

NH-functionalized tungsten complexes of 2-(dimethylphosphino)imidazole

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Abstract

Ligand substitution in $W(CO)_4(NO)(ClAlCl_3)$ with 2-(dimethylphosphino)imidazole (dmpi) bearing an acidic NH functionality afforded $W(Cl)(CO)(NO)(bdmpi)(dmpi)$ (**1**) (bdmpi = 1,2-bis(dimethyl-phosphino)imidazole), while the reaction of dmpi with $W(Cl)(NO)(P(OMe)_3)_4$ led to the isolation of $W(Cl)(NO)(dmpi)_4$ (**2**) together with $W(Cl)(NO)(bdmpi)(dmpi)_2$ (**3**). Attempts to replace the chloride by a hydride ligand in **1–3** applying various hydride reagents did not lead to stable products. The soluble compound $W(Cl)(NO)(dmpe)(dmpi)_2$ (**5**) was prepared by an alternative route from $W(Cl)(NO)[P(OMe)_3]_4$ via the intermediacy of $W(Cl)(NO)(P(OMe)_3)_2(dmpe)$ (**4**). The protection of the NH function in **5** was approached applying BuLi and subsequently Me_3SiCl to afford $[W(Cl)(NO)(dmpe)(tmsdmpi)_2]$ (tmsdmpi = 1-trimethylsilyl-2-dimethylphosphino-imidazole) (**6**) which could not be isolated in pure form. The reaction of **5** with $NaHBET_3$ led to the formation of a deprotonated and nitrogen-coordinated salt $Na[W(NO)(dmpe)(dmpi)(tebdmpi)]$ (**7**) (tebdmpi = 2-dimethylphosphino-3-triethylboro-imidazole). Compound **7** crystallized from CH_3CN to establish a one-dimensional chain structure in the solid state. The structures of compounds **1–5** and **7** were studied by single-crystal X-ray diffraction.

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1. Introduction

Catalytic hydrogenations play a pivotal role in homogeneous catalysis. Recently, major research efforts were devoted to the development of catalytic ionic hydrogenations using H^+ and H^- as a H_2 equivalent. One sub-class of this latter type of reaction follows a concerted mechanism [1–4], where the hydride and proton transfer to the unsaturated substrate occur more or less simultaneously requiring, in addition, the hydride and proton sources to be arranged in close spatial vicinity. The hydrogenation of organic carbonyl compounds could thus take place in

the secondary coordination sphere of complexes and would not require a vacant site, which middle transition elements like tungsten normally cannot easily provide. The design of efficient such bifunctional hydrogenation catalysts or pre-catalysts would, however, demand a transition metal hydride of appropriate hydricity and ligands with an acidic function, for instance, coordinated or noncoordinated NH or OH groups [2–8,6,9,10]. The coordinated forms of such moieties usually possess increased acidities with the possibility of facile deprotonation. In this paper, we intended to approach the preparation of complexes with acidic ligands of the non-ligating NH type and it seemed appropriate to build these functionalities into strongly cis- σ -donating phosphines, the latter to enhance hydricity of the M–H bond [11–16]. We therefore approached the preparation of 2-(dimethylphosphino)imidazole (dmpi) to apply this ligand in tungsten nitrosyl complexes.

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2. Results and discussion

2.1. Preparation of 2-(dimethylphosphino)imidazole (dmpi)

Starting from *N*-(diethoxymethyl)imidazole dmpi was prepared by a route analogous to that of tris(4,5-dimethylimidazol-2-yl)phosphine [17]. The reaction of Me₂PCl with the lithium salt of *N*-(diethoxymethyl)imidazole gave the *N*-protected 2-(dimethylphosphino)imidazole (Scheme 1). The latter characterized through NMR spectroscopy including ¹H, ³¹P, ¹³C NMR, NOESY, ¹H-COSY and ¹³C–¹H correlation spectra. Deprotection of the *N*-functionalized group was effected by dissolution in 10:1 acetone–water and heating to 50 °C for 8 h. A too large excess of water reduced the yield of dmpi greatly. The crude mixture was purified by recrystallization from dry CH₂Cl₂ to give dmpi as white needles in a yield of 75% based on *N*-(diethoxymethyl)imidazole. dmpi was fully characterized by IR, NMR, elemental analysis, MS and a single crystal X-ray analysis. The ³¹P NMR spectrum of dmpi in CD₂Cl₂ reveals a singlet at –58.7 ppm and its ¹H NMR spectrum displays a broad resonance at 11.31 ppm characteristic for the NH function. Its structure revealed a pyramidal geometry at the phosphorus atom.

2.2. Reactions of dmpi with tungsten nitrosyl complexes

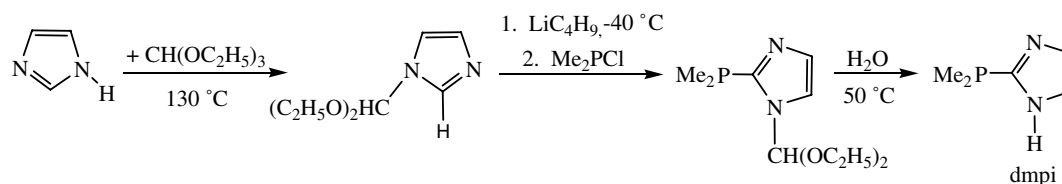
The reaction of W(NO)(CO)₄(ClAlCl₃) [18] with a 6-fold excess of dmpi in THF at 85 °C for 6 d gave W(Cl)(CO)(NO)(dmpi)(bdmpi) (**1**) (bdmpi = 1,2-bis(dimethylphosphino)imidazole) in 71% yield (Scheme 2), which was characterized by IR, NMR, elemental analysis and single crystal X-ray diffraction.

In **1**, a new ligand 1,2-bis(dimethylphosphino)imidazole (bdmpi) was generated bearing a new P–N bond. It is suggested that **1** was produced via an intermediacy of [W(Cl)(CO)(NO)(dmpi)₃] in which two neighbouring dmpi

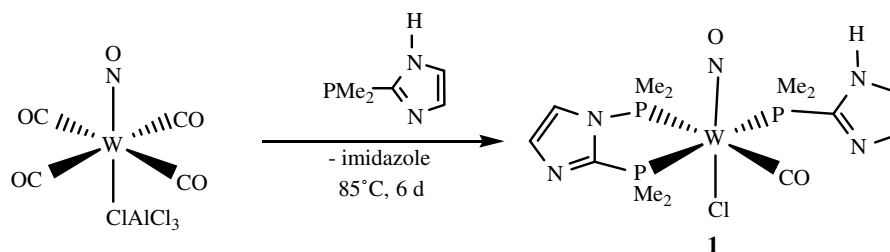
ligands underwent an imidazole disproportionation forming a coordinated bdmpi ligand and a free imidazole molecule.

The IR spectrum of **1** showed ν(CO) and ν(NO) bands at 1952 and 1599 cm^{–1}, which confirmed the presence of both types of ligands. The ³¹P NMR spectrum in CDCl₃ displayed three groups of doublet of doublet resonances with satellites at 82.7 ppm (²J_{PP-trans} = 159 Hz, ²J_{PP-cis} = 25 Hz, ¹J_{PW} = 463 Hz), –11.5 ppm (²J_{PP-cis} = 25 Hz, ²J_{PP-cis} = 19 Hz, ¹J_{PW} = 235 Hz) and –26.3 ppm (²J_{PP-trans} = 159 Hz, ²J_{PP-cis} = 18 Hz, ¹J_{PW} = 451 Hz) indicating that all phosphorus nuclei coordinate to the tungsten centre and are chemically inequivalent and in meridional positions. The P atom corresponding to the signal at –11.5 ppm is located between the other two. Furthermore, in the ¹H NMR spectrum the NH proton was shifted to 10.87 ppm somewhat up-field in comparison to the free dmpi ligand and in the ¹³C NMR spectrum two distinct resonances are assigned to the imidazole carbon atoms bearing the phosphorus substituents. They appear as a doublet of doublet of doublet at 157.0 ppm (¹J_{CP} = 66 Hz, ²J_{CP} = 33 Hz, ³J_{CP} = 7 Hz) for the bdmpi and as a doublet signal at 150.9 ppm (²J_{CP} = 48 Hz) for the dmpi ligand. The spectroscopically derived structure of **1** was in full agreement with the structure obtained from the single crystal X-ray diffraction analysis.

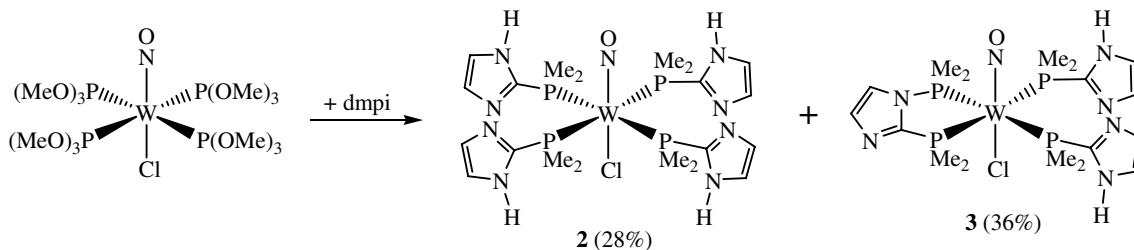
A ligand substitution related to Scheme 2 was then attempted starting from W(Cl)(NO)[P(OMe)₃]₄ [19] and dmpi in THF at 70 °C. After 10 d the reaction was complete and the NMR spectra of the mixture showed that several compounds were formed. The crystallization of the crude product in a THF solution at –30 °C gave two main products subsequently in a turn of [W(Cl)(NO)(dmpi)₄]·2THF (**2**·2THF) as a crystalline form and [W(Cl)(NO)(bdmpi)(dmpi)₂] (**3**) (Scheme 3) as powder. The latter was purified again by recrystallization from CH₃CN giving crystals of **3**·CH₃CN.



Scheme 1.



Scheme 2.



Scheme 3.

The IR spectrum of **2** in THF revealed a $\nu(NO)$ band at 1515 cm^{-1} . In the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ a singlet was found bearing satellites at -21.4 ppm ($^1J_{PW} = 288\text{ Hz}$) proving the four chemically equivalent phosphine ligands. The 1H NMR spectrum of **2** revealed a broad resonance at 10.94 ppm for the NH moieties.

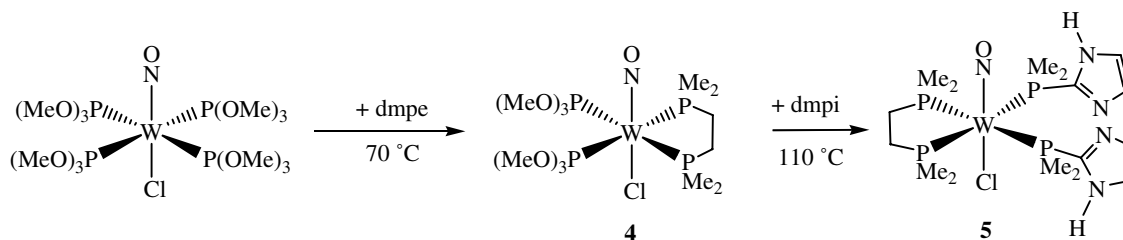
The IR spectrum of **3** showed a $\nu(NO)$ band in CH_2Cl_2 at 1517 cm^{-1} very close to that of **2** indicating similar ligand environments for both complexes. The $^{31}P\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ displayed three groups of resonances: a doublet of doublet at 89.6 ppm ($^2J_{PP-trans} = 162\text{ Hz}$, $^2J_{PP-cis} = 22\text{ Hz}$, $^1J_{PW} = 318\text{ Hz}$), a doublet of doublet of doublet at -6.3 ppm ($^2J_{PP-trans} = 142\text{ Hz}$, $^2J_{PP-cis} = 13\text{ Hz}$, $^2J_{PP-cis} = 21\text{ Hz}$, $^1J_{PW} = 281\text{ Hz}$) and two partly overlapping resonances at -24.8 ppm ($^2J_{PP-trans} = 141\text{ Hz}$, $^2J_{PP-cis} = 12\text{ Hz}$, $^1J_{PW} = 290\text{ Hz}$) and at -25.1 ppm ($^2J_{PP-trans} = 163\text{ Hz}$, $^2J_{PP-cis} = 11\text{ Hz}$, $^1J_{PW} = 282\text{ Hz}$) appearing in a 1:1:2 ratio. They were assigned to the Me_2N group of $bdmpi$, the Me_2P-C group of $bdmpi$ and to the two chemically different $dmpe$ ligands, respectively. In the 1H NMR spectrum **3** displayed two partly overlapping resonances at 11.19 and 11.09 ppm for the NH groups, which again proved chemically different environments for the $dmpe$ ligands. The formation of a new P–N bond is also supported by the ^{13}C NMR data, which similar to **1** revealed a doublet of doublet of doublet resonance at 159.2 ppm ($^1J_{CP} = 66\text{ Hz}$, $^2J_{CP} = 30\text{ Hz}$, $^3J_{CP} = 6\text{ Hz}$) for the N–C–P moiety of the $bdmpi$ ligand, different from the related $dmpe$ doublets at 151.5 ppm ($^1J_{CP} = 63\text{ Hz}$) and 149.9 ppm ($^1J_{CP} = 60\text{ Hz}$).

Compound **2** had low solubility in organic solvents, which caused difficulties in the attempt to prepare the related hydride complex. Therefore, we considered to additionally introduce the more soluble ligand $dmpe$. $W(Cl)(NO)(dmpe)_2(dmpe)$ (**5**) was eventually obtained as

pure product starting from $W(Cl)(NO)[P(OMe)_3]_4$ via the intermediacy of a $W(Cl)(NO)[P(OMe)_3]_2(dmpe)$ complex (**4**) (Scheme 4). Two $P(OMe)_3$ ligands of $W(Cl)(NO)[P(OMe)_3]_4$ could indeed be substituted by $dmpe$ at $70\text{ }^\circ\text{C}$ within 8 h to afford **4** in high yield (95%). The composition and structure of **4** was derived from IR, NMR spectroscopies, elemental analysis and single crystal X-ray diffraction. In the IR spectrum **4** showed in THF a band at 1557 cm^{-1} , which gave evidence to the presence of a NO group. Furthermore, the $^{31}P\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ displayed two multiplets with satellites at 161.2 ppm ($^2J_{PP-trans} = 205\text{ Hz}$, $^1J_{PW} = 484\text{ Hz}$, $P(OMe)_3$) and 20.6 ppm ($^2J_{PP-trans} = 205\text{ Hz}$, $^1J_{PW} = 266\text{ Hz}$, PCH_3) consistent with the in plane arrangement of *cis* pairs of phosphorus nuclei.

The subsequent substitution of the other two $P(OMe)_3$ substituents of **4** was accomplished by the reaction of $W(NO)(Cl)[P(OMe)_3]_2(dmpe)$ (**4**) with $dmpe$ in THF. The reaction mixture was heated over $105\text{ }^\circ\text{C}$ and free $P(OMe)_3$ was produced, which was removed from time to time. After one week the reaction was complete and **5** was isolated in high yield (89%). Full characterization was achieved by IR, NMR, elemental analysis, MS and single crystal X-ray diffraction confirming the given composition and structure.

The IR spectrum of **5** showed a $\nu(NO)$ band at 1494 cm^{-1} confirming the presence of a NO group. Just like for **4**, the ^{31}P NMR spectrum ($CDCl_3$) of **5** displayed two multiplets with satellites at 19.6 ppm ($^2J_{PP-trans} = 142\text{ Hz}$, $^1J_{PW} = 282\text{ Hz}$) for $dmpe$, and at -23.3 ppm ($^2J_{PP-trans} = 142\text{ Hz}$, $^1J_{PW} = 298\text{ Hz}$) for the $dmpe$ ligands. Interestingly, these groups of signals showed different intensities, which were attributed to different relaxation times of the various types of phosphorus nuclei. The phosphorus atoms of the $dmpe$ ligand were found to relax slower than those of the $dmpe$ ligand. The routinely used relaxation delay ($d_1 = 0.4\text{ s}$) was



Scheme 4.

therefore too short to allow for a complete relaxation. When the relaxation delay was set to $d_1 = 20$ s, signals of nearly the same intensities appeared. The ^1H NMR spectrum of **5** revealed one broad resonance at 11.24 ppm for both NH functions. The other NMR data of **5** including ^1H , ^{31}P , ^{13}C and ^1H - ^{31}P correlation supported the proposed structure further.

In further experiments, silyl protection of the NH function was approached via deprotonation of the NH groups of **5** with LiC_4H_9 in THF at -75°C for 3 h and subsequent addition of Me_3SiCl (Scheme 5). The reaction mixture was warmed to room temperature and **6** was spectroscopically assigned a $[\text{W}(\text{Cl})(\text{NO})(\text{dmpe})(\text{tmsdmpi})_2]$ structure ($\text{tmsdmpi} = 1$ -trimethylsilyl-2-dimethylphosphino-imidazole). Compound **6** could not be obtained totally pure, since it was found to be very sensitive to traces of water and hydrolyzed even in dry solvents, however, it was pure enough to extract most of the spectroscopic data.

The NMR spectra of **6** (^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR), 1D-NOE, ^1H - ^{29}Si correlation and ^{31}P - ^1H correlation spectra confirmed that its structure is related to that of **5**. The ^{31}P NMR spectrum in THF- d_8 showed two multiplets with satellites at 21.5 ppm ($^2J_{\text{PP-trans}} = 150$ Hz, $^1J_{\text{PW}} = 287$ Hz) and -12.2 ppm ($^2J_{\text{PP-trans}} = 150$ Hz, $^1J_{\text{PW}} = 301$ Hz). In comparison with the ^{31}P NMR resonances of compound **5**, both these resonances were shifted to lower field. The 1D ^1H -NOE experiment of **6** revealed upon irradiation at the resonance of the SiMe_3 group enhancement of the resonance at 7.18 ppm of the NCH moieties, and of the resonance at 1.90 ppm of the dmpci ligands. A negative NOE was observed for the resonance at 1.16 ppm attributed to the dmpe ligand. When the NCH resonances were irradiated, NOE enhancement of the SiMe_3 signal at 0.59 ppm became visible. Furthermore, the ^1H - ^{29}Si correlation spectrum of **6** demonstrated coupling of the resonance at 15.4 ppm in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum with the resonance at 0.59 ppm in the ^1H NMR spectrum, which proved the existence of a N-SiMe₃ bond. Other ^1H NMR resonances were assigned by aid of a ^1H - ^{31}P correlation spectrum.

2.3. Attempts to prepare the hydride derivatives of **1–3** and **5**

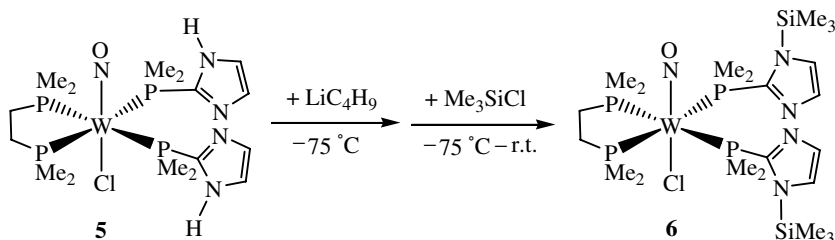
The preparation of hydride complexes starting from **1–3** and **5** was attempted at various temperatures and with various hydride reagents including $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$, NaBH_4 , Bu_4NBH_4 , LiH , KH , and NaHBET_3 .

^1H NMR spectroscopic pursuit of all these reactions did not reveal the presence of any hydride species. It was often seen, however, that H_2 evolved and in addition that ligands were liberated from **1–3** and **5**, which indicated that the NH functions may have been deprotonated and that the resulting anions expelled at least some parts of the molecule.

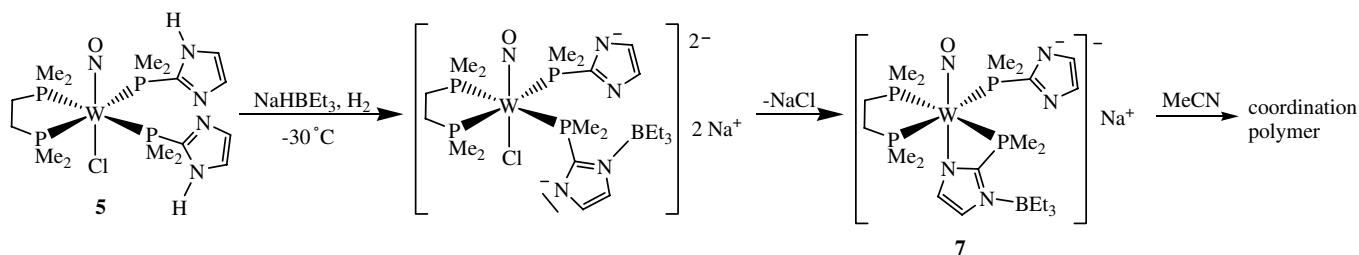
It is noteworthy that the reaction of $\text{W}(\text{Cl})(\text{NO})(\text{dmpi})_2(\text{dmpe})$ (**5**) with NaHBET_3 led at -30°C to the formation of a precipitate identified as $\text{Na}[\text{W}(\text{NO})(\text{dmpe})(\text{dmpi})(\text{tebdmpi})]$ ($\text{tebdmpi} = 2$ -dimethylphosphino-3-triethylboro-imidazole) (**7**). The precipitate possessed low solubility in THF and CH_3CN and was therefore suspected to be ionic. Its composition and structure was derived from IR and NMR spectroscopies, MS, elemental analysis and single crystal X-ray diffraction. The IR spectrum of **7** showed a band at 1495 cm^{-1} attributed to the nitrosyl ligand. The ^{31}P NMR spectrum of **7** in $\text{CH}_3\text{CN}-d_3$ displayed three groups of resonances between 24.9 and 26.7, and at -17.1 and -25.9 ppm with a 2:1:1 ratio. The earlier group of resonances was assigned to the two phosphorus atoms of the dmpe ligand and the latter two resonances were attributed to the dmpi phosphorus atoms. All of them appear as doublets due to a strong trans $J_{\text{P-P}}$ coupling. In the ^1H NMR spectrum of **7** three resonances were found at 6.97, 6.88 and 6.38 ppm for the N-CH=CH-N moieties possessing an integration ratio of 2:1:1. This means two CH groups of one dmpi ligand are chemically identical, while the two hydrogen nuclei of the other dmpi ligand are chemically different. In the ^1H NMR spectrum signals at 0.27 and 0.49 ppm (2:3 ratio) gave evidence to the presence of a BEt_3 unit.

The course of the formation of $\text{Na}[\text{W}(\text{NO})(\text{dmpe})(\text{dmpi})(\text{tebdmpi})]$ (**7**) is sketched in Scheme 6. First a deprotonation of the NH function is thought to occur upon attack of the $[\text{HBET}_3]^-$ base and then the remaining BEt_3 adds to a $\text{N}_{\text{imidazole}}$ atom. It is this imidazolyl anion, which then substitutes the chloride ligand to form **7**. Compound **7** slowly self-assembles into a chain-like 1D polymer and with an increasing degree of aggregation it eventually precipitates from solution. This coordination polymer is nearly insoluble in any organic solvent.

The aggregation was thought to be prevented by silyl protection of the $\text{H}_{\text{imidazolyl}}$ protons. Therefore, the reaction of **5** dissolved in THF was carried out with BuLi in hexane at -75°C followed by addition of Me_3SiCl .



Scheme 5.



Scheme 6.

However, this derivatization led to an unstable product, which was too difficult to be handled in further experiments.

2.4. Crystal structure determinations

Crystals of **1–3** suitable for X-ray diffraction were obtained by evaporation of an ether solution at ambient temperature, cooling a THF solution to $-30\text{ }^{\circ}\text{C}$, and evaporation of a CH_3CN solution at ambient temperature, respectively. Their structures determined by single crystal X-ray diffraction. Their structures are displayed in Figs. 1–3. Selected bond distances (\AA) and bond angles ($^{\circ}$) are listed in Table 1.

As shown in Figs. 1–3, the structures of **1–3** and exhibit pseudo-octahedra at the tungsten centres with disordered trans nitrosyl and chloride groups. The structures of **1** and **3** possess the newly formed ligand bdpmp. The P–N bond lengths (1.736(4) \AA and 1.781(4) \AA , for **1** and **3**, respectively) are somewhat longer than related ones [20,21]. The W–P bond lengths of the three compounds are in the range of 2.4195(13)–2.492(2) \AA similar to those of other phosphine tungsten complexes [11,12]. In comparison with $[\text{W}(\text{Cl})(\text{NO})(\text{dmp})_4]$ (**2**), compound **3** possesses a less sterically hindered ligand sphere with four phosphorus atoms located nearly in a plane.

Crystals of **4** and **5** suitable for X-ray diffraction were grown by slow evaporation of ether solutions at ambient

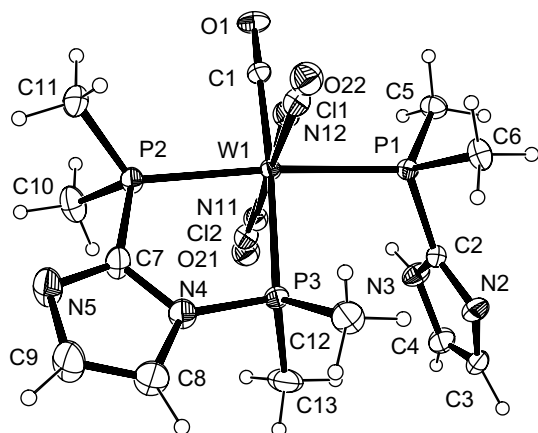


Fig. 1. ORTEP plot of the structure of **1**. The displacement ellipsoids are drawn with 30% probability.

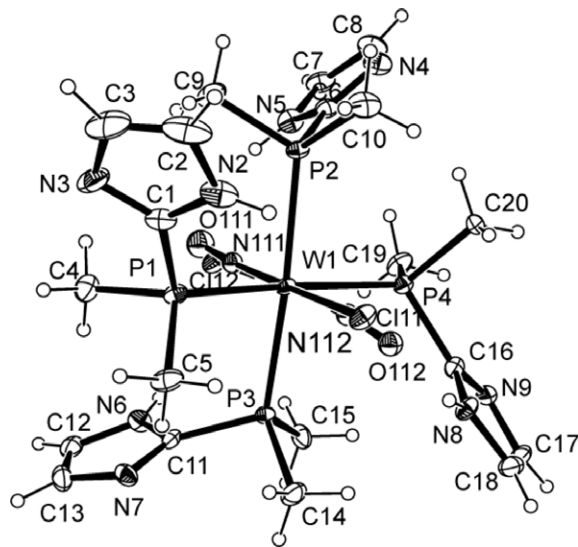


Fig. 2. ORTEP plot of the structure of **2**. The displacement ellipsoids are drawn with 30% probability. The structure consists of two independent complexes, of which only complex **1** is shown.

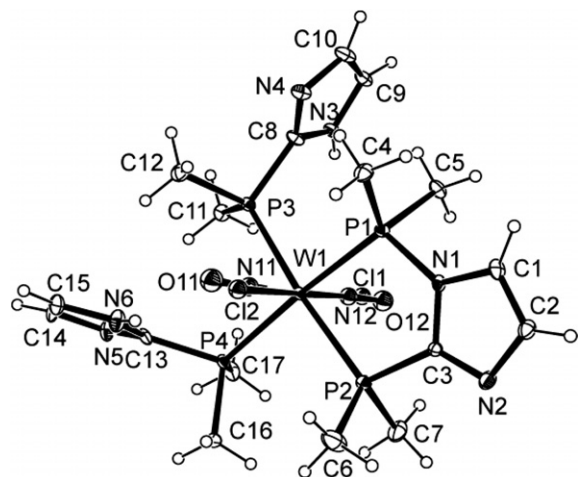


Fig. 3. ORTEP plot of the structure of **3**. The displacement ellipsoids are drawn with 30% probability.

temperature, while crystals of **7** were obtained by cooling a CH_3CN solution to $-30\text{ }^{\circ}\text{C}$ over one month. Selected bond distances (\AA) and bond angles ($^{\circ}$) of the single crystal X-ray diffraction analysis for **4**, **5** and **7** are listed in Table 2.

Table 1
Selected bond distances (Å) and bond angles (°) of **1–3**

1		2		3	
W1–P1	2.4793(11)	W1–P1	2.467(2)	W1–P1	2.4195(13)
W1–P2	2.4590(11)	W1–P4	2.481(2)	W1–P2	2.4617(15)
W1–P3	2.4894(11)	W1–P3	2.4876(18)	W1–P4	2.4759(13)
P3–N4	1.736(4)	W1–P2	2.492(2)	W1–P3	2.4819(14)
W1–C1	2.025(4)			P1–N1	1.781(4)
		P1–W1–P4	168.59(6)		
C1–W1–P2	95.06(13)	P1–W1–P3	89.17(6)	P1–W1–P2	82.59(5)
C1–W1–P1	90.39(13)	P4–W1–P3	91.73(6)	P1–W1–P4	175.59(5)
P2–W1–P1	174.53(4)	P1–W1–P2	92.58(7)	P2–W1–P4	93.08(5)
C1–W1–P3	176.44(13)	P4–W1–P2	88.17(7)	P1–W1–P3	93.97(4)
P2–W1–P3	81.51(4)	P3–W1–P2	171.60(6)	P2–W1–P3	174.23(5)
P1–W1–P3	93.05(4)			P4–W1–P3	90.41(5)
O1–C1–W1	178.4(4)				

Table 2
Selected bond distances (Å) and bond angles (°) of **4, 5 and 7**

4		5		7	
W1–P3 2.4216(15)		W1–P1 2.4613(14)		W1–N1 1.782(3)	P2–W1–P1 79.58(4)
W1–P4 2.4274(19)		W1–P2 2.4736(14)		W1–N2 2.234(3)	N1–W1–P4 93.62(11)
W1–P2 2.4672(17)		W1–P4 2.4637(13)		W1–P2 2.4485(10)	N2–W1–P4 88.17(9)
W1–P1 2.4704(16)		W1–P3 2.4507(13)		W1–P1 2.4562(11)	P2–W1–P4 93.66(4)
				W1–P4 2.4815(11)	P1–W1–P4 171.87(4)
P3–W1–P4 97.38(6)		P3–W1–P1 93.28(5)		W1–P3 2.4831(10)	N1–W1–P3 108.38(10)
P3–W1–P2 91.10(6)		P3–W1–P4 94.52(4)		Na1–O1 2.342(3)	N2–W1–P3 64.92(9)
P4–W1–P2 170.53(7)		P1–W1–P4 172.19(4)		Na1–N5 2.362(4)	P2–W1–P3 159.66(3)
P3–W1–P1 168.97(6)		P3–W1–P2 173.19(5)		Na1–N4i 2.368(4)	P1–W1–P3 93.57(3)
P4–W1–P1 91.56(7)		P1–W1–P2 80.05(5)		Na1–N6 2.389(5)	P4–W1–P3 91.30(3)
P2–W1–P1 80.53(6)		P4–W1–P2 92.16(4)		N1–O1 1.239(4)	O1–Na1–N5 116.11(13)
				N3–B1 1.630(6)	O1–Na1–N4i 101.84(13)
				N1–W1–N2 73.14(13)	N5–Na1–N4i 118.47(14)
				N1–W1–P2 90.99(10)	O1–Na1–N6 97.19(16)
				N2–W1–P2 95.50(9)	N5–Na1–N6 99.18(16)
				N1–W1–P1 91.02(11)	N4i–Na1–N6 122.92(17)
				N2–W1–P1 88.00(9)	O1–N1–W1 178.3(3)
					N1–O1–Na1 95.0(2)

Symmetry operation: $i = -x, y + 1/2, -z + 1/2$, $ii = -x, y - 1/2, -z + 1/2$.

The coordination geometries around the tungsten centres of **4** and **5** are best described as pseudo octahedra with four P atoms in a plane and trans-NO, Cl ligands at axial positions as shown in Figs. 4 and 5. The latter show disorder.

The structure of **7** was also determined by single crystal X-ray diffraction and confirmed the structure of a coordination polymer with the repeat unit of Na[W(NO)(dmpe)-(dmpi)(tebdmpi)] (tebdmpi = 2-dimethylphosphino-3-triethylboro-imidazole) (Fig. 6). The inner coordination sphere is a severely distorted octahedron surrounded by one chelating *P,N*-ligand, one unidentate dmpi ligand, one chelating dmpe and one nitrosyl ligand (N1–W1–P1: 91.02(11)°, N1–W1–P2: 90.99(10)°, N1–W1–P3: 108.38(10)°, N1–W1–P4: 93.62(11)°). Both dmpi ligands are deprotonated and one of them became chelating via the coordination of its phosphorus atom and an amide function forming a four-membered ring. Furthermore, the other nitrogen atom of the chelating dmpi ligand bears

the BEt_3 group (Fig. 6). The N(3)–B(1) bond length of 1.630(6) Å is comparable to reference values of related boron–nitrogen compounds [22,23]. One of the ethyl groups from BEt_3 is disordered. The sodium atoms are four coordinated binding to one oxygen atom of the nitrosyl group (Na(1)–O(1): 2.342(3) Å), to the nitrogen atom of a CH_3CN molecule (Na(1)–N(6): 2.389(5) Å) and two nitrogen atoms of two imidazolyl rings (Na(1)–N(5): 2.362(4) Å, Na(1)–N(4i): 2.368(4) Å). As shown in Fig. 7, the sodium cations are bridged by μ -imidazolyl rings to form a 1D infinite chain along the *b*-axis of the crystal.

2.5. Conclusions

In this work, a new ligand 2-(dimethylphosphino)imidazole (dmpi) bearing an acidic NH group was probed for its co-existence with hydride functions in nitrosyl tungsten complexes. A series of chloro complexes containing the dmpi ligand were prepared first applying the reactions

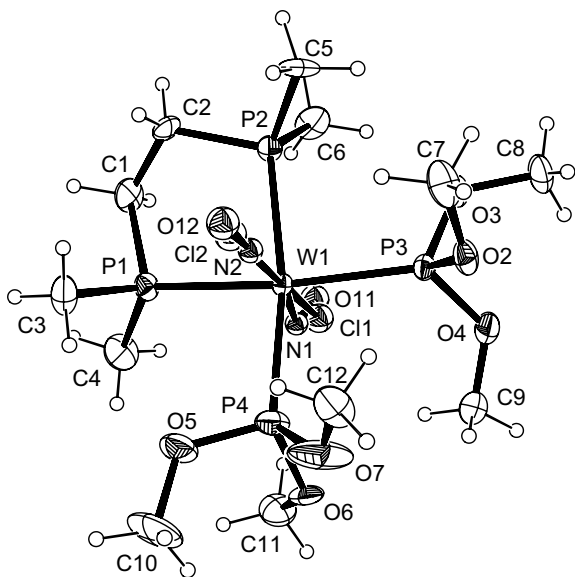


Fig. 4. ORTEP plot of the structure of **4**. The displacement ellipsoids are drawn with 30% probability.

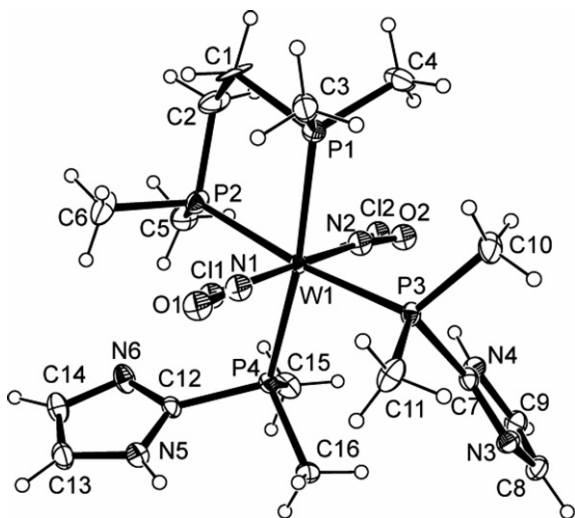


Fig. 5. ORTEP plot of the structure of **5**. The displacement ellipsoids are drawn with 30% probability.

of *dmp*i with $W(CO)_4(NO)(ClAlCl_3)$ or $W(Cl)(NO)(P(OMe)_3)_4$. However, it was recognized that the *dmp*i ligands were partly unstable under the reaction conditions and tended to form P–N bonds by substitutional processes generating for instance the new ligand system of 1,2-bis(dimethylphosphino)imidazole (*bdmp*i). Furthermore, any of these chloro compounds did not revealed the corresponding hydride complexes in reactions with various hydride reagents rather effected deprotonation of the *dmp*i ligands with subsequent decomposition of the formed anions. In the case of the deprotonation of **5** the stable anion $[W(NO)(dmp)e(dmp)i(tebdmp)i)]^-$ was formed. All of these reactions seemed to indicate that the acidity of the NH functions was too high to allow easy access to the corresponding hydride complexes. Attempts to protect

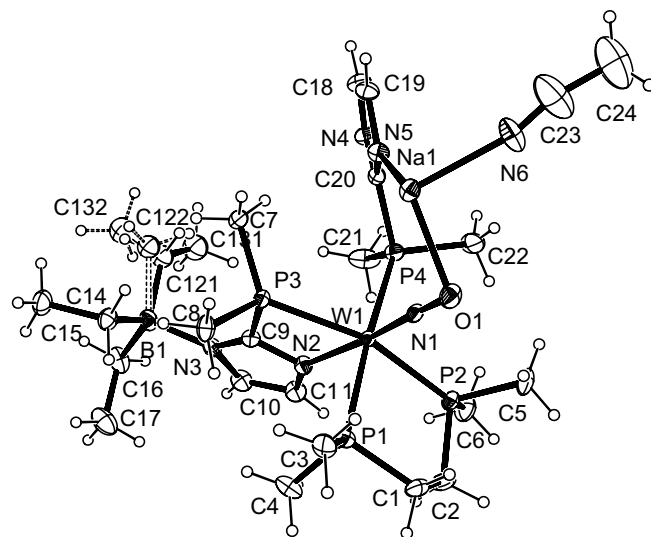


Fig. 6. ORTEP plot of the structure of **7-CH₃CN** crystallized from CH_3CN . The displacement ellipsoids are drawn with 30% probability.

the NH moieties via silylation did not afford compounds stable enough for further transformations.

3. Experimental

General considerations: All reactions and manipulations were performed under an atmosphere of dry nitrogen using conventional Schlenk techniques or a glove box. Solvents were dried by standard methods and freshly distilled before use. Reagents of commercial quality were obtained from commercial suppliers and used as received. NMR spectra were recorded on the following spectrometers: Varian Gemini-300 instrument; 1H at 300.08 MHz, ^{13}C at 12.46 MHz, ^{19}F at 282.33 MHz, ^{31}P at 121.47 MHz. Bruker DRX-500 instrument; 1H at 500.13 MHz, ^{13}C at 125.23 MHz, ^{31}P at 202.51 MHz. Chemical shifts δ (1H) and δ (^{13}C) relative to $SiMe_4$, δ (^{31}P) relative to 85% H_3PO_4 . IR spectra: Biorad FTS-45 instrument and FTS-3500 instruments. Raman spectra: Renishaw Labram Raman microscope. Mass Spectra: Finnigan-MAT-8400 spectrometer. FAB spectra in 3-nitrobenzyl alcohol matrix. Elemental analyses: Leco CHN(S)-932 instrument.

(2-Imidazolyl)dimethylphosphine (*dmp*i): To 200 ml of dry ether containing 23.23 g of *N*-(diethoxymethyl)imidazole kept under N_2 at $-40^\circ C$ was syringed 85.3 ml (8.74 g, 0.136 mol) of 1.6 M *n*-BuLi in hexane at such a rate that the temperature did not exceed $-40^\circ C$. After the addition of the BuLi solution, the yellow solution was stirred for additional 2 h. Then, to the solution was added 13.38 g (0.139 mol) of newly prepared $(CH_3)_2PCl$. The resulting white slurry was allowed to stir and warm overnight. Then, 250 ml of concentrated NH_4OH was cautiously added and the resulting mixture stirred for 2 h. The ether layer was separated and the NH_4OH layer extracted with ether (100 ml \times 3). The combined ether solutions were dried over Na_2SO_4 , and the solvent was removed in vacuo to give

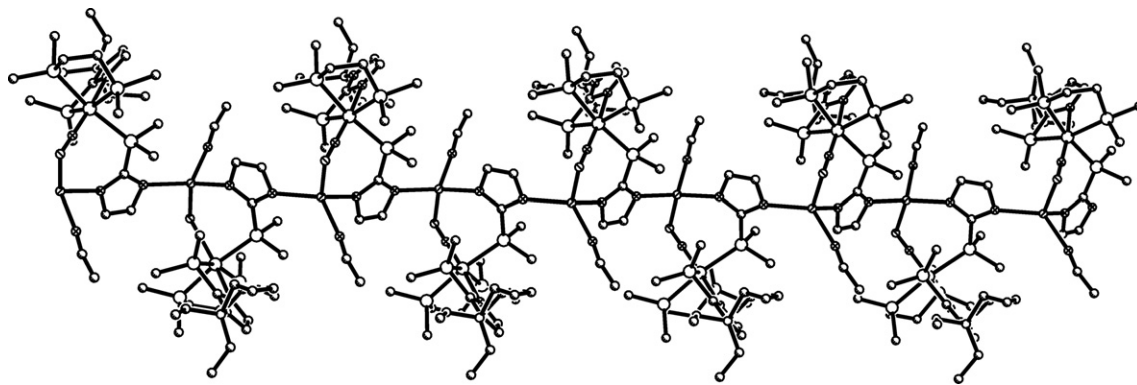


Fig. 7. 1D arrangement of 7-CH₃CN. Na⁺ ions connect two imidazole nitrogens to form an almost linear chain.

2-dimethylphosphino-*N*-(diethoxymethyl)imidazole. It was identified by NMR spectroscopy: ¹H NMR (500.2 MHz, THF-*d*₈): δ 7.19, 7.18 (m, 2H, N-CH=CH-N=), 6.32 (d, 1H, ²J_{HN} = 5.3 Hz, NCH), 3.29–3.1 (m, 4H, CH₂), 1.31 (d, ²J_{HP} = 3.4 Hz, 6H, PMe₂), 0.91 (t, ³J_{HH} = 7.1 Hz, 6H). ³¹P{¹H} NMR (202.5 MHz, THF-*d*₈): δ -64.8. ¹³C{¹H} NMR (125.8 MHz, THF-*d*₈): δ 149.4 (d, ¹J_{CP} = 13 Hz, P-C-N), 130.4, 118.3 (m, N-CH=CH-N=), 101.3 (d, ¹J_{CN} = 16 Hz, N-CH), 61.5 (s, CH₂), 14.8 (s, CH₃), 13.3 (d, ¹J_{CP} = 9 Hz, PMe).

The deprotection of 2-dimethylphosphino-*N*-(diethoxymethyl)imidazole was effected by dissolution in 165 ml of 10:1 acetone–water and heated to 50 °C for 8 h. Removal of the volatiles under reduced pressure yielded 16.59 g of a white solid, which was recrystallized twice from dry CH₂Cl₂ to give pure *dmp*i as colourless needles. Yield: 13.08 g (75%). mp.: 150 °C. IR (cm⁻¹, ATR): 3100–2300 (br), 1542 (m), 1428 (m), 1407 (m), 1396 (m), 1325 (m), 1238 (m), 1097 (m), 962 (s), 945 (s), 893 (s), 871 (m), 759 (s), 701 (s), 676 (m). ¹H NMR (300.1 MHz, CD₂Cl₂): δ 11.31 (br, 1H, NH), 7.20 (s, 2H, -CH-CH-), 1.38 (d, ²J_{HP} = 2.7 Hz, 6H, PMe). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ -58.7 (s). ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂): δ 150.4 (d, ¹J_{CP} = 11 Hz, P-C), 120.5 (s, -CH-CH-), 13.4 (d, ¹J_{CP} = 10 Hz, PCH₃). Anal. Calc. for C₅H₉N₂P: C, 46.83; H, 7.08; N, 21.87. Found: C, 47.16; H, 7.27; N, 22.09%. EI-MS: 128 [M⁺], 113 [M⁺-CH₃].

[W(Cl)(CO)(NO)(*bdmp*i)(*dmp*i)] (1): To a solid mixture of W(NO)(CO)₄(ClAlCl₃) (0.64 g, 1.57 mmol) and *dmp*i (1.20 g, 9.38 mmol) 20 ml of THF was added. The resulting mixture was refluxed at 70 °C for 1 d, 85 °C for 6 d, then filtered. The precipitate was washed with THF (4 × 10 ml). The combined THF solutions are concentrated. Diffusion of pentane into the THF solution at -30 °C gave pure product 1. Yield: 0.665 g (71%). IR (cm⁻¹, CH₂Cl₂): 1952 (CO), 1599 (NO). ¹H NMR (300.1 MHz, CDCl₃): δ 10.87 (br, 1H, NH), 7.73, 7.29 (s, 2H, -CH-), 7.27, 7.17 (m, 2H, -CH-), 2.16 (t, ²J_{HP} = 7 Hz, 6H, PMe), 2.14 (dd, ²J_{HP} = 8.1 Hz, ⁴J_{HP} = 0.7 Hz 3H, PMe), 2.10 (dd, ²J_{HP} = 8.3 Hz, ⁴J_{HP} = 0.7 Hz 3H, PMe), 1.61 (d, ²J_{HP} = 7.5 Hz, 3H, PMe), 1.44 (d, ²J_{HP} = 8.3 Hz, 3H, PMe). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ

82.7 (dd with satellites, ²J_{PP-trans} = 159 Hz, ²J_{PP-cis} = 25 Hz, ¹J_{PW} = 463 Hz, P-C from *bdmp*i), -11.5 (dd with satellites, ²J_{PP-cis} = 25 Hz, ²J_{PP-cis} = 19 Hz, ¹J_{PW} = 235 Hz, P-N from *bdmp*i), -26.3 (dd with satellites, ²J_{PP-trans} = 159 Hz, ²J_{PP-cis} = 18 Hz, ¹J_{PW} = 451 Hz, P-C from *dmp*i). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ 219.5 (dt, ²J_{CP-trans} = 49 Hz, ²J_{CP-cis} = 5 Hz) 157 (ddd, ¹J_{CP} = 66 Hz, ²J_{CP} = 33 Hz, ³J_{CP} = 7 Hz, P-C from *bdmp*i), 150.9 (d, ²J_{CP} = 48 Hz, N-C-P from *dmp*i), 147.1 (d, ²J_{CP} = 61 Hz, P-N-CH- from *bdmp*i), 140.3 (m, N-CH), 120.8 (m, N-CH), 120.3 (m, -CH-), 19.1 (d, ¹J_{CP} = 30 Hz, PMe), 17.9–16.8 (m, 3 PMe), 13.0 (d, ¹J_{CP} = 29 Hz, PMe), 12.1 (d, ¹J_{CP} = 11 Hz, PMe), 10.4 (d, ¹J_{CP} = 28 Hz, PMe). Anal. Calc. for C₁₃H₂₃ClN₅O₂P₃W: C, 26.31; H, 3.91; N, 11.80. Found: C, 26.71; H, 4.35; N, 12.18%.

W(Cl)(NO)(*dmp*i)₄ (2) and W(Cl)(NO)(*bdmp*i)(*dmp*i)₂ (3): The mixture of [W(Cl)(NO)-(P(OMe)₃)₄] (2.76 g, 3.71 mmol) and *dmp*i (2.11 g, 16.50 mmol) in THF (50 ml) was placed in a Young tap Schlenk tube and was stirred at 70 °C. During the reaction time, the P(OMe)₃ formed in the reaction was occasionally removed. After 10 d the resultant mixture was filtered over celite, the solid residue extracted with THF (20 ml × 3). Concentration and cooling of the combined solution at -30 °C gave two main products in a turn of pure 2 · 2THF (0.94 g, 28%) and W(Cl)(NO)(*bdmp*i)(*dmp*i)₂ (3). The latter was purified again by recrystallization from CH₃CN giving crystals of 3 · CH₃CN (0.93 g, 36%).

Data for 2: IR (cm⁻¹, THF): 1515 (NO). ¹H NMR (300.1 MHz, CDCl₃): δ 10.94 (s, 4 H, NH), 7.18 (s, -CH-8H), 1.50 (s, 24H, PMe). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ -21.4 (s, with satellite, ¹J_{PW} = 288 Hz). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ 151.6 (m, P-C), 129.6 (s, -CH-), 119.0 (s, -CH-), 15.3 (m, PMe). Anal. Calc. for C₂₈H₅₂ClN₉O₃P₄W: C, 37.12; H, 5.78; N, 13.91. Found: C, 36.67; H, 5.52; N, 14.09%.

Data for 3: IR (cm⁻¹, CH₂Cl₂): 1517 (NO). ¹H NMR (300.1 MHz, CDCl₃): δ 11.19 (s, 1H, NH), 11.09 (s, 1H, NH), 7.75 (s, 1H, -CH-), 7.17 (m, 5H, -CH-), 1.94 (d, ²J_{HP} = 6.9 Hz, 3H, PMe), 1.83 (d, ²J_{HP} = 7.2 Hz, 3H, PMe), 1.78 (d, ²J_{HP} = 6.6 Hz, 6H, PMe), 1.70 (d, ²J_{HP} = 8.1 Hz, 3H, PMe), 1.66 (d, ²J_{HP} = 6.6 Hz, 6H,

PMe), 1.61 (d, $^2J_{\text{HP}} = 7.2$ Hz, 3H, PMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 89.6 (dd with satellites, $^2J_{\text{PP-trans}} = 162$ Hz, $^2J_{\text{PP-cis}} = 22$ Hz, $^1J_{\text{PW}} = 318$ Hz, P–N), –6.3 (ddd with satellites, $^2J_{\text{PP-trans}} = 142$ Hz, $^2J_{\text{PP-cis}} = 13$ Hz, $^2J_{\text{PP-cis}} = 21$ Hz, $^1J_{\text{PW}} = 281$ Hz, P–C), –24.8 (dd with satellites, $^2J_{\text{PP-trans}} = 141$ Hz, $^2J_{\text{PP-cis}} = 12$ Hz, $^1J_{\text{PW}} = 290$ Hz, P–C), –25.1 (dt with satellites, $^2J_{\text{PP-trans}} = 163$ Hz, $^2J_{\text{PP-cis}} = 11$ Hz, $^1J_{\text{PW}} = 282$ Hz, P–C). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 159.2 (m, P–C), 151.5 (d, $^1J_{\text{CP}} = 63$ Hz, P–C), 149.9 (d, $^1J_{\text{CP}} = 60$ Hz, P–C), 140.6 (d, $^3J_{\text{CP}} = 3$ Hz, –CH–), 140.5 (d, $^3J_{\text{CP}} = 3$ Hz, –CH–), 130.0 (m, –CH–) 129.5 (m, –CH–), 129.4 (t, $^3J_{\text{CP}} = 3$ Hz, –CH–), 119.2 (m, –CH–), 18.3 (m, $^1J_{\text{CP}} = 28$ Hz, 2PMe), 18.3 (d, $^1J_{\text{CP}} = 27.9$ Hz, PMe), 17.6 (d, $^1J_{\text{CP}} = 29$ Hz, PMe), 17.0 (dd, $^1J_{\text{CP}} = 25$ Hz, $^3J_{\text{CP}} = 2$ Hz PMe), 16.8 (d, $^1J_{\text{CP}} = 29$ Hz, PMe), 15.1 (d, $^1J_{\text{CP}} = 30$ Hz, PMe), 12.7 (d, $^1J_{\text{CP}} = 28$ Hz, PMe). Anal. Calc. for $\text{C}_{17}\text{ClH}_{32}\text{N}_7\text{OP}_4\text{W}$: C, 29.44; H, 4.65; N, 14.13. Found: C, 29.69; H, 5.03; N, 13.97%.

$W(\text{Cl})(\text{NO})[(\text{P}(\text{OMe})_3)_2(\text{dmpe})]$ (**4**): $W(\text{Cl})(\text{NO})[\text{P}(\text{OMe})_3]_4$ (3.24 g, 4.34 mmol) was dissolved in THF (30 ml) in a Young tap Schlenk tube, and dmpe (0.0667 g, 4.34 mmol) was added. After the mixture was heated to 70 °C for 8 h, the solvent, excess of dmpe and the $\text{P}(\text{OMe})_3$ formed in the reaction were slowly removed *in vacuo* to give pure **4**. Yield: 2.68 g (95%). IR (cm^{-1} , THF): 1557 (NO). ^1H NMR (300.1 MHz, CDCl_3): δ 3.70

(d, $^3J_{\text{HP}} = 10.8$ Hz, 18H, $\text{P}(\text{OMe})_3$), 1.71 (br, m, 4H, PCH_2), 1.57 (m, 6H, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 161.2 (m with satellites, $^2J_{\text{PP-trans}} = 205$ Hz, $^1J_{\text{PW}} = 484$ Hz, $\text{P}(\text{OMe})_3$), 20.6 (m with satellites, $^2J_{\text{PP-trans}} = 205.2$ Hz, $^1J_{\text{PW}} = 265.5$ Hz, PCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 52.0 (s, $\text{P}(\text{OMe})_3$), 30.5 (m, CH_2), 13.4 (d, $^1J_{\text{CP}} = 26$ Hz, PCH_3), 12.3 (d, $^1J_{\text{CP}} = 25$ Hz, PCH_3). Anal. Calc. for $\text{C}_{12}\text{ClH}_{34}\text{NO}_7\text{P}_4\text{W}$: C, 22.00; H, 5.49; N, 2.13. Found: C, 22.26; H, 5.29; N, 2.16%.

$W(\text{Cl})(\text{NO})(\text{dmpe})(\text{dmpi})_2$ (**5**): To a solid mixture of **4** (2.50 g, 3.86 mmol) and dmpi (1.09 g, 8.54 mmol) in a Young tap Schlenk tube was added THF (40 ml). The resulting mixture was heated to 105 °C. During the reaction, the $\text{P}(\text{OMe})_3$ formed was removed every 2 d. After one week, the reaction mixture was dried *in vacuo* and then washed with pentane (10 ml \times 3) and ether (10 ml \times 3) to give pure **5**. Yield: 2.25 g (89%). IR (cm^{-1} , CH_2Cl_2): 1494 (NO). ^1H NMR (300.1 MHz, CDCl_3): δ 11.24 (s, br, 2H, NH), 7.16 (s, 2H, –CH=CH–), 7.07 (m, 2H, –CH=CH–), 1.87 (d, $^2J_{\text{HP}} = 6.9$ Hz, 6H, PMe from dmpi), 1.76–1.42 (br, 4H, PCH_2), 1.64 (d, $^2J_{\text{HP}} = 6.9$ Hz, 6H, PMe from dmpi), 1.355 (d, $^2J_{\text{HP}} = 7.8$ Hz, 6H, PMe from dmpe), 1.281 (d, $^2J_{\text{HP}} = 7.5$ Hz, 6H, PMe from dmpe). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 19.6 (m with satellites, $^2J_{\text{PP-trans}} = 142$ Hz, $^1J_{\text{PW}} = 282$ Hz, dmpe), –23.3 (m with satellites, $^2J_{\text{PP-trans}} = 142$ Hz, $^1J_{\text{PW}} = 298$ Hz, dmpi). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 152.2 (d, $^1J_{\text{CP}} =$

Table 3

Crystallographic data and structure refinement parameters for dmpi, **1** and **2**

	dmpi	1	2
Formula	$\text{C}_5\text{H}_9\text{N}_2\text{P}$	$\text{C}_{13}\text{H}_{23}\text{ClN}_5\text{O}_2\text{P}_3\text{W}$	$\text{C}_{28}\text{H}_{52}\text{ClN}_9\text{O}_3\text{P}_4\text{W}$
Color	Colourless	Yellow	Yellow
Mr (g mol $^{-1}$)	128.11	593.56	905.96
Crystal dimensions (mm)	0.36 \times 0.19 \times 0.12	0.39 \times 0.23 \times 0.17	0.22 \times 0.20 \times 0.16
Temperature (K)	183(2)	183(2)	183(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	9.8252(9)	11.6569(11)	12.2098(12)
b (Å)	13.6816(12)	9.9554(7)	15.2110(16)
c (Å)	17.4743(15)	19.0686(15)	20.708(2)
α (°)	100.675(10)	90	97.428(12)
β (°)	104.843(10)	101.143(10)	98.827(12)
γ (°)	103.516(11)	90	90.131(12)
V (Å 3)	2131.3(3)	2171.2(3)	3767.6(7)
Z	12	4	4
D_c (Mg m $^{-3}$)	1.198	1.816	1.597
μ (mm $^{-1}$)	0.288	5.681	3.349
$F(000)$	816	1152	1832
θ Range (°)	2.78–30.42	2.32–27.92	2.75–30.23
Reflections collected	38,570	22,015	47,694
Reflections unique (R_{int})	11,740 (0.0901)	4873 (0.0528)	20,114 (0.0648)
Completeness to θ (%)	30.42, 91.0	27.92, 92.5	30.23, 89.6
Maximum/minimum transmission	0.968/0.921	0.4439/0.1807	0.6277/0.5621
Data/restraints/parameters	11,740/0/454	4873/0/232	20,114/14/864
Goodness-of-fit on F^2	0.766	1.050	0.838
R_1, wR_2 (observed)	0.0621, 0.1682	0.0274, 0.0634	0.0462, 0.1112
R_1, wR_2 (%) (all data)	0.1390, 0.1963	0.0373, 0.0726	0.1035, 0.1324

Details in common: numerical absorption correction; refinement method: full-matrix least-squares on F^2 .

$$^a R_1 = \Sigma(F_o - F_c)/\Sigma F_o; I > 2\sigma(I); wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}.$$

Table 4
Crystallographic data and structure refinement parameters for **3–5**, and **7**

	3	4	5	7
Formula	C ₁₉ H ₃₅ ClN ₈ OP ₄ W	C ₁₂ H ₃₄ ClNO ₇ P ₄ W	C ₁₆ H ₃₄ ClN ₅ OP ₄ W	C ₂₄ H ₅₀ BN ₆ NaOP ₄ W
Color	Yellow	Yellow	Yellow	Yellow
Mr (g mol ⁻¹)	734.72	647.57	655.65	780.22
Crystal dimensions (mm)	0.26 × 0.22 × 0.15	0.41 × 0.38 × 0.35	0.41 × 0.29 × 0.20	0.15 × 0.06 × 0.06
Temperature (K)	183(2)	183(2)	183(2)	183(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	^b Pna2 ₁	P2 ₁ /c	^b P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c
a (Å)	11.6147(10)	14.4628(10)	10.6813(7)	14.7704(13)
b (Å)	15.8674(12)	9.3958(6)	11.2256(8)	11.8644(6)
c (Å)	15.5596(11)	17.7580(13)	21.7296(14)	21.3650(17)
α (°)	90	90	90	90
β (°)	90	94.760(8)	90	103.767(10)
γ (°)	90	90	90	90
V (Å ³)	2867.6(4)	2404.7(3)	2605.5(3)	3636.5(5)
Z	4	4	4	4
D _c (Mg m ⁻³)	1.702	1.789	1.671	1.425
μ (mm ⁻¹)	4.373	5.211	4.798	3.390
F(000)	1456	1280	1296	1576
θ Range (°)	3.11–30.36	2.78–30.34	2.79–30.31	2.29–28.08
Reflection collected	38264	33517	32449	38070
Reflections unique (R _{int})	8571 (0.0606)	6779 (0.0978)	7750 (0.0554)	8597 (0.0487)
Completeness to θ (%)	30.36, 99.5	30.34, 93.8	30.31, 99.4	28.08, 92.6
Maximum/minimum transmission	0.5758/0.4273	0.3039/0.2076	0.4665/0.3048	0.8608/0.7387
Data/restraints/parameters	8571/2/291	6779/6/240	7750/6/257	8597/0/340
Goodness-of-fit on F ²	1.007	1.011	1.047	0.646
R ₁ , wR ₂ (observed) (%)	0.0288, 0.0770	0.0428, 0.1091	0.0273, 0.0670	0.0253, 0.0582
R ₁ , wR ₂ ³ (%) (all data)	0.0363, 0.0811	0.0582, 0.1154	0.0340, 0.0708	0.0454, 0.0639

Details in common: numerical absorption correction; refinement method: full-matrix least-squares on F².

^a R₁ = Σ(F_o - F_c)/ΣF_o; I > 2σ(I); wR₂ = {Σw(F_o² - F_c²)₂/Σw(F_o²)^{1/2}}.

^b The Flack parameters for achiral space group Pna2₁ (**3**) and chiral space group P2₁2₁2₁ (**5**) refined to 0.001(7) and 0.023(7), respectively [29,30].

59 Hz, PC), 129.4 (m, CH=CH-), 118.7 (s, -CH=CH-), 31.9 (m, PCH₂), 19.1 (d, ¹J_{CP} = 28 Hz, PCH₃), 17.8 (d, ¹J_{CP} = 29 Hz, PCH₃), 13.9 (d, ¹J_{CP} = 26 Hz, PCH₃), 12.7 (d, ¹J_{CP} = 24 Hz, PCH₃). Anal. Calc. for C₁₆H₃₄ClN₅OP₄W: C, 29.31; H, 5.23; N, 10.68. Found: C, 29.50; H, 4.89; N, 10.33%. EI-MS: 655 [M⁺], 527 [M⁺-dmp_i], 399 [M⁺-2dmp_i], 311 [M⁺-dmp_i-imidazole-NO-2CH₃].

W(Cl)(NO)(dmpe)(tmsdmp_i)₂ (**6**): *n*-Butyllithium (1.6 M in *n*-hexane, 0.43 ml, 0.68 mmol) was added to a solution of **5** (0.2055 g, 0.31 mmol) in THF (20 ml) at -75 °C within half an hour. The solution was maintained at this temperature for an additional 3 h. Me₃SiCl (0.074 g, 0.68 mmol) was added dropwise to the cooled solution over 20 min. The reaction mixture was stirred further at -75 °C for 1 h and then brought to room temperature and stirred at this temperature for 30 min. Compound **6** was obtained by removal of the solvent, but was not analytically pure. ¹H NMR (500.2 MHz, THF-*d*₈): δ 7.18 (s, 2H, -CH-), 7.07 (s, 2H, -CH-), 1.95 (d, ²J_{HP} = 6.4 Hz, 6H, PMe₃ from dmp_i), 1.90 (d, ²J_{HP} = 6.4 Hz, 6H, PMe₃ from dmp_i), 1.48 (br, 4H, PCH₂), 1.16 (d, ²J_{HP} = 8.4 Hz, 6H, PMe₃ from dmpe), 1.07 (d, ²J_{HP} = 8 Hz, 6H, PMe₃ from dmpe), 0.59 (s, 18H, SiMe₃). ³¹P{¹H} NMR (202.5 MHz, THF-*d*₈): δ 21.5 (m with satellites, ²J_{PP-trans} = 150 Hz, ¹J_{PW} = 287 Hz, dmpe), -12.2 (m with satellites,

²J_{PP-trans} = 150 Hz, ¹J_{PW} = 301 Hz, dmp_i). ¹³C{¹H} NMR (125.8 MHz, THF-*d*₈): δ 130.0 (m, -CH-), 125.9 (s, -CH-), 32.6 (m, PCH₂), 22.1 (d, ¹J_{CP} = 8 Hz, PCH₃ from dmp_i), 21.9 (d, ¹J_{CP} = 8 Hz, PCH₃ from dmp_i), 12.2 (d, ¹J_{CP} = 23 Hz, PCH₃ from dmpe), 11.3 (d, ¹J_{CP} = 25 Hz, PCH₃ from dmpe), 3.2 (s, SiMe₃). ²⁹Si{¹H} NMR (99.4 MHz, THF-*d*₈): δ 15.4 (s, SiMe₃).

Na[W(Cl)(NO)(dmpe)(dmp_i)(tebdmp_i)] (**7**): Compound **5** (0.135 g, 0.21 mmol) was dissolved in THF (30 ml) and 0.65 ml of NaHBEt₃ in THF (1 mol / L) was added at -30 °C. The resulting mixture was allowed to stir for 8 h at this temperature, then warmed up to room temperature overnight. After filtration the precipitate was washed with ether (5 ml × 4) and dried to afford a pure product. Yield: 0.136 g (89%). IR (cm⁻¹, ATR): 1487 (NO). ¹H NMR (300.1 MHz, CD₃CN): δ 6.97 (s, 2H, NH), 6.88 (s, 1H, NH), 6.384 (s, 1H, NH), 1.2–1.8 (m, 28H, 8PMe₂ and 2PCH₂). ³¹P{¹H} NMR (121.5 MHz, CD₃CN): δ 26.1 (d, ²J_{PP} = 142 Hz, dmpe), 25.4 (d, ²J_{PP} = 105 Hz, dmpe), -17.1 (d, ²J_{PP} = 147 Hz, tebdmp_i), -25.9 (d, ²J_{PP} = 109 Hz, dmp_i). A ¹³C{¹H} NMR spectrum of **7** could not be recorded due to its low solubility in all organic solvents. Anal. Calc. for C₂₂H₄₇BN₅OP₄NaW: C, 35.75; H, 6.41; N, 9.47. Found: C, 36.14; H, 6.11; N, 9.29%. EI-MS: 619 [M⁺-Na-NO-imidazole-H], 573 [M⁺-Na-BEt₃-3CH₃], 529 [M⁺-Na-NO-imidazole-

6CH₃-H], 491 [M⁺-Na-tebdmpi], 401 [M⁺-Na-tebdmpi-6CH₃].

X-ray data collection and structure refinement Single Crystals of dmpi, **1–5**, and **7** were mounted on top of a glass fibre using polybutene oil as protecting agent, and immediately transferred to the diffractometer. There the crystals were cooled to 183(2) K by an Oxford cryogenic system. The determination of the unit cell parameters and the collection of intensity data were performed with an image plate detector system (Stoe IPDS diffractometer) with graphite monochromated Mo K α radiation using the STOE IPDS software [24]. A total of 273, 220, 167, 250, 218, 233 and 220 images were exposed at constant times of 2.3, 1.60, 2.00, 1.50, 1.30, 1.30 and 4.00 min/image for dmpi, **1–5**, and **7**, respectively. The total exposure and read-out times for the five compounds were 29, 21, 17, 24, 20, 21 and 30 h. The crystal-to-image distances were set to 50.0, 60.0, 50.0, 50.0, 50.0, 50.0 and 60.0 mm. Totals of 11,740 ($2.78 < \theta < 30.42$), 22,015 ($2.32 < \theta < 27.92$), 47,694 ($2.76 < \theta < 30.23$), 38,264 ($3.11 < \theta < 30.36$), 33,517 ($2.78 < \theta < 30.34$), 32,449 ($2.79 < \theta < 30.31$), and 38,070 ($2.29 < \theta < 28.08$), reflections were, respectively, collected for dmpi, **1–5**, and **7**, which yielded 11,740, ($R_{\text{int}} = 0.0901$), 4873 ($R_{\text{int}} = 0.0528$), 20,114 ($R_{\text{int}} = 0.0648$), 8571 ($R_{\text{int}} = 0.0606$), 6779 ($R_{\text{int}} = 0.0978$), 7750 ($R_{\text{int}} = 0.0554$), and 8597 ($R_{\text{int}} = 0.0487$) unique reflections, respectively. ϕ rotation (**1–5**) or oscillation scan modes (**7**) were selected for the ϕ increments of 1.1, 1.0, 1.2, 1.2, 1.1, 0.9, 1.0 per exposure. Lorentz and polarization corrections were done with INTEGRATE [24]; numerical absorption corrections (10, 11, 12, 13, 21, 17 and 8 indexed crystal faces measured) were performed with XRED [24] using a video camera installed at the IPDS diffractometer. All of the structures were solved by direct methods using the Programme SHELXS-97 [25] and they were refined by full-matrix least squares methods on all F^2 data with SHELXL-97 [26]. ORTEP ellipsoid plots were made with PLATON [27]. Full matrix least squares refinements on F^2 converged to R_1/wR_2 ($I > 2\sigma(I)$) of 0.0621/0.1682, 0.0274/0.0634, 0.0479/0.1083, 0.0288/0.0770, 0.0428/0.1091, 0.0273/0.0670 and 0.0253/0.0582 for dmpi, **1–5**, and **7**, respectively. The X ray data collections and the processing parameters are given in Tables 3 and 4. Structures **1–5** exhibited Cl/N=O positional disorder with 0.64:0.36, 0.80:0.20, 0.62:0.38, 0.70:0.30, 0.46:0.54 ratios. All structures were checked with check-def, Version 2005 of the programme PLATON [28].

Supplementary material

CCDC 630926, 620854, 630927–630930 contain the supplementary crystallographic data for **1**, **2**, **3–5** and **7**. These

data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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