WILEY-VCH

UNUSUAL REACTIVITY OF *cyclo*-(P$_5$Ph$_5$): OXIDATIVE ADDITION AT A GROUP 6 METAL CARBONYL AND INSERTION OF ACETONITRILE INTO A P−P BOND

Divine Mbom Yufanyi,[a,b] Toni Grell[a] and Evamarie Hey-Hawkins*[a]

Abstract: The reaction of [M(CO)$_4$L$_x$] (M = Cr, W, L = MeCN, x = 2; M = Mo, L = 2,5-norbornadiene (nbd), x = 1) with *cyclo*-(P$_5$Ph$_5$) led to an unusual transformation reaction including the oxidative addition of a P–P bond to the Group 6 metal carbonyl, the insertion of MeCN into a P−P bond, and the formation of an M–M bond. The products were characterized by IR and ^{31}P{^{1}H} NMR spectroscopy, ESI mass spectrometry and single crystal X-ray crystallography. The complexes contain a metal–metal unit bridged by two terminal phosphanido groups of the novel ligand, (PPh-PPh-PPh-PPh-CMe=N-PPh)$^{2-}$. The ^{31}P{^{1}H} NMR spectrum shows an ABCDE spin system consistent with the molecular structure observed in the solid state. Furthermore, the thermal properties of the complexes were evaluated.

Introduction

Scientific interest in the fundamental chemistry of cyclophosphanes *cyclo*-(P$_n$R$_n$) (n = 3-6) has gone from a period of intense research between 1960 and 1990 to a period of low activity in the past two decades, but has received renewed interest lately.[1] These compounds, which display diverse reactivity with transition metal carbonyls, have been used for the synthesis of phosphorus-rich main group and transition metal complexes.[1] Especially reactions of *cyclo*-(P$_5$Ph$_5$) with metal carbonyls at room temperature have been explored.[2,3]

Furthermore, P–P bonds can be cleaved homolytically[4] or, when polarised, especially when activated through coordination to a metal atom, heterolytically.[5,6] Both of these processes can result in the insertion of unsaturated small molecules into the homonuclear σ-bonds.[7–9] The insertion of small molecules into homo- and heteronuclear element–element (E–E) single bonds has been the subject of intense research, since this important transformation can be of significance in catalytic processes. Thus, the insertion of molecules like CO, alkene, alkyne, CO$_2$, CS$_2$, RCN, isothiocyanate (NCS), etc. into E–E bonds (E = C, N, O, halogen, P, S, metal) is known.[10,11] The activation of P−P bonds in cyclophosphanes is particularly interesting as a potential route to unique oligophosphorus-containing species. Burck *et al.* observed that the reaction of N-heterocyclic diphosphines with [W(CO)$_4$(cod)] (cod = 1,5-cyclooctadiene) in
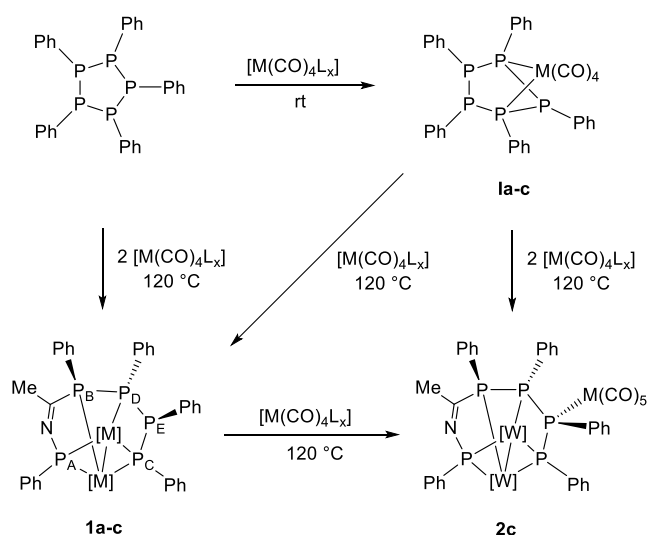
acetonitrile resulted in a mixture of two complexes arising from insertion of an acetonitrile molecule or a metal dicarbonyl fragment into the P–P bond of the starting material.[9] When [AuCl(SMe$_2$)] was reacted with an azadiphosphiridine, the P–P bond was cleaved to give a gold(I) complex with a PNP type ligand.[12] Wolf *et al.* reported the reversible insertion of the C=S or C=N bond of phenyl isothiocyanate into a P–P bond of [{CpNi(IMes)}$_2$(μ-η^1:η^1-P$_4$)] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene).[13] Furthermore, a highly selective metal-mediated insertion of nitriles into a nonpolar P–P bond of a substituted hexahydro-1,4-diaza-2,3,5,6-tetraphosphorine has been reported by Rosenthal *et al.*.[7] Recent studies by Manners *et al.* have shown that nitrile or isonitrile insertion into P–P bonds of phosphorus homocycles takes place easily for polarized molecules, such as {*cyclo*-(P$_3$*t*Bu$_3$)Me}$^+$ and {*cyclo*-(P$_4$*t*Bu$_4$)Me}$^+$, but does not proceed with the neutral molecules, *cyclo*-(P$_3$*t*Bu$_3$) and *cyclo*-(P$_4$*t*Bu$_4$).[6] In addition, stoichiometric and acid-catalyzed insertion of nitriles into a P−P bond of *cyclo*-(P$_3$*t*Bu$_3$) resulted in the first free 1-aza-2,3,4-triphospholenes.[14]

As for small molecules, the insertion of metal atoms into E–E bonds is also relevant. Such oxidative addition reactions are an important step in many catalytic cycles based on transition metals.[15] Furthermore, these reactions may result in unusual compounds. Thus, the homoleptic cobalt(III) phosphanido complex [K(thf)$_4$][Co{1,2-(P*t*Bu)$_2$C$_2$B$_{10}$H$_{12}$}$_2$], prepared by an unprecedented oxidative addition of the P–P bond of an *ortho*-carborane-substituted 1,2-diphosphetane to cobalt(–1) has been reported[16] and oxidative addition of a P–P bonds in *cyclo*-(P$_5$Et$_5$) to rhodium(I) resulted in the metallacyclic complex [(NacNac)RhP$_5$Et$_5$)] (NacNac = HC(CMeN(*i*Pr$_2$C$_6$H$_2$))$_2$).[17]

Recently, we reported the synthesis of phosphorus-rich complexes of Group 6 metal carbonyls, namely [Cr(CO)$_5${*cyclo*-(P$_5$Ph$_5$)-κ*P*^{1}}], [{Cr(CO)$_5$}$_2${μ-*cyclo*-(P$_5$Ph$_5$)-κ*P*^{1},*P*^{3}}], and [M(CO)$_4${*cyclo*-(P$_5$Ph$_5$)-κ*P*^{1},*P*^{3}}] (with M = Cr, Mo, W (**Ia-c**)). For tungsten, we observed *exo* and *endo* isomers, which gradually interconverted in solution to give a mixture of both isomers.[2] The reaction of these complexes with [M(CO)$_4$L$_x$] (M = Cr, W, L = MeCN, x = 2; M = Mo, L = nbd, x = 1) (Scheme 1) resulted in an unusual transformation reaction including the insertion of MeCN into a P−P bond, the oxidative addition of a P–P bond to the metal carbonyl fragment and the formation of an M–M bond. These new complexes contain a novel bis-phosphanido ligand, (PPh-PPh-PPh-PPh-CMe=N-PPh)$^{2-}$. All products were characterised by elemental analyses, IR and ^{31}P{^{1}H} NMR spectroscopy, mass spectrometry and single crystal X-ray crystallography. Furthermore, their thermal properties were evaluated.

[a] Dr. D.M. Yufanyi, Dr. T. Grell, Prof. Dr. E. Hey-Hawkins
Faculty of Chemistry and Mineralogy
Institute of Inorganic Chemistry
Leipzig University
Johannisallee 29, 04103 Leipzig, Germany
E-mail: hey@uni-leipzig.de
[b] Dr. D.M. Yufanyi
Department of Chemistry
The University of Bamenda
P.O. Box 39 Bambili, Bamenda, Cameroon

Scheme 1. Synthesis of **1a-c** and **2c** and labelling of phosphorus atoms in the clusters **1a-c** for NMR assignment.

[M] = M(CO)$_3$

a: M = Cr, L = MeCN, x = 2
b: M = Mo, L = nbd, x = 1
c: M = W, L = MeCN, x = 2

Results and Discussion

Reacting **Ia-c** with [M(CO)$_4$L$_x$] (M = Cr, W, L = MeCN, x = 2; M = Mo, L = nbd, x = 1) in the appropriate stoichiometric ratio (1:1) in refluxing toluene affords **1a-c** as the only products detected by $^{31}P\{^1H\}$ NMR spectroscopy. The pure complexes were isolated as air-stable black crystals, suitable for X-ray diffraction, in high yields by crystallization from dichloromethane n-hexane.

The complexes **1a-c** are isostructural and crystallize in the space group $P\bar{1}$ ($Z = 2$); **2c** crystallizes in the space group $P2_1/n$ ($Z = 4$) (Table S1, ESI, summarizes the crystallographic data). The molecules (Figs. 1, 2 and Figs. S1–S3 ESI) contain an M–M unit bridged by the two terminal phosphanido groups of the novel ligand, (PPh-PPh-PPh-PPh-CMe=N-PPh)$^{2-}$, with an all-trans arrangement of the phenyl groups. Although heteroleptic dinuclear bis-phosphanido-bridged complexes with M$_2$P$_2$ units are known,[7,9] these are the first examples in which the bridging phosphorus atoms are linked to a chain of phosphorus atoms. Both metal atoms are in the formal oxidation state +I and have a distorted octahedral geometry with a planar M$_2$P$_2$ unit. The coordination sphere for each metal atom is completed by three terminal carbonyl ligands and one coordinating phosphorus atom (P3 for W2 and or P4 for W1) of the novel ligand. The M1−M2 distances (Table 1 and Table S2, ESI) are 2.8930(1) Å for **1a**, 3.0253(2) Å for **1b**, 3.0279(2) Å for **1c** and 3.0279(2)Å for **2c**, and fall within the range of metal-metal bonds for other M$_2$P$_2$(CO)$_x$ units in similar Cr [2.8925(8)–2.949(1) Å],[7,18] Mo [3.022(4)–3.057(6) Å][19,20] and W [(3.017(2)–3.078(5) Å][18–20,21] complexes. The bridging M–P bonds fall in the ranges 2.297(2)–2.337(2) Å (**1a**), 2.4335(5)–2.4668(5) Å (**1b**), 2.4363(9)–

2.4675(9) Å (**1c**) and 2.431(1)–2.4951(9) Å (**2c**). These values are close to reported values for Cr–P [2.2858(9)–2.3176(8) Å];[7,18] Mo–P [2.49(1)–2.51(1) Å],[19] and W–P [2.467(2)–2.616(1) Å] single bonds.[18]
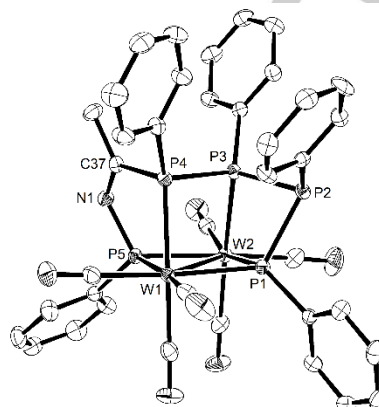

Figure 1. Molecular structure and atom-labelling scheme for **1c** with ellipsoids drawn at 50% probability level. H atoms are omitted for clarity.
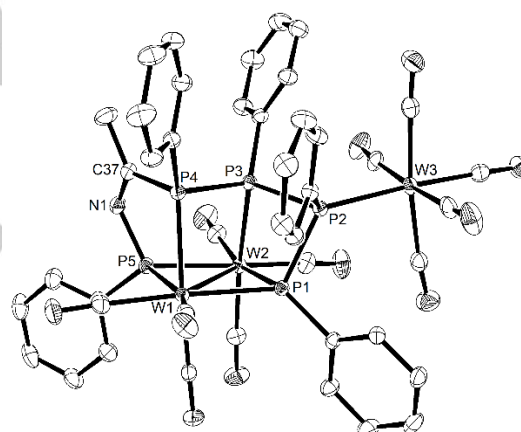

Figure 2. Molecular structure and atom-labelling scheme for **2c** with ellipsoids drawn at 50% probability level. H atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **1a-c** and **2c**.

Bond Length (Å); Bond Angle (°)	1a (M = Cr)	1b (M = Mo)	1c (M = W)	2c (M = W)
M(1)–M(2)	2.8930(1)	3.0253(2)	3.0279(2)	3.0279(2)
P(1)–M(1)	2.3154(2)	2.4538(5)	2.4539(1)	2.4948(8)
P(1)–M(2)	2.3367(2)	2.4668(5)	2.4675(9)	2.4758(8)
P(2)–M(3)				2.5274(8)
P(3)–M(2)	2.3872(2)	2.5161(5)	2.5091(9)	2.5161(8)
P(4)–M(1)	2.3232(2)	2.4688(5)	2.4629(9)	2.4986(8)
P(5)–M(1)	2.297(2)	2.4335(5)	2.4363(9)	2.4361(8)
P(5)–M(2)	2.3029(2)	2.4412(5)	2.4424(1)	2.4349(9)
P(1)–P(2)	2.204(2)	2.2028(7)	2.2050(1)	2.2098(1)
P(2)–P(3)	2.192(2)	2.2008(7)	2.2023(1)	2.2445(1)
P(3)–P(4)	2.219(2)	2.2245(6)	2.2295(1)	2.2242(1)
P(5)–N(1)	1.748(5)	1.7425(2)	1.743(3)	1.719(3)
C(37)–P(4)	1.859(6)	1.8795(2)	1.883(4)	1.889(3)
C(37)–N(1)	1.280(6)	1.276(2)	1.274(4)	1.266(4)
M(1)–P(1)–M(2)	76.90(6)	75.87(8)	75.94(3)	75.06(2)

M(1)–P(5)–M(2)	77.95(6)	76.72(2)	76.72(3)	76.87(2)
P(2)–P(3)–P(4)	105.12(1)	106.29(3)	106.22(5)	103.09(4)
P(3)–P(2)–P(1)	77.69(7)	80.22(2)	79.76(5)	80.34(4)
P(5)–M(1)–P(1)	102.98(7)	103.86(2)	103.81(3)	103.61(3)
C(37)-N(1)-P(5)	115.7(4)	118.29(2)	118.30(3)	119.3(2)

In contrast, W–P double bonds are usually much shorter (2.28 Å).[22] The P(2)–W(3) bond (2.529(1) Å) is longer than the other W–P bonds in complex **2c**, but still in the range of literature values.[23] In **1a-c**, the P–P bonds [2.192(2)–2.230(1) Å] are in the typical range for P–P single bonds,[2,24] with two bonds, P1–P2 (2.204(2)–2.205(1) Å) and P2–P3 (2.2008(7)–2.192(2) Å), being slightly shorter than the other bonds, P3–P4 (2.219(2)–2.230(1) Å). In all complexes, the C(37)–P(4) [1.859(6)–1.889(3)Å] bonds are slightly longer than P–C bonds of known P–C=N–P moieties (1.803–1.870 Å), while the P(5)–N(1) [1.719(3)–1.748(3) Å] bonds are within the reported range (P–N 1.697–1.802 Å).[14,23,24] However, the P(5)–N(1) and C(37)–P(4) bonds are longer than P–N bonds [1.665(2)–1.710(2) Å][7,23,25] in diazaphospholene and P–C bonds (1.799(2)–1.835(5) Å)[26] in phosphole rings. The C(37)–N(1) bonds [1.265(4)–1.280(6) Å] correspond to C=N double bonds[11] and are similar to the C–N bond lengths [1.261(4)–1.276(4))][6,9,27] in P–C=N–P moieties, but shorter than that [1.320(3) Å] reported by Hoffmann et al.[23] for a hexahydro-1,4-diaza-2,3,5,6-tetraphosphorine derivative ($C_{32}H_{26}Cr_2N_2O_6P_4$). The C(37)–N(1)–P(5) bond angles of 115.7(4)°, 118.3(1)°, 118.3(3)°, and 119.3(3)° for **1a-c** and **2c**, respectively, are similar to known values[28] of other five-membered MP–C=N–P (M = Cr, Mo, W) rings. These values are of course larger than in a four-membered PC=N–P ring (101.9(1)°).[29]

The small M–P–M bond angles (75.00(3)–77.95(6)°) for the complexes are similar to literature values,[7,18,27] as are the large P–M–P bond angles [102.12(7)–104.19(3)°].[7,8,18,30] The P(2)–P(3)–P(4) [103.10(5)–106.29(3)°] bond angles fall within the range [94.1(2)–107.2(2)°] for *cyclo*-(Ph₅P₅)[31] and similar compounds like P[P(S)Me₂]₃.[32]

The ³¹P{¹H} NMR spectra of **1a-c** and **2c** (Fig. 3 and Figs. S4-S7, ESI) in C_6D_6 show five complex multiplets for an ABCDE spin system consistent with five different P atoms. The NMR data indicate that the clusters are diamagnetic. The chemical shifts and coupling constants of **1a-c** were extracted from these spectra by simulation (Table 2). The large coupling constants correspond to ¹*J*(P,P) couplings (-177 to -321 Hz) and allow the identification of the single P atom (P_A) and the chain of four P atoms (P_B-P_E) (labelling scheme is given in Scheme 1). The right assignment of the P atoms of the chain to the structure was achieved by investigation of the ¹⁸³W satellites of each multiplet in **1c**. The phosphanido P atoms (P_A, P_C) each show two different ¹*J*(P,W) coupling constants (132–183 Hz), while the remaining coordinating P atoms show only one. This allows the unambiguous assignment of P_E, which shows no satellite signals in **1a-c**. There is a large ²*J*(P_A,P_C) coupling between the phosphanido P atoms.
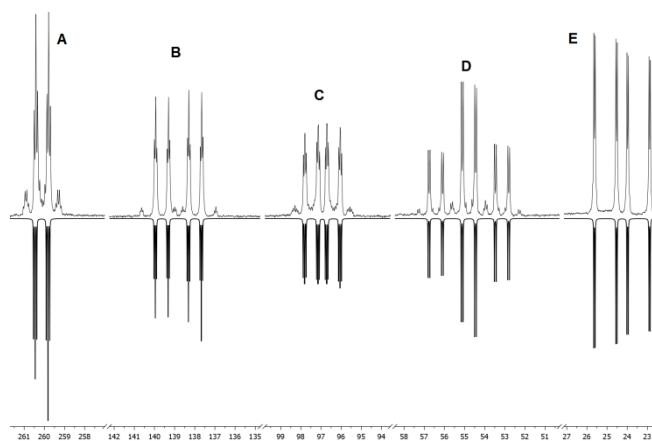

Figure3. Experimental (top) and simulated (bottom) ³¹P{¹H} NMR spectrum of complex **1c** in C_6D_6 (for details see Table S3, ESI).

Table 2. ³¹P{¹H} NMR data (δ (ppm) and *J* (Hz), standard deviations in brackets) of compounds **1a-c** in C_6D_6 at 25°C. Numbering scheme is given in scheme 1.

	1a	**1b**	**1c**	**2c**
Chemical Shift (ppm)				
δ(P_A)	343.09(1)	305.12(1)	260.10(1)	260.57(1)
δ(P_B)	195.55(1)	145.56(1)	138.79(1)	116.97(1)
δ(P_C)	162.80(1)	141.20(1)	96.92(1)	115.75(1)
δ(P_D)	79.62(1)	62.07(1)	54.77(1)	90.28(1)
δ(P_E)	7.27(1)	19.09(1)	24.27(1)	60.53(1)
***J*_P-P (Hz) and *J*_W-P (Hz)**				
²*J*(P_A,P_B)	1.49(8)	10.21(3)	13.35(1)	
²*J*(P_A,P_C)	89.69(7)	87.66(3)	103.05(1)	
²*J*(P_A,P_D)	-0.00(7)	-0.00(3)	-0.03(9)	
²*J*(P_A,P_E)	20.06(7)	14.65(5)	14.10(1)	
²*J*(P_B,P_C)	10.99(8)	10.01(1)	10.16(1)	
¹*J*(P_B,P_D)	-187.04(8)	-181.54(2)	-177.38(1)	
²*J*(P_B,P_E)	-92.75(8)	-99.47(3)	-107.58(1)	
²*J*(P_C,P_D)	10.48(7)	10.06(2)	10.83(1)	
¹*J*(P_C,P_E)	-321.32(7)	-290.51(3)	-266.70(1)	
¹*J*(P_D,P_E)	-268.68(7)	-270.37(3)	-266.23(9)	
¹*J*(P_A,W1)			159	
¹*J*(P_A,W2)			144	
¹*J*(P_C,W1)			183	
¹*J*(P_C,W2)			132	
¹*J*(P_B,W1)			227	
¹*J*(P_D,W2)			170	
²*J*(P_E,W)			20	

The IR spectra of **1a-c** and **2c** (Fig. S9, ESI) show the stretching frequencies for the carbonyl ligands in the ranges 1991–2009 (s) cm⁻¹, 1954–1964 (vs) cm⁻¹, 1938–1954 (vs) cm⁻¹, 1906–1920 (s) cm⁻¹ and 1880–1891 cm⁻¹ (sh), respectively. These values (summarised in Table S4, ESI) are consistent with literature values for terminal carbonyl groups.[33] The decrease in

the vibrational frequencies of the main CO absorptions indicates weaker CO bonds.[34] This observation is consistent with the shorter P–M bonds and longer M–M (M = Cr, Mo, W) bonds in the M_2P_2 unit, indicating that the P−M bonds are stronger due to metal-to-ligand back bonding.[20,27] Consequently, the P(5)−N(1) and C(37)−P(4) bonds are also weakened by conjugation.[27]

For the formation of **1a-c** (Scheme 2), several possibilities were considered (Schemes S1 and S2, ESI) and the following mechanism is proposed: initially the chelate complexes **Ia-c** are formed, which are transformed to the key intermediates **i1** by an oxidative insertion reaction. This intermediate was in fact isolated for the Rh[III] complex [(NacNac)RhP_5Et_5].[17] In the transition state (TS), a carbonyl group is replaced by an acetonitrile ligand. This induces a positive polarisation on the nitrogen atom which enables a bond formation with a negatively polarised phosphanido atom. The reaction sequence is completed by coordination of a second metal carbonyl fragment and subsequent syn-proportionation.
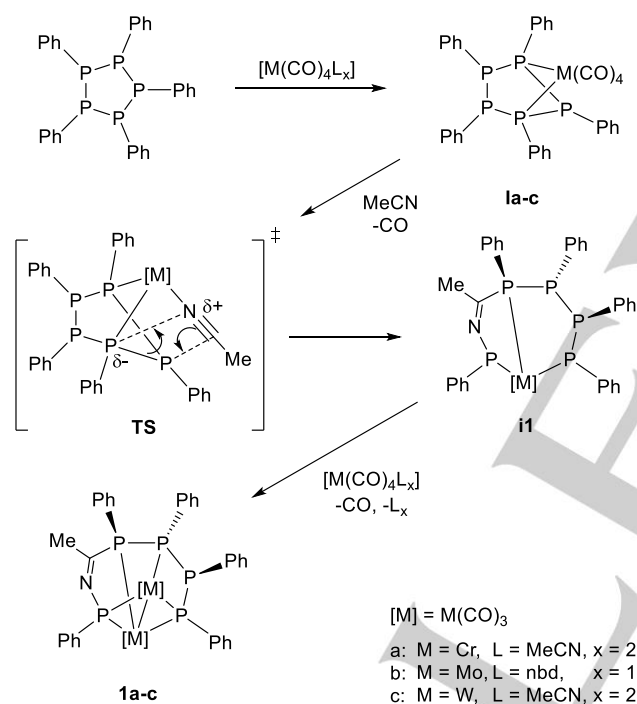
Scheme 2. Proposed mechanism of oxidative addition and MeCN insertion to give **1a-c**.

The following observations support the proposed mechanism. No reaction, according to ^{31}P NMR spectroscopy, was observed when cyclo-(P_5Ph_5) was refluxed in MeCN at 120 °C for 12 hours. This confirms that transition metal-mediated activation of the P–P bond is necessary for MeCN insertion.[6,7,27] Reaction of [M(CO)_4L_x] and cyclo-(Ph_5P_5) in a 1:1 ratio led to the chelate complexes **Ia-c** as previously reported.[2] The complexes **1a-c** are only formed when the starting materials [M(CO)_4L_x] and cyclo-(P_5Ph_5) are reacted in the ratio 2:1 at high temperatures, or when **Ia-c** are reacted with [M(CO)_4L_x] under the same conditions (Scheme 1). Reaction of [W(CO)_4(MeCN)_2] and cyclo-

(P_5Ph_5) in the ratio 3:1 led to a mixture of **1c** and **2c** as shown by ^{31}P NMR spectroscopy (Fig. S8, ESI). When the Mo complex **Ib** was reacted with [W(CO)_4(MeCN)_2], a trinuclear complex was obtained, which is isostructural to **2c** and where all metal sites are occupied (disordered) by Mo and W (see ESI, Fig. S1). The insertion of acetonitrile was found to be irreversible as opposed to the reversible insertion reported by Burck et al.[27].

The thermal properties of complexes **1b** and **1c** were studied by simultaneous TG/DTA/MS analyses in the temperature range 30–900 °C under an argon atmosphere (Fig. S10 and Table S5, ESI). The first decomposition step up to ~290 °C is attributed to the loss of six CO and MeCN (for **1b** and **1c**). A broad exothermic peak observed between 290 and 840 °C in both compounds can be attributed to the decomposition of the phenyl substituents within this range. A loss of two (for **1b**) or three (for **1c**) phosphorus atoms occurs at higher temperatures. The powder XRD patterns of the residues (Fig. S11, ESI) indicate that they contain only small fractions of crystalline material, and the very low intensity peaks could not be indexed to any known phase. The percent weight of the experimentally obtained residues (54.71% and 58.27%, respectively) differ a lot from the calculated amounts for the potential phosphorus-rich metal phosphides (MoP_3 (20.07%) and WP_2 (21.99%)), indicating the presence of impurities, probably carbon.

Conclusions

In summary, a novel route to complexes that contain a dinuclear metal core bridged by the two terminal phosphanido groups of the novel ligand $(PPh-PPh-PPh-PPh-CMe=N-PPh)^{2−}$ has been achieved. The products are formed via oxidative addition of a P–P bond at a metal carbonyl fragment and transition metal-assisted insertion of MeCN into a P–P bond. The dinuclear clusters can further utilize the uncoordinated P atom (P2) to coordinate another metal atom, resulting in homonuclear (**2c**) or heteronuclear clusters.

Experimental Section

Data Collection and Structure Refinement

X-ray data were collected with a GEMINI CCD diffractometer (Rigaku Inc.), λ(Mo-K_α) = 0.71073 Å, T = 130(2) K, empirical absorption corrections with SCALE3 ABSPACK.[35] All structures were solved by dual space methods with SIR-92.[36] Structure refinement was done with SHELXL-2016[37] by using full-matrix least-square routines against F^2. All hydrogen atoms were calculated on idealized positions. The pictures were generated with the program Mercury.[38] CCDC 1888485 (**1a**), CCDC 1888484 (**1b**), CCDC 1888482 (**1c**), CCDC 1888486 (**2**, Mo/W disordered) and CCDC 1888488 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

Keywords: N,P ligands • Nitriles • Insertion • Thermolysis

References

[1] S. Gomez-Ruiz, E. Hey-Hawkins, *Coord. Chem. Rev.* **2011**, *255*, 1360–1386.

[2] D. M. Yufanyi, T. Grell, M.-B. Sárosi, P. Lönnecke, E. Hey-Hawkins, *Pure Appl. Chem.* **2019**, 1259.

[3] a) H.-G. Ang, S.-G. Ang, Q. Zhang, *J. Chem. Soc, Dalton Trans.* **1996**, 2773–2778; b) H.-G. Ang, S.-G. Ang, Q. Zhang, *J. Chem. Soc, Dalton Trans.* **1996**, 3843–3851;

[4] a) N. A. Giffin, A. D. Hendsbee, T. L. Roemmele, M. D. Lumsden, C. C. Pye, J. D. Masuda, *Inorg. Chem.* **2012**, *51*, 11837–11850; b) N. A. Giffin, A. D. Hendsbee, J. D. Masuda, *Dalton Trans.* **2016**, *45*, 12636–12638;

[5] S. Burck, D. Gudat, M. Nieger, D. Vindus, *Eur. J. Inorg. Chem.* **2008**, 704–707.

[6] S. S. Chitnis, R. A. Musgrave, H. A. Sparkes, N. E. Pridmore, V. T. Annibale, I. Manners, *Inorg. Chem.* **2017**, *56*, 4521–4537.

[7] M. Höhne, B. H. Müller, N. Peulecke, A. Spannenberg, H. Jiao, U. Rosenthal, *Eur. J. Inorg. Chem.* **2017**, 3008–3014.

[8] M. A. Alvarez, M. E. Garcia, D. Garcia-Vivo, R. Lozano, A. Ramos, M. A. Ruiz, *Inorg. Chem.* **2014**, *53*, 11261–11273.

[9] S. Burck, D. Gudat, M. Nieger, *Organometallics* **2009**, *28*, 1447–1452.

[10] a) P. Braunstein, D. Nobel, *Chem. Rev.* **1989**, *89*, 1927–1945; b) G. Qiu, Q. Ding, J. Wu, *Chem. Soc. Rev.* **2013**, *42*, 5257–5269; c) M. F. Lappert in *Inorganic reactions and methods*, *Inorganic Reactions and Methods*; (Eds. J. J. Zuckerman, A. P. Hagen), VCH Publishers, Deerfield Beach, Fla, **1986-<c1999>**, pp. 439–444;

[11] M. Schiffer, M. Scheer, *Angew Chem Int Edit* **2001**, *40*, 3413–3416.

[12] A. Hinz, A. Schulz, A. Villinger, *Chem. Commun.* **2015**, *51*, 1363–1366.

[13] S. Pelties, A. W. Ehlers, R. Wolf, *Chem. Commun.* **2016**, *52*, 6601–6604.

[14] S. S. Chitnis, H. A. Sparkes, V. T. Annibale, N. E. Pridmore, A. M. Oliver, I. Manners, *Angew. Chem, Int. Ed.* **2017**, *56*, 9536–9540.

[15] a) B. M. Gardner, C. E. Kefalidis, E. Lu, D. Patel, E. J. L. McInnes, F. Tuna, A. J. Wooles, L. Maron, S. T. Liddle, *Nature Commun.* **2017**, *8*, 1898; b) S. T. H. Willems, P. H. M. Budzelaar, N. N. P. Moonen, R. de Gelder, J. M. M. Smits, A. W. Gal, *Chem. - Eur. J.* **2002**, *8*, 1310–1320;

[16] P. Coburger, S. Demeshko, C. Rödl, E. Hey-Hawkins, R. Wolf, *Angew. Chem, Int. Ed.* **2017**, *56*, 15871–15875.

[17] S. J. Geier, D. W. Stephan, *Chem. Commun.* **2008**, 2779–2781.

[18] S. Bauer, C. Hunger, M. Bodensteiner, W.-S. Ojo, A. Cros-Gagneux, B. Chaudret, C. Nayral, F. Delpech, M. Scheer, *Inorg. Chem.* **2014**, *53*, 11438–11446.

[19] M. H. Linck, L. R. Nassimbeni, *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1105–1113.

[20] P. Planinic, D. Matkovic-Calogovic, *Struct. Chem.* **2001**, *12*, 439–444.

[21] a) R. L. Keiter, J. S. Martin, E. A. Keiter, A. L. Rheingold, *J. Chem. Crystallogr.* **2003**, *33*, 491–495; b) G. Huttner, J. Borm, L. Zsolnai, *J. Organomet. Chem.* **1986**, *304*, 309–321; c) U. Vogel, P. Hoemensch, K.-C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. - Eur. J.* **2003**, *9*, 515–519;

[22] L. D. Field, N. G. Jones, P. Turner, *J. Organomet. Chem.* **1998**, *571*, 195–199.

[23] N. Hoffmann, C. Wismach, P. G. Jones, R. Streubel, N. H. T. Huy, F. Mathey, *Chem. Commun.* **2002**, 454–455.

[24] M. Höhne, M. Joksch, K. Konieczny, B. H. Müller, A. Spannenberg, N. Peulecke, U. Rosenthal, *Chem. Eur. J.* **2017**, *23*, 4298–4309.

[25] Z. Benko, S. Burck, D. Gudat, M. Hofmann, F. Lissner, L. Nyulaszi, U. Zenneck, *Chem. - Eur. J.* **2010**, *16*, 2857–2865.

[26] a) C. Lescop, L. Toupet, R. Reau, *Heteroat. Chem.* **2011**, *22*, 339–347; b) Z. Hu, Z. Li, K. Zhao, R. Tian, Z. Duan, F. Mathey, *Org. Lett.* **2015**, *17*, 3518–3520;

[27] S. Burck, D. Gudat, M. Nieger, *Angew. Chem, Int. Ed.* **2007**, *46*, 2919–2922.

[28] N. Thirupathi, P. M. Stricklen, X. Liu, R. Oshel, I. Guzei, A. Ellern, J. G. Verkade, *Inorg. Chem.* **2007**, *46*, 9351–9363.

[29] R. Streubel, M. Bodea, U. Schiemann, C. Wismach, P. G. Jones, A. Monsees, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1215–1219.

[30] a) U. Vogel, A. Y. Timoshkin, K.-C. Schwan, M. Bodensteiner, M. Scheer, *J. Organomet. Chem.* **2006**, *691*, 4556–4564; b) M. A. Alvarez, M. E. Garcia, R. Lozano, A. Ramos, M. A. Ruiz, *Inorg. Chem.* **2015**, *54*, 2455–2466;

[31] M. Baudler, K. Glinka, *Chem. Rev.* **1993**, *93*, 1623–1667.

[32] M. Scheer, P. G. Jones, *J. Organomet. Chem.* **1992**, *434*, 57–61.

[33] M. Scheer, E. Leiner, P. Kramkowski, M. Schiffer, G. Baum, *Chem. - Eur. J.* **1998**, *4*, 1917–1923.

[34] R. L. Keiter, E. A. Keiter, K. N. Mittelberg, J. S. Martin, V. M. Meyers, J. G. Wang, *Organometallics* **1989**, *8*, 1399–1403.

[35] *CrysAlis Pro:* Empirical absorption correction; Oxford Diffraction Ltd, **2014**.

[36] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J Appl Crystallogr* **1994**, *27*, 435.

[37] G. M. Sheldrick, *Acta crystallogr. Sect. C* **2015**, *71*, 3–8.

[38] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J Appl Crystallogr* **2006**, *39*, 453–457.
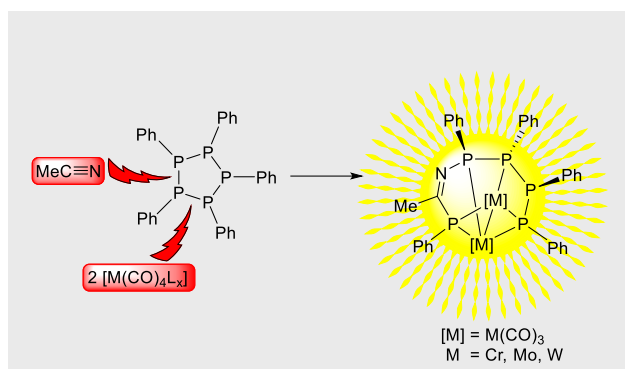
Entry for the Table of Contents (Please choose one layout)

Layout 2:

COMMUNICATION

Divine Mbom Yufanyi, Toni Grell and Evamarie Hey-Hawkins*

Page No. – Page No.

Unusual Reactivity of *cyclo*-(P$_5$Ph$_5$): Oxidative Addition at a Group 6 Metal Carbonyl and Insertion of Acetonitrile into a P−P bond

A novel and very efficient route to complexes that contain a dinuclear metal core bridged by the two terminal phosphanido groups of the novel ligand (PPh-PPh-PPh-PPh-CMe=N-PPh)$^{2-}$ is reported. The products are formed via oxidative addition of a P–P bond at a metal carbonyl fragment and transition metal-assisted insertion of MeCN into a P–P bond.