H	**W**–P_3C_3–B	**W**–P_3C_3–Si	**W**–P_3C_3–H
Δδ	166	161	191	176	167	193	185	177	198
M–ct	1.6407(8)	1.6499(5)	1.6817(8)	1.753(1)	1.778(6)	1.8157(11)	1.7462(11)	1.7743(19)	1.802(5)
P–C	1.7578(13)	1.7577(7)	1.7597(9)	1.765(4)	1.769(2)	1.7717(18)	1.7687(18)	1.767(3)	1.773(8)
M–CO	1.8947(18)	1.8714(11)	1.8667(12)	2.022(4)	2.005(2)	1.989(3)	2.024(3)	2.009(5)	2.001(12)
C–O	1.1370(18)	1.1453(12)	1.1487(16)	1.139(5)	1.143(2)	1.156(4)	1.129(3)	1.137(5)	1.130(13)
C–P–C	101.46(7)	102.25(5)	102.69(8)	101.19(2)	101.93(8)	102.7(3)	101.13(11)	101.37(18)	102.2(6)
P–C–P	138.53(10)	137.7(6)	137.28(8)	138.7(2)	137.88(2)	137.3(18)	138.8(12)	138.4(3)	137.7(6)

For every metal, the M–ct distance is the longest with $P_3C_3(OH)_3$ as ligand (**Cr**–P_3C_3–H = 1.682 Å, **Mo**–P_3C_3–H = 1.816 Å, **W**–P_3C_3–H = 1.802 Å), followed by the siloxylated complexes (**Cr**–P_3C_3–Si = 1.650 Å, **Mo**–P_3C_3–Si = 1.778 Å, **W**–P_3C_3–Si = 1.774 Å) and the boryloxylated P_3C_3 metal complexes (**Cr**–P_3C_3–B = 1.619 Å, **Mo**–P_3C_3–B = 1.753 Å, **W**–P_3C_3–B = 1.746 Å). Although the differences are small (within 3σ), the Mo-complexes show always slightly longer Mo–ct distances compared to the corresponding W–ct distances despite the increasing covalent radii [r_{cov}(Mo) = 1.54 Å; r_{cov}(W) = 1.62 Å]. Complexes with chromium show expectedly significantly shorter Cr–ct distances [r_{cov}(Cr) = 1.39 Å].[43] (The atomic van der Waals radii of Cr, Mo, and W [r_{vdW}(Cr) = 1.89 Å; r_{vdW}(Mo) = 2.09 Å, r_{vdW}(W) = 2.10 Å] reflect better the observed trends in the **M**–P_3C_3–X complexes with M in the oxidation state 0, but also suggest that the M–ct bond lengths should steadily increase in the order W > Mo > Cr).[44] Indeed this trend is observed for [M[$P_3C_3(^t\mathrm{Bu})_3$](CO)$_3$] (M = Cr, Mo, W), whose structures were calculated by DFT methods. Here the increase in M–ct distances corresponds to the van der Waals radii of the metals.[23,44]

In [M(L)$_x$(CO)$_y$] complexes, a ligand L with π-accepting properties competes with carbonyl co-ligands for M → π*(CO) electron back donation. Consequently the electronic properties of a ligand L in [M(L)$_x$(CO)$_y$] complexes are reflected in the M–C and C–O distances as well as in the CO stretching frequencies ν(CO) of the carbonyl co-ligands.[45] A ligand L of high π-electron accepting property will lead to long M–C bonds to the CO ligand, short C–O bonds and ν(CO) at high wave numbers. In case of complexes with Cr(CO)$_3$ or Mo(CO)$_3$ fragments, the ones with P_3C_3–B rings show the longest M–CO distances while, on the contrary, the M–CO distances are the shortest in complexes with the P_3C_3–H ligand. As expected, the opposite trends are observed with respect to the C–O bond lengths.

Another frequently used instrument in order to evaluate the electronic properties of L in$[M(L)_x(CO)_y]$ complexes are the ν(CO) of the carbonyl co-ligands. It is generally accepted that the relative ratio of ligand-to-metal electron donation d (M ← L) to metal-to-ligand back donation b (M → L), denoted here as d/b, decreases in the order CO ≈ alkynes < olefins < carbenes < phosphines < amines (simplified meaning that the π-electron accepting property of the respective ligand decreases in this order).[46–48] Consequently a decrease of ν(CO) is expected along this ligand line. In Tables 2–4 a compilation of IR data is given for selected, comparable chromium, molybdenum, and tungsten tricarbonyl complexes with simple monodentate σ-donor/π-acceptor ligands, arene ligands, and phosphinine ligands. In all complexes the $M(CO)_3$ fragment (M = Cr, Mo, W) adopts a facial coordination mode and reference is made only to the symmetrical ν(CO) stretching frequency of A_1 symmetry at higher wave numbers (in case of deviation from local C_{3v} symmetry of the $M(CO)_3$ fragment, reference is made to ν(CO) at the highest wave number). As reference compounds the hexacarbonyl complexes $[M(CO)_6]$ are chosen, for which ν(CO) is quite similar independently on the metal (M = Cr: 1985 cm^{-1}; Mo = 1985 cm^{-1}; M = W: 1981 cm^{-1}). As expected, the replacement of three CO groups in facial position by ligands with an increasingly stronger σ or π-donating but poorer π-accepting property – that is an increasingly higher d/b ratio – as in the series $P(OMe)_3$ < PMe_2Ph < NCMe – will increasingly lower the ν(CO) stretching frequency as a result of increasing electron density on the metal centre (see entries 2–4 in each table). This effect is remarkably similar for each metal and the variation $\Delta\nu$(CO) from $[M(CO)_6]$ to $[M(NCMe)_3(CO)_3]$ is about 70 cm^{-1} to lower wave numbers. In the benzene complexes $[M(C_6H_6)(CO)_3]$ a slight blue-shift of ν(CO) to higher wave numbers is observed for M = Mo (1987 cm^{-1}) or W (1990 cm^{-1}) (entries 5 in Tables 3 and 4), while in $[Cr(C_6H_6)(CO)_3]$ (1971 cm^{-1}) a red-shift by 14 cm^{-1} to lower wave numbers occurs (entry 5 in Table 2). σ-Donating substituents like methyl groups in 1,3,5-position of the arene ring increase the d/b ratio and lower the ν(CO) by 6 to 15 cm^{-1} (entries 6 in Tables 2–4). The IR data for a range of Cr(0) complexes with arene ligands functionalised in 1,3,5-position are available (see entries 7–10 in Table 2). σ-Electron and π-electron donating substituents like *t*Bu or hydroxyl groups shift ν(CO) by about 25 cm^{-1} to lower wave numbers. Electron accepting groups like carboxy groups, CO_2Me, or triflate groups, OSO_2CF_3, in 1,3,5-position shift ν(CO) to higher wave numbers by 32 cm^{-1} or 48 cm^{-1}, respectively. Hence, the range by which A_1 ν(CO) can be changed in these type of complexes is about 70 cm^{-1}.

Table 2 IR stretching frequencies in cm^{-1} for the CO groups in various chromium tricarbonyl complexes with σ-donor/π-acceptor, arene, and phosphinine ligands. The streching frequencies ν(CO) of **Cr–P_3C_3–B**, **Cr–P_3C_3–Si**, and **Cr–P_3C_3–H** were recorded by ATR-IR spectroscopy from crystalline products. Substituents in the arene ring are in 1,3,5-position, in phosphines in 2,4,6-position

		ν_{CO} (cm^{-1})
1	$[Cr(CO)_6]$[49]	1985
2	$[Cr\{P(OMe)_3\}(CO)_3]$[50]	1962, 1888, 1874
3	$[Cr\{PMe_2Ph\}(CO)_3]$[51]	1920, 1820
4	$[Cr(NCMe)_3(CO)_3]$[52]	1910, 1782
5	$[Cr(C_6H_6)(CO)_3]$[53]	1971, 1860
6	$[Cr(Mes)(CO)_3]$[54]	1965, 1852
7	$[Cr\{C_6H_3(t\mathrm{Bu})_3\}(CO)_3]$[55]	1947, 1871
8	$[Cr\{C_6H_3(OH)_3\}(CO)_3]$[56]	1945, 1850
9	$[Cr\{C_6H_3(CO_2Me)_3\}(CO)_3]$[57]	2003, 1947
10	$[Cr\{C_6H_3(OSO_2CF_3)_3\}(CO)_3]$[56]	2019, 1947
11	$[Cr\{PC_5H_2(Ph)_3\}(CO)_3]$[58]	1976, 1915, 1907
13	$[Cr\{P_3C_3(t\mathrm{Bu})_3\}(CO)_3]$[23]	1979, 1926
14	$[Cr\{P_3C_3(OH)_3\}(CO)_3]$ **Cr–P_3C_3–H**	1980, 1921
15	$[Cr\{P_3C_3[O(Sit\mathrm{BuPh}_2)]_3\}(CO)_3]$ **Cr–P_3C_3–Si**	1983, 1927
16	$[Cr\{P_3C_3[OB(ipc)_2]_3\}(CO)_3]$ **Cr–P_3C_3–B**	2012, 1967

Table 3 IR stretching frequencies in cm^{-1} for the CO groups in various molybdenum tricarbonyl complexes with σ-donor/π-acceptor, arene, and phosphinine ligands. The streching frequencies ν(CO) of **Mo–P_3C_3–B**, **Mo–P_3C_3–Si**, and **Mo–P_3C_3–H** were recorded by ATR-IR spectroscopy from crystalline products. Substituents in the arene ring are in 1,3,5-position, in phosphines in 2,4,6-position

		ν_{CO} (cm^{-1})
1	$[Mo(CO)_6]$[49]	1985
2	$[Mo\{P(OMe)_3\}(CO)_3]$[50]	1974, 1898, 1884
3	$[Mo\{PMe_2Ph\}(CO)_3]$[51]	1939, 1832, 1824
4	$[Mo(NCMe)_3(CO)_3]$[52]	1915, 1783
5	$[Mo(C_6H_6)(CO)_3]$[49]	1987, 1916
6	$[Mo(Mes)(CO)_3]$[49]	1973, 1901
7	$[Mo\{PC_5H_2(Ph)_3\}(CO)_3]$[42]	1996, 1942, 1933
8	$[Mo\{P_3C_3(OH)_3\}(CO)_3]$ **Mo–P_3C_3–H**	1988, 1925
9	$[Mo\{P_3C_3[O(Sit\mathrm{BuPh}_2)]_3\}(CO)_3]$ **Mo–P_3C_3–Si**	1993, 1941
10	$[Mo\{P_3C_3[OB(ipc)_2]_3\}(CO)_3]$ **Mo–P_3C_3–B**	2022, 1972

Table 4 IR stretching frequencies in cm^{-1} for the CO groups in various tungsten tricarbonyl complexes with σ-donor/π-acceptor, arene, and phosphinine ligands. The streching frequencies ν(CO) of **W–P_3C_3–B**, **W–P_3C_3–Si**, and **W–P_3C_3–H** were recorded by ATR-IR spectroscopy from crystalline products. Substituents in the arene ring are in 1,3,5-position, in phosphines in 2,4,6-position

		ν_{CO} (cm^{-1})
1	$[W(CO)_6]$[49]	1981
2	$[W\{P(OMe)_3\}(CO)_3]$[50]	1970, 1893, 1878
3	$[W(PMe_2Ph)_3(CO)_3]$[51]	1932, 1926
4	$[W(NCMe)_3(CO)_3]$[52]	1915, 1793
5	$[W(C_6H_6)(CO)_3]$[59]	1990, 1916
6	$[W(Mes)(CO)_3]$[59]	1975, 1902
7	$[W\{P_3C_3(OH)_3\}(CO)_3]$ **W–P_3C_3–H**	1987, 1921
8	$[W\{P_3C_3[O(Sit\mathrm{BuPh}_2)]_3\}(CO)_3]$ **W–P_3C_3–Si**	1989, 1921
9	$[W\{P_3C_3[OB(ipc)_2]_3\}(CO)_3]$ **W–P_3C_3–B**	2019, 1963

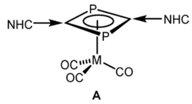
What effect will be evoked when one CH unit is replaced by a phosphorus centre? In the monophosphinine complexes $[Cr\{PC_5H_2(2,4,6\text{-}Ph)_3\}(CO)_3]$ (1976 cm^{-1}, entry 11 in Table 2) and $[Mo\{PC_5H_2(2,4,6\text{-}Ph)_3\}(CO)_3]$ (1996 cm^{-1}, entry 7 in Table 3) ν(CO) shifts slightly (5, 9 cm^{-1}) with respect to the benzene complexes, or modestly (11, 23 cm^{-1}) with respect to the mesitylene complexes to higher wave numbers indicating indeed some depletion of the electron density at the metal centre with respect to an arene ligand. The further substitution of two additional CH units by phosphorus leading to triphosphinine ligands raises the A_1 ν(CO) to even higher frequencies. A significant blue-shift of 32 cm^{-1} is observed comparing [Cr{C_6H_3(*t*Bu)$_3$}(CO)$_3$] (1947 cm^{-1}; entry 7 in Table 2) and [Cr{P_3C_3(*t*Bu)$_3$}(CO)$_3$] (1979 cm^{-1}; entry 13 in Table 2). As in arene complexes, σ-donating *t*Bu substituents in 1,3,5-position of a triphosphinine ligand have a very similar effect than π-donating hydroxyl groups as a comparison between [Cr{P_3C_3(OH)$_3$}(CO)$_3$] (**Cr**–P_3C_3–H) (1980 cm^{-1}, entry 14 Table 2) and [Cr{P_3C_3(*t*Bu)$_3$}(CO)$_3$] (1979 cm^{-1}, entry 13 Table 2) shows.

How is ν(CO) influenced by electronically different substituents in 2,4,6-position of a triphosphinine ligand? This question can be partly answered by inspecting the last three entries 14–16 in Table 2. While replacing hydroxyl groups in **Cr**–P_3C_3–H by siloxy groups has a marginal influence, the replacement by boryloxy groups has a significant impact. The complex [Cr{P_3C_3[OB(ipc)$_2$]$_3$}(CO)$_3$] (**Cr**–P_3C_3–B) has the highest ν(CO) = 2012 cm^{-1} (entry 16 Table 2) of all triphosphinine complexes indicating that a B(ipc)$_2$ group efficiently abstracts electron density from the π-electron donating oxygen centres connected to the P_3C_3 ring thereby depleting the overall electron density at the chromium centre. But the variation between the complex with an "electron rich" P_3C_3(*t*Bu)$_3$ [or P_3C_3(OH)$_3$] ligand and the one with an "electron poor" P_3C_3[OB(ipc)$_2$]$_3$ ligand is smaller [$\Delta\nu$(CO) = 32 cm^{-1}] than the one seen between "electron rich" and "electron poor" arene ligands (70 cm^{-1}; *vide supra*). This span of $\Delta\nu$(CO) is seen for all [M{P_3C_3(OX)$_3$}(CO)$_3$] complexes independently on the metal centre M = Cr, Mo, W (see the last three entries in every Tables 2–4).

The nature of the metal centre has also an influence on the ν(CO) stretching frequencies but this is rather small and for all type of ligands the largest step is seen between the Cr(0) and Mo(0) complexes (shift of about 10 cm^{-1} to higher wave numbers) while there is almost no change between Mo(0) and W(0) complexes.

That for every [M{P_3C_3(OH)$_3$}(CO)$_3$] (entry 14, entry 8, entry 7 in Tables 2, 3 and 4, respectively) or [M{P_3C_3[O(Si*t*BuPh$_2$)]$_3$}(CO)$_3$] complex (M = Cr, Mo, W; entry 15, entry 9, entry 8 in Tables 2, 3 and 4, respectively) the A_1 ν(CO) is quite similar to the one observed in the corresponding parent benzene complex [M(C_6H_6)(CO)$_3$] (entry 5 in Tables 2, 3 and 4, respectively) may be due to counterbalancing effect of the π-electron donating hydroxyl groups and π-electron withdrawing P_3C_3 core.

^{183}W satellites (natural abundance 14.3%)[60] were observed in the ^{31}P{^{1}H} NMR spectra of the W(0) triphosphinine complexes prepared in this work. The J_{WP} couplings decrease very slightly from **W**–P_3C_3–B (21.4 Hz) to **W**–P_3C_3–Si (19.1 Hz) and **W**–P_3C_3–H (16.4 Hz). These data demonstrate that, as expected, a shorter W–ct distance correlates with a larger ^{31}P–^{183}W coupling constant as a result of a stronger π-accepting ligand (see Fig. 1 and 2, in the ESI† for a correlation of W–ct, J_{WP}, ν(CO), and δ ^{183}W). No J_{WP} coupling has been reported for [W($P_3C_3{}^t$Bu$_3$)(CO)$_3$] and a η^6-coordinated monophosphinine tungsten complex has not been prepared yet. Only the J_{WP} coupling constants of η^1-phosphinine tungsten complexes are reported in the literature, as for example in the hexakis-(η^1-phosphinine)tungsten complex [W(η^1-PC_5H_5)$_6$], which has a much larger direct P–W coupling of 304 Hz.[61]



A
M = Cr, Mo

Fig. 2 M(CO)$_3$ complex of bis(imidazolium)-1,3-diphosphete-diide (IPD) (M = Cr, Mo).

Lastly, ^{183}W resonances were measured using a triple resonance broad-band (TBI) probe with ^{1}H/^{2}D/^{31}P/BB channels. A ^{31}P–^{183}W heteronuclear multiple-quantum coherence (HMQC) experiment was performed, enhancing the sensitivity of the low γ ^{183}W nucleus. The resonances in the ^{183}W NMR spectrum shift very slightly to higher frequencies in the order **W**–P_3C_3–B (δ ^{183}W = −3146 ppm) < **W**–P_3C_3–Si (δ ^{183}W = −3140 ppm) < **W**–P_3C_3–H (δ ^{183}W = −3110 ppm). The number of reported ^{183}W NMR chemical shifts for tungsten(0) complexes is rather limited and span from about −3500 to −2500 ppm. The most shielded ^{183}W NMR shift is observed for [W(CO)$_6$], which shows a ^{183}W NMR resonance at δ ^{183}W = −3446 ppm and is chosen as reference compound here.[62] Replacement of three CO groups by a phosphite ligand like P(OMe)$_3$ (a strong σ-donor and medium π-acceptor) leads to a high frequency shift of about 150 ppm to δ ^{183}W = −3297 ppm in [W{P(OMe)$_3$}$_3$(CO)$_3$].[63] This deshielding effect becomes even more pronounced (630 ppm) in [W(PMe$_2$Ph)$_3$(CO)$_3$] (δ ^{183}W = −2818 ppm) where three strong σ-electron donor but relatively weak π-acceptor ligands were incorporated in the ligand sphere.[64] To the best of our knowledge, no δ^{183}W NMR shifts are reported for any arene tungsten carbonyl complex. The shifts of the ^{183}W resonances of [W{P_3C_3(OX)$_3$}(CO)$_3$] to higher frequencies by about 300–336 ppm places them in between [W(CO)$_6$] and [W(PMe$_2$Ph)$_3$(CO)$_3$] indicating that to some extent the electronic effect on the ^{183}W resonance caused by the replacement of three CO groups in facial position by one P_3C_3(OX)$_3$ ligand may be comparable to three P(OMe)$_3$ ligands.

Conclusions

The successful preparation, and isolation of a 3 × 3 matrix of complexes [M{P_3C_3(OX)$_3$}(CO)$_3$] using three different metals M = Cr, Mo, W and three different substituents X = B(ipc)$_2$, Si*t*Bu Ph$_2$, H allowed to systematically study and evaluate the effects provoked by these variations on a variety of spectroscopic data. The η^6-binding mode entails a large coordination shift of >160 ppm to lower frequencies regardless the nature of the phosphinine. As has been observed in the coordination chemistry of 2,4,6-*t*Bu-1,3,5-triphosphinine, the C–P–C angles are narrowed while the P–C–P angles are widened upon binding to a $M(CO)_3$ fragment (note that the bulky and σ-electron donating *t*Bu groups lead to slightly larger C–P–C and more acute P–C–P angles in both the uncoordinated molecule as well as in the complexes).[23] As expected, the distances between the Cr centre and the centroid of the P_3C_3 rings in all complexes are significantly smaller (by about 8%) than the Mo–Ct and W–ct distances, which are almost identical. This is attributed to the contracted d-orbital shell of Cr *versus* those of Mo and W.[65,66] This contraction may also be seen as reason for the fact that in all Cr(0) complexes listed in Table 2 independently of the type of ligand the ν(CO) is somewhat smaller than in analogous Mo and W complexes because efficient M → L electron back donation (which raises ν(CO)) requires an efficient orbital overlap.

As mentioned in the introduction, phosphinines are considered as especially good π-electron density accepting ligands. We recalculated the HOMO–LUMO gap of C_6H_6 (6.60 eV), PC_5H_4 (5.23 eV), 1,3-$P_2C_4H_4$ (4.88 eV), and 1,3,5-$P_3C_3H_3$ (4.63 eV) with density functional theory (DFT) methods (B3LYP/6-311+G**) (see ref. 27 and the ESI† for details). While indeed there is a significant closing of the gap by ΔE = 1.37 eV when converting C_6H_6 to PC_5H_5, additional substitution leads to much smaller changes (<0.4 eV). That $P_3C_3(OH)_3$ has an especially small HOMO–LUMO gap of 4.27 eV is mainly due to the fact that the three hydroxyl groups in 1,3,5-position lift the HOMO in energy. Given these data, it is not surprising that the effect of replacing a monophosphinine by a triphosphinine has only a modest effect on the ν(CO) stretching frequencies and thereby the electron density at the metal centre. The variation of the substituents in 1,3,5-position of an arene ligand or 2,4,6-position of a 1,3,5-triphosphinine allows to modify ν(CO) over an range of about 70 cm^{-1} or 30 cm^{-1}, respectively, fully in accord with expectations (that is an electron donating ligand lowers ν(CO); an electron accepting ligand raises ν(CO)). However, it remains surprising that in comparison to benzene complexes phosphinines provoke only modest (<10 cm^{-1} when the parent molecules without strong electronic substituent effects are taken into account) blue-shifts of ν(CO). Under the assumption that these heterocycles are really "strong π-electron acceptor" ligands more pronounced deviations might have been expected. For example, we observed that the coordination of bis(imidazolium)-1,3-diphosphete-diide (IPD) – an unsual molecule with a central 6π-aromatic C_2P_2 ring of biradicaloid character – to form $M(CO)_3$ complexes **A** (Fig. 2) in which ν(CO) is shifted by about 100 cm^{-1} to lower frequencies indicating strong electron donation to the metal centre by these cycles, indeed.[67] There is no question that phosphinines act as strongly binding ligands to metals (in their synthesis frequently an arene ligand in a precursor complex is displaced by a phosphinine). But we feel that the characterization of phosphinines as electron accepting ligands is an oversimplification and the electronic structure of phosphinine complexes is not fully understood yet. High-level quantum chemical methods should be applied to gain a better insight into electrostatic interactions and the electron donating properties of phosphinines as well.

Conflicts of interest

There are no conflicts to declare.

References

1 G. Märkl, *Angew. Chem.*, 1966, **78**, 907–908.
2 A. J. Ashe, *J. Am. Chem. Soc.*, 1971, **93**, 3293–3295.
3 P. L. Floch, *Coord. Chem. Rev.*, 2006, **250**, 627–681.
4 P. Le Floch and F. Mathey, *Coord. Chem. Rev.*, 1998, **178–180**, 771–791.
5 N. Mezailles, F. Mathey and P. Le Floch, *Prog. Inorg. Chem.*, 2001, **49**, 455–550.
6 L. Weber, *Angew. Chem., Int. Ed.*, 2002, **41**, 563–572.
7 L. Kollar and G. Keglevich, *Chem. Rev.*, 2010, **110**, 4257–4302.
8 C. Müller, L. E. E. Broeckx, I. de Krom and J. J. M. Weemers, *Eur. J. Inorg. Chem.*, 2013, **2**, 187–202.
9 C. Müller and D. Vogt, *Dalton Trans.*, 2007, **47**, 5505–5523.
10 C. Müller and D. Vogt, *C. R. Chim.*, 2010, **13**, 1127–1143.
11 N. T. Coles, A. S. Abels, J. Leitl, R. Wolf, H. Grützmacher and C. Müller, *Coord. Chem. Rev.*, 2021, **433**, 213729–213756.
12 H. Heydt, *New Asp. Phosphorus Chem. II. 223*, 2003, vol. 223, pp. 215–249.
13 R. L. Falconer and C. A. Russell, *Coord. Chem. Rev.*, 2015, **297–298**, 146–167.
14 A. R. Barron and A. H. Cowley, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 907–908.
15 R. Milczarek, W. Rüsseler, P. Binger, K. Jonas, K. Angermund, C. Krüger and M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 908–909.
16 P. Binger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger and S. Leininger, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2227–2230.
17 F. Tabellion, C. Peters, U. Fischbeck, M. Regitz and F. Preuss, *Chem. – Eur. J.*, 2000, **6**, 4558–4566.
18 P. L. Arnold, F. G. N. Cloke, P. B. Hitchcock and J. F. Nixon, *J. Am. Chem. Soc.*, 1996, **118**, 7630–7631.
19 P. Binger, S. Stutzmann, J. Stannek, B. Gabor and R. Mynott, *Eur. J. Inorg. Chem.*, 1999, **1**, 83–86.
20 C. W. Tate, P. B. Hitchcock, G. A. Lawless, Z. Benkő, L. Nyulászi and J. F. Nixon, *C. R. Chim.*, 2010, **13**, 1063–1072.
21 M. D. Francis, C. Holtel, C. Jones and R. P. Rose, *Organometallics*, 2005, **24**, 4216–4225.
22 K. Eggers, F. W. Heinemann, M. Hennemann, T. Clark, P. Binger and U. Zenneck, *C. R. Chim.*, 2010, **13**, 1203–1212.
23 S. B. Clendenning, J. C. Green and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 2000, **9**, 1507–1512.

24 J. Waluk, H. P. Klein, A. J. Ashe and J. Michl, *Organometallics*, 1989, **8**, 2804–2808.

25 C. Elschenbroich, M. Nowotny, B. Metz, W. Massa, J. Graulich, K. Biehler and W. Sauer, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 547–550.

26 R. Gleiter, H. Lange, P. Binger, J. Stannek, C. Krüger, J. Bruckmann, U. Zenneck and S. Kummer, *Eur. J. Inorg. Chem.*, 1998, **1998**, 1619–1621.

27 R. Suter, Y. Mei, M. Baker, Z. Benkő, Z. Li and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2017, **56**, 1356–1360.

28 A. M. Cook and R. Huetter, *J. Agric. Food Chem.*, 1981, **29**, 1135–1143.

29 H. J. Sanders, *Chem. Eng. News*, 1981, **59**, 20–36.

30 Y. Yu, J. C. Yu, C.-Y. Chan, Y.-K. Che, J.-C. Zhao, L. Ding, W.-K. Ge and P.-K. Wong, *Appl. Catal., B*, 2005, **61**, 1–11.

31 P. Gijsman, R. Steenbakkers, C. Fürst and J. Kersjes, *Polym. Degrad. Stab.*, 2002, **78**, 219–224.

32 P. Zhao, M. Zhang, D. Wu and Y. Liu, *Korean J. Chem. Eng.*, 2013, **30**, 1687–1690.

33 D. Jiang, C. Sun, Y. Zhou, H. Wang, X. Yan, Q. He, J. Guo and Z. Guo, *Fibers Polym.*, 2015, **16**, 388–396.

34 K. P. Nair, V. Breedveld and M. Weck, *Macromolecules*, 2008, **41**, 3429–3438.

35 K. P. Nair, V. Breedveld and M. Weck, *Soft Matter*, 2011, **7**, 553–559.

36 B. Roy, P. Bairi and A. K. Nandi, *RSC Adv.*, 2014, **4**, 1708–1734.

37 E. E. Simanek, M. Mammen, D. M. Gordon, D. Chin, J. P. Mathias, C. T. Seto and G. M. Whitesides, *Tetrahedron*, 1995, **51**, 607–619.

38 D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229–2260.

39 D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154–1196.

40 L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem., Int. Ed.*, 2001, **40**, 2382–2426.

41 H. Fenniri, B. L. Deng and A. E. Ribbe, *J. Am. Chem. Soc.*, 2002, **124**, 11064–11072.

42 J. Deberitz and H. Nöth, *Chem. Ber.*, 1973, **106**, 2222–2226.

43 B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832–2838.

44 S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871–885.

45 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 2019, ch. 4, pp. 98–133.

46 G. Frenking and N. Frohlich, *Chem. Rev.*, 2000, **100**, 717–774.

47 G. Frenking, *J. Organomet. Chem.*, 2001, **635**, 9–23.

48 G. Frenking, *Coord. Chem. Rev.*, 2003, **238–239**, 55–82.

49 C. J. Breheny, J. M. Kelly, C. Long, S. O'Keeffe, M. T. Pryce, G. Russell and M. M. Walsh, *Organometallics*, 1998, **17**, 3690–3695.

50 J. A. S. Howell, P. C. Yates, N. F. Ashford, D. T. Dixon and R. Warren, *J. Chem. Soc., Dalton Trans.*, 1996, 3959–3966.

51 J. M. Jenkins, J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 1969, 2796–2800.

52 B. L. Ross, J. G. Grasselli, W. M. Ritchey and H. D. Kaesz, *Inorg. Chem.*, 1963, **2**, 1023–1030.

53 R. D. Fischer, *Chem. Ber.*, 1960, **93**, 165–175.

54 G. Davidson and E. M. Riley, *J. Organomet. Chem.*, 1969, **19**, 101–114.

55 J. A. S. Howell, C. J. Beddows, P. J. O'Leary, P. C. Yates, P. McArdle, D. Cunningham and H. E. Gottlieb, *J. Organomet. Chem.*, 1997, **527**, 21–27.

56 Z. Zhao, J. Messinger, U. Schon, R. Wartchow and H. Butenschön, *Chem. Commun.*, 2006, 3007–3009.

57 A. D. Hunter, V. Mozol and S. D. Tsai, *Organometallics*, 1992, **11**, 2251–2262.

58 J. Deberitz and H. Nöth, *Chem. Ber.*, 1970, **103**, 2541–2547.

59 R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837–1846.

60 P. S. Pregosin, in *Encyclopedia of Magnetic Resonance*, 2011.

61 C. Elschenbroich, S. Voss, O. Schiemann, A. Lippek and K. Harms, *Organometallics*, 1998, **17**, 4417–4424.

62 R. L. Keiter and D. G. Vander Velde, *J. Organomet. Chem.*, 1983, **258**, C34–C36.

63 G. T. Andrews, I. J. Colquhoun, W. McFarlane and S. O. Grim, *J. Chem. Soc., Dalton Trans.*, 1982, **12**, 2353–2358.

64 H. C. E. McFarlene, W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1976, **1**, 1616–1622.

65 M. Kaupp, *J. Comput. Chem.*, 2007, **28**, 320–325.

66 F. Weinhold and C. R. Landis, *Valency and bonding: a natural bond orbital donor-acceptor perspective*, Cambridge University Press, 2005.

67 Z. Li, X. Chen, L. L. Liu, M. T. Scharnholz and H. Grutzmacher, *Angew. Chem., Int. Ed.*, 2020, **59**, 4288–4293.